

## **A solid-state IR laser for two-step desorption/ionization processes in single-particle mass spectrometer**

Note:

Reviewer comments are in normal format.

*Author responses are in italics, blue.*

**Changes** that were made to the manuscript are in **bold** face.

### **Referee 1**

#### **General comments:**

The authors discuss the advantages and disadvantages of using a new type of IR-laser for laser desorption followed by REMPI and LDI by an UV laser. The use of a solid-state Er:YAG instead of the widely used CO<sub>2</sub> laser offers a more compact design with less maintenance required. However the prototype character of the Er:YAG still leads to instabilities in laser energy and less reproducibility.

The authors show on a variety of aerosol species, that the new laser leads to reasonable and qualitatively good spectra with similar quality compared to the established method, still pointing out the existing problems and differences.

The comparison of the LD/REMPI on three species and LD/REMPI+LDI on the same three species seems very repetitive and does not provide the necessary insight justifying for 6 plots. I suggest, reducing this part to 3 plots, shifting Fig. 2,4 and 6 along with its corresponding text into the supplement. In the main article a short note to the results of Fig. 2,4, and 6 with reference to the supplement should suffice.

*We agree with the reviewer on the length issues. As suggested by the reviewer, we have moved three figures with mass spectra including the corresponding text to the Supplement and added short notes on the respective results in the manuscript.*

Instead the description of the Er:YAG laser falls short, since it is the main news of the publication. Please consider adding more info, e.g. about the dimensions, pulse shape and pumping.

*We added the required information in a new section.*

All-in-all the writing and the structure of the paper is very clear, enabling a good understanding of the topic and what the authors are trying to get across. The supplement is useful and offers a reasonable amount of extra information.

I suggest publication in AMT after some minor to major revision.

*We thank the reviewer for his/her time and positive feedback about the manuscript.*

#### **Specific comments:**

Consider shifting some figures and text for the spectral comparisons into the supplement (eg. Fig. 2,4, and 6)

*Figure 3, 4 and 7 were shifted to the supplement, the text was also shortened in the main article and a full explanation can be found in the supplement now.*

Consider a more detailed description of the Er:YAG laser, e.g. about the dimensions, pulse shape and pumping.

*We added a section about Er:YAG laser including a detailed description in the methods section of the paper.*

The spectra are compared in detail, however, it is not clear, whether minor differences state a problem. Please state at some point, that due to the missing quantitiveness of the measurement method, minor differences in the acquired spectra do not undermine the applicability of the new laser.

*We added a corresponding statement early in the results section 3.1: "It is also important to note that in SPMS, due to the limits in quantitative measurement, minor differences in the mass spectra obtained do not undermine the applicability of the Er:YAG laser."*

line 100: "(Zhuo, Z., Su, B., Xie, Q., Li, L., Huang, Z., Zhou, Z., Mai, 2021)."

This should be abbreviated as Zhuo, Z. et al., 2021. Name of Mai is missing the Z. and last author Tan, G. is not mentioned, rework the reference.

*Thank you! Corrected.*

line 108f: "a 14-bit digitizer card (ADQ14..."

To my knowledge the ADQ14 provides 4 channels. If this instrument uses all four channels, similar to PALMS-NG, ALABAMA, ERICA and others, clarify here: "2 channels per polarity"

*The ADQ14 card is available with 1,2 or 4 channels. We use the 2-channel version, with only one channel per polarity and added a respective statement in the manuscript.*

line 124: "This is due to the lack of Q-switching. Within the 200  $\mu$ s pulse duration,"

It is not 100% clear, that the lack of Q-switching and the pulse duration both refer to the Er:YAG laser. Please rephrase.

*Thank you. Corrected: "This is due to the lack of Q-switching for the Er:YAG laser. Within the 200  $\mu$ s pulse duration,..."*

line 129: ", see Fig. S2)"

This can be more specific, like "a histogram of laser energies can be found in Fig. S2)"

*Ok. Done. "(up to  $\pm 50$  % calculated on the average pulse energy, a histogram of pulse energies can be found in Fig. S2)."*

line 144: "no LD"

strictly LDI is a form of LD, thus rather write "no prior LD"

*Thank you. Corrected accordingly.*

line 153: "was not exposed to LD"

compare comment above, rather write "was not exposed to the IR LD laser"

*Corrected.*

Fig. 1

The distance between LD and REMPI/LDI seems pretty large. This is totally ok for a sketch, but somewhere it should be clarified, how small the distance is in reality.

*The distances differ slightly between the Er:YAG and CO<sub>2</sub> lasers due to the broad beam of the Er:YAG laser, which spatially overlaps with the unfocused UV beam used for REMPI. To clarify the dimensions without overcomplicating the description, we included two brief notes at the beginning of the respective sentences, as*

*follows: "In the ion source, the two desorption lasers, i.e., the "standard" CO<sub>2</sub> laser and the experimental Er:YAG laser, are alternately fired at the respective particles, generating a small gas plume for each particle. Few  $\mu$ s later, the unfocused UV laser pulse ionizes the PAHs in the expanding plume via REMPI. "*

line 251: "resulting in cluster #4 with dominant fragments"

I am not convinced by the interpretation of a very small peak at ~178 as the only parent molecule and everything else as fragments. All other spectra show more parent molecules than fragments. Can the peaks not be explained by a different parent molecule, possibly hydrogenated or methylated PAH?

*Thank you for the comment and discussion! The mass spectrum of cluster #4 can be identified as a typical fragmentation pattern for several reasons. Oxidized PAHs exhibit a significantly lower REMPI cross section and therefore typically do not contribute to the major peaks. Methylated PAHs, on the other hand, have even m/z numbers (e.g., 192, 206, 220, etc.). The strongest peaks in this spectrum, however, display odd m/z numbers, which is characteristic of PAH fragments (e.g., resulting from H-atom abstraction). Although a detailed discussion of this is beyond the scope of this paper, we have added a note regarding the odd m/z values to the text.: "The primary difference between the two lasers is the higher fragmentation caused by the CO<sub>2</sub> laser, which leads to the formation of cluster #4, characterized by dominant fragments **with odd m/z values.**"*

line 258f: "The results indicate that the compact Er:YAG laser can replace the more commonly used CO<sub>2</sub> lasers for single-particle LD also in ambient air studies."

This conclusion is not part of the graph description and should only be mentioned in the plain text, not in the caption.

*Yes, we agree. Accordingly, **we removed the conclusion from the caption and added into the text.***

line 263f: "We investigated the capability of the Er:YAG laser for its implementation in this ionization technique"

This sounds like the Er:YAG does the REMPI/LDI, which is not the case. Rephrase like "We investigated the capability of LD by the Er:YAG laser in combination with this ionization technique"

*Thank you! **Changed accordingly.***

line 281f: "but there are some differences of unknown origin, e.g., enhanced phosphate signals when the CO<sub>2</sub> laser is used for LD."

In the LD scheme without LDI, only cations have been investigated. Do the wood ash LD/Rempi spectra show the phosphate signal in the anions as well? Since only the LD laser is changed between 7a and 7b, a difference in the LDI spectrum would indeed be astonishing.

*No mass spectrometric peaks were visible for anions using LD-REMPI without LDI. We believe that the relatively short and intense CO<sub>2</sub> laser pulse excites the particle in such a way as to enhance ion formation of some particle components in the subsequent LDI process, possibly by selectively vaporizing different materials. In contrast, the long and low intensity pulse of the Er:YAG laser results in a slow heating of the whole particle. However, the data presented here do not allow a sophisticated investigation of the underlying processes.*

line 320: "the vast majority of mass spectra were dominated by fragments"

At this point I am not sure, whether I know what you mean. Since you differentiate between LDI spectrum and PAH spectrum within the same spectrum and you use the term fragment mainly in the context of PAHs, I would guess you mean most of the PAH spectra (m<sub>z</sub>>140) were dominated by fragments.

*Yes, exactly. We added this information to the sentence: "For the LDI process only, without previous LD and REMPI ionization in the plume, **the vast majority of the PAH mass spectra were dominated by fragments.**"*

**Technical comments:**

line 161: "isobar substances"

I think the correct term is isomeric

*Sorry, of course. Corrected.*

line 161f

several parts of the sentence are written in italic for no obvious reason

*Corrected.*

line 162f

replace above and below by upper panel and lower panel or similar (top panel, bottom panel)

*Thank you. Corrected.*

Table 2

Some lines are not separated by an empty line, in some lines the m/z are not aligned with the species

*Corrected and aligned.*

line 181: "of each 500 diesel soot particles"

The expression sounds unfamiliar, shouldn't it be "of 500 diesel soot particles, each"

*Corrected.*

line 235: "from each 500 PAH-containing particles"

What does each 500 mean in the context of 1450 measured spectra? Should it be "from a representative set of 500 PAH-containing particles, each"

*Yes, thank you. Corrected and clarified.*

line 280, line 292, line 305: "Each n = 500."

n=500 each.

*Corrected.*

line 370: "LDI ionization"

This is a pleonasm. Rather write LDI method or LDI scheme.

*Corrected to "...LDI method...".*

line 536f: "...Con- centrator... Spectrome- try..."

Please check spelling

*Corrected.*

line 543

The title of the reference is in capitals, not in agreement with the other references

*Capitalization seems to be common for patent titles. We would leave the decision to the editorial team.*