



High-Mass Cluster Ions of Ionic Liquids in Positive-Ion and Negative-Ion DART-MS and their Application for Wide Range Mass Calibrations

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Idea and Concept

- Direct analysis in real time (DART) [1] has found manifold applications [2] calling for a reliable and facile mass calibration, especially when accurate mass measurements are intended [3,4].
- Recently, DART-MS was demonstrated for the analysis of ionic liquids (ILs) [5]. There, positive IL cluster ions, $[C_nA_{n-1}]^+$ (as in field desorption spectra [6]), and negative $[A_nC_{n-1}]^-$ ions were reported up to m/z 1200.
- Cluster ion series are ideally suited for mass calibration, providing the respective IL cluster ions cover a wide mass range. Here, an IL is applied for mass calibration covering m/z 100–4000 in positive-ion and m/z 100–2500 in negative-ion DART-MS.
- A high-mass record of $m/z > 5000$ for positive-ion DART-MS is presented here [7].

Ionic Liquids Studied

IL No.	Compound Name	Cation and Anion Formulas and Nominal Masses [u] Separately	Structure	Accurate Mass of [CA] in [u]
1	N-hexylpyridinium tetrafluoroborate	$[C_{11}H_{18}N]^+$ [BF ₄] ⁻ 164 87		251.147049
2	1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate	$[C_9H_{20}N]^+$ [CF ₃ SO ₃] ⁻ 142 149		291.111599
3	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	$[C_9H_{20}N]^+$ [C ₂ F ₆ NO ₅ S ₂] ⁻ 142 280		422.076868
4	1-butyl-3-methylimidazolium methylsulfate	$[C_8H_{15}N_2]^+$ [CH ₃ SO ₄] ⁻ 139 111		250.098728
5	1-ethyl-3-methylimidazolium trifluoroacetate	$[C_8H_{11}N_2]^+$ [C ₂ F ₃ O ₂] ⁻ 111 113		224.077262
6	1-ethyl-3-methylimidazolium thiocyanate	$[C_8H_{11}N_2]^+$ [SCN] ⁻ 111 58		169.067368
7	1-butyl-3-methylimidazolium tricyanomethide	$[C_8H_{15}N_2]^+$ [C ₃ N ₃] ⁻ 139 90		229.132746
8	N-butyl-3-methylpyridinium dicyanamide	$[C_{10}H_{16}N]^+$ [C ₂ N ₃] ⁻ 150 66		216.137497

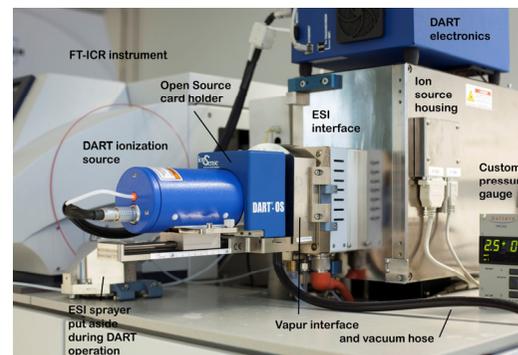
The eight ILs used in this study are compiled in the table.

In our laboratory, ten ILs employed in previous work [6] were still in stock. From this set of ILs, those with a heavy cation and/or anion were ruled out as potential mass calibrants as these ILs would have caused too large mass differences ($\Delta m/z > 450$) between adjacent cluster ions.

The widest cluster ion spacing is provided by 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($\Delta m/z = 422$).

IL 7 presents the optimum combination of width of cluster ion distribution and cluster ion spacing on the m/z scale.

Experimental



Left Side: DART-SVP with OpenSource option and Vapour Interface mounted to the electrospray interface of a Bruker ApexQe instrument in the author's laboratory. The DART supply electronics (blue box) is placed on top of the ion source housing. The ESI sprayer is placed aside (lower left) without disconnecting supply lines. For exchange, the units are simply lifted out of the hinges (right of center). The pressure reading of 2.5 mbar (custom-installed gauge) indicates nitrogen flow in DART standby mode, while 3.0 mbar are observed when helium is used in operation. The compact membrane pump of the Vapour interface is not shown; it is connected via the black hose exiting to the lower right.

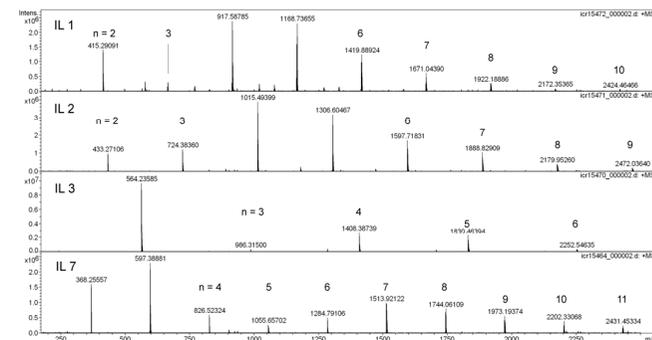
Lower Right: Insertion of an OpenSpot card in the OpenSource sample holder.



Experiments were performed on a Apex-Qe FT-ICR instrument (Bruker Daltonik). A DART-SVP ionization source (IonSense) equipped with the OpenSource that provides transmission mode DART was mounted onto the ESI interface via the VapourInterface. The DART helium gas was set to 450 °C. Ions were accumulated for 0.5–1.5 s prior to ICR mass analysis. Ions were excited and detected using standard setting from previous DART work [3,4]. Broadband spectra were acquired with 512 k to 1 M data points. Per magnitude spectrum, 6–12 transients were accumulated. Initial positive-ion mode mass calibration was established in DART mode using silicone oil [3] while Agilent ES tune mix with 2 % (v/v) of trifluoroacetic acid was used in negative-ion mode [4].

Searching for Wide Cluster Ion Distributions

In general, ILs form positive $[C_nA_{n-1}]^+$ ions and negative $[A_nC_{n-1}]^-$ ions, the abundance of which strongly depends on the IL. Most of the ILs form cluster ions up to about m/z 2500. The spectra of some ILs indicate that the series may expand well beyond that value. The figure compares the positive-ion DART spectra of ILs 1, 2, 3, and 7 to exemplify the general behavior of the ILs upon DART ionization. The cluster ion of highest m/z in these spectra is identified as the $[C_{10}A_9]^+$ ion of 1. The relative ion abundances as derived from the relative intensity



of the corresponding signals are 3% for the $[C_{10}A_9]^+$ ion of 1, 5% for the $[C_6A_5]^+$ ion of 2, 4% for the $[C_6A_5]^+$ ion of 3, and finally 9% for the $[C_{11}A_{10}]^+$ ion of 7. Among these and all others, 7 turns out to form the cluster ions of highest m/z . Analogous behavior is observed in negative-ion spectra where 6 and again 7 show the widest cluster ion distribution.

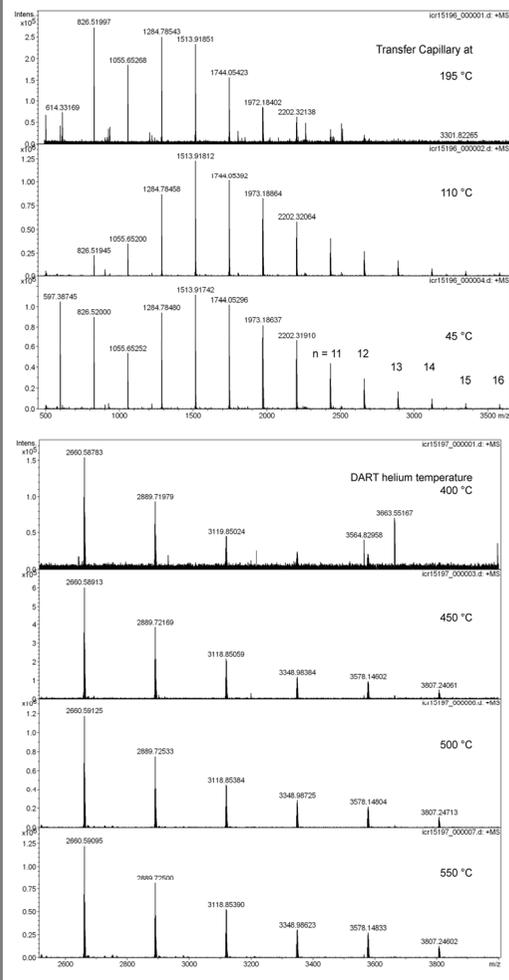
Handouts

Handouts of this poster in PDF format can be downloaded after this ASMS conference from www.ms-ocihd.de

Acknowledgment

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Optimization of Cluster Ion Distributions



Effect of the temperature of the ion transfer capillary on cluster ion abundances and widths of cluster ion distributions.

Using IL 7 and with the DART gas set to 450 °C, the temperature of the capillary is stepwise reduced from 195 °C (top), to 110 °C (middle), to 45 °C (bottom). High-mass cluster ions are detected when the capillary approaches the lower temperature limit posed by typical temperature of the ion source housing.

Influence of the temperature of the DART helium gas.

Increasingly larger cluster ions of IL 7 can be observed when the temperature of the DART helium gas is raised from 400 to 550 °C. The spectra show the effect of increments of 50 °C. Other than variation of He temperature all measurements are made using under standard DART conditions and instrument settings.



Take-Home Message

- DART-MS in positive-ion and negative-ion mode can be used to identify ILs.
- Cluster ions are formed that cover a wide m/z range, some even beyond m/z 5000.
- Transmission mode DART at 450–550 °C provides widest cluster ion distributions.
- The cluster ion series of IL 7 serves well to set up a mass calibration for DART-MS.

References

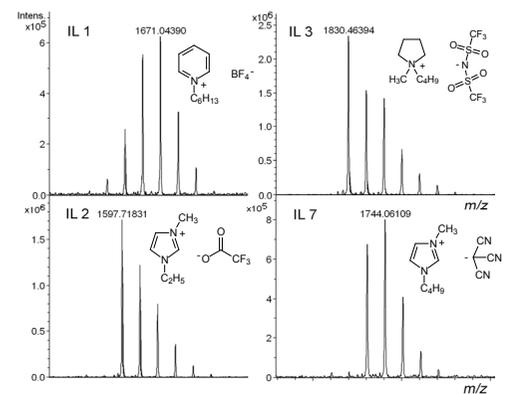
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Finding the Ideal Reference

Mass calibration compounds should deliver numerous evenly spaced peaks over a wide m/z range, i.e.,

- the sum of cation and anion mass should be in the order of 200–300 u,
- the isotopic pattern should not be complicated by chlorine, bromine, sulfur, boron or other elements, and
- cluster ions should be covering a wide m/z range in either ion polarity.

Just one S atom per anion as in trifluoromethane sulfonate of **2** and **4** or in thiocyanate of **6**, broadens the isotopic pattern; two S atoms per anion as in bis(trifluoromethyl-sulfonyl)imide of **3** do so even stronger. Overall, **7** presents the most promising IL to serve as a mass calibrant.

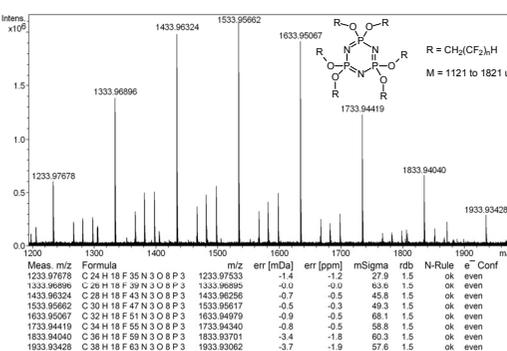


Example of Application

Ultramark 1621, a mixture of hexakis-(fluoroalkoxy)-phosphazenes, has been analyzed by negative-ion DART-MS. The phosphazenes therein differ by a nominal mass of 100 u, i.e., by two CF_2 units.

The negative-ion DART spectrum of a solution of Ultramark 1621 in ACN/water/HTFA (93:5:2, v/v) exemplifies the use of the IL-based calibration to higher-mass analytes in the range of m/z 1200–2000.

Ultramark 1621 forms $[\text{M} + \text{CF}_3\text{COO}]^-$ adduct ions when analyzed by DART-MS.



Building Mass Reference Lists

Mass reference list for mass calibration in positive-ion DART-MS using IL 7. All ions are singly charged even-electron species and m/z values refer to monoisotopic ions.

Positive Cluster Ion Formulas	Calculated m/z
$[\text{C}]^+$	139.122975
$[\text{C}_2\text{A}]^+$	368.255720
$[\text{C}_3\text{A}_2]^+$	597.388466
$[\text{C}_4\text{A}_3]^+$	826.521211
$[\text{C}_5\text{A}_4]^+$	1055.653956
$[\text{C}_6\text{A}_5]^+$	1284.786702
$[\text{C}_7\text{A}_6]^+$	1513.919447
$[\text{C}_8\text{A}_7]^+$	1743.052192
$[\text{C}_9\text{A}_8]^+$	1972.184937
$[\text{C}_{10}\text{A}_9]^+$	2201.317683
$[\text{C}_{11}\text{A}_{10}]^+$	2430.450428
$[\text{C}_{12}\text{A}_{11}]^+$	2659.583173
$[\text{C}_{13}\text{A}_{12}]^+$	2888.715919
$[\text{C}_{14}\text{A}_{13}]^+$	3117.848664
$[\text{C}_{15}\text{A}_{14}]^+$	3346.981409
$[\text{C}_{16}\text{A}_{15}]^+$	3576.114155
$[\text{C}_{17}\text{A}_{16}]^+$	3805.246900
$[\text{C}_{18}\text{A}_{17}]^+$	4034.379645

Mass reference list for mass calibration in negative-ion DART-MS using IL 7. All ions are singly charged even-electron species and m/z values refer to monoisotopic ions.

Negative Cluster Ion Formulas	Calculated m/z
$[\text{A}]^-$	90.009771
$[\text{CA}_2]^-$	319.142516
$[\text{C}_2\text{A}_3]^-$	548.275262
$[\text{C}_3\text{A}_4]^-$	777.408007
$[\text{C}_4\text{A}_5]^-$	1006.540752
$[\text{C}_5\text{A}_6]^-$	1235.673498
$[\text{C}_6\text{A}_7]^-$	1464.806243
$[\text{C}_7\text{A}_8]^-$	1693.938988
$[\text{C}_8\text{A}_9]^-$	1923.071733
$[\text{C}_9\text{A}_{10}]^-$	2152.204479
$[\text{C}_{10}\text{A}_{11}]^-$	2381.337224
$[\text{C}_{11}\text{A}_{12}]^-$	2610.469969
$[\text{C}_{12}\text{A}_{13}]^-$	2839.602715
$[\text{C}_{13}\text{A}_{14}]^-$	3068.735460
$[\text{C}_{14}\text{A}_{15}]^-$	3297.868205
$[\text{C}_{15}\text{A}_{16}]^-$	3527.000951
$[\text{C}_{16}\text{A}_{17}]^-$	3756.133696
$[\text{C}_{17}\text{A}_{18}]^-$	3985.266441

To obtain the method file for use with Bruker ApexQe instruments and the mass reference list files for IL7 in both ion polarities (suitable for direct use with Bruker FT-ICR, quadrupole-TOF, and quadrupole ion trap instruments) email your request to juergen.gross@oci.uni-heidelberg.de

DART High-Mass Record

By optimization of the instrument parameters for higher m/z range and concomitant increase of the DART gas temperature, it was possible to detect IL 7 cluster ions above m/z 5000.

Best high-mass cluster ion abundances and peak shapes were observed at an ion transfer time of 3.3 ms and at an argon buffer gas flow of 0.55 L s^{-1} into h2.

Setting DART gas temperature to 550 °C yielded a substantial shift to higher mass cluster ions. The last well-defined signal finally obtained at m/z 5183 is correlated to $[\text{C}_{23}\text{A}_{22}]^+$, the highest mass detected by DART-MS to date.

