Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2016-411-AC1, 2017


Atmospheric Measurement Techniques Discussions

# *Interactive comment on* "Laser Ablation ICP-MS of Size-Segregated Atmospheric Particles Collected with a MOUDI Cascade Impactor: A Proof of Concept" *by* Marin S. Robinson et al.

**Marin S. Robinson et al.**

elteren@ki.si

Received and published: 1 March 2017

The paper dedicated to the analysis by LA ICP-MS of atmospheric particles collected with a MOUDI cascade impactor fit well with the scope of the AMT journal. However, many questions arise. The study which intended to demonstrate the value of this combination (MOUDI / LA ICP-MS) not treated and discussed a lot of keypoints that deserved the proof of concept. The main problem comes with the lack of a real reference material characterized for the different particle sizes tested here. The urban particulate matter of the SRM 2783 used as reference in this study has a median particle size of 3.2 $\mu$m and a size range of 2.5 $\mu$m and particles are collected on nuclepore polycarbonate membrane filters of 0.4 $\mu$m pore size. How it can be possible for the authors to



compare its response by LA ICPMS with what they obtained on their particulate samples of lower sizes, collected on PTFE filters? This is not discussed (influence of the particle size and the filter type on the laser ablation efficiency / influence of the laser beam mask size on the laser ablation efficiency and the mapping...)

Authors' response: We used NIST SRM 2783 as an absolute calibration standard, i.e. the LA ICP-MS parameters were such that the laser beam completely penetrated the nucleopore filter, making matrix-matching unnecessary. The PTFE filters were not completely obliterated after ablation, probably due to the fact they were thicker, but the size-segregated particles on the filter were in most instances completely removed as observed by optical microscopy under 100$\times$ magnification, except maybe for the deepest impacted, smallest particles in the case of MOUDI sampling without rotation, making quantification by one-point calibration of the rotational filters on the NIST standard accurate. Since we use a laser beam diameter of 150 $\mu$m with a square mask it is obvious that the particles ablated are much smaller and as such the influence of particle size on the quantification is negligible.

The authors claimed that "The laser beam energy was sufficient to remove all of the particles during ablation, allowing elemental concentrations to be determined via a one-point calibration with the NIST standard" (P3L12). The authors have to prove that it is realistic. What's about deep-impacted particles into filters? As they mentioned in their previous paper published in Science of the Total Environment in 2008 ("A multi-element mapping approach for size-segregated atmospheric particles using laser ablation ICP-MS combined with image analysis") distribution of particulate matter in SRM 2783 is non-homogeneous... Why is it not taking into account here?

Authors' response: Visual inspection of the post-ablation filters under 100$\times$ magnification showed that the selected laser parameters (e.g., fluence/mask size/repetition rate) were sufficient to remove multiple layers of PTFE in each particle stage; hence, we assumed that the particles themselves were also ablated. However, it is possible that the deepest impacted particles were missed, especially in the smallest size ranges in

the case of MOUDI sampling without rotation and high loading of particles. MOUDI with rotation prevents such potential problems altogether. We are aware of the heterogeneity of the NIST standard as the certificate declares that a sampling area of 1 cm2 is deemed necessary for reaching the certified uncertainty. In the current manuscript we routinely analyzed 1 cm2 to comply with these requirements.

LA ICP-MS and "wet chemical" ICP-MS of several samples had been also compared for 5 samples which is informative but non-sufficient to understand the effect of the particulate size on the LA ICP-MS response.

Authors' response: We did not specifically examine the effect of particulate size on the LA ICP-MS response; however, we did optimize the laser parameters so that particles in all stages appeared to be ablated. Furthermore, section 2.4 (QA/QC) clearly shows that there is a good agreement between LA CP-MS and bulk ICP-MS after digestion for most elements and for stages 6-10 with cut-point dia. of 0.56, 0.32, 0.18, 0.10, and 0.0156 $\mu$m, respectively.

Particulate collection is another keypoint of this particulate matter analysis. However, collection particle losses during MOUDI collection was not investigated (nozzle wall loss which is dependent on the size but also on the particle composition / clogging effects). Moreover, the effect of the rotation of the filter was studied by comparing the results got from two different cities, at different days and different climatic conditions...too much parameters varied to get really confident comparison.

Authors' response: It is true that there may have been particle losses during MOUDI collection, but this was not our focus. Our focus was to use LA ICP-MS (as an alternative to wet-chemical ICP-MS) to determine the elemental composition of the particles that were successfully collected. We also used laser ablation to investigate the uniformity of the particles that were deposited when the MOUDI was rotated.

Moreover, no validation data are given on this new measurement system. Validation steps of the concept should be considered (repeatability integrating the collection step).



Authors' response: Based on the concentration levels found in the filters, validation with similar imaging techniques like XRF, PIXE, etc. is questionable as LA ICP-MS is the most sensitive technique for elemental microanalysis. However, by comparing the elemental concentration in size-segregated particles with a sensitive bulk analytical technique like ICP-MS, after digestion of the filter, an indirect comparison can be made as explained in section 2.4 and highlighted in Table 3. As such we feel that the LA ICP-MS imaging method used yields accurate and precise data.

Why no conclusion was drawn on the proof of concept ...?

Authors' response: The current manuscript contains a "Conclusions" section.

I suggest conducting the proof of concept on a very well characterized particulate sample (size/composition by other analytical tools), to study systematically each critical parameter and compare with the author's previous work and the literature (one important paper in this field is missed: Hsieh, Chen et al. "Elemental analysis of airborne particulate matter using an electrical low-pressure impactor and laser ablation/inductively coupled plasma mass spectrometry" J.Anal.At.Spectrom., 2011, 26, 1502).

Authors' response: The current manuscript, although it does not study systematically each critical parameter, shows that LA ICP-MS yields accurate data and superior detection limits for elemental analysis of size-segregated aerosols collected by MOUDI in rotation mode. The mentioned reference is included in the current manuscript.

---

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-411, 2017.