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Atmospheric Measurement Techniques Discussions

Interactive comment on "Development and characterization of a single particle laser ablation mass spectrometer (SPLAM) for organic aerosol studies" *by* F. Gaie-Levrel et al.

Anonymous Referee #1

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General Comments

The submitted manuscript "Development and characterization of a single particle laser ablation mass spectrometer (SPLAM) for organic aerosol studies", Atmos. Meas. Tech. Discuss., 4, 4165–4208, 2011 from F. Gaie-Levrel1, S. Perrier, E. Perraudin, C. Stoll, N. Grand, and M. Schwell is eligible for publication at AMT (Atmospheric Measurement Techniques) since it addresses "laboratory measurement techniques for the constituents ... of the Earth's atmosphere", "development ... and validation of measurement instruments" and "aerosols" as listed in the "Aims and scope" para-

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graph of the AMT journal presentation page (http://www.atmospheric-measurement-techniques.net/home.html")

Globally the manuscript is well written and honest with important efforts to present the newly developed instrument in a very pedagogic manner that would help readers who do not know this technique to understand the basic setup and the role of its different parts. Indeed after a quite extensive presentation of the historical development of this technique and highlighting the milestones, the authors present the role and characteristics of the different components of this instrument in dedicated paragraphs with precision and attempts to compare how good is their instrument with other similar instruments when possible. Then first measurements with gas phase sample (2-methylnaphthalene), model aerosols (DOP) and then a model secondary organic aerosol (SOA) system (from the reaction of indene with ozone) are presented to illustrate the capabilities and the applications, present or future, of this instrument.

The aim of the instrument is to contribute to a better description of the organic fraction of aerosols at single particle level as a function of time with the aerosol mass spectrometry technique. The authors apparently orient, on the long term, the mass spectrometric approach to laser soft desorption ionization (L2DI with R2PI or SPI) that has the advantage of limiting considerably the molecular fragmentation what is of particular importance for speciation studies. Single particle laser mass spectrometry, even after almost 2 decades of development, is still hindered in its potential by sample fragmentation and modification, reproducibility and mass spectrum variability issues. Thus any progresses to access reliably molecular speciation of organic molecules in aerosol (single) particles will benefit the community. Molecular speciation, in particular, is needed to better understand chemical and physical processes that let the aerosol particle properties and composition evolve with time and its reactivity towards its environment.

By taking the example of an anthropogenic SOA system. (indene+O3) that was also investigated with another more conventional technique, the authors can, only supported with their own observations, evaluate in which extent their instrument allow the or-

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ganic speciation. The manuscript lets sense that the authors probably have a long term plan/project to specialize their instrument to organic molecule speciation in single particles and target very specific aerosol system (SOA from aromatic precursors).

On the technical aspects, some corrections of the English style are required. More frequently the choice of the vocabulary would gain to be better chosen and some phrases also need to be reformulated to avoid unambiguity and for clarity purposes (see Technical corrections for details)

The choice of references is globally fine. However at some other places, references are needed to strengthen the author points (for example for paragraph p.4182, line 13-21, p. 4188, line 6-12, see section of specific comments for details). Indeed although the SPLAM setup has been newly brought into operation and this is the first publication of this group about this instrument, the authors can support their own findings with some existing references.

Figures can be completed with more labels, in particular scale and orientation axes. The details are listed in the subsequent sections.

Considering this, I support this manuscript for publication in this journal with the suggested modifications.

Specific comments

p. 4167, line 13-14: please precise that the LDI process in this study is performed in one step. It will make clear that the desorption proceeds also via the same laser.

p. 4167, line 17: express also 0,85 attograms in SI, give a representative number of molecules

p. 4167, line 20: define "global hit rate“

p. 4168, line 3: references can be strengthen, Hallquist et al., 2010 for example

p. 4168, line 11: can you add some adjectives or examples that illustrate in which

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sense it is “difficult to describe” the organic aerosol (elemental composition, speciation, reliability, variability of the measurement)

p. 4168, line 18: the reference of Cocker et al., 2001 is quite old. Since a lot of groups put efforts on better describing the organic fraction these last years, some more recent references are welcome.

p. 4169, line 20 : "impact, and several m/z could be scanned at a time using an ion trap mass spectrometer“. It gives the impression that instrument from Jayne et al., 2000, Drewnick et al., 2005, ... can not give complete mass spectrum and that only ion-trap do. It is suggested to reformulate.

p. 4169, line 28 : "two detection lasers“: You can also write 2 laser beams since the most important is that the particles cross successively 2 laser beam. Similar setup using a single laser whose beam is splitted can do the same job.

p. 4170, line 8: the references all pointing to the group of Prather could be completed by some references pointing to other groups as you did in p.4170, line 20-23. It would be fair since the group of K. Prather was not the only one to start that early with this technique, you mentioned Hinz et al., 1994 ...

p. 4170, line 11: The acronym LDI is here defined. Maybe it is a good thing to stress that LDI here refers to “one-step LDI” exclusively since the acronym L2DI is also used and is also “technically” a LDI in the broad sense.

p.4170, line 15: you may replace the word "solid“ by "particulate phase“ or "condensed phase material“ since studies involved either solid or liquid particles.

p. 4171, line 10-15: It would be fair to mention here the work of the group of Reilly and Whitten (Lazar et al., 1999). Eventually the recent work of A. Zelenyuk’s group can also be mentioned here as well.

p. 4171, line 25: Here it would be a good thing to indicate clearly that the SPLAM instrument performed the single particle analysis via a one-step laser desorption ionization.

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It is not very clear otherwise.

p. 4172, line 9: please tell what very compact means here. For example tell in which box dimension you can pack the SPLAM (aerodynamic lens, inlet body and ToF-MS). Since miniaturization of such instrument is a permanent goal, people would be interested to know how compact is the SPLAM.

p. 4174, line 14: "These cw laser beams are spaced by 41$\pm$0.5mm". Is it possible to precise the reasons of this choices ? (geometry of the system or electronic reasons).

p. 4175, line 1-2: "According to Mie theory, the maximum of scattered light is in the forward direction, independent of wavelength.". Please try to relate more this sentence to the previous one to strengthen the choice of the PMT orientation.

Paragraph 2.2.1: Is it possible to precise in this paragraphs how the different lasers beam are technically and materially positioned ?

p. 4176, line 2 : the variable topt refers in the paper to "transit time, travel time and to residence time". Please choose one and keep it. The word residence time for topt is quite misleading.

p. 4176, line 21-27: Please explain more in details the way the SPLAM DE is defined. In particular, does it include the fact that SPLAM DE accounts only for the number of particles that cross at least the laser beam L2 OR both laser beams L1 AND L2 ? Since it is indicated that the number of particles crossing the laser L1 and L2 is different, it seems necessary to precise this point.

p. 4178, line 1-2: "our TOF-MS will exclusively detect compounds from the aerosol phase.". Please precise "with the current ionization method" or equivalent. With EI ionization, ion signal from air components will be detected.

p. 4178, line 9: what is meant here with "off-focus" ?

p. 4179, line 22: maybe it is necessary to mention "optimal spatial and time overlap"

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since the Excimer laser must be triggered at a very defined time.

p. 4180, line 10: "residence time topt". See comments for p. 4176, line 2 :

p. 4180, line 24: "recorded". It appears necessary to precise in the paper if it is planned (or not) at some point to record the "topt time" with the corresponding mass spectrum. The power (and great interest) of this technique is not only to get mass spectrum of single particles but also to investigate the particle composition size dependency. Please precise clearly this point and mention it either here or in the conclusion. This is a very important.

p.4182, line 3: "travel time". See comments for p. 4176, line 2.

p.4182, line 13-21: "with the photon ...of different size". Here are some critical points that the authors address carefully. The authors would benefit significantly in trying to support/illustrate more their claims (as listed below):

variability of the mass spectra due to the laser power variation over time (p. 4182, line 15-16), "peak intensity variation" associated with the DOP particle size variation (p. 4182, line 17-21), "Differences in signal intensity can be interpreted in terms of different particles sizes." (p. 4186, line 7-8), "particles of different size could give different fragmentation pattern " (p. 4190, line 2-4), "This is significant since we are convinced that LDI of single chemical substances present in the aerosol phase always yield approximately the same mass spectra with our experimental set-up (see Sect. 3.1)". (p.4186, line 12-15)

References would illustrate/support, here, the fact that the mass spectra variabilities is not an artifact specific of the SPLAM instrument but of the technique. It will also give more credits to the author claims in the rest of the manuscript in particular when they address the pertinence of the results and the possibility to access speciation. It seems necessary knowing that though the particle size can be inferred with the SPLAM instrument in the current state, it is not recorded along the the mass spectrum. Thus

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relationship “particle size – composition – mass spectrum pattern/variability” can only be addressed using conditional tense. Since the authors mention these aspects, some references on this aspects are welcome.

Indeed, the question of the variability of the mass spectra in single particle aerosol mass spectrometry (which depends on many factors (laser energy incident on the particles, particle size and composition, ...) is critical for this technique. The mass spectrum variability is a major drawback and limiting factor of this technique. Since the technique is operated since almost 2 decades, many studies addressed these aspects.

It is strongly recommended to authors to take advantages of these studies (and citing them) and strengthen thereby their manuscript accordingly.

p. 4182, line 22-23: Add some supporting elements/arguments, if available, would strengthen the claim.

p. 4182, line 29: It may help the reader to add the EI-MS mass spectrum in figure 7. to ease the comparison

p. 4183, line 2-10: It is not certain that these lines bring something valuable for the reader. The comparison with the EI-MS is valuable since NIST EI-MS are standard comparison material and it is good to know if the mass spectrum from obtained with LDI is coherent / comparable with comparable technique. The lines 2-10 appears to be a start of explanation of the physics of the ionization processes that, if interesting, deviates from the topic of the manuscript. Unless the authors have major reasons to keep it, removing this point will not affect the content of the manuscript.

p. 4183. line 15-16 : It is strongly suggested to the authors to be coherent and propose references concerning the different "other single particle aerosol mass spectrometers“ they refer to. One reference sounds poor.

p. 4184, line 27: Add "size“ to "distribution“

p. 4185, line 25 – p.4186, line 3: Since these lines refer to the text p. 4183, line 2-10:,

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the authors may consider to remove it unless they have a specific point to make. If yes, the point must be clearly mentioned and argumented.

p. 4186, line 7-8: the sentence "Differences in signal intensity can be interpreted in terms of different particles sizes." It probably refers to the text p.4182, line 13-21: but according to the authors, the SPLAM do not record topt (and as a result the particle size) with the corresponding mass spectrum. Since there is no experimental data from this work to support this, the authors should precise what make them suggest this, add references or remove this statement since it does not affect the content of the paragraph 3.2.3. Please consult comment for p.4182, line 13-21

p. 4186, line 13-15: " this is significant ... with our experimental setup": It is suggested to the authors to be careful with this statement and use/adapt it according to the remarks for p.4182, line 13-21

p. 4186, line 15-17: "We can thus expect that specific molecules present in the aerosol phase will always leave the same typical fingerprint which could be used, in principle, for molecular speciation.". If the authors do not have experimental data for other pure organic aerosols, they may here add references that support their claim since the presented data in the manuscript do not support this.

p. 4188, line 6-12: It is not straightforward to understand why the authors mention studies with AMS Aerodyne instrument at this stage. It would make more sense to do it at the end of the same paragraph after comparison attempts with the work of Huang et al., 2007. Hence, before the conclusion, it will highlight more the advantages of the SPLAMS compared to the AMS. It is surprising that the authors did not looked for comparison elements with aerosol mass spectrometers using one-step LDI at 248 nm. The work of Rodgers et al., 200 from Reilly's group may be provide elements ....

p. 4188, paragraph 3.2.4, line 12-28: If data are available in the paper of Huang, 2007 , it could helpful for the readers to report the fraction of mass spectra showing a significant signal at high m/z ratio (upon the authors criteria) to ease comparison.

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p. 4188, line 1-2: "to be less problematic compared to a thermal desorption AMS“. It is suggested to develop what is meant here by “problematic“.

p. 4189 line 14-15. "The optical detection limit in terms of particle size was determined to be at 100nm approximately. The two-fold optical detection efficiency DE is measured to be 0.4% at daev =10nm and 74% at daev =350 nm.“ The close mention of 100 nm and 10 nm may be confusing. Maybe there is a way to avoid confusion.

p. 4189, line 19-20: see comment for p.4178, line 1

p. 4190, line 2-4:. It is not clear from which “under LDI conditions” the authors are referring to. In the discussion of the results of the analysis of the indene ozonolysis induced aerosol , there are no elements justifying/suggesting this point. Please consult comment for p.4182, line 13-21 and modify this sentence accordingly.

p. 4190, line 8: please precise the similarities that were found (i.e. Small fraction of mass spectra with ions of large m/z ratios, ions of identical m/z ?).

p. 4191, line 6: "Different chemical sub-groups of single particle MS could still be identified in parallel.“ What is the meaning of parallel ?

p. 4191 Conclusion: In the conclusion different works directions are listed without giving to the readers a clear idea on the immediate future development of the SPLAM instrument. The authors report the need of “more statistics”, the unrecorded particle size for each mass spectrum, the variability of the mass spectra, the “high potential” of the SPLAM, the use of SPI or L2DI. The reader may be confused.

Technical corrections

- Grammatic

general: expression use rather "permit/allow + name“ than "permit/allow to + verb“ (p. 4171, line 7, p. 4173, line15, p.4190, line 16-17

p. 4167, l. 6: replace by: "realized by using“

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p. 4168, line 20: replace by "for the analysis“

p. 4171, line 16: reformulate: "can be achieved yielding“

p. 4177, line 21-22: Cut the word "analyzers“ between "y“ and "z“

p. 4183, line 20: "In these cases,“ can be replaced by "For these cases“

- Reformulate or complete more clearly:

p. 4167, line 22-23: "particles, and most of the detected mass peaks are attributed to oxidized products of indene“. What is mass peaks ?

p. 4167, line 25: "known to impact on human“. Please reformulate.

p. 4169, line 27: "perpendicularly crossed to the particle beam". It is ambiguous. Please reformulate.

p. 4172, line 24-25: "(3) acceleration of particles to a specific speed in function of their diameters“. It is needed to be reformulated. It is misleading and it masks the principles upon which particles can be aerodynamically sized.

p. 4173, line 4-5: "spacers. Note that these orifices can be exchanged if different lens properti μm critical orifice (Microcontrole) into the aerodynamic lens.“. Please correct or complete this sentence.

p. 4173, line 20-21: "MS (20 cm downstream the accelerating nozzle).2. Try to merge it with the previous sentence or reformulate. The current version is misleading.

p. 4174, line 4 : "One way to provide improved size information is achieved by incorporating a two-laser particle velocity measurement as implemented in the SPLAM instrument.“ . Please reformulate.

p. 4175, line 11: "light generates a signal to the first PMT“. Please reformulate.

p. 4176, line 9-12: please rephrase more clearly these line "using counting DOP . . ..optical characterization (Sect. 2.2.3).

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p. 4180, line 22-23: please rephrase this sentence since it is quite misleading for the readers not familiar with this technique. "rate. In its current state, the synchronization of the SPLAM instrument allows the laser triggering from topt determination“

- Vocabulary

General: watch your writing when speaking about the ion mass to charge ratio: one speak of “m/z value”, “m/z ratio” and not “mass”. Please consider the remark for the next expressions located at: p. 4167, line 22 : “detected mass peaks” p. 4170, line 15: "independent of mass“ p. 4186, line 23: "The m/z mass of“

p. 4167, line 18: "functioning of the instrument“. Please find an other word for “functioning”

p. 4168, line 29: the word "region“ is not always appropriated. For example p.4168, l. 29, authors speak of sizing region“ as part of the instrument. Maybe word like: "unit“,“device“,equipment“ would be more appropriate

p. 4170, line 3: " by mass spectrometry“ can be replaced "by a mass spectrometer“. Actually the detector is a mass spectrometer.

p. 4172, line 5, line 8: see comment for p. 4168, line 29:

p. 4173, line 26: the word "extension“ should be replaced. It is not clear what is meant here.

p. 4173, line 22: "particle traveling“. This expression be exchange by a more appropriate one. For example "particle flight“

p.4176, line 6 : replace "avoid coincidences during" by "avoid coincidence events during“

p.4176, line 13: Be careful with the vocabulary choice. It does not fit together: "The particle velocity variability observed for the smaller aerodynamic diameters can“.

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p. 4189, line 6 and 14: "two-fold optical detection“. Maybe it exists a more appropriate expression for this.

p. 4189, line 17: replace by "one step laser desorption/ionization (LDI).“ remove the word “particle”.

p. 4190, line 11: what is the difference for authors between "statistics“ and "larger number of mass spectra“ ?

Comments on figures

Fig. 1: Maybe locating by a letter or number the different processes in the picture can help the reader. For example: Particles are focused by an aerodynamic lens system (a), ... (b), ...(c)

Fig. 2 and Fig 3. Please add a frame (O,x,y,z) and corresponding scale

Fig 4. Add the y-legend to plot a and c

Fig 6. Maybe add typical values of topt, trig and explain to what the HV impulsions relate to (delayed extraction ?)

Fig 7 Add the total numbers of taken mass spectrum used for the plot and specific the particle size range. There is a mistake at the end of the legend text: mass peak identifications (no "s“ for "peaks“). Maybe add the NIST MS of DOP above Fig 7b

Fig 8: Even though the information may be in the text body, precise in the text the evolution trends of the particle size and which curves correspond to the experiment start and to the experiment end.

Fig 9 – 10 please specify the number of particles for each group 1 and 2

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