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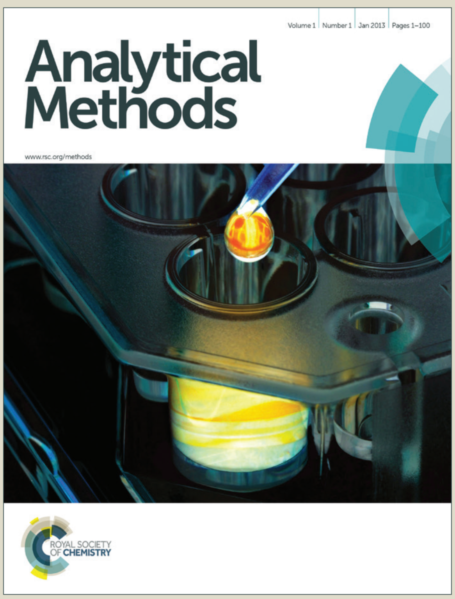

A Rapid Approach to Isolating Nitroexplosives from Imidazolium and Pyrrolidinium Ionic Liquid Solutions Using Solid Phase Extraction (SPE)

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ABSTRACT

Ionic liquids have received considerable attention as ideal green solvents for synthesis and extraction applications. Ionic liquids, because of their unique set of properties such as low volatility, high stability, excellent solvation ability, ionic strength, and tunable structure, are frequently utilized as alternate environmentally friendly solvents to conventional solvents. It is these same properties, however, that present analytical challenges, particularly with liquid chromatography (LC) or gas chromatography (GC) analysis of compounds of interest dissolved in ionic liquid media. A simple solid phase extraction (SPE) sample preparation method is described for isolating nitroexplosive compounds from solutions containing 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (DMPIm-NTf_2) or 1-methyl-3-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPy-NTf_2) prior to analysis. High recoveries of the compounds of interest are achieved with substantial removal of the ionic liquid, thus avoiding significant interferences and time-consuming and costly instrumental problems.

INTRODUCTION

Ionic liquids, because of their many unique properties, have attracted considerable interest across many fields of chemistry for use in a wide range of applications. Their versatility is largely due to their ability to be "tuned" with the appropriate combination of cation and anion to influence their physical properties.[1,2] They are frequently utilized as alternate environmentally friendly solvents to conventional solvents in chemical processes including organic synthesis and catalysis, biomass dissolution and biocatalysis, and extraction [3-10]. Ionic liquids have large electrochemical windows, high thermal stabilities, and good conductivity that is desirable for electrochemical applications in lithium-ion secondary batteries, dye-sensitized solar cells, and supercapacitors.[11-13] Ionic liquids have also gained popularity in chromatographic separations with the emergence of supported ionic liquid stationary phases for sorptive solid–liquid extractions and separations.[14,15]

Solid Phase Extraction (SPE) columns or cartridges and discs have been commercially available since the late 70's for the removal of impurities, isolation of substances of interest, and concentration of samples. SPE is the most widely-used sample preparation technique used for the purification of a variety of compounds prior to analysis [16]. The commercial availability of SPE columns has expanded to include a variety of sorbent properties and configurations including mix-mode sorbents and specialized sorbents with modified silica or polymeric surfaces that enhance sorbent selectivities and optimize extractions for the preparation of samples for analysis. [17,18]

Historically, gas chromatography-mass spectrometry (GC/MS) has been the preferred method for identification of small molecules. [19] GC analysis requires vaporization of the sample upon introduction into the GC inlet in order to be detected. This creates a problem when analyzing samples containing ionic liquids with very low volatilities and high viscosities. Liquid chromatography-mass spectrometry (LC/MS) has also evolved as powerful tools for identifying and quantifying compounds of interest. Contrary to GC/MS, low concentrations of ionic liquid in the LC mobile phase have been found to be excellent ion pairing agents for affecting the free silanol groups of the silica resins that would otherwise interact with basic analytes.[20,21] However, introduction of significant amounts of ionic liquid into the LC system can also lead to destructive adsorption of the ionic liquid, degradation of the column performance, and contamination of the instrument.

To effectively utilize LC/MS and GC/MS for the analysis of compounds dissolved in ionic liquid media, it is necessary to remove the interfering ionic liquids before analysis. A solid phase extraction method was developed for the concurrent removal of imidazolium or pyrrolidinium ionic liquid cation and anions from sample solutions and the recovery of neutral nitroexplosive compounds. The eluate, void of ionic liquid cations and anions, can be collected and analyzed by liquid or gas chromatography without concern for significant interferences and time-consuming and costly instrumental problems.

EXPERIMENTAL SECTION

Materials

The ionic liquids, DMPIm-NTf_2 and BMPy-NTf_2, were purchased from Sigma-Aldrich (St. Louis, Missouri, USA) and TCI America (Portland, OR), respectively. The solvents, reagents, and individual explosive chemicals were also obtained from Sigma- Aldrich. The explosive mix standard solution (p/n ERE-042) was acquired from Cerilliant Corporation (Round Rock, Texas, USA). The SPE columns (STRATA®-XC strong cation exchange p/n 8BS029-TAK and STRATA®-SAX strong anion exchange p/n 8B-S008-EAK) and the SPE vacuum manifold were purchased from Phenomenex (Torrance, California, USA). The reversed-phase columns utilized in the LC separations, the Phalanx C18 (5um, 2.5 x 150mm) and the Synergi MAX-Polar (mixed-bed, 2.5um, 2.5 x 100 mm), were acquired from Higgins Analytical (Mountain View, California, USA) and Phenomenex, respectively. Finally, the GC column used for the GC analyses (HP-5MS, 5% Phenyl, 30 ft x 0.25 mm ID) was purchased from Agilent Technologies (Santa Clara, California, USA).

Instrumentation

A Buchi R215 rotary evaporator (Flawil, Switzerland) was used for the removal of the solvents. The samples were analyzed using a 5975C GC/MS with an electron impact ionization source and/or a G1969 ESI-LC/MS-TOF consisting of a gradient LC system coupled to a time-of-flight mass spectrometer and electrospray ionization source. Both chromatography systems are manufactured by Agilent Technologies (Santa Clara, California, USA).

Solid Phase Extraction

The SPE method employs a dual ion exchange separation whereby both anion exchange and cation exchange sorbents are combined for each extraction for the simultaneous removal of the ionic liquid ions. A one- or two-column SPE configuration was utilized for the extractions. For the one-column configuration, the sorbents of the STRATA®-SAX (100 mg bed size) and STRATA®-XC (30 mg bed size) were packed in a single column with the anion exchange sorbent stacked on top of the cation exchange sorbent. For the two-column configuration, the individual ion exchange columns were coupled together via a coupling adapter (Figure 1). It should be noted, however, that both SPE configurations gave identical results and that the two-column configuration was used for most of the experiments simply because of ease of experimental set-up.

A stopcock between the column assembly and the vacuum manifold allowed regulation of the eluent flow (approximately 2 drops/sec) while the manifold was maintained under vacuum (20–30 mmHg). The column assembly was conditioned with at least 3 mL of methanol. 1 ml of sample solution was loaded onto the column assembly immediately after the conditioning step to avoid drying of the sorbent. The sample was eluted with a minimum of one column volume (1 - 2 mL) of methanol, collected, and analyzed by LC/MS or GC/MS to determine the percent recovery of the analytes and percent removal of the ionic liquid ions. NOTE: We found that no residual analytes were recovered with subsequent elution with methanol. The used SPE column assembly can be washed further with a minimum of one column volume (1 - 2 mL) of 0.1 *M* NaCl and methanol (10:90 v/v) to completely remove the ionic liquid ions adsorbed on the sorbent surface. This process allows for regeneration and reuse of the columns. All the samples collected from the extractions were diluted with methanol or concentrated as needed before analysis by LC/MS-TOF and GC/MS.

Instrumental Analysis

The analytes and ionic liquid solutions were dissolved in methanol with concentrations of 10−200 ug/mL and 2−3 mg/mL, respectively, unless otherwise noted. The ionic liquids were added to the sample solutions to obtain final analyte to ionic liquid weight ratio of 1:50 (w/w) unless otherwise noted. The eluate from the extractions were diluted an additional 1:10 (v/v) with methanol for the LC/MS analyses. A gradient elution from 30% to 80% organic composition was employed for the reversed-phase LC separations. The mobile phase consisted of 5 m*M* ammonium formate and methanol. For the GC/MS samples, the eluate from three extractions were combined, dried down with N_2 purging, and reconstituted in 1 mL of methanol then injected into the GC. The GC oven temperature was ramped at a rate of 20 ^{o}C min^{-1} from 70 ^{o}C to 280 ^{o}C.

RESULTS AND DISCUSSION

A non-retentive ion exchange solid phase extraction method was developed for the removal of 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonimide) (DMPIm-NTf_2) and 1-methyl-3-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPy-NTf_2) ionic liquids from the sample matrix to isolate and purify explosive compounds. The chemical structures of all the compounds examined are illustrated in Table 1. Typical ion exchange sorbents contain hydrophilic functional groups bonded to a silica or polymeric resin that can exchange with the free anions or cations in the sample solution. In conventional non-retentive ion exchange SPE, aqueous samples are introduced into pre-conditioned anion or cation exchange columns and the compound(s) of interest are eluted and collected. The SPE method described utilizes a combination of strong anion exchange and strong cation exchange sorbents to allow for exchange of DMPIm-NTf_2 or BMPy-NTf_2 anions and cations in a single non-aqueous non-retentive extraction.

Removal of the ionic liquid

The significance of the removal of the ionic liquid ions in sample solutions is realized in the severe tailing peaks observed for the ionic liquid by LC/MS analysis, particularly in the positive mode (Figures 2a and 3a) which is indicative of adsorption either on the column or instrumentation. Problems with carryover or bleeding of the ionic liquid to subsequent runs made identification and quantitation of trace compounds near impossible, necessitating a sample preparation step to remove the interfering ionic liquid from the sample solution prior to analysis.

Figures 2 and 3 illustrate the LC/MS-TOF extracted ion chromatograms (EIC) of sample solutions containing DMPIm-NTf_2 and BMPy-NTf_2, respectively, before and after solid phase extraction (m/z = 139-140 for $DMPIm^+$, m/z = 142-143 for $BMPy^+$, and m/z = 279-280 for NTf_2^-). The amount of ionic liquid ions removed after solid phase extraction were found to be >95% for $DMPIm^+$, $BMPy^+$ and NTf_2^- as long as the ionic liquid mass loads were kept below the ionic capacities of the ion exchange sorbents. The breakthrough mass for $DMPIm^+$ ion with the STRATA®-CX column was determined to be approximately 4.0 mg. The observed value is in close agreement to the theoretical value of 4.17 mg which suggests the interaction between $DMPI^+$ and the benzylsulfonic acid mixed-mode functionality of the sorbent is primarily ionic. In consequence, the breakthrough mass for $DMPIm^+$ was reduced when competing cations were present in the sample matrix (Figure 4). Similar results were observed for $BMPy^+$.

The method described was also observed to be easily scalable to larger sorbent bed sizes to enable removal of higher concentrations of ionic liquid in the sample media. The % removal of the ionic liquid was found to be comparable to those observed for the smaller bed size columns. Other SPE sorbents including weak cation exchange, weak anion exchange, and C18 reversed-phased sorbents were also examined for the removal of ionic liquids. However, the percent removal calculated for the experiments were very poor (< 35%).

Recovery of the explosive compounds

The percent recoveries after SPE treatment of three explosive compounds (2,4-dinitrotoluene, trinitrotoluene, and 1,3-dinitrobenzene) with analyte to ionic liquid ratios from 1:25 to 1:150 (w/w) were determined by LC/MS-TOF. We found that within the analyte to ionic liquid ratio range studied, recoveries for the explosives were >85% as long as the total mass of ionic liquid loaded on the SPE cartridges were below the breakthrough mass. In addition, results showed that the recoveries of the explosives increased slightly with increasing ionic liquid concentrations until the ionic capacities of the SPE sorbents were exceeded, beyond which point the ionic liquid signal often masked or interfered in the detection of the analytes. We can conclude that weak interactions between the neutral explosives and available active sites on the ion exchange surfaces must also exist. The likely interaction mechanism would involve π-π bonding or hydrophobic interaction with the benzyl functionality of the cation exchange sorbent. Because the recoveries of the analytes are dependent to a small extent on the ionic liquid concentration in the sample matrix, quantitation of the analytes after SPE treatment was not straightforward. However when the concentrations of the explosives were varied but the ionic liquid concentration in the sample matrix was kept constant, excellent recovered analyte concentration to peak area linearity was achieved for dinitrobenzene and trinitrobenzene with correlation coefficient values (R^2) of 0.9998 and 0.9971, respectively.

To demonstrate the effectiveness of the SPE method for clean-up of a variety of common explosives, sample solutions of the Cerilliant explosives standard mixture (Table 1) in BMPy-NTf_2 ionic liquid media were prepared, extracted, and analyzed by GC/MS. The explosives, with the exception of 2-amino-3,5-dinitrotoluene, 3-amino-1,5-dinitrotoluene, 3,5-dinitroaniline, RDX and Tetryl, were successfully isolated. For the purpose of this experiment, only qualitative data was collected. The identities of the recovered explosives were determined by GC/MS mass spectral matching using the NIST spectral library (match values of > 95%).

The compounds retained on the SPE columns are all amino-functionalized explosives (designated with a † in Table 1). Amines are notorious for interacting with free silanol groups on the sorbent surface by hydrogen bonding [19, 20]. Since the STRATA®-SAX column employs a silica-based sorbent, it would certainly be the most credible explanation. To test this theory, sample solutions of the amino explosives in methanol were eluted through each of the ion exchange columns separately then analyzed by GC/MS. Correspondingly, the compounds were recovered from the STRATA®-XC column (polymeric-based sorbent) and were fully retained on the STRATA®-SAX column. Regrettably, a polymeric-based strong anion exchange column (e.g. Phenomenex STRATA®-XA) was not available for testing at the time of this study but is certainly worth investigating for the sample preparation of amino compounds in ionic liquid media.

CONCLUSIONS

Analyzing sample solutions containing ionic liquids by LC/MS or GC/MS can be a challenging task due to interactions associated with the ionic liquid that can lead to poor chromatography and instrumental problems. Ion exchange SPE is one of the oldest chromatographic techniques for desalting and removal of ionic impurities or interferences and continues to evolve as new sorbents, applications, and configurations are developed even to this day. In this study, a novel SPE ion exchange method is introduced that incorporates both cation and anion exchange sorbents in a single extraction for the removal of interfering ionic liquid and isolation of neutral explosive compounds prior to analysis. With this method, > 95% removal of DMPIm-NTf_2 or

BMPy-NTf_2 in the sample matrix can be achieved, allowing for problem-free analysis of compounds of interest.

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FIGURE CAPTIONS:

1. **Figure 1**: SPE column assembly with SPE vacuum manifold
2. **Table 1**: Chemical structures of the compounds examined

   †Retained on the STRATA-SAX/STRATA-XC column assembly

3. **Figure 2:** Extracted Ion Chromatograms (EIC) of DMPI-Tf_2N before (blue) and after (red) SPE in the positive (a) and negative (b) MS mode.
4. **Figure 3:** Extracted Ion Chromatogram (EIC) of BMPyr-Tf_2N before (blue) and after (red) SPE in the positive (a) and negative (b) MS mode.
5. **Figure 4:** Retention of $DMPI^+$ on the Strata-XC SPE column: (◆) Ionic liquid only, (■) Ionic liquid with 8.0 wt% tetramethylammonium hydroxide.

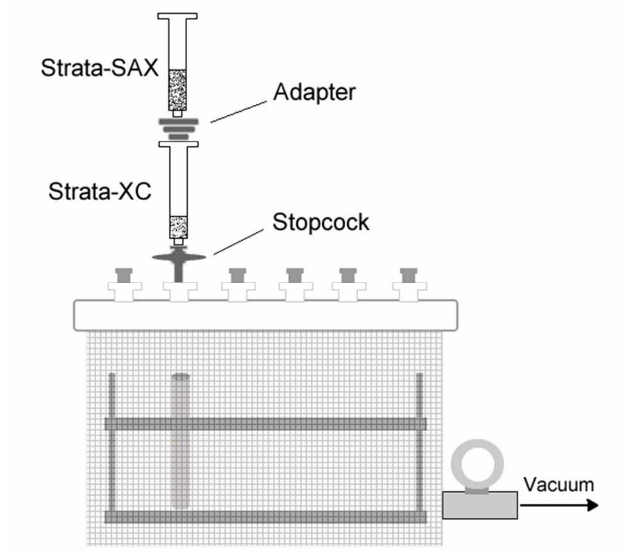
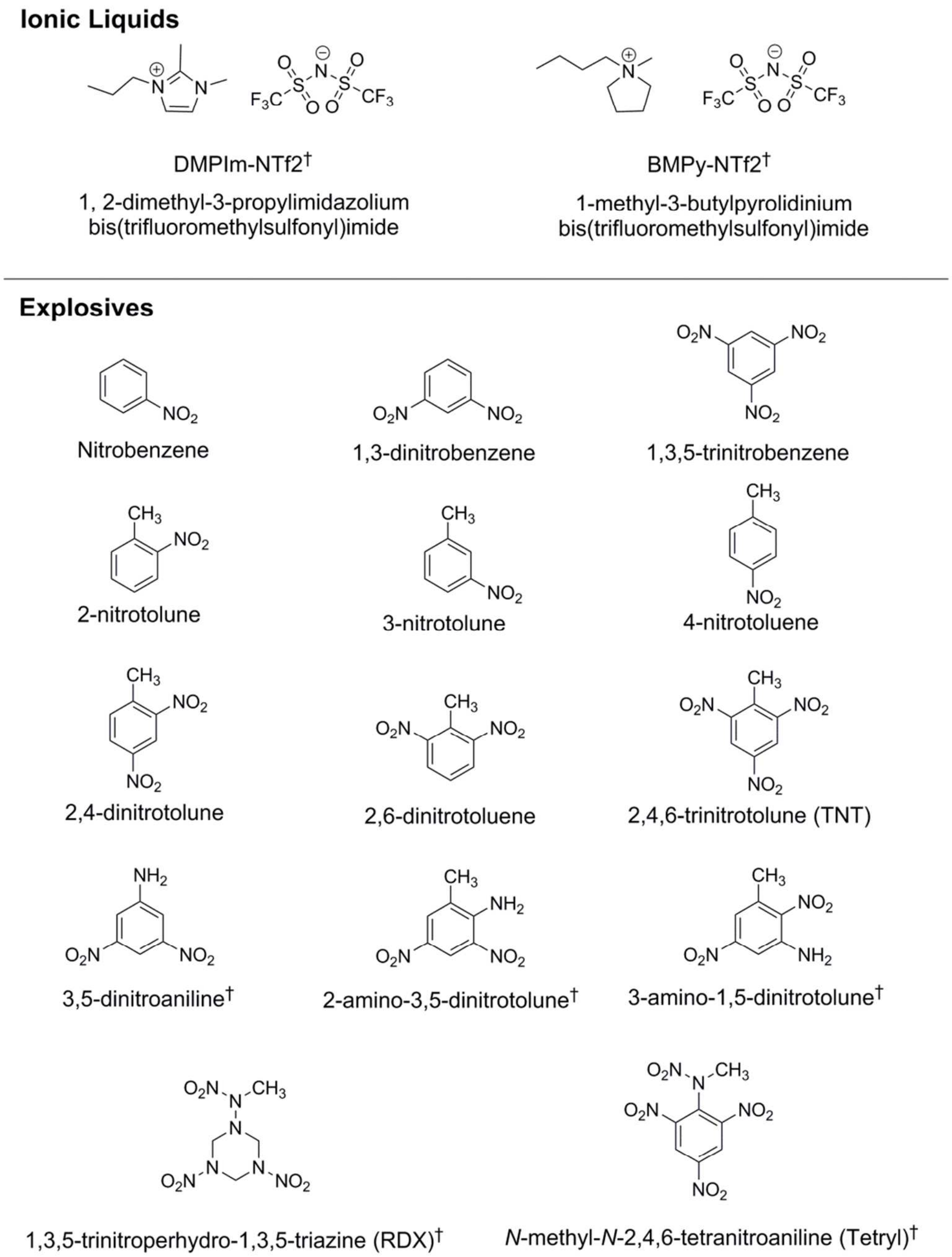


Figure 1. SPE column assembly with SPE vacuum manifold.

Table 1. Chemical structures of the ionic liquids studied and explosives contained in the Cerilliant Explosive Standard Mix
†Retained on the STRATA-SAX/STRATA-XC column assembly



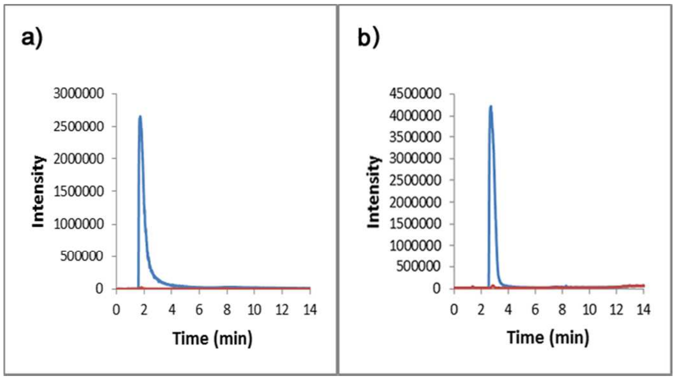


Figure 2. Extracted Ion Chromatograms (EIC) of DMPI-Tf_2N before (blue) and after (red) SPE in the positive (a) and negative (b) MS mode.

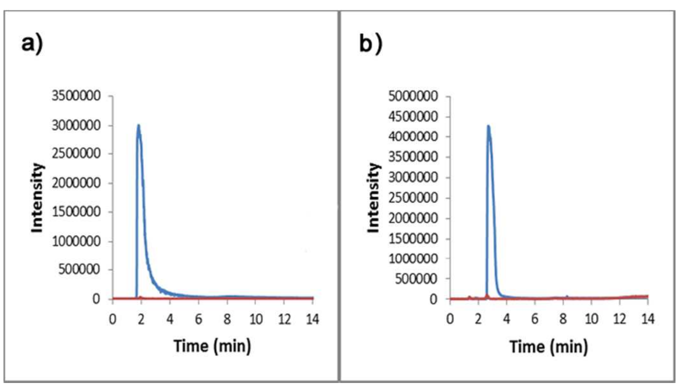


Figure 3. Extracted Ion Chromatogram (EIC) of BMPyr-Tf_2N before (blue) and after (red) SPE in the positive (a) and negative (b) MS mode.

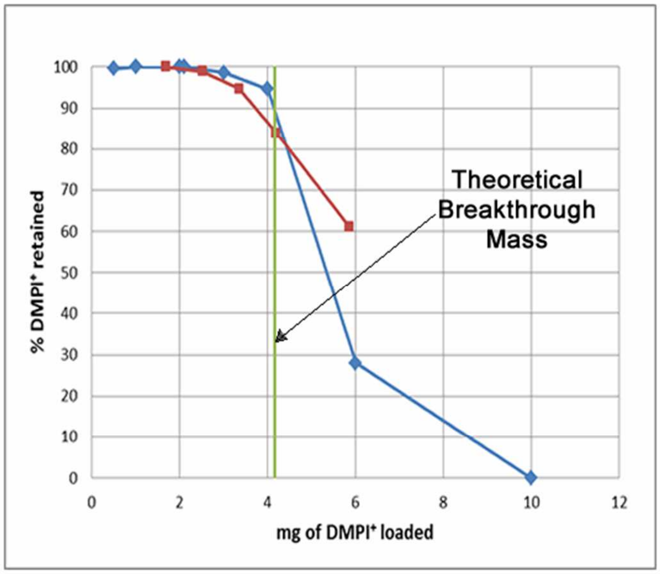


Figure 4. Retention of $DMPI^+$ on the Strata-XC SPE column: (◆) Ionic liquid only, (■) Ionic liquid with 8.0 wt% tetramethylammonium hydroxide.