Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2017-357-RC2, 2018

Atmospheric Measurement Techniques Discussions

Interactive comment on "Exploring femtosecond laser ablation in single particle aerosol mass spectrometry" *by* Ramakrishna Ramisetty et al.

Anonymous Referee #2

Received and published: 10 February 2018

General comments

This paper deals with the single particle mass spectrometry (SPMS) of atmospherically relevant aerosol particles (or laboratory surrogates) in the one-step (ablation/ionization) laser approach, comparing the performances of ns (193 nm) and fs (800 nm and 266 nm) laser irradiation. As a preliminary comment, although this technique can be useful for classifying atmospheric particles based on their (fragmentation) mass spectral fingerprints, it does not provide detailed molecular information on the actual chemical composition of the particles. The two-step (separate ablation and ionization lasers) approach is much more effective on this (see, e.g., Zimmermann's group studies, Anal. Chem. 2017, 89, 6341). The introduction should better acknowledge this, i.e. mention the actual chemical analysis capabilities, not only the improvement of quantitative

abilities in SPMS.

The paper presents an important amount of experimental data. However, it is written mostly at a descriptive and comparative level, with no deeper insight into the actual mechanisms involved in the ablation and ionization processes. Purely speculative assertions (e.g. "... which again indicates a more complex ionization mechanism during fs-laser ablation", rows 212-213, or rows 179-182, 334-336 etc.), cannot contribute much to advancing our knowledge on this technique. Moreover, as the authors acknowledge themselves, this paper is an extension of a previous one (Zawadowicz et al., Anal. Chem., 2015), the difference being an "in-line" laser irradiation, compared to the orthogonal one used in the previous paper. The choice of this new configuration is not justified by the authors. It introduces an important experimental uncertainty on the actual ablation/ionization position in the ion source of the bipolar mass spectrometer (evaluated by the authors at 2-4 cm from the focus – how was this calculated?), which further generates a lack of precision in the discussion (see, e.g., rows 179-182). Additionally, this results into significant uncertainty on the laser irradiance actually experienced by the particles at the ablation/ionization spot. The reported laser irradiances, calculated in the focal plane, are therefore mostly useless for comparison with experiments performed by other groups in different geometries. The conclusion of the paper is that the use of a fs laser presents rather limited interest, when compared to much common (and cheaper) ns sources. This conclusion can be a bit rushed. Although not evident here, the fs approach can still have an interesting application in depth profiling of phase-separated or mixed aerosol particles, but for this a precise and reproducible alignment of the laser beam with respect to the particle must be achieved, which is clearly not the path followed in this study.

It is very surprising that the two wavelengths (800 nm and 266 nm) used for fs ablation/ionization returned absolutely similar results. On one hand, the multi-photon ionization (MPI) invoked by the authors is very different at the two wavelengths (three times more photons needed in IR to reach the same ionization energy), this should re-

sult in orders of magnitude difference in the MPI yield, which could not be compensated by the 20-fold higher IR energy/pulse. On the other hand, the optical properties of the studied particles (although extensively mentioned in the Introduction) are not properly used in the text to account for the experimental observations. Most of the discussion (e.g. high reflectance of Au at 800 nm) is based on single-photon interaction assumptions, while at the high intensities reached in fs regime everything is so multi-photonic (i.e. non-linear). Moreover, the optical properties at 266 nm are completely ignored.

Specific comments

1. Rows 68-69: "The energy per unit volume is greater for femtosecond laser pulses compared to nanosecond laser pulses" – why? The energy/pulse is comparable for ns and fs (800 nm). Is the focusing different? Can you clearly specify the beam diameter at the focus (or better, at the interaction) spot for all three beams used? For each experiment: please indicate clearly the energy per pulse used.

2. Rows 81-83: "In the case of fs-laser ablation, the higher photon density may favour multi-photon ionization, which may lead to the formation of new species from the ablated plume in subsequent Coulomb or phase explosion" – the formulation is not clear. Please state clearly what processes are taking place in the condensed phase (particle) and which ones in the gas phase (plume).

3. Rows 120-122: "beam diameter is $\sim$300 μm" – how was this value obtained? Calculated/measured? If calculated, were the lens aberrations taken into account? If the same lens was used for 193 nm and 800 nm, how the focal length and all subsequent calculations change between these two wavelengths? What is the error bar on the beam diameter? Error bars should be indicated also on the irradiance values all over the manuscript (including Figures). How was the 2-4 cm position after the focus determined? Does this translates into 1-3 cm for F1 focusing? How these values change between the three wavelengths, considering the change in the focal length? F1 and F2 mentioned here are not indicated in Figure 1. Please give the beam diameter limits in

the (2-4 (1-3) cm ?) laser-particle interaction region for all wavelengths, this would be much more useful than diameter at the focus. Indicate also the irradiance limits with the error bars related to calculations and measurements.

4. Please report mass resolution for both polarities. From Figures, this seems to be around 100. In these conditions, how certain can be the assignment of some mass peaks, e.g. m/z 16, 18?

5. Rows 179-182: the explanation for observation of type 1 vs type 2 spectra is not convincing. Can the authors provide a more developed explanation, based on experimental evidence? Generally speaking, a more thorough discussion on type 1 vs type 2 spectra is needed (see also comment 12 below), as this can have practical implications on particle classification in "real world" (field) experiments.

6. Rows 183-188: formation of larger carbon clusters for fs-ablation: "This may be due to the higher power density of the fs-laser, and reactions of the primary ion species with the source plume forming larger clusters as secondary products" – what is the experimental evidence for the in-plume growth of these clusters? How their intensity changes with the increase in laser irradiance? Please show the data (at least in Supplementary Information), they must be available from studies performed in section 3.2. In the Conclusion sections, the in-plume reactions are not mentioned, but only formation at the ablation stage (rows 366-367). Please put in agreement the conclusions with the main text assertions.

7. Section 3.1.2: the optical properties of NaCl particles are quite well-known and should be used to explain the low efficiency in generating mass spectra in fs AND ns regimes.

8. Rows 211-213: please clarify what you mean. Are these species generated in the ablation process, or by subsequent interactions in the plume? What is the role of the ionization here?

9. Section 3.1.3: an explanation should be advanced for the very low efficiency in generating mass spectra in both positive (10%) and negative (1%) polarities with the (800nm?) fs laser, with respect to the much higher (100%?) efficiency achieved with the ns one.

10. Section 3.1.4: less intense signal at 266 nm compared to 800 nm – please try to relate this to the optical properties of the SiO2 particles.

11. Rows 290-292: "The high reflectance of gold in the IR likely leads to reduced ablation of the core" – beside the fact that the absorption processes in the fs regime must be highly multi-photonic, this conclusion is questionable, as similar spectra are observed for 266 nm fs irradiation, or at this wavelength the reflectance of gold and silver is much reduced ($\sim$30%). How can the authors interpret this? The same explanation is given rows 311-312, although the same similarity is observed between 800 nm and 266 nm irradiation.

12. Rows 305-309: an explanation for the existence of two types of spectra must be advanced.

13. Row 329: is this average factor relevant, considering the huge variability in efficiently generating usable mass spectra?

14. Rows 334-336: "... saturation effect ... may be due to coulombic repulsion ..." – please develop. Why this effect would occur only for NaCl particles? How this saturation correlates with the low efficiency (16%) in generating non-empty mass spectra with the fs laser? How is this saturation effect related to the optical properties of the NaCl particles (vs the others)?

15. Row 345: factor 7 claimed is not evident from Fig. 10, please check.

16. Row 348: Factor 8 in volume is not "much larger" than factor 7 in ion intensity (if confirmed).

17. Rows 350-351: "This demonstrates the quantitative limitations of both ns- and fs-

laser ablation". However, can the authors infer something about the fraction of particle mass which is vaporized from the measured data in Figure 10?

Technical corrections

18. Rows 80-81: ablated particles cannot move 5 μm during 5 ns and 0.1 μm during 100 fs, please check

19. Rows 301-303: 44% + 66% = 110%

20. Rows 387-388: please check English

21. Tables 1 and 3 can go to Supplementary Information

22. Table 2 is useless in this form, everyone can apply the proportionality on the energy/pulse. Give instead proper beam diameters in the interaction zone for each wavelength (see above)

23. Fig. 10 caption: inversion red-green

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-357, 2017.