

## ***Interactive comment on “A Vacuum Ultraviolet Ion Source (VUV-IS) for Iodide-Chemical Ionization Mass Spectrometry: A Substitute for Radioactive Ion Sources” by Yi Ji et al.***

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Referee comment: “A general point. I- CIMS was first deployed for measurement of PAN and this method is still widely used. Why was PAN not tested in the lab? It appears from fig. 4 that the signal at 59 amu is much larger when using the VUV (config a) compared to Po210. Is this due to a better sensitivity, a worse background or changing ambient conditions? If the latter is true, it is not clear what this figure hopes to convey. As mentioned below, a spectra obtained in zero-air should be presented in order to assess the potential of the VUV-source properly.”

Author response: We chose to focus on an unheated I-CIMS for this work as this is

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probably the most common CIMS method used in the community. The PAN detection by TD-CIMS is more specialized, involves a heated inlet, and is not as widely used. The mass spectrum with the VUV source in configuration (a) does have an obvious background at 59 amu as well as other masses. We showed this mass spectrum to demonstrate the issue of stray photoelectrons which would impact many measurements. We also showed simple solutions to minimize this issue. We have added a mass spectrum to the SI (Figure S3) to show that PAN can be detected with TD-CIMS using a VUV-IS. We have also a short section in the results to report the quick tests requested by the reviewer.

Referee comment: “L23 How does deploying the instrument in the field for a month demonstrate reliability? Section 3.4 and Fig 7 do not really help convince (beyond simply stating that it was operated continuously for a month) that the VUV source can be operated under field conditions. The data (HC(O)OH measurements) are not discussed in terms of their quality or compared to other measurements. Did the primary ion-current (lamp output) change over one month of operation? What does the manufacturer state concerning the operational lifetime (in hours) of the PKS 106?”

Author response: Running the CIMS with a lamp for a month in a remote location does demonstrate reliability but we agree it doesn't demonstrate the quality of the measurement. Our primary goal for this CIMS during the OPECE campaign was to measure halogen containing compounds. However, we found the presence of halogens to be intermittent so we chose to show the formic acid data. Formic acid is routinely measured by I- CIMS and is ubiquitous in the atmosphere as both an emission and a secondary chemical product. So the formic data offers a way to show the CIMS with a lamp could be operated continuously for an extended period. This was one of our major concerns going into the field campaign as we were deploying in an unheated shelter in a remote location in a bird sanctuary in the Yellow River Delta with intermittent power issues. For this reason, we have provided more details of the physical setup and describe the temperature variance experienced by the CIMS.

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In order to address the data quality question, we have added a figure with representative observations of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> for this site when halogens were observed (Figure 6). This figure is consistent with expected behavior of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> as they accumulate during night time and decay after sunrise. This indicates the performance of the CIMS is reasonable.

The lifetime of this lamp is claimed to be 4000 hours (~5.5 months) by the manufacturer, and we did not observe an obvious degradation of CIMS sensitivity. The CIMS sensitivity to formic acid was measured to be  $185.2 \pm 48.3$  Hz pptv<sup>-1</sup> during the first 24 hours, and  $180.5 \pm 24.3$  Hz pptv<sup>-1</sup> during the last 24 hours of the mission. So we did not observe any drop in sensitivity that could be attributed to a decrease in light intensity from the lamp. We have reported the starting and ending sensitivity in the results section.

Referee comment: “L26 The spectrum in ambient air was cleaner. This could mean that the VUV source does not detect everything the Po210 source does. Alternatively, it could imply that the primary ion spectrum is less complex. Please clarify. Again, it would be nice to see a comparison of the primary ion spectra in zero air, at least in the supplement.”

Author response: Both the VUV and polonium sources produce similar amounts of I- as well as other ions. So it is hard to understand why the VUV source does not detect everything in the same manner as the polonium source. They both utilize reactions of I-. We can certainly obtain a mass spectra in zero air, although we note that most complications with CIMS come from the presence of ozone and water, but we have trouble accessing our laboratory at this time due to COVID.

Referee comment: “L34 . . . used to detect many atmospheric trace gases. . . . But then only BrO and PAN are named. Why not simply list what classes of trace gases have been measured (organic, halogen, nitrates etc)?”

Author response: We have modified the texts as suggested.

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Referee comment: “L43 “little” = “few”?”

Author response: We have modified the texts as suggested.

Referee comment: “L60 . . .which can be attached by CH3I. . . = which can attach to CH3I. . .?”

Author response: We have modified the texts as suggested.

Referee comment: “L78/80 Benzene has a larger cross-section (than CH3I). Please quote the cross-sections (and wavelengths) for benzene and CH3I here as well as the ionisation potentials (or refer to a section where they are listed/tabulated)”

Author response: This values was quoted in line 65.

Referee comment: “L103 Some details pertaining to the detection of Cl2 (a reference to the instrument, total uncertainty, cross-section used etc) would be appropriate here.”

Author response: We have provided more detailed information and reference in the text.

Referee comment: “L110 Was the DC power supply a commercial one (also from Heraeus?)”

Author response: We have added the model and manufacturer.

Referee comment: “L134 The terms IMR and flow-tube (eg. In Fig.1) are used interchangeably. Please stick to one. As it is not strictly a “flow-tube” Ion Molecule Reactor might be the better choice.”

Author response: The terms of IMR is more commonly used when talking about Aerodyne TOF-CIMS, and “flow tube” are more commonly used when talking about quadrupole CIMS, so we prefer to stick to the convention to avoid confusion to readers.

Referee comment: “L144 What is special about the photoelectrons generated on the metal surfaces. Explain why they are a problem? (Presumably because they can attach

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to O<sub>2</sub> in this part of the instrument). On the other hand, could metal surfaces in N<sub>2</sub> / CH<sub>3</sub>I gas provide a useful source of photo-electrons upstream of the IMR?”

Author response: The photoelectrons generated in the flow tube are exposed to O<sub>2</sub> which electron attaches to make O<sub>2</sub><sup>-</sup> and leads to a series of interfering masses. Our preliminary tests shows that using metal surfaces can produce only about 1% I<sup>-</sup> of that achieved with using a gas phase absorber (CH<sub>3</sub>I or C<sub>6</sub>H<sub>6</sub>).

Referee comment: “Section 3, Results. The first paragraph in the results section summarises all of the results and introduces all of the Figures from the laboratory tests. As the same conclusions are made in the individual sections that follow (but with the underlying data to support them) this paragraph is redundant. I suggest it can be removed and integrated with the conclusions.”

Author response:

Good comment – We have moved this to the end of the paper and used as the first paragraph of a summary and conclusion section.

Referee comment: “L158 Are the mixing ratios of CH<sub>3</sub>I those in the ion-source-flow or in the IMR (after dilution)? Please make this clear throughout the manuscript.”

Author response: All the mixing ratios of CH<sub>3</sub>I and benzene in the manuscripts are those in the ion source flow. We mentioned this in line 151 for TOF-CIMS and line 159, 201 for Q-CIMS. We have also clarified it in line 144.

Referee comment: “L199 I’m surprised that the authors did not add SF<sub>6</sub> to test the potential of extension to the use of the VUV-IS. This would have been a very simple experiment. I would encourage the authors to do this “10 minute experiment” and add the qualitative observation (formation of SF<sub>6</sub><sup>-</sup> ?) to this manuscript.”

Author response: We are working on using SF<sub>6</sub><sup>-</sup> with the lamp. This is really not a “10 minute experiment”, because SF<sub>6</sub>-chemistry is more complicated than I<sup>-</sup> chemistry. E.g. its reaction with water vapor and O<sub>3</sub> are troublesome to both its selectivity and

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stability, so we have to minimize the reaction time and number density in the flow tube. So we don't have extensive or conclusive results at this time. We have added a figure (S4) that shows preliminary measurements of formic and acetic acid using an SF<sub>6</sub>-during test flights.

Referee comment: "Are other lamps available (different noble gases and emission energies) to extend the use of photo-ionisation sources to generate other primary ions for CIMS. Or, put another why, why choose a Krypton line?"

Author response: Photoionization detector lamps (PID) are available with a variety of gas fills including argon, krypton and xenon gas. However xenon's photon energy (9.6 eV) is lower than krypton (10 and 10.6 eV). The argon lamp has a higher photo energy (11.8 eV) but it also lithium fluoride (LiF) as a window material which is hygroscopic. The krypton lamp uses a magnesium Fluoride (MgF<sub>2</sub>) window which is less hygroscopic.

Referee comment: "L200 "electron attaching compounds" = trace gases with large electron affinities?"

Author response: Electron attaching compound are molecules like O<sub>2</sub>, SF<sub>6</sub>, CH<sub>3</sub>I that attach electrons to make species such as O<sub>2</sub><sup>-</sup>, SF<sub>6</sub><sup>-</sup>, I<sup>-</sup>. However, SF<sub>6</sub> and O<sub>2</sub> don't have particularly large electron affinities and the electron affinity of CH<sub>3</sub>I is a more difficult concept as it dissociative attaches to form I<sup>-</sup>, so we prefer electron attaching compounds,

Referee comment: "Section 3.4 I'm not sure what this section seeks to achieve. The information that the lamp can be used for 18 months without degradation of the signal is important but was not gleaned from a 1 month campaign and is lost in this section. I suggest adding this information to the methods section, perhaps with manufactures data about the lifetime of the lamp. Also "no obvious degradation of signal" could be presented in a more quantitative manner. What "signal" is referred to here? What information (Fig. 7) do the J-NO<sub>2</sub> values convey? Seeing that there is no discussion of

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the data, the J-values simply delineate night and day. But what does that tell us? Why were HC(O)OH mixing ratios chosen to illustrate that the ion-source worked? Was nothing else measured? Why do the formic acid mixing ratios maximise at nighttime (expected?). I recommend removing this section completely unless significantly more use is made of the field data (a comparison with another instrument would e.g. have been useful).”

Author response: We have been using the same VUV-IS since the OPECE field mission (Spring 2018) till 2020 for both lab studies and field measurements, and we have not found significant degradation of CIMS sensitivity. As mentioned before, the krypton lamp’s lifetime is expected to ~5.5 month of continuous use

Yes the JNO<sub>2</sub> is to simply delineate night and day. As mentioned above, Figure 7 is to show that the VUV-IS was operated continuously for a month. We are choosing formic acid because it is ubiquitous and easy to measure and calibrate. We are not claiming anything about the quality of the formic acid measurements. As discussed before, we also presented our measurements on ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> as a support of our data quality (Figure 6).

Referee comment: “Section 4. The “discussion” is weak. I suggest taking this text and combining it with the (weak) “conclusions” text to generate a section “discussion of results and conclusions” or something like that.”

Author response: We have modified the text by moving the intro paragraph to an end summary and conclusion sections. We also feel that we have made a strong conclusion – The VUV lamp can eliminate the use of radioactivity for CIMS.

Referee comment: “L255 Extend the conclusions by taking the first paragraph of text from the results section.”

Author response: We have moved the summary paragraph to the conclusion and make it a “summary and conclusion section”.

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Referee comment: “Fig 4 (1) and (3). It would be good to add the ions to the figures. The  $\text{HNO}_3\text{I}^-$  ion at 1190 amu is the main difference between the Po210 and VUV ion sources and this would be nicely highlighted if the ion-peaks were labelled. In this context, what is the ion at  $m/z$  144 amu (next to  $\text{I-H}_2\text{O}$ )? and at  $m/z$  170 amu?”

Author response: We have added labels to the larger signal ions in the spectra. Please refer to Figure 5 and 8 above. There is no peak at 144 but there is a peak at 143 amu that corresponds to  $\text{IO}^-$ . The peak at  $\sim 170$  corresponds to  $\text{HCOOH}\cdot\text{I}^-$  at  $m/z$  173.

Referee comment: “SI: The cross-section of  $\text{CH}_3\text{I}$  is  $\times 10^{-17}$  (not  $\times 10^{-17}$ ). Give a citation for the cross-section.”

Author response: We have modified the texts as suggested.

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