Dear Editor,

We thank the reviewers for taking the time to review our manuscript and for their valuable feedback. We have carefully considered their suggestions and made the necessary revisions to enhance the clarity and accuracy of the manuscript. Below, we provide a detailed response to each of their comments. For your convenience, we have marked the reviewer comments in blue, our responses in black and parts of the text reflecting changes in the manuscript in purple. Please note that the line numbers in our responses correspond to the manuscript with tracked changes. Thank you once again for the feedback.

Reply to Reviewer 1:

This manuscript presents sensitivity estimates for Br- and I- CIMS using the voltage scanning method. It follows several earlier studies where this approach has been utilized, and it is likely a useful addition to the growing literature on the subject. I recommend publication after revisions, and list my main comments and concerns below, with the major one relating to lack of novelty.

We appreciate the valuable feedback from Reviewer 1 and provide the response to each of comments in the following.

General comment

Comment1: It is not very clear to what the novelty in this specific work is. Lopez-Hilfiker et al. presented a very similar set of results for I- CIMS in 2016, and there have been several other papers following up with additional details after that. I started reading this manuscript with high hopes for some new insight, methodologies, or guidelines. In particular as the title said "From Signal to Sensitivity", suggesting that the manuscript would contain new and in-depth methodology. However, now I have to suggest to the authors to more clearly showcase what this manuscript presents that is actually new in the context of "Atmospheric Measurement Techniques". The authors themselves note in the introduction that "voltage scanning is one of the most frequently used semi-quantitative calibration methods".

This is my only general comment, since in general the manuscript reads well and is quite straightforward, but this is partly because the authors are following similar steps as earlier studies.

Reply1. We thank the reviewer for this comment. The aim of this study is to demonstrate how voltage scanning can be implemented in the newly developed Vocus AIM IMR, which is grounded and operates at a fixed potential. In addition, it provides theoretical and experimental insight into how different functional groups influence molecular sensitivity in Br-CIMS and I-CIMS.

In the revised manuscript, we present an expanded discussion on the necessity of implementing the voltage bias in Vocus AIM IMR and how this bias enables accurate voltage scanning results. The method is further applied to our Vocus CI-TOF, demonstrating that it is broadly applicable across instruments employing grounded IMR designs.

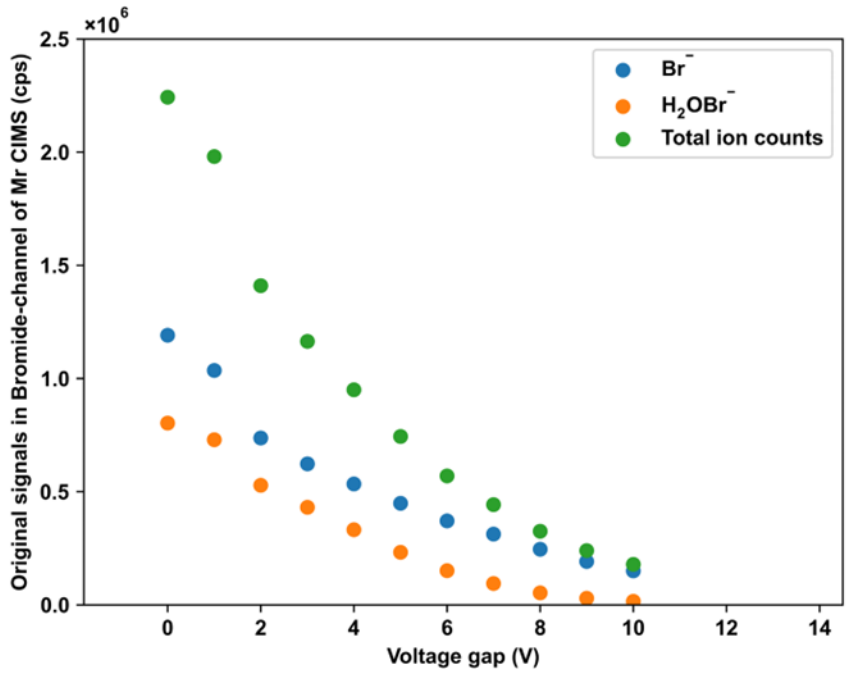
We revised Page 5, Line 10 to Page 6, Line 6 as: 'The Vocus AIM IMR is configured to be electrically grounded, which differs from earlier CIMS designs (Lopez-Hilfiker et al., 2016). For anions, an increase in the voltage gap between SQ and BSQ will lower the potential of SQ relative to the grounded IMR and thus can generate a retarding electric field at the reactor exit. This will reflect ions back toward the IMR because anions are decelerated when moving toward regions of lower electric potential. A similar argument applies to cations in positive channels. This effect results in ion repulsion, i.e., reduced ion transmission, and can result in a decrease in ion signals. Consequently, the measured signal decay rate reflects not only the declustering

processes occurring after Skimmer, which indicates the cluster binding energy, but also variations in ion transmission across the IMR–SQ interface. Since voltage scanning is used to derive the cluster binding energy based on the signal decay, we have to minimize the above issue and ensure that signal decay rate is primarily determined by cluster binding energy.

Total ion counts (TIC) serve as a useful indicator of changes in ion transmission efficiency **(Figure S3)** (Lopez-Hilfiker et al., 2016). In this work a pinhole bias of −4 V in negative channels and +4 V in positive channels is implemented across the IMR–SQ interface, i.e., Reactor Back, at the start of scanning. This approach results in a fixed ion transmission offset from IMR to pinhole, but it ensures that the subsequent signal decay is dominated by variations in relative binding energies rather than by transmission artefacts from pinhole to SQ. This behavior arises because the strong gas expansion from IMR (~52 mbar) into SQ (~1.5 mbar) can efficiently drive the initial transport of ions, allowing anions to be transmitted with comparable efficiency from pinhole to SQ. It makes ion transmission relatively insensitive to variations in the SQ potential as long as the retarding electric field across the pinhole-SQ region remains moderate. Although ion transmission eventually decreases as the field becomes sufficiently strong, most clusters have already reached their dV_{50} by that stage.'

Figure S3 was added to help better understand the changes of transmission:

(a)



(b)

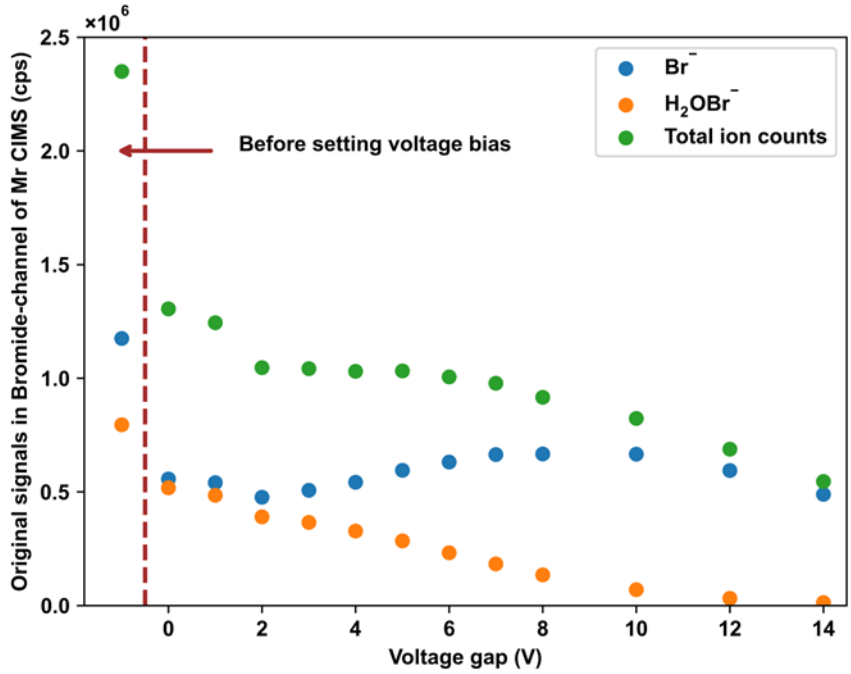


Figure S3. Signal variations of total ion counts (TIC), Br^- and H_2OBr^- (a) without a voltage bias and (b) with a voltage bias during the voltage scanning.

Specific comments

Comment2: Page 1, Line 17: How is the feasibility of the method actually shown? There is a figure with time series of different molecules, but those are not compared against anything else.

Reply2. The comparison with HONO is used to show the feasibility of this method and then applied to obtain the time series of the concentrations of these oxidation products. We revised Page 1, Line 16 – 17 as 'were taken as examples to show the results of this method for a daytime oxidation chamber experiment.'

Comment3: Page 2, Line 3: This reference seems limited concerning to generality of the sentence. Perhaps the authors could cite some recent review touching the subject, e.g. Zhang et al., 2023 (https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/mas.21857), or some CIMS comparison, e.g. Riva et al., 2019 (https://amt.copernicus.org/articles/12/2403/2019/).

Reply3. We revised Page 2, Line 4 as: 'It uses soft ionization to charge analytes and has the advantage of allowing in situ measurements that preserve the structure of the analytes (Riva et al., 2019; Zhang et al., 2023).'

Comment4: Page 3, lines 5-8. This is a key sentence of the manuscript, but it is now very long and hard to follow. I suggest splitting it in two and making it clearer. In addition, this paragraph is followed by two more, which read more as summaries and feel a bit misplaced at the end of an introduction.

Reply4. We revised Page 3, Line 6 – 11 as: 'Here we present an approach to estimating sensitivities of a wide range of compounds using multiple reagent ion chemistries in the grounded Vocus AIM IMR, whilst simultaneously tracking the collision limit sensitivity based on the method reported by Aggarwal et al. (2025). Based on this, sensitivities were for a wide range of species were obtained with this voltage scanning approach. We assessed the performance of this approach using a wide range of calibrants, chamber experiments and quantum chemical calculations.'

Comment5: Page 4, line 7: What does it mean that the VUC sources were switched?

Reply5. It means that the two VUV sources were alternately operated at a frequency of 1 Hz, with only one source active at any given time. We revised Page 4, Line 11 as: 'the two VUV sources were alternately operated at a frequency of 1 Hz to generate …'.

Comment6. Page 4, lines 8-9. Please add citation since you say it is well-known.

Reply6. We added the citations in the revised manuscript.
We revised Page 4, Line 13 as: 'on the sensitivity of CIMS (Huey, 2007; Lee et al., 2014).'

Comment7: Page 4, lines 18-21. I had to re-read these sentences several times and am still not sure I understood the details. Please try to make this more clear and easy to understand.

Reply7. We revised Page 4, Line 21 – 25 as: ''Data consist of four segments, each corresponding to a different reagent ion and were recorded with a time resolution of 0.5 Hz. For data processing, each segment was averaged by a factor of 2 and thus had an integration time of 1 s.

Comment8: Fig. 1, caption: I am used to seeing "SSQ", but is the first quadrupole not segmented in this instrument? In addition, quadrupole is misspelled in the figure.

Reply8. The first quadrupole in our Vocus B and Vocus CI-TOF is not segmented. Riva et al. reported that the optimal voltage gradients in the first quadrupole region are typically all 0 V between electrodes, as ions are focused on the radial direction efficiently by the RF but transported axially by the gas flow (Riva et al., 2024). Consequently, Tofwerk opts not to implement a segmented quadrupole.

Thank you for pointing out the spelling error. We have revised this figure according to reviewers' comments as:

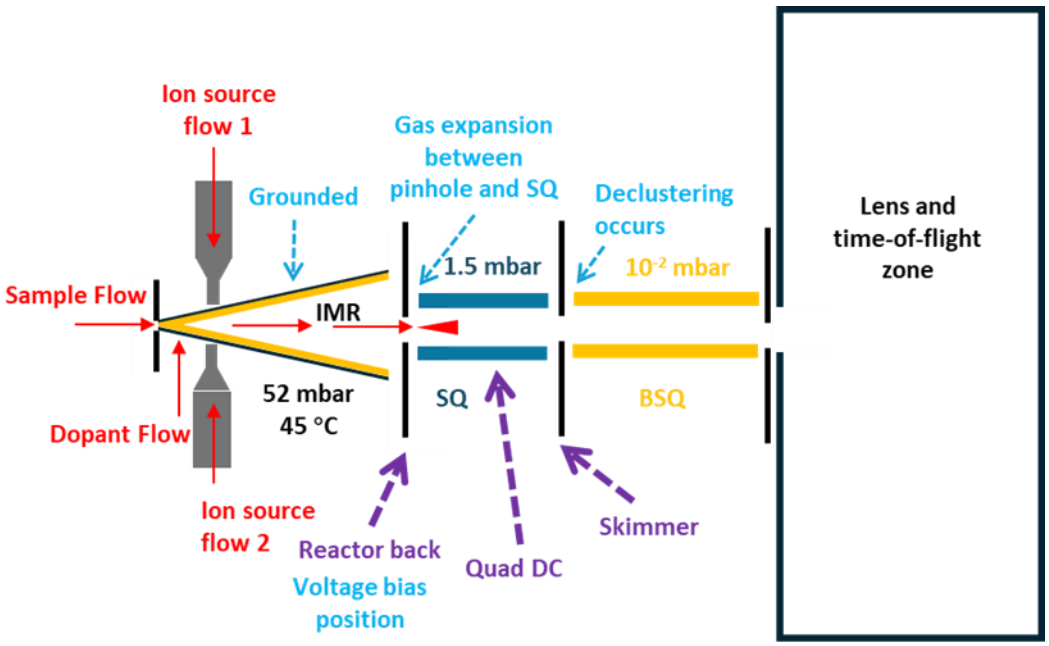


Figure 1. Schematic of the MR-CIMS structure. Gas flow paths are indicated in red, and key electrodes are highlighted by purple dashed arrows and texts. Explanatory annotations are denoted by blue dashed arrows and words. Pressures of the IMR, SQ (short quadrupole), and BSQ (big-segmented quadruple), as well as the temperature of the IMR, are labeled to facilitate understanding of the operating conditions in MR-CIMS.

Comment9: Page 5, line 4: Which are these "other voltages". The last mentioned one was the orifice plate, and if also all others were kept constant, then there would not be much changed at all? In addition, Table S1 provides voltages that were varied, but using nomenclature that is not used elsewhere, making it hard to relate to.

Reply9. We revised this section and give a detailed description and explanation for this voltage scanning method as well as its voltage bias setting. This can be found in Reply1.

We revised Page 4, Line 32 – 37 as: 'A schematic of the main elements of MR-CIMS including the IMR and quadrupoles, highlighting the region where the voltage was scanned, and the transfer of molecular ions to the TOF MS are shown in Figure 1. Three electrodes/voltages were adjusted in upstream of big-segmented quadruple (BSQ), including Reactor back, Quad DC, and Skimmer. Reactor back is the direct currency (DC) potential applied at pinhole between IMR and SQ, which is set as 0 V in the routine operation. Quad DC refers to the DC potential applied to the four quadrupole rods that carry the radio frequency (RF) field of SQ. Skimmer voltage corresponds to the DC potential applied to the skimmer electrode, which controls ion extraction and transmission efficiency across the SQ-BSQ interface. An increase in the voltage difference between the BSQ and region upstream of it induces dissociation of the adduct.'

Comment10: Page 6, line 12: KDE was applied to investigate the oxygen levels. How does KDE serve that particular purpose? And in the SI it says "We introduced it to ensure the completeness of the manuscript", which also confused me.

Reply10. KDE is principally a method to present the distributions of a finite sample of data. It overcomes the key limitations of traditional histograms, providing a better visualization of dV_{50}'s distribution. We revised Page 7, Line 15 – 16 as: 'Kernel density estimation (KDE) was applied to estimate the probability density functions of dV_{50} in both channels, in order to provide better visualization of the effects of …'

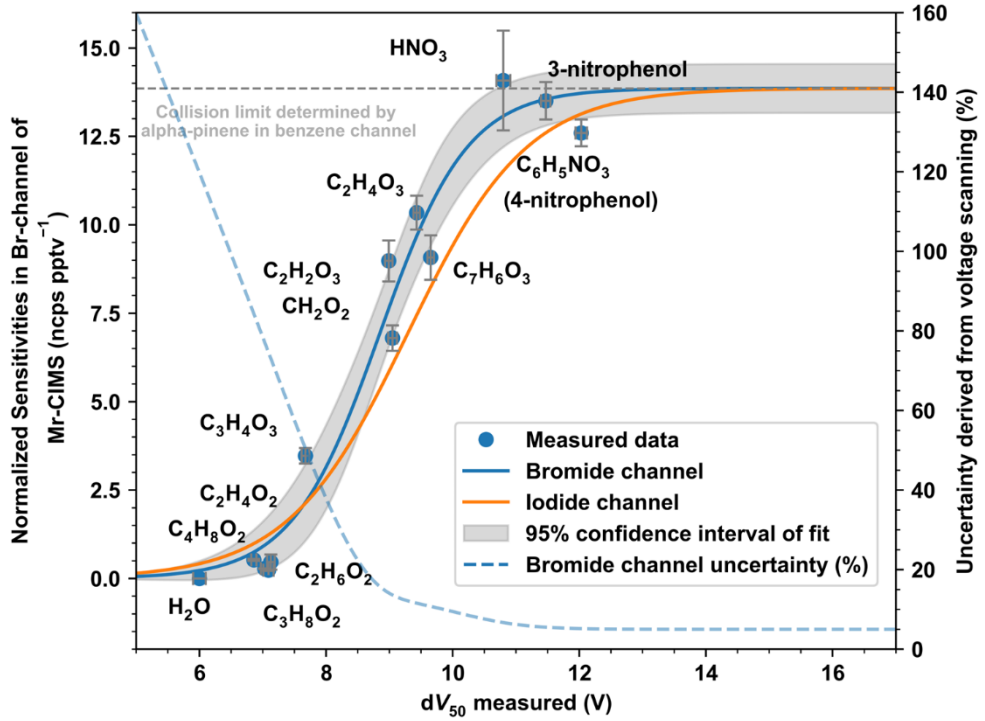
With respect to the latter query, this is probably a language misunderstanding. We revised the Section S1 in the supplement as 'We described it to ensure the completeness of the manuscript.'

Comment11: Figure 2: 1) The figures have two lines that refer to "uncertainty", and they are very different, and on different axes. 2) nitrophenol is misspelled in panel a. 3) Having the "I" in the formulas in panel b in the middle of the formulas, although they are adducts with I-, seems incorrect.

Reply11. 1) We already explained the uncertainty in the Page 7, Line 2 – 4 of original manuscript: 'The uncertainty in the estimation was defined as half the width of the 95% confidence interval of the sigmoid fit, divided by the corresponding fitted value, and was also treated as a systematic error associated with the use of this method.' The shadow indicates 'half the width of the 95% confidence interval of the sigmoid fit'. The right axis is the systematic error, which is the sum of squares of 5% uncertainty from collision limit determination and the standard error of sigmoid fit divided by the corresponding fitted value. This is further explained this in the revised version. 2) Revised. 3) We followed the ion formulas detected by mass spectrometer. To avoid misunderstanding, we only labelled formulas of analytes in the revised version.

We revised Figure 2 as:

(a)



(b)

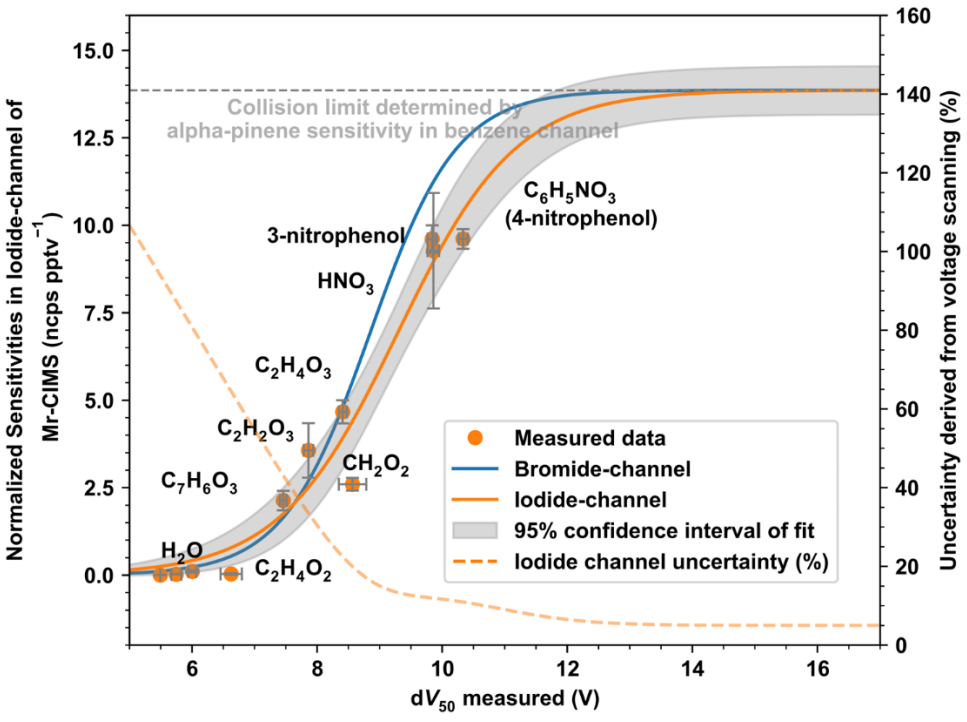


Figure 2. Relationships between dV_{50} of adducts and sensitivities to the corresponding species in the (a) bromide channel and (b) iodide channel of MR-CIMS. Fitting curves and 95% confidence intervals of dV_{50} and sensitivity are shown. For comparison, the sigmoidal fit line from the iodide channel is also plotted in (a) and that from the bromide channel is also plotted in (b). The systematic uncertainty derived from voltage scanning is the sum of squares of 5% uncertainty from collision limit determination and half the confidence interval of sigmoid fit divided by the corresponding fitted value.

Comment12: Page 11, lines 17-18: Is this information on fragments not something that could be utilized for other types of analyses? Not in this manuscript, but it seems like an interesting topic to explore.

Reply12. Thanks for this suggestion. We checked the signals obtained in the chamber experiments. But it is difficult for us to conclude a tendency based on this dataset. The primary problem is that we cannot establish a one-to-one correspondence between fragmentation signals and their parent compound due to the simultaneous detection of hundreds of species. To solve this problem, the most feasible approach is to design experiments that significantly reduce the number of species introduced into the instrument, thereby enabling an unambiguous elucidation of the relationship between fragmentation and their respective parent molecules. However, this is obviously out of the scope of this paper.

Comment13: Page 11, line 22: "more than 2" would be ">2".

Reply13. Thanks. We revised Page 13, Line 22 as: 'only compounds with at least 2 oxygen atoms …'. We revised Page 13, Line 26 as: 'For nitrogen-free compounds with at least 5 oxygen atoms…'.

Comment14: Page 12, line 14: I am not sure what this sentence means.

Reply14. We revised Page 14, Line 14 – 16 as: 'The signals that yielded successful voltage scanning were evaluated relative to the widely used limit-of-detection threshold of SNR = 3 (Yuan et al., 2017), in order to understand the signal strength necessary for a successful scanning.'.

Comment15: Page 14, lines 12-14: This reads as if also the latter series of compounds would have bene injected, but from later sentences, this seems not to be the case. Please make sure it is clear and correct.

Reply15. Thanks for reading carefully. We revised Page 16, Line 12 – 14 as: 'Several precursors were injected, including gasoline, biogenic, cooking, and VCP sources. During the oxidation experiments, a series of compounds that have been previously identified to be formed from certain precursors were detected.'

Comment16: Page 14, lines 18-21: What is the purpose of this sentence? If only to list the VOCs, it is unnecessarily complicated to list what they were injected as. Also, the following sentence then starts "All of these oxidation products", although they are not oxidation products.

Reply16. We removed these sentences, since the precursor-product relationships were described in the previous sentences.

Technical comments

Comment17: Page 1, Lines 3 and 21: Sensitivities of adduct ions are mentioned. Is it really the sensitivity of those that you are reporting, or is it the sensitivity of the CIMS to different molecules?

Reply17. The sensitivity we reported are all derived from calibration curves of adduct ion signal intensity versus neutral analyte concentration. Indeed, the value derived solely from the adduct ion is slightly lower than that obtained by summing the intensity of all ions originating from the analyte, including fragmentation ions and adduct ions. However, because the principle of voltage scanning is to infer sensitivity form the binding energy of the adduct formed between reagent ion and analyte, it is methodologically necessary to restrict the analysis to adduct ion alone.

Comment18: Page 1, Line 6 and elsewhere: Sensitivities are given with four significant digits in many cases. Is this possible? Given e.g. that standard gas concentrations are typically accurate to two significant digits.

Reply18. We confirm that the reported sensitivities with four significant digits are justified and reflect the precision of our calibration sources. The certified concentration on the gas cylinder label provided by the manufacturer is 6 significant digits and is gravimetrically prepared primary standards used for instrument calibration. For liquid standards and permeation tubes, the preparation involved gravimetric weighing using calibrated analytical balances with a readability of 0.1 mg, which yields four significant digits of precision.

Comment19: Page 2, lines 35 and 36. Why not simple add the year to the first mention of Lopez-Hiilfiker et al and Song et al, instead of separately adding the full citations again in the end of the sentence?

Reply19. We revised Page 2, Line 36 – 37 as: 'Lopez-Hilfiker et al. (2016) was the …Song et al. (2024) established …'

Comment20: Page 3, line 24: "SAPHIR"

Reply20. We revised Page 3, Line 28 as: 'in the SAPHIR-CHANEL campaign …'.

Comment21: Page 3, lines 40-42: Seems like some repetition from what was already said concerning definitions and acronyms.

Reply21. Corrected it. We have revised the Page 3, Line 44 – 45 in the manuscript as: 'MR-CIMS is a newly designed instrument equipped with a bipolar time-of-flight (TOF) mass spectrometer…'

Comment22: Page 5, line 3: Please rephrase "primarily purely"

Reply22. We revised this section in the revised manuscript, as replied in Reply1.

Comment23: Page 6, line 37: S4?

Reply23. Corrected it. Currently, it is Figure S5. We revised Page 7, Line 41 as 'are shown in Figure S5.'

Comment24: Page 9, line 6: Check the sentence.

Reply24. Sorry for the typo. We revised Page 11, Line 2 as: '4-nitrophenol exhibited a high dV_{50} and a sensitivity close …'

References

Riva, M., Pospisilova, V., Frege, C., Perrier, S., Bansal, P., Jorga, S., Sturm, P., Thornton, J. A., Rohner, U., and Lopez-Hilfiker, F.: Evaluation of a reduced-pressure chemical ion reactor utilizing adduct ionization for the detection of gaseous organic and inorganic species, Atmos. Meas. Tech., 17, 5887–5901, https://doi.org/10.5194/amt-17-5887-2024, 2024.

Reply to Reviewer 2:

Comment1. Overall, the manuscript is well-written and presents a valuable methodology for estimating the sensitivity of a wide range of atmospheric trace gases using the Multi-Reagent Chemical Ionization Mass Spectrometer (MR-CIMS) platform. By combining collision-limit determinations with a voltage scanning approach, the authors address the challenges of quantifying diverse compounds in the atmosphere. The authors identify three gaps that motivate this work: the evaluation of bromide CIMS chemistry in scanning, the application to a new Ion-Molecule Reactor (IMR) design, and the determination of the signal-to-noise ratio (SNR) required for this approach. However, since bromide voltage scanning is fundamentally similar to iodide chemistry and SNR requirements are often implied in previous literature, I believe that the true novelty of this work should lie in investigating how the unique Vocus AIM IMR design and Vocus B fast-switching capabilities influence standard voltage scanning protocols. Currently, the manuscript does not clearly articulate the implementation of the voltage bias in the new Vocus AIM IMR or how this specific IMR configuration changes the scanning procedure. Furthermore, the methodology as presented feels equally applicable to a standard Vocus AIM with slower switching, potentially failing to highlight the unique electrical and chemical challenges posed by the rapid polarity and reagent switching of the Vocus B. My major comments are as follows:

As pointed out by the authors, one main difference between the VOCUS-AIM-IMR and the traditional CIMS is that we can no longer change a set of voltages at the same time upstream of the BSQ. Instead, there is a voltage bias setting. This changes a lot of the difference in how we should do voltage scanning. I think there is still a lack of explanation on how this voltage bias changes the de-clustering, even though the authors have a short paragraph in the supporting information Page 5 line 1-15. While I appreciate the authors explaining the use of voltage bias in the new IMR, it's still not quite clear to me whether they change the voltage bias between a regular sampling mode and a voltage scanning mode. I think one of the reasons for the confusion is the use of different terminology for the same voltage setting (for example, Quad DC(bias) in Table S1 vs voltage bias on Page 5). My understanding is that the voltage bias was adjusted at each step during scanning, but why does the change in voltage bias not influence the transmission efficiency (i.e., reduce TIC as suggested by Figure S3)? Also, should the voltage bias setting be different between Vocus AIM and Vocus B during voltage scanning?

Reply1. We appreciate the reviewer's comments and agree that the necessity and theoretical basis of the voltage bias were not sufficiently clarified in the original manuscript. Therefore, Section S1 has been expanded and moved into the revised main text.

First, we clarify that the voltage bias referred to in this manuscript specifically denotes the -4 V potential (4 V for positive channels) applied at the electrode 'Reactor back', which is located at the pinhole between the IMR and the first quadrupole, i.e., SQ. This voltage bias is applied only in the voltage scanning mode and remains fixed throughout the scanning. The parameter labelled 'Quad DC (bias)' refers to the direct currency (DC) potential applied to the four quadrupole rods that carry the radio frequency (RF) field of SQ, which is unrelated to the voltage bias discussed above. To avoid misunderstanding, we use the name 'Quad DC' in the

revised version. We clarified this in Table S1 and also labelled their positions in Figure 1. We revised Page 4, Line 32 – 37 as: 'Three electrodes/voltages were adjusted in upstream of big-segmented quadruple (BSQ), including Reactor back, Quad DC, and Skimmer. Reactor back is the direct currency (DC) potential applied at pinhole between IMR and SQ, which is set as 0 V in the routine operation. Quad DC refers to the DC potential applied to the four quadrupole rods that carry the radio frequency (RF) field of SQ. Skimmer voltage corresponds to the DC potential applied to the skimmer electrode, which controls ion extraction and transmission efficiency across the SQ-BSQ interface. An increase in the voltage gap between the BSQ and the region upstream of it induces …'

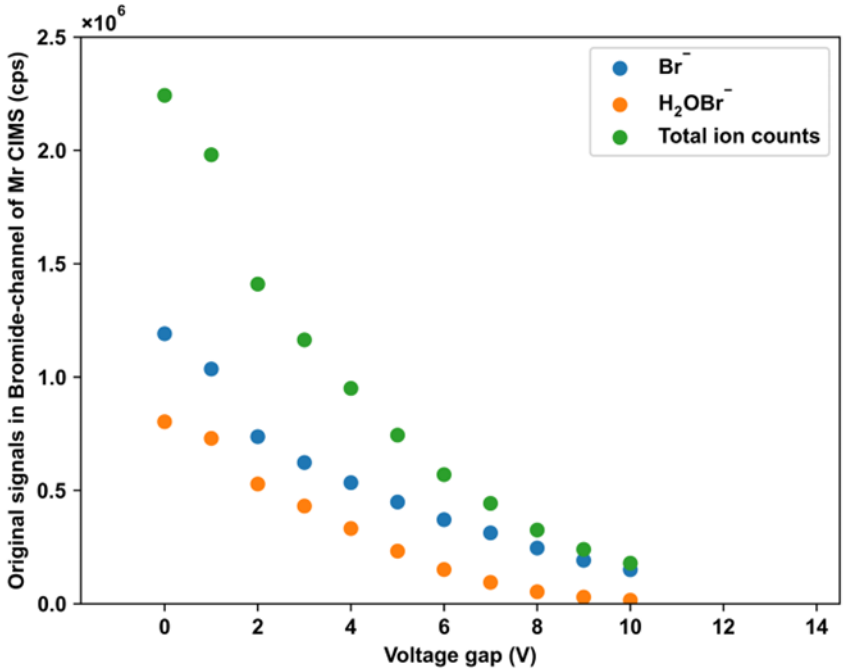
Section S1 has been revised and incorporated into the manuscript to explain the voltage settings more clearly. We revised Page 5, Line 10 to Page 6, Line 11 as: '

The Vocus AIM IMR is configured to be electrically grounded, which differs from earlier CIMS designs (Lopez-Hilfiker et al., 2016). For anions, an increase in the voltage gap between SQ and BSQ will lower the potential of SQ relative to the grounded IMR and thus can generate a retarding electric field at the reactor exit. This will reflect ions back toward the IMR because anions are decelerated when moving toward regions of lower electric potential. A similar argument applies to cations in positive channels. This effect results in ion repulsion, i.e., reduced ion transmission, and can result in a decrease in ion signals. Consequently, the measured signal decay rate reflects not only the declustering processes occurring after Skimmer, which indicates the cluster binding energy, but also variations in ion transmission across the IMR–SQ interface. Since voltage scanning is used to derive the cluster binding energy based on the signal decay, we have to minimize the above issue and ensure that signal decay rate is primarily determined by cluster binding energy.

Total ion counts (TIC) serve as a useful indicator of changes in ion transmission efficiency (Figure S3) (Lopez-Hilfiker et al., 2016). In this work, a pinhole bias of −4 V in negative channels and +4 V in positive channels is implemented across the IMR–SQ interface, i.e., Reactor Back, at the start of scanning. This approach results in a fixed ion transmission offset from IMR to pinhole, but it ensures that the subsequent signal decay is dominated by variations in relative binding energies rather than by transmission artefacts from pinhole to SQ. This behavior arises because the strong gas expansion from IMR (~52 mbar) into SQ (~1.5 mbar) can efficiently drive the initial transport of ions, allowing anions to be transmitted with comparable efficiency from pinhole to SQ. It makes ion transmission relatively insensitive to variations in the SQ potential as long as the retarding electric field across the pinhole-SQ region remains moderate. Although ion transmission eventually decreases as the field becomes sufficiently strong, most clusters have already reached their dV_{50} by that stage. The increased voltage gap between SQ and BSQ accelerates the velocity of ions. Clusters collided with buffer gas at the entrance of BSQ, and those with higher binding energies required larger kinetic energies to dissociate. Thus, their strengths were inferred from the voltage gaps needed for efficient dissociation. The detailed voltage settings during the scanning are listed in Table S1.'

We revised Figure S3 as:

(a)



(b)

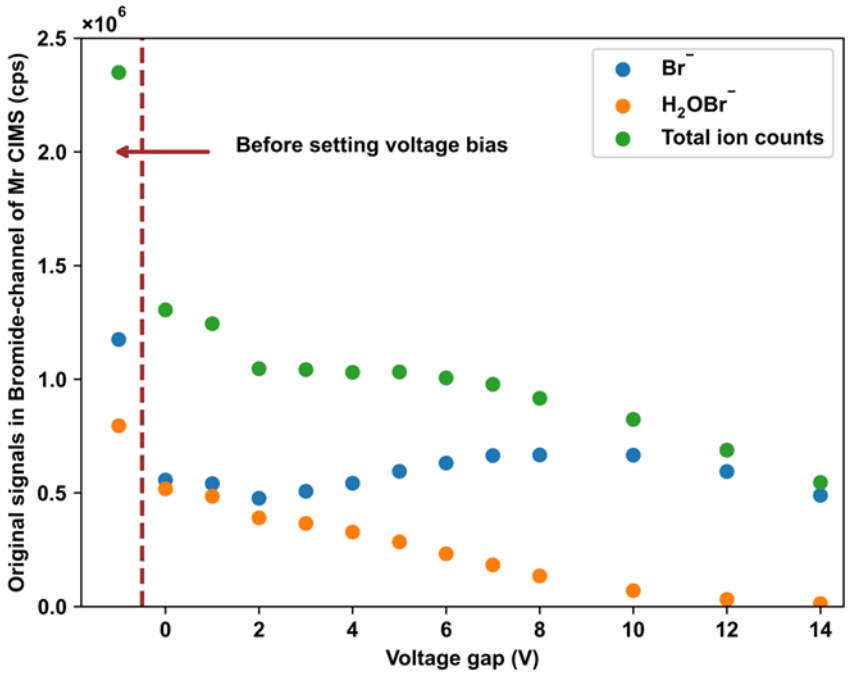


Figure S3. Signal variations of total ion counts (TIC), Br^- and H_2OBr^- (a) without a voltage bias and (b) with a voltage bias during the voltage scanning.

This voltage scanning method is applicable on other instruments using Vocus AIM IMR. In order to show this, we have also included additional data from another Vocus AIM instrument. We employed the same voltage settings on our Vocus chemical ionization time-of-flight mass spectrometer (Vocus CI-TOF, Vocus 2R, Tofwerk AG.). We followed the default operating pressure of Vocus CI-TOF, with its IMR and SQ maintained at 60 mbar and 2.0 mbar, respectively. We set the voltage bias at its electrode 'Vocus/Reactor back' and adjusted the potential before BSQ with its electrodes 'RF DC' and 'Skimmer' by the same increment. The results

obtained are comparable to those from MR-CIMS, though the absolute sensitivities of same compounds differed between the two instruments. This is likely due to factors such as instrument tuning, microchannel plate (MCP) settings, and pressure. In addition, because we did not have an extra dopant flow heater, the water ratio of the Vocus CI-TOF in iodide channel and bromide channel were 0.09 and 0.3, respectively. However, the relative ordering of dV_{50} and the relationship between dV_{50} and sensitivities was preserved. This application is discussed in the revised version.

We revised Page 3, Line 21 – 22 as: 'This voltage scanning method was further demonstrated to be applicable to other CIMS using Vocus AIM IMR. To better investigate the …'

We revised Page 10, Line 18 – 26 as: 'This voltage scanning method incorporating a voltage bias is also applicable to other instruments utilizing Vocus AIM IMR. We employed it on our Vocus chemical ionization time-of-flight mass spectrometer (Vocus CI-TOF, Vocus 2R, Tofwerk AG.). We followed the default operating pressure of Vocus CI-TOF, with its IMR and SQ maintained at 60 mbar and 2.0 mbar, respectively. We set the voltage bias at its electrode 'Vocus/Reactor back' and adjusted the potential before BSQ with its electrodes 'RF DC' and 'Skimmer' by the same increment. The results obtained are comparable to those from MR-CIMS, though the absolute sensitivities of same compounds differed between the two instruments (**Fig. S7**). This is likely due to factors such as instrument tuning, microchannel plate (MCP) settings, and pressures. In addition, because we did not have an extra dopant flow heater, the water ratio of the Vocus CI-TOF in iodide channel and bromide channel were 0.09 and 0.3, respectively. However, the relationship between dV_{50} and sensitivities was preserved.'.

We added Figure S7 in the supplement.

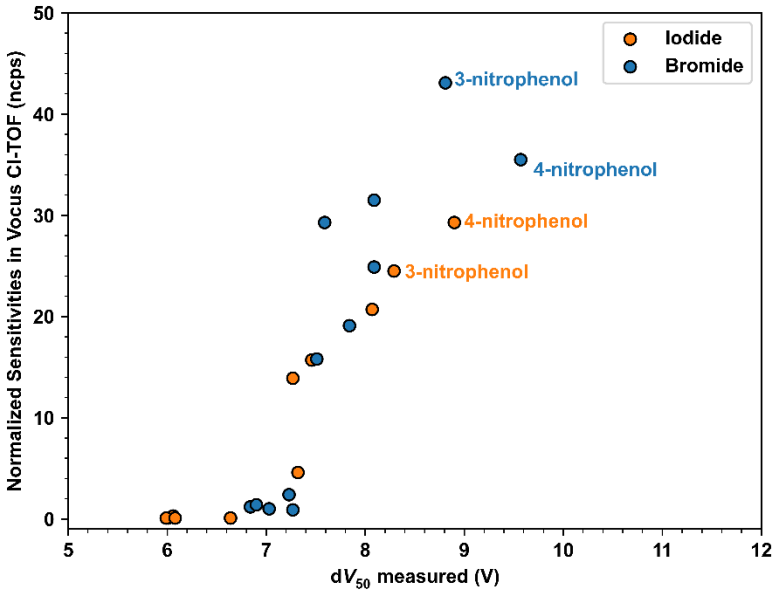


Figure S7. Relationships between dV_{50} of adducts and sensitivities to the oxygenated organic compounds in Vocus CI-TOF. High sensitivity compounds, i.e., nitrophenols, are labelled. Orange and blue text indicate the iodide and bromide channels, respectively.

Therefore, the application of voltage scanning on Vocus CI-TOF is actually very similar to that of MR-CIMS. However, since the Vocus CI-TOF was not operated in positive ion mode, we were unable to determine

a collision limit using the same method as applied in MR-CIMS, which relies on measuring the sensitivity of alpha-pinene in the benzene channel. Therefore, we do not fit the relationship in Figure S7.

Comment2. Page 5 Line 16-19. Rapid switching between four reagent ions at a frequency of 1 Hz is impressive but introduces the risk of chemical interference or competition. Given that the authors indicate that benzene and acetone dimer chemistries can overlap, I think that it is important to demonstrate whether this fast-switching environment leads to residual "cross-talk" that might corrupt the dV50 determination for any single reagent ion.

Reply2. A control experiment was conducted by operating each VUV lamp individually without switching. The dV_{50} of lactic acid retrieved from both negative channels deviated by less than 3% from values obtained during standard operation. Therefore, the fast-switching environment does not influence the dV_{50} determination. We revised Page 10, Line 14 – 17 as: 'A test experiment was conducted to confirm that fast-switching settings of MR-CIMS do not influence the determination of dV_{50} for the analytes. We measured the dV_{50} of lactic acid under routine operation and under conditions where the VUV lamps were operated without switching. The results of both negative channels are shown in **Figure S6**, demonstrating that the differences were within 3%.'

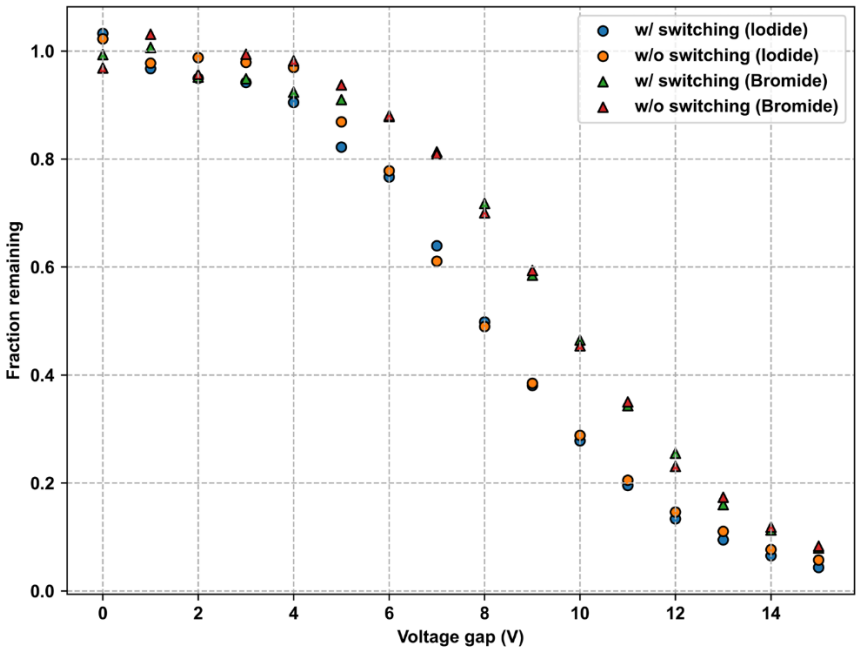


Figure S6. Dissociation of lactic acid-reagent ion adducts during the voltage scanning, with and without fast switching of the VUV lamps. Circles represent the iodide channel and triangles represent the bromide channel. Signals of adducts have been normalized to the sum of reagent ions and hydrated reagent ions and to the maximum at the start of the voltage scanning.

Comment3. Table S1. What is Quad linac? Is this specific to Vocus B? My recollection is that this setting is not on a Vocus AIM. On Page 3 Line 42, the authors state that the MR-CIMS uses the Vocus AIM IMR. These additional settings suggest minor differences between the AIM and Vocus B platforms that are not clearly

documented. The manuscript might be easier to follow if the methodology focused entirely on the Vocus AIM, as the Vocus B details increase complexity without necessarily helping to validate the scanning approach.

Reply3. We thank the reviewer for drawing attention to this point. We contacted Tofwerk to clarify the function of this parameter and confirmed that the "Quad Linac" voltage is associated with ion mobility spectrometry–mass spectrometry (IMS–MS) configurations. Although the same graphical user interface (GUI) is implemented in the Vocus B software, this port is not physically connected to any electrodes in our instrument. We further verified this experimentally by varying the "Quad Linac" voltage over its available range and observed no measurable effect on the detected ion signals. Therefore, we revised Table S1 and deleted this column. The voltage settings on the Vocus CI-TOF during the scanning are actually the same as those on Vocus B, as described in Reply1.

Comment4. With over 260 compounds identified in chamber experiments, structural isomers are highly probable, particularly as oxygen content increases. The manuscript would be strengthened by a discussion on the capability, or inherent limitations, of this voltage scanning approach to differentiate between isomers that share a molecular formula but possess different binding energies.

Reply4. We appreciate this suggestion. Because structural isomers share the same elemental composition, the voltage scanning signal might represent a sum of their individual responses. If multiple isomers contribute significantly to the ion signal and have different binding energies, the resulting voltage scanning profile cannot be well represented by a single sigmoid fitting. This limitation motivates the use of a sigmoid fitting quality threshold, i.e., $R^2 > 0.5$, below which signals are not retained. In addition, the voltage scanning method can provide insight into compound functionality. As discussed above, different oxygenated functional groups have distinct binding energies, which can be captured in their corresponding dV_{50} values derived from voltage scanning.

We add the discussion on this in the Page 17, Line 14 – 18 of revised version: 'It deserves notification that the voltage scanning signal might represent a sum of individual responses of structural isomers. If multiple isomers contribute significantly to the ion signal and have different binding energies, the resulting voltage scanning profile cannot be well represented by a single sigmoid fitting. This limitation motivates the use of a sigmoid fitting quality threshold, i.e., $R^2 > 0.5$, below which signals are not retained. In addition, the voltage scanning method can provide insight into compound functionality. As discussed above, different oxygenated functional groups have distinct binding energies, which can be captured in their corresponding dV_{50} values derived from voltage scanning.'

Minor comments:

Comment5. There is a typo on Page 2, Line 68, where a double period follows the phrase "voltage scanning methods..".

Reply5. Thanks a lot for reading carefully. We removed it.

Comment6. The reference to Figure S1 in Section S1 regarding Total Ion Counts (TIC) appears incorrect, as

Figure S1 in the text pertains to IMR stability; the authors likely intended to reference Figure S3.

Reply6. Sorry for this incorrect reference. We corrected it in the revised manuscript as 'Figure S3' .

Comment7. It would be clearer if Figure 1 could be annotated to show exactly where the specific voltage settings mentioned in Table S1 are applied within the instrument, which would clarify how the electrical gradient differs in the AIM IMR compared to older designs

Reply7. Thanks for this suggestion. We revised Figure 1 and show the positions of relevant voltage settings. We revised Figure 1 as:

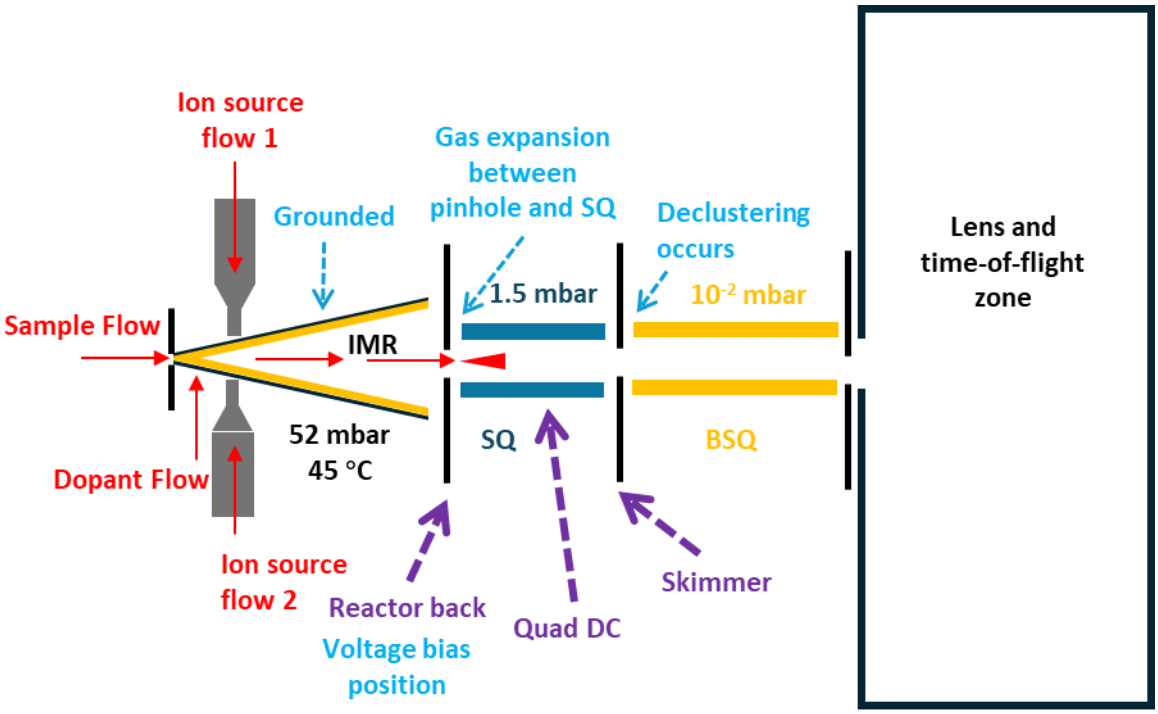


Figure 1. Schematic of the MR-CIMS structure. Gas flow paths are indicated in red, and the electrodes/voltages adjusted during voltage scanning are highlighted by purple dashed arrows and texts. Explanatory annotations are denoted by blue dashed arrows and words. Pressures of the IMR, SQ (short quadrupole), and BSQ (big-segmented quadruple), as well as the temperature of the IMR, are labeled to facilitate understanding of the operating conditions in MR-CIMS.

In summary, this is a strong paper that merits publication. However, I found the methodology difficult to follow from the perspective of a user looking to implement voltage scanning on their own instrumentation. This is partly due to the nuanced differences between the Vocus AIM and Vocus B. The manuscript would benefit from a clearer differentiation between these two inlets/instruments, or perhaps a reorganization specifically tailored to the implementation of voltage scanning within the Vocus AIM framework.

Reply8. We really appreciate the suggestions from Reviewer 2. We gave a better description of electrodes and voltages in the revised manuscript and explained the voltage bias and scanning strategies from the fundamental perspective. We also applied the voltage scanning on the Vocus CI-TOF, another CIMS employing Vocus AIM IMR, and showed the obtained results. As mentioned above, though the absolute sensitivities varied due to a

lot of factors, a similar relationship between dV_{50} and sensitivities can be observed by utilizing the same voltage bias and scanning strategies. Therefore, voltage scanning is implemented using a similar strategy in Vocus CI-TOF and Vocus B and produces consistent results.

We still want to keep this manuscript mainly discussing about the application on MR-CIMS, i.e., Vocus B framework, but will also show the feasibility of voltage scanning on other instruments employing Vocus AIM IMR with the same scanning methods. This is because, in previous investigations, the determination of collision-limit sensitivity in negative channels is quite challenging. The compounds reported to be charged at the collision limit either require complex synthesis, e.g., N_2O_5 (Huey et al., 1995; Lopez-Hilfiker et al., 2016), or have volatilities that are too low to establish a quantifiable gas-phase standard, e.g., levoglucosan (Aggarwal et al., 2025). Aggarwal et al. showed that we can determine the collision limit sensitivity of negative channels by measuring the sensitivity of alpha-pinene in the benzene channel of the same IMR (Aggarwal et al., 2025). This is the advantage of Vocus B framework which can readily switch between positive and negative ion modes without additional tuning or modification, thereby simplifying the experimental workflow and presentation of the results.

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