Review of “Resonance-Enhanced Detection of Metals in Aerosols using Single Particle Mass Spectrometry”

General comments

In this study, the authors combined laboratory experiments and field measurements to demonstrate resonant ionization enhancement of particle-bound metals, i.e., Fe, Mn, Zn, and Li, by single particle mass spectrometry (SPMS). The authors show a new way to improve the detection capabilities of single particle mass spectrometer to specific species in aerosol particles. A tuneable laser system was used in the laboratory to investigate the wavelength-dependent resonance effects, which rarely applied in SPMS. Given the resonant ionization with KrF excimer laser (λ=248 nm), ambient particle-bound iron can be detected with much higher sensitivity, such that its source information can be well preserved. Considering the profound impact of particle-bound metals in marine environments and for human health, this study is quite helpful also in a broader research field. However, the method description is inadequate, some laboratory measurements and more discussions are needed. The atmospheric implication section should be strengthened to better fit for this journal. Therefore, I recommend it to be published after major revisions.

Major comments

1. The authors state that resonant ionization of metals in single particles is becoming independent of the particle matrix and its atmospheric changes. This is an important point, however, there is not enough evidence to support it. Although the enhancement effect has been observed not only in Fe-rich but also in other Fe-containing particles, it doesn’t mean that the particle matrix won’t play a role. I would argue that the degree of enhancement may change in different particle types. This is actually shown in Fig 2: when comparing the wavelength at 248. 3 and ~247 nm, an enhancement of the Fe-54 signal is above 2 and below 2 for diesel soot and Arizona test dust, respectively. Please add more discussions, rephrase the abstract and the conclusion sections.

2. Experimental Section (consider to change the header to “Methods”)

1) This study focused on both technical improvements and application, thus more description of the instrument should be added, even though it has been described in other publications. The following points should be addressed in the main manuscript and/or supporting information. Briefly describe the inlet system (inlet type? transmission efficiency of the inlet to standard samples, e.g., PSL?), particle detection region (what is the detection limit of particle size? Scattering efficiency?), LDI region (hit rate for ArF and KrF?), spectra generation (e.g., some descriptions of data analysis in section 3.3 should be moved to the method section), and what is the overall transmission efficiency/detection efficiency of this instrument to PSL particles or other standard samples? In the field measurement, a custom electronic circuit was applied to trigger the lasers alternately. What is the firing time for each one?

2) In the manuscript, “delayed ion extraction” was used and mentioned in section 3.3 Line 234, but not described in method section. Please add it at least in the supporting information.

3) Regarding surrogates. Why was the diesel soot chosen as the anthropogenic Fe-containing particles? I suggest that some standard samples with specific Fe signal, e.g., hematite, should also be measured. This allows to see

more prominent resonant enhancement and the ratio of Fe-56/Fe-54 can be determined, which could help to refine the enhancement effect for other particle types.

3. Results and discussion

1) The mass spectra are shown in an accumulated way, without normalization or further processing. However, the accumulation method is not able to reduce the shot-to-shot difference, which might bring big uncertainty to the results. As stated in the manuscript, the irregularly triggered OPO system reduced its pulse stability. In the ambient, more stable excimer lasers were used, but the ambient particles are more dispersed and complicated. Therefore, further processing is highly recommended. For individual particles, normalization to the total ion intensity can account for shot-to-shot variability (Hatch et al., 2014; Shen et al., 2018). Afterwards, averaging the normalized ones can give statistically more relevant results.

In order to further investigate the resonant enhancement, the authors measured the wavelength-dependent total ion yield of Fe-54 shown in Figure 2. It would be better to show the averaged relative ion yield with standard deviation, which may give an ion yield curve with less broadening.

2) Bias induced by organics and uncertainty of the results should be discussed. For diesel soot, m/z 56+ could also originate from organics e.g., C_4H_8+. Similar interference effects could rise from m/z 56 CaO+ for Arizona Test Dust. Therefore, the enhancement of Fe signals could be underestimated (based on the results that KrF excimer laser leads to ionization enhancement of Fe, but does not change or even reduce the signals of organics). It would be great if this can be discussed more. M/z 54+ is a more characteristic peak for iron, but it is rather weak compared to m/z 56+. Such weak signals can be close to the noise level. As mentioned above, measurement of some standard samples like hematite may provide useful information for discussion.

3) In section 3.1 and Fig. 1. Why were wavelengths at 250 nm and 242.2 nm chosen to compare with 248.3 nm for diesel soot and Arizona test dust, respectively? Please clarify the reasons (242.2 was chosen to show the enhancement effect for Li?). Please consider to show more wavelengths (e.g., <248, 248, >248) for comparison and keep consistency for different samples. Similar questions and comments apply to section 3.3 and Fig. 3.

4. Atmospheric implications and conclusions should be strengthened. Consider to add an implication section or implement it to the conclusion section as it is now. However, several points should be addressed. For the conclusions, the authors should answer e.g., how much enhancement (%) can be achieved? What about the uncertainty? What are the weaknesses of the technique? E.g., resonant ionization enhancement can only be obtained for a few metals simultaneously. In addition, the sensitivity to the other species, e.g., organics, might be reduced while it is enhanced to metals. Hence, tuneable laser systems are required. For the implications consider mentioning that particle-bound metals, such as iron, can also serve as catalyst or reactant in chemistry. Consider to add more discussions on how this study can help understand/investigate the role of particle-bound metal and/or metal oxides in atmospheric processes, e.g., heterogeneous chemistry, transportation, etc.

Minor comments

Page(P) 3 Line (L)64: Regarding typical ionization products, metals especially alkaline metals (e.g., Na, K) and mineral components such as silicate should be mentioned.

P3L65: Change “EC, OC” to “EC or OC”.

P3L66: Why is it “unique” compared to the other kinds of source information?

P3L75: “Herein” would mislead the reader to think that the two-step technique was used in this study. However, one step LDI was used.

P4L101: What does “meaningful” mean? Please describe.

P4L106: “0-3 μm” change the short line to a long one “–” and mention the diameter type (physical?).

P4L107: “modelled” might cause ambiguity. Consider another word, e.g., mimic.

P4L112–115: Is the concentration factor (=3000?) stable? What was the upstream particle number concentration to the inlet of the instrument? What were the particle number and mass concentrations during the measurement time?

P5L120: Table1 Change “x” to multiplication sign “×”. Change “…” to “to” or “–” and throughout the manuscript.

P5L127: Aren't those accumulated spectra rather than averaged ones? I am confused here.

P6L132: “much stronger Fe-signals”. Please quantify such enhancement. How much % stronger?

P6L141: In the histogram plots of Fig.1, what is the difference between the light red and dark red? Please add descriptions in the figure caption as well. Similar comment is applied to Fig. 3.

P6L147: This is the first time to mention supporting information, thus it should be Fig. S1 rather than S4. Please revise accordingly throughout the manuscript.

P7L151: Such signal enhancement of 4 is compared to which value at which wavelength? As shown in Fig2, when compared to the lowest value, they are 7 for diesel soot and 4 for mineral dust; comparing the wavelength at 248.3 and ~247 nm, an enhancement of Fe-54 signal is >2 and <2 for diesel soot and Arizona test dust, respectively.

P7L155–160: Change this sentence to “Thomson et al. (1997) observed ….bulk material.” Similarly, please revise the sentence “Wade et al…”.

P7L158: Give the full name of “MALDI”.

P7L160: Add reference.

P7L164: Fig. 2 please use the same scale for OPO wavelength in panel (a) and (b). Add Y axis with the corresponding units for atomic absorption spectrum and for KrF laser spectrum.

P7L170–172: Move to introduction.

P7L178: Give the full name of “RIMS”.

P7L183–187: Move to introduction.

P8L192–193: Please keep consistency, either use % or mg/kg for mass fraction.

P10L244: If refer to organics, m/z 39+ should be C_3H_3+.

P10L245–252: Move the data analysis part to the method section.

P11L259: Add more references for TMA, e.g., Angelino et al., 2001; Pratt et al., 2009; Köllner et al., 2017.

P11L269–270: What it the threshold of Fe signal(s) to identify Fe-containing particles.

P12L290–292: Fe can be detected in different particle types does not suggest less particle matrix effect. Please see the first major comment and rephrase the sentence, as well as the following statement.

Supplement Figure S4: Can you really detect particles in the size range from 0 to 200 nm? What is the detection limit of this instrument? Please add such information in the method section in the main manuscript, and only show the data within the detection limits.

References:

Angelino, S., Suess, D. T., and Prather, K. A.: Formation of aerosol particles from reactions of secondary and tertiary alkylamines: Characterization by aerosol time-of-flight mass spectrometry, Environ Sci Technol, 35, 3130–3138, 2001.

Hatch, L. E., Pratt, K. A., Huffman, J. A., Jimenez, J. L., and Prather, K. A.: Impacts of aerosol aging on laser desorption/ ionization in single-particle mass spectrometers, Aerosol Sci. Tech., 48, 1050–1058, 2014.

Köllner, F., Schneider, J., Willis, M. D., Klimach, T., Helleis, F., Bozem, H., Kunkel, D., Hoor, P., Burkart, J., Leaitch, W. R., Aliabadi, A. A., Abbatt, J. P. D., Herber, A. B., and Borrmann, S.: Particulate trimethylamine in the summertime Canadian high Arctic lower troposphere, Atmos Chem Phys, 17, 13747–13766, 2017.

Pratt, K. A., Hatch, L. E., and Prather, K. A.: Seasonal Volatility Dependence of Ambient Particle Phase Amines, Environ Sci Technol, 43, 5276–5281, 2009.

Shen, X., Ramisetty, R., Mohr, C., Huang, W., Leisner, T., and Saathoff, H.: Laser ablation aerosol particle time-of-flight mass spectrometer (LAAPTOF): Performance, reference spectra and classification of atmospheric samples. Atmos. Meas. Tech., 11, 2325–2343, 2018.