Final author comments

We would like to express our gratitude to the reviewers 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.

Reviewer #2 comment:

This paper compares two atmospheric pressure chemical ionization geometries using a detailed model simulations. Results from ion current measurements are presented and compared to simulations of the two different geometries. The overall goal of this manuscript is interesting and the results would be useful to the community. However I find the paper inconsistent or confusing at the least.

From my understanding, the advective velocities used in the model (Figures 1 and 7) are too large for the typical operation of either case of the CIMS. This is especially true for the Eisele design. For the MION described in Wang et al. [2021] with a 22 mm flow tube, a velocity of 2 m s^{-1} equates to a total flow of ~45 slpm which is on the higher end of the 20-30 slpm typically described (Wang et al. [2021] used 32 slpm for example). For the Eisele design using the 44 mm diameter flow tube described in the model, 1.7 m s^{-1} equates to a total flow of ~160 slpm. Well above the 20-45 slpm typically described (Tanner and Eisele [1995] and Sipila et al. [2018] used 45 and 30 slpm respectively). Later however, in Table 1, values more consistent with previously published operating parameters are presented for both systems.

The authors state that a reaction time of 113 ms is assumed for the Eisele configuration. Using a flow of 30 slpm as stated in Table 1 and the 44 mm diameter, a flow velocity of ~30 cm s^{-1} is obtained, yielding a reaction distance of only 3-4 cm? The physical length of the actual IMR cylinder is ~15 cm. The 113 ms reaction time IS greater than the calculated ~88 ms geometric reaction.

This inconsistency/confusion furthered in the topic of turbulence. The authors state that a Reynolds number, R_e, of ~1600 was assumed. Using 45 slpm in a 22 mm dia. flow tube, as in the MION model, yields a R_e of ~2800, well into the transition zone towards turbulent flow. The 160 slpm flow in a 44 mm flow tube, as in the Eisele model, yields a R_e >4000, well into the turbulent flow regime. If, however, the flows from Table 1 are used laminar conditions are maintained.

Overall, as a person familiar with both systems, I find this work inconsistant and/or confusing and hard to follow. The manuscript should be rewritten with an eye towards addressing these inconsistencies or making things more understandable. The work is interesting and will provide insight for users of either technique. The visualizations are quite useful. However, it needs more work before I would recommend publication.

Quick reply to reviewer comment #2

We appreciate the critical review. We deem it appropriate to provide a swift comment to clarify that there is no inconsistency with the fundamental model setup in the study. We are under the impression that the confusion caused to the reviewer stems from assuming certain approximations of the advective velocity profile in conjunction with the peak advective velocity, resulting in flow rates putatively incompatible with values from Table 1.

The modeling indeed uses the flow rates from Table 1 (20 slpm for MION, 30 slpm total for Eisele), consistent with what is in the literature.

The reviewer seems to use a constant velocity profile ("plug flow") to derive the high flow rates calculated in the comment (45 slpm for MION, 160 slpm for Eisele) that are indeed not compatible with the literature (too high). Assuming a parabolic velocity profile (a fully developed laminar flow) leads to flow rates that are lower by a factor of 2 (22 slpm for MION, 80 slpm for Eisele). For the MION inlet, this flow rate is compatible with the values shown in Table 1. For the Eisele inlet, this still seems incompatible. Here, it turns out that the velocity profile is neither constant nor parabolic, but rather behaves as depicted in Figure C1 (blue line). The flow velocity has a pronounced peak in the center, the velocity of the sheath flow is modeled to be rather weakly varying. This profile establishes as there is not much time for a fully parabolic flow to develop in the IMR after the core and sheath flow (green lines in Fig. C1) merge. Contributing to this non-parabolic profile is the fact that the velocity profile downstream of the IMR (close to the pinhole plate) is not parabolic, either. This is an interesting observation which is not obvious from the manuscript figures in their current form.

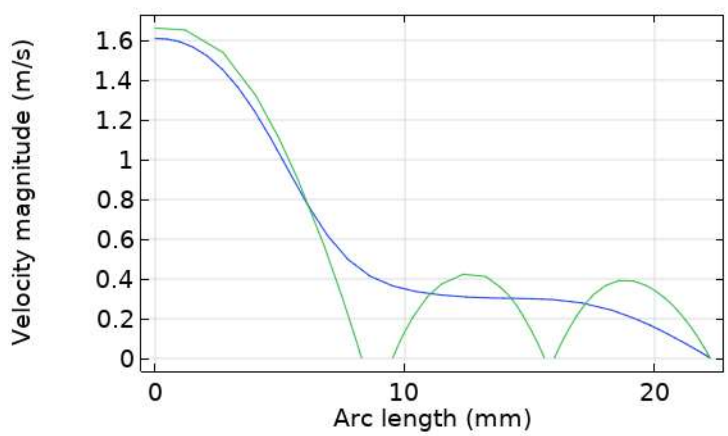

Figure C1: Flow velocity as function of radius (arc length) in the Eisele-type inlet. Profile before merging of sheath and core flow (green) and in center of IMR (blue). While the individual flow profiles are parabolic before merging, a parabolic flow in the IMR does not fully develop.

Effectively, we are confident that there is no fundamental problem with the study and that we will be able to clarify the profile of flows throughout the Eisele and MION inlet in a revised version of the manuscript that avoids confusion or misinterpretation. In due time, we will provide such a revised manuscript that also incorporates modifications motivated from the other reviewer comments.

Amendment to quick reply to reviewer comment #2

Following the reasoning outlined in the "Quick reply to reviewer comment #2", we have revised the manuscript to clarify the flow rates used in the modelling, the flow profiles, and that using laminar flow in the model is justified. Specifically, we addressed these issues in the following sections:

1. Clarification of flow rates for each inlet, Section 2.2 (Model setup)

   For the modelling of the Eisele-type inlet, 10 slpm sample, 20 slpm sheath, and 1 slpm flow to the mass spectrometer are used (Tanner and Eisele, 1995). For the MION2 inlet, 20 slpm exhaust flow (Wang et al., 2021) and 0.8 slpm flow to the mass spectrometer are used. The auxiliary reagent, purge, and reagent exhaust flow are J_R = 10 smlpm, J_{RE} = 50 smlpm, and J_{RP} = 100 smlpm.

2. Clarification of flow profiles in both MION2 and Eisele-type, and respective Reynolds numbers (including the parameters used for their derivation), Section 3.1 and 3.2 (Results)

   MION2, Section 3.1 (Results MION2 inlet):

   Assuming an interface upstream of the MION2 inlet that creates laminar flow (Reynolds number Re ≈ 2100 (using D = 20 mm, u = 1.6 m s^{-1}, ν = 1.48 · 10^{-5} m^2 s), the flow velocity profile is parabolic throughout the sample tube and IMR close up to the pinhole plate, where the flow splits to the exhaust and pinhole.

   Eisele-type, Section 3.2 (Results Eisele type inlet):

   Considering the paramount importance of the flow field throughout the inlet for the gas and ion transport, we added Figure 8 and an accompanying paragraph, which effectively communicates the modelled velocity profile within the Eisele-type inlet before and after merging the sample and the sheath flow.

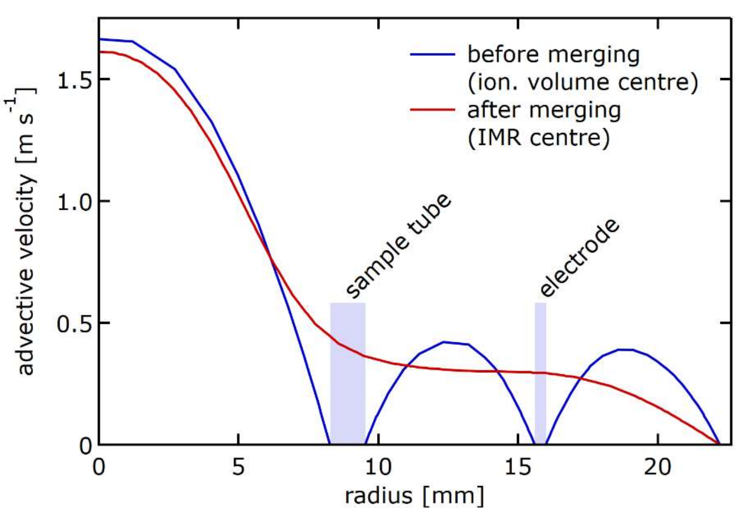

Fig. 8: Modelled velocity profile within the Eisele-type inlet before and after merging sample and sheath flow, using 10 slpm sample flow and 20 slpm sheath flow. The

composite profile establishing in the IMR has a pronounced maximum in the centre and a rather flat shoulder.

Figure 8 shows the velocity profile of the advective velocity upstream of the flow merging at the x-ray lamp plane and downstream after mixing at the IMR mid plane. Before merging, the flow profiles within the different channels are near-parabolic, as expected for fully developed laminar flows. After merging, the individual flow profiles combine to form a transition composite that maintains a near-parabolic shape in the innermost 5 mm with a pronounced maximum at the centre line and a rather flat shoulder with low velocity. The profile is the result of the relatively little interaction with the IMR surface after merging: The IMR radius (22 mm) is relatively large in comparison to the total IMR length (15 cm). Additionally, the velocity profile at the downstream end of the IMR (close to the pinhole plate) is not parabolic, either. The Reynolds number $Re \approx 1840$ (using $D = 16$ mm, $u = 1.7$ m s^{-1}, $v = 1.48 \cdot 10^{-5}$ m^2 s) at the downstream end of the sample tube, the location most prone to cause turbulence, supports assuming laminar flow in the modelling.

We remain convinced that there is no fundamental problem with the study and believe to have appropriately addressed the raised concerns about the clarity of presentation and consistency of the study.