

## ***Interactive comment on “The performance and the characterization of Laser Ablation Aerosol Particle Time-of-Flight Mass Spectrometry (LAAP-ToF-MS)” by Rachel Gemayel et al.***

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We sincerely appreciate the constructive comments of the reviewer. Laboratory measurements with model spherical particles revealed that LAAP-TOFMS is able to detect particles in the range between 350 nm and 600 nm. However, during the measurements performed at ambient air the particles ranging between 200 nm and 3  $\mu$ m were detected which was ascribed to the influence by several parameters such as the refractive index, the chemical composition, the factor shape . . .), as was detailed in the core of the article. Nevertheless, the scattering efficiency exhibits maximal value for the particles in the size range between 350 and 600 nm. For the particles sizes lower than 350 nm, the scattering efficiency is very low which makes the comparison with other

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instruments very difficult. In summary, LAAP-TOFMS is able to detect and analyze particles with diameter > 200 nm, in particular the particles ranging between 350 nm and 600 nm. Reviewer # 1: Primary comments: Comment 1: Reviewer: More description is needed for the inlet system. For example, is the aerodynamic lens a commercial system or home built? If the former, then please provide a literature reference. If the latter, then please provide specific dimensions so that this could be replicated. Author: The particle inlet of the LAAP-TOFMS built by Aeromegt, GMBH is identical to the one used in the Aerosol Mass Spectrometer (AMS) and it is based on the design of Liu et al., (1995) and Zhang et al., (2004). It consists of a 100 micrometer critical orifice and an aerodynamic lens composed of six precision-machined orifice lenses mounted in a precision bore stainless steel tube. This aerodynamic lens transmits the particles with an aerodynamic diameter between 80 nm and 600 nm.

Zhang, X., Smith, K. A., Worsnop, D. R., Jim'enez, J. L., Jayne, J. T., Kolb, C. E., Morris, J., and Davidovits, P. Numerical Characterization of Particle Beam Collimation: Part II Integrated Aerodynamic Lens-Nozzle System, *Aerosol Sci. Technol.*, 38, 619–638, 2004.

Comment 2: Reviewer: Line 89-91: “[This technique] would allow . . . quantitative information about ambient particle ensembles. . .” I disagree that any “quantitative information” could be obtained from this instrument. First, only 2.5 % of the particles are detected. Of those, less than 2/3 are analyzed (hit rate). Second, of the particles which are hit by the laser, there is no evidence that 1) the particle is fully ablated or 2) the species of interest are fully ionized for MS detection. Unless the authors provide other compelling evidence, I would consider this instrument qualitative, similar to other LA instrumentation.

Author: We agree with the reviewer about his comments. As mentioned in the text this instrument is able to follow the evolution of the number of particles; hence, it is perhaps more correct to describe it as a “semi-quantitative” instrument. This is especially true because we are on the way to develop the instrument in order to obtain quantitative

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information. The outcomes of this analytical development will be published elsewhere.

Comment 3:

Referee: The authors do a good job of comparing their technique to other airborne LA techniques. However, since the focus is largely on trace elements (more so than most other LA techniques), the authors should also compare (both positives and negatives) their technique to advances in airborne single particle ICPMS. For example, Myojo T et al, 2002, *Aerosol Science and Technology* and Suzuki, Sato, Hiyoshi, and Furuta, 2012, *Spectrochimica Acta Part B*, among several others.

Author: We thank the reviewer for this comment. However, the goal of this study was to test the performance of this instrument. Even though we compared the performances of LAAP-TOFMS with some other instruments. Please note that, this manuscript it will be the first one published related to this commercial instrument. In the future comparison can be carried out with other available instruments based on LA technique.

Other Comments: Comment 1:

Reviewer: The English needs fine tuning. There are more than several errors, including references not capitalized (line 54), incorrect grammar (line 63), sometimes the reference C2 AMTD Interactive comment Full screen / Esc Printer-friendly version Discussion paper is after the punctuation and sometimes before, and other issues which need to be addressed.

Author: These comments have been considered in the revised version of the manuscript Comment 2:

Reviewer: Line 199: The authors claim “excellent repeatability” for the hit rate. Please explain why an RSD of 18% is considered “excellent” in this application as, in most instrumental analyses, this is not the case. Author: We remove the “excellent” since the comparison with other similar instruments cannot be performed. However, we are still on opinion that the repeatability of the instrument is very good. In the future, the

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comparison with other available instruments will confirm this very good repeatability.

Comment 3:

Reviewer: Lines 205-208 and Figure 3: The authors state that, after 4 weeks, the hit rate goes to 0%. Yet, Figure 3 only goes out to 12 days. The authors should either adjust Figure 3 or specify that these data are “not shown” as this could be confusing to the reader. Related, it would be useful for the authors to give some context as to why the hit rate would be “constant” for 8 days after refilling the laser only to suddenly drop thereafter. Author: We did not change Figure 3 for the following reasons. According to the Laser Gam Ex5 specifications, laser energy drops to 50 % after a shelf life of 12 days or after 12 million pulses with ArF (<http://www.gamlaser.com/Brochures/EX5.pdf>). It seems that the shelf file is the limiting factor when using the laser in association with single particle mass spectrometer, at least in the diode trigger modes. However, we specified in the core of the manuscript that “these data are not shown” as suggested by the reviewer.

Comment 4: Referee: Line 244: Authors mention “sulfate” in the text, but show “bisulfate” as the chemical formula in parenthesis. Author: In the text “sulfate” is used as a general term to refer to the various sulfate species associated to particles.  $\text{HSO}_4^-$  is the ion produced by laser desorption ionization that has been chosen to represent these species. Comment 5: Reviewer: Line 303-306: Can the authors elaborate on which design parameters are responsible for the improved hit rate relative to SPLAT? And, in which size range are these improvements observed? Author: It is an omission in the text. We changed it accordingly i.e. SPLAM instead of SPLAT. the size range of detected particles is between 200 and 900 nm.(Gaie-Levrel et al. 2012). The low hit rate can be ascribed to the effect of different wavelengths of the ionization lasers (at LAAP-TOFMS;  $\lambda = 193 \text{ nm}$ ; at SPLAM;  $\lambda = 248 \text{ nm}$ ) or the difference in the distance between the laser diodes and the ionization laser. The hit rate for SLAT is 15%.

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