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Atmospheric Measurement Techniques Discussions

Interactive comment on "Coupling a gas chromatograph simultaneously to a flame ionization detector and chemical ionization mass spectrometer for isomer-resolved measurements of particle-phase organic compounds" *by* Chenyang Bi et al.

Anonymous Referee #2

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Review of Bi et al., "Coupling a gas chromatograph simultaneously to a flame ionization detector and chemical ionization mass spectrometer for isomer-resolved measurements of particle-phase organic compounds"

Summary:

The authors describe a new instrument configuration using a TAG column upstream of both an FID and a ToF-CIMS. The goal was to address several current measurement

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issues by 1) using the GC to separate isomers in the CIMS spectrum, and 2) using the FID as a means of quantifying unknown compounds in the CIMS spectrum. They also show the simultaneous use of I- and O2- as reagent ions, with the goal of expanding CIMS sensitivity to generally less oxidized compounds. Generally, this is an interesting and well written paper that attempts to address several of the critical issues with CIMS spectrum interpretation of ambient or complex data. Separation of isomers seems be useful (at least for compounds that can make it through a GC column, which will be a subset of what I- usually can measure). This technique may well be very useful (especially for simplified systems), however I don't think the authors have fully illustrated this yet. I have a major issue with some of the methods and interpretations thereof that require major revisions. Mainly, the data shown for iodide ionization shows that the ionization process is different than in typical iodide ionization CIMS setups (at least for some compounds including vanillin). This will diminish the ability to use this instrument to guide interpretation of other typical iodide CIMS measurements. I believe the authors need to address this issue (likely by showing more measurements) before making some of the conclusions drawn here. I also have questions about decomposition, and the utility of interpreting multiple reagent ion spectra.

Main comments:

Line 112: Is there a risk of decomposition of organic analyte molecules at this 225C temperature in the IMR, especially on metal surfaces? I would also be worried about fragmentation at the 300C temps upstream. Previous FIGAERO CIMS research has suggested decomposition of oligomers and/or highly functionalized molecules when heating at even lower temperatures than 300C. Please add some references to this previously observed issue, and also add some discussion somewhere in the manuscript of how decomposition would affect your measurements.

Line 211: Related to my previous comment, how much of these early eluting compounds might be fragmentation products as an artifact of the sampling technique?

Fig 4: Regarding decomposition again, one way to investigate would be to show the FID signal for Fig 4 and maybe for more examples where you are injecting single known compounds. How much signal is in the FID but not the CIMS, i.e., how much fragmentation occurs throughout the sampling process? I think this would be important information for a reader to judge the utility of the technique.

Line 297: This inset in Fig 4a indicates a major issue. In a typical iodide CIMS setup, vanillin would be sampled almost completely at the [M+I]- cluster with iodide, but you're showing that in your instrument it is predominantly sampled at the deprotonated [M-H]-. Therefore, the ionization process is different from a normal iodide CIMS. I think this is a major problem that you need to address before publishing under the pretext that your instrument can be used to help generally interpret iodide CIMS measurements. The most likely answer that I see could be that holding the IMR at 225C is causing the changes? Perhaps at those temperatures (and with metal surfaces?), vanillin becomes a gas phase acid and C8H8O3 + I- –> C8H7O3- + HI proceeds? At line 300, you try to address the [M-H]- by stating that vanillin "produces a large number of detectable ions through reactions with other reagents in the IMR." But, there are no other reagent ions there (except NO2- maybe, but that is often present in typical iodide CIMS spectra and is therefore not the cause), so this statement is probably not accurate. So, please address this issue thoroughly. A first step could be to do the same vanillin injection but hold the IMR at room temp. The vanillin signal may smear, but does is show up at [M+I]-? Again, this seems like a major issue since you're trying to say (eg lines 372-374) that you can use this method to investigate non-iodide clusters separated by the 'iodide valley', but you're apparently also drastically changing the ionization method.

Line 303: Interesting that the lower volatility compounds or more polar compounds appear to have different ionization processes relative to the more volatile or less polar compounds like vanillin. Since one of the advantages of I- ionization has been a more consistent (and single) ionization process for the majority of compounds, do you have any thoughts on how this affects interpretation of the spectra?

Line 318: Since you're seeing the deprotonated ions using both ionization methods (just I-, and both I- and O2-), it seems like it would be really hard to convert the signal in multiple reagent ion mode to mixing ratios as the sum of two ionization processes with variable sensitivities. Especially this would be hard if you have are sampling a complex mixture. It makes me wonder if it's feasible to use both reagent ions at the same time, or if you should instead use them one at a time in series. No doubt that O2- ionization gives you a lot of extra information about the less oxidized/polar compounds that I- can't see. Please discuss this to give the reader confidence that using two reagent ions simultaneously is actually a practical scientific improvement. Best would be to show a quantitative example of a calibration curve using both reagents, but possibly this will be the subject of a future manuscript.

Technical comments:

Fig. 3 Caption: extra 's' after SOA

Line 324: This sentence just needs some clarification. You're either adding zero air to the ionizer alongside methyl iodide, or adding O2- to the ionization region (aka IMR) alongside iodide. Also "ionization region" is ambiguous because that could be the ionizer or the IMR.

Line 326: This was confusing to me because you list the numbers with multi-reagent ion first and iodide second, right after referring to Figs. 4b (iodide) and 4d (multi) in the reversed order. Please reverse the order of listing the numbers in order to stay consistent with the Fig.

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