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Silver-based polymeric ionic liquid sorbent coatings for solid-phase microextraction: Materials for the selective extraction of unsaturated compounds

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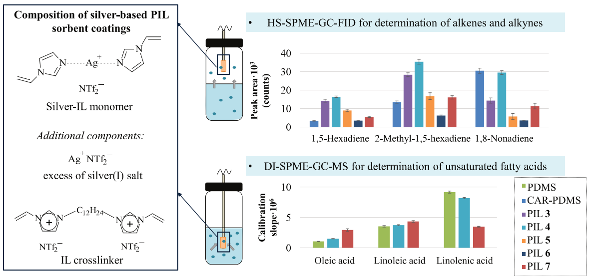
HIGHLIGHTS

- Silver-based polymeric ionic liquid (PIL) coatings are developed for the determination of unsaturated compounds.
- The thermal stability of the silver-based PILs is higher in comparison with silver ionic liquids.
- The coatings are selective for analytes with terminal double bonds in headspace solidphase microextraction.
- The coatings extract unsaturated analytes by a competitive partitioning mechanism.
- The coatings are valid for determining unsaturated fatty acids in rinse water by directimmersion SPME.

GRAPHICAL ABSTRACT



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ABSTRACT

A new generation of silver-based polymeric ionic liquid (PIL) sorbent coatings has been developed and applied in solid-phase microextraction (SPME). The new materials are based on ionic liquid monomers formed by cations containing the silver(I) ion coordinated with two 1-vinylimidazole ligands. Up to seven different silver-based PIL sorbent coatings were developed by polymerizing the silver-IL monomer in the presence of either silver bis[(trifluoromethyl)sulfonyl]imide, and/or a dicationic ionic liquid crosslinker. The obtained sorbent coatings were found to possess adequate thermal stability despite the presence of the silver(I) ions. Thermal desorption of the analytes at 175 °C was effectively used without any significant decrease in extraction efficiency. The developed sorbent coatings were used in two different applications: the determination of alkenes/alkynes via headspace SPME and the determination of unsaturated fatty acids using direct-immersion SPME. In the former approach, the silver-based PILs were particularly selective for the determination of unsaturated compounds with terminal double bonds such as 1,5-hexadiene, 2-methyl-1,5-hexadiene, and 1,8-nonadiene. A study of the extraction mechanism of the analytes to the sorbent coating revealed a competitive partitioning of the analytes. In the second approach, the most selective silver-based PILs were applied for the determination of oleic acid, linoleic acid, and linolenic acid. After proper optimization of the method, the coatings were found to be more or as sensitive as the commercial polydimethylsiloxane fiber. Limits of detection between 2.6 and 8.2 $\mu g\, L^{-1}$ in ultrapure water and from 12 to 14 $\mu g\, L^{-1}$ in tap water were obtained for the best silver-based PIL, with relative standard deviations lower than 13% in all cases at a spiked level of 160 $\mu g\, L^{-1}$. Finally, the fiber

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was effectively applied for the analysis of rinse water from a dairy farm, with adequate detection of the analytes at concentrations between 52 and 179 μg L^{-1}.

1. Introduction

Solid-phase microextraction (SPME) is a fast, simple, and powerful sample preparation technique for the determination of a wide variety of compounds [1–3]. The technique is based on the mass transfer of analytes initially within the sample to a small amount of sorbent, typically coated on a solid support [4]. The success of the technique is directly linked to the nature of the sorbent coating. Therefore, the development of selective and sensitive materials for SPME is a current trend in analytical chemistry [5]. Several types of materials have been employed in SPME, including molecular recognition sorbents like immunosorbents [6], aptamers [7] or molecular imprinted polymers (MIPs) [8], carbonaceous nanomaterials such as carbon nanotubes (CNTs) [9] or graphene [10], metal and/or metal oxide nanoparticles [11], metal-organic frameworks (MOFs) [12], ionic liquids (ILs) [13] and polymeric ionic liquids (PILs) [14].

Among the aforementioned materials, PILs are a group of interesting polymers that are generated by the polymerization of IL monomers [15]. PILs possess low to negligible vapor pressure at room temperature, high chemical and electrochemical stability, and the ability to promote different interactions with analytes, properties that are altogether directly linked to their nature. However, in comparison to ILs, PILs generally have higher thermal and chemical stability and their viscosity is not significantly affected by temperature, properties that makes PILs interesting materials for high temperature applications [16].

It is well-known that silver ions can interact specifically and strongly via chemical complexation with compounds possessing double bonds [17]. The interaction is established by the formation of a σ-bond due to electron donation of the occupied π_{2p} hybrid orbital of the unsaturated compound to the empty *s* orbital of the silver ion. A π-bond is also formed due to electron donation from the occupied *d* orbitals of the silver ion to the empty π^*_{2p} antibonding orbital of the unsaturated compound [18]. The bonds formed by chemical complexation are stronger than those formed by van der Waals forces. In addition, the interaction is reversible and the bonds can be broken under elevated temperatures [17]. Silver chemistry has been investigated in the development of stationary phases in chromatography [19,20] (e.g, argentation chromatography) and facilitated transport membranes [17,18], applied for the separation of olefin/paraffin mixtures [17–19] and unsaturated fatty acids [20]. It is important to mention that some of these applications have used silver-based room temperature ionic liquids (RTILs) instead of common silver salts [18,19]. In this sense, Brooks et al. have introduced silver-based RTILs [21]. The cation structure of these reported RTILs is based on silver(I) ions that are coordinated with two N-alkylimidazole ligands [21]. The strategy was to develop a silver-based platform with lower melting points than common silver salts, facilitating faster diffusion of the unsaturated compounds to be complexed. A primary issue with the aforementioned materials is their limited thermal stability. However, this problem can be partially solved by designing PILs that contain silver(I) ions instead of the previously reported silver-RTILs.

For this study, a new class of silver-based PIL sorbent coatings for SPME was developed. The coatings were designed with the objective of exploiting silver(I)-double bond complexation to achieve/enhance selectivity and sensitivity for the extraction of unsaturated compounds. At the same time, our goal was to improve the thermal stability with respect to the previously reported silver-based ILs. With these objectives, the coatings were prepared from silver-based IL monomers in which the silver(I) ion was coordinated with 1-vinylimdiazole ligands, which permits subsequent polymerization to generate the corresponding silver-based PIL. Apart from the neat silver-based IL, several SPME fibers were also prepared by using the silver-IL monomer in the presence of silver bis[(trifluoromethyl)sulfonyl]imide, and/or in the presence of a dicationic IL crosslinker. Another objective of the work was to apply the silver-based PILs towards the determination of unsaturated compounds. Thus, two different methods were developed, namely, headspace (HS)-SPME for the selective determination of alkenes/alkynes and direct-immersion (DI)-SPME for the sensitive determination of unsaturated fatty acids.

2. Experimental

2.1. Chemicals, reagents, materials and samples

The group of alkenes and alkynes studied included 1,4-pentadiene (1,4-PDE, 99%), hexane (HA, 97%), 1-hexene (1-HE, 99.8%), 1,3-hexadiene, mixture of isomers (1,3-HDE isomers 1, 2, 3, 95%), 2,4-hexadiene, mixture of isomers (2,4-HDE, isomers 1, 2, 3, 90%), 2-methyl-1,5-hexadiene (2-M-1,5-HDE, 97%), 2,3-dimethyl-1,3-butadiene (2,3-DM-1,3-BDE, analytical grade), 1-nonene (1-NE, 96%), and 1,8-nonadiene (1,8-NDE, 99%), all purchased from Sigma-Aldrich (St. Louis, MO, USA). The analytes *trans*-2-hexene (trans-2-HE, 98%), *cis*-2-hexene (cis-2-HE, 6%), 1,5-hexadiene (1,5-HDE, 98%), 3-hexyne (3-HY, 99%), and 2-hexyne (2-HY, 98%) were acquired from Alfa Aesar (Ward Hill, MA, USA). The studied unsaturated fatty acids were oleic acid ($C_{18:1}$, ≥99%), linoleic acid ($C_{18:2}$, ≥99%), and linolenic acid ($C_{18:3}$, ≥99%). These analytes were purchased from Sigma-Aldrich.

For studies involving the extraction of alkenes and alkynes, two standard solutions containing mixtures of the analytes were prepared by dissolving the analytes as two groups using pentane (analytical grade, Fisher Scientific, Geel, Belgium) at a concentration of 10000 mg L^{-1}. A 1 μL volume of each intermediate solution was used to compare the selectivity of the SPME fibers, with the concentration of the analytes at 0.5 mg L^{-1} in the headspace of the vial. For the study of the extraction mechanism, two intermediate solutions containing 1-HE and 1,5-HDE were prepared in pentane. Working solutions containing 5–12000 μg of the analytes were prepared by dilution of these solutions in pentane (10 μL of total volume).

For the determination of the unsaturated fatty acids, individual stock solutions were prepared by dissolving each analyte in acetonitrile (analytical grade, Sigma Aldrich) at concentrations of 2000 mg L^{-1} for $C_{18:1}$ and $C_{18:3}$, and 1200 mg L^{-1} for $C_{18:2}$. An intermediate solution of the three analytes in acetonitrile was prepared by dilution of the stock solutions to achieve a concentration of 300 mg L^{-1}. Standard working solutions were prepared by diluting the intermediate solution in ultrapure water, with concentrations between 50 and 1200 μg L^{-1}. The organic content was always lower than 0.7% (v/v).

Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

For the synthesis of the IL monomers and crosslinkers, as well as the ensuing polymerization reaction, the following reagents were required: imidazole (≥99.0%), 1-vinylimidazole (≥99.0%), 1,12-dibromododecane (98.0%), 2-hydroxy-2-methylpropiophenone (>96.0%, DAROCUR 1173) and silver(I) oxide (≥99.0%), all purchased from Sigma-Aldrich. Lithium bis[(trifluoromethyl)sulfonyl] imide ($[Li^+][NTf_2^-]$) was purchased from SynQuest Laboratories (Alachua, FL, USA). Acetonitrile, methanol, ethyl acetate, and *iso*-propanol (≥99.0%) were acquired from Sigma-Aldrich. Elastic nitinol wires (external diameter of 127 μm) were acquired from Nitinol Devices & Components (Fremont, CA, USA) and were used as solid supports in the preparation of the SPME fibers. For the derivatization of nitinol wires, hydrogen peroxide (30.0%, w/w) was purchased from Fisher Scientific and vinyltrimethoxysilane (VTMS) (98.0%) was obtained from Sigma-Aldrich. Blank SPME assemblies (24 Ga) were provided by Millipore-Sigma (Bellefonte, PA, USA).

The commercial polydimethylsiloxane (PDMS, 100 μm film thickness), carboxen-polydimethylsiloxane (CAR-PDMS, 75 μm film thickness), divinylbenzyl-polydimethylsiloxane (DVB-PDMS, 65 μm film thickness), and divinylbenzyl/carboxen-polydimethylsiloxane (DVB/CAR-PDMS, 50/30 μm film thickness) SPME fibers were obtained from Millipore-Sigma.

Rinse water from a milk pipeline rinse cleaning process was obtained from a dairy farm in Ames, IA, USA. The samples were collected in amber glass bottles and kept in the freezer until analysis.

2.2. Instrumentation

The alkene/alkyne separation was carried out using an Agilent Technologies 6890N GC (Santa Clara, CA, USA) equipped with flame ionization detection (FID) and an Agilent Technologies HP-Al_2O_3/KCl PLOT column (30 m L ×0.535 mm ID ×15.00 μm). Ultrapure helium was used as carrier gas at a flow rate of 5 mL min^{-1}. The inlet was always operated in *splitless* mode, with an inlet temperature of 175 °C. Two different oven temperature programs were performed for the separation of the olefins and are shown in Fig. S1 (A) and (B) of the SM of the Supplementary Material (SM). The temperature of the FID was 220 °C, using an air flow of 450 mL min^{-1}, a hydrogen flow of 40 mL min^{-1}, and a helium make-up flow of 45 mL min^{-1}. The retention time and peak area were considered for the identification and quantification of the analytes, respectively. Table S1 of the SM includes the retention time of the analytes.

The fatty acid separation was performed using an Agilent Technologies 7890B GC equipped with a 5977A MS detector (single quadrupole) and a MEGA-FFAP EXT crossbonded capillary column (50 m L × 0.20 mm I.D. × 0.20 μm film thickness) purchased from Mega s.n.c (Legnano, MI, Italy). Ultrapure helium was used as carrier gas at a flow rate of 1 mL min^{-1}. The inlet was operated in *splitless* mode, with an inlet temperature of 290 °C for PA and CAR-PDMS, 260 °C for PDMS and DVB-PDMS, and 175 °C for the silver-based PIL fibers. The following temperature program was used: the temperature was increased at 15 °C·min^{-1} from 100 °C up to 200 °C, followed by an increase at 5 °C·min^{-1} up to 240 °C and held for 16 min (Fig. S1 (C)). The transfer line from the GC to the MS was kept at 250 °C. The MS was operated in electron ionization (EI) mode at 70 eV, employing gain factor mode and using 230 °C and 150 °C as the source and quadrupole temperatures, respectively. Data was acquired using the single ion monitoring (SIM) mode. For identification of fatty acids, the retention time and the presence of two characteristic ions for each analyte (denoted as quantifier and qualifier ions), as well as their ratio were considered, as provided in Table S2 of the SM. The peak area corresponding to the quantifier ion was used for quantitative purposes.

2.3. Procedures

2.3.1. Synthesis of the silver-based IL monomers and IL crosslinker

The silver-based IL monomer was synthesized using a modification of a previously published method [21]. Briefly, 5 mmol of silver(I) oxide was reacted with 10 mmol of bis(trifluoromethane) sulfonimide in acetonitrile with stirring at room temperature for 2 h. Then, the solvent was removed via rotary evaporation and the obtained solid ($[Ag^+(ACN)][NTf_2^-]$) was dried under vacuum. To obtain the neat silver-based IL monomer ($[Ag^+(VIM)_2][NTf_2^-]$), $[Ag^+(ACN)][NTf_2^-]$ and 1-vinylimidazole were stirred and reacted at a 1:2 molar ratio in acetonitrile at room temperature for 2 h. After the reaction, the solvent was removed by rotary evaporation, and the product was dried under vacuum at 35 °C. In addition, mixtures containing the $[Ag^+(VIM)_2][NTf_2^-]$ monomer and $[Ag^+][NTf_2^-]$ were obtained by reacting $[Ag^+(ACN)][NTf_2^-]$ and 1-vinylimidazole at 1:1, 1.3:1, 1.5:1 or 2:1 molar ratios.

The 1,12-di(3-vinylimidazolium)dodecane bis[(trifluoromethyl) sulfonyl]imide ($[(VIM)_2C_{12}^{2+}]\ 2[NTf_2^-]$) IL crosslinker was synthesized according to previously published methods [22].

2.3.2. Preparation of the silver-based PIL sorbent coatings

A total of 7 SPME fibers were developed in this study. There are two main features that distinguish the fibers from each other: (1) the type of IL monomer (neat silver-based IL or silver-based IL mixtures) and (2) the structure of the final polymer (linear or crosslinked co-polymer). Table 1 provides a summary of all developed fibers.

All of the silver-based PIL sorbent coatings were generated by *on fiber* free radical polymerization. Prior the polymerization, nitinol elastic wires were derivatized according to previously published methods [23]. Briefly, the nitinol support was treated with hydrogen peroxide and then with VTMS to install free vinyl groups on the surface. The derivatized nitinol wires were subsequently glued onto a commercial SPME assembly.

Linear polymers (PILs **1**–**5**) were obtained by mixing the silver-based IL (or silver-based mixture) monomer with a free radical initiator (DAROCUR 1173, 5%, w/w, with respect to the monomer). Crosslinked polymers (PILs **6**–**7**) were generated by adding the crosslinker (50%, w/w, with respect to the monomer) as an extra component to the mixture. Each binary or ternary mixture was placed onto the surface of a 1.3 cm derivatized nitinol support, and exposed to UV irradiation (360 nm) for 1 h using a RPR-100 UV reactor featuring a spinning carousel purchased from Southern New England Ultraviolet Company (Bradford, CT, USA). The fibers were then conditioned in the GC injector at 150 °C for 1 h. Representative scanning electron microscopy (SEM) images of the silver-based PILs, obtained with a JEOL JSM-6060 LV microscope, are shown in Fig. 1.

2.3.3. HS-SPME-GC-FID procedure for the determination of alkenes and alkynes

HS-SPME extractions were performed with all studied commercial and silver-based PIL fibers. A volume of 1 μL of the analyte working solution dissolved in pentane was added to a 20 mL headspace vial (Restek, Bellefonte, PA, USA). The concentration of the analytes in the headspace was 0.5 mg L^{-1} and the pentane content was 0.005% (v/v). The vial was immediately sealed using a polytetrafluoroethylene (PTFE) crimp cap (Agilent Technologies), and extractions were performed for 6 min at 25 °C. Analytes were then thermally desorbed in the GC inlet for 10 min at 175 °C, followed by GC-FID according to Fig. S1 (A) and (B) of the SM. After

Table 1
Composition of the developed silver-based PIL sorbent coatings.

PIL abbreviation	Molar ratio of $[\mathrm{Ag^+(ACN)}][\mathrm{NTf_2^-}]$: 1-vinylimidazole reacted to prepare the IL monomer	IL monomer	Molar excess of $[\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[a]	IL crosslinker
PIL **1**	1: 2	Neat $[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}]$[b]	0	–
PIL **2**	1: 1	$[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}] + [\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[c]	0.5	–
PIL **3**	1.3: 1	$[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}] + [\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[c]	0.8	–
PIL **4**	1.5: 1	$[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}] + [\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[c]	1.0	–
PIL **5**	2: 1	$[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}] + [\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[c]	1.5	–
PIL **6**	1: 1	$[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}] + [\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[c]	0.5	$[\mathrm{(VIM)_2C_{12}^{2+}}]\ 2[\mathrm{NTf_2^-}]$[d]
PIL **7**	1.5: 1	$[\mathrm{Ag^+(VIM)_2}][\mathrm{NTf_2^-}] + [\mathrm{Ag^+}][\mathrm{NTf_2^-}]$[c]	1.0	$[\mathrm{(VIM)_2C_{12}^{2+}}]\ 2[\mathrm{NTf_2^-}]$[d]

[a] Molar excess with respect to the monomer.
[b] Referred to in the text as neat silver-based IL.
[c] Referred to in the text as silver-based IL mixtures.
[d] Crosslinker amount was 50% (w/w) with respect to the monomer.

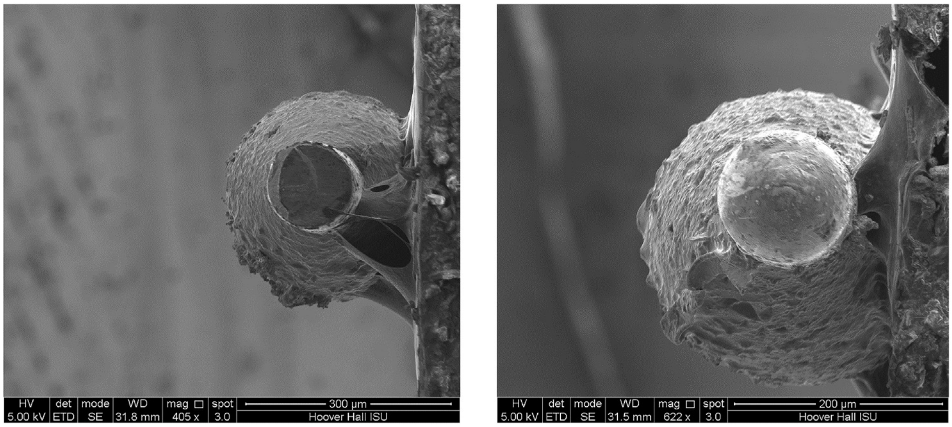

Fig. 1. Representative scanning electron microscopy (SEM) images of the silver-based PIL **4**. Note: Estimated film thickness: ~76 µm; estimated volume: ~0.625 µL.

each desorption, a cleaning step of the fiber was performed in the GC inlet for 10 min.

2.3.4. *Study of the extraction mechanism for the studied fibers*

The extraction mechanism of 1-HE in the presence of 1,5-HDE was evaluated for the CAR-PDMS, PDMS, and PIL **4** and PIL **7** fibers. A volume of 10 µL of analyte working solution in pentane was added to a 20 mL vial and sealed with a PTFE crimp cap. Therefore, a 5–100 µg amount of 1-HE and 5–1000 µg of 1,5-HDE was added to the vial, depending on the experiment, while the pentane content in the headspace of the vial was always kept to 0.05% (v/v). HS-SPME extractions were performed at 25 °C for a time corresponding to the equilibrium time of each fiber (6 min for commercial fibers and 60 min for silver-based PILs fibers, according to Fig. S2 of the SM). Thermal desorption was then performed at 175 °C for 10 min, using GC-FID according to Fig. S1 (C) of the SM. After each desorption, a cleaning step of the fiber was performed in the GC inlet for 10 min.

The pentane content did not affect the selectivity of the fibers towards 1,5-HDE *versus* 1-HE in the range between 0.005% and 0.05% (v/v).

2.3.5. *DI-SPME-GC-MS procedure for the determination of fatty acids*

A sample volume of 19 mL (or aqueous standard solution) was added to a 20 mL vial containing a stir bar (1 cm length × 0.5 cm diameter, from Fisher Scientific). The vial was sealed with a metallic screw cap containing a PTFE/silicone septum and placed on a Corning PC-420D magnetic stirring hotplate (Corning, NY, USA). DI-SPME was performed by directly exposing the fiber to the solution. Under optimum conditions, extractions were performed at 25 °C for 60 min at a stirring rate of 600 rpm. Thermal desorption was then performed in the GC inlet for 10 min using the temperatures detailed in Section 2.2, resulting in the chromatograms shown in Fig. S1 **(D)** of the SM.

3. Results and discussion

3.1. *Development of silver-based PIL sorbent coatings*

The development of materials with relatively high thermal stability is of vital importance in SPME, especially when the technique is coupled with thermal desorption of the analytes. For that reason, one of the main goals of this study was to improve the thermal stability of the silver-based ILs that have been previously reported in the literature [19,21]. In one of these studies, an analogous class of silver-based ILs was used as GC stationary phases, with maximum allowable operating temperatures of 125–150 °C being reported [19]. In the current study, the introduction of polymerizable moieties within the structure of the IL (i.e., the vinyl groups appended to the imidazole ligands) allows polymerization of the silver-based IL to generate the corresponding PIL. As expected, PIL **1**, obtained by the polymerization of the neat silver-based IL monomer, was stable at temperatures higher than 200 °C when exposed to the GC inlet, a notable increase over previously reported works [19]. PILs **2**–**7** were prepared by the polymerization of different silver-IL mixtures containing a certain amount of $[\mathrm{Ag^+(ACN)}][\mathrm{NTf_2^-}]$ (as shown in Table 1). As the free silver(I) cannot be polymerized, it likely affects the properties of the final polymer. However, the experimental results showed only slightly lower thermal stabilities compared to PIL **1** (up to 200 °C). Finally, a thermal desorption temperature of 175 °C was selected for all silver-based PIL sorbent coatings in order to ensure adequate desorption of the analytes and to extend the lifetime of the fibers.

Additionally, it was observed that the viscosity of the silver-based PILs significantly decreased when the amount of [Ag$^+$(ACN)][NTf$_2$] within the sorbent coating was increased. Thus, fibers with a molar excess of [Ag$^+$(ACN)][NTf$_2$] greater than 1.5 (PIL **5**) were not practical to be successfully supported on the fiber.

3.2. Silver-based PIL sorbent coatings for the selective extraction of unsaturated compounds by HS-SPME

3.2.1. Selectivity comparison of the silver-based PILs

The selectivity of the developed silver-based PILs towards the extraction of unsaturated compounds was evaluated by performing HS-SPME extractions from a standard solution containing a variety of alkenes and alkynes consisting of five to nine carbon atoms. This group of compounds included linear alkenes and alkynes, substituted alkenes, mono-unsaturated alkenes, and alkenes with two terminal or non-terminal double bonds. Different isomers were also studied, including *trans*- and *cis*-2-HE, and the three most stable conformational isomers of 1,3-HDE and 2,4-HDE (anti, gauche, and eclipsed conformers). HA was also included as an analyte. Table 2 shows the peak area ratios obtained by dividing the chromatographic peak area of each analyte with respect to the chromatographic peak area of HA for all studied SPME fibers. These values allow for a crude comparison of the selectivity offered by the fibers for the extraction of unsaturated compounds.

Considering only the studied commercial SPME fibers, the lowest peak area ratios in all cases was achieved for 1,4-PDE. For this analyte, peak area ratios lower than 1 were obtained, indicating that the commercial fibers were more suitable for the extraction of HA than for 1,4-PDE. The same observation was made in the case of up to 10 unsaturated compounds for PDMS, up to 6 for DVB-PDMS, up to 5 for DVB/CAR-PDMS, and up to 3 for CAR-PDMS. On the other hand, the highest peak area ratios were obtained for 1-NE and 1,8-NDE using all commercial fibers (and also for one of the isomers of 2,4-HDE using the CAR-PDMS fiber). This observation suggests that the commercial fiber exhibits more interactions with long-chained unsaturated compounds. In general, CAR-PDMS was the most selective commercial fiber in the determination of the target alkenes and alkynes.

Completely different behavior was observed for the silver-based PILs. Considering only those fibers composed of linear polymers (PIL **1**–**5**, see Table 1), it is interesting to highlight the behavior of PIL **1**, prepared by polymerizing the neat silver IL monomer. For this fiber, peak area ratios lower than 1 were achieved for the majority of analytes, with the exception of 1-NE, 2-M-1,5-HDE and 1,8-NDE. This indicates that this particular fiber is not especially selective toward this group of unsaturated compounds. However, for the remaining group of linear PILs that contain silver IL mixtures (e.g., [Ag$^+$(VIM)$_2$][NTf$_2$] and [Ag$^+$][NTf$_2$], PIL **2**–**5** according to Table 1), much greater peak area ratios were obtained (on average, 20 for PIL **2**, 203 for PIL **3**, 202 for PIL **4**, and 106 for PIL **5**). In comparison, the highest peak area ratio obtained for all commercial fibers was 16.

In general, an increase in the selectivity was observed for the analytes when the [Ag$^+$][NTf$_2$] molar excess in the PIL increased from 0.5 mol (PIL **2**) to 1.0 mol (PIL **4**), followed by a decrease in selectivity at higher molar excess. The increased selectivity in the presence of excess [Ag$^+$][NTf$_2$] is in agreement with a previous study using analogous silver-based ILs as GC stationary phases [19]. In the case of PIL **5**, a thinner sorbent coating was prepared due to the lower viscosity of the IL mixture used as monomer, likely the result of a higher excess of free [Ag$^+$][NTf$_2$], which yielded decreased selectivity. On the other hand, peak areas ratios similar to or lower than PILs **2**–**4** were achieved for the two crosslinked silver PILs (PIL **6**–**7**). The lower selectivity of these SPME fibers can be attributed to the presence of the [(VIM)$_2$C$_{12}^{2+}$] 2[NTf$_2$] crosslinker, which may reduce interactions of the analytes with the silver (I) ions.

PILs **2**–**7** exhibited remarkable selectivity in the extraction of analytes possessing terminal double bonds, including 1,5-HDE, 2-M-1,5-HDE, and 1,8-NDE. For these analytes, peak area ratios up to 1970, 1953, 1104, and 1008 were achieved for PILs **3**, **4**, **7**, and **4**, respectively. Furthermore, for these three analytes extraction efficiencies higher than CAR-PDMS were achieved for PILs **3**–**7** in the case of 1,5-HDE, and for PILs **3**–**5** and **7** in the extraction of 2-M-1,5-HDE. Similar extraction efficiency to CAR-PDMS was achieved for PIL **4** in the extraction of 1,8-NE, as shown in Fig. 2. Previous studies have indicated that the maximum stability of the chelate silver (I) – double bond in the case of terminal diolefins is achieved for molecules with six carbon atoms, such as 1,5-HDE [24]. Although the extraction efficiency of the silver-based PILs **2**–**7** was similar to or

Table 2

Peak area ratios (peak area of each analyte with respect to the peak area of hexane) obtained after employing the HS-SPME-GC-FID method with both commercial and silver-based PILs. Experimental conditions (n = 3): 1 μL of standard solution of the analytes, HS-SPME extraction (6 min, 25 °C), thermal desorption (10 min, 175 °C), and GC-FID. See Table 1 for the composition of the silver-based PIL fibers.

Analyte	Peak area ratio										
	DVB/CAR-PDMS	CAR-PDMS	PDMS	DVB-PDMS	PIL 1	PIL 2	PIL 3	PIL 4	PIL 5	PIL 6	PIL 7
1,4-PDE	0.06	0.09	0.03	0.04	0.04	0.52	5.2	1.9	2.3	3.3	0.41
trans-2-HE	1.1	1.4	0.89	1.1	0.67	1.8	11	12.9	6.3	7.6	4.2
1-HE	0.94	1.1	0.84	0.93	0.80	4.2	29	31	15	16	11
cis-2-HE	1.3	1.4	1.1	1.3	0.83	4.3	32	32	16	16	13
1,3-HDE (1)	1.4	2.9	0.53	0.89	0.23	2.6	19	22	9.1	11	9.1
1,3-HDE (2)	2.0	4.2	0.69	1.3	0.37	3.5	30	31	13	16	14
1,3-HDE (3)	0.37	0.72	0.09	0.22	0.05	0.50	1.2	1.4	0.63	0.89	0.64
2,4-HDE (1)	0.28	0.63	0.08	0.17	0.04	0.34	2.7	3.4	1.3	1.4	1.5
2,4-HDE (2)	7.4	15	1.1	2.5	0.52	4.3	29	33	14	17	15
2,4-HDE (3)	3.2	7.3	0.68	1.5	0.33	3.1	22	27	11	12	13
2,3-DM-1,3-BDE	0.80	1.2	0.70	0.81	0.55	2.0	6.9	11	4.1	6.4	3.5
3-HY	1.3	1.9	1.0	1.4	0.78	4.2	22	31	11	17	11
2-HY	1.7	3.0	1.1	1.4	0.76	3.9	21	30	10	16	10
1-NE	15	15	13	16	2.6	10	54	108	34	26	36
1,5-HDE	1.3	1.8	0.79	1.1	0.69	103	991	904	540	329	376
2-M-1,5-HDE	4.5	7.1	2.5	3.8	1.5	177	1970	1953	1008	595	1104
1,8-NDE	15	16	11	15	2.9	115	997	1629	343	341	780
Average	*2.7*	*4.0*	*1.6*	*2.7*	*1.0*	*20*	*203*	*202*	*106*	*68*	*101*

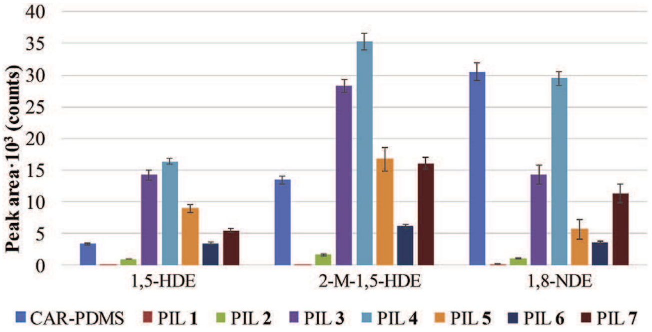

Fig. 2. Extraction efficiency, expressed as chromatographic peak area, obtained for the studied analytes after performing HS-SPME with seven silver-based PIL fibers and CAR-PDMS. Experimental conditions (n = 3): 1 µL of standard solution containing 10 µg of each analyte, HS-SPME (6 min, 25 °C), thermal desorption (10 min. at 175 °C), and GC-FID.

lower than commercial fibers (Fig. S3 and S4 of the SM), higher peak area ratios were achieved for the remaining unsaturated compounds in the majority of cases for the silver-based PILs.

3.2.2. *Extraction mechanism of the silver-based PILs*

The extraction mechanism refers to the mode in which analytes undergo sorption from the sample to the sorbent coating. The two primary sorption modes are absorption or adsorption. In absorption-based fibers such as PDMS and PA, diffusion in the coating enables the analytes to freely partition into the sorbent. Therefore, non-competitive partitioning of the analytes from the sample (or HS) to the fiber generally results and, under optimum conditions, the concentration of each extracted analyte will depend on the coating volume [25]. In adsorption-type extractions such as those exhibited by CAR-PDMS, DVB/CAR-PDMS, or DVB-PDMS, there is substantial reduction in diffusion through the coating, resulting in sorption that often occurs on the surface of the fiber. Thus, when the analyte concentration is relatively high, analytes undergo competition in interacting with the limited sites available in the coating. As a result, the concentration of the analytes can be affected under equilibrium conditions, especially for those compounds that possess less affinity to the sorbent coating [4]. Therefore, the competitive or adsorption-type extraction mechanism can be evaluated by studying changes in the sensitivity of a target analyte extracted in the presence of one or various interfering species [25,26].

The two silver-based PILs selected for evaluating the sorption mechanism were PIL **4**, which exhibited the highest selectivity toward the entire group of studied unsaturated compounds according to Section 3.2.1, and an analogous silver-based PIL with crosslinker, PIL **7**. The extraction mechanism of the PDMS and CAR-PDMS fibers was also evaluated and compared to the silver-based PILs. The study was performed using a similar approach previously reported in which calibration curves of the target analyte in the presence of different concentrations of a possible interfering compound were developed [26]. In this study, 1-HE was selected as the target analyte and 1,5-HDE was selected as the interfering compound. This implies that if a competitive partitioning mechanism is observed for the silver-based PILs, 1,5-HDE will preferably interact with the surface of the sorbent coating and, as the concentration of the analytes increases, competition will be more pronounced resulting in a decreased amount of 1-HE extracted.

Two types of calibration curves were developed for each SPME fiber in the range between 5 and 110 µg for 1-HE, and in the presence of 1,5-HDE at the relative concentration ratios of 1:1 and 1:10 (1-HE:1,5-HDE ratio). Fig. 3 shows the plots representing the peak area *versus* the spiked amount of 1-HE obtained for each fiber at the two aforementioned ratios. From a direct comparison of the plots, it can be concluded that the silver-based PILs exhibit similar behavior to the CAR-PDMS fiber. For these three fibers, a decrease in the 1-HE peak area is observed in the 1:1 to 1:10 ratio of 1-HE:1,5-HDE, indicating that adsorption is more prevalent. On the contrary, the extraction mechanism was very different than that observed for PDMS. For this fiber, no significant change in the peak area of 1-HE was observed when the relative ratio of 1-HE:1,5-HDE was increased from 1:1 to 1:10, which is in agreement with the typical non-competitive partitioning behavior described for these fibers.

A deeper evaluation of the fibers can be conducted by comparing the calibration slopes obtained for the linear segments of the curves included in Fig. 3 (in the 5–64 µg range of 1-HE for PIL **4**, and in the 5.0–85 µg range for the remaining fibers). As shown in Table S3 of the SM, the calibration slopes decreased by 89%, 63%, and 53% for PIL **4**, PIL **7** and CAR-PDMS, respectively, when the 1-HE:1,5-HDE ratio was increased from 1:1 to 1:10. For PDMS, there was no significant change in the calibration slope when the ratio was increased. Previous studies in our group showed that conventional PIL sorbent coatings containing imidazolium-based IL monomers (and crosslinkers, depending on the fiber), extracted analytes via a non-competitive partitioning mechanism [26]. Therefore, it can be concluded that the incorporation of silver(I) into the PIL structure plays a significant role in the observed adsorptive-type extraction mechanism. Furthermore, this likely explains why the decrease in the calibration slopes from the 1:1 to 1:10 ratio is more pronounced for PIL **4** than for PIL **7** as the presence of the crosslinker in PIL **7** decreases the total concentration of silver(I) in the coating, thereby limiting the adsorption tendency of the fiber.

3.3. *Silver-based PIL sorbent coatings for the sensitive preconcentration of fatty acids by DI-SPME*

After demonstrating the selectivity of the silver-based PILs for the extraction of unsaturated compounds in the HS-SPME mode, the fibers were applied for the determination of three unsaturated fatty acids containing up to 3 double bonds (e.g. $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$). DI-SPME was selected for this application due to the non-volatile nature of the selected analytes and to demonstrate the suitability of the silver-based PILs in this sampling mode. Among all of the developed silver-based PILs, PIL **4** and PIL **7** were studied for the reasons explained in Section 3.2.2.

3.3.1. *Optimization of the DI-SPME procedure*

Firstly, a screening of different commercial SPME fibers was performed in order to select the most ideal commercial fiber for the determination of the unsaturated fatty acids. The commercial fibers tested included PDMS, DVB-PDMS, CAR-PDMS, and PA. The results, shown in Fig. S5 of the SM, demonstrated that PDMS was the most suitable commercial fiber for the determination of the three analytes. The entire method was optimized and validated using PDMS, PIL **4**, and PIL **7**.

The most influential parameters in the method including the stirring rate, extraction time, and desorption time were optimized for each selected fiber. Extractions were performed at a fixed volume of 19 mL to ensure adequate preconcentration of the analytes, with desorption temperatures of 260 °C and 175 °C for the PDMS fiber and the silver-based PILs, respectively.

The stirring rate in the extraction vial plays an important role in DI-SPME. The stirring of the sample promotes the convection of analytes from the bulk of the solution to the fiber, thereby increasing the extraction efficiency and decreasing the equilibrium time [4]. Therefore, the influence of stirring in the extraction was

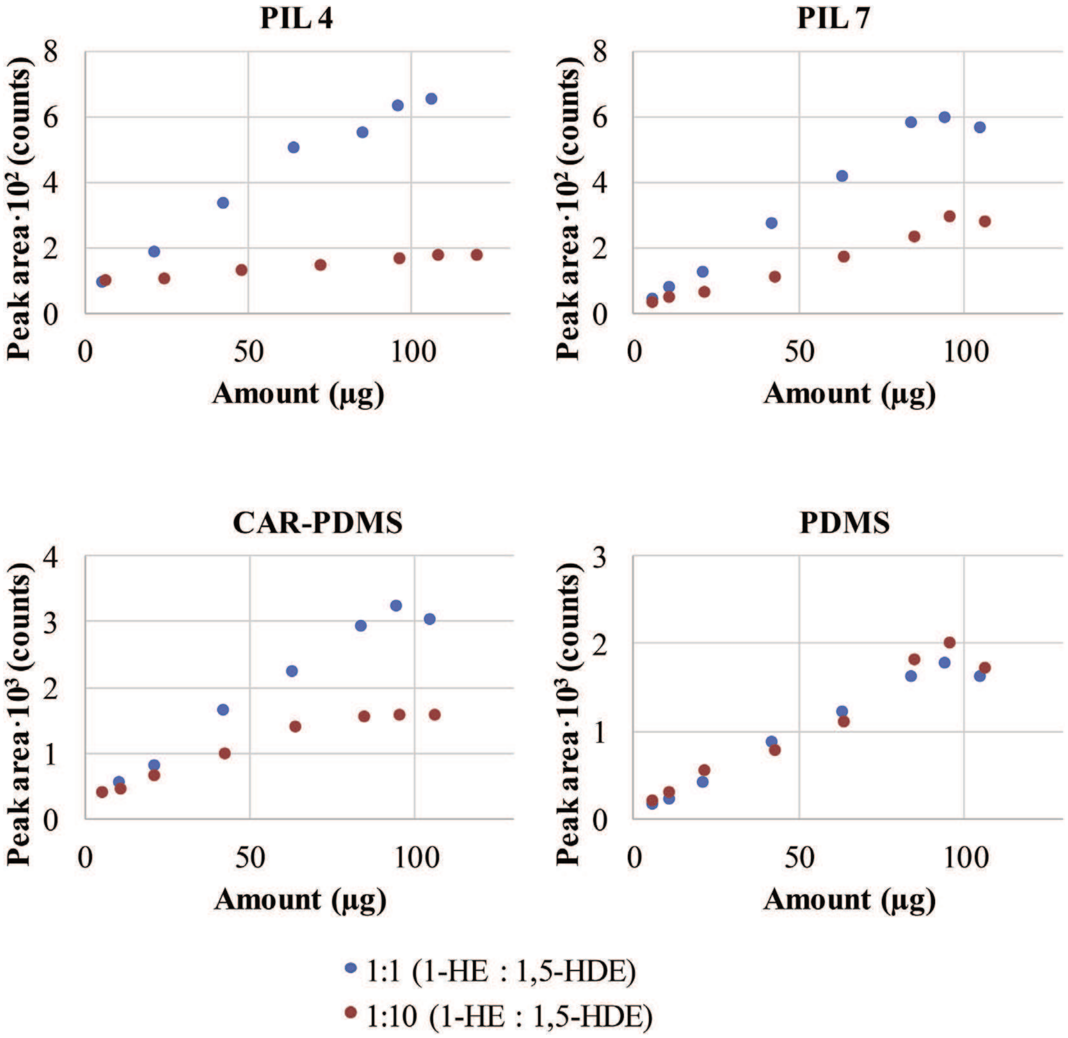

Fig. 3. Calibration curves of 1-HE in the presence of 1,5-HDE at two different ratios: 1:1 and 1:10 (excess of 1,5-HDE) using four SPME fibers. Experimental conditions (n = 3): 10 µL of standard solution containing 1-HE and 1,5-HDE. HS-SPME (6 min for commercial fibers, 60 min for silver-based PILs, 25 °C), thermal desorption (10 min at 175 °C), and GC-FID.

studied for each fiber in the range between 200 and 600 rpm, as shown in Fig. S6 of the SM. The results are similar for all studied fibers and indicate an enhancement in the extraction efficiency when the stirring speed is increased. A stirring rate of 600 rpm was selected as optimum in all cases. Higher stirring rates were not studied to avoid the damage to the sorbent coating.

The extraction time was studied in the range between 15 and 100 min for each fiber (Fig. S7 of the SM). The behavior of the three fibers was similar and the extraction time profiles indicated that the analytes did not achieve equilibrium in the studied time range. It was observed that the extraction efficiency continued to increase with prolonged extraction time for all analytes/fibers studied. In light of these results, an intermediate extraction time of 60 min was selected as optimum for all fibers. This time was chosen in order to achieve a compromise between extraction time while achieving adequate sensitivity.

The desorption time was also studied for each fiber in the range between 2 and 10 min. The results, included in Fig. S8 of the SM, indicated that 6 min was adequate for the desorption of the analytes using the PDMS fiber whereas 10 min was required for PIL **4** and **7**. Finally, a desorption time of 10 min was selected for all fibers to ensure no analyte *carry over*; this desorption time did not reduce the extraction efficiency of the PDMS fiber.

3.3.2. Analytical performance of the developed DI-SPME methods

External calibration curves for the unsaturated fatty acids were developed with the three studied fibers under optimum conditions. The analytical performance metrics of the fibers, including linear range, correlation coefficient (R), sensitivity, limit of detection (LOD), reproducibility and relative recovery (RR) are shown in Table 3.

Wide linear ranges were obtained for the PDMS fiber (50–1000 µg L^{-1}) and for PIL **7** (50–1000 µg L^{-1}), whereas PIL **4** exhibited a narrower range (from 50 to 600 µg L^{-1} for $C_{18:1}$ and $C_{18:2}$, and from 50 to 1000 µg L^{-1} for $C_{18:3}$). The R values were higher than 0.990 for all fibers.

The sensitivity of the fibers was evaluated based on the calibration slope. The obtained values ranged from $(105 \pm 6)\cdot 10^4$ to $(916 \pm 35)\cdot 10^4$ for PDMS, from $(293 \pm 41)\cdot 10^4$ to $(434 \pm 28)\cdot 10^4$ for PIL **4,** and from $(149 \pm 7)\cdot 10^4$ to $(817 \pm 24)\cdot 10^4$ for PIL **7**. It is important to highlight that the silver-based PILs were more sensitive than the PDMS fiber for the determination of $C_{18:1}$ and $C_{18:2}$. For these analytes, the calibration slopes of PIL **4** were between 1.2 ($C_{18:2}$) and 2.8 ($C_{18:1}$) times higher than the calibration slopes of PDMS, and between 1.1 ($C_{18:2}$) and 1.4 ($C_{18:1}$) times higher than PDMS in the case of PIL **7**.

The LODs were estimated as the concentration corresponding to

Table 3
Analytical performance of the DI-SPME-GC-MS method for the determination of unsaturated fatty acids using different SPME fibers and 6–7 calibration levels.

Analyte	Working range (μg·L^{-1})	(Slope ± SD[a])·10^{-4}	R[b]	$S_{y/x}$[c]·10^{-5}	LOD[d] (μg·L^{-1})	Spiked level 1[e]		Spiked level 2[f]	
						RSD[g] (%)	RR[h] (%)	RSD[g] (%)	RR[h] (%)
PDMS									
$C_{18:1}$	50–1000	105 ± 6	0.995	0.45	17	4.3	120	2.4	119
$C_{18:2}$	50–1000	353 ± 26	0.990	2.3	4.6	4.5	111	2.5	120
$C_{18:3}$	50–1000	916 ± 35	0.997	3.1	1.4	2.6	101	6.5	108
PIL **4**									
$C_{18:1}$	50–600	293 ± 41	0.991	1.9	5.2	4.3	85.9	2.0	98.0
$C_{18:2}$	50–600	434 ± 28	0.994	1.3	2.1	2.9	84.3	3.1	88.2
$C_{18:3}$	50–1000	345 ± 15	0.996	1.4	5.5	4.1	90.2	12	102
PIL **7**									
$C_{18:1}$	50–1200	149 ± 7	0.995	0.80	8.2	8.5	115	17	110
$C_{18:2}$	50–1200	371 ± 19	0.993	2.2	3.2	2.8	109	4.0	108
$C_{18:3}$	50–1200	817 ± 24	0.998	2.8	2.6	1.3	107	4.8	112

[a] Standard deviation of the slope.
[b] Correlation coefficient.
[c] Standard deviation of the residuals (error of the estimate).
[d] Limit of detection, calculated as 3 times the signal-to-noise ratio.
[e] 160 μg L^{-1}.
[f] 500 μg L^{-1}.
[g] Relative standard deviation (n = 3).
[h] Relative recovery.

three times the signal-to-noise ratio, and the values were verified by performing extractions at the obtained levels. The LODs ranged from 1.4 to 17 μg L^{-1} for PDMS, from 2.1 to 5.5 μg L^{-1} for PIL **4**, and from 2.6 to 8.2 μg L^{-1} using PIL **7**.

The reproducibility was calculated as the relative standard deviation (RSD) obtained for three replicates at two spiked levels of fatty acids, namely, 160 and 500 μg L^{-1}. For the lower spiked level, the RSDs oscillated between 2.6% and 4.5% for PDMS, between 2.9% and 4.3% for PIL **4**, and between 1.3% and 8.5% for PIL **7**.

The percent relative recovery (RR) was determined as the ratio of the predicted concentration using the calibration curves of Table 3 and the spiked concentration. For the lower spiked level, they ranged from 101% to 120% for PDMS, from 84.3% to 90.2% for PIL **4**, and from 107% to 115% for PIL **7**.

The lifetime of the developed silver-based PILs was also evaluated. If both PIL **4** and PIL **7** are compared, a limited lifetime was observed in the DI-SPME mode for PIL **4** (~48 extraction/desorption cycles per fiber). On the other hand, PIL **7** was used for more than 80 extraction/desorption cycles without a significant loss in the extraction efficiency. This behavior can be easily explained based on the structure of both PILs. The absence of crosslinker in the case of PIL **4** likely prompts a decrease in the stability of the fiber when it is directly exposed to the aqueous sample, resulting in reduced its lifetime. However, this situation was not observed when the fibers were applied in the HS-SPME mode (Section 3.2). In this case, the lifetime of the fibers was completely comparable independent of the polymer type (linear or crosslinked) and was limited by the thermal stability of the silver(I) complexes that are part of the PIL structures.

3.3.3. *Analysis of real samples*

The final step of the study was to demonstrate the applicability of the developed silver-based PILs for the analysis of real samples. Rinse water was obtained from a dairy farm milk pipeline cleaning process and analyzed by the DI-SPME-GC-MS method. Three rinse water samples, denoted as rinse water (1), (2), and (3), were collected at the beginning, middle, and end of the cleaning process, respectively. Among the two studied silver-based PILs, PIL **7** was selected for analysis due to its enhanced stability when exposed to aqueous samples. For the analysis, matrix matched calibration in tap water was used for the prediction of the concentration of rinse water. Table 4 shows the analytical figures of merit obtained in the tap water calibrations. LODs ranging from 12 to 14 μg L^{-1} in tap water were obtained, values that are especially low for the determination of fatty acids [27,28]. Fig. 4 shows the predicted concentration for the samples. A decrease in the concentration of the three unsaturated fatty acids was observed from the beginning to the end of the cleaning procedure, with analytes detected at concentrations between 52 and 179 μg L^{-1}.

4. Conclusions

A total of seven silver-based PIL sorbent coatings were successfully developed and applied in HS- and DI-SPME. The fibers

Table 4
Analytical performance of the DI-SPME-GC-MS method for the determination of unsaturated fatty acids in tap water using silver-based PIL **7** (5 calibration levels).

Analyte	Working range (μg·L^{-1})	(Slope ± SD[a])·10^{-5}	R[b]	$S_{y/x}$[c]·10^{-5}	LOD[d] (μg·L^{-1})	Spiked level of 160 μg L^{-1}	
						RSD[e] (%)	RR[f] (%)
$C_{18:1}$	50–400	145 ± 6	0.991	1.7	12.0	6.0	109
$C_{18:2}$	50–400	47 ± 12	0.994	3.3	14.4	10.1	99.8
$C_{18:3}$	50–400	18 ± 2	0.996	0.53	13.5	13.4	97.5

[a] Standard deviation of the slope.
[b] Correlation coefficient.
[c] Standard deviation of the residuals (error of the estimate).
[d] Limit of detection, calculated as 3 times the signal-to-noise ratio.
[e] Relative standard deviation (n = 3).
[f] Relative recovery.

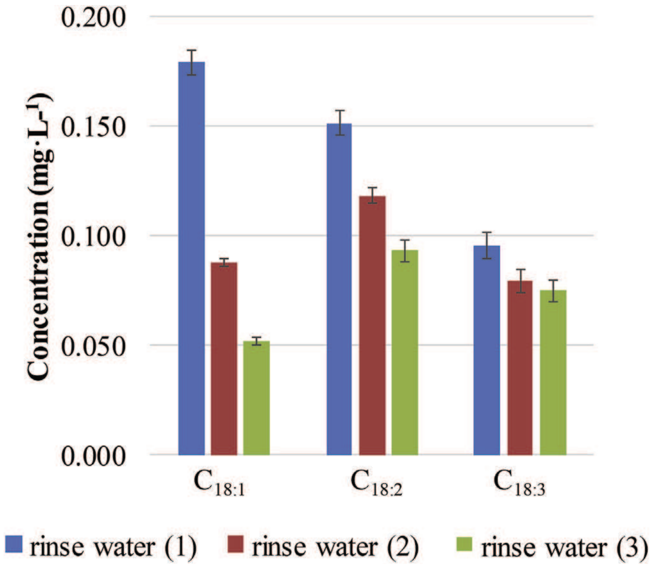

Fig. 4. Analysis of rinse water obtained from a dairy farm milk pipeline rinse cleaning process using PIL **7** coupled to DI-SPME-GC-MS. Samples were collected at the beginning (1), middle (2), and end (3) of the cleaning process.

were prepared by the polymerization of the silver-based IL monomer ($[Ag^+(VIM)_2][NTf_2]$) and, in some cases, different molar excesses of $[Ag^+(ACN)][NTf_2]$. Crosslinked co-polymers were prepared by adding the $[(VIM)_2C_{12}^{2+}]$ $2[NTf_2]$ IL crosslinker.

The silver-based PILs exhibited unique selectivity in the determination of alkenes and alkynes via HS-SPME, and were particularly selective for analytes with terminal double bonds, including 1,5-HDE, 2-M-1,5-HDE, and 1,8-NDE. The silver-based PILs extracted these types of unsaturated compounds by a competitive partitioning mechanism. This extraction mechanism is the result of silver(I) within the PIL structure, and can be modulated by increasing or decreasing the amount of free $[Ag^+(ACN)][NTf_2]$ and IL crosslinker.

In DI-SPME, the silver-based PILs were found to exhibit sensitivity in the determination of unsaturated fatty acids including $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$. In particular, the calibration slopes of PIL **4** and PIL **7** were are up 2.8 times higher than the calibration slopes of PDMS, which was the most suitable commercial fiber for the determination of these analytes. Low LODs were achieved for these fibers, and ranged from 2.1 to 5.5 $\mu g\ L^{-1}$ for PIL **4** and from 2.6 to 8.2 $\mu g\ L^{-1}$ for PIL **7**, values that are especially low in the determination of fatty acids [27,28].

The lifetime of the fibers in DI-SPME (number or extraction/desorption cycles without a significant loss of the extraction efficiency) was ~48 cycles for PIL **4** and 80 cycles for PIL **7**. The crosslinked PIL **7** fiber was applied for the analysis of rinse water samples. The analytes were successfully detected and quantified in the real samples, with concentrations between 52 and 179 $\mu g\ L^{-1}$.

Ongoing work is devoted towards improving the mass transfer and analyte capacity of the silver-based PILs by using different SPME geometries. The objective is to employ supports that permit a thin film of the sorbent to be attached to the support while featuring high surface area, facilitating large preconcentration of analytes [29].

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2018.09.051.

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