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Technical Report

Desorption of Positive and Negative Ions from Areoles of *Opuntia microdasys* Cactus at Atmospheric Pressure: Cactus-MS

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The areoles and spines of cacti can be used to desorb ions of ionic liquids (ILs) by the mere action of an electric field into the atmospheric pressure (AP) interface of a mass spectrometer. The small cactus species *Opuntia microdasys* bears numerous very fine hairs on its areoles and tiny sharp spines that appeared suited to serve as needle electrodes sharp enough for field desorption of ions to occur. In fact, positive and negative ions of four ILs could be desorbed by a process analogous to AP field desorption (APFD). In contrast to APFD where activated field emitters are employed, the ILs were deposited onto one or two adjacent areoles by applying 1–3 μL of a dilute solution in methanol. After evaporation of the solvent, the cactus was positioned next to the spray shield electrode of a trapped ion mobility-quadrupole-time-of-flight instrument. Desorption of IL cations and IL anions, respectively, did occur as soon as the electrode was set to potentials in the order of ±4.5 kV, while the cactus at ground potential was manually positioned in front of the entrance electrode to bring the areole covered with a film of the sample into the right position. Neither did mixing of ILs occur between neighboring areoles nor did the cactus suffer any damage upon its use as a botanical field emitter.

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1. INTRODUCTION

The advent of ambient desorption/ionization[1–3] led to a plethora of emerging techniques of ion desorption and desorption/ionization. Among those techniques, there were some where strong electric fields played a role in analyte ion desorption.[4–9] In particular, the use of fine bamboo fiber in front of an atmospheric pressure (AP) interface inspired the idea that essentially anything having sharp enough edges or tips should be able to deliver ions to a mass spectrometer equipped with an AP interface of similar design. Being fond of cacti, the author's initial inspiration was that even the spines of a cactus should do the trick. However, the cactus concept was not immediately followed. Instead, an activated tungsten field emitter, that is, an object from the analytical world, appeared as a reasonable substitute for the spines of a cactus. This eventually led to the development of AP field desorption (APFD).[10]

Traditional field ionization (FI) and field desorption (FD), which have been known for decades as very soft ionization techniques in mass spectrometry (MS), are both high-vacuum ionization methods.[11–14] While the FI process yields intact positive molecular ions, $M^{+\bullet}$, the FD process transfers preformed ions into the gas phase.[11–14] In contrast to FI, FD of preformed ions only needs field strengths that are about a hundred times lower than those required FI.[15–19]

While established as a high vacuum ionization technique, FD has nonetheless also been performed at super-atmospheric pressure.[19] Furthermore, there were two studies presenting special cases of FD at atmospheric conditions: while one employed activated emitters to study reaction kinetics in strong electric fields,[20] the other also described the use of the hairy leg of a *Drosophila* fly as a field emitter.[21]

Activated field emitters, as used in vacuum FI or FD, were demonstrated to deliver sufficiently strong electric fields to allow for FI and FD at AP.

In APFD, the voltages required to achieve ion desorption were in the order of 4.5–5.5 kV.[10] It turned out that not only positive even-electron ions of highly polar or ionic compounds could be desorbed but even positive molecular ions, $M^{+\bullet}$, could be generated in APFD.[22] APFD also worked in negative-ion mode and delivered negative even-electron ions of highly polar or ionic compounds, for example, of surfactants in commercial detergents.[23]

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As the further advancement of APFD was hampered by the practical limitation inherent to the first simplistic source design, a more robust and reproducible means of positioning and aligning the emitter was constructed. This dedicated APFD source allowed for robust operation, implemented the observation of the emitter during operation, and most importantly, provided resistive emitter heating as in traditional FD.[24–26] Using this robust and versatile APFD source[27] also enabled the coupling of APFD with trapped ion mobility separation (TIMS).[28] Meanwhile, APFD has been explored in some depth.[10,22,23,27,28]

The spines of cacti emerge from a special structure that typically is a woolly or hairy area on the stem. These structures are termed areoles. In the case of the small-growing species *Opuntia microdasys*, the areoles have numerous very fine hairs and also bear tiny sharp spines. In addition, *Opuntia microdasys* is commonly among the offerings of garden centers, and thus, easy to obtain. Therefore, the experiments were carried out using one cactus of this species. The work presented here is a proof of principle type of study, admittedly with some playful aspects.

2. EXPERIMENTAL

2.1 Mass spectrometer

A TIMS-quadrupole-time-of-flight (TIMS-Q-TOF) instrument (timsTOFflex, Bruker Daltonics, Bremen, Germany) was used. The instrument was equipped with an ESI-to-MALDI switchable Dual Source. The mass spectrometer was controlled by the Bruker timsControl software (V 2.0) and data analysis was performed using the Bruker DataAnalysis software (V 6.0).

External mass calibrations were established in ESI mode using Agilent Tune Mix (G1969-85000) for the *m/z* 50–800 or *m/z* 80–2000 range.[29,30] Mass accuracy was generally in the order of 2–5 ppm.

2.2 Samples

Four ionic liquids (ILs), one of which was previously used to establish the basics of APFD mode,[10] and all of which had been characterized by LIFDI-MS,[31] were employed. Methanol of LC-MS grade was obtained from Merck KGaA (Darmstadt, Germany). The ILs are compiled in Table 1.

2.3 APFD source

A recently described APFD source[27] based on an aluminum frame that fits the hinges and source clamp of the AP interface of the timsTOFflex mass spectrometer was exclusively used to (i) activate the high-voltage interlock switch and (ii) to serve as a hand rest while placing the cactus in front of the interface. The mounting stage that would carry the APFD probe with the emitter was retracted as far as possible to give free access to the AP interface (Fig. 1).

2.4 Cactus-MS

A 10-µL microliter syringe was used to apply the sample solutions to the areoles situated along the rim of a cactus cladode. The ILs were used as solutions of concentrations of 0.1–1 µL ml^{-1} in methanol. After the solvent had completely been evaporated, the cactus was ready to serve as a field emitter. Thus, the rim of the cactus was positioned horizontally in the center of the aperture of the spray shield electrode of the Bruker AP interface where the spray shield served as the counter electrode. High voltage was only applied to the counter electrode provided by the API interface, whereas the cactus remained at ground potential. High voltage of the spray shield and the cap on the transfer capillary underneath were set using the API source controls of the instrument. In positive-ion mode, these voltages were negative to attract cations while in negative-ion mode they were positive to attract anions. The spray shield voltages were in the order of ±4.5 kV while the cap was set to 200 V higher voltage. The desolvation gas at the spray shield was set to 4.0 L min^{-1} at 150°C as this was a proven mid-level setting established in previous work on APFD using the same mass spectrometer.[27,28] All remaining instrument settings were used as in ESI operation for the respective *m/z* range.

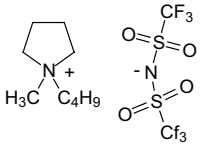
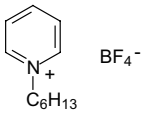
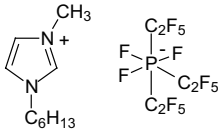
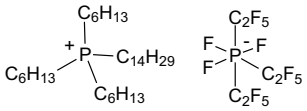
Caution: High voltage is applied to the spray shield without cover. Provided that basic care is applied, the user is nonetheless safe from getting into contact with high voltage during operation as all other parts are at ground potential. Also, note that the spines of *Opuntia microdasys* penetrate the skin even upon slight contact and can be a bit nasty.

3. RESULTS AND DISCUSSION

In positive-ion mode, signals corresponding to the IL cations were observed as soon as an areole loaded with an IL was suitably positioned in front of the entrance of the spray shield electrode, that is, at a location where the emitter would have been in APFD. Thus, the desorption of IL cations of the four ILs from areoles of *Opuntia microdasys* occurred upon positioning the respective areole at about 2 mm distance to the entrance of the shield electrode of the AP interface. The relevant portions of those mass spectra are compiled in Fig. 2. From *top* to *bottom*, the left column shows 1-butyl-1-methylpyrrolidinium, $[C_9H_{20}N]^+$, *m/z* 142.1584 (calc. *m/z* 142.1590), *N*-hexylpyridinium, $[C_{11}H_{18}N]^+$, *m/z* 164.1433 (calc. *m/z* 164.1434), 1-hexyl-3-methylimidazolium, $[C_{10}H_{19}N_2]^+$, *m/z* 167.1531 (calc. *m/z* 167.1543), and trihexyl(tetradecyl)phosphonium, $[C_{32}H_{68}P]^+$, *m/z* 483.5059 (calc. *m/z* 483.5053). The spectra of the first three IL cations also exhibited peaks of about 5%–10% relative intensity due to fragment ions by losses of butene and also butane from 1-butyl-1-methylpyrrolidinium, and by losses of hexene from either *N*-hexylpyridinium or 1-hexyl-3-methylimidazolium. The intensities of the IL cation signals varied due to slight positional changes of the hand-held cactus plant during the period of data acquisition. Provided that the areole loaded with sample was correctly placed in front of the entrance of the spray shield electrode, the intensities of the cation peaks were in the range of 10^4 to 10^7 counts depending on the actual IL and probably on the "quality" of the selected areole in terms of its hairs and spines.

An example of the temporal variation of the signal and the entire procedure of spectral acquisition from the cactus spines is provided in the Supplementary Material (Fig. S1). There, the initial period until about 0.15 min in the base peak chromatogram (BPC) reflects the time span between the start of the acquisition and the final positioning of the cactus with the loaded areole placed right in front of the interface. The last segment of the BPC, from about 0.45 min to the end, corresponded to the time for retracting the cactus and stopping the actual run. This BPC also showed a strong fluctuation in

Table 1. Compilation of ionic liquids studied by cactus-mass spectrometry in the order of increasing cation mass.

Compound name	Formula of cation and anion	Structure	Calculated mass of C^+ and A^- [u]
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	$[C_9H_{20}N]^+$ $[C_2F_6NO_4S_2]^-$		142.1590 279.9178
N-Hexylpyridinium tetrafluoroborate	$[C_{11}H_{18}N]^+$ $[BF_4]^-$		164.1434 87.0035
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate	$[C_{10}H_{19}N_2]^+$ $[C_6F_{18}P]^-$		167.1543 444.9456
Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)-trifluorophosphate	$[C_{32}H_{68}P]^+$ $[C_6F_{18}P]^-$		483.5053 444.9456

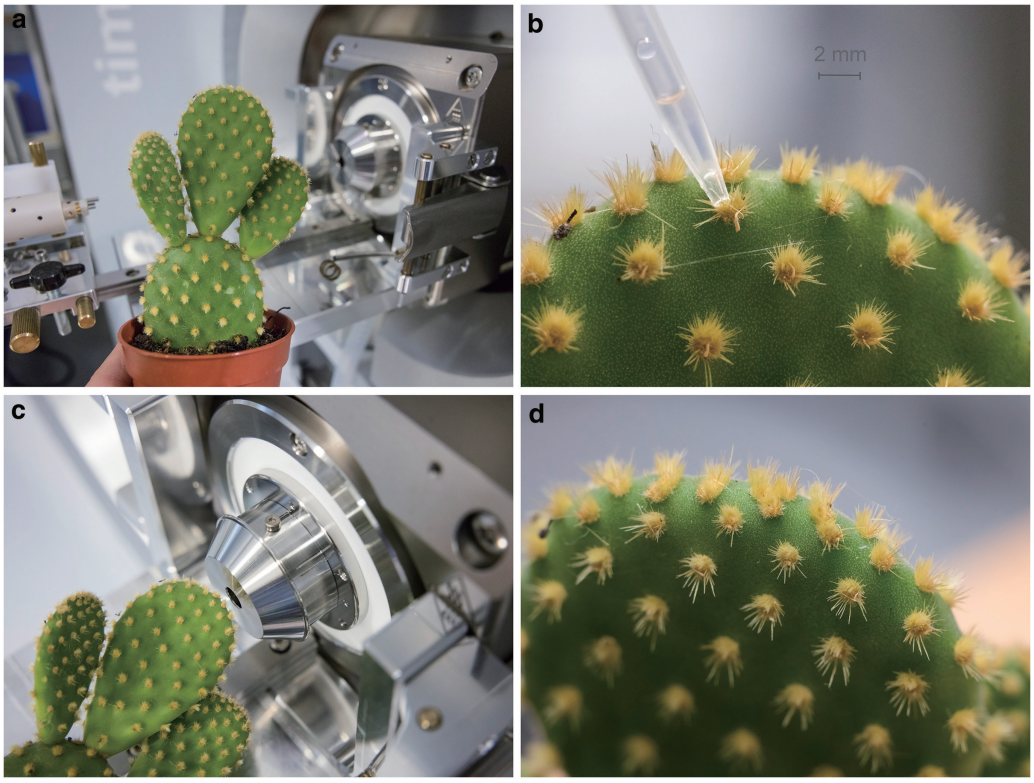


Fig. 1. Performing cactus-mass spectrometry. (a) To get ready for using *Opuntia microdasys* as field emitter the slider with the emitter mount of atmospheric pressure field desorption source is fully retracted. (b) Next, 1–3 µL of sample solution is loaded onto a selected areole and allowed to dry. (c) The cactus is then manually positioned as to align the areole of interest at about 2 mm distance in front of the entrance of the spray shield electrode to start ion desorption. (d) No damage was observed at the rim of cactus cladode after more than a dozen runs. For a sense of scale: the diameter of the straight part of the pipette tip in (b) is 2.1 mm while the portion of the cactus cladode shown in (d) is about 30 mm wide, that is, the spines are typically 0.5–1.5 mm long.

signal intensity due to slight dislocations of the hand-held cactus during acquisition. Generally, useful spectra could be collected for several seconds within each single run. It should also be mentioned that the period of desorption happened to be shorter and the signals were of about one order of magnitude lower intensity than what would have been obtained in APFD with an activated emitter and the same amount of sample loaded onto it.[10,27)]

In negative-ion mode, the anions of these four ILs were also detected (right column of Fig. 2). Thus, signals due to bis(trifluoromethylsulfonyl)imide, $[C_2F_6NO_4S_2]^-$, *m/z* 279.9174 (calc. *m/z* 279.9178), tetrafluoroborate, *m/z* 87.0035

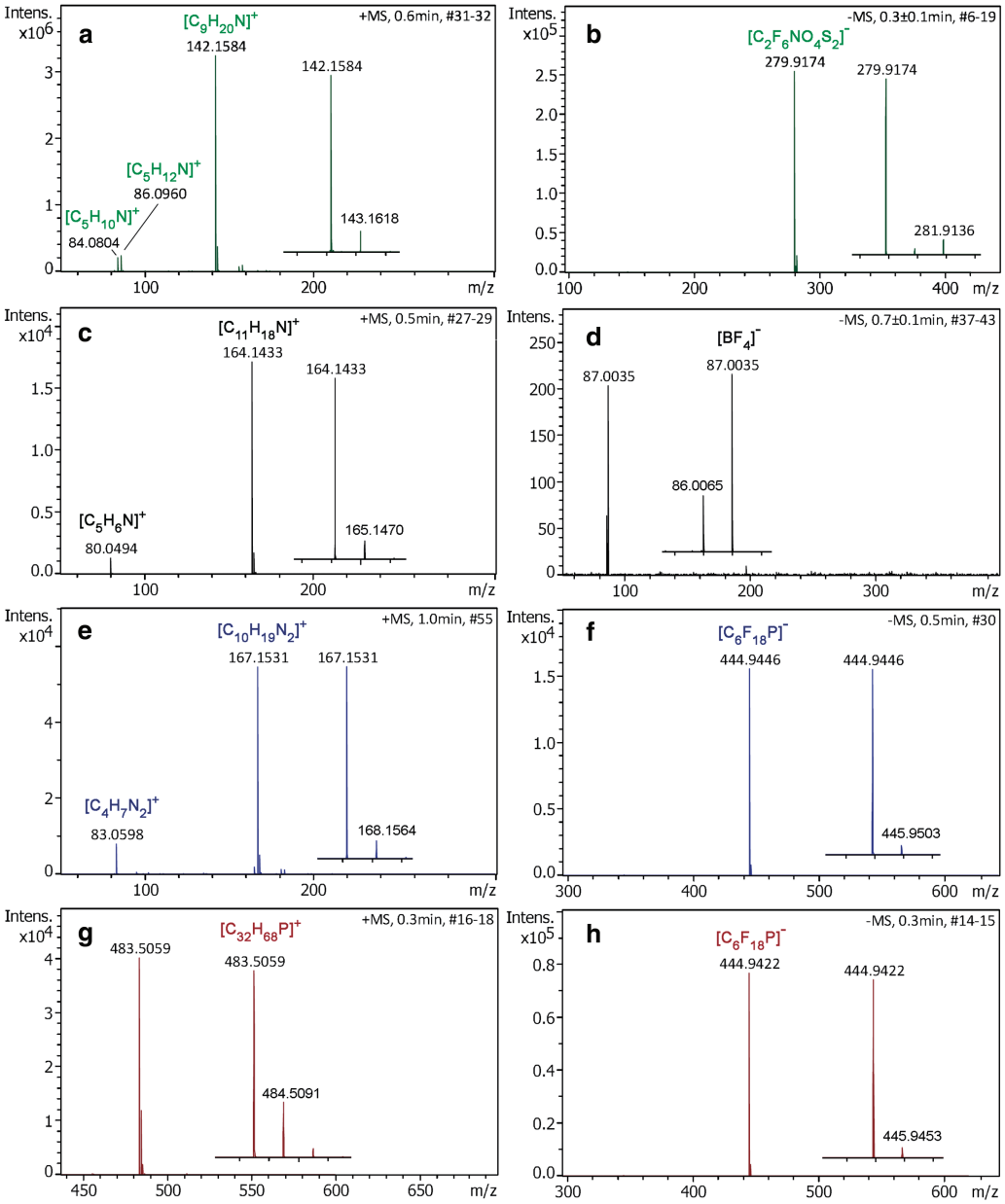


Fig. 2. Desorption of IL cations (left column) and anions (right column) of four ILs (each IL in the same line and all in order of Table 1) from areoles of *Opuntia microdasys* upon positioning the respective areole at about 2 mm distance to the entrance of the shield electrode of the AP interface. (a) 1-Butyl-1-methylpyrrolidinium, (b) bis(trifluoromethylsulfonyl)imide, (c) *N*-hexylpyridinium, (d) tetrafluoroborate, (e) 1-hexyl-3-methylimidazolium, (f) tris(pentafluoroethyl)trifluorophosphate, (g) trihexyl(tetradecyl)phosphonium, and (h) also tris(pentafluoroethyl)trifluorophosphate. Each spectrum shows the relevant portion of the *m/z* scale and an inset with an expansion of the signals of the respective cation or anion. AP, atmospheric pressure; IL, ionic liquid.

(calc. *m/z* 87.0035), and tris(pentafluoroethyl)trifluorophosphate, *m/z* 444.9446 (calc. *m/z* 444.9456) were observed. The latter anion was identical for the last two ILs. The isotopic patterns in the anion spectra revealed the presence of two sulfur atoms due to ^{34}S in the case of bis(trifluoromethylsulfonyl)imide and of boron due to ^{10}B in the case of tetrafluoroborate. Apart from tetrafluoroborate, the anions yielded signal intensities in the order of 10^4–10^5 counts. Tetrafluoroborate never delivered better than a few hundred counts. The signal was yet clear enough to show the boron isotopic pattern and to allow for its assignment to $[BF_4]^-$ based on accurate mass.

All spectra could be repeated, sometimes even without reloading the sample to an areole, and more importantly, using the same cactus plant on different days. Even several weeks after the first experiments, there is no visible damage to the rim of the cactus. The ILs also did not migrate on the cactus surface as demonstrated by moving the cladode along the different areoles (Fig. S2). Depending on the position of the cactus, either just one or in case of overlap two IL cations did appear.

Finally, it is worth noting that some signals of low intensity (several hundred to two thousand counts) did occur when an areole that was not loaded with sample happened to be in front of the interface. Mainly two peaks occurred repeatedly, in particular during the first experiments, and were thus examined more closely. These were detected at *m/z* 283.2626 and *m/z* 311.2941 and could be assigned to ions of the formula $[C_{18}H_{35}O_2]^+$, and $[C_{20}H_{39}O_2]^+$, respectively. The peaks would

thus correspond to $[M+H]^+$ ions of unsaturated fatty acids, that is, of oleic acid and eisosenoic acid or isomers thereof. Furthermore, there were some hydrocarbon fragment ions such as $[C_6H_9]^+$, $[C_6H_{11}]^+$, $[C_6H_{13}]^+$, $[C_7H_9]^+$, and $[C_7H_{11}]^+$ that were in line with the presence of long alkyl chains (Fig. S3). All of those ionic compositions could be expected to arise from the waxy compounds forming the cuticle of the plant.[32,33)]

A second cactus was thus purchased and analyzed as a control sample free of any IL. Depending on the exact position along the rim of cladodes of this second *Opuntia* as well as from a side cladode of the first Opuntia that had never been loaded with an IL, some additional signals did appear that might be related to cuticle compounds of these plants (Fig. S4). However, these desorptions from blank cladode areas were quite sporadic as compared to what could be achieved with the ILs and were not pursued any further.

4. CONCLUSIONS

Inspired by the recently developed APFD method, the areoles of the cactus species *Opuntia microdasys* carrying very fine hairs and spines were demonstrated to serve as needle electrodes sharp enough for FD of ions to occur. Both cations and anions of four ILs could be desorbed from these areoles when positioned in front of the AP interface of a TIMS-Q-TOF instrument (Bruker timsTOFflex). To do so, the areole loaded with some micrograms of the sample just needed to be at a position where the emitter would have been located in the APFD operation.

This study demonstrates that almost any sort of sharp tips may allow for ion desorption in strong electric fields at a level high enough to serve as a kind of ion source in MS. In particular, ILs resulted in strong ion desorption from the areoles, whereas ions related to compounds presumably being contained in the cuticle of the plant did only occur sporadically from blank portions of the plant.

Cactus-MS admittedly may not present the most elaborate technique and may also not be able to compete with other ambient ion sources. Nonetheless, this contribution might remind us that playful research beyond direct application or even commercial uses can bring about interesting results and may yet contribute to our understanding of ion formation processes.

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CONFLICTS OF INTEREST

J. H. Gross declares no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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