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Discussions

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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.

Anonymous Referee #2

Received and published: 13 February 2020

Ji et al present experimental data pertaining to the characterisation and deployment of a VUV ion-source using a commercially available photo-ionisation lamp that provides a viable alternative to use of polonium in an I-CIMS, at least for some trace-gases.

The VUV source appears to provide sensitivities for detection of HC(O)OH, ClNO2 and Cl2 that are comparable to those achieved with Po210, but without the logistic disadvantages related to deployment of radioactive sources in field measurements. A further advantage is that, unlike Po210, the VUV source does not generate HNO3.

The manuscript is short and to the point, which is fine; but its organisation could be substantially improved and there are many minor errors/omissions that need attention.

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Discussion paper

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.

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?

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.

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 etc)?

L43 "little" = "few" ?

L60 . . .which can be attached by CH3I. . . = which can attach to CH3I. . ..?

L61 "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)

L78/80 The acronyms Q-CIMS and I- -CIMS appear to be used randomly. In Fig. 1 the term I–Q-CIMS is also used. Please unify throughout the manuscript.

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

L110 Was the DC power supply a commercial one (also from Heraeus ?)

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.

L144 What is special about the photoelectrons generated on the metal surfaces. Explain why they are a problem ? (Presumably because they can attach to O2 in this part of the instrument). On the other hand, could metal surfaces in N2 / CH3I gas provide a useful source of photo-electrons upstream of the IMR ?

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.

L158 Are the mixing ratios of CH3I those in the ion-source-flow or in the IMR (after dilution) ? Please make this clear throughout the manuscript.

L199 I'm surprised that the authors did not add SF6 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 SF6- ?) to this manuscript. 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 ?

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

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-NO2 values convey? Seeing that there is no discussion of the data, th 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).

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.

L255 Extend the conclusions by taking the first paragraph of text from the results section.

Fig 4 (1) and (3) It would be good to add the ions to the figures. The HNO3I- 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 $\sim$ 144 amu (next to I-H2O)? and at $\sim$ 170 amu ?

SI: The cross-section of CH3I is x 10-17 (not e17). Give a citation for the cross-section.