Ionic liquids have been analyzed in undiluted form using electrospray mass spectrometry (ES-MS); results indicate that signal-to-noise ratios for minor constituents are comparable to those observed in conventional, diluted ES-MS and that this approach could be readily applied for mass spectrometric analysis of ionic liquids and ionic impurities/additives dissolved therein, especially those that are solvent reactive.

Room temperature ionic liquids (RTILs) have received major attention recently as replacements for conventional solvents in synthesis, catalysis, electrochemistry and separations. With their widespread application comes an inherent requirement to determine the nature and purity of synthesized ionic liquids, and to characterize and quantify the variety of compounds dissolved within them. This poses an interesting analytical problem, because the properties of RTILs do not always readily lend themselves to conventional analytical techniques.

Early attempts to obtain electron ionization (EI) mass spectra and chemical ionization (CI) mass spectra were unsuccessful, presumably because RTILs have very little vapor pressure and cannot be readily transferred to the gas phase. Because of their inherently low vapour pressure, fast atom bombardment (FAB) MS has been the most extensively used MS technique for characterizing RTILs. The RTILs may be dissolved in a matrix such as glycerol, or analyzed without dissolution. FAB-MS spectra of RTILs are typically characterized by a dominant peak for the unbound cation, observable with the naked eye or under significant magnification. Solvents such as methanol, the electrospray plume was not observed at low vapour pressure, fast atom bombardment (FAB) MS has been the most extensively used MS technique for characterizing RTILs. The RTILs may be dissolved in a matrix such as glycerol, or analyzed without dissolution. FAB-MS spectra of RTILs are typically characterized by a dominant peak for the unbound cation, observable with the naked eye or under significant magnification.

Fig. 1(a) shows a mass spectrum obtained from an undiluted and under heated conditions, but was probably not greater than 80 °C. Future work will need to clarify the heating effect and any potential problems regarding the heating of thermally sensitive analytes that might decompose at these operating temperatures. ES-MS of undiluted ionic liquids was usually performed at an infusion rate of 0.4 M tetrabutylammonium iodide (TBAI) and stable ion signal could often be achieved with no active infusion. Unlike ES plumes generated from conventional solvents such as methanol, the electrospray plume was not observable with the naked eye or under significant magnification. In an effort to alleviate problems associated with dissolution and solvent effects, we have performed the first studies to evaluate the possibility of generating mass-spectrometric information from undiluted ionic liquids. Two reports can be found in the literature on the electrospray of undiluted ionic liquids, although these reports are not analytical in nature. In addition, these reports utilize an electrospray plume under vacuum and not at atmospheric pressure.

Applying a heated curtain gas in opposition to the electrospray plume enables consistent ion signals to be recorded from an undiluted sample of 1-butyl-3-methyl imidazolium pentafluorophosphate (BMIM-PF$_6$). However, the effect of the heated curtain gas (250 °C) is not immediate. The benefit arises from the reduced viscosity of the heated ionic liquid in the electrospray needle caused by convective heating by the curtain gas. Very little, and in some cases no ion signal is observed in the absence of the heated curtain gas. The exact temperature of the ionic liquid was not determined under heated conditions, but was probably not greater than 80 °C. Future work will need to clarify the heating effect and any potential problems regarding the heating of thermally sensitive analytes that might decompose at these operating temperatures. ES-MS of undiluted ionic liquids was usually performed at an infusion rate of 0.2 μL min$^{-1}$, but stable ion signal could often be achieved with no active infusion. Unlike ES plumes generated from conventional solvents such as methanol, the electrospray plume was not observable with the naked eye or under significant magnification.

Fig. 1(a) shows a mass spectrum obtained from an undiluted and purified sample of BMIM-PF$_6$ containing 4 × 10$^{-4}$ M tetrabutylammonium iodide (TBAI). Clearly evident is the BMIM$^+$ cation signal at m/z 139, and the trimolecular cluster ([BMIM]$_2$PF$_6$)$^+$ at m/z 424. The peak at m/z 84 is due to the following reaction mechanism: B$+$ (where B is the anion) reacts with the negatively charged RTIL component to form the observed signal.
fragmentation of the BMIM\textsuperscript{+} cation, the extent of which could be readily altered by the acceleration potential between the capillary exit and the skimmer cone. MS/MS of isolated BMIM\textsuperscript{+} also gave this peak as one of the major fragmentation products.

The TBA\textsuperscript{+} peak is readily observable at m/z 242 and the spectrum is relatively free from other major peaks. Fig. 1(b) shows the same sample dissolved to \(2 \times 10^{-4}\) M BMIM-PF\textsubscript{6} in the methanolic solution (final concentration of TBA\textsuperscript{+} = \(1 \times 10^{-7}\) M). In general, the two spectra show the same major ions in similar relative abundance. Although the plots have been normalized to the largest peak in each case, absolute ion abundances were reasonably similar for the two methods when using a 50 ms injection period. Closer inspection of the baseline of the two spectra, shown in the insets, reveals interesting differences. The spectrum for the undissolved RTIL displays considerably less chemical noise and shows the TBA\textsuperscript{+} peak at \(\sim 0.3\%\) of the base peak height, whereas the baseline for the dissolved RTIL shows significant ion signal at nearly every mass and a TBA\textsuperscript{+} peak at \(1\%\) of the base peak height. In this example, dissolution of the RTIL matrix provides better absolute signal response for the dissolved “impurity” ions, but at the expense of higher background noise. The minor peaks in the m/z 200–700 window have not been identified; presumably, they are due to methanol or water clusters of impurity ions. Calculation of the signal-to-noise ratio for the two methods (dilution versus no dilution) gave very similar results. Approximate detection limits for methanol or water clusters of impurity ions. Calculation of the window have not been identified; presumably, they are due to

The TBA\textsuperscript{+} peak at ~ 0.3% of the base peak height, whereas the baseline for the dissolved RTIL shows significant ion signal at nearly every mass and a TBA\textsuperscript{+} peak at 1% of the base peak height. In this example, dissolution of the RTIL matrix provides better absolute signal response for the dissolved “impurity” ions, but at the expense of higher background noise. The minor peaks in the m/z 200–700 window have not been identified; presumably, they are due to methanol or water clusters of impurity ions. Calculation of the signal-to-noise ratio for the two methods (dilution versus no dilution) gave very similar results. Approximate detection limits for TBA\textsuperscript{+} showed no measurable drift over a ten minute acquisition period. Iso

Notes and references
