Letter to the editor addressing comments of referees 1 and 2
by F. Gaie Levrel on behalf of the authors.

Development and characterization of a single particle laser ablation mass spectrometer (SPLAM) for organic aerosol studies

by François Gaie-Levrel, Sébastien Perrier, Emilie Perraudin, Christoph Stoll,
Noël Grand, and Martin Schwell

Atmos. Meas. Tech. Discuss., 4, 4165–4208, 2011
www.atmos-meas-tech-discuss.net/4/4165/2011/

General comments of the authors to both referees:
We thank both anonymous referees for careful reading of the manuscript and detailed remarks. The principal criticism of referees 1 and 2 concern our conclusions drawn from observed differences in the single particle mass spectra, in the sense that these reflect real chemical differences of the particles. Unfortunately, at the moment, we do not have sufficient experimental material in terms of statistics to support this claim. Also, the *associated* recording of size and single particle mass spectra is not yet implemented in the SPLAM instrument.
We therefore substantially revised section 3 and the conclusion of the manuscript. In a first paragraph (3.1.1), we point out and discuss the variability of the observed DOP single particle mass spectra. The reasons for this observation, mainly inherent to the methodology of LDI, are now clearly stated and explained (see pages 14/15 of the revised manuscript). We finish this paragraph with the conclusion that interpretation of LDI single mass spectra of chemically complex aerosols has to be done with extreme caution, but that nevertheless qualitative chemical analysis should be possible since single particle DOP mass spectra resemble grossly the EI-MS found in MS data bases.
In the following paragraphs of section 3, all too speculative statements and uncertain conclusions have been cut, especially those with respect to the discussion of single particles MS of indene SOA. In this sense we follow the suggestion of referee 2 to take out the too speculative discussion on chemical difference of SOA particles.
The conclusion has been revised in this sense too. Some other paragraphs of the conclusion have been cut for clarity and in order to avoid confusion.
Since the important part 3 of the manuscript is completely revised, we submit the revised manuscript together with the comments presented in this letter, because it will probably be more easier for the associated editor to follow the philosophy of the revision we propose.
Our comments to the more specific and technical remarks of the referees are listed in the following.

Author's comments (in green) to the specific comments of referee 1 (in black)

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.
This was specified in the revised manuscript.

p. 4167, line 17: express also 0,85 attograms in SI, give a representative number of molecules
Attograms were changed to 10^{-15} kg and the corresponding number of molecules was added in the text.

p. 4167, line 20: define "global hit rate“
“Global hit rate” was changed to “effective hit rate” as defined in section 3.1.3.

p. 4168, line 3: references can be strengthen, Hallquist et al., 2010 for example
This reference was added in the text.

p. 4168, line 11: can you add some adjectives or examples that illustrate in which sense it is “difficult to describe” the organic aerosol (elemental composition, speciation, reliability, variability of the measurement)
It was specified in the text that *“OA is indeed composed of a complex mixture of compounds with a wide range of polarity, functional groups, molecular weight… and present at trace levels”*.

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.
A few more recent references were added here:

-
- **Chiappini,** L., Perraudin, E., Durand-Jolibois, R., and Doussin, J. F.: Development of a supercritical fluid extraction-gas chromatography-mass spectrometry method for the identification of highly polar compounds in secondary organic aerosols formed from biogenic hydrocarbons in smog chamber experiments, Anal. Bioanal. Chem., 386, 1749–1759, 2006.
- **Hamilton**, J. F., Lewis, A. C., Carey, T. J., and Wenger, J. C.: Characterization of polar compounds and oligomers in secondary organic aerosol using liquid chromatography coupled to mass spectrometry, Anal. Chem., 80, 474–480, 2008.
- **Gómez-González**, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, J. Mass Spectrom., 43, 371–382, 2008.

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, ... cannot give complete mass spectrum and that only ion-trap do. It is suggested to reformulate.
This misleading phrase has been modified for the sake of clarity as: *“Thereafter, Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS) (Hoffmann et al., 2002) has been used as a soft ionization technique”*

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.
This was corrected in the text.

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.
Two other references (“Hinz et al., 1994” and “Weiss et al., 1997”) were added.

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.
It was specified at that point that LDI refers to “one step”. It was also mentioned further in the text that LDI refers in the whole manuscript to one-step laser desorption/ionization process only.

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.
Correction has been made in the text.

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.
The suggested reference (Lazar et al., 1999) was cited but not Zelenyuk et al.

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. It is not very clear otherwise.
It was clearly specified that SPLAM instrument proceeds with a one-step LDI.

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.
The adjective "compact" was removed and dimensions of the set-up were provided : *"The TOF-MS with its aerosol inlet is mounted on a scientific table with rolls (WxL=0.6 x 1 m; H = 2,5m) and can be moved easily."* It was also clarified further in the paragraph that "*The present configuration is suitable only for laboratory use, not in the field".*

p. 4174, line 14: "These cw laser beams are spaced by 41±0.5mm". Is it possible to precise the reasons of this choices ? (geometry of the system or electronic reasons).
The following sentence was added for a better understanding : "*This distance was imposed by the optomechanical elements used for laser beam introduction into the detection chamber: Microbench elements (Linos), integrating a glass window, are fixed directly to the detection chamber (not shown in Fig. 3). The two lasers themselves are placed outside the vacuum system on the 1.2 x 2.2m optical table where also...."*

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.
The paragraph was reformulated in this sense as : *"According to Mie theory, the maximum of scattered light is in the forward direction, independent of wavelength. That is why the two photomultiplier tubes (PMT, Photonis, model XP2930), used for the detection of scattered light from the particles, are placed at an angle of 34° with respect to the forward direction of the laser beams. As can be seen in Figure 3, mechanical constraints do not permit to set the PMT even closer to the laser beam in our configuration since the PMT have circular active areas of ∅=23 mm and are placed at 37 mm distance only from the particle/laser intersection zone, in order to cover a maximum solid angle*"

Paragraph 2.2.1: Is it possible to precise in this paragraphs how the different lasers beam are technically and materially positioned ?
This should be clear now by taking into account our comment/text modification for the p. 4174, line 14 remark of referee 1.

p. 4176, line 2 : the variable t_{opt} 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.
We choose "transit time" and this was corrected in the whole article.

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.
This point was precised by adding the following sentence : *"This means that SPLAM DE takes into account the number of particles that cross both laser beams L1 and L2 since a detection in L2 position necessarily implies a detection in L1. Different reasons may explain the observed higher L1 count rate...."*

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.
We add *"during sampling"* after *"detect compounds from the aerosol phase".*

Author's comment: In fact we do not completely agree with the referee's suggestion for modification (....*"with the current ionization method"*)'. We agree that with EI ionization, *background* air (due to the base pressure of the machine which is 10e-7 mbar)) would probably be visible. But during sampling, these background air signals would not be enhanced (in the case of EI ionization) because of our efficient differential pumping. This was proven by the toluene experiment depicted in the next phrase, since REMPI of toluene is a much more efficient ionization method (in terms of ionization cross sections) than EI ionization of N_2 or O_2.

p. 4178, line 9: what is meant here with "off-focus" ?
We reformulated as: *"off the focal point"*.

p. 4179, line 22: maybe it is necessary to mention "optimal spatial and time overlap" since the Excimer laser must be triggered at a very defined time.
This was added in the text.

p. 4180, line 10: "residence time topt". See comments for p. 4176, line 2 :
This was corrected in the text.

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.
The end of the paragraph was reformulated as: *"In the current state of SPLAM, t_{opt}, associated with the single particle mass spectrum, is not recorded yet. This has to be programmed in the future on the FPGA card, in order to investigate the particle composition size dependency and fully exploit the scientific potential of SPLAM's single particle measurement capacity."*

p.4182, line 3: "travel time". See comments for p. 4176, line 2.
This was corrected in the text.

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)
Section 3 of the paper has been completely revised due to serious criticisms of the two referees concerning conclusions drawn by us from the measured DOP and SOA single particle mass spectra (please see revised version which is also submitted).
In a first paragraph (3.1.1) we point out the apparent difficulties in interpreting single particle LDI mass spectra, in connection with the variability of the observed DOP single particle mass spectra. The reasons for the variability, inherent to the LDI method, are now clearly stated and explained (see pages 14/15 of the revised manuscript). We finish this part with the conclusion that interpretation of LDI mass spectra of real aerosols has to be done with extreme caution, but that nevertheless, qualitative chemical analysis should be possible since single particle DOP mass spectra resemble grossly the EI-MS found in MS data bases. In the following, all too speculative statements and uncertain conclusions have been cut, especially with respect to the discussion of single particles MS of indene SOA. The conclusion has been revised in this sense too.

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 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.
See our comment with respect to p.4182, line 13-21.

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.
See our comment with respect to p.4182, line 13-21. We added also the following: *"We also note that charge transfer processes occurring in the ablation plume depend on the aerosol matrix, and therefore on the chemical nature of the particles which thus is expected to influence the fragment ion intensity ratios observed in the LDI mass spectra. These effects can be minimized using L2DI where desorption and ionization are separated. These effects have been discussed, for example, by Lazar et al. (1999) and work cited there."*

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

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

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.
This paragraph was removed almost completely. We just say that m/z 279 is a striking difference between EI-MS and LDI-MS suggesting that a little more internal energy is released to particles by LDI in our conditions, as compared to EI ionization.

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.
Another reference was cited here (“Zelenyuk et al., 2005”).

p. 4184, line 27: Add "size“ to "distribution“
This was added in the text.

p. 4185, line 25 – p.4186, line 3: Since these lines refer to the text p. 4183, line 2-10:, 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.
This sub-paragraph has been removed.

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 t_{opt} (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
The sentence *"Differences in signal intensity can be interpreted in terms of different particles sizes.“* has been removed since it is too speculative and not corroborated by experimental data.

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
See comment on referee comment on p. 4186, line 15-17 (just below).

"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.
This paragraph has been cut and a new paragraph has been added, with much more cautious statements:
"From figure 10, one can easily notice that the obtained mass spectra of the second group do not resemble to each other. In principle, these differences could originate from real chemical difference of the particles. Since current understanding of SOA formation implies dynamic mechanisms of enrichment/depletion processes due to evaporation and condensation of compounds of different saturation vapor pressure (see for example Hallquist et al., 2009), chemical composition differences are expected to depend mostly on size. As has been discussed above, the LDI process itself yields a certain variability of mass spectra. The dependence of LDI fragmentation patterns on particle size could in principle be wiped out by classifying the observed mass spectra additionally by particle size (which is not possible yet with our experimental setup). The dependence of LDI fragmentation patterns on the chemical nature of SOA condensed phase matrix is, as discussed above, uncertain. Therefore, in the absence of size resolved MS measurements and more statistics, we cannot conclude on the detection of further chemical sub-groups among group 2 particles."

We were in fact convinced by the two referees that the so far obtained experimental data do probably not permit conclusions on chemical differences of the observed indene SOA particles.

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 ....
This refers to paragraph 3.2.4 (Discussion of the first results of SPLAM). This paragraph has been substantially revised too. Please see in the text of the revised manuscript (pages 20/21). The confrontment of our results with AMS studies has been moved at the end of section 3.2.4, and reformulated. Our work is also compared now to results the study of Narukawa et al., 2007. However, it is not useful to compare our results to the work of Rodgers/Reilly et al., 2000 because their work concerns combustion type aerosols: This is explained in the text too (page 21).

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.
This kind of data are not available in the work of Huang et al. 2007, unfortunately.

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“.

This phrase has been removed.

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.
This was a type setting error by the editor. The right sentence is: *“The optical detection limit in terms of particle size was determined to be at 100 nm approximately. The two-laser optical detection efficiency DE is measured to be 0.4 % at* d_{aev} *= 100 nm and 74 % at* d_{aev} *= 350 nm.”*

p. 4189, line 19-20: see comment for p.4178, line 1
As mentioned before, it is clear to us that the SPLAM instrument only sees particulate phase compounds due to efficient differential. See our comment on the referee comment on p. 4178, line 1-2.

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.
This paragraph has been revised. LDI conditions mean 1.4 Wcm^{-2} irradiation power density at λ = 248nm. This clarification has been added to the text.

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 ?).
This has been clarified.

p. 4191, line 6: "Different chemical sub-groups of single particle MS could still be identified in parallel.“ What is the meaning of parallel ?
The related paragraph has been cut to reduce confusion (see next remark of Referee 1)

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.
The last part of the conclusion has been revised in order to be clearer in terms of perspectives and avoid confusion. Some aspects have been cut. Please refer to the text of the new revised manuscript.

Technical corrections of referee 1

- **<u>Grammatic</u>**

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

p. 4167, l. 6: replace by: "realized by using“
This is corrected in the text.

p. 4168, line 20: replace by "for the analysis“
This is corrected in the text.

p. 4171, line 16: reformulate: "can be achieved yielding“
This is corrected in the text.
p. 4177, line 21-22: Cut the word "analyzers“ between "y“ and "z“

This is a mistake from the editor.

p. 4183, line 20: "In these cases," can be replaced by "For these cases"
This is corrected in the text.

- 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 ?
This is corrected in the text.

p. 4167, line 25: "known to impact on human". Please reformulate.
This is corrected in the text as *"Atmospheric aerosols are known to have a large impact on human health"*.

p. 4169, line 27: "perpendicularly crossed to the particle beam". It is ambiguous.
This is corrected in the text as: *"They are perpendicularly aligned to the particle beam"*.

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.
This is corrected in the text as : *"the possibility for each single particle to obtained its aerodynamic diameter from its velocity (small particles are accelerated to higher velocities than large particles)."*

p. 4173, line 4-5: "spacers. Note that these orifices can be exchanged if different lens properti □m critical orifice (Microcontrole) into the aerodynamic lens.". Please correct or complete this sentence.
This is a type setting error. A part of the phrase was cut.

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.
This is corrected in the text as: *"Up to the ion source of the TOF-MS (20 cm downstream the accelerating nozzle), the theoretical particle beam diameter is calculated to be smaller than 1 mm."*

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.
This is corrected in the text as: *"One way to provide improved size information is to use a two-laser particle velocity measurement as implemented in the SPLAM instrument."*

p. 4175, line 11: "light generates a signal to the first PMT". Please reformulate.
This is corrected in the text as: *"the scattered light is detected by the first PMT"*.

p. 4176, line 9-12: please rephrase more clearly these line "using counting DOP ….optical characterization (Sect. 2.2.3).
This is corrected in the text as: *"Using counting of size-selected DOP particles, the calibration measurements provided a detection limit of* d_{aev} *= 100-110 nm (see section 2.2.3)"*.

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"
This is corrected in the text as: *"In its current state, the appropriate time to fire the excimer laser pulse, used for the one step particle desorption/ionization, is calculated from the transit time* t_{opt}*."*

- **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 18: "independent of mass“ p. 4186, line 23: "The m/z mass of“
This is corrected in the text.

p. 4167, line 18: "functioning of the instrument“. Please find an other word for “functioning”
This is corrected in the text as *“operation”*.

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
This is corrected in the text as *“device”*.

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

p. 4172, line 5, line 8: see comment for p. 4168, line 29.
This is corrected in the text as *“device”*.

p. 4173, line 26: the word "extension“ should be replaced. It is not clear what is meant here.
This is corrected in the text as *“separated by”*.

p. 4173, line 22: "particle traveling“. This expression be exchange by a more appropriate one. For example "particle flight“
This is corrected in the text as *“in the particle beam direction”*.

p.4176, line 6 : replace "avoid coincidences during" by "avoid coincidence events during“
This is corrected in the text.

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“.
We do not understand the referee remark here.

p. 4189, line 6 and 14: "two-fold optical detection“. Maybe it exists a more appropriate expression for this.
This is corrected in the text by *“two-laser”*.

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

p. 4190, line 11: what is the difference for authors between "statistics“ and "larger number of mass spectra“ ?
The term “statistics” is of course related to a large number of mass spectra and also to the appearance frequency analysis done by Huang et al. (2007).

Comments by referee 1 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)
This is added in Fig.1

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

Fig 4. Add the y-legend to plot a and c
This is added in Fig.4

Fig 6. Maybe add typical values of topt, trig and explain to what the HV impulsions relate to (delayed extraction ?)
This is added in Fig.6. We do not indicate typical values of topt, trig to not confuse the reader.

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
This is added and corrected in Fig.7 and in its caption.

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.
This is added in Fig.8

Fig 9 – 10 please specify the number of particles for each group 1 and 2
This is added in the caption of Fig.9 and 10.

Author's comments (in green) to minor comments of referee 2 (in black)

page 4172 “: : : as function of their diameter: : :”
The word *"in"* has been replaced by *"as"*.

page 4178 “: : : sensibility: : : “ ?? (better sensitivity ?)
We use the term *"sensitivity"* now.

page 4184 “: : : 4 x 10ˆ3 to 1 x 10ˆ3 : : :” ????
Correct symbols are used now.

page 4184 “As for DOP experiment, : : :.” The whole sentence is very difficult to understand. Please rephrase, perhaps by using several shorter sentences.
This sentence has been simplified and rephrased.