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Modular Development of Plasma-Source Ultra-High-Resolution Mass Spectrometry with Constitutional Isotopic Information

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High-field asymmetric-waveform ion mobility spectrometry (FAIMS) allows for the separation of molecules based on their ion mobility in an electrical field with an asymmetric waveform.[1] FAIMS allows for the differentiation of constitutional isotopes, often linear and cyclic compounds, which would usually be non-differentiable with just a mass spectrometer. FAIMS is typically coupled to electrospray ionisation (ESI) sources. A drawback of ESI is its limited range of ionisable molecules, often needing a functional group to allow for the ion detection in the mass analyser. This leaves a plethora of molecules such as apolar molecules or those without a functional group to be invisible during analysis. The coupling of a liquid sampling atmospheric pressure glow discharge (LS-APGD) would allow for such molecules to be analysed.[2] Coupling APGD with FAIMS could unlock new analytical possibilities which are not yet available. By integrating this instrument further with an absorption-mode FT 'booster system', which includes an FPGA module for real-time data display and processing, the analysis achieves ultra-high resolution. The spectrum is then generated by the Spectroswiss software peak by peak (Fig. 1).[4–5]

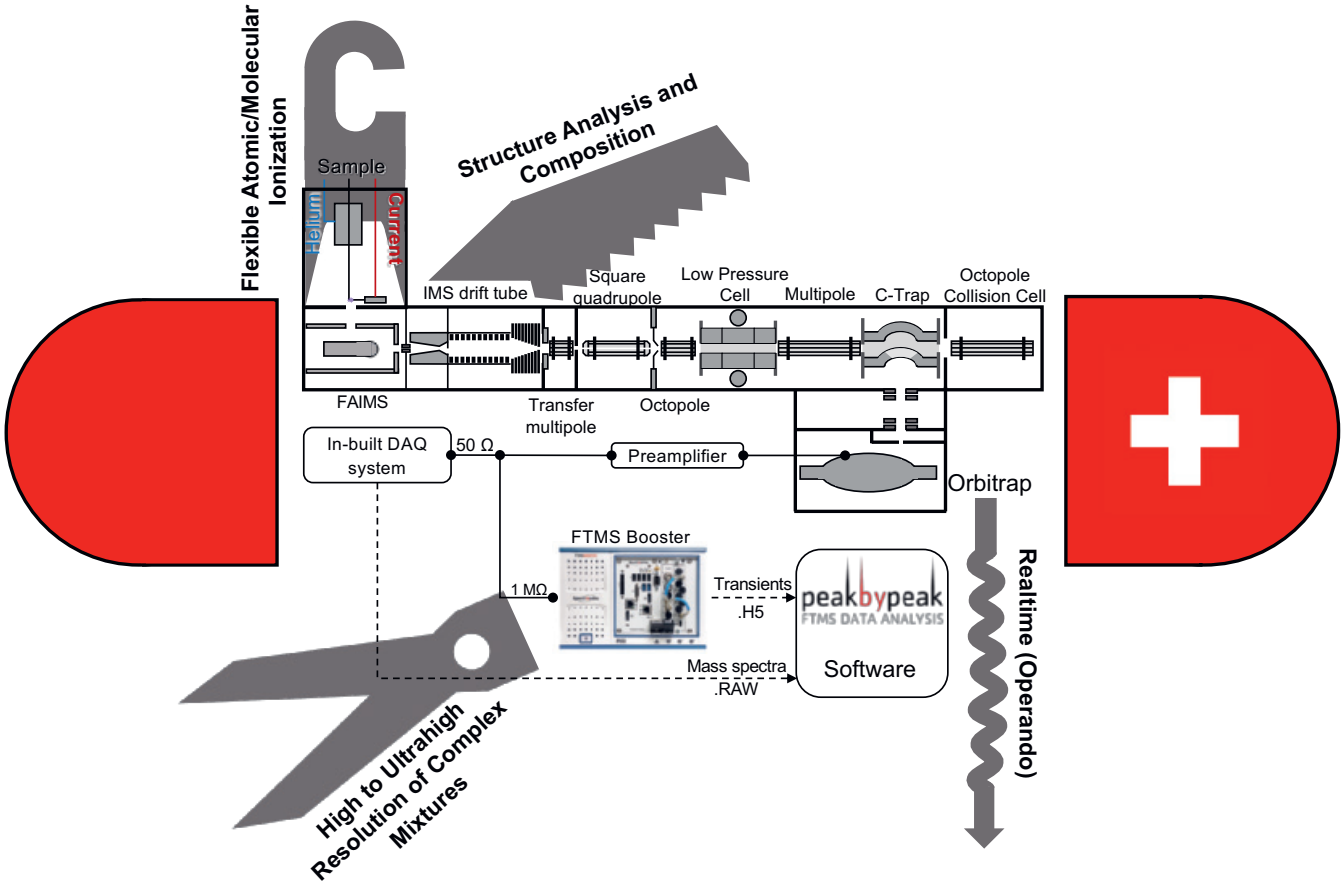

Fig. 1. The desired experimental setup described in this paper. The experiments were conducted with ESI and CAMS without the FAIMS coupled to the system. Each tool represents an important component of the mass spectrometer. The instrument would consist of an APGD, FAIMS, orbitrap and FTMS booster system. Some parts of the figure have been adapted from D. Bleiner *et al.* and A. A. Shvartsburg *et al.* refs. [3,4].

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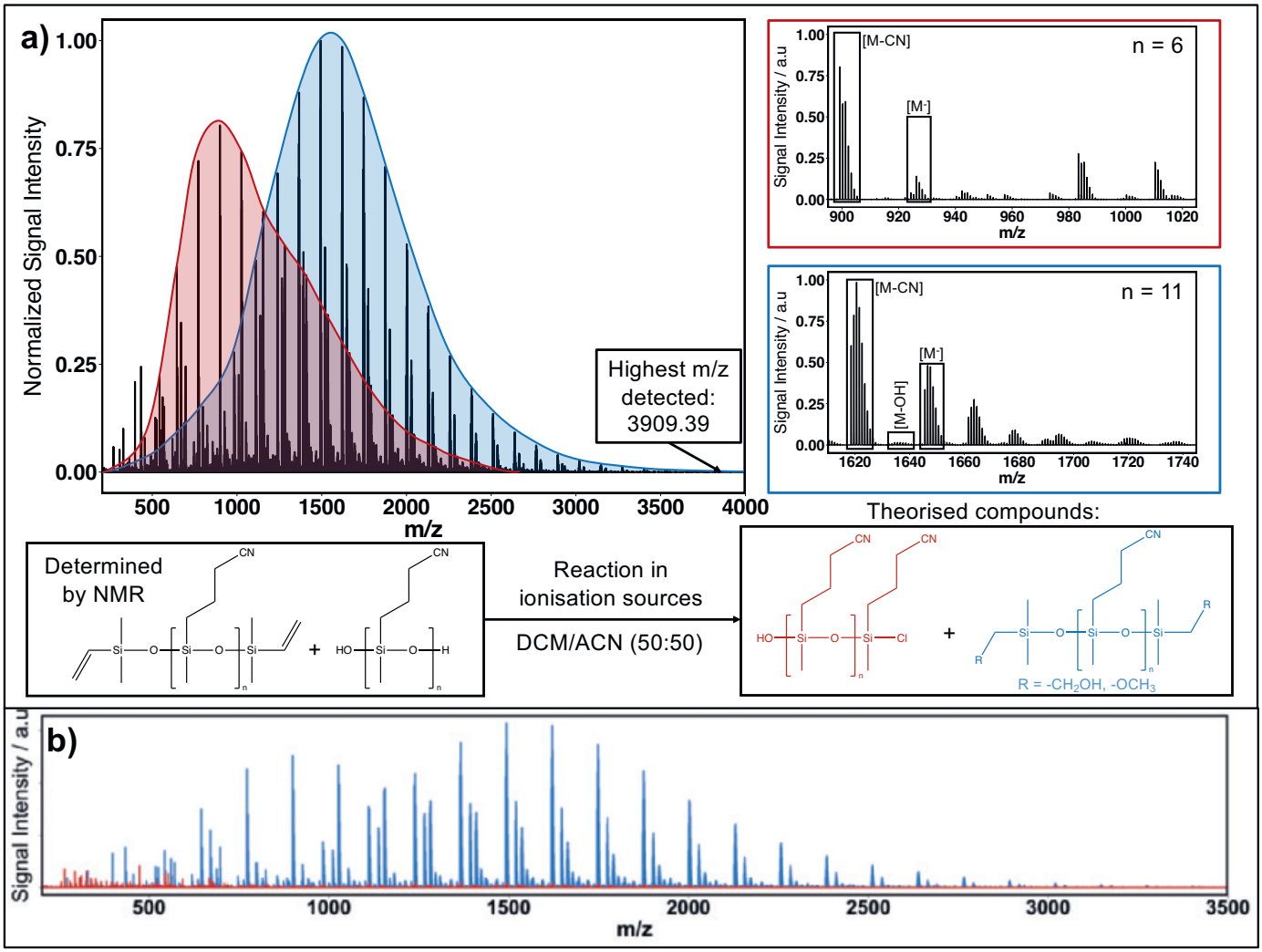

Fig. 2. a) The obtained mass spectrum of the polymer depicted on the bottom left with the theorised compounds that are created during ionisation. The colours correspond to the spectra created by these products. The two spectra on the top right correspond to the highest intensity of the blue and red mass distribution with the corresponding fragments. The red product could either be a reaction from the starting polymer with the hydroxyl end groups or could be a product of a ring opening reaction of the cyclic byproducts of the polymerisation; b) A comparison of the signal intensity between LS-APGD (blue) and ESI (red) as an ionisation source.

To demonstrate the system's applicability, a polymer with two potential end groups was chosen for its complex analysis and ability to form linear and cyclic compounds during polymerisation (Fig. 2).

APGD offers a much more complex and detailed mass spectrum due to more species being ionised and detected compared to ESI. ESI furthermore also shows more background due to the lower intensity of the detected species. By coupling FAIMS with APGD the differentiation between cyclic and linear polymers would be simplified and the product created by the ionisation source would be allowed to be analysed more easily. The booster could enhance the contrast for poorly resolved peaks and allow for isotope pattern analysis.

By achieving such high flexibility and utility in the fashion of a 'Swiss army knife', each module synergises with the other to compensate for what it is lacking, making the analysis of complex mixtures possible.

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