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Atmospheric
Measurement
Techniques
Discussions

Interactive comment on "Atmospheric trace gas measurements using ion mobility spectrometer" *by* A.-K. Viitanen et al.

Anonymous Referee #1

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In this paper, the authors present an Ion Mobility Spectrometer as an instrument for in situ measurement of trace gases. However, they do not state which trace gases they measure, nor do they describe any novel or new instrument components. There is no quantification, merely a time series of unidentified peaks. I cannot recommend this paper for publication. Overall, the authors have not demonstrated any new insight, development of any new component, or analysis of any data that provides scientifically credible information. I have several serious qualms with this paper, which can be divided into (a) Lack of any science, technological development or insight, (b) Extremely poor writing, and (c) A lack of understanding of the physical principles involved in the instrument described.

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In more detail: (a) Lack of new development. According to the AMT website, "the main subject areas [of the journal] comprise the development, intercomparison and validation of measurement instruments and techniques of data processing and information retrieval for gases, aerosols, and clouds". This paper does not fit within the scope of the journal as it does not describe any new development (ion mobility spectrometers as used in this paper have been previously described), no intercomparison (as the authors seem to be unsure as to the identity of molecules detected by the instrument, they were unable to provide any intercomparison), and no validation of the instrument (no calibrations were performed, no proof provided that the instrument could provide any quantitative or qualitative data of any form).

There are additional items of concern under this heading.

First, as described, the instrument provided no usable information: peaks were observed in the ion mobility spectrometer, but no serious attempt was made to identify them. The authors claim that one peak might be amines and ammonia, but did not run standards to confirm this and provide no convincing evidence for the claim. The system requires calibrations, which were apparently not done. The remaining peaks are vaguely speculated upon, but not identified. The fact that no correlations between the peaks and other environmental variables is worrisome - it implies that the peaks were not representative of either short-lived or long-lived components at the site. Many VOCs are measured at the SMEAR-II station - I am surprised the authors made no attempt to use the vast data from the site to provide insight on their observations.

Second, with regards to the motivation for the instrument: I fundamentally disagree with the premise of the paper that "the main disadvantage of [mass spectrometry is] the need for vacuum". As the authors point out, PTR-MS, CIMS, and GC-MS have all been used in the field for atmospheric chemistry measurements with great success. Further, most other state-of-the-art atmospheric chemistry measurements use vacuum (LIF for measurements of OH or NO2, for example). In fact, almost every form of atmospheric chemistry instrumentation, with perhaps the exception of long-path DOAS

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require air samples to be pulled into the instrument, thus requiring some form of pump. Not to mention that PTR-MS, CIMS and GC-MS have all provided useful data about compounds in the atmosphere, unlike this study. The authors need to find a better reason for their study.

The only compounds the authors identified were amines and ammonia, which were not quantitatively observed. As this result has been observed in previous work (papers that are cited in this manuscript), I see no evidence of new information. This is not the first use of IMS in atmospheric chemistry field measurements. What makes this study unique from the others, warranting a 'techniques' paper in AMT? The authors state "In this study the ion mobility spectrometer (IMS) is implemented for direct atmospheric sampling on site in order to find out the potential of this technique for current measurement requirements in atmospheric studies". Not only does this sense make no sense in English, it also provides no justification for the publishing of this paper.

(b) Extremely poor writing and use of the English language. I highly recommend that the authors use a professional editing service to correct and proofread the paper. Many sentences are so grammatically incorrect as to render them unintelligible to the native English speaker.

(c) A lack of understanding of the physical principles involved in the instrument described

I am concerned by an apparent lack of understanding by the authors on how the instrument works. This may, however, be a result of poor use of the English language. For example, how is O+(H2O)n 'protonated'? Either the term 'protonated' is used incorrectly, or the ion is identified incorrectly! Protonation typically refers to the addition of an H+ or H3O+ ion. In this case, the authors have written that the ionizing agent is a positively charged oxygen atom clustered with H2O molecules. If the oxygen atom is positively charged, that is the result of a loss in one electron, not the gain in a proton (which would change the chemical identity of oxygen!).

Further, on p. 4963, l.15: the authors describe the comparison between the proton affinity of water vs. other compounds. This suggests that water is used as an ionizing agent. This is not at all what is suggested in the instrument description, suggesting that the instrument description is poorly written (it just maintains the use of a radioactive source, but it appears that this source ionizes a reagent ion - in this case H2O?) If O+(H2O)n is indeed the ionizer, then the proton affinity of water is not the important component to compare! The charge lies on the oxygen, and the transfer of an electron (and thus ionization) would depend on differences in electron affinity of the analytes compared to that of oxygen atoms.

Similarly, how is the O2-(H2O)n formed? I am confused. This suggests that O2 molecules are ionized, and then form clusters with water? I suspect that the authors have confused (or poorly described) the ionization scheme. Again, if O2- is the charged component of the ionizer, than proton affinity is not the appropriate physical property to use for peak prediction.

Overall, the authors need to explain what causes differential mobility of ions in the instrument (i.e., why do they separate? what is the physical principle behind the instrument?).

The authors state that observations of natural sulphate-based ions and reduced nitrogen compounds in small particles "support [their] hypothesis". I fail to understand a) what scientific hypothesis the authors are proposing, and b) how the observation of ions in the atmosphere supports this observation? As I understand the instrument, the authors are measuring gas-phase molecules that are ionized in the instrument, not ions.

Lastly, differences between the two instruments are attributed to "data processing". This is worrisome: were the two systems analyzed differently, resulting in different peaks, different trends, and/or different signal intensities? The authors need to explain their statement.

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Details. pg. 4963, l. 7: the code "recorded"? Or did it calculate? There is a large difference between the two terms.

- comparison to APi-TOF was completely inappropriate and seemed like a shameless attempt to add citations to another paper: that instrument directly measured ions in the atmosphere, not reactive trace gases.

- what is the resolution of the instrument? (i.e., what is the minimum difference in reduced mobility for two adjacent ions that the instrument can separate?) Namely, on p.4965, the authors write that the instrument cannot separate 2.02 and 2.12 cm2/V/s for acetaldehyde and formaldehyde.

- p.4964, l.4: the authors claim to calculate the mass of the ion based on mobility calculated from the peak "based on Kilpatrick's old data (Makela et al. 1996)". There are multiple problems of this: why isn't Kilpatrick cited for the use of his/her data? Why "old data"? (This implies there is new data instead, so the use of old data should be justified).

- citations are not entirely correct (e.g.pp.4960, l.19 should read "...the station can be found in Hari and Kulmala (2005)."

- Figure 3 is unnecessary

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 4957, 2011.