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# Negative-Ion Field Ionization and Liquid Injection Field Desorption/Ionization-Mass Spectrometry on Recent Instrumentation

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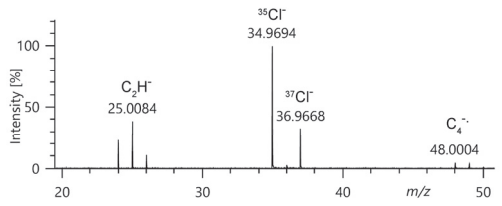
## Idea and Concept

- Field ionization (FI) [1], field desorption (FD) [2] and liquid injection field desorption/ionization (LIFDI) [3] are known to provide soft positive ionization of gaseous (FI) or condensed phase analytes (FD and LIFDI) [2-4].
- LIFDI provides sample deposition under inert conditions, i.e., the exclusion of atmospheric oxygen and water. Thus, negative-ion LIFDI could potentially be applied to highly sensitive anionic compounds.
- In contrast to the well-established positive-ion mode, negative-ion FI or FD have remained rare exceptions [5-6].
- We explore negative-ion LIFDI when modern mass spectrometers (JEOL AccuTOF GCx and Waters Micromass Q-TOF Premier) are employed with a LIFDI source .
- This work describes the instrumental setups, identifies operational parameters relevant for robust operation, and presents the application of negative-ion LIFDI-MS using two different instruments [7].

## A Signal for Tuning

When it come to ion source tuning, a compound reliably delivering a constant signal is of great help. Preferably, this tuning compound can be delivered as vapor and be ionized in FI mode.




Dichloromethane vapor could be admitted via the transfer capillary but failed to form a molecular anion. Nonetheless, it yielded a $^{35}Cl^-$ ion signal, *m/z* 35, and a $^{37}Cl^-$ ion signal, *m/z* 37 (intensity ratio 3 : 1) at a s/n of up to 200. Some other background ions already noted in [5] were also observed at low intensity.

In contrast to positive-ion FI, the chloride signals occurred at almost equal intensity across the 0-80 mA EHC range.

Their intensity was slightly improved by a stepwise increase of the emitter potential from 5.0 kV to 5.5 kV while potentials above 6.0 kV increased the risk of discharges leading to destruction of the emitter.

Even though the chloride ion signals were still a bit weak, they could serve as a convenient indicator of proper ion source operation and permit some basic tuning prior to admission of samples.

## Experimental

Two different mass spectrometers were employed for negative-ion LIFDI work:

- JEOL AccuTOF GCx orthogonal-acceleration time-of-flight mass spectrometer (Jeol, Tokyo, Japan).
- Waters Micromass Q-TOF Premier quadrupole-orthogonal-acceleration time-of-flight mass spectrometer (Waters, Manchester, United Kingdom).

Both were used with LIFDI sources from Linden CMS (Weyhe, Germany). Emitter high voltage and emitter heating current were controlled using the Linden LIFDI-700 electronics and LIFDI-700 control software. A

Analytes including ionic liquids, acidic compounds, anionic surfactants, dichloromethane, a fullerene derivative, and samples sensitive to moisture and air were analyzed.

The field emitters (13 µm activated tungsten wire) were set to 5-6 kV relative to the counter electrode at positive potential and heated at 20-60 mA $min^{-1}$ during spectral acquisition [7].

## Take-Home Messages

- Negative-ion liquid injection field desorption/ionization works surprisingly well on modern mass spectrometers of oaTOF type.
- Two different mass spectrometers were used thus proving general applicability of the method.
- Negative-ion LIFDI can be applied to a wide range of ionic, acidic, and even neutral samples.
- Even samples sensitive to air and moisture can be analyzed by negative-ion LIFDI.
- Some experience in FI, FD, and LIFDI provided, negative-ion LIFDI works equally well.

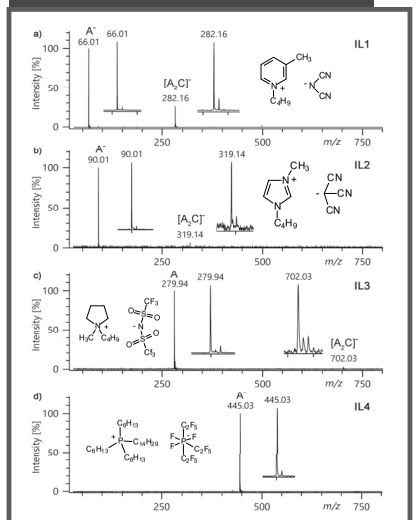
## Handout

Download a handouts of this poster from www.ms-ocihd.de

## References

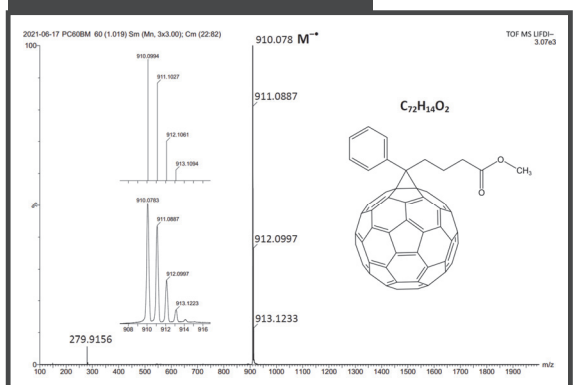
1. Beckey, H.D. Pergamon, Elmsford (1971)
2. Beckey, H.D. Pergamon Press, Oxford (1977)
3. Linden, H.B. Eur. J. Mass Spectrom. **10**, 459-468 (2004)
4. Gross, J.H. Eur. J. Mass Spectrom. **26**, 33 (2020)
5. Robertson, A.J.B., Williams, P. Proceedings of the Chemical Society. **Sep.**, 286-287 (1964)
6. Anbar, M., St. John, G.A. J. Am. Chem. Soc. **97**, 7195-7197 (1975)
7. Linden, M.H., Linden, H.B., Gross, J.H. Anal. Bioanal. Chem. **413**, 6845-6855 (2021)
8. Hartmann, D., Schädler, M., Greb, L. Chem. Sci. **10**, 7379-7388 (2019)
9. Weitkamp, R.F., Neumann, B., Stammler, H.-G., Hoge, B Chem. Eur. J. **27**, 915-920 (2021)
10. Drusgala, M., Linden, M.H., Knoechl, A., Torvisco, A., Fischer, R.C., Bernhard Linden, H., Haas, M. Eur. J. Inorg. Chem. **2021**, 3091-3096 (2021)

## Ionic Liquids



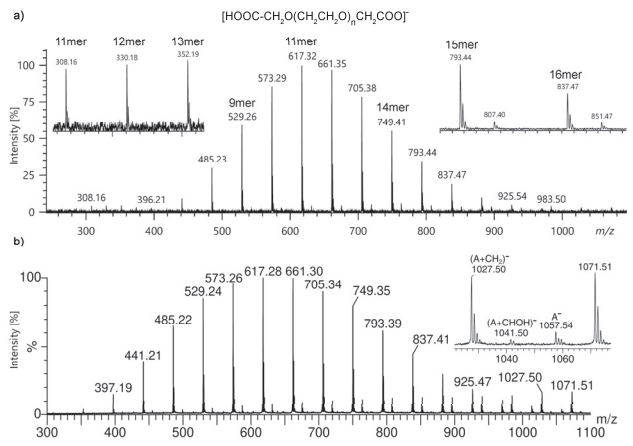

Negative-ion LIFDI spectra of ionic liquids (ILs) showed intensive anion signals of the respective IL, and the first cluster ion, $[A_2C]^-$, was observed. A mixture of ILs was also employed for mass calibration of the instruments in negative-ion LIFDI mode.

## Radikal-Anions $M^{-\bullet}$




Compounds of high electron affinity may undergo electron capture, and thus, form a molecular radical anion, $M^{-\bullet}$. Provided this negative molecular ion is stable like in case of the above fullerene derivative, it can be detected by negative-ion LIFDI-MS. This spectrum has been obtained using the Waters Micromass Q-TOF instrument.
The inserts show that the calculated (*top*) and experimental isotopic pattern (*lower*) for $[C_{72}H_{14}O_2]^{-\bullet}$ are in very good agreement. Here, neither hydride adduct formation nor deprotonation play a role in analyte ion formation.

## Acidic Compounds

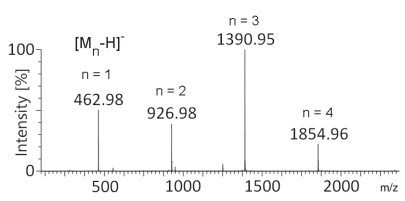



LEFT: Polyethylene glycol diacid, $HOOC-CH_2O(CH_2CH_2O)_nCH_2COOH$ (average molecular weight 600 u), yielded $[M-H]^-$ ions under negative-ion LIFDI conditions.

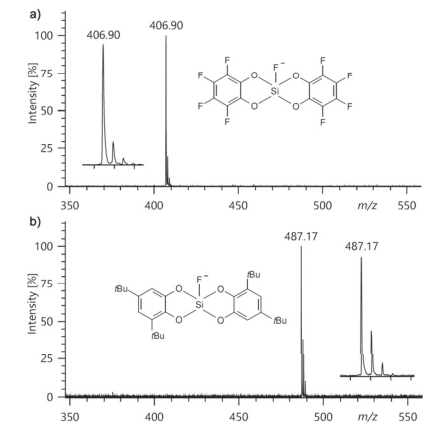
On either mass spectrometer the ions ranged from the 6mer to the 20mer. Nonetheless, the spectrum was more intensive and showed an additional ion series more clearly when the Q-TOF Premier instrument was used.

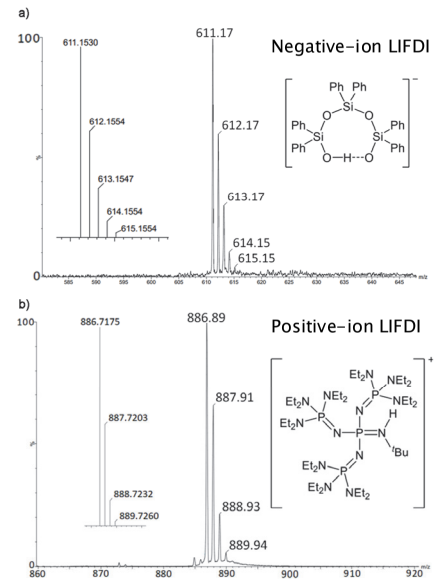
While caculated and measured *m/z* values are within 0.03 u, the results are not accurate enough to permit formula determination, e.g., $[C_{26}H_{49}O_{16}]^-$, *m/z* 617.3026 (calc.).

RIGHT: Perfluorononanoic acid (PFNA) exhibited the anion $[C_9F_{17}O_2]^-$, *m/z* 462.98, by deprotonation and several very intensive peaks due to $[M_n-H]^-$ cluster ions ranging from $n = 1$ through $n = 3$. This amount of cluster ion formation is indicative of a soft ion formation process in negative-ion LIFDI. The spectrum was obtained by using the Waters Q-TOF Premier mass spectrometer.




## Sensitive Samples




TOP: Bis(catecholato)silanes are highly sensitive to moisture [8]. They were supplied as solutions in dry dichloromethane and analyzed using the JEOL AccuTOF GCx instrument. Both yielded spectra showing the respective anions, i.e., *m/z* 406.90 due to $[C_{12}F_9O_4Si]^-$ and *m/z* 487.17 corresponding to $[C_{28}H_{40}FO_4Si]^-$.

BOTTOM: Silanol-sinalolates also require the strict exclusion of moisture during handling to avoid decomposition [9]. A solution of tetra-phosphazene silanol-silanolate $[C_{40}H_{100}N_{13}P_4]^+$ $[C_3{}_6H_{31}O_4Si_3]^-$, anion *m/z* 611.15, in dry THF was analyzed by negative- and positive-ion LIFDI-MS using the Waters Micromass Q-TOF instrument. Triacyl-germenolates have also recently been analyzed this way [10].