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Comment on amt-2021-228

Anonymous Referee #1

Referee comment on "A new method to quantify particulate sodium and potassium salts (nitrate, chloride, and sulfate) by thermal desorption aerosol mass spectrometry" by Yuya Kobayashi and Nobuyuki Takegawa, Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-228-RC1>, 2021

In their manuscript "A new method to quantify particulate sodium and potassium salts (nitrate, chloride, and sulfate) by thermal desorption aerosol mass spectrometry", Kobayashi and Takegawa present measurements of sodium and potassium sulfates, nitrates, and chlorides with their 'refractory aerosol thermal desorption mass spectrometer' (rTDMS). The rTDMS collects particles on a graphite collector and vaporizes them using a focused CO₂ laser before electron ionization and quadrupole MS analysis. This instrument was presented in a recent publication by the authors as well as the analysis of various sulfate salts.

In this manuscript, the sulfate salts analysis is presented again, however in a different setting together with chloride and nitrate salt measurements, focusing on the analysis of sodium and potassium salts. The authors present vaporization time series of single- and multi-component samples, analysis of linearity of the analysis, and detection limits for the various components.

While this presentation of measurement capabilities of the rTDMS in little slices (first various sulfate salts, now various sodium and potassium salts – including the sulfates) seems to be an attempt to improve the number of publications on the measurement capabilities of the instrument, they deliver a thorough characterization of the rTDMS capabilities to separate and quantify these kinds of salts with a reasonable attempt to explain the observed features, presented in a clear way. Since the subject of the manuscript fits well into the scope of AMT and since quantitative (semi-)online aerosol mass spectrometry of sodium and potassium salts is still not established in the aerosol community, I recommend publishing this manuscript after the following rather minor issues have been reasonably addressed.

Detailed comments

P1L10-11: "refractory" is defined as material that keeps its structural properties at very high temperatures. Examples are oxides or carbides of metals like aluminum or magnesium. In this manuscript, materials are analyzed with the rTDMS that have bulk decomposition temperatures from 142 up to 850 °C – with the exception of K₂SO₄ - and at temperatures of the graphite collector up to 930 °C. These are temperatures of which most are within the accessible range of e.g. the vaporizer of the Aerodyne AMS (typical 550-600 °C, 800 °C can be reached), an instrument which claims to measure "non-refractory" aerosol components. I wonder whether the name "refractory TDMS" is adequate for an instrument with these features; most of the really refractory materials could probably not be measured with this instrument.

P1L29-P2L36: This text largely repeats the information from the lines above it.

P2L42-43: The PILS-IC measures ion concentrations after dissolving the soluble aerosol components in water. It does not care about whether the material is refractory or not, just whether it is soluble or not. All the salts presented in this study could be measured with the PILS-IC.

P4L100: It is unclear to me what the benefit of repeating the information from the text within this figure is. The concentration information could easily be added to the respective information in the text and then the figure could be omitted.

P5L120-121: Instead of presenting the method how mass loadings were calculated, the authors refer to their recent paper (Kobayashi et al., AS&T 2021). For some readers it is quite unfortunate that this paper is not openly accessible, and therefore the open access benefit of AMT is somewhat limited for readers without AS&T access.

P5L127: The particle collection efficiency discussion in this manuscript is a weak point of the whole presentation. From other particle-collecting devices it is known that particle collection efficiency can vary strongly. Here, some assumptions about collection efficiency were made, however, no measurements were presented which provide a basis for these assumptions. At the end, particle collection efficiency differences between single component particles which might be used for calibration and real-world particles with different components and under different RH conditions could result in much larger errors than the 15-30% uncertainty presented here.

P6L140: Some of the ions of Table 2 require some more information. For SS m/z 23 (Na⁺) and 48 (SO⁺) are listed in the table. According to Figure 2, the SO₂⁺ signal (m/z 64) is larger than the m/z 48 signal. Why is it not included in the table?

Furthermore, for PN, PC, and PS the C₃H₃⁺ ion is listed in the table. What is the origin of this ion?

P6L158: For m/z 39 and 48 from PS small increases at ~30s were observed. For m/z 39 also a peak at ~7-15 s can be seen in Figure 2(f). This is not mentioned or explained.

P7L161-167: How was the background signal, i.e. the signal outside the peak integration area, accounted for? For some of the m/z signals in Figure 2 it does not return to zero after the peak, how is this handled?

P7L164: Please define "Q_i" and "W_i".

P7L168-169: What causes the variability in sensitivity for certain ions with respect to the difference in the chemical form? Is this caused by differences in collection efficiency or vaporization efficiency/incomplete vaporization? The efficiency of electron ionization should be the same.

P7L178: Is the relative peak area in the measurements proportional to the relative composition of the particles, i.e. can the composition of a multi-component particle be reliably calculated from single-component calibrations? This should be stated clearly.

P8Figure2: Why is the NO⁺ signal in Figure 8(a) and (d) about 10 times more intense than the Na⁺/K⁺ signals (similar intensity after multiplication with 0.1)? Are Na and K incompletely vaporized?

P10Figure4: In Figure 4(b) the m/z 39 signal (K⁺) is strongly enhanced after the first group of peaks and even more after the second peak (40-50s). What causes this enhanced background signal? How do you deal with it when calculating the total signal area? Is this slowly vaporizing potassium?

P10L205: "pure seawater" should probably be "diluted seawater".

P12Figure6: The y-axis captions "Molar ratio of Na₂SO₄/NaNO₃ to NaCl in collected particles" should rather read "Molar ratio of Na₂SO₄/NaNO₃ to NaCl from ion signal intensities" since the real ratio in the particles is not known (but probably is the same as in the solution) and the ion signal intensities are used for this comparison.

P13L243-249: These decomposition equations do explain the occurrence of the m/z 30 (NO⁺) signal, however, they do not explain the occurrence of the m/z 23 and 39 signals. Is the final product of these equations (Na₂O₂, K₂O₂) vaporized or is it further decomposed into Na/K and O₂? Are these ions (Na₂O₂⁺, K₂O₂⁺) observed in the mass spectra?

P13L250-251: I do not understand how the sequential thermal decomposition of the Nitrate salts causes the bimodal peaks at m/z 23 and 39. This would only be the case if the intermediate Na- and K-containing products would vaporize to form the Na⁺/K⁺ peaks. However, if this would be the case, why is not all the material vaporized during the first peak? Furthermore, if e.g. NaNO₂ is vaporized, is the respective ion observed in the mass spectra?

P14Table3: Why are not the same collection times used in the LOD measurements as in the other measurements of this study (i.e. 6 min instead of 2 or 4 min)?

P14L292: What could these "matrix effects" be? What could cause these differences in signal intensities? How would mixtures of K- and Na-salts behave? These results show that Na cannot be quantitatively measured with this method. This should be stated clearly in Abstract and Conclusions.

P15L311: In this work it was not shown that the "current system achieved collection efficiencies of ~70% for solid sulfate particles". This was rather an assumption, based on previous measurements.

P15L315: Here, an alternative for the current ADL is discussed. Unfortunately, the authors do not mention the features or limitations of the current ADL in this paper.