Final author comments

We would like to express our gratitude to the reviewer for taking the time and providing comments and a critical review to the manuscript.

Below, we provide point-to-point responses to the comments in red and document changes to the manuscript in blue.

Additional to the changes in direct context of the reviews, we have corrected multiple typographical errors in the manuscript, harmonized the panel labels of Figures 1 and 7, corrected the affiliations for one co-author, and amended the acknowledgments.

Henning Finkenzeller, on behalf of all co-authors

Reviewer #1 comment:

Report to the manuscript "Multiphysical description of atmospheric pressure interface chemical ionisation in MION2 and Eisele type inlets"

This manuscript presents multiphysics simulations of two atmospheric pressure chemical ionization sources frequently used in analyzing atmospheric samples with a mass spectrometer. The authors validate the theoretical results with current measurements at specified electrodes and also compare them with general observations having made while working with these sources. In general, this manuscript provides interesting and valuable insights into the physical and chemical working principles of these devices. Hands-on visualizations of parameters impacting the operation are given.

In accordance with AMTs referee guideline, following aspects are addressed:

1. *Does the paper address relevant scientific questions within the scope of AMT?*

--- To users of these sources the presented simulations might be relevant, also in view of further improvements.

1. *Does the paper present novel concepts, ideas, tools, or data?*

--- According to the authors it is the first time that a multiphysics simulation tool has been applied to describe and visualize the physical and chemical principles of these devices.

1. *Are substantial conclusions reached?*

--- In my opinion, no further substantial conclusions are reached despite the insightful visualizations.

1. *Are the scientific methods and assumptions valid and clearly outlined?*

--- In principal yes, specific points are discussed further below.

1. *Are the results sufficient to support the interpretations and conclusions?*

--- In principal yes, specific points are addressed further below.

1. *Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?*

--- Yes.

1. *Do the authors give proper credit to related work and clearly indicate their own new/original contribution?*

--- Yes.

1. *Does the title clearly reflect the contents of the paper?*

--- Yes.

1. *Does the abstract provide a concise and complete summary?*

--- Yes.

1. *Is the overall presentation well-structured and clear?*

--- Appropriate.

1. *Is the language fluent and precise?*

--- Appropriate, specific points are addressed further below.

1. *Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?*

--- Yes.

1. *Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?*

--- Generally okay, specific clarification is addressed further below.

1. *Are the number and quality of references appropriate?*

--- Yes.

1. *Is the amount and quality of supplementary material appropriate?*

--- Not applicable.

In compliance with the AMT referee guideline I do recommend publishing this article, however, with some minor changes/additions and requested comments presented in the following:

(i) lines 147 and 148: Please comment on the measured ion currents in the order of 10^{-11} A. The used Tenma (72-2595) can only measure in the µA range according to its specification.

The reviewer is correct in that the regular measurement range of the multimeter in current mode only extends down to µA. Here, we measured in voltage mode the voltage-drop over the multimeter-internal 10 MOhm resistor. Usually, the 10 MOhm present an “infinitely large resistance” for measuring voltages, and the voltage drop across the resistor is essentially the source voltage which is meant to be measured. Here, adding the resistor does not introduce a voltage-drop significant enough to bias the system (burden voltage of single mV out of hundreds or few thousands V) but the voltage-drop is measurable.

We agree that this could be made clearer in the manuscript and revise the passage as follows:

The currents to the two topmost electrodes of the MION2 inlet ($4 \cdot 10^{-11}$ A, attraction of H^+) and for the ion cage of the Eisele inlet ($6 \cdot 10^{-11}$ A, attraction of H^+, negligible adsorption of NO_3^-) were determined via the voltage-drop across the internal 10. MΩ resistor dedicated to measure voltages in a simple multimeter (Tenma 72-2595). The voltage-drop of 0.6 mV is measurable by the voltmeter and does not constitute a measurement bias under the test conditions.

(ii) line 60: "…by 40…" please revise

Added missing "%."

(iii) line 76: "a narrow…(A)…" please revise

Revised description to clarify analogy as follows:

Analogous to narrowing riverbanks that increase the water flow velocity (v) by reducing the cross-section area of the flow (A) but do not change the composition of the water (c), electric fields defined by electrodes affect the ion trajectories without changing their concentration.

(iv) fig 4d and e: U_A = -3000 V instead of U_A = 3000 V

Added missing minus signs.

(v) line 202: "The pinhole current is measured at a higher voltage than predicted." Please clarify.

We modified and expanded the discussions of Figure 5 substantially by a paragraph as follows to improve clarity:

The maximum pinhole current is measured at a higher accelerator voltage than predicted. Although the deflector voltage U_D was chosen in the measurement to maximise the ion delivery, it is possible that the ion beam was not always axially centred to be contained within or to fully illuminate the pinhole flow. In very narrow ion beams (low U_A, compare Fig 4a) that are not aligned with the flow going to the pinhole, most ions entering the IMR would be lost to the exhaust flow (J_E). This is a plausible explanation for the gradual onset of the observed measured total pinhole current. We note that the measured pinhole current in Figure 5 apparently decreases faster towards higher accelerator voltages U_A than expected from model simulations. Insufficient centring of the beam does not explain this observation, as the ion concentration within the beam varies only slightly. While shying from pinpointing a specific mechanism, we hypothesise that the effect originates in the volume controlled by U_A, i.e., the ionisation volume or the buffer volume between the ionisation volume and IMR. Actual ion mobilities considerably higher than assumed in the model at high U_A would lead to a more rapid decrease. A lower degree of reagent ion hydration and cluster formation between the reagent ion and reagent gas at high field strength would increase the effective electrical mobility. The field strength sensitivity of the reagent ion mobility itself is less likely to be significant because of the still relatively weak field strength (Viehland and Mason, 1995). Space charge losses during transport (especially within the IMR) are found to be not yet significant for the ion concentrations of few 10^6 cm^{-3}. In the model, the ion delivery efficiency η_D (eq. 4) is larger than 90 %, essentially unity, for $|U_A|$ > 3000 V: The ion concentration is maintained from the ion source to the pinhole.

(vi) line 204: "This could lead to a softening of the voltage sensitivity." Please clarify.

See comment v.

(vii) Please clarify the argumentation for the significantly differing slope of the measured pinhole current in contrast to the simulated ion concentration in figure 5.

See comment v.

(viii) line 288: "cm^{-3}" instead of "cm^{-1}"

Changed.