



## Ionic liquid-functionalized silica for selective solid-phase extraction of organic acids, amines and aldehydes

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### ABSTRACT

Three ionic liquid (IL)-functionalized silica materials, imidazolium, N-methylimidazolium and 1-alkyl-3-(propyl-3-sulfonate) imidazolium, were synthesised and applied in solid-phase extraction (SPE) of organic acids, amines and aldehydes, which are important compound families in atmospheric aerosol particles. 1-Alkyl-3-(propyl-3-sulfonate) imidazolium-functionalized silica was tested as sorbent for SPE for the first time. The analytes were separated and detected by liquid chromatography–mass spectrometry (LC–MS). To confirm the results achieved by LC–MS, the acids were additionally determined by gas chromatography–mass spectrometry (GC–MS). The stability of the IL-functionalized silica materials was tested at low and high pH. The effect of the pH on the extraction was also informative of the retention mechanism of the materials. The results showed anion exchange to be the main interaction, but hydrophobic and  $\pi$  interactions and hydrogen bonding also played a role in the extraction. Extraction efficiencies for organic acids ranged from 87 to 110%, except for *cis*-pinonic acid (19–29%). Lower extraction efficiencies for amines and aldehydes confirmed that anionic exchange was the predominant interaction. Comparisons made with two commercial SPE materials—silica-based strong anion exchange (SAX) and polymer-based mixed-mode anion exchange and reverse-phase (MAX)—showed the IL-functionalized materials to offer different selectivity and better extraction efficiency than SAX for aromatic compounds. Finally, the new materials were successfully tested in the extraction of an atmospheric aerosol sample.

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### 1. Introduction

Ionic liquids (ILs) are molten salts consisting of organic cations (e.g., imidazolium, pyrrolidinium, pyridinium, tetraalkyl ammonium, tetraalkyl phosphonium) and numerous different inorganic or organic anions (e.g., tetrafluoroborate, hexafluorophosphate, bromide). The potential of ILs in chemistry is related to their unique properties as non-molecular solvents, negligible vapour pressure associated with high thermal stability, tunable viscosity, miscibility with water and organic solvents, and good extractability for various organic compounds and metal ions [1]. Their polarity, hydrophobicity, viscosity, and other chemical and physical properties can be tailored through choice of the cationic and anionic constituents [1].

The growing interest in ILs in analytical chemistry is evident in the dramatic increase in the number of publications during the last

decade and the excellent reviews published in 2010 [1–5]. Studies of ILs in analytical chemistry have mostly been related to extraction [4] and separation [6]. In the last two decades, ILs have taken a step forward and been immobilized on silica particles, thereby providing new sorbents with interesting properties. The new sorbents have been applied as stationary phases in liquid chromatography (LC) [7–9] and as sorbents in solid-phase extraction (SPE) [10–16]. The power of these sorbents rests on their dual nature: they act as low-polarity phases for non-polar compounds and in the opposite manner for compounds bearing strong proton-donor groups [1]. This behaviour depends on the separation mechanism, which involves multiple interactions (electrostatic, hydrophobic,  $\pi$ ). It is important to note that once the IL is immobilized on a surface it loses its liquid state [17]. However, its other unique properties, such as low volatility and its polarity supporting non-polar and ionic interactions, are maintained [18].

Use of imidazolium-based zwitterionic IL-silica as stationary phase in LC has shown promising results [9]. In the preparation of this material, 1,3-propane sultone was added to imidazolium IL-functionalized silica to give 1-alkyl-3-(propyl-3-sulfonate) imidazolium (SilmPS). The main difference between imidazolium and N-methylimidazolium IL-functionalized silica materials and SilmPS is the longer alkyl chain and the presence of the sulfonate group.

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Hence, the immobilized group can play two different roles by enhancing hydrophobicity and/or by acting as ion exchange site [9].

A few studies have described the use of IL-functionalized silica for SPE of organic compounds [10–16]. Tanshinone I and tanshinone IIA have been extracted from *Salvia miltiorrhiza bunge* [10,11] and ginseng drinks [11], 12 sulfonylurea herbicides from environmental water and soil samples [12], lactic acid from fermentation broth [13], liquiritin and glycyrrhizic acids from licorice [14], essential fatty acid methyl esters from soy-derived biodiesel [15] and polyunsaturated fatty acid methyl esters from fish oil [16]. The ILs most often covalently bonded to silica, as sorbent for SPE, have been imidazolium [11,13], N-methylimidazolium [10,12,13,15,16] and 2-ethyl-4-methylimidazolium [13,14], with chloride [10,11,13,14], tetrafluoroborate [15,16] or hexafluorophosphate [12,15,16] as anion.

Up to now, most studies on the extraction capability of IL-functionalized silica have focused on specific applications. No study has focused on how these materials behave in SPE at different pH for compounds with diverse properties (i.e., acidic, basic and neutral). We investigated the behaviour of three IL-functionalized silica materials at different pH to clarify the retention mechanisms in SPE for different compounds. Organic acids, amines and aldehydes were selected on the basis of their different properties and their presence in atmospheric aerosols, whose chemical composition is of keen interest in our understanding of climate change. Highly oxidized compounds, such as carboxylic acids and keto- and dicarboxylic acids, are of particular interest because of their low saturation pressure and consequent high aerosol-forming potential [19,20]. Amines and aldehydes, in turn, may play a vital role at the beginning of the aerosol cycle [21–23]. The chemical complexity of these compounds requires the use of highly selective sample treatment techniques, such as SPE.

In the present work three IL-functionalized silica materials, imidazolium (SilprIm), N-methylimidazolium (SilprMim) and SilmPS, were synthesized and applied in SPE, one of them (SilmPS) for the first time. After the stability of the materials was determined at low and high pH, cartridges packed with the silica materials were applied to the extraction of atmospherically relevant organic compounds: six acids (azelaic, adipic, vanillic, sebacic, *cis*-pinonic and pinic), three amines (triethylamine, quinoline and tripropylamine) and two aldehydes (cinnamaldehyde and  $\beta$ -caryophyllene aldehyde). The three groups of analytes were separated and detected by liquid chromatography–mass spectrometry (LC–MS). To confirm the LC–MS results, the acids were additionally determined by gas chromatography–mass spectrometry (GC–MS). The results obtained with the IL-functionalized silica materials were compared with results obtained with commercial SPE cartridges packed with silica-based strong anion exchange (SAX) and polymer-based mixed-mode anion exchange and reverse-phase (MAX) sorbent. Finally the silica materials were tested in the extraction of an atmospheric aerosol particle sample.

## 2. Experimental

### 2.1. Materials and reagents

The reagents for preparation of IL-functionalized silica materials were silica gel 60 (0.063–0.2 mm, 500 m<sup>2</sup> g<sup>-1</sup>) from Fluka (Sigma–Aldrich Chemie GmbH, Steinheim, Germany), nitric acid (65%) from Riedel-de Haën (Sigma–Aldrich Laborchemikalien GmbH, Seelze, Germany), N-methylimidazole (99%) from Alfa Aesar GmbH & Co. KG (Karlsruhe, Germany), and imidazole (puriss. p.a.), (3-chloropropyl)trimethoxysilane (97%), 1,3-propane sultone and triethylamine (99%) from Sigma–Aldrich (Steinheim, Germany).

Toluene (HPLC grade) was purchased from LAB-SCAN Analytical Sciences (Gliwice, Poland), acetone (>99%) and acetonitrile (HPLC grade) were from VWR International bvba. (Leuven, Belgium), methanol and ethanol (HPLC grade) were from Aldrich (Steinheim, Germany) and dichloromethane was from Sigma–Aldrich.

Acetonitrile, Milli-Q water (DirectQ-UV, Millipore Corp., Billerica, USA) and acetic acid (99%) from Fluka were used for the HPLC analysis.

Anhydrous sodium sulphate from Riedel-de Haën was used for drying organic solvents.

Dipotassium hydrogen phosphate from J.T. Baker Chemicals B.V. (Deventer, Holland), potassium dihydrogen phosphate from Fisher Scientific (Fair Lawn, NJ, USA), orthophosphoric acid (85%) and formic acid (suprapur) from Merck KGaA (Darmstadt, Germany), and ammonium formate ( $\geq 99.995\%$ ) from Sigma–Aldrich were used to prepare buffers and adjust pH of samples.

Pyridine from J.T. Baker Chemicals B.V. and a solution of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) purchased from Sigma–Aldrich were used in the derivatization of organic acids.

Two commercial SPE cartridges, packed with a silica-based strong anion exchange (SAX) sorbent (HyperSep, 100 mg/1 mL, Thermo Electron Corporation, Waltham, MA, USA) and a polymer-based mixed-mode anion exchange and reverse-phase (MAX) sorbent (Oasis, 30 mg/1 mL, Waters, Milford, MA, USA), were tested for comparison with the IL-functionalized silica materials.

Three groups of analytes were selected to evaluate the sorbents: (i) azelaic acid (>99%), vanillic acid (97%) and sebacic acid (purum.) from Fluka Chemie GmbH (Buchs, Switzerland), adipic acid (99%) from BDH Chemicals Ltd (Poole, England), and pinic acid (library of rare chemicals, no purity available) and *cis*-pinonic acid (98%) from Sigma–Aldrich; (ii) triethylamine (99%) from Sigma–Aldrich, tripropylamine ( $\geq 99\%$ ) from Aldrich and quinoline (98%) from Sigma (Steinheim, Germany); (iii) cinnamaldehyde (99%) from Aldrich and  $\beta$ -caryophyllene aldehyde (BCA), which was synthesised in our laboratory according to Parshintsev et al. [22]. The structures, pK<sub>a</sub> and log P values of the analytes are shown in Table 1.

Standard stock solutions (1000 mg L<sup>-1</sup>) of each analyte were prepared in methanol. Working solutions were prepared in buffer at different pH before the extraction. Amine and aldehydes were studied together and working solutions containing the five compounds were prepared. All solutions were stored at 4 °C.

### 2.2. Atmospheric aerosol sample

A real atmospheric aerosol sample was used to test the applicability of the three IL-functionalized silica materials in SPE of complex matrices. The measurement site (SMEAR II station in Hyytiälä, Finland), meteorological conditions and procedure for the ambient aerosol sampling have been described elsewhere [24]. A quartz filter (240 mm diameter, Munktell, Grycksbo, Sweden) was used in high volume sampling with a flow rate of 80–90 m<sup>3</sup> h<sup>-1</sup>. The filter was preheated at 880 °C for 5 h to remove organic impurities and stored in aluminum foil until needed. Sampling time was 24 h (February 2003). After collection, the sample was kept in a clean glass jar in a freezer at –25 °C. Five pieces (2.5 cm × 2.5 cm) were cut from the filter and put in a beaker with 30 mL of a mixture of acetone and methanol (50:50, v/v) as extraction solvent. The sample was extracted by sonication for 60 min in an ultrasonic bath Eurosonic 44 (J. Dienes Anwendungstechnik, Offenbach, Germany). The extract was evaporated with a gentle flow of nitrogen. Before SPE extraction, the sample was reconstituted in 1.5 mL of phosphate buffer (pH 6.0). The solution was passed through the SPE cartridge, with the conditions described in Section 2.6 for washing and elution. Finally, 40  $\mu$ L of the extract was injected in the

**Table 1**  
Structures,  $pK_a$  and  $\log P$  values of the studied analytes.

Analyte	Structure	$pK_{a1}^a$	$pK_{a2}$	$\log P^f$
Azelaic acid		4.47	5.33 <sup>d</sup>	1.196
cis-Pinonic acid		4.72	N.A. <sup>c</sup>	1.062
Pinic acid		4.64	N.A. <sup>c</sup>	0.820
Adipic acid		4.39	5.41 <sup>d</sup>	-0.105
Sebacic acid		4.48	5.59 <sup>d</sup>	1.706
Vanillic acid		4.50	8.54 <sup>e</sup>	1.304
Triethylamine		10.62 <sup>b</sup>	-	1.647
Quinoline		4.97 <sup>b</sup>	-	2.131
Tripropylamine		9.99 <sup>b</sup>	-	3.175
Cinnamaldehyde		N.A. <sup>c</sup>	-	1.900
$\beta$ -Caryophyllene aldehyde		N.A. <sup>c</sup>	-	N.A. <sup>c</sup>

<sup>a</sup>  $K_a$  = acidic constant, obtained from SciFinder Scholar Database 2007.

<sup>b</sup> Deprotonation of amino moiety.

<sup>c</sup> Not available.

<sup>d</sup> Values obtained from R. Kvaratskhelia, E. Kvaratskhelia, Russ. J. Electrochem. 46 (2010) 952.

<sup>e</sup> Value obtained from F.Z. Erdemgil, S. Şanlı, N. Şanlı, G. Özkan, J. Barbosa, J. Guiteras, J.L. Beltrán, Talanta 72 (2007) 489.

<sup>f</sup> Logarithm of the partition coefficient, obtained from SciFinder Scholar Database 2007.

LC-MS system. The procedure was done three times to test the three IL-functionalized silica materials.

### 2.3. Preparation of ionic liquid-functionalized silica

The silica gel used as support material was activated to enhance the content of silanol groups on the silica surface and to eliminate

metal oxide and nitrogenous impurity. Silica gel (18 g) was stirred with 200 mL nitric acid–water (50:50, v/v) at room temperature for 2 h and refluxed for 8 h. The activated silica was filtered and washed thoroughly with deionized water until the effluent pH was neutral and acetone, then dried overnight at 60 °C [10].

Activated silica (10 g) was suspended in 100 mL of dry toluene, and 10 mL of (3-chloropropyl)trimethoxysilane was added,

followed by 1 mL of triethylamine (added as a catalyst). The suspension was mechanically stirred and refluxed for 24 h. The reaction was then stopped and the functionalized silica was cooled to room temperature, filtered and washed with toluene, ethanol–water mixture (50:50, v/v), deionized water and methanol. The chloropropyl silica (SilprCl) was dried overnight at 60 °C.

### 2.3.1. *N*-methylimidazolium-functionalized silica (SilprMim)

SilprCl silica (5 g) was mixed with 5 mL of *N*-methylimidazole in 60 mL of dry toluene. The mixture was refluxed with stirring for 24 h. The reaction was stopped and the IL-functionalized silica (SilprMim) was cooled to room temperature, filtered and washed with methanol, deionized water and again with methanol, and dried overnight at 60 °C.

### 2.3.2. Imidazolium-functionalized silica (SilprIm)

The modification of silica with imidazole [25] was carried out as for the *N*-methylimidazolium (Section 2.3.1), except that 5 g of imidazole was used.

### 2.3.3. 1-Alkyl-3-(propyl-3-sulfonate) imidazolium-functionalized silica (SilmPS)

For the synthesis of the zwitterionic IL-functionalized silica, 3 g of SilprIm was allowed to react with 3.3 mL of 1,3-propane sulfone in 50 mL of dry toluene [9]. The mixture was refluxed with stirring for 24 h. After refluxing, the reaction was stopped and the IL-functionalized silica (SilmPS) was cooled to room temperature, filtered, washed with toluene, ethanol and acetone, and finally dried overnight at 60 °C.

## 2.4. Characterization of materials

To confirm the immobilization reaction, the amounts of nitrogen, carbon and hydrogen in the activated silica, SilprCl and IL-functionalized silica materials were determined by elemental analysis performed on a Vario MICRO analyser from Elementar Analysen Systeme GmbH (Hanau, Germany). In addition, FT-IR spectra between 650 and 4000 cm<sup>-1</sup> were measured with a Spectrum one FT-IR spectrometer from Perkin Elmer (Waltham, MA, USA).

## 2.5. Stability study of ionic liquid-functionalized silica

Since silica is pH sensitive [26], a stability study of the IL-modified silica materials was carried out to confirm their applicability at the pH values (2, 8, 10 and 12) of interest in this work. Each IL-functionalized material (100 mg) was suspended in 4 mL of phosphate buffers of pH 2, 8, 10 and 12 for 2, 5 and 24 h. Mixtures were mechanically stirred during the whole process. After the selected time, the silica was washed with deionized water until neutral pH was achieved, and then dried at 100 °C. Elemental analysis was carried out to determine the amount of imidazole groups still attached to the silica surface. After the extraction study, 100 mg of the IL-functionalized silica materials treated for 24 h at pH 10 was packed in SPE cartridges and the three groups of compounds were extracted as described in Section 2.6. Amines and aldehydes were also extracted with IL-functionalized silica materials treated for 24 h at pH 12. The results were compared with those obtained with the freshly prepared IL-functionalized silica materials.

## 2.6. Solid-phase extraction

Empty polypropylene cartridges (1 mL) equipped with two polyethylene discs were filled with 100 mg of IL-functionalized silica and equilibrated by flushing with 6 mL of methanol and 6 mL

of deionized water. Cartridges were connected to an SPE manifold (IST VacMaster-20, Biotage AB, Uppsala, Sweden), which was connected to a vacuum pump. The deionized aqueous samples (500 µL), adjusted to pH 6 or 10 depending on the group of analytes, were uploaded onto cartridges and washed with 1 mL of water. Elution was done with 500 µL of acetic acid–water (10:90, v/v) for organic acids and with acetic acid–methanol (10:90, v/v) for amines and aldehydes. In the case of the commercial MAX cartridge, the organic acids were eluted with 500 µL of formic acid–methanol (2:98, v/v) as recommended in the technical specification. Extracts were directly injected to the LC–MS system, but derivatization was required before GC–MS determination of the acids.

## 2.7. Liquid chromatography–mass spectrometry

Analysis was performed with a Hewlett-Packard Series 1100 liquid chromatograph (Palo Alto, CA, USA) coupled to an Esquire 3000 plus ion trap mass spectrometer (Bruker Daltonics, Billerica, MA, USA). Electrospray ionization (ESI) in negative ion mode was used for organic acids and ESI in positive mode for amines and aldehydes. Chromatographic separation was carried out in an XBridge C18 column (4.6 mm × 75 mm, 2.5 µm, Waters Corp., Milford, MA, USA) with gradient 0–2 min 100% of A (1% acetic acid in water), 2–5 min 50% A, 5–7.5 min 25% A, 7.5–15 min 100% B (1% acetic acid in acetonitrile), 15–20 min 100% A. Flow rate was 0.5 mL min<sup>-1</sup> and analysis was done at room temperature. Injection volume was 40 µL for organic acids and 20 µL for amines and aldehydes. Parameters for the ESI–MS were capillary voltage +3600 V (–3600 V for positive mode), end plate offset –500 V, nebulizer pressure 2.76 bar (nitrogen), 12 L min<sup>-1</sup> of drying gas (nitrogen) and drying temperature 350 °C. For organic acids the mass range was 80–230 amu. To ensure identification, MS<sup>2</sup> was used in single reaction monitoring mode for the following ions: 185 amu (pinic acid), 183 amu (*cis*-pinonic acid), 187 amu (azelaic acid), 201 amu (sebacic acid), 167 amu (vanillic acid) and 145 (adipic acid). For amines and aldehydes the mass range was 73–300 amu and the parent ions selected for identification were 102 amu (triethylamine), 130 amu (quinoline), 144 amu (tripropylamine), 133 amu (cinnamaldehyde) and 237 amu (β-caryophyllene aldehyde). Quantitation of target compounds was done with use of extracted ion chromatograms for the parent ions and/or fragments.

## 2.8. Gas chromatography–mass spectrometry

Acids were derivatized before GC–MS analysis. The extract from SPE (500 µL) was dried with a gentle stream of nitrogen and the residue was reconstituted with 20 µL of pyridine and 20 µL of a solution containing BSTFA and 1% TMCS. The vial containing the mixture was heated in a heating module (Dri-Block® DB-3, Techne, Staffordshire, UK) at 60 °C for 60 min, after which 500 µL of dichloromethane was added. The derivatized sample (1 µL) was injected into the GC. An Agilent 6890N gas chromatograph (Agilent Technologies, Pittsburgh, PA, USA) was used with DB5–MS fused silica capillary column (30 m × 0.25 mm I.D., 0.25 µm film thickness, Agilent) coupled with a 3-m deactivated retention gap (I.D. 0.53 mm, Agilent). The injector temperature was set to 280 °C, and the injection was done in splitless mode. Helium at a constant flow rate of 1.0 mL min<sup>-1</sup> was used as carrier gas. The oven temperature program was as follows: initial temperature 30 °C (held for 4 min), increase at 10 °C min<sup>-1</sup> to 300 °C (held for 5 min). The total analysis time was 36 min, plus 5 min for re-establishing and equilibrating the initial conditions. The mass spectrometer was operated in electron impact ionization (EI) mode with ionization energy of 70 eV. Transfer line and ion source temperatures were set to 300 and 230 °C, respectively. The MS detector was operated in SCAN mode,

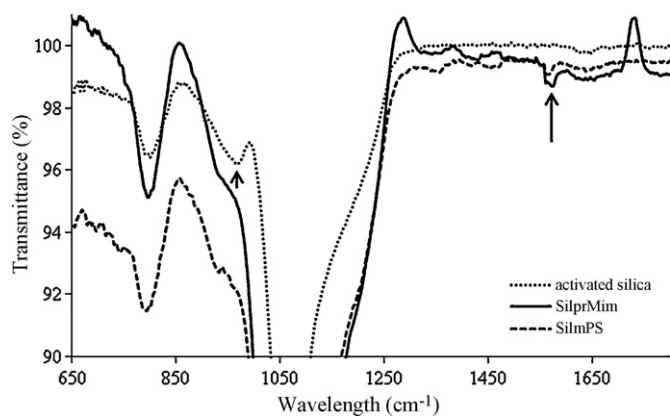


Fig. 1. FT-IR spectrum of activated silica and IL-functionalized silica materials.

and mass-to-charge ratios were measured from 50 to 370 amu. The base peaks were used for quantitation.

### 3. Results and discussion

#### 3.1. Characterization of materials

##### 3.1.1. Elemental analysis

Nitrogen, carbon and hydrogen data from elemental analyses and the surface coverage of nitrogen and carbon on functionalized silica gel are summarized in Table 2. Carbon and nitrogen coverage was calculated according to Ref. [9]. From the percentage of carbon (%C), the concentration of organic groups attached to the silica surface was calculated as  $4.8 \mu\text{mol}/\text{m}^2$  for SilprCl,  $3.7 \mu\text{mol}/\text{m}^2$  for SilprIm,  $3.2 \mu\text{mol}/\text{m}^2$  for SilprMim and  $3.0 \mu\text{mol}/\text{m}^2$  for SilmPS. From the percentages of nitrogen (%N), the concentrations of imidazolium groups bonded to the SilprCl were calculated as  $3.5 \mu\text{mol}/\text{m}^2$  for SilprIm,  $3.1 \mu\text{mol}/\text{m}^2$  for SilprMim, and  $3.0 \mu\text{mol}/\text{m}^2$  for SilmPS. We conclude that the presence of nitrogen enabled the successful immobilization of the imidazole ring onto the silica surface. Moreover, because SilmPS has the same carbon and nitrogen coverage values, it can be assumed that nearly all 1,3-propane sultone was bonded to the imidazolium ring.

##### 3.1.2. FT-IR analysis

FT-IR spectra of the activated silica and two of the IL-functionalized silica materials were recorded between 650 and  $4000 \text{ cm}^{-1}$ . Fig. 1 shows the part of the spectra recorded from 650 to  $1800 \text{ cm}^{-1}$  and clearly displays the distinguishing bands for the activated and IL-functionalized silica. Corresponding to silanol groups (Si–OH) [27] a band around  $950 \text{ cm}^{-1}$  is observed for the activated silica, while a weak band at around  $1575 \text{ cm}^{-1}$  corresponding to characteristic frequency of the imidazole ring [27] can be seen for the IL-functionalized silica materials SilprMim and SilmPS. These results, together with the results of elemental analysis, confirm that SilprCl was covalently modified with the imidazole ring.

#### 3.2. Stability of IL-functionalized silica

Stability of the IL-functionalized silica materials was investigated at pH 2, 8, 10 and 12 and the results are shown in Table 3. The relative percentage of nitrogen was calculated as the ratio of the nitrogen content after pH adjustment to the content of nitrogen before. Inspection of these values allowed us to determine whether if the imidazole ring was still covalently attached to the silica surface after the pH treatment. No important decrease in nitrogen content was observed after pH treatment at pH 2, 8 and 10: the

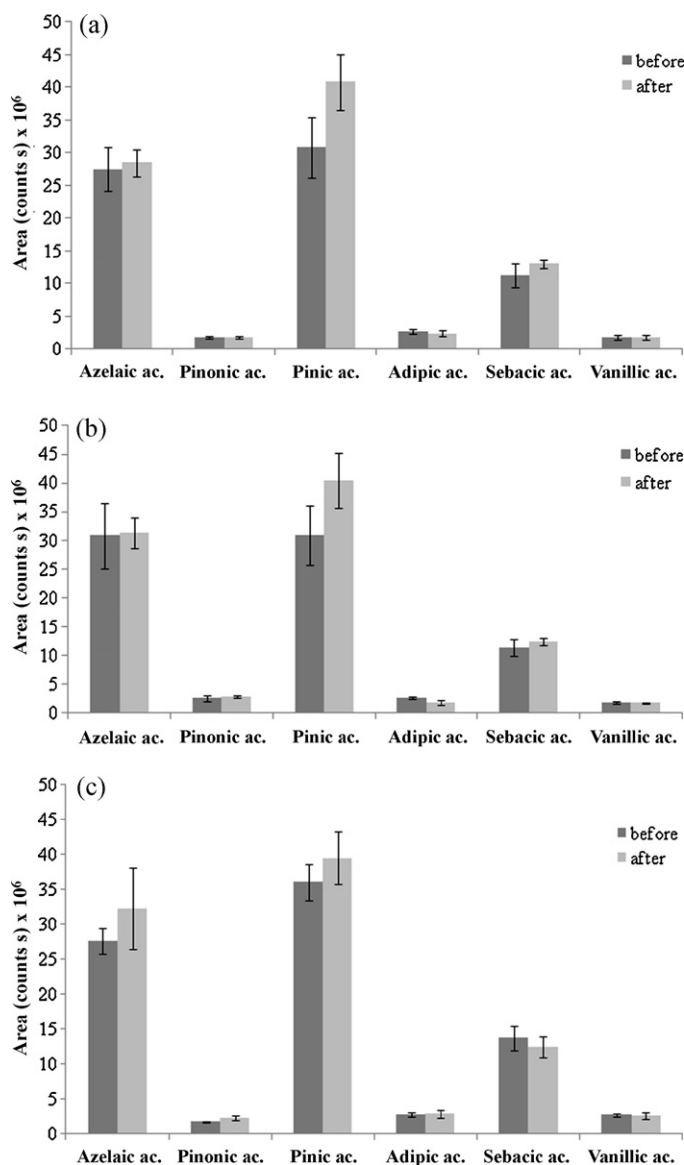


Fig. 2. Results obtained for SPE of organic acids before and after treatment of the IL-functionalized silica materials at pH 10 for 24 h. (a) SilprIm; (b) SilprMim; (c) SilmPS. Error bars correspond to standard deviation values.

relative values ranged from 71 to 98%, except for SilprMim at pH 8 and 10 pH, where the values were between 55 and 62%. However, the values for SilprMim and SilmPS after treatment at pH 12 ranged between 40 and 61%, indicating a marked decrease in the nitrogen content. We conclude that SilprIm is the most stable material.

The effect of pH treatment on the extraction properties of the materials was then clarified. The IL-functionalized silica treated at pH 10 for 24 h was tested for the extraction of organic acids at pH 6 (Fig. 2) and amines and aldehydes at pH 12. In addition, amines and aldehydes were also extracted with IL-functionalized silica treated at pH 12.

No marked differences were observed in the amounts of organic acids extracted with the IL-functionalized silica materials before and after treatment of the materials at pH 10 except for the slightly higher value for pinic acid with SilprIm (Fig. 2a) after pH treatment. Therefore, we conclude that the three IL-functionalized silica materials are stable under the conditions employed in the extraction of organic acids.

Notable differences were found when amines and aldehydes were extracted with materials treated at pH 10 for 24 h (results

**Table 2**  
Results of elemental analyses and surface coverage of carbon and nitrogen on functionalized silica gel.

Material	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Nitrogen coverage ( $\mu\text{mol}/\text{m}^2$ )	Carbon coverage ( $\mu\text{mol}/\text{m}^2$ )
Activated silica	0	0	1.2	–	–
SilprCl	0	7.8	1.9	–	4.8
SilprIm	4	11.0	2.5	3.5	3.7
SilprMim	3.6	11.0	3.1	3.1	3.2
SilmPS	3.4	13.0	3.2	3.0	3.0

not shown); the extraction efficiencies of SilprIm and SilprMim for quinoline and of SilprIm for tripropylamine were visibly increased. Cinnamaldehyde was the only aldehyde that could be extracted with SilmPS, but the amount was too small to allow conclusions. For  $\beta$ -caryophyllene aldehyde a significant decrease in extraction was observed with SilprMim. This decrease can be attributed to the smaller amount of IL groups attached to the silica surface and, therefore, decrease in interactions. After treatment at pH 12 for 24 h, the extraction efficiencies for amines were improved and those for  $\beta$ -caryophyllene aldehyde poorer. These results are probably explained by detachment of IL groups from the silica surface, leaving behind extra silanol groups to interact with amines. The finding are supported by the results of elemental analysis.

### 3.3. Conditions of the solid-phase extraction

The conditions used in the SPE of organic acids with SAX were studied and optimized in our previous study [19]. Organic acids were eluted from SAX with a mixture of acetic acid and water (10:90, v/v), and the same mixture was used with the three IL-functionalized silica materials. The elution mixture for MAX, as described in Section 2.6, was as recommended in the technical specifications. A mixture of acetic acid and methanol (10:90, v/v) was used for all five materials to elute amines in protonated form and neutral aldehydes. Since our aim was to study the extraction of neutral and negatively and positively charged compounds of different polarities, extracts (500  $\mu\text{L}$ ) were directly injected to LC–MS without a pre-concentration step.

### 3.4. Extraction of organic acids

#### 3.4.1. LC–MS

The anionic exchange interactions of the IL-functionalized silica materials were explored in detail for the organic acids. A variety of acids were selected—linear acids adipic, azelaic and sebacic; cyclic acids pinonic and pinic; and aromatic vanillic acid—to enable study of hydrophobic and  $\pi$  interactions and hydrogen bonding at the same time. In addition, the IL-functionalized silica materials were compared with two commercial extraction materials.

Theoretically, if the efficiency of the IL-silica materials was due to anion exchange interaction, extraction of the acids should be maximum at two units above their  $\text{p}K_{\text{a}1}$  values (Table 1), that is, at about pH 6 where the acids would be in deprotonated form. A pH study was carried out at pH values from 2 to 12, and the results are presented in Fig. 3. As can be seen, the optimum pH for the

extraction is about pH 4–6 for all three materials. The deprotonation of the second acidic group (Table 1) was not determinant in the extraction because the extraction efficiencies decrease above pH 6, probably due to anionic exchange of phosphate anions of the buffer, as indicated by the GC–MS results (see Section 3.4.2).

The presence of other interactions ( $\pi$  and hydrophobic interactions and hydrogen bonding), in addition to anionic exchange, can be deduced from Fig. 3. The differences in the extractions at pH 4 and 6 relative to the extractions at other pH values are less pronounced with SilprIm (Fig. 3a) than with SilprMim (Fig. 3b) and SilmPS (Fig. 3c). For three of the acids there are virtually no pH-dependent differences with SilprIm. These results can be attributed to the stronger  $\pi$  interactions and hydrogen bonding in SilprIm than in SilprMim and SilmPS due to the lack of alkyl chain in SilprIm [28]. In the case of SilprMim, the presence of other interactions, mainly  $\pi$ – $\pi$  interaction, is evident with vanillic acid, where the extraction efficiency was not dependent on pH. The extraction of vanillic acid with SilmPS was slightly dependent on pH due to longer alkyl chain, which serves to decrease  $\pi$  interactions [28].

SAX material exhibits solely anion exchange interactions, and vanillic acid extraction was dependent on the pH. Comparison of the results obtained with SAX (not shown) and the IL-functionalized silica materials showed that the extraction efficiencies with the IL-functionalized silica materials are higher at pH values different from the optimum, allowing the conclusion that, in addition to the anion exchange interaction, hydrophobic and  $\pi$  interactions and hydrogen bonding are present in the IL materials. The extraction efficiency of MAX (results not shown) was less dependent on pH due to the mixed-mode nature of the phase. From the results presented in Fig. 4 for the extraction of acids at pH 6 with the five SPE materials, we conclude that IL-functionalized silica materials provide about the same extraction efficiencies as SAX. Comparison with MAX is not meaningful owing to its different particle size (25–35  $\mu\text{m}$ ), specific surface area (727–889  $\text{m}^2 \text{g}^{-1}$ ) and elution solvent. Moreover, the amount of MAX in the cartridge was only 30 mg (100 mg for the other four materials).

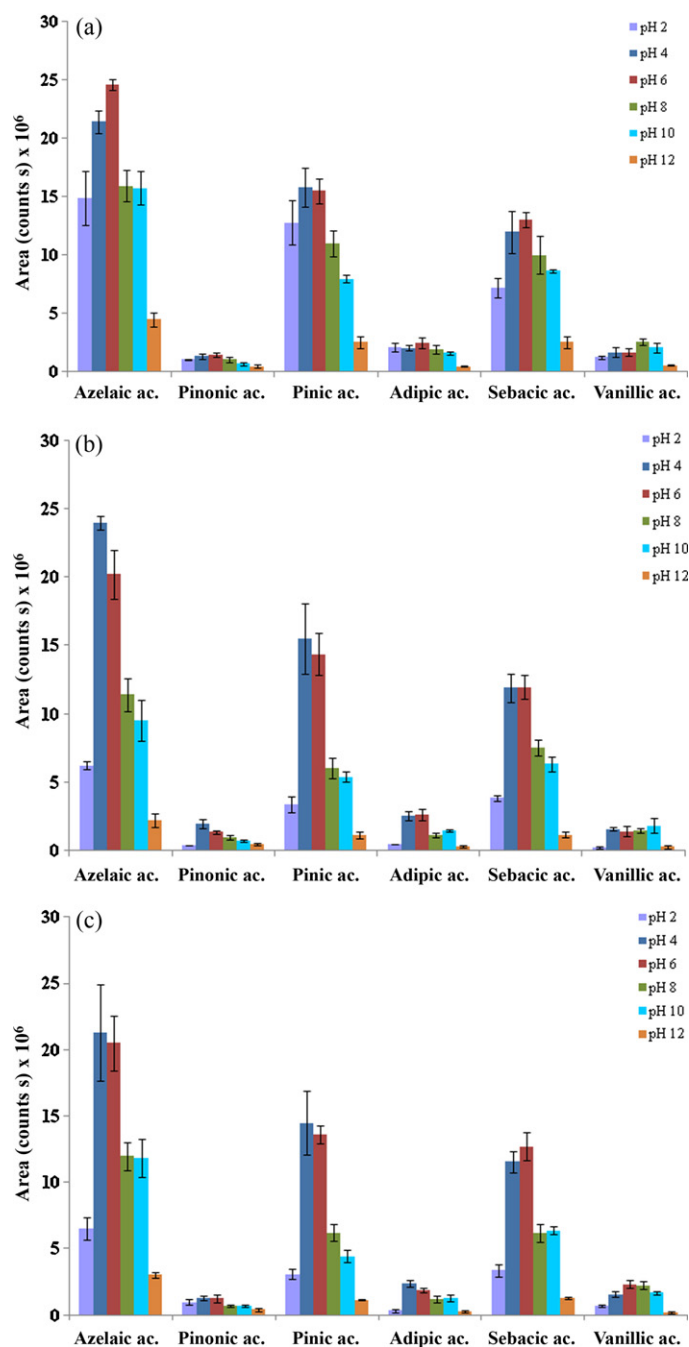
#### 3.4.2. GC–MS

The GC–MS results support the results obtained by LC–MS. The pH study could be carried out by GC–MS only at pH 4 and 6, with formic acid/ammonium formate buffer. Phosphate buffer could not be used for studies owing to competition of the anionic phosphate ion with the analytes in derivatization. In preliminary studies carried out at pH 6 with phosphate buffer, the size of the peak of

**Table 3**  
Nitrogen content of IL-functionalized silica material after pH treatment.

Material	% Nitrogen (relative) <sup>a</sup>											
	pH 2			pH 8			pH 10			pH 12		
	2 h	5 h	24 h	2 h	5 h	24 h	2 h	5 h	24 h	2 h	5 h	24 h
SilprIm	88	81	82	91	91	88	93	92	83	68	62	71
SilprMim	83	80	71	62	59	55	62	57	59	40	44	48
SilmPS	93	98	97	86	79	76	89	81	73	57	57	61

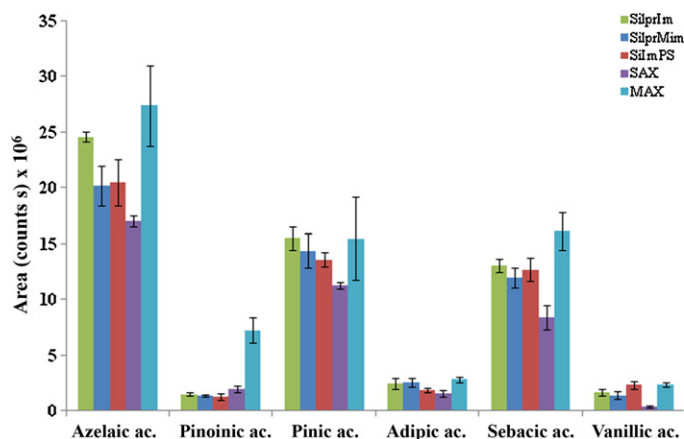
<sup>a</sup> Ratio of nitrogen contents (%) after and before pH treatment.



**Fig. 3.** Effect of pH on the extraction of organic acids with IL-functionalized silica materials. (a) SilprIm; (b) SilprMim; (c) SilmPS. Error bars correspond to standard deviation values.

the derivatized phosphate anion was much smaller with SilprIm and MAX than with SilprMim, SilmPS and SAX. Thus, peaks for all six acids were seen with SilprIm and MAX, but only a few or no peaks were seen with SilprMim, SilmPS and SAX. These findings improved our understanding of the extraction mechanisms of the different extraction materials. SilprIm exhibits stronger hydrogen bonding and stronger  $\pi$  interactions than do SilprMim, SilmPS and SAX.

Extraction efficiencies of the three IL-functionalized silica materials for the organic acids at optimum pH with formate buffer were not markedly different (data not shown). This is in agreement with the LC-MS results presented in Fig. 4.

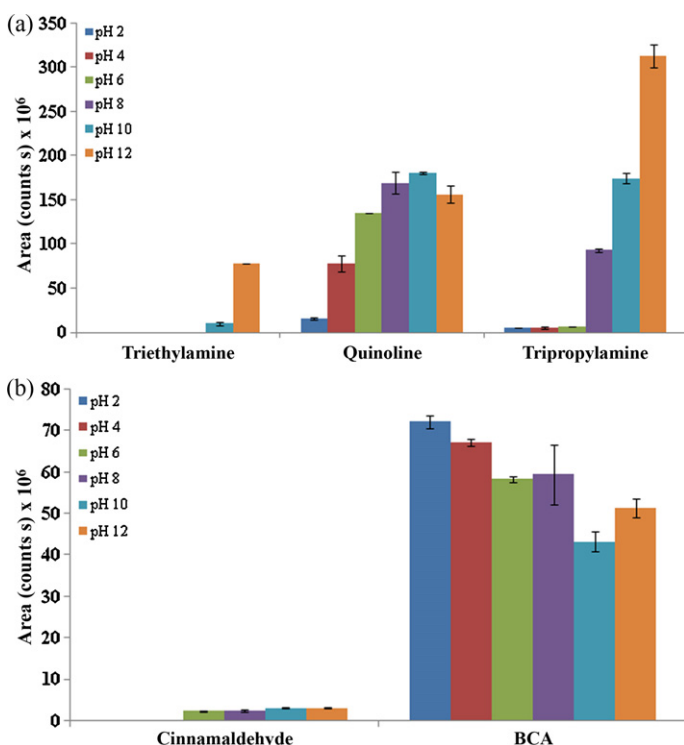


**Fig. 4.** Effect of sorbent material on the extraction of organic acids at pH 6. Error bars correspond to standard deviation values.

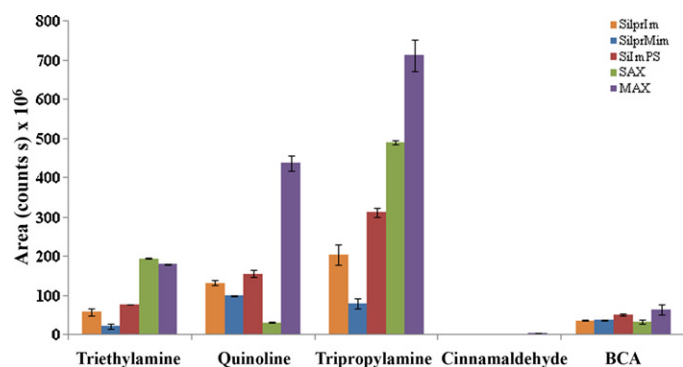
### 3.5. Extraction of amines and aldehydes

Amines and aldehydes were included to study the extraction of positively charged and neutral compounds. In addition, the extraction of amines was expected to reveal the cation exchange properties of the materials.

pH study was carried out from pH 2 to 12. Hydrophobic and  $\pi$  interactions and hydrogen bonding should be available over the whole pH range, which means that aldehydes should be extractable over a wide pH range. The optimal extraction pH for amines should be 12, about two units higher than the  $pK_a$  of the linear amines (10.78), since they are in neutral form and there is no repulsion between the imidazole ring (positively charged) and the protonated amine. The behaviour of the three silica materials was similar and only the results for SilmPS are presented (Fig. 5).



**Fig. 5.** Effect of pH on the extraction of amines and aldehydes with SilmPS. (a) Amines; (b) aldehydes. Error bars correspond to standard deviation values.



**Fig. 6.** Effect of sorbent material on the extraction of amines and aldehydes at pH 12. Error bars correspond to standard deviation values.

Extraction efficiencies for triethylamine and tripropylamine, with  $pK_a$  values of 10.78 and 10.65, respectively, were maximum at pH 12 with all IL-silica materials (Fig. 5a). For quinoline, with  $pK_a$  value of 4.94, no substantial improvements were seen at pH higher than 8 (Fig. 5a). In the case of aldehydes,  $\beta$ -caryophyllene aldehyde was extracted with all three extraction materials, while cinnamaldehyde was only extracted with SilmPS. The amount of  $\beta$ -caryophyllene aldehyde extracted decreased with increasing pH (Fig. 5b). Results for the extraction of amines with the five materials at optimum pH (12) are shown in Fig. 6. As can be seen, amines and  $\beta$ -caryophyllene aldehyde were also extracted by SAX, most probably thanks to the presence of the silanol groups and the propyl chain on the silica surface. Of the three IL-functionalized silica materials, SilmPS with longest hydrophobic alkyl chain and negatively charged sulfonic group gave highest extraction efficiencies, being also the only SPE material that could extract cinnamaldehyde. Nevertheless, the highest extraction efficiencies for almost all compounds were achieved with mixed phase MAX. In addition, SAX and MAX extracted more of the linear amines than did the IL-functionalized silica materials (Fig. 6), but the IL phases were better than SAX in extracting quinoline, indicating that  $\pi$ - $\pi$  interactions make an important contribution to the extraction.

### 3.6. Efficiency and repeatability of the extractions with IL-functionalized silica materials

The extraction efficiency, expressed as percentage recovery, was calculated as ratio of the peak area obtained after extraction of the analyte with IL-functionalized silica to the peak area obtained after direct injection of the analyte to LC-MS without prior extraction. The results are shown in Table 4 for organic acids and in Table 5 for amines and aldehydes. Extraction efficiencies for organic acids at optimum pH 6 ranged from 87 to 110%, except for *cis*-pinonic acid, where the extraction efficiency ranged from 19 to 29%. The results confirmed the anion exchange properties of the three IL materials.

In view of the stability problems encountered at pH 12 (Section 3.2) the extraction of amines and aldehydes was done at pH 10 (Table 5). The lower extraction efficiencies than for acids confirmed

**Table 4**  
Recoveries obtained in the SPE of organic acids at pH 6.

Analyte	Recovery $\pm$ SD (%)		
	SilprIm	SilprMim	SilmPS
Azelaic acid	105 $\pm$ 21	103 $\pm$ 29	105 $\pm$ 18
<i>cis</i> -Pinonic acid	21 $\pm$ 4	29 $\pm$ 7	19 $\pm$ 3
Pinic acid	93 $\pm$ 14	94 $\pm$ 16	109 $\pm$ 8
Adipic acid	91 $\pm$ 20	89 $\pm$ 17	93 $\pm$ 18
Sebacic acid	87 $\pm$ 19	87 $\pm$ 17	106 $\pm$ 20
Vanillic acid	93 $\pm$ 24	109 $\pm$ 22	110 $\pm$ 20

**Table 5**  
Recoveries obtained in the SPE of amines and aldehydes at pH 10.

Analyte	Recovery $\pm$ SD (%)		
	SilprIm	SilprMim	SilmPS
Triethylamine	1.6 $\pm$ 0.2	2.5 $\pm$ 0.5	6 $\pm$ 1
Quinoline	22 $\pm$ 2	18 $\pm$ 2	32 $\pm$ 6
Tripropylamine	3.8 $\pm$ 0.5	6 $\pm$ 1	11 $\pm$ 2
Cinnamaldehyde	N.D. <sup>a</sup>	N.D. <sup>a</sup>	36 $\pm$ 3
$\beta$ -Caryophyllene aldehyde	23 $\pm$ 2	37 $\pm$ 4	36 $\pm$ 4

<sup>a</sup> Not detected.

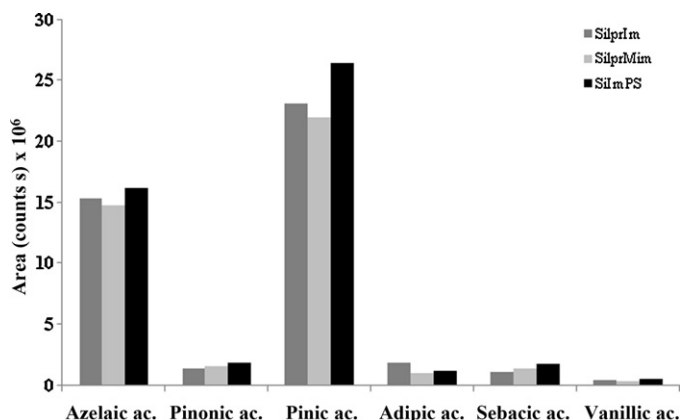
the dominance of the anion exchange properties of the silica materials. However, as noted above, the sulfonic group and the longer alkyl chain of SilmPS improved the extraction of the amines and aldehydes in comparison with SilprIm and SilprMim. The better results with SilmPS are in agreement with results reported in the literature [9]. The negatively charged sulfonic group attracts amines and the longer alkyl chain gives hydrophobicity and, as noted above, SilmPS was the only phase capable of extracting cinnamaldehyde. We conclude that, although the three IL-functionalized silica materials exhibit different properties (anion exchange, hydrophobic and  $\pi$  interactions, hydrogen bonding), anion exchange is the dominant property in SPE, as expected.

The repeatability of the extractions was calculated to obtain information about the precision of the method. Successive extractions were made with the same and with three different cartridges during the same day (intraday) and with the same cartridge during three different days (interday). The extractions were carried out at pH 6 for organic acids and at pH 10 for amines and aldehydes.

Three replicates or three cartridges were used in measurements of the repeatability. As can be seen from Table 6, the repeatability in terms of coefficient of variation (CV) ranged from 3.7 to 22.1% for extraction of acids with SilprIm, from 4.2 to 21.4% with SilprMim and from 5.9 to 19.9% with SilmPS. In the case of the amines and aldehydes (Table 7), the repeatability ranged between 3.4 and 22.5% for SilprIm, between 4.4 and 22.5% for SilprMim, and between 7.9 and 23.1% for SilmPS. Note that the repeatability of the LC-MS instrument was about 10%. We consider the repeatability values to be acceptable, therefore.

### 3.7. Atmospheric aerosol sample

Finally, we studied the suitability of the three IL-functionalized silica materials for the extraction of organic acids from a complex atmospheric aerosol sample collected on quartz filter for 24 h (Fig. 7). Zwitterionic SilmPS was a slightly better material for SPE of most of the compounds. Usually, extraction efficiencies for aerosol



**Fig. 7.** Extraction of acids from atmospheric aerosol sample with IL-silica materials.



**Table 6**  
Interday and intraday CV values for organic acids.

Analyte	CV (%) intraday			CV (%) interday			CV (%) intraday cartridges		
	SilprIm	SilprMim	SilmPS	SilprIm	SilprMim	SilmPS	SilprIm	SilprMim	SilmPS
Azelaic acid	12.0	18.5	6.5	9.3	13.6	12.6	16.5	17.3	19.9
Pinonic acid	9.8	19.0	5.9	12.6	7.2	14.9	3.7	4.4	16.4
Pinic acid	15.0	16.7	7.1	17.2	17.1	8.0	6.3	21.4	16.5
Adipic acid	14.1	9.8	11.3	22.1	4.7	17.2	4.7	16.4	17.3
Sebacic acid	15.6	12.8	12.8	20.0	7.4	7.7	7.0	21.4	14.3
Vanillic acid	19.8	17.0	7.7	18.5	4.2	12.4	18.0	16.2	9.6

**Table 7**  
Interday and intraday CV values for amines and aldehydes.

Analyte	CV (%) intraday			CV (%) interday			CV (%) intraday cartridges		
	SilprIm	SilprMim	SilmPS	SilprIm	SilprMim	SilmPS	SilprIm	SilprMim	SilmPS
Triethylamine	13.7	18.6	9.7	13.3	20.0	16.1	22.5	9.0	8.2
Quinoline	5.6	4.4	18.8	12.7	14.9	17.2	20.2	22.5	23.1
Tripropylamine	12.7	12.4	16.7	10.0	16.3	12.8	14.8	15.0	7.9
Cinnamaldehyde	N.D. <sup>a</sup>	N.D. <sup>a</sup>	8.9	N.D. <sup>a</sup>	N.D. <sup>a</sup>	9.5	N.D. <sup>a</sup>	N.D. <sup>a</sup>	12.3
β-Caryophyllene	7.6	7.7	8.8	3.4	14.5	11.8	5.1	7.9	14.0

<sup>a</sup> Not detected.

samples are calculated in percents for standard samples, and the results are applied without corrections [19,29]. The standard addition method is seldom applied since the standard solution might not be integrated into the sample matrix in the same way as compounds are in nature. In the absence of reference aerosol samples with known acid concentrations, recoveries obtained for the acid standard solution with SilmPS (Table 4) could be used for the calculation of efficiencies.

#### 4. Conclusions

Three IL-functionalized silica materials with predominantly anion exchange properties were synthesised as sorbents for solid-phase extraction. SilprIm exhibited stronger hydrogen bonding and  $\pi$  interactions than SilprMim or SilmPS. The sulfonic group and longer alkyl chain in zwitterionic SilmPS offered an additional active centre for the extraction, and extraction of amines and aldehydes was better than with SilprIm or SilprMim.

All IL materials exhibited equal or higher extraction capacities than commercial SAX. In addition, they offered different selectivity from both commercial sorbents, and more efficient extraction than SAX for aromatic compounds.

Biogenic compounds were successfully extracted with IL-functionalized silica for the first time. The successful extraction of biogenic compounds from an atmospheric aerosol sample confirmed the suitability of the synthesised materials for extractions from complex sample matrices.

The study revealed that different types of interaction are involved in the extraction of chemically different compounds.

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