Liquid Injection Field Desorption/Ionization-Mass Spectrometry of Ionic Liquids

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Ten ionic liquids based on four types of organic cations, C^+ (imidazolium, pyrrolidinium, pyridinium, and phosphonium), combined with various types of anions, A^- , were analyzed by liquid injection field desorption/ionization- (LIFDI) mass spectrometry. For the purpose of LIFDI analysis the ionic liquids were dissolved in methanol, acetonitrile or tetrahydrofuran at concentrations of 0.01–0.1 $\mu\text{l mL}^{-1}$. The measurements were performed on a double-focusing magnetic sector instrument. In all ionic liquid LIFDI spectra, the intact cation of the compound yielded the base peak accompanied by cluster ions of the general formula $[C_2A]^+$ and occasionally $[C_3A_2]^+$. Tandem mass spectrometry and reconstructed ion chromatograms were employed to reveal the identity of the observed ions. Although limited to positive-ion mode, LIFDI also provided analytical information on the anions due to cluster ion formation. Depending on actual emitter condition and ionic liquid the limit of detection in survey scans was determined to 5–50 pg of ionic liquid. (J Am Soc Mass Spectrom 2007, 18, 2254–2262) © 2007 American Society for Mass Spectrometry

Ionic liquids (ILs) have recently received widespread interest among many areas of chemical research as they act as highly polar thermally stable solvents in chemical synthesis [1–3]. Consequently, there is a need for the development of methods for their analysis, be it for the sake of checking their purity, to verify their absence in products from processes where ILs are involved, or to monitor their distribution in the environment as a result of their long-term usage.

Mass spectrometry (MS) offers various methods for the analysis of ionic analytes, with electrospray ionization (ESI) [4, 5] and matrix-assisted laser desorption/ionization (MALDI) [6, 7] presently being the widest known techniques for that purpose. In addition, fast atom bombardment (FAB) [8, 9] as well as field desorption (FD) [10–12] are capable of delivering the required analytical information. Indeed, analyses of ILs with MALDI [13], ESI [14–17], and FAB [18] have already been conducted, and those methods were found to serve nicely for the analysis of ILs. Vice versa, ILs have been used as matrices or matrix dopants to alter the properties of established matrix compounds in MALDI-MS [19–27].

Although being the longest established method for ionic analyte analysis, FD has been overlooked in this scenario of mass spectral techniques for IL analysis. Field desorption (FD) is known since the 1970s as a soft desorption/ionization method in mass spectrometry [10, 28–30]. FD-MS has proven capabilities in analyzing nonionic low- to medium polarity compounds [12].

FD employs strong electric fields in the order of 10^{10} V m^{-1} ($1 \text{ V \AA}^{-1}$) to effect the ionization of atoms and molecules [11, 12, 31]. The necessary field strength is normally achieved by setting whisker-bearing wires—so-called activated emitters [32–34]—to high electric potential of typically 10–12 kV opposed to a counter electrode at $\sim 2 \text{ mm}$ distance. With the emitter at positive polarity, electron tunneling becomes possible from the analyte residing on the activated emitter's large surface into the emitter material. The analyte is thereby ionized very softly and the molecular ions generated are immediately extracted into the mass analyzer by action of the same electric field.

Due to the advent of liquid injection field desorption/ionization (LIFDI) [35–37] the FD experiment can now be conducted easier, faster, and with more reproducibility than with the previous methodology of sample supply outside the ion source. If required, LIFDI offers fully inert sample transfer from septum vials to the emitter positioned inside the ion source. So far, LIFDI has been applied to nonpolar constituents of crude oils and petroleum fractions [38–40], fullerene derivatives [41, 42], transitions metal complexes [43], and other compounds of high reactivity towards moisture and air [37].

FD, like FAB and MALDI, is not restricted to the analysis of ionic species, but may also yield ions of neutral analytes, e.g., of nonionic impurities in case of ILs. In contrast to the above ionization methods, FD does not exhibit any background peaks such as matrix or solvent ions. Thus, it was tempting to apply the traditional method FD in its comparatively new implementation as LIFDI to the mass spectral analysis of ILs.

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Experimental

The LIFDI measurements were performed on a JEOL JMS-700 (JEOL, Tokyo, Japan) double-focusing reversed-geometry magnetic sector instrument set to scan the m/z 50–800 range in 7 s with the resolving power adjusted to $R = 1000$ –1200, or the m/z 200–2550 range in 12 s at $R = 2500$, respectively. For tuning, toluene was admitted to the ion source from the reservoir inlet and field ionized to yield the molecular ion peak at m/z 92. The unmodified manufacturer's FD/FI ion source was kept at 80 °C; the emitter potential was 11.0–11.5 kV.

The LIFDI unit comprising a LIFDI probe and observation optics with CCD camera was the commercial product of Linden CMS (Linden CMS, Leeste, Germany) based on the prototype for this mass spectrometer, which had previously been tested in our laboratory; a detailed description of this assembly [43] and its basic operation have been published [37, 43].

Activated tungsten wire (13 μm) LIFDI emitters (Linden CMS) were employed. During the experiments, the emitter heating current (EHC) was ramped from 2 to 50 mA at (2–)16 mA min⁻¹. Fast heating rates were preferred and only diminished when desorption otherwise would have occurred too fast or too intense to allow for registration of reproducible spectra, or when extreme desorption rates would have presented the risk of emitter-destroying discharges. Repeated short baking at 90 mA was used to clean the emitter after each measurement.

Normally, ILs were provided as solutions in methanol, for testing purposes also in acetonitrile or tetrahydrofuran (Sigma-Aldrich, Taufkirchen, Germany), at concentrations of 0.01–0.1 $\mu\text{L mL}^{-1}$. The sample solutions were transferred onto the emitter by means of a fused silica transfer capillary of 50 μm i.d. and about 80 cm long. The atmospheric pressure entrance of the capillary was dipped into the sample solution for 5 s whereby a volume of roughly 100 nL was sucked onto the emitter inside the ion source. The transfer through the capillary took about 15 s; further 30–60 s were necessary to allow for evaporation of the solvent and for further pumping to recover the ion source vacuum. To ensure smooth operation without discharges, the pressure inside the ion source housing was allowed to fall to at least 8×10^{-4} Pa before switching on the high voltage. During measurements this pressure typically settled around 4×10^{-4} Pa. (Note: our JMS-700 recently had the original 520 L s⁻¹ turbomolecular pump at the ion source housing replaced by a 330 L s⁻¹ pump. The exchange of 75 μm i.d. transfer capillaries for 50 μm i.d. nicely compensated for the associated lack of pumping capacity.)

Linked scans at constant B/E [44] were employed to acquire the first field-free region metastable ion or collision-induced dissociation (CID) [45, 46] spectra of the selected precursor ions. For CID measurements helium was used as collision gas. As the collision cell is located within the ion source housing, its pressure rose

to 1.8×10^{-3} Pa while the precursor ion intensity was reduced to 50%–60% during CID measurements.

Results and Discussion

All but one of the ILs studied were based upon a nitrogen heterocyclic cation, i.e., derivatized pyridinium, pyrrolidinium, or imidazolium ions, and an organic or inorganic counterion (IL 1–9). Among these, the two pyrrolidinium salts exhibit the same cation but different anions (2, 3). The same sort of variation is realized with two pairs of imidazolium structures (6, 7, and 5, 8). The last IL in the series (10) consists of a phosphonium cation and a trifluorophosphate anion. The complete set of ILs under study and their structures are collected in Table 1 (additional survey scan spectra and selected tandem mass spectra are provided as Supplementary Material, which can be found in the electronic version of this article).

LIFDI basically tolerates a wide range of solvents including dichloromethane, tetrahydrofuran, methanol, toluene, and acetonitrile. Highly volatile solvents such as dichloromethane tend to elute in a somewhat irregular manner onto the emitter, while acetonitrile freezes upon evaporation in the vacuum of the ion source and needs elongated periods to thaw and wet the emitter. Tetrahydrofuran, methanol, and toluene show the most convenient behavior. Because some ILs needed a polar solvent, methanol was finally selected for LIFDI analysis of all ten ILs. In case of those compounds that were initially measured from tetrahydrofuran or acetonitrile solutions, no changes in the appearance of LIFDI spectra was observed when their spectra were recorded from methanol.

Full Scan LIFDI Mass Spectra of IL

The full scan spectrum of *N*-hexylpyridinium tetrafluoroborate (1) presents a typical example for the appearance of all ILs LIFDI mass spectra (Figure 1). The *N*-hexylpyridinium clearly presents the base peak of the spectrum at m/z 164.2, which is accompanied by a peak of 27% relative intensity at m/z 415.3 and a minor one of just 1.3% at m/z 666.4 (m/z values of the most abundant ion among isotopomers are given). It is clearly visible from the insets that the latter pair of signals corresponds to the $[\text{C}_2\text{A}]^+$ and $[\text{C}_3\text{A}_2]^+$ cluster ions, respectively. Formation of cluster ions of the general formula $[\text{C}_n\text{A}_n - 1]^+$ is a long known phenomenon in FD mass spectra of salts [47, 48]; the value of n rises the larger the amount of sample placed onto the emitter surface and also depends on the actual salt. The assignment of the signals at higher m/z is further justified from the comparison of the experimental and calculated isotopic patterns, which reveal the presence of one boron atom at m/z 415.3 and two at m/z 666.4 due to the content of ¹⁰B besides the most abundant boron isotope ¹¹B. The signal-to-noise ratio (s/n) of 1400 of this spectrum where a solution of 1 in methanol at a concentration of

Table 1. Compilation of ILs studied by LIFDI-MS

No.	Compound name	Formula; cation and anion separate	Structure	Mass of C ⁺ , A ⁻ , [C ₂ A] ⁺ [u]
1	<i>N</i> -hexylpyridinium tetrafluoroborate	[C ₁₁ H ₁₈ N] ⁺ [BF ₄] ⁻		164, 87, 415
2	1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate	[C ₉ H ₂₀ N] ⁺ [CF ₃ SO ₃] ⁻		142, 149, 433
3	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[C ₉ H ₂₀ N] ⁺ [C ₂ F ₆ NO ₄ S ₂] ⁻		142, 280, 564
4	1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	[C ₁₀ H ₁₉ N ₂] ⁺ [C ₆ F ₁₈ P] ⁻		167, 445, 779
5	1-Butyl-3-methylimidazolium methylsulfate	[C ₈ H ₁₅ N ₂] ⁺ [CH ₃ SO ₄] ⁻		139, 111, 389
6	1-Ethyl-3-methylimidazolium trifluoroacetate	[C ₆ H ₁₁ N ₂] ⁺ [C ₂ F ₃ O ₂] ⁻		111, 113, 335
7	1-Ethyl-3-methylimidazolium thiocyanate	[C ₆ H ₁₁ N ₂] ⁺ [SCN] ⁻		111, 58, 280
8	1-Butyl-3-methylimidazolium tricyanomethide	[C ₈ H ₁₅ N ₂] ⁺ [C ₄ N ₃] ⁻		139, 90, 368
9	<i>N</i> -Butyl-3-methylpyridinium dicyanamide	[C ₁₀ H ₁₆ N] ⁺ [C ₂ N ₃] ⁻		150, 66, 366
10	Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate	[C ₃₂ H ₆₈ P] ⁺ [C ₆ F ₁₈ P] ⁻		483, 445, 1411

Figure 1. LIFDI mass spectrum of *N*-hexylpyridinium tetrafluoroborate (**1**) in methanol at a concentration of 0.1 $\mu\text{L mL}^{-1}$ scanned over the m/z 50 to 800 range. The insets show the $[\text{C}_2\text{A}]^+$ and $[\text{C}_3\text{A}_2]^+$ cluster ions for comparison of the experimental and calculated isotopic patterns.

0.1 $\mu\text{L mL}^{-1}$ has been transferred onto the emitter roughly falls in the middle of the range between s/n 900 and s/n 2500 that has been obtained for LIFDI spectra of ILs. It exemplifies that peaks down to about 1% relative intensity can still be distinguished from the electronic background, and moreover, that their isotopic patterns still serve as a source of information.

The same characteristics can be observed in the LIFDI mass spectrum of 1-butyl-3-methylimidazolium methylsulfate (**5**), cation at m/z 139.1, where the cluster ions $[\text{C}_2\text{A}]^+$ at m/z 389.2 and $[\text{C}_3\text{A}_2]^+$ 639.3 are even more pronounced, i.e., their relative intensities have increased to 63% and 0.4%, respectively (cf. Supplementary Material section, which can be found in the online version of this article). The formation of those cluster ions and, thus, setting of a scan range to include at least the first of them, is essential for the determination of the anion of the IL. FD mass spectrometry with activated emitters is basically restricted to positive-ion mode, because in negative-ion mode the (often emitter destroying) emission of electrons from the emitter tends to precede the desorption of anions, thus making negative-ion FD the rare exception [49, 50]. This behavior is the reason why the JMS-700 instrument used in this work cannot even be switched to negative-ion operation in FD mode. Nonetheless, the cluster ions provide the information necessary for the identification of the anions, because they obey the rule of adding complete "salt molecules," $[\text{CA}]$, to the cation or a lower-order member in the series to form the higher-order cluster ions. Therefore, the mass difference between the base peak of the LIFDI spectrum and the ion of second highest intensity or between neighboring cluster ions always corresponds to the mass of the complete IL, i.e., to $[\text{CA}]$. Subtraction of the cation mass as obtained from

the base peak of the spectrum then unambiguously provides the anion mass. In addition, the eventual changes in isotopic pattern between cation and cluster ion peaks provide information on the anion's isotopic composition.

Tandem MS for Cluster Ion Identification

Tandem mass spectrometry may further assist in the assignment of peaks to cluster ions. Linked scans at constant B/E [44] present the preferred technique of accomplishing this on a double focusing magnetic sector instrument, because linked scans at constant B/E deliver good resolution of the fragment ions plus sufficient ion abundances since ion dissociations in the first field-free region are observed.

Figure 2 compares the metastable ion dissociation of the $[\text{C}_3\text{A}_2]^+$ ion of **5**, m/z 639.3, with the collision-induced dissociation of the same species. Although only contributing to a peak of about 0.4% relative intensity in the LIFDI mass spectrum of this IL, the $[\text{C}_3\text{A}_2]^+$ ion of **5** still delivers highly useful tandem mass spectra in both modes. Despite their very low abundance, the relevant fragment ions can already be observed under metastable ion conditions, but the corresponding signals are significantly stronger under CID. Clearly, the $[\text{C}_3\text{A}_2]^+$ ion dissociates in the expected manner to form $[\text{C}_2\text{A}]^+$, m/z 389.2, and C^+ , m/z 139.2, fragment ions by subsequent elimination of $[\text{CA}]$. The low intensity of fragment ions upon collision gas-free conditions demonstrates the extraordinary softness of ion formation under FD conditions. The internal energy of the cluster ions is low enough to prevent the vast majority of them from metastable dissociation. Instead, collisions are required to supply additional excitation to induce $[\text{CA}]$

Figure 2. Metastable ion dissociation of the $[C_3A_2]^+$ ion of 5, m/z 639.3 (a), and collision-induced dissociation of the same species (b). $[C_3A_2]^+$ dissociates to form $[C_2A]^+$, m/z 389.2, and C^+ , m/z 139.2, fragment ions by subsequent elimination of [CA].

losses at significant rates to yield fragment ion peaks of reasonable intensity for analytical purposes. The absolutely minor degree of metastable dissociation of IL cations as well as of their cluster ions was common of all ions generated from 1–10.

Residual Collisions or Real Metastable Dissociation?

The question arises as to whether the small peaks in the metastable ion spectrum of 5 are really due to metastable ions and thus result from internal energy received during field desorption. The increased pressure during LIFDI measurements compared with conventional FD might cause some CID with residual gas. To eliminate the influence of residual gas as much as possible, the transfer capillary was capped by sticking a septum on its exit towards atmosphere. After an additional delay

of 5 min to allow the remaining solvent vapor to escape from the capillary, the pressure in the ion source housing had fallen to 2.6×10^{-4} Pa, which is 65% of the usual value of 4×10^{-4} Pa during LIFDI operation; a further reduction of the pressure could not be achieved. In a first experiment with the $[C_2A]^+$ cluster ion, m/z 564.3, of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (3), this drop in pressure did not affect the very low fragment ion intensity of 0.03% compared with 4% in the respective CID spectrum (Figure 3). Analogous observations were made for the fragmentation of the $[C_3A_2]^+$ cluster ion of 5. However, this cluster ion started to show considerable loss of one [CA] when the EHC exceeded 30 mA, whereas loss of two [CA] moieties as observed in the corresponding CID spectrum (Figure 2) did not occur. This supports the assumption that thermal energy at high EHC still presents the most relevant source of internal energy for

Figure 3. Comparison of fragment ion mass spectra of the $[C_2A]^+$ ion of **3**, m/z 564.3; (a) metastable ion dissociation at reduced pressure, (b) metastable ion dissociation at standard pressure of LIFDI operation, and (c) collision-induced dissociation of the same species. The intensity scale is amplified by a factor of 1000 in (a) and (b), by 20 in (c). The precursor ions are in scale.

ions generated by FD and that the somewhat elevated pressure during LIFDI compared with conventional FD has only very minor if any effect on the internal energy of the ions.

Tandem MS of the Cation

The inherent softness of LIFDI requires tandem MS experiments to be performed for structure elucidation of the IL cation. The full scan spectra shown here were the results of accumulating the whole desorption period, but the process of desorption was found to last sufficiently long to allow for CID spectra of the cations to be acquired after about 10 survey scans had been obtained. Thus, a more economical measurement procedure would yield both spectra from one sample run. In some cases, even two tandem mass spectra were run in addition, e.g., those of two presumed cluster ions or of IL cation plus one cluster ion. The *N*-hexylpyridinium ion, $[C_{11}H_{18}N]^+$, m/z 164, from **1** fragments by competitive losses of methane, ethane, propane, and butane to yield fragment ions at m/z 148, 134, 120, and 106, respectively. Due to the occurrence of peaks at m/z 107, 93, and 79, ion **1** also shows homolytic C–C bond cleavages causing butyl, pentyl, and hexyl loss. Finally, it undergoes another rearrangement to yield the pyridinium ion, m/z 80, upon loss of hexene (Figure 4).

Accordingly, the rather large trihexyl(tetradecyl)phosphonium ion, $[C_{32}H_{68}P]^+$, m/z 483.5, shows its many alkyl chains by homolytic cleavages at any C–C and C–P bond.

A preference for C–P bond cleavages is revealed by the appearance of prominent peaks due to hexyl loss from the cation at m/z 398.4 and tetradecyl loss at m/z 286.3. This allows identifying the substitution pattern at the phosphorus atom (cf. Supplementary Material section).

Recognition of Cluster Ions from Ion Chromatograms

While tandem mass spectrometry is the tool of choice for structure elucidation of the cations and for identification of cluster ions, it is not always necessary to perform such additional experiments just to recognize a peak as being related to a cluster ion. As the emitter is heated during the measurement by ramping the EHC from zero or very low values to a level generating several hundred degrees Celsius (2 to 50 mA in this study), there is some fractionation to be observed. Normally, ions of lower mass desorb at lower EHC than heavier ones, but cluster ions behave the opposite way. This is because cluster ion formation depends on a high particle density to favor condensation products over desorption of isolated ions. The emitter gets depleted as desorption proceeds, i.e., the density of molecules on the emitter surface or in the selvedge region is largely diminished, thereby reducing cluster ion formation. Consequently, high cluster ion intensities are observed in the period after onset of ion desorption, whereas neat cation desorption prevails towards the end of the process. In addition, at high temperature ample thermal energy is present to bring about spontaneous evaporation

Figure 4. CID mass spectrum of *N*-hexylpyridinium ion, $[C_{11}H_{18}N]^+$, m/z 164, from 1.

of neutrals from cluster ions. A simple plot of the respective reconstructed ion chromatograms (RICs) therefore reveals whether an ion is a cluster ion of one component or an isolated cation of another component having different mass. As an example, the total ion chromatogram (TIC) of the measurement of 5 and the RICs of $[C_3A_2]^+$, m/z 639, $[C_2A]^+$, m/z 389, and C^+ , m/z 139, are shown in Figure 5. The larger cluster ion clearly predominates at the beginning, while the cation alone exhibits the highest abundance relative to the other species at the end of the trace.

Obviously, this simple approach applies only for mixtures with significant differences in cation mass and

if only two or eventually three components are to be distinguished.

Limit of Detection

The limit of detection (LOD) in LIFDI full scan spectra has been determined for some of the ILs. It is a general fact that the sensitivity of FD depends on the cleanliness of the ion source, especially on that of the surface of the counter electrode, and on the actual condition of the emitter. ILs were found to desorb without notable residue from the emitter preventing emitter degradation along a series of measurements from becoming a

Figure 5. Total ion chromatogram (TIC) of the measurement of 5 and reconstructed ion chromatograms (RICs) of $[C_3A_2]^+$, m/z 639, $[C_2A]^+$, m/z 389, and C^+ , m/z 139. The larger cluster ion clearly predominates at the beginning. Each curve is normalized to 100% intensity to simplify their comparison in time.

Figure 6. Partial LIFDI mass spectrum of a solution containing **1** and **6** in a 1:1 ratio. The cluster ion constituents are color-coded for easy of assignment.

major issue; a single emitter could serve for a whole day of measurements. Nonetheless, there is an influence of those parameters, and therefore, LODs may vary. Depending on the IL and actual ion source conditions, an amount of 5–50 pg IL was sufficient to yield an *s/n* better than 10 when the instrument was scanned from *m/z* 50 to 800 at *R* = 1000. The amount of sample has been determined based on the concentration of the analyte solution (here 0.0001 $\mu\text{L mL}^{-1}$) and on the estimate that a volume of 100 nL is transferred by a single dipping event of 5 s [37].

Mixture Analysis

A solution containing **1** and **6** in a molar 1:1 ratio was prepared, which yielded a mixture of two cations, i.e., *N*-hexylpyridinium, *m/z* 164, and 1-ethyl-3-methylimidazolium, *m/z* 111, and of two anions, i.e., tetrafluoroborate and trifluoroacetate. The intensity ratio of the cation peaks was 10:7, i.e., *N*-hexylpyridinium was desorbed more efficiently than the lighter 1-ethyl-3-methylimidazolium.

As predicted by statistics, cluster ions can be formed, having grouped together two cations of the same kind with either the tetrafluoroborate or the trifluoroacetate as counterion, thereby giving rise to four cluster ion compositions. Furthermore, a mixed pair of cations can either attach to tetrafluoroborate or the trifluoroacetate to yield another two cluster ion composition. In the spectrum, a total of six cluster ions has indeed been observed. Statistics would dictate intensity ratios of 1:1:2:2:1:1 and the increased abundance of the *N*-hexylpyridinium, *m/z* 164, suggests even higher probability to detect its clusters. However, the experimental distribution was roughly 3:3:3:3:1:1 (Figure 6). This reflects the unfortunate tendency

towards discrimination among competing ionic species, where the higher intensity of the isolated cation is not necessarily reflected in the intensities of the respective cluster ions.

Nonetheless, a full discrimination of one component did not occur, which is consistent with earlier findings in mixture analysis in this laboratory. Thus, one may rely on FD's capability not to hide one component in favor of another, but one should remain aware of the fact that the relative intensities of peaks in LIFDI spectra are indications rather than measures for the relative concentrations of components in mixtures.

Conclusions

LIFDI mass spectrometry was successfully applied to the analysis of 10 ILs with different types of anions and cations. For LIFDI measurements the ILs were provided as dilute solutions preferably in methanol, were transferred directly into the ion source, and desorbed from the emitter after complete solvent evaporation. For each IL, the intact cation of the compound yielded the base peak of the mass spectrum. In addition, cluster ions of the general formula $[\text{C}_2\text{A}]^+$ and occasionally $[\text{C}_3\text{A}_2]^+$ were detected. Ion currents were high enough to permit tandem mass spectrometry to be employed for the identification of the observed ions. Thus, the inherent limitation of LIFDI to the positive-ion mode did not prevent acquisition of analytical information on the anions. The limit of detection in survey scans should be low enough to detect IL impurities in chemical products. Altogether, LIFDI-MS served as a reliable tool for the mass spectral analysis of ILs. Due to the absence of any solvent or matrix background peaks, LIFDI-MS should be particularly useful for purity control of such compounds.

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