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Versatile atmospheric pressure field desorption ion source allowing for robust operation, emitter observation, and emitter heating

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APFD Source design

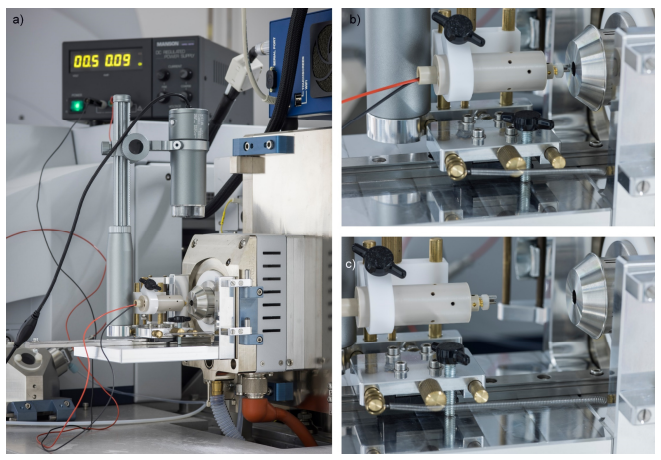
Status of APFD so far

- Atmospheric pressure field desorption (APFD) mass spectrometry (MS) has been introduced as a new variant of field desorption (FD) mass spectrometry [1].
- APFD aims at combining the capabilities of FD-MS with instruments equipped with an atmospheric pressure (AP) interface.
- APFD yields both positive and negative even electron ions of highly polar or ionic compounds [1, 2] and it enables the generation of positive molecular ions, $M^{+\bullet}$, e.g., of polycyclic aromatic compounds [3].
- The prototype setup for APFD was based on a nano-ESI source slightly modified to allow for emitter positioning in front of the AP interface of a Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker ApexQe).
- In APFD, the entrance electrode of the interface was set to a voltage of ± 3.5–5.0 kV with respect to the emitter at ground potential, thereby providing the high voltage required for FI and FD [1–3].

Advancements made

- Here, a new custom-built assembly for quick and reproducible sample loading on the field emitter and positioning at the entrance electrode of the AP interface is described.
- The APFD source provides means for observation of the emitter during operation and enables an emitter heating current (EHC) to be applied as in traditional FD-MS.
- Using an EHC both speeds up the desorption of the analytes and allows for the desorption/ionization of analytes of higher molecular weight than without emitter heating, e.g., polystyrenes.
- The new setup enables robust and reliable operation in APFD-MS [4].
- It is compatible with a range of instruments, i.e., it fits the Bruker ApexQe and the trapped ion mobility-quadrupole-time-of-flight instrument (Bruker timsTOFflex), and thus, all current Bruker instruments with AP interface.

APFD Source attached to ApexQe



a) The entire APFD source assembly shown mounted to the AP interface of the Bruker ApexQe FT-ICR mass spectrometer. The DC power supply for the EHC is placed on top of the instrument in the background (showing 0.09 A at 0.5 V). The USB microscope camera rests on the sliding rail together with the probe mount.

b) The probe tip with emitter positioned at the spray shield electrode as in APFD operation.

c) The probe tip in retracted position for emitter loading or swapping without the need to unmount the probe.

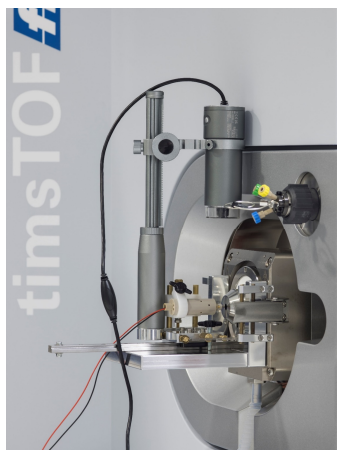
Versatile for use on any Bruker instrument

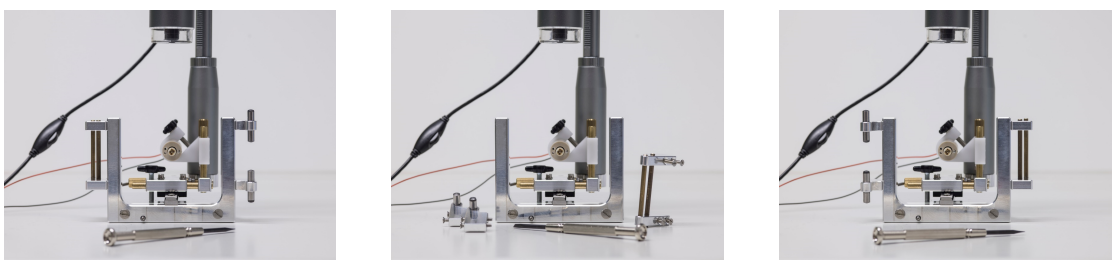
The APFD source can be modified for mounting to the timsTOFflex instrument within minutes.

Using the timsTOFflex, spectra were acquired using source settings analogous to those reported for the FT-ICR mass spectrometer and common in ESI operation of this instrument.

The spectra of 1,1,4,4-tetraphenylbutadiene, of fluoranthene, and of polystyrene were recorded, and were found to exhibit the same characteristics as previously observed with the ApexQe.

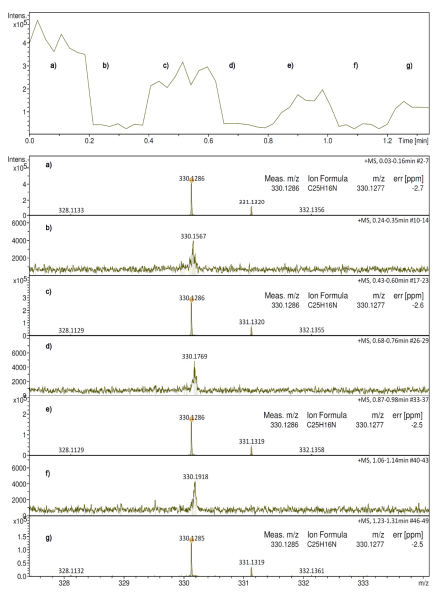
The spectrum of fluoranthene was clearly better in terms of signal-to-noise ratio and the duration the instrument was capable of recording a signal. The timsTOFflex already detected the molecular ion from the beginning, i.e., without or very low EHC at an intensity of about 3×10^4 counts while the signal reached higher level of 4×10^6 counts during the most active desorption period. This is where the low-mass cut-off at around *m/z* 170 of the ApexQe mass spectrometer already had an adverse effect on ion transmission whereas the timsTOFflex played to its strengths.



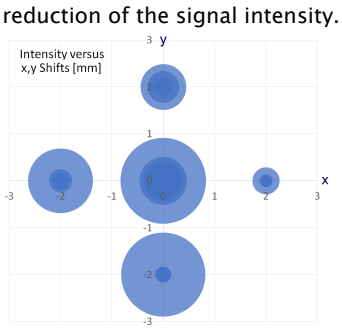


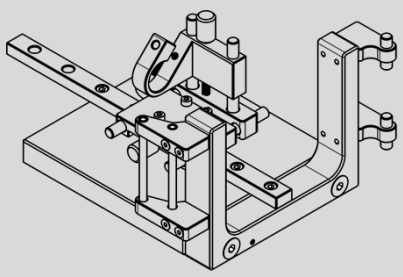
Configured for ApexQe → Unscrew hinges and source clamp, swap sides and screw on again → For timsTOF

Robust Operation



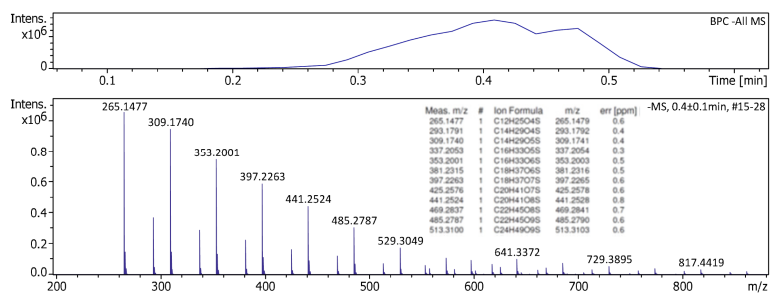
Cycles of attaching and retracting the probe with the emitter at and from the spray shield electrode: The $[M+H]^+$ peak of 1-aza[6]helicene reappeared as soon as the emitter approached the spray shield. Also, vertical and horizontal misalignments by 2 mm caused only moderate reduction of the signal intensity.





Surfactants and PFNA in negative-ion APFD

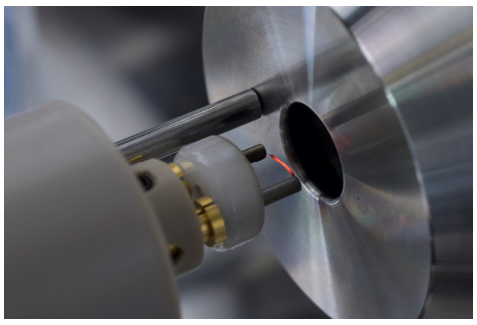
Below: Negative-ion APFD mode using the timsTOFflex. The spectrum of a shower gel appeared the same as on the ApexQe instrument. It desorbed upon gentle heating of the emitter and exhibited the series of organic sulfate ions already known. APFD settings: ion accumulation 1.0 s per spectrum, shield at 4.3 kV, dry gas at 4.0 l min^{-1} and 150 °C, and EHC ramp up to 0.14 A.

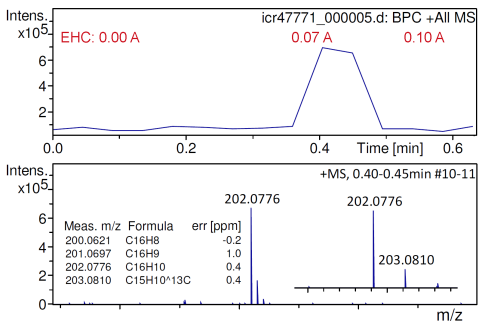


Further, a spectrum of perfluorononanoic acid (PFNA) also showed the $[M-H]^-$ ion, $[C_9F_{17}O_2]^-$, a fragment by loss of CO_2, $[C_8F_{17}]^-$, and the $[2M-H]^-$ cluster ion, $[C_{18}HF_{34}O_4]^-$, as the base peak. The EHC permitted to analyze neat PFNA by negative-ion APFD, i.e., using glycerol as matrix was not anymore needed to provide sufficient surface mobility on the emitter.

Emitter loading and heating

Right: Manual control of the DC voltage supply worked well. At 2.2 V an EHC of 0.16 A caused the emitter to glow red hot. Voltages of >2.3 V and currents >0.17 A tended to destroy the emitter. An emitter operated at <0.16 A could be run for tens of acquisitions. The currents were reproducible within about 0.01 A among different emitters. Activated 13-µm tungsten wire emitters of Linden CMS (as for JEOL AccuTOF series) were used here.





Left: Upon gentle emitter heating, the molecular ion, $M^{+\bullet}$, of fluoranthene, *m/z* 202.0776, was observed at very good intensity. An EHC of just 0.07 A was sufficient in this case. In the absence of an EHC, the $M^{+\bullet}$ ion could only be observed when related compounds assisted the APFD process. The use of an EHC furthermore enabled APFD of polystyrene of average MW of 1 ku (PS 1k), which also formed molecular ions in APFD.

Handouts?

Handouts of this posters in PDF format are available for download from www.ms-ocihd.de cf. topic > Publications > Conference Contributions.

Thanks

Many thanks to the Deutsche Forschungsgemeinschaft (DFG) for granting the Bruker timsTOFflex mass spectrometer (INST 35/1640-1 FUGG).

Perspective?

Using APFD in combination with the timsTOFflex instrument called for the exploration of APFD-TIMS coupling. In between, it worked very well.

References

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3) Matthias Hoyer, Jürgen H. Gross, "Molecular ion formation on activated field emitters in atmospheric pressure field desorption-mass spectrometry", *Anal. Bioanal. Chem.* **2023,** 415(12), 2307–2315. DOI 10.1007/s00216-023-04652-4.

4) Jan Schweinfurth, H. Bernhard Linden, Jürgen H. Gross "Robust and versatile assembly for emitter positioning, observation, and heating in atmospheric pressure field desorption mass spectrometry" *Eur J Mass Spectrom* **2024;** DOI 10.1177/14690667241236073.