

Introduction

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

The underlying concept behind the novel source is to utilize surface decomposition reactions of gaseous species into the elements on selected surfaces (**step 1**). It is crucial that the **desired decomposition products** remain on the surface and accumulate there, while other **atoms or molecules** are desorbed back into the gas phase (**step 2**). In a subsequent step, the **accumulated products** are desorbed from the surface as ions upon exposure to **accelerated electrons or radicals** (**step 3**). These cations are further guided into a mass analyzer.

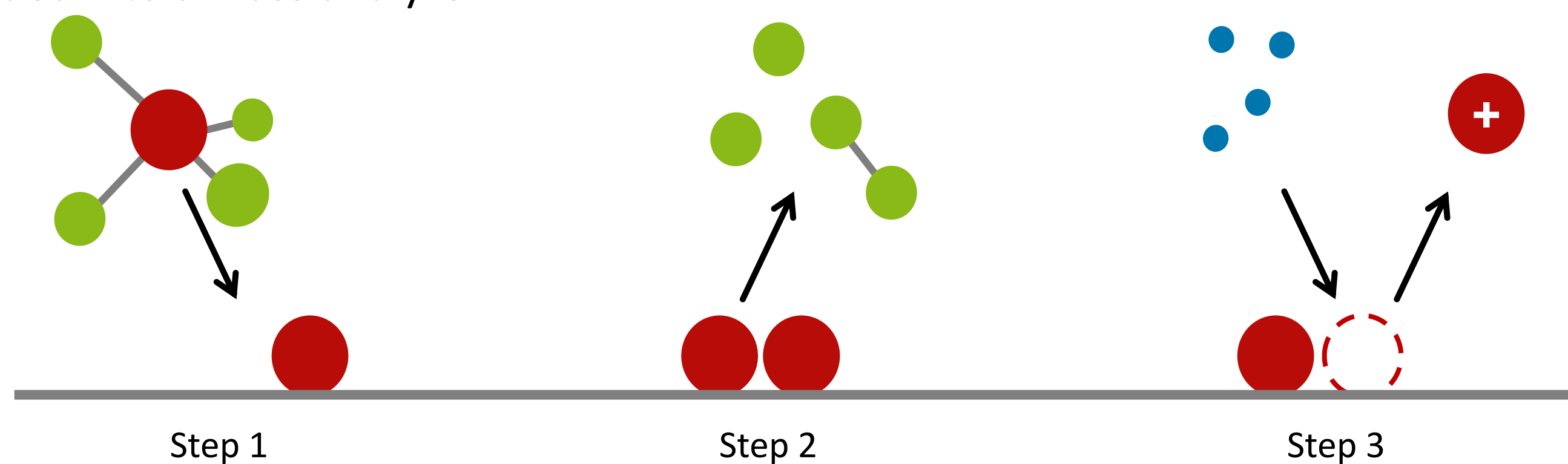


Fig. 1: Proposed mechanism

Proof of Concept

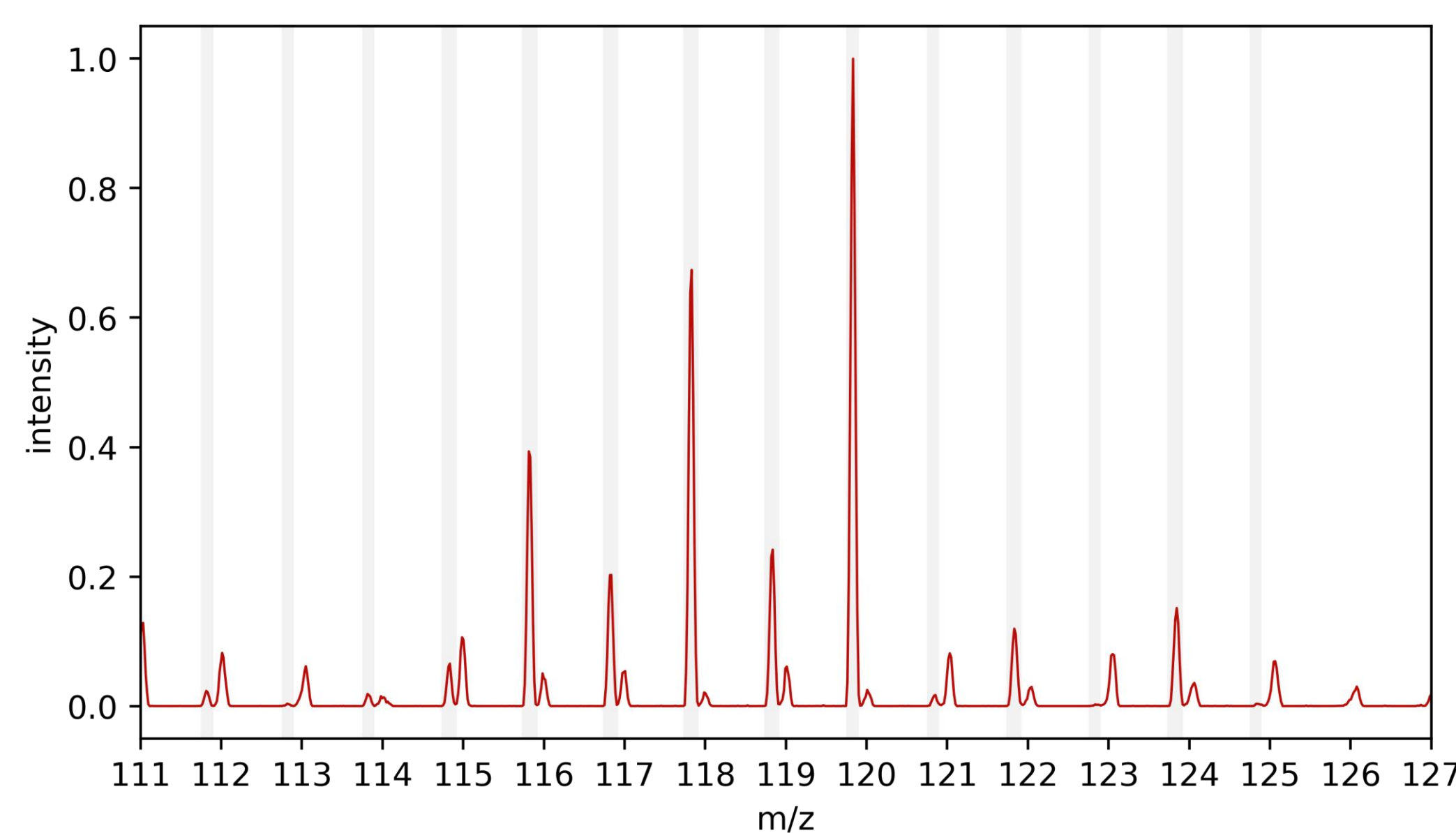


Fig. 2: Mass spectrum of Sn⁺

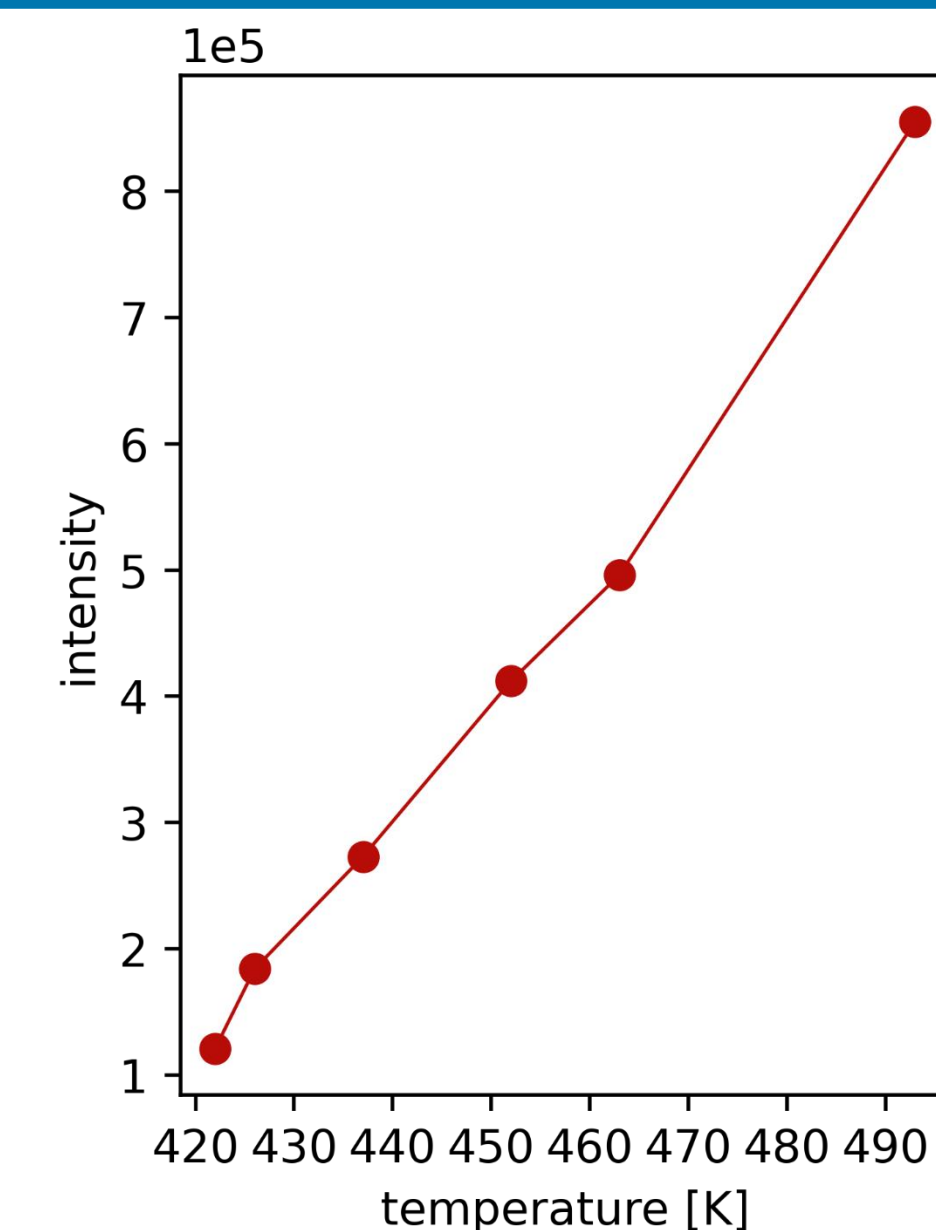


Fig. 3: Temperature dependency

As a proof of concept, a steel surface was coated with a metal (tin in the example here) and placed in a commercial EI ion source of a MAT95XP sector field MS. The electrons generated by the filaments were accelerated to the surface to 70 eV. Due to the high resolution of the mass spectrometer, it is possible to discern the tin M⁺ signals (highlighted in the mass spectrum) from background signals (mostly from hydrocarbons). The isotopic pattern of the corresponding metal is fully present. In the absence of background gas, almost exclusively M⁺ is observed in the mass spectrum. However, as hydrogen is added the [M+H]⁺ peaks appear. The ion signal is directly proportional to the temperature of the ion source over a wide range.

Source design

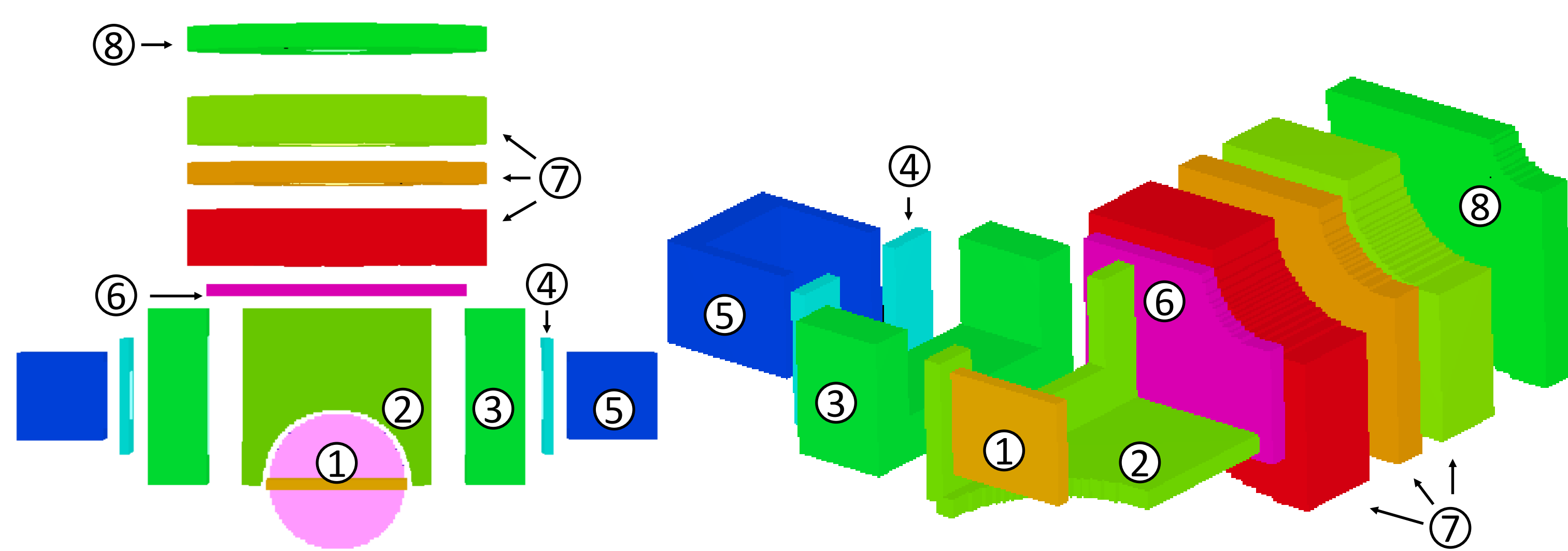


Fig. 4: Geometric representation of the electrodes in SIMION: ① Sampling tip, ② Ionization area, ③ Defocus, ④ Electron extraction, ⑤ Wehnelt electrode, ⑥ Ion extraction, ⑦ Focus 1–3, ⑧ Exit

A linear actuator allows a movement of the **sampling tip** from the exposure environment into the custom ion source, located directly in front of the ion optics of a high resolution LTOF time-of-flight mass spectrometer. 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**. Additionally, an integrated lens system facilitates efficient ion transmission towards the mass analyzer. Specifically shaped **defocusing electrodes** broaden the electron beam to increase bombardment coverage on the **sample tip**. Located opposite of the sample tip are electrodes for **extraction** and subsequent focusing (**Focus 1–3, Exit**) into the LTOF analyzer. However, 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. Alternating between the electron bombardment mode and the ion extraction mode (Pulsing) allows to adjust both modes for optimum performance.

In addition to detecting the desorbed ions, this ion source also allows for standard EI acquisition, which provides residual gas analysis and calibration of the MS.

Simulated Trajectories

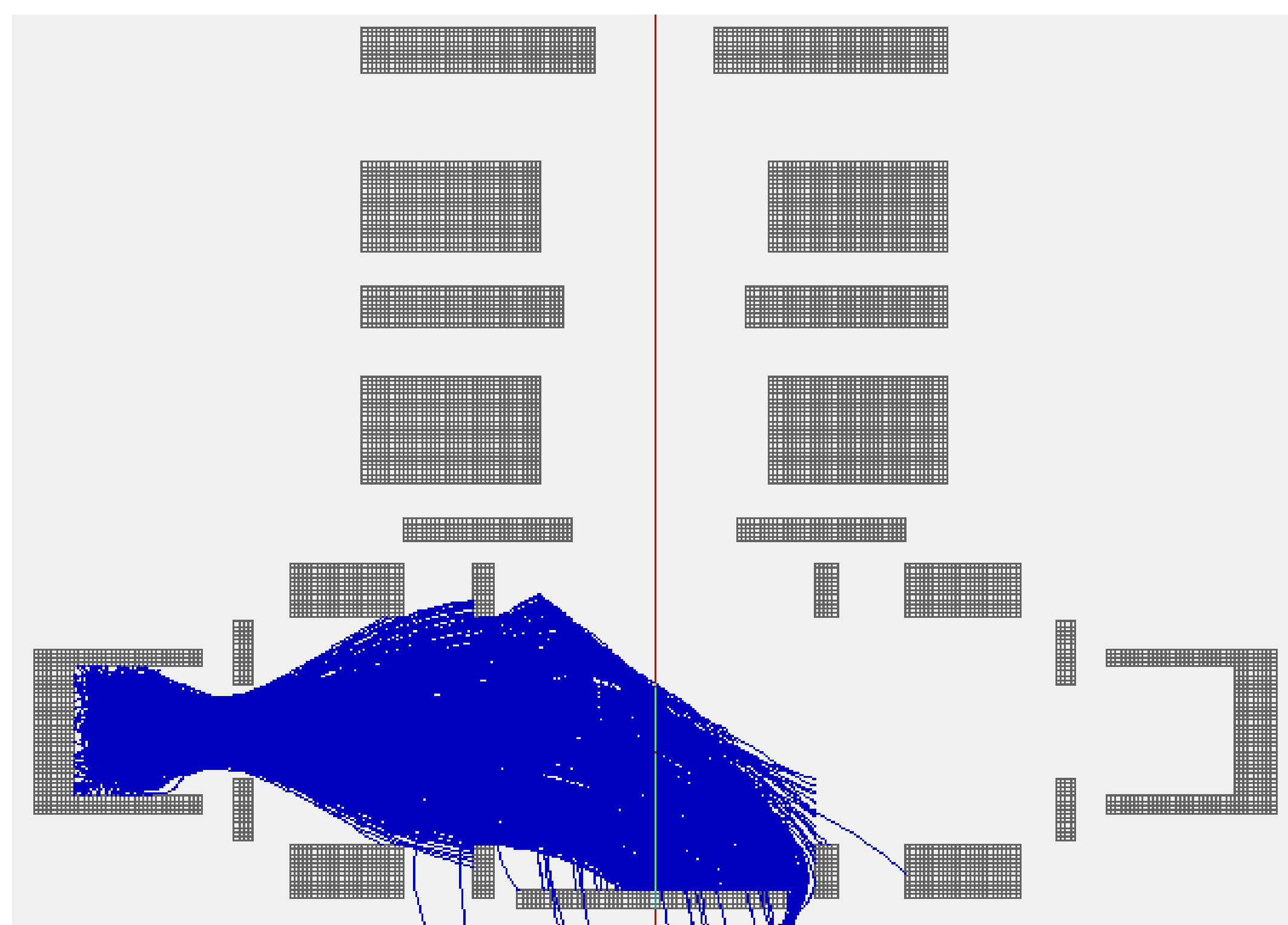


Fig. 5: Trajectories of the electrons from a filament to the sample

The simulated trajectories of the **electrons** (cf. **fig. 5**) with 70 eV kinetic energy show their paths from the filament (left) through the defocusing unit onto the sampling tip surface. An electron beam in a standard EI ion source is intentionally focused, which provides several advantages, but this would result in an unfavorable electron coverage of the sample tip. The defocus unit leads to a large area electron beam. Caused by the geometry, only half of the surface is covered. However, the second filament (not shown due to clarity) efficiently covers this missing area.

Figure 7-8 show the sample surface. The upper figure displays a heatmap of the electron bombardment by electrons and the lower figure maps the areas, which are counted as hits by the algorithm to determine the covered areal percentage (divided into bins of 0.12 mm²). According to the simulations, 67.5 % of the emitted electrons reached the sample surface, whereby 74.3 % of the surface is sufficiently covered.

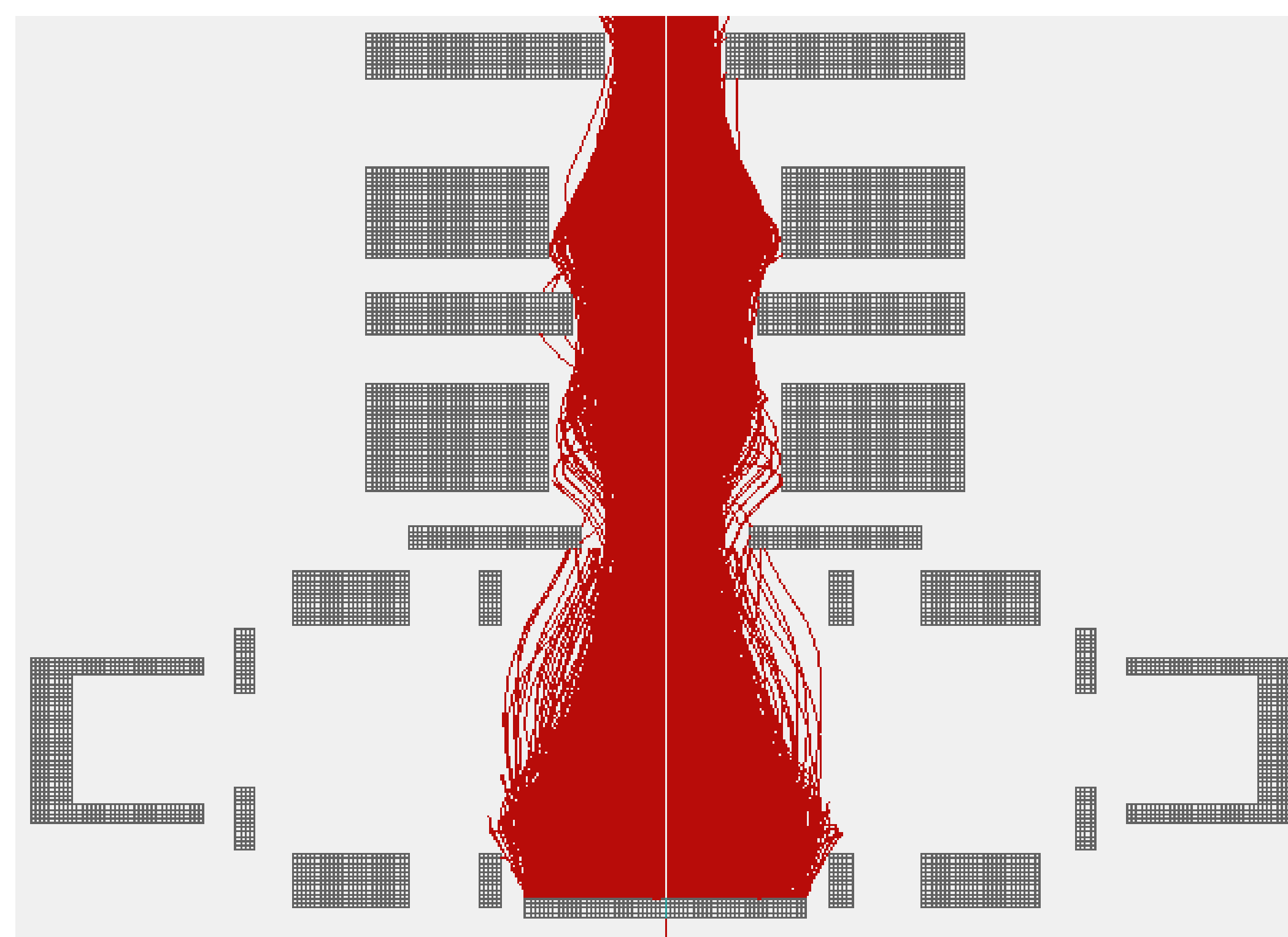


Fig. 6: Trajectories of the generated ions from the sample into the analyzer

The **ions** generated by the electrons are extracted from the sample by adjusted 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.

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 to be carried out very soon.

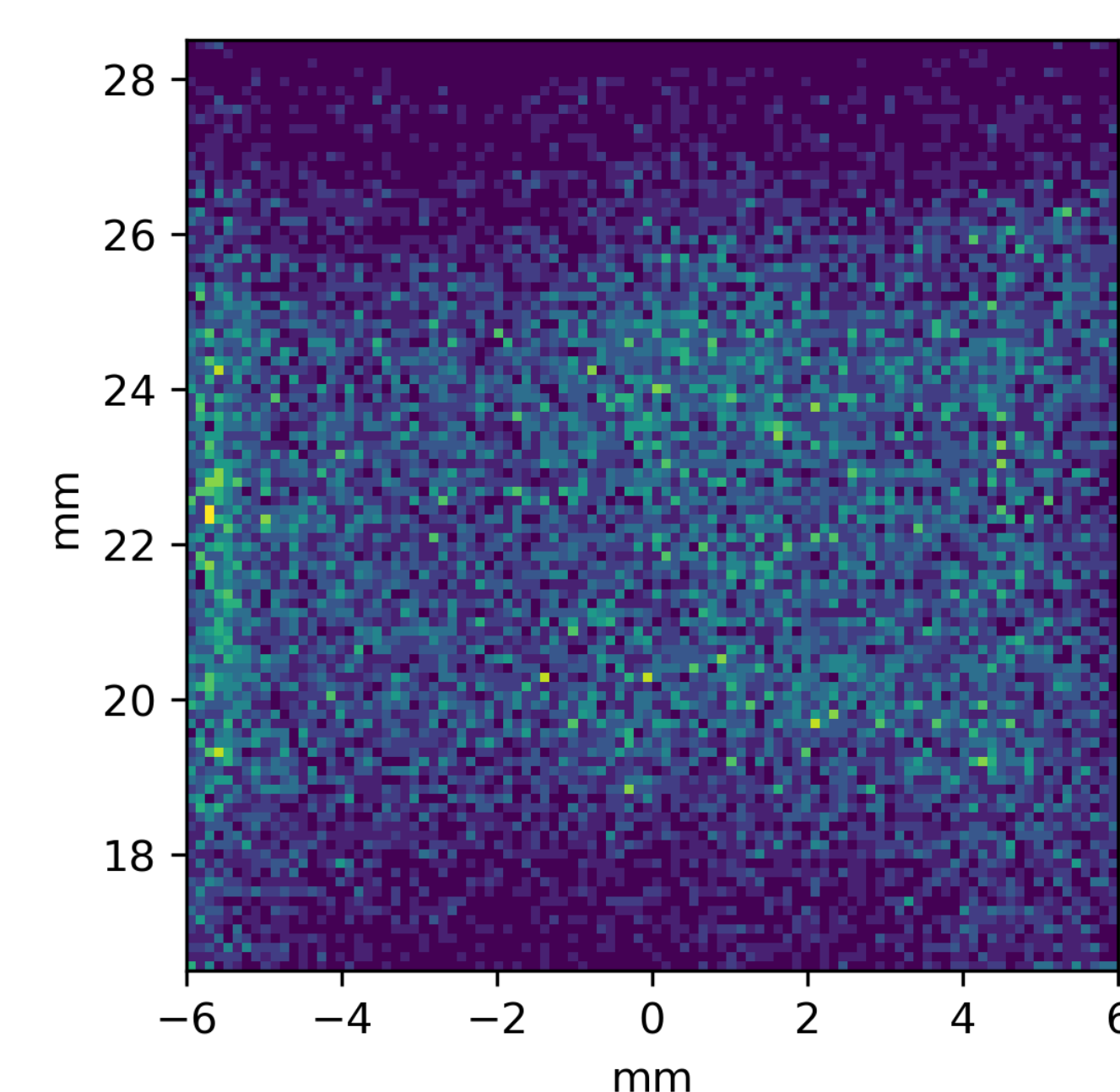


Fig. 7: Heatmap of the electron impact on the sample surface.

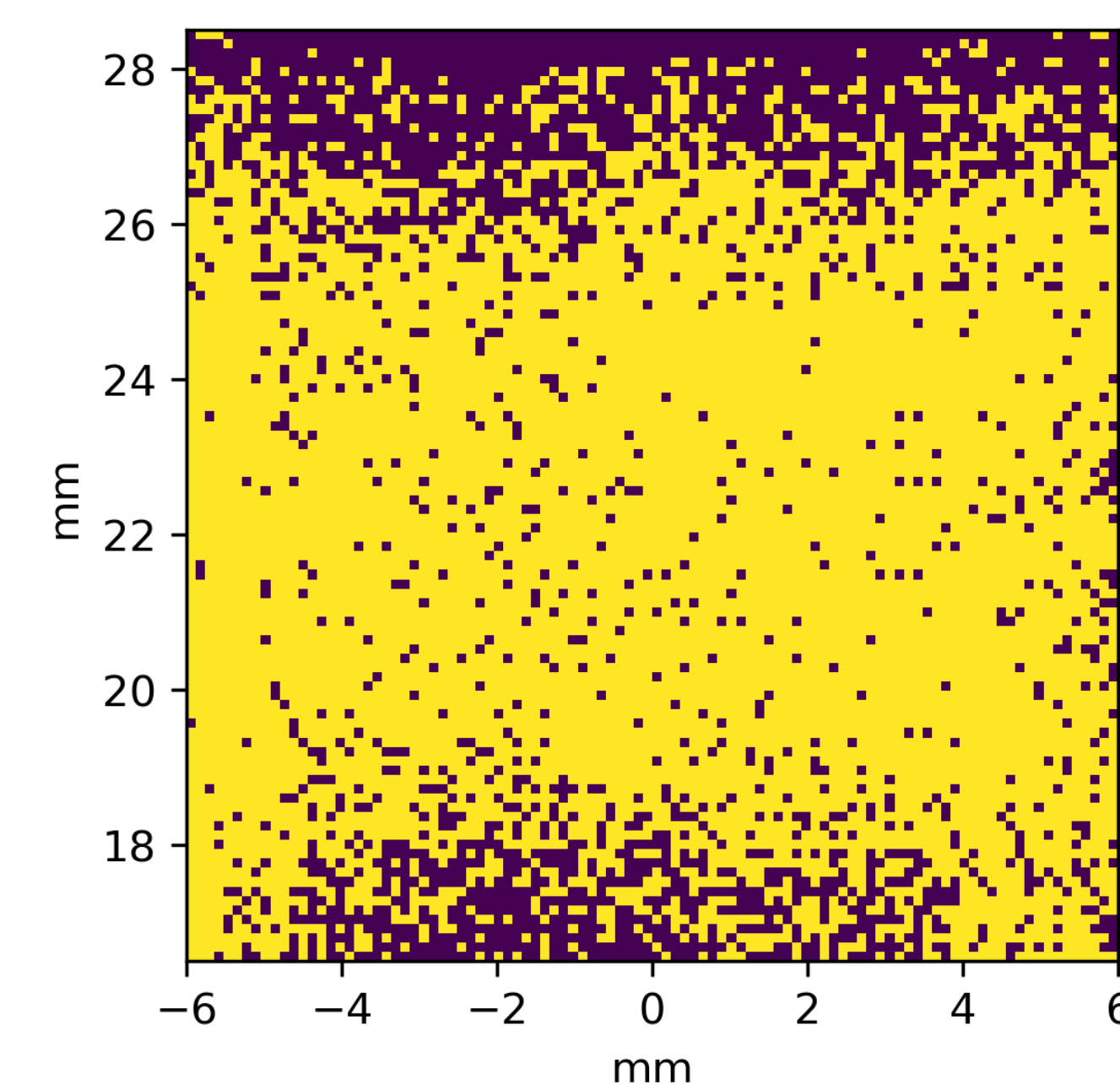


Fig. 8: Areas evaluated as electron hits

Acknowledgment

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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*