

Interactive comment on “Aerosol mass spectrometry: particle–vaporizer interactions and their consequences for the measurements” by F. Drewnick et al.

Anonymous Referee #2

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The paper by Drewnick et al. presents laboratory data for a number of particle types analyzed by several Aerodyne Aerosol Mass Spectrometers (AMS). These instruments are used by many groups, sometimes without fully appreciating the complexities of the detection process. The authors should be commended for conducting and documenting this interesting set of experiments that will serve as an excellent reference for AMS practitioners. The paper contains new data on AMS measurements of several semi-refractory species and is of high interest for the audience of AMTD and generally well written. However in places it is not completely clear. I recommend that the paper is accepted into AMTD after the issues listed below are addressed.

Abstract

1) Line 6: suggest changing "various ambient aerosol components" to "various non-refractory ambient aerosol components"

2) Line 6-8: I assume that the authors are referring to the assignment of metal species to organic in the default analysis procedure when they say that results can be "misinterpreted". To my knowledge, this issue should only affect unit mass resolution analyses, and not high-resolution analyses. Moreover, since the metal species have unique ions and isotope patterns that do not resemble typical AMS organic spectra observed in ambient environments they can be readily distinguished and identified with additional analysis even in unit mass resolution.

I suggest changing the last sentence to clarify this as follows: " However, when measuring close to certain anthropogenic and marine sources of semi-refractory aerosol particles, several of these assumptions may not be met and unit-mass resolution spectra should be carefully analyzed for unique ions and isotope patterns associated with semi-refractory species."

3) Line 16: as discussed below, the differences in evaporation kinetics can lead to higher noise, but not to biases in ion ratios.

4) Line 26: clarify that the biases are due to semi-refractory species by changing the sentence as follows:

" while laboratory experiments and measurements and measurements close to anthropogenic or marine sources of semi-refractory aerosol can be biased by these effects".

A quantitative description of the magnitude of the effects studied would be useful.

Introduction

5) p. 3528, Line 2: The assumptions are not "hard-coded", they are user editable and users in fact are required to edit several entries for quantitative results with a specific

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instrument. Users are also strongly encouraged and responsible for adapting the fragile framework for their purposes and specific species studied, which the software interface makes easy to do. I suggest replacing with “hard-coded” with “user-editable,” and potentially explaining what the possibilities and responsibilities of users in a little more detail.

6) p. 3528, Line 3: Huffman et al. (ACP 2009) also report the increase of the background (“closed”) concentrations as a fraction of the difference concentrations, for both ambient sampling and when sampling through a thermal denuder, for two different field studies. See Figures 4 & 8 on that paper.

7) p. 3528, Line 28. The text “For less volatile or very “sticky” species” can be confusing, since it is not clear what the volatility of the species is, relative to non-refractory species. For example, sulfate is non-volatile from an atmospheric point of view, but is still non-refractory for AMS detection purposes. It would be better to say “For semi-refractory species” which is clearer in the context of the AMS.

Measurement Setup

8) The time resolution at which the measurements were averaged and saved (in MS mode) should be described, since this may affect the interpretation of the fastest transitions observed (if the averaging time is longer than the timescale of the transition). Recent versions of the ToF-AMS acquisition software (since ~2009 or so) allow acquiring data with time resolution of 1 second (Kimmel et al., 2011).

9) The data analysis software used and any relevant adjustments and settings should be described.

10) p. 3530, Line 23: it should be specified whether V or W mode was used for the HR-ToF-AMS measurements.

11) p.3530, Line 29: how was the vaporizer temperature determined? The thermocouple on the vaporizer is known to not be very accurate, and this temperature has an

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important influence on the results discussed in the paper. Due to the known limitations of the thermocouple measurement, a procedure has been developed by Aerodyne for more accurate setting of this parameter, see:

http://cires.colorado.edu/jimenez-group/UsrMtg/UsrMtg13/AMSUsersMtg_2012_VapT.pdf

Was that procedure or a similar method used for the work reported here?

Also a range of 50 degrees C can make a difference for some experiments. The authors should make sure that the vaporizer temperature is given for each one of the experiments for which they report results.

Particle Vaporization Kinetics

12) p. 3531, Line 12: Fig. 2 is similar to Fig. 6 of Jayne et al. (2000), suggest citing that paper here.

13) p. 3531, Lines 18-20: a reference should be given for these reactions. If they are speculative, this should be noted.

14) The meaning of the vertical arrows in the first reaction should be explained. Does this mean that the species evaporate? Then that would mean that the second reaction happens in the gas-phase, but it is not plausible for 4 HNO₃ molecules to collide in the gas-phase and react in this way. This also relates to the text on Lines 23-24 that seems to assume gas-phase reactions.

The third reaction should be written as $2 \text{NO}_2 \leftrightarrow 2 \text{NO} + \text{O}_2$.

15) p. 3531 Line 16-26: this section reads as if gas-phase reactions were most important. However hot tungsten is known to be a good catalyst: for example a search for “tungsten catalyst*” returns almost 2000 records in Google Scholar, most of which appear to concern organic reactions. The potential for reactions on the tungsten surface should be acknowledged in this section and throughout the manuscript.

16) Page 3532, Line 1: The authors mention several of the processes that can give rise

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to signal during the AMS vaporization process, but they do not provide a summary of these processes in one place. For example, at the start of section 3 (just before section 3.1) the authors could have a summary paragraph in which they clearly state the main processes that likely contribute to AMS particle vaporization kinetics including:

a) Fast flash vaporization of aerosol species of interest off the AMS vaporizer b) Slow thermal decomposition of species of interest on the AMS vaporizer c) Condensation of flash vaporized species and/or decomposition products on cooler surfaces such as the ionizer surfaces on which they may undergo subsequent slower desorption and further thermal decomposition. d) Particle bounce off the AMS vaporizer followed by slow vaporization/decomposition of bounced particles from cooler ionizer surfaces (or occasionally the filament surface which is hotter).

The authors refer to a - c in the discussion but they surprisingly do not mention the contribution of particle bounce (d) at all. Previous work has shown that particle bounce does not significantly affect the vaporization process of NH_4NO_3 (Cross et al. 2009), but it is expected to affect all the aerosol particles measured in this work including $(\text{NH}_4)_2\text{SO}_4$ (Middlebrook et al. 2012) and the other solid semi-refractory aerosols (Matthew et al. 2008). The bounced fractions for some of these species may be quite high, comparable with $\sim 70\%$ for PSLs. Thus, it is important the authors should explicitly consider and mention the possible role of particle bounce in the various observations.

17) Page 3532, Line 1: It would be useful along with statements in comment 16 above for the authors to summarize the timescales with which the different measurement modes provide information about vaporization. For example, the single particle measurements take place on timescales of tens of microseconds and average PToF measurements are on timescales of milliseconds. MS open/closed measurements, on the other hand, are typically on timescales of seconds and most likely to reflect the all the vaporization processes mentioned in comment 16.

18) p. 3532, Line 5-7: The authors are suggesting that NO is the slowest vaporizing

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component because it does not decompose and it slowly adsorbs and desorbs off the ionization surface. While this is certainly one possible scenario, another likely scenario is that the vaporized HNO₃, which is stickier than NO, adsorbs onto the cooler ionization surface and undergoes extensive slow decomposition that gives rise to the slow NO signal. This should at least be mentioned as another possibility.

It should also be noted that some form of surface chemistry must be involved, as otherwise the NO⁺ signal would be expected to decay the fastest if it was present on the gas-phase (or was the product of gas-phase reactions of the other faster-decaying species), due to its higher thermal speed.

19) p. 3532, Line 8: Please state at the beginning of this paragraph that the discussion deals with measurements of single particle vaporization events at different ion extraction frequencies. Also mention in this discussion that while faster extraction frequencies would provide a more precise measurement of any given single particle, the choice of extraction frequencies is often limited by the m/z range that is needed for the MS measurements. When slow extraction frequencies that are on the order of vaporization timescales are used, accurate measurements of the average single particle can still be obtained with sufficient particle counting statistics. For ensemble aerosol measurements, the S/N decreases at slower extraction frequencies, but the accuracy of the measurements are not affected if they are referenced to NO₃ calibrations performed under (or scaled to) the same extraction conditions.

20) p.3532 Line 17-18: the statement on the change of the fragmentation pattern of ammonium nitrate as the pulser frequency changes is incorrect. Lower pulser frequencies will result in noisier fragmentation patterns on a particle by particle basis, but since the arrival of the particles is uncorrelated with the pulsing times, ratios of averages using PToF or MS modes will still be correct and not change with the pulsing frequency. If the authors have data that suggests differently, it should be presented here, or otherwise this statement should be removed.

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21) It should be mentioned that a possible reason to observe an artificial change in fragmentation patterns would be if the ion-detection threshold is not set properly, as in that case the weaker signals would be discriminated against (Hings et al., 2007). Also in Brute Force Single Particle mode there could be an artificial bias depending on the threshold settings for single particle detection. The latter error should not affect averaging modes such as MS and PToF.

22) p. 3532, Line 21: It is important to recommend that since the AMS reports mass concentrations measured in MS mode, the IPP measured from single particle measurements should be checked against ionization efficiencies measured by comparing ensemble MS and CPC measurements before it is used in mass concentration calculations. Also it is standard practice to determine RIE_{NH4} using the measured NH₄/NO₃ ratio in MS mode, rather than using the single particle measurements.

23) p. 3533, Line 1-4: Why do these reactions not include HSO₃⁺ which is the source of m/z 81?

Also, as for NH₄NO₃ and based on the same arguments, the longer evaporation timescales for SO₃⁺ and SO₂⁺ relative to the larger sulfate fragments indicate that surface chemistry is important for the smaller fragments. This needs to be mentioned.

It is also of interest to note that NH₄ fragments desorb more slowly from ammonium sulfate than ammonium nitrate, and as fast as the fastest anion fragments.

24) p. 3533, Line 8-10: again this statement is incorrect, fragmentation patterns will not change with the pulser frequency.”

25) p. 3533, Line 25-28: How are the vaporizer temperatures determined- are they the temperature readouts from the AMS vaporizer thermocouple? Was a NaNO₃ temperature calibration performed before these experiments?

26) Same section: a recent paper (Docherty et al., 2015) reports results when an AMS was operated in a field study with varying temperature of the vaporizer. The results of

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that paper appear to be consistent with those of the present one, and we suggest that this is mentioned here.

27) p. 3533, last paragraph: the procedure for setting the temperature of the AMS vaporizer is based on this principle of measuring the size distribution width for NaNO_3 , and that could be mentioned here.

28) p. 3534 Line 9: as mentioned earlier a similar report was given by Huffman et al. (2009).

29) p. 3534, Line 10-12: Why was 17 min chosen as opposed to other timescales? It would be useful to point out that this operating condition is way outside the typical AMS operating mode of switching between open and closed modes on the order of 5 seconds. Also, what were the mass concentrations that were used? In the figures these concentrations are quite high (again atypical compared to typical operation). Mass concentrations would likely affect observed timescales as well, with higher concentrations possibly resulting in longer timescales, as an insulating layer might be built up on the vaporizer by the accumulated particle mass. This should be discussed.

30) p. 3534, Line 12. I don't understand why 5 seconds is the best possible time resolution. Measurements can be obtained with 1 second time resolution in Fast MS mode (Kimmel et al., 2011), and the AMS is capable of 10 Hz measurements in Eddy correlation mode (Farmer et al., 2011). Perhaps it was the best time resolution at the time the experiments were done, but if so this qualifier should be added.

31) p. 3534, Line 13-17: Why is the NH_4NO_3 signal increasing in the first two open time periods? Is this due to source variability? Are the signals normalized to the input particle concentration?

32) p. 3534, 2nd paragraph: it is unclear what signal is shown, open, closed, diff, or total. It would seem that the total signal is shown, but this should be clarified. This should also be clarified for Figure 4, and perhaps elsewhere.

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33) p. 3534, Line 19: The background value of H₂O is always high in the AMS, due to the particular vacuum technology used. How does the closed signal that is measured during these experiments compare to typical background H₂O in this instrument? (before the experiments started). Otherwise the background H₂O is not particularly meaningful for this discussion.

Also was the increase in H₂O signal when sampling nitrate due to particle-phase H₂O (particles were not dried)? Or was it due to gas-phase H₂O if the particles were dried?

34) p. 3535, Line 18-22: Since the mechanisms of decomposition are different between the two (as KNO₃ cannot make HNO₃), it is not clear how the NH₄NO₃ observations are necessarily related to KNO₃ measurements.

35) p. 3535 Line 23 to P.3536 Line 7: the slower behavior of SO⁺ and SO₂⁺ again suggests that the vaporizer surface plays a larger role for generating those fragments. Alternatively, could the slower fraction of those signals be dominated by particles that bounced and deposited into surfaces colder than the vaporizer?

36) p. 3536, line 14-16: It is not clear that SO₂ will stick more efficiently to the ionizer walls than H₂SO₄. It seems more likely that gas phase H₂SO₄ that is flash vaporized sticks to the ionizer surfaces and then undergoes slower vaporization and increased decomposition at the cooler ionizer surface temperatures. (NH₄)₂SO₄ is also known to undergo bounce. So, slow vaporization from bounced particles should also contribute significantly to the observations. This should be discussed here in the context of the observations.

37) p. 3536, line 22: The time per half cycle that is typically used when performing ambient measurements, for example, should be mentioned somewhere for reference.

38) p. 3536, line 27: The "significant reduction" mentioned in text should be quantified by comparing the PToF and MS measurements for these experiments, if available.

39) p.3537 Line 11, can the authors quantify "not far above." This information would be

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quite useful.

40) p.3537, Line 15: elemental Hg is a gas, and should be removed from this list.

41) p.3537, some of the species mentioned may decompose in the tungsten vaporizer and some decomposition products may partially evaporate be measurable. This possibility should be mentioned.

Also, and as discussed earlier in the paper, the vaporizer temperature can be increased to at least 750-800C, which may allow the measurement of additional species. This should be mentioned as well. (Custom vaporizers to reach higher temperatures have also been demonstrated (Svane et al., 2004)).

42) p. 3538, Line 29: have size distribution measurements been attempted with the fast-vaporizer ZnI₂⁺ fragment that was discussed earlier?

43) p.3539, Line 7: “measured” should be changed to “difference-mode” to clarify that this is a problem with that mode. I.e. when species evaporate slowly, the assumptions that underlie the difference mode are not true, and thus the concentrations reported are wrong (and this is not surprising, it is expected). We suggest explaining this more clearly in this section.

Also, the method of Salcedo et al. (2010) can be used to quantify semi-refractory species by using the open and closed signals directly. We suggest discussing that method here briefly and referring to readers to that publication for further details.

44) p. 3539 L16-19, again it should be noted that this change only concerns the difference mode, but that additional analyses may improve the results.

45) p. 3540, Line 5-7: The NaCl that is being vaporized off ionizer surfaces also likely comes from bounced particles. This should be mentioned.

46) p.3541: the dash should be removed from the Y-axis labels, as it appears to indicate “minus the ratio

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47) Line 3541, Line 6-10: How do you distinguish between slow decomposition and vaporization processes off the oven and slow adsorption/desorption processes off the ionizer surfaces? It is also possible that FeCl₃ sticks to ionizer walls and slowly decomposes at the lower temperatures as opposed to FeCl₂, Fe, and FeCl₂ sticking to ionizer walls and slowly desorbing.

48) p.3541, last paragraph: using the “extended RIE” idea carries the risk that its value will only be valid for the same conditions where it was acquired. The alternative quantification method of Salcedo et al. (2010), that uses both the open and closed signals (rather than only the difference signals) and takes the slow evaporation into account directly, should also be mentioned here.

49) p. 3542, Line 20: It is not clear from Table 2 that there is a relationship between RIE and c/o ratios. The authors should clarify what they mean.

50) p. 3542, Line 26: Since this is the first main discussion of matrix effects involving reaction of two aerosol components with each other on the oven, it would be useful to see an example of the data that the authors are referring to. If the authors prefer not to show the data, I suggest removing the reference to matrix effects after line 26 on this section.

Chemical Reactions on the vaporizer

51) p. 3544 Line 26 and 3545 lines 11-13: the percent increases in the CO₂⁺ signal have no meaning, since they depend on the gas-phase concentration of CO₂ as well as on the particular concentration of particles used in these experiments. We suggest removing these values and instead stating that the increases were clearly measurable. This focuses the discussion on the increase in measured O/C etc., which is the important result here.

52) p. 3545. Line 5-7: It would be useful to have an example of these PToF data as a supplementary figure.

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53) p. 3545. Line 19-21: It would be useful if the authors note here that the increases in O/C that are observed in these studies are very small compared to the increases of interest for atmospheric aerosol particles.

54) p. 3546, line 23: Why does 80 go up with background H₂O if Reaction R5 is shifting towards reactants?

55) p. 3546, line 23-24: Given the fact that the changes are not statistically significant, it seems that a more reasonable conclusion is that carrier gas humidity does not have a strong observable effect on the observed sulfate mass spectra.

56) p. 3546, line 25: Was there evidence of increased collection efficiency for the SO₄ with increased RH? This is expected from Allan et al. and Matthew et al. measurements.

57) p. 3547, Line 1: It would be useful if the authors provided an introductory sentence that specified whether the chemical reactions discussed in this section are observed only for semi-refractory species or both semi-refractory and non-refractory species.

58) p. 3547, line 1-4: Why do you not show the contrast between HR and UMR spectra for these municipal waste incinerator? The non-organic signals should clearly split out from the organic signals in HR.

59) p. 3547, Line 7: It is useful to more clearly point out that even though UMR does not allow for separation of the metals from organics, in practice there are several methods that can be used to identify and confirm the contribution of semi-refractory species to the signals at these m/zs. These include: unusual spectra with signal at m/zs that are not typical for organic species, isotope patterns that can be used to identify the presence of specific elements, and, as discussed in this manuscript, large $\delta^{13}C$ ratios that are characteristic of semi-refractory behaviour.

60) p. 3547, Line 13: Are these effects only observed with semi-refractory chlorides? Are similar observations seen for NH₄Cl? It would be useful to specify the difference if

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possible.

61) p. 3547, Line 15: an indication of the magnitude of the observed effects is needed. Are these WO₂Cl signals 50%, 1%, 0.01% of the main peaks observed for those species? The reactions are interesting, but their impact on atmospheric measurements is limited unless the fractional signal is substantial.

62) p. 3457, consistent with what is reported here, Jimenez et al. (2003) reported the detection of MoO⁺ and MoO₂⁺ when sampling particles containing iodic acids into an AMS, that had an older Mo vaporizer, and attributed them to reactions between particle materials and the vaporizer.

63) p. 3547, Line 17: a reference or other supporting information is needed for the production of WO₃ in the vaporizer, otherwise this seems like a unsupported hypothesis.

What is the source of the O₂ thought to be, given that the WO₂Cl signals are still observed when sampling aerosols under argon? Is it O₂ adsorbed to the vaporizer surface, or from remaining from previous compounds sampled?

64) Is this slow corrosion of the vaporizer a cause of concern in the use of the instrument? Can the authors use the range of RIEs determined here to estimate the mass lost from the vaporizer? If someone was doing these experiments 24/7, would it take a month, a year, or a century to corrode enough vaporizer material to be a concern?

65) p. 3549, Line 1: FeSO₄ is not listed among the sulfates potentially detectable by the AMS in the Table.

66) p. 3549, Line 7-8: what is the magnitude of those signals, relative to the nitrate peaks?

67) p. 3550, Line 15: It is known that vaporizer temperature as well as heater bias and instrument tuning can affect sensitivity to surface ionization. In practice, the heater bias is often tuned while monitoring the K⁺ signal to limit the instrument sensitivity to surface ionization. Was the heater bias adjusted to investigate the efficiency with which

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surface ions were detected?

70) p. 3550, Line 29: Please specify what is meant by "the assumption of the above-mentioned separation of vaporization and surface ionization".

71) p. 3551, Line 13: should it be a decrease on the work function, rather than an increase?

Discussion 72) p. 3551, Line 21-24: As discussed above the ratios of the different ions will not be affected by the pulsing frequency, other than due to an increase of the noise. We suggest restating the last sentence as follows:

73) "Since these vaporization timescales are often on the timescale of extraction pulser periods, single particle measurements and associated IPP values must be obtained with sufficient particle statistics to accurately capture the average single particle vaporization event."

74) p. 3352, Line 1: please quantify "not well above".

75) p. 3552, Line 7: is it possible that for some species size distribution measurements are possible using some m/z and not others? It seems that for many species different fragments exhibit very different timescales, so just because some fragments show a slow evolution it does not mean that all fragments do.

76) p. 3552, Line 10: the alternative quantification method using the open and closed signals (Salcedo et al., 2010) mentioned earlier should be more robust than using the difference signals, and can be mentioned here as an alternative.

77) p. 3352, Line 22: suggest replacing "under general conditions" with "unless an instrument is carefully calibrated with the species and particle mixtures of interest".

78) p. 3553, Line 7: It is important to specify that in environments with large concentrations of semi-refractory aerosol, metal signals can appear at m/z 's that are typically assigned as "organic" in UMR spectra. In cases where HR capability is available the

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metals can be readily separated from organic species. However, even in the absence of HR capability, the existence of peaks at atypical organic m/z s and isotope patterns can be used to recognize this misidentification. Also, large closed to open ratios can be used to confirm semi-refractory behaviour.

79) p. 3553, Line 10-15 and 25-end: here the magnitude of some of the effects are finally quantified. This information would be more useful when those experimental data are being presented, otherwise it is confusing when isolated in this discussion section.

80) p. 3553, Line 20: I suggest deleting the line "chemical reactions of particle components with oxygen or water in the carrier gas or with components from previous experiments which were accumulated on the vaporizer can result in ion signals in the mass spectra which do not reflect components of the measured aerosol" since the data from this experiment does not strongly support it.

81) p. 3554, Line 7: From the results in this manuscript, it looks as though the statement that "the AMS vaporizer does not always behave inertly towards particles" should be qualified to specify "semi-refractory particles" since the experiments do not show this effect strongly or clearly for non-refractory particles. In fact, the long vaporization timescales of the semi-refractory species (as opposed to the shorter timescales of more non-refractory species) likely contribute to the observed lack of inertness.

82) p. 3554, line 15: This line should also include a reference to particle bounce as well as slow decomposition of vapors of cooler ionizer surfaces.

83) p. 3554, Line 15-17, again this refers to the incorrect assumption that pulsing frequency biases the averages of the ion ratios.

84) p. 3554, Line 25-26: While it is possible that the end products of the thermal products can stick with some probability to the ionizer walls, particle bounce and slow decomposition of adsorbed species on the cooler ionizer surfaces are probably more likely to play a role. Since the experiments that have been performed cannot distinguish

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between these mechanisms, they should be mentioned.

85) p. 3555, Line 15: The data does not show any clear influence of carrier gas or humidity on the mass spectra. It is more accurate to say that these effects were investigated and they were not observed to be significant compared to the uncertainties of the measurements.

86) p. 3556, Line 2: is there any evidence that the RIE of the non-refractory species can change due to these “conditioning” effects? That would be quite surprising. Or are the authors referring to the “apparent RIEs” of the semi-refractory species? This should probably be clarified.

87) p. 3556, Line 7: please add "when semi-refractory aerosol species can be significant." at the end of the last sentence.

Minor items, grammar, spelling etc.

p. 3257, Line 9: suggest changing “and with subsequent” to “and in later experiments with”. Otherwise a reader may think that SI and EI happen sequentially in the same experiment.

p. 3528, Line 29: suggest removing the word “mainly.” This depends on the interests of the user. It is true that semi-refractory species can act as contaminants for determining other species, but if the user is interested on them, then that’s not an issue.

p. 3549, Line 18: the word “veritable” seems out of place here.

Figures Figure 2: Please specify vaporizer temperature used for the measurements shown in 2a,2b,and 2c in the caption.

Figure 3: Please include vaporizer information in caption. Why are NH₄⁺ ions not shown? Figure 4: It would be more appropriate to show the trends of individual ions in units of Hz rather than mass concentrations which require knowledge of appropriate RIEs for each ion.

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