BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry

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Development and evaluation of a novel accumulation ion source for chemically instable compounds

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Introduction

Mass spectrometric detection of molecules and ions at the ultra-trace level requires specifically tailored and optimized sampling and acquisition systems. Even highly sensitive instruments cannot reliably detect analytes at concentrations this low due to chemical noise. Analyte accumulation is a common technique used in analytical chemistry but has not yet been used for sampling of chemically fragile gas phase compounds.

Step 1: Utilization of surface decomposition reactions of gaseous species into elements.
Step 2: Desired decomposition products remain on the surface and accumulate there, while other atoms or molecules are desorbed back into the gas phase.
Step 3: In a subsequent step, the accumulated products are desorbed from the surface as ions upon exposure to accelerated electrons or radicals.

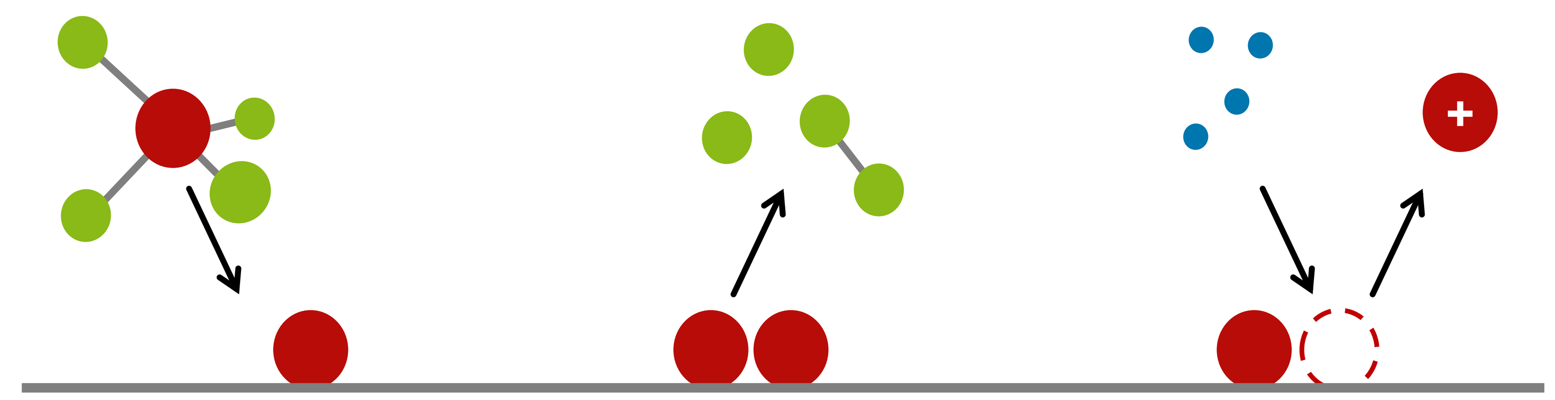

Fig. 1: Proposed mechanism

Source Design

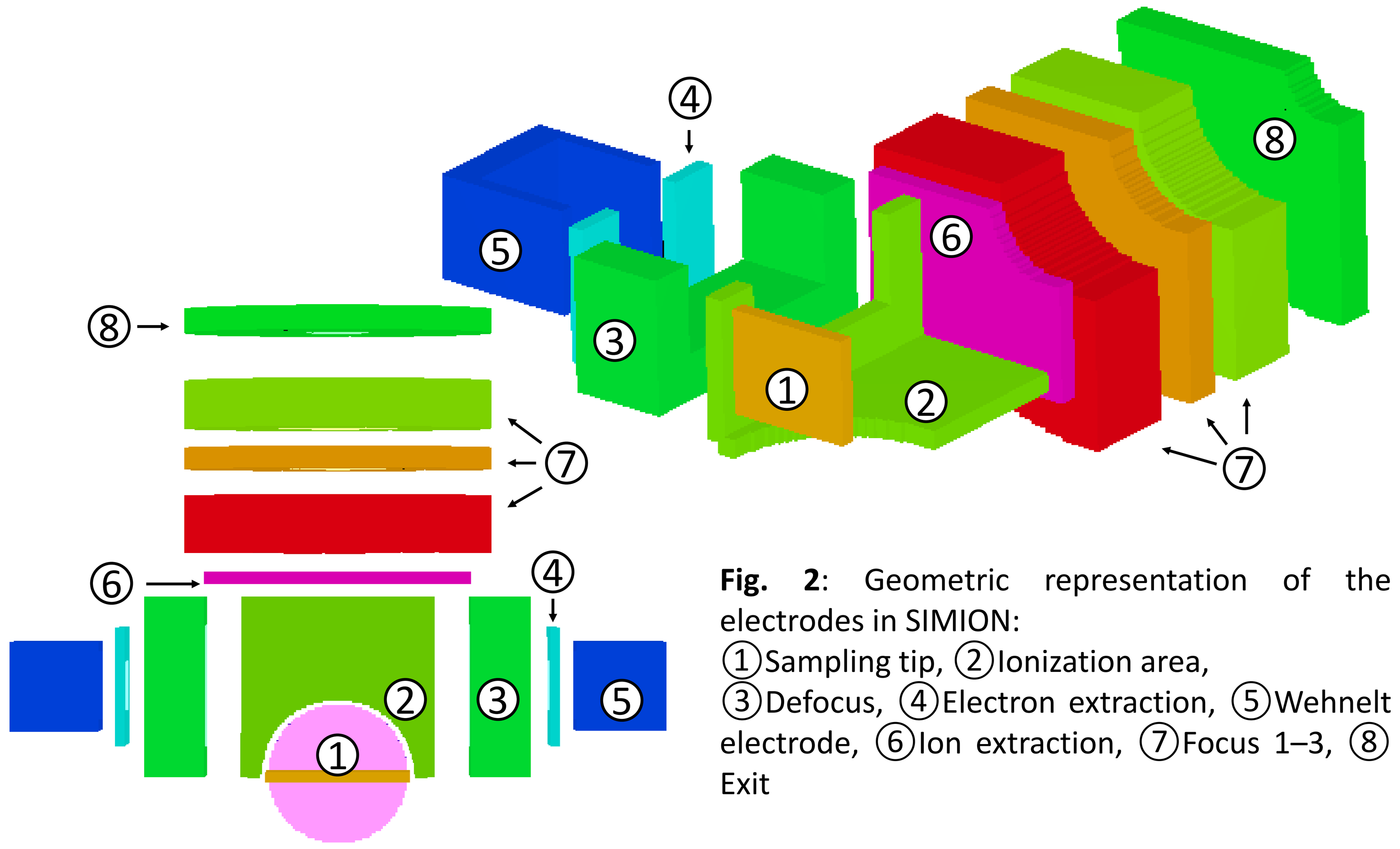

Fig. 2: Geometric representation of the electrodes in SIMION:
①Sampling tip, ②Ionization area, ③Defocus, ④Electron extraction, ⑤Wehnelt electrode, ⑥Ion extraction, ⑦Focus 1–3, ⑧ Exit

Setup: A linear actuator allows movement of the **sampling tip** from the exposure environment into the custom ion source. The design of the source ensures wide area bombardment of the sample tip by electrons, generated by two opposing filaments, each surrounded by a **Wehnelt electrode**. Specifically shaped **defocusing electrodes** broaden the electron beam to increase surface coverage of the **sample tip**. Electrodes located opposite of the sample tip are electrodes are employed for **extraction** and subsequent focusing (**Focus 1–3, Exit**) into the LTOF analyzer.

Operation: A potential array that *simultaneously* efficiently guides a) the electrons onto the sample tip and b) surface released ions into the analyzer is not feasible. However, pulsing between electron bombardment and ion extraction modes optimizes performance for both modes. The ion source supports both desorbed ion detection and standard electron ionization acquisition for residual gas analysis and MS calibration.

Proof of Concept

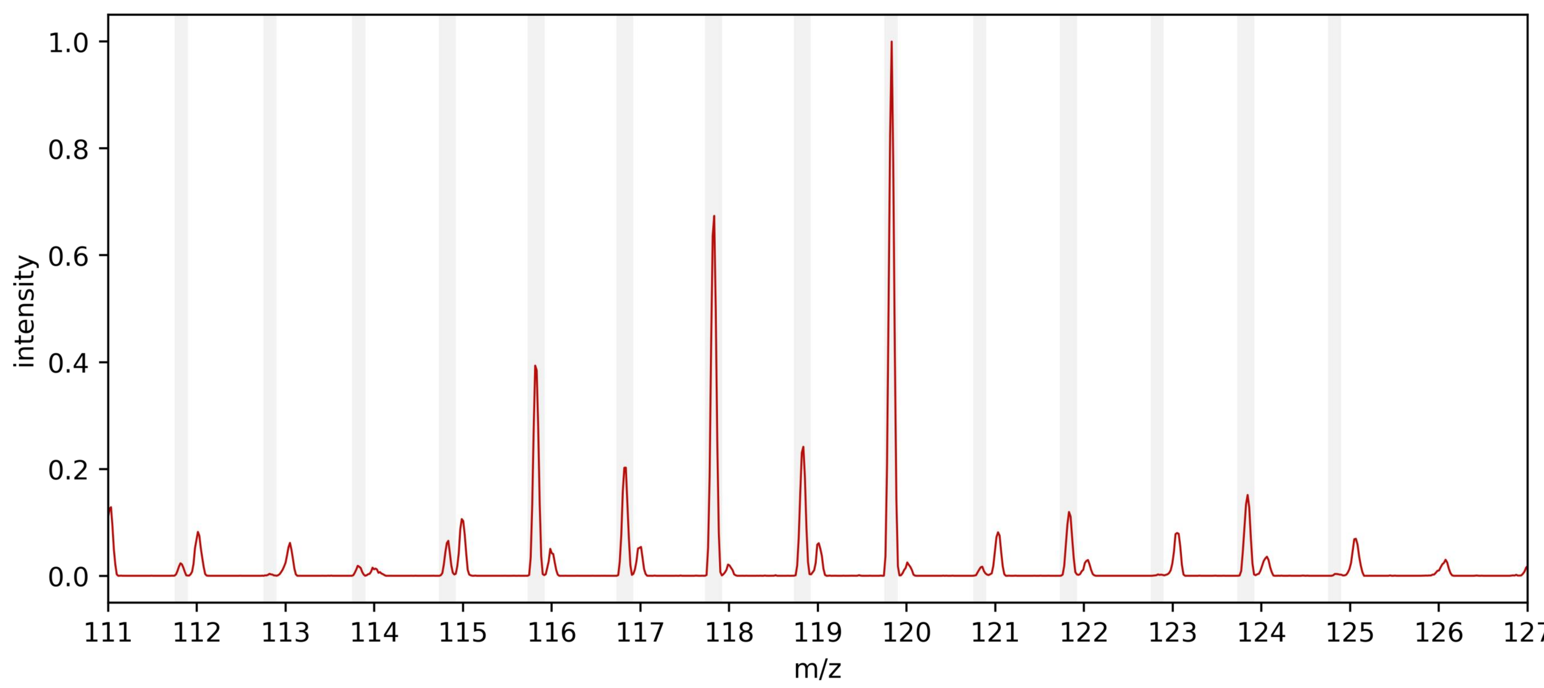

Fig. 3: Mass spectrum of Sn^+

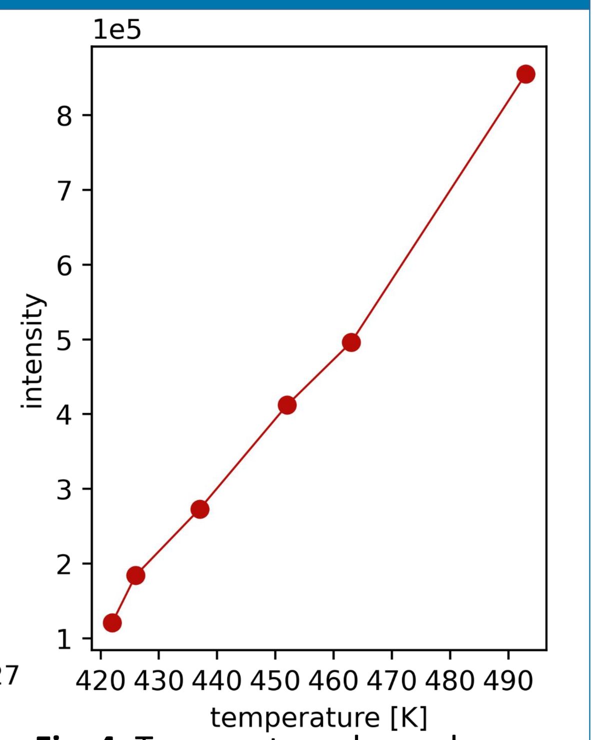

Fig. 4: Temperature dependency

- Metal surface coated with tin, placed in a commercial ion source of a MAT95XP mass spectrometer.
- Electrons accelerated to the surface at 70 eV.
- The high-resolution mass spectrometer can distinguish tin M^+ signals from background signals (mainly hydrocarbons). Isotopic pattern of tin metal is fully present.
- In the absence of background gas primarily M^+ is observed in the mass spectrum. Addition of hydrogen leads to appearance of $[M+H]^+$ peaks.
- Ion signal correlates with ion source temperature over a wide range.

Simulations

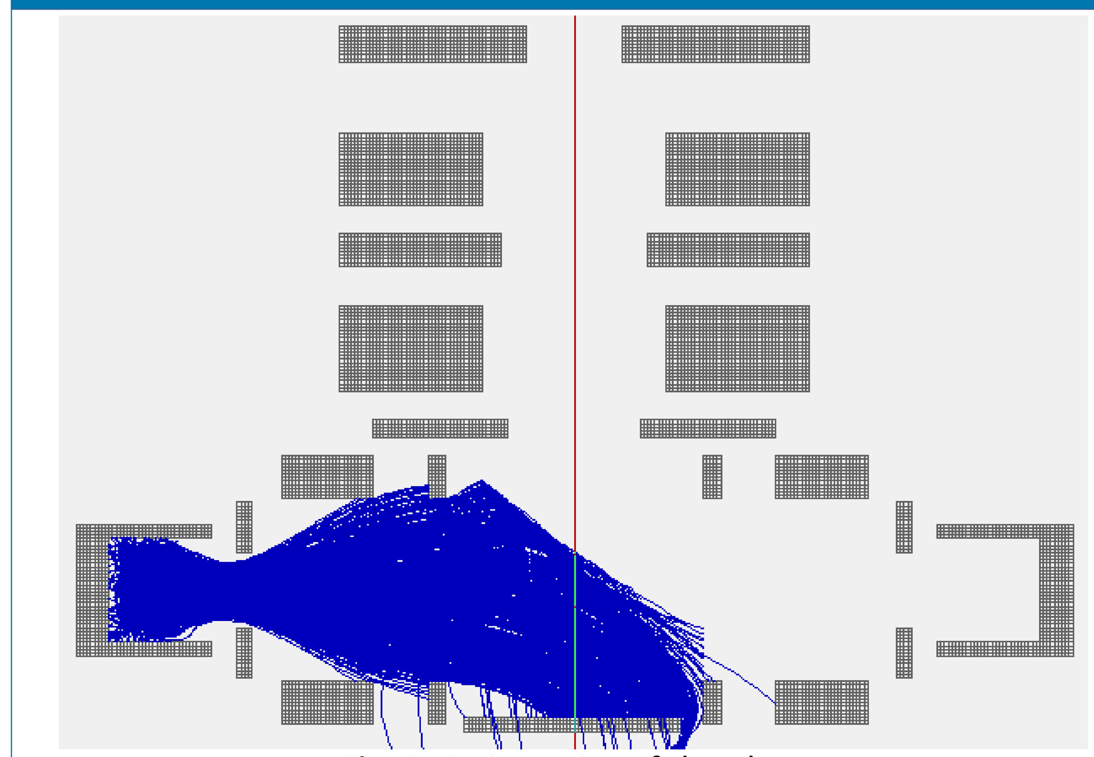

Fig. 5: Trajectories of the electrons

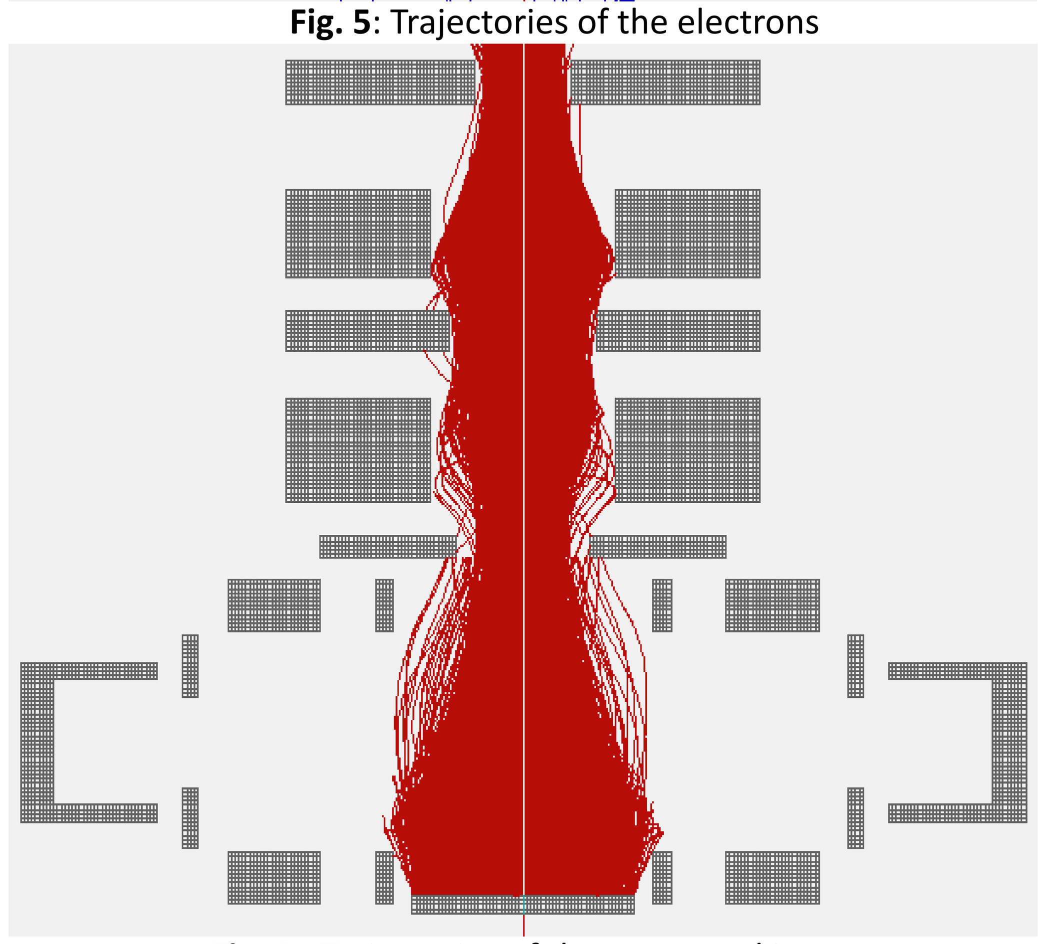

Fig. 6: Trajectories of the generated ions

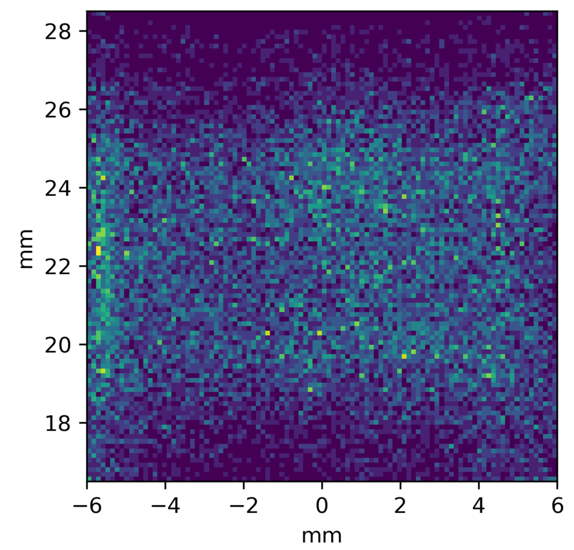

Fig. 7: Heatmap of the electron impact on the sample surface.

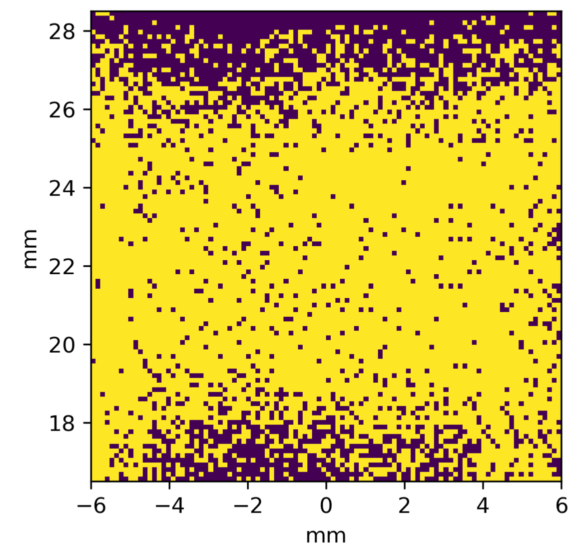

Fig. 8: Areas evaluated as electron hits

Simulated 70 eV electron trajectories (cf. **fig. 5**) displays an efficient trajectory from the filament through the defocusing unit onto the sampling tip surface. The defocusing unit creates a large-area electron beam, covering half of the surface. However, a second filament (not shown due to clarity) efficiently covers the remaining area.
Figures 7&8 illustrate the sample surface. The left figure portrays a heat map of electron bombardment and the right figure indicating areas counted as hits for determining the covered areal percentage. Simulations indicate that 67.5 % of emitted electrons reached the sample surface, and 74.3 % of the surface is adequately covered.

The generated ions (cf. **fig. 6**) are extracted from the sample by fitting potentials. According to the calculations, 82.1 % of the generated ions reach the exit of the source, with the majority impinging on the last electrode. The simulation was based on singly charged ions with a mass of 121 Da. A starting energy of 5 eV and a half angle of 30° were chosen for the calculation. These values correspond to the worst possible conditions under which the ions still can pass successfully through the entire source region.

Conclusion: The concept of such an ion source for the detection of trace elements is shown to be suitable by the simulations in combination with the proof of concept. The experimental confirmation and testing are still be carried out very soon.

Acknowledgment

Generous support from the BUW ipaMS (Institute for Pure and Applied Mass Spectrometry), Germany, is gratefully acknoweldged.

References

- SIMION (v. 8.1.2.30); ion optics and trajectory simulation program; http://simion.com/
- MAT95XP double focusing sector field MS; *Thermo Fisher Scientific, Waltham, MA, USA*
- LTOF time-of-flight mass spectrometer; *Tofwerk AG, Thun, Switzerland*