

Interactive comment on “Near-infrared laser desorption/ionization aerosol mass spectrometry for measuring organic aerosol at atmospherically relevant aerosol mass loadings” by S. Geddes et al.

Anonymous Referee #1

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This manuscript describes a new type of mass spectrometer for the near real-time analysis of organic aerosols. The novel aspects of this instrument are the use of near-IR laser desorption ionization (LDI) to create quasi-molecular ions and the low limits of detection. The simplicity of the design with a single, inexpensive Nd:YAG laser and the ability to characterize atmospherically relevant loadings of organic aerosols in a matter of minutes will make this work of interest to many researchers in atmospheric science.

The paper is appropriate for AMT, presents a novel tool, and reaches substantial conclusions supported by sufficient results and conclusions. The description of the ex-

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periments is sufficient (with the exceptions pointed out below) and credit is given to previous work appropriately (again, with the exceptions pointed out below). The title clearly represents the nature of the work, and the abstract provides a clear and precise summary. The overall structure of the paper is appropriate as are the figures and the number of references.

Specific comments:

Mechanism of Ionization:

There is no discussion of the mechanism of ionization of the particle material following desorption by the near-IR laser. It may be that the exact details of that mechanism are beyond the scope of the present manuscript, but the authors need to offer some possible explanations. Along these lines, some discussion of similar, previous LDI work needs to be included. In particular, the IR-LDI work of Kermit Murray and colleagues (e.g. Bhattacharya et al. "Infrared laser desorption/ionization on silicon. *Analytical Chemistry*" (2002) vol. 74 (9) pp. 2228-2231; Rousell et al. Matrix-free infrared soft laser desorption/ionization. *Journal of Mass Spectrometry* (2004) vol. 39 (10) pp. 1182-1189) needs to be cited and discussed. It would be helpful to the reader if the authors could comment on whether near-IR LDI has been used previously, too, to put the present work in context.

Is there any precedent for the formation of [M-H]⁻ ions from LDI? Again, a brief mention of what is known from previous LDI work would help to put this work into context.

Are ions other than [M-H]⁻ ions generated with this approach? Are any positive ions created? Even if the authors did not find any or did not look for positive ions, these facts should be mentioned as they may be useful to others.

Assuming that the exact mechanism for near-IR LDI is not known, it would be helpful and interesting from a practical standpoint to know what types of organic molecules can be detected. It appears from the oleic acid data and the α -pinene ozonolysis data that

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aldehydes and carboxylic acids can be detected. This suggests that only species with labile hydrogens/protons and/or carbonyl moieties can be ionized. Could the authors provide any more information to rationalize these observations?

Experimental Details:

How big is the particle beam compared to the Al wire?

What is the near-IR laser spot size? It would be helpful to know this or at least the laser fluence (W/cm²).

Is the Al wire biased, floating or grounded?

Was any aging of the wire noticed? How reproducible are the spectra after repeated use of the wire?

Were wires of any other metals tried? How did the spectra and limits of detection compare to Al?

Does the probe on which the particles are collected even need to be metal?

In Figure 2 there is significant scatter in the mass spectral signal vs. particulate mass sampled. Please comment on the nature of this scatter. Could it be shot-to-shot fluctuation in the near-IR laser?

Please explain how the 532-nm laser is used for alignment of the particle beam.

Are the particle transmission and deposition efficiencies known? It would be interesting to know how much the limit of detection is determined by these.

Please describe how the mass spectra are collected and averaged in more detail. How long does the vapor from desorbed particulate matter last? How many laser shots are averaged or summed to obtain spectra? Do the spectra from a single deposition look qualitatively similar from shot to shot?

Why is that the data collection is limited to only one mass spectrum per second with

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a sampling rate of 1 GSa/s? Even if an entire mass spectrum took 100 microseconds and points were collected every nanosecond (for a total of 10^5 points), it should be possible to collect 10 mass spectra every second. This is an important point to clarify since it seems possible to improve the signal-to-noise and the detection limit.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 2013, 2010.

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