

This manuscript presents an exploration into technical developments in single particle mass spectrometry (SMPS) aimed to improve the detection and identification of various PAHs in individual aerosol particles. From the onset the authors note that to generate high-quality single particle mass spectra of particle-bound PAHs requires evaporating/desorbing the PAHs and ionizing them in the gas phase by REMPI. Indeed, two-laser schemes using a CO<sub>2</sub> laser in the IR to evaporate semi-volatile molecules, followed by UV ionization have previously been shown to yield significant improvements in SPMS. In addition to reducing fragmentation and matrix effects, it also was shown to result in highly reproducible mass spectra with significantly smaller particle-to-particle fluctuations (e.g. (Zelenyuk, Yang et al. 2009)).

The central issue here is to explore the use of a solid state Er:YAG laser producing light at ~3 μm as an alternative to the CO<sub>2</sub> laser. However, while the authors emphasize the cost-effectiveness and compact size of the Er:YAG laser, no details on its size, weight, cost, and ease of operation are provided. The discussion of the Er:YAG laser features and performance should be extended prior to manuscript publication.

It is important to note that aside from the wavelength, there are other important differences between the CO<sub>2</sub> and Er:YAG that are clearly listed in Table 1. Most notably, the Er:YAG pulse length is 200 μs and the laser beam, as used, is 5x5 mm, as compared to 250 ns pulse width and a 1x1 mm beam size for the CO<sub>2</sub> laser. This translates to a difference in irradiance of a factor of 5,000!

A note on IR wavelengths used here. As it turns out the absorption by PAHs at both the Er:YAG, at 3 μm and CO<sub>2</sub>, at 10.6 μm, are on the edges of the IR absorption bands of PAHs. This brings out the question of the role of differences in IR absorption cross-section of the various PAHs in determining their absolute and relative abundance using the observed mass spectral peak intensities. It is rather surprising to find that despite the large differences between the two IR light sources, the mass spectra generated using CO<sub>2</sub> and Er:YAG presented in the manuscript, are nearly the same.

To assure gentle REMPI, the evaporated gas plume is ionized using a 4 mJ/pulse KrF excimer laser pulse (248 nm), operated with a 5x10 mm laser beam. As a result, the LD mass spectra of particles used in this study are generally of high quality and relatively easy to assign.

The manuscript presents a series of measurements on what the authors call “laboratory particles”: diesel soot, wood ash, and tar balls particles, which all exhibit nearly IR laser independent mass spectra. It is most interesting that for most of the mass spectra, the absolute and relative peak intensities are independent of desorption laser. Why, I am not clear. Could the authors discuss the possible reasons for these observations? Are both IR lasers evaporate the whole particle over the entire particle size range? Given the significant pulse-to-pulse energy variations reported in Figure S2 for the Er:YAG laser, are particles completely evaporated at lower pulse energies? If so, the histograms of the total PAH ion yield per particle for the Er:YAG laser, shown in Figures 2 and 3, seems to be inconsistent with the histogram of the pulse energies presented in Figure S2. The authors state that “*The total reduction in hit rate resulting from the combined loss in duty cycle and*

*pulse-to-pulse variations is estimated to be  $\approx 30\text{--}50\%$ , compared to a hypothetical stable Er:YAG laser to be developed for irregular triggering in SPMS.*, which seems to suggest that lower pulse energies are insufficient to generate “a sufficient plume”. The authors also state that “*the pulse energy required to generate a sufficient plume is highly dependent on the particle properties and composition.*” Do these particle properties include particle size? I expect that both, particle size and laser power, can significantly affect the observed mass spectra and apparent hit rate, but were not investigated in the present study.

It also important to note that the reported hit rates for wood ash particles were  $\sim$  an order of magnitude lower compared to those observed for diesel soot 2% (4%) vs. 38% (49%) for the CO<sub>2</sub> and (Er:YAG) lasers. The authors state that “*This is due to the nature of the sample, which contains many burnt ash particles and fewer OC/soot particles containing PAHs.*” Ash particles should have been efficiently detected and identified by the LDI. Was the observed hit rate for the data presented in Figure 6 a factor of  $\sim 10$  higher compared to those in Figure 3? Moreover, the mass spectra of ash-rich particles would be very different compared to the PAH-containing particles. Were different types of the mass spectra observed in the cases where the LDI was used?

The experiments on ambient particles are clearly more challenging. Despite this fact, the results on PAH-containing particles for the two IR lasers are again very similar. This set of experiments clearly demonstrates that the solid state Er:YAG can be used to evaporate semi-volatile molecules from particles, much like the CO<sub>2</sub> laser, which is the central point of the paper.

Characterization of mixed particles, containing semi-volatiles and nonvolatile species, requires a more intense UV laser to ablate the nonvolatile fraction in the particle. It is accomplished by using a reflector that focuses the Excimer laser pulse, such that each particle is hit with the IR laser first, then the evaporated plume is ionized with unfocused excimer laser, that same beam is reflected and focused to hit what remains in the particle for LDI.

The authors apply this scheme to all three laboratory particle samples, presenting the data for the two of the IR lasers, including the LDI step, as well as the mass spectra generated by the excimer laser only (LDI). The first two examples provide a clear demonstration of how much better the mass spectra are when IR laser is used. Surprisingly, the LDI mass spectra for tar ball particles are nearly the same as those with IR evaporation, which the authors explain by the presence of soot in these particles. If so, why the LDI mass signatures of soot are “missing” in panels (a) and (b) of Figure 8?

The ambient particles experiment also show improved mass spectral signatures with IR evaporation. At present, the Er:YAG is clearly less efficient than the CO<sub>2</sub> laser. However, as the authors note, future developments of the Er:YAG could result in significant improvements.

The weakest aspect of this manuscript relates to particle size. Particle evaporation and the amount of material in the plume are expected to be strongly dependent on particle size and hence affect the results of the entire study. The size distributions (aerodynamic diameters in the free molecular regime?) are shown in the supplement. All these size distributions show particles that

are significantly larger than what I would expect for “real” diesel soot, wood ash, and ambient particles. I assume this is due to the particle generation (dispersion of the collected and milled bulk samples) and aerosol concentration methods used.

The manuscript notes that “the instrument in this configuration could not record individual particle size information but only average size distributions.” and, “size information is only available at the ensemble average,” which I find confusing. You must detect each particle twice and “a hit” means it was properly detected (i.e. it was not a false detection or free-running laser) does that not yield a size for each particle? As I mentioned above, the size-dependent information would be critical to understand the performance of the new Er:YAG laser, which is/should be a focus of this paper.

Overall, the paper is well-written and is suitable for publication in AMT after revision.

Zelenyuk, A., J. Yang and D. Imre (2009). "Comparison between mass spectra of individual organic particles generated by UV laser ablation and in the IR/UV two-step mode." International journal of mass spectrometry **282**(1): 6-12.