AMT-2021-271

Design, characterization, and first field deployment of a novel aircraft-based aerosol mass spectrometer combining the laser ablation and flash vaporization techniques

Hünig et al.

Replies to the comments by Dr. Nicholas Marsden, Referee #3

General Reply:

First of all, we would like to thank Dr. Nicholas Marsden from the University of Manchester for reviewing our manuscript and for his helpful comments to improve it. In the following we will comment on the individual points.

The reviewer comments are written in this font style and color.

Our answers are written in this font style and color.

Changes to the revised version of the manuscript are printed in red.

The authors present the design and development of a mass spectrometry system for comprehensive measurement of aerosol composition, in which two commonly used techniques, single particle mass spectrometry (SPMS) and aerosol mass spectrometry (AMS) are combined in a single tandem instrument. The manuscript represents a substantial body of work that required considerable expertise in instrument design including differential pumped vacuum systems, optical particle detection and time-of-flight mass spectrometry (TOFMS). A substantial amount of data is presented to evaluate the instrument design. The subject matter is very suitable for this journal but some important issues need to be addressed in the content if this manuscript is to be used as an instrument characterisation reference for future publications.

Major Comments

Both instrument use TOFMS as an analyser. This should be introduced and the benefits explained.

We included a short introduction of the TOFMS technique in Sect. 1 and refer to the rich literature on this topic:

"For single particle analysis by the LDI method, a Time-Of-Flight Mass Spectrometer (TOFMS) is a suitable choice, because in this way a full bipolar mass spectrum of a single particle can be recorded (Hinz et al., 1996). The trigger signal for firing the laser pulse that causes the ionization of the particle can be used as the trigger of the TOFMS. Thereby, the ions are separated from neutral molecules in less than a microsecond, preventing further reactions between ions and molecules as for example in an ion trap mass spectrometer (Fachinger et al., 2017). For the TD-EI technique (Aerodyne AMS), a quadrupole mass spectrometer was used in the beginning (Jayne et al., 2000) until it was replaced by TOFMS (Drewnick et

al., 2005; DeCarlo et al., 2006). The advantages of the TOFMS are higher m/z resolution, higher sensitivity and thereby lower detection limits compared to the quadrupole technique (DeCarlo et al., 2006). Additionally, the TOFMS makes it also possible to perform single particle analysis using thermal desorption technique, provided an optical triggering of the detected particles (Cross et al., 2009; Freutel et al., 2013). Furthermore, TOF mass spectrometers are compact and rugged (Noble et al., 1994)."

They both also use aerodynamic lens inlet. The main difference is with the ionisation techniques employed to achieve the desired measurement. The pros and cons to each technique and the consequences on the data should be developed in the introduction. Both techniques are hard ionisation that causes intense fragmentation that has to be dealt with in the data analysis. In the case of laser desorption ionisation (SPMS), this renders the measurements inherently non-quantitative for molecular ion species. The thermal desorption ionisation method used in the AMS method is only quantitative with careful calibration. The authors present some details of the mass calibration in terms or the relative ionisation efficiencies (RIE) of nitrate, sulphate, and ammonium using the same method used for the Aerodyne AMS family of instruments. This is where my first major concern with the work arises.

In various places throughout the document the authors state the ERICA-AMS is 'similar' in design to the Aerodyne AMS, but the similarity is not described nor are the differences. In fact, no detailed description of the vaporiser, ioniser and ion extraction optics is given. The Thermal Desorption ionisation technique (TDI) is not well understood and Quantitative nature of the Aerodyne AMS instrument is underpinned by a large body of publications and method development (See Jimenez 2016 and references therein). If the authors wish to convey these characteristics onto their instrument, they need demonstrate equivalence in the design, particularly regarding the geometry of the ionisation source and the incident particle beam.

Vaporizer, ioniser and ion extraction, as well as the C-ToF mass spectrometer are exactly the same as in the commercial C-ToF-AMS, ToF-ACSM and miniAMS. The details are described in Drewnick et al. (2005), Canagaratna et al. (2007), and Fröhlich et al. (2013).

There are two marked differences: The use of a shutter unit instead of a chopper and a longer particle flight path between aerodynamic lens exit and vaporizer. In the ERICA AMS, quantification is given in the same way as in the commercial AMS, since the shutter performs the same function as the chopper in the AMS.

The corresponding paragraph was revised (including revisions due to other reviewer comments).

"During the idle time of the Nd:YAG laser particles remain unablated, even if they are successfully detected by the units PDU1 and PDU2. This actually is by far the largest fraction of the sampled particles emerging from the ADL. If, for example, the ambient number density of particles with diameters above the detection limit is 100 cm^{-3}_{Std}, then, at most only 5.4 % (8 shots per second and sampling volumetric flow rate of 1.48 $cm^3\ s^{-1}$) of the detectable particles are hit by the laser. Second, particles for which the calculation of the trigger failed continue their travel towards the ERICA-AMS vaporizer. Third, particles that primarily consist of materials that are transparent at a UV wavelength of 266 nm, such as pure sulfuric acid, are hard to ablate (Murphy, 2007). We selected a UV laser with 266 nm wavelength due to smaller

dimensions and the fact, that chemical substances show less fragmentation compared to ablation with shorter wavelengths (Thomson et al., 1997). In general, however, it is also possible to implement excimer lasers operating at shorter wavelength to ablate pure sulfuric acid droplets. Also, pure sulfuric acid is detected by the ERICA-AMS."

was changed to (Numbers of sections refer to the revised manuscript)

"All particles which are not ablated in ERICA-LAMS (see Sect. 2.3) continue their flight towards the ERICA-AMS instrument part. The design of the ERICA-AMS is the same as the design of the commercial Aerodyne AMS, which is described in the literature (Drewnick et al., 2005; Canagaratna et al., 2007). However, a major difference to the commercial AMS is the use of the SU in the ERICA-AMS instead of a chopper and a longer particle flight path between the ADL and the vaporizer (see below). In the ERICA AMS, quantification is given in the same way as in the commercial AMS, since the shutter performs the same function as the chopper. The vaporizer, ionizer and ion optics, as well as the C-ToF-MS are identical to those in the commercial Aerodyne C-ToF-MS, ToF-ACSM, and miniAMS. The details are described in Drewnick et al. (2005), Canagaratna et al. (2007), and Fröhlich et al. (2013)."

This leads to the second point of major concern with this manuscript regarding the measurement/calculation the particle beam width. The method description is extremely difficult to follow in the current version of the document and it is impossible to get any sense of the error in the calculation. This needs to be addressed. The authors use a method in which the particle beam is tracked across optical detection system which is kept static, in a very similar method to that presented in Marsden 2016 (not cited here) with the LAAPTOF single particle mass spectrometer, an instrument with many common features to the ERICA LAMS. The results are quite different regarding the ratio of particle beam and detection laser beam width compared to the LAAPTOF. This may be due to a superior quality aerodynamic lens, but the result should be discussed with respect to LAAPTOF and other instrument design as this is an important factor in instrument design.

(Numbers of sections and figures refer to the revised manuscript)

The approach of the ADL scan, which is similar to Marsden et al. (2016), was included in the description of the method in Sect. 3.1.1.: „ This approach, which is similar to the method reported by e.g., Marsden et al. (2016) and Clemen et al. (2020), is described by Molleker et al. (2020)."

Based on a comment from Referee #1, Sect. 3, which contains the basic method description, has been restructured. Therefore, the method should be better presented in the revised manuscript. Details on the method to determine the detection efficiencies for AN particles (carrying single or double electrical charges) are provided in the supplement (Sects. S5.2, S5.3, and S5.5). The calculations of the effective laser radii $r_{eff,L}$ for PSL particles (108 nm) and for AN particles (138 nm and 91 nm) are also provided in the supplement (Sect. 5.1). As described in Sect. 3.1.1, the alternative determination of $r_{eff,L}$ of the latter three measurements was necessary, because the losses between PDU1 and PDU2 seemed reasonable due to the particle beam divergence (Huffman et al., 2005).

The visibility of error bars in the graphs (Figs. 3, 4, 5, 6, 7, 8, 12, 14, 15, 16, S6, S7, S10, S13, S14, S15, S16, S17, S18, and S21) has been improved by using non-filled markers.

As mentioned in the captions of the figures (Figs. 3, 4, 5, S16, S17, and S18), the uncertainties of w_{part}, $r_{eff,L}$, $r_{eff,V}$, $S_{detect,L}$, $S_{detect,V}$, and $S_{ablation}$ (and $x_{0,shift}$, particle beam divergence α, and A_{scan}; latter three see Sect. S5.7 in the supplement) result from the curve-fittings (one standard deviation). The uncertainty of $r_{eff,L}$ for the PSL measurement with particle size of 108 nm was estimated to be 0.002 mm (PDU1) and 0.004 mm (PDU2) and the uncertainties of $r_{eff,L}$ for the AN measurements with particle sizes of 138 nm and 91 nm are conservatively estimated to be 0.009 mm at PDU1 and 0.014 mm at PDU2. These values are the approximated maximum uncertainties of $r_{eff,L}$ in the considered size range of 213 nm to 814 nm at PDU1 and PDU2. For the measurement with AN particles of 91 nm in diameter, the uncertainty of $r_{eff,V}$ was estimated to be 0.08 mm, since this was the maximum found for the measurements with AN particles at the vaporizer.

A comparison of ERICA with the LAAPTOF is a logical consequence, since ERICA consists of the basic framework of the LAAPTOF. However, the components that would justify a direct comparison have been replaced with components of a different design. For example, the ERICA contains a different critical orifice, a different ADL, a different optical detection unit (including ellipsoidal reflectors and a different ablation laser (including optics) than the LAAPTOF. The components remaining from the LAAPTOF (the vacuum chamber (including the four-stage TMP), the ADL adjustment mechanics, and the B-ToF-MS) were included in the text (Sect. 2.3):

„The ERICA-LAMS is based on the commercial LAAPTOF (Gemayel et al., 2016; Marsden et al., 2016). However, it had been thoroughly modified, so only the vacuum chamber (including the four-stage TMP), the ADL adjustment mechanics, and the B-ToF-MS remained."

Finally, I have concerns about the dynamic range of the ion detection system in ERICA LAMS. The A/D has only 8bits if vertical dynamic range which equates to 3 orders of magnitude within spectrum signal. This is insufficient in the reviewers experience and will either produce excessive saturation of intense ion signals or the complete loss of minor signals depending on the gain setting. Can the authors comment on this in section 3.5.2?

For each polarity (anions and cations) two channels record the amplified mass spectrometer signal. One channel with a small full range to cover mass spectra of low signal intensities and a second channel with a large full range to cover mass spectra, in case the small channel is saturated. Overall, all four channels are in use. For the cations Channel A is set to 200 mV and Channel B is set to 4 V. For the anions Channel C is set to 100 mV and Channel D to 4 V. During the evaluation, all mass spectra from each channel for small signals (Channel A for cations and Channel C for anions) are checked for saturation. In case a saturation is detected, the channel for large signals (Channel B for cations and Channel D for anions) is used for further evaluation. When no saturation is detected, the spectra from the channel for small signals are used. Both polarities are treated independently for each mass spectrum.

The text in P6 L30 (Sect. 2.4; Number of section refers to the submitted manuscript for review) was revised:

"The two MCP detector outputs for the anions and cations are conditioned and sampled concurrently by two separate channels with different input voltage ranges, an approach for extending the dynamic range of the A-to-D conversion."

was changed to:

"Each of the two MCP outputs, for the anions and cations, is conditioned and sampled simultaneously by two separate channels (two channels for cations and two channels for anions) of different input voltage ranges (full range: cations 200 mV and 4 V, respectively, anions 100 mV and 4 V, respectively), an approach for extending the dynamic range of the A-to-D conversion (Brands et al., 2011)."

Minor Comments

Take care to make accurate definitions upfront in the introduction, and then stick to those definition throughout the document.

We checked the entire manuscript for undefined terms and introduced the terms 'Laser Desorption and Ionization (LDI)' and 'Thermal Desorption and Electron impact Ionization (TD-EI)'.

Please check the correct use of commas throughout the document and avoid excessive paragraph length.

The manuscript was revised regarding the use of commas and the length of paragraphs.

The writing style changes part way through the document which is rather odd.

The manuscript was revised regarding the writing style.

Introduction

Page 1 ln 35 Chemical composition measurements can provide…

Done

Ln39 Comma after 'in situ' not required

Done

Page 2, Ln 1 Define the 'pulsed laser technique' as 'single particle mass spectrometry (SPMS)'

Reply:

LDI and SPMS were defined and the sentence was changed: "The first method uses a pulsed laser to vaporize and ionize individual submicron to micrometer sized particles by Laser Desorption and Ionization (LDI; Suess and Prather, 1999) for single particle mass spectrometry (SPMS)."

Page2, Line 5 the correct term is 'Thermal Desorption (TD)' and should be used throughout the document.

TD-EI was defined and the sentence changed to:
"The second method is based on the Thermal Desorption and electron impact Ionization (TD-EI) method, to quantitatively measure non-refractory species (sulfate, nitrate, ammonium, chloride, and organic compounds) in ensembles of particles (Drewnick et al., 2005)."

Page2, Ln8 This sentence is a little muddled. Maybe replace 'previous' with 'former'?

"previous method" was replaced by "LDI method"

Page2, Ln10 Froyd et al. (2019) demonstrates a method for quantifying particle classes, not absolute mass concentrations of specific ions. There is an important distinction.

"Within certain limitations this may become possible, if the data of other instruments are included in the analysis (e.g., in Froyd et al. (2019)).

was changed to:

„ Within certain limitations this may become possible, if the data of other instruments are included in the analysis (e.g., Ault et al., 2009; Healy et al., 2012; Gunsch et al., 2018; Köllner et al., 2021)."

Page2, Ln 11 Consider starting a new paragraph

Done

Page2, Ln 30 Perhaps introduce the term 'tandem measurement'

We do not consider the term "tandem measurement" to be appropriate here.

For us the term "tandem measurement" means that two measurements are carried out which, coupled with different approaches, investigate the same thing and thus provide a more comprehensive understanding. A typical tandem measurement is possible using GC-MS (Gas Chromatography–Mass Spectrometry), for example. This type of tandem measurement has not yet been realized with the ERICA. Tandem measurements are only realized when the same particle would be analyzed with both (ERICA-LAMS *and* ERICA-AMS) methods. If only a part of the aerosol is measured with one method and another part with another method, this is not yet a tandem measurement, even if both instruments are connected in a rack and vacuum system, because they are not coupled.

Page2, Ln31 Replace 'repetition rate' with the term 'temporal resolution'

The term 'repetition rate' was replaced with the term 'temporal resolution'.

Page2, Ln37 ' Tandem Instrument'?

We do not consider the term "tandem" to be appropriate here (see our reply to the comment on Page2, Ln 30).

Instrument Description

I brief principal of operation required before getting into the detail. Both techniques are sampling to same particle beam with the ERICA AMS at the end of the particle path. The LDI is requires optical detection to size particles and trigger the pulsed laser part way along the path.

Page3, Ln12 More effort should be made to describe Fig1.

The entire paragraph (until line 28, revised manuscript) is intended to be the description of Fig. 1. Thus, we changed as follows:

"The principal configuration of the ERICA with its inlet system, the laser ablation section (denominated as ERICA-LAMS), and the thermal vaporization section (ERICA-AMS) is shown in Fig. 1."

was changed to

"The principal configuration of the ERICA with its inlet system, the LDI section (denominated as ERICA-LAMS), and the TD-EI section (ERICA-AMS) is shown in Fig. 1 and is described in the following."

Page3, Ln12. Define LAMS and AMS in the introduction or consider changing to Laser desorption ionisation (LDI) and Thermal desorption Ionisation (TDI) therefor highlight the actual distinction between the two techniques.

The laser desorption and ionization method and the thermal desorption and electron impact ionisation method (with the terms LDI and TD-EI) were introduced and explained in Sect. 1. In Sect. 2, the terms ERICA-LAMS and ERICA-AMS were introduced and the methods (LDI and TD-EI) linked to the instrument parts:

"The principal configuration of the ERICA with its inlet system, the laser ablation section (denominated as ERICA-LAMS), and the thermal vaporization section (ERICA-AMS) is shown in Fig. 1."

was changed to:

"The principal configuration of the ERICA with its inlet system, the LDI section (denominated as ERICA-LAMS), and the TD-EI section (ERICA-AMS) is shown in Fig. 1 and is described in the following."

Page3, Ln14 Why is a constant pressure inlet required? Should this have already been introduced as part of the challenges of aircraft measurement?

(Numbers of sections refer to the revised manuscript)

Yes, the reviewer is right, challenges of aircraft operation under conditions of rapidly changing ambient pressure. This is briefly mentioned in Section 2.2 but the detailed explanations are provided in Molleker et al. (2020). For clarification, the abbreviation "CPI" for Constant Pressure Inlet was introduced:

"During aircraft operation the sample air flow is provided by a constant pressure inlet (Molleker et al., 2020) serving as a critical orifice at the instrument's front end."

was changed to:

"During aircraft operation, the sample air flow is provided by a Constant Pressure Inlet (CPI; Molleker et al., 2020) serving as a critical orifice at the instrument's front end (see Sect. 2.2)."

And

"However, in order to achieve a constant pressure in the ADL (p_{ADL} = 4.5 hPa), the mass flow rate needs to be kept constant during flight operations with largely varying ambient pressures (for the M-55 *Geophysica* ranging from ground pressure to 50 hPa). If p_{ADL} is not maintained constant, the transmission of the particles through the inlet into the vacuum system becomes altitude dependent (Zhang et al., 2002). For this purpose, a newly developed, automatically-controlled compressible rubber O-ring setup is deployed (Molleker et al., 2020)."

was changed to

"However, in order to achieve a constant pressure in the ADL (p_{ADL} = 4.5 hPa), the mass flow rate needs to be kept constant during flight operations with largely varying ambient pressures (for the M-55

Geophysica ranging from ground pressure to 50 hPa). If p_{ADL} is not maintained constant, the transmission of the particles through the inlet into the vacuum system becomes altitude dependent (Zhang et al., 2002). For this purpose, a newly developed, automatically-controlled compressible rubber O-ring setup, the so-called CPI, is deployed (Molleker et al., 2020)."

Page 3, Ln23 The term 'ion extraction' instead of acceleration would be more appropriate

"The resulting cations and anions are accelerated into a bipolar time-of-flight mass spectrometer (B-ToF-MS) and detected by micro-channel plates (MCPs)."

was changed to

"The resulting cations and anions are extracted into a bipolar time-of-flight mass spectrometer (B-ToF-MS) and detected by micro-channel plates (MCPs)."

Page3, Ln25 Some particles are partially vaporised. What happens to particle fragment and partly ablated material?

This is a very interesting and important question, which up to now could not be studied further, because the optical triggering for the AMS part of ERICA had not been implemented during the time of this study, but is currently work in progress. The so-called OT-AMS (optically triggered AMS) will allow to record quantitative information of single particles. If both MS (LAMS and AMS) are triggered by the detection unit, we will be able to see if a non-ablated remainder of a particle will hit the vaporizer. This was briefly touched upon in the "summary and outlook" section (submitted manuscript, page 24, lines 32 - 41). However, the paragraph was revised:

„For the same point in time, a data acquisition card is triggered and, similar to the procedure with a light scattering probe on the AMS (Cross et al., 2007; Freutel, 2012), the single particle mass spectrum is recorded. In this way it is possible to quantify the non-refractory components of a single particle. In addition, the size information of the measured single particle is obtained by means of the particle flight time between the two PDUs. Here, a future characterization of interest is the ablation laser's effect to the particles that are only partly ablated and the residuals reach the vaporizer of the ERICA-AMS. For this purpose, a method has to be developed to ensure the linkage of the results to the very same particle. Such a procedure needs more implementations and further laboratory studies."

was changed to

„For the same point in time, the data acquisition card is triggered and the single particle mass spectrum is recorded. For the ERICA this mode is called optically triggered AMS (OT-AMS) mode. With the method of the OT-AMS mode, it is possible to quantify the non-refractory components of single particles when the ablation laser is in idle mode. This method is similar to the procedure with a light scattering probe on the AMS (Cross et al., 2007; Freutel et al., 2013). In addition, the size information of the measured single particle is obtained by means of the particle flight time between the two PDUs. One possible future investigation by means of the OT-AMS mode is the ablation laser's effect on the particles that are only partly ablated and where the residuals reach the vaporizer of the ERICA-AMS. This investigation is only

possible with the unique feature, the serial configuration of SMPS and AMS, as in the OT-AMS mode. A method has to be developed to ensure the linkage of the results to the very same particle. Such a procedure needs more implementations and further laboratory studies. “

Page3, Ln28 Un-ablated particles do not pass through the B-TOF-MS section because they are not extracted.

“B-ToF-MS section” was changed to „ablation region“.

Page3, Ln31 use ‘extracted’ instead of ‘injected.

Done

Page3, Ln31 C-TOF-MS has not been properly introduced.

The term ‘C-ToF-MS’ is introduced in Sect. 1 as ‘Compact Time-of-Flight Mass Spectrometer’. For clarification, we added the manufacturer:

“The thermal vaporization and electron impact ionization technique were deployed on research aircraft using a C-ToF-MS (Compact Time-of-Flight Mass Spectrometer) beside others by Bahreini et al. (2009), Morgan et al. (2010), Schmale et al. (2010), Brito et al. (2018), Schulz et al. (2018), and Haslett et al. (2019), while a mAMS (mini Aerosol Mass Spectrometer) was used for example by Vu et al. (2016) and Goetz et al. (2018).”

Was changed to

“The TD-EI technique were deployed on research aircraft using a C-ToF-MS (Compact Time-of-Flight Mass Spectrometer from Tofwerk AG, Switzerland) e.g., by Bahreini et al. (2009), Morgan et al. (2010), Schmale et al. (2010), Brito et al. (2018), Schulz et al. (2018), and Haslett et al. (2019), while a mAMS (mini Aerosol Mass Spectrometer) was used for example by Vu et al. (2016) and Goetz et al. (2018).”

Page3, Ln31, You have to be more specific than ‘Detectable particle size’ as that would appear to conflict the next sentence. Do you mean you get composition measurement from that size range?

(Number of sections refer to the submitted manuscript for review)

“The detectable particle size range (d_{va}) of the ERICA-LAMS is between ~180 nm and 3170 nm (see Sect. 3.3.3). However, the signal-to-noise ratio of optical particle detection is sufficient for particle time-of-flight calibration between 80 nm and 5 µm (see Sect. 3.2).”

was changed to (Number of sections refer to the revised manuscript):

“The particle size range within the 50 % cut-off in detection efficiency (d_{50}) of the ERICA-LAMS is between 180 nm and 3170 nm (see Sect. 3.2.2). The signal-to-noise ratio of optical particle detection is sufficient for particle time-of-flight calibration between 80 nm and 5000 nm (see Sect. S4 in the supplement).”

Page3, Ln33 Xu 2017 describes the ACSM – please state that. Is it valid to assume the detectable particle size range is the same as the ACSM? This requires some discussion.

(Number of figures refer to the revised manuscript)

The detectable particle size of the thermal desorption instrument is determined by the transmission and focussing properties of the aerodynamic lens. Therefore, we refer to the paper by Xu et al. (2017), who used the same aerodynamic lens. The fact that they used an ACSM does not make a fundamental difference here. The longer particle flight path in the ERICA compared to the ACSM may cause that small particles that show a wider divergence do not hit the vaporizer to 100%, thereby reducing detection efficiency for small particles. However, as our measurements show (Fig. 12) this is not the case for particles down to 90 nm.

"The detectable particle size range (d_{va}) of the ERICA-LAMS is between ~180 nm and 3170 nm (see Sect. 3.3.3). However, the signal-to-noise ratio of optical particle detection is sufficient for particle time-of-flight calibration between 80 nm and 5 µm (see Sect. 3.2). The detectable particle size range of the ERICA-AMS is assumed to be the same as published by Xu et al. (2017) for the deployed lens type.: ~120 nm to 3.5 µm."

was changed to (Numbers of sections and figures refer to the revised manuscript; see also reply to RC1 and RC3):

"The particle size range within the 50 % cut-off in detection efficiency (d_{50}) of the ERICA-LAMS is between 180 nm and 3170 nm (see Sect. 3.2.2). The signal-to-noise ratio of optical particle detection is sufficient for particle time-of-flight calibration between 80 nm and 5000 nm (see Sect. S4 in the supplement). For the ERICA-AMS, the detectable particle size range is determined by the transmission and focusing properties of the aerodynamic lens. For the ADL used in our instrument, Xu et al. (2017), who used this lens in combination with an ACSM (Aerosol Chemical Speciation Monitor), determined a transmission range from ~120 nm to 3500 nm. We assume that the detectable particle size range of the ERICA-AMS matches this transmission range."

Page 3, Ln39 Consider putting the final paragraph of this section as part of the introduction.

Done

Page4, Ln 30 Are the vacuum pressures measured or calculated? A schematic of the vacuum system would be helpful.

The presented pressures values were measured. A schematic of the vacuum system and a table of the pressures and pumping rates (read out from the manuals) are now included in the supplement (Sect. S1.2 in the supplement; revised manuscript).

Page5, Ln15 How is the vacuum seal achieved on a movable assembly?

We added following sentence:

"An O-ring around the holding tube for the four aperture rings seals the vacuum at the pivot point."

Page 5, Ln20 How do you know that the system collects 75% of the scattered light. Has this been modelled or measured?

We had to correct the value to 70 %. The value of the total scattered light has been modelled considering Mie-Theory and the geometry of the elliptical reflectors.

"This design collects approximately 75 % of the total scattered light, not considering the losses at the pinholes."

was changed to

"This design collects in maximum 70 % of the total scattered light from a spherical particle (100 nm), according to model calculations adopting Mie theory and using the geometry of the detection unit except for the pinholes (which cause losses)."

Page6, Ln10 What shape beam profile is produced by the pulsed laser system. Is there variation in the power density with respect to position on the particle beam axis?

The beam shape of the ablation laser is considered to be Gaussian. Thus, the power density is depending on the position of the particle beam axis.

"Gaussian beam shape" was added in parenthesis for the detection lasers and the ablation laser in Section 2.1 (revised manuscript)

Following sentence was added (Number of the section refers to the revised manuscript):

"Considering a nearly Gaussian beam shape, as measured and confirmed by the fitting method in Sect. 3.2.1, the power density available to ablate the particle is depending on the position of the particle beam axis."

Page6, Ln29 8bits the effective dynamic range including the noise? This equates to around 3 orders of magnitude.

Yes, the noise is included and is < 1bit. Please note: The text was revised (see answer to ‚Major comment' No. 4)

Page6, Ln30 The positive and negative ion signals are measured by separate detection systems. Whilst having different gain on each channel is beneficial, it does not actually increase the dynamic range of the A/D, nor the dynamic range within the spectra. This is misleading.

The text was revised (see answer to ‚Major comment' No. 4). The explanation of the extension of the dynamic range should be much clearer now.

Section 2.5 The writing style changes to prose, which is rather odd.

Section 2.5 (submitted manuscript for review) was revised regarding the writing style.

Page 8, Ln1 Replace 'serial configuration' with 'tandem configuration'

We do not consider the term "tandem" to be appropriate here (see our reply to the comment on Page2, Ln 30).

Section 2.6 Is the data for 5% reduction in particle mass on the AMS with LAMS switched on actually presented in this paper? Where?

We removed the statement, since the presentation of this measurement will be part of an upcoming publication about the OT-AMS mode.

Section 3.1 The detection laser beam waist (250um) is much smaller than particle beam, but much larger that the particle diameters. Particles can encounter very different laser fluence depending on their trajectory through the Gaussian profile, therefore the effective irradiance encountered cannot be calculated by diciding the laser power by the beam area. See Marsden et al 2018.

Here, the average irradiance E_e over the beam cross section (1/e^2 of intensity) of the laser is presented to provide a value for an instrument-specific parameter. It is calculated by (with beam waist radius w_0 and intensity P):

$$E_e = P/(\pi * {w_0}^2)$$

The statement from Marsden et al. (2018) that particles can encounter very different laser irradiance depending on their trajectory through the Gaussian profile, since the detection laser beam waist diameter (250 µm) is much larger than the particle diameters was added in the text.

„The irradiance can be estimated as $2.1 \cdot 10^3$ W cm^{-2}."

was changed to:

„The average irradiance over the beam cross section (1/e^2 of intensity) of the laser can be estimated as 2.1×10^3 W cm^{-2}."

and

„Thus, the beam waist diameter $w_{0,dia}$ is approximately 250 µm, resulting in an irradiance of $1.36 \cdot 10^9$ W cm^{-2}."

was changed to

„Thus, the beam waist diameter $w_{0,dia}$ is approximately 250 µm, resulting in an average irradiance over the beam cross section (1/e^2 of intensity) of the laser of 1.36×10^9 W cm^{-2}. It has to be mentioned that particles can encounter very different laser irradiance depending on their trajectory through the Gaussian profile, since the detection and the ablation laser beam waists are much larger than the diameters of the sampled particles (Marsden et al., 2018)."

References

Ault, A. P., Moore, M. J., Furutani, H., and Prather, K. A.: Impact of Emissions from the Los Angeles Port Region on San Diego Air Quality during Regional Transport Events, Environ. Sci. Technol., 43, 3500-3506, https://10.1021/es8018918, 2009.

Bahreini, R., Ervens, B., Middlebrook, A. M., Warneke, C., de Gouw, J. A., DeCarlo, P. F., Jimenez, J. L., Brock, C. A., Neuman, J. A., Ryerson, T. B., Stark, H., Atlas, E., Brioude, J., Fried, A., Holloway, J. S., Peischl, J., Richter, D., Walega, J., Weibring, P., Wollny, A. G., and Fehsenfeld, F. C.: Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas, J. Geophys. Res.-Atmos., 114, https://doi.org/10.1029/2008JD011493, 2009.

Brands, M., Kamphus, M., Böttger, T., Schneider, J., Drewnick, F., Roth, A., Curtius, J., Voigt, C., Borbon, A., Beekmann, M., Bourdon, A., Perrin, T., and Borrmann, S.: Characterization of a Newly Developed Aircraft-Based Laser Ablation Aerosol Mass Spectrometer (ALABAMA) and First Field Deployment in Urban Pollution Plumes over Paris During MEGAPOLI 2009, Aerosol Sci. Technol., 45, 46-64, https://doi.org/10.1080/02786826.2010.517813, 2011.

Brito, J., Freney, E., Dominutti, P., Borbon, A., Haslett, S. L., Batenburg, A. M., Colomb, A., Dupuy, R., Denjean, C., Burnet, F., Bourriane, T., Deroubaix, A., Sellegri, K., Borrmann, S., Coe, H., Flamant, C., Knippertz, P., and Schwarzenboeck, A.: Assessing the role of anthropogenic and biogenic sources on PM1 over southern West Africa using aircraft measurements, Atmos. Chem. Phys., 18, 757-772, https://doi.org/10.5194/acp-18-757-2018, 2018.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, Mass Spectrom. Rev., 26, 185-222, https://doi.org/10.1002/mas.20115, 2007.

Clemen, H. C., Schneider, J., Klimach, T., Helleis, F., Köllner, F., Hünig, A., Rubach, F., Mertes, S., Wex, H., Stratmann, F., Welti, A., Kohl, R., Frank, F., and Borrmann, S.: Optimizing the detection, ablation, and ion extraction efficiency of a single-particle laser ablation mass spectrometer for application in environments with low aerosol particle concentrations, Atmos. Meas. Tech., 13, 5923-5953, http://10.5194/amt-13-5923-2020, 2020.

Cross, E. S., Slowik, J. G., Davidovits, P., Allan, J. D., Worsnop, D. R., Jayne, J. T., Lewis †, D. K., Canagaratna, M., and Onasch, T. B.: Laboratory and Ambient Particle Density Determinations using Light Scattering in Conjunction with Aerosol Mass Spectrometry, Aerosol Sci. Technol., 41, 343-359, https://doi.org/10.1080/02786820701199736, 2007.

Cross, E. S., Onasch, T. B., Canagaratna, M., Jayne, J. T., Kimmel, J., Yu, X. Y., Alexander, M. L., Worsnop, D. R., and Davidovits, P.: Single particle characterization using a light scattering module coupled to a time-of-flight aerosol mass spectrometer, Atmos. Chem. Phys., 9, 7769-7793, https://10.5194/acp-9-7769-2009, 2009.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, Anal. Chem., 78, 8281-8289, https://doi.org/10.1021/ac061249n, 2006.

Drewnick, F., Hings, S. S., DeCarlo, P., Jayne, J. T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J. L., Demerjian, K. L., Borrmann, S., and Worsnop, D. R.: A New Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS)—Instrument Description and First Field Deployment, Aerosol Sci. Technol., 39, 637-658, https://doi.org/10.1080/02786820500182040, 2005.

Fachinger, J. R. W., Gallavardin, S. J., Helleis, F., Fachinger, F., Drewnick, F., and Borrmann, S.: The ion trap aerosol mass spectrometer: field intercomparison with the ToF-AMS and the capability of differentiating organic compound classes via MS-MS, Atmos. Meas. Tech., 10, 1623-1637, https://10.5194/amt-10-1623-2017, 2017.

Freutel, F.: Einzelpartikel- und Ensemblemessungen mit dem Aerosolmassenspektrometer (AMS): Untersuchungen zu Quellen und chemischer Prozessierung von Aerosolpartikeln im Submikrometerbereich, PhD thesis, Johannes Gutenberg-Universität Mainz, Mainz, Germany, https://doi.org/10.25358/openscience-4367, 2012.

Freutel, F., Drewnick, F., Schneider, J., Klimach, T., and Borrmann, S.: Quantitative single-particle analysis with the Aerodyne aerosol mass spectrometer: development of a new classification algorithm and its application to field data, Atmos. Meas. Tech., 6, 3131-3145, https://10.5194/amt-6-3131-2013, 2013.

Fröhlich, R., Cubison, M. J., Slowik, J. G., Bukowiecki, N., Prévôt, A. S. H., Baltensperger, U., Schneider, J., Kimmel, J. R., Gonin, M., Rohner, U., Worsnop, D. R., and Jayne, J. T.: The ToF-ACSM: a portable aerosol chemical speciation monitor with TOFMS detection, Atmos. Meas. Tech., 6, 3225-3241, https://doi.org/10.5194/amt-6-3225-2013, 2013.

Froyd, K. D., Murphy, D. M., Brock, C. A., Campuzano-Jost, P., Dibb, J. E., Jimenez, J. L., Kupc, A., Middlebrook, A. M., Schill, G. P., Thornhill, K. L., Williamson, C. J., Wilson, J. C., and Ziemba, L. D.: A new method to quantify mineral dust and other aerosol species from aircraft platforms using single-particle mass spectrometry, Atmos. Meas. Tech., 12, 6209-6239, https://doi.org/10.5194/amt-12-6209-2019, 2019.

Gemayel, R., Hellebust, S., Temime-Roussel, B., Hayeck, N., Van Elteren, J. T., Wortham, H., and Gligorovski, S.: The performance and the characterization of laser ablation aerosol particle time-of-flight mass spectrometry (LAAP-ToF-MS), Atmos. Meas. Tech., 9, 1947-1959, https://doi.org/10.5194/amt-9-1947-2016, 2016.

Goetz, J. D., Giordano, M. R., Stockwell, C. E., Christian, T. J., Maharjan, R., Adhikari, S., Bhave, P. V., Praveen, P. S., Panday, A. K., Jayarathne, T., Stone, E. A., Yokelson, R. J., and DeCarlo, P. F.: Speciated online PM1 from South Asian combustion sources – Part 1: Fuel-based emission factors and size distributions, Atmos. Chem. Phys., 18, 14653-14679, https://doi.org/10.5194/acp-18-14653-2018, 2018.

Gunsch, M. J., May, N. W., Wen, M., Bottenus, C. L. H., Gardner, D. J., VanReken, T. M., Bertman, S. B., Hopke, P. K., Ault, A. P., and Pratt, K. A.: Ubiquitous influence of wildfire emissions and secondary organic aerosol on summertime atmospheric aerosol in the forested Great Lakes region, Atmos. Chem. Phys., 18, 3701-3715, https://10.5194/acp-18-3701-2018, 2018.

Haslett, S. L., Taylor, J. W., Evans, M., Morris, E., Vogel, B., Dajuma, A., Brito, J., Batenburg, A. M., Borrmann, S., Schneider, J., Schulz, C., Denjean, C., Bourrianne, T., Knippertz, P., Dupuy, R., Schwarzenböck, A., Sauer, D., Flamant, C., Dorsey, J., Crawford, I., and Coe, H.: Remote biomass burning dominates southern West African air pollution during the monsoon, Atmos. Chem. Phys., 19, 15217-15234, https://doi.org/10.5194/acp-19-15217-2019, 2019.

Healy, R. M., Sciare, J., Poulain, L., Kamili, K., Merkel, M., Müller, T., Wiedensohler, A., Eckhardt, S., Stohl, A., Sarda-Estève, R., McGillicuddy, E., O'Connor, I. P., Sodeau, J. R., and Wenger, J. C.: Sources and mixing state of size-resolved elemental carbon particles in a European megacity: Paris, Atmos. Chem. Phys., 12, 1681-1700, https://10.5194/acp-12-1681-2012, 2012.

Hinz, K.-P., Kaufmann, R., and Spengler, B.: Simultaneous Detection of Positive and Negative Ions From Single Airborne Particles by Real-time Laser Mass Spectrometry, Aerosol Sci. Technol., 24, 233-242, https://10.1080/02786829608965368, 1996.

Huffman, J. A., Jayne, J. T., Drewnick, F., Aiken, A. C., Onasch, T., Worsnop, D. R., and Jimenez, J. L.: Design, Modeling, Optimization, and Experimental Tests of a Particle Beam Width Probe for the Aerodyne Aerosol Mass Spectrometer, Aerosol Sci. Technol., 39, 1143-1163, https://doi.org/10.1080/02786820500423782, 2005.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, Aerosol Sci. Technol., 33, 49-70, https://doi.org/10.1080/027868200410840, 2000.

Jimenez, J. L., Canagaratna, M. R., Drewnick, F., Allan, J. D., Alfarra, M. R., Middlebrook, A. M., Slowik, J. G., Zhang, Q., Coe, H., Jayne, J. T., and Worsnop, D. R.: Comment on "The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer", Aerosol Sci. Technol., 50, i-xv, https://10.1080/02786826.2016.1205728, 2016.

Köllner, F., Schneider, J., Willis, M. D., Schulz, H., Kunkel, D., Bozem, H., Hoor, P., Klimach, T., Helleis, F., Burkart, J., Leaitch, W. R., Aliabadi, A. A., Abbatt, J. P. D., Herber, A. B., and Borrmann, S.: Chemical composition and source attribution of sub-micrometre aerosol particles in the summertime Arctic lower troposphere, Atmos. Chem. Phys., 21, 6509-6539, https://doi.org/10.5194/acp-21-6509-2021, 2021.

Marsden, N., Flynn, M. J., Taylor, J. W., Allan, J. D., and Coe, H.: Evaluating the influence of laser wavelength and detection stage geometry on optical detection efficiency in a single-particle mass spectrometer, Atmos. Meas. Tech., 9, 6051-6068, https://10.5194/amt-9-6051-2016, 2016.

Marsden, N. A., Flynn, M. J., Allan, J. D., and Coe, H.: Online differentiation of mineral phase in aerosol particles by ion formation mechanism using a LAAP-TOF single-particle mass spectrometer, Atmos. Meas. Tech., 11, 195-213, https://10.5194/amt-11-195-2018, 2018.

Molleker, S., Helleis, F., Klimach, T., Appel, O., Clemen, H.-C., Dragoneas, A., Gurk, C., Hünig, A., Köllner, F., Rubach, F., Schulz, C., Schneider, J., and Borrmann, S.: Application of an O-ring pinch device as a constant pressure inlet (CPI) for airborne sampling, Atmos. Meas. Tech., 2020, 1-13, https://doi.org/10.5194/amt-2020-66, 2020.

Morgan, W. T., Allan, J. D., Bower, K. N., Highwood, E. J., Liu, D., McMeeking, G. R., Northway, M. J., Williams, P. I., Krejci, R., and Coe, H.: Airborne measurements of the spatial distribution of aerosol chemical composition across Europe and evolution of the organic fraction, Atmos. Chem. Phys., 10, 4065-4083, https://doi.org/10.5194/acp-10-4065-2010, 2010.

Murphy, D. M.: The design of single particle laser mass spectrometers, Mass Spectrom. Rev., 26, 150-165, https://doi.org/10.1002/mas.20113, 2007.

Noble, C. A., Nordmeyer, T., Salt, K., Morrical, B., and Prather, K. A.: Aerosol characterization using mass spectrometry, TrAC, Trends Anal. Chem., 13, 218-222, https://doi.org/10.1016/0165-9936(94)85042-9, 1994.

Schmale, J., Schneider, J., Jurkat, T., Voigt, C., Kalesse, H., Rautenhaus, M., Lichtenstern, M., Schlager, H., Ancellet, G., Arnold, F., Gerding, M., Mattis, I., Wendisch, M., and Borrmann, S.: Aerosol layers from the 2008 eruptions of Mount Okmok and Mount Kasatochi: In situ upper troposphere and lower stratosphere measurements of sulfate and organics over Europe, J. Geophys. Res.-Atmos., 115, n/a-n/a, https://doi.org/10.1029/2009JD013628, 2010.

Schulz, C., Schneider, J., Amorim Holanda, B., Appel, O., Costa, A., de Sá, S. S., Dreiling, V., Fütterer, D., Jurkat-Witschas, T., Klimach, T., Knote, C., Krämer, M., Martin, S. T., Mertes, S., Pöhlker, M. L., Sauer, D., Voigt, C., Walser, A., Weinzierl, B., Ziereis, H., Zöger, M., Andreae, M. O., Artaxo, P., Machado, L. A. T., Pöschl, U., Wendisch, M., and Borrmann, S.: Aircraft-based observations of isoprene-epoxydiol-derived secondary organic aerosol (IEPOX-SOA) in the tropical upper troposphere over the Amazon region, Atmos. Chem. Phys., 18, 14979-15001, https://doi.org/10.5194/acp-18-14979-2018, 2018.

Suess, D. T., and Prather, K. A.: Mass spectrometry of aerosols, Chem. Rev., 99, 3007-3036, https://doi.org/10.1021/cr980138o, 1999.

Thomson, D. S., Middlebrook, A. M., and Murphy, D. M.: Thresholds for Laser-Induced Ion Formation from Aerosols in a Vacuum Using Ultraviolet and Vacuum-Ultraviolet Laser Wavelengths, Aerosol Sci. Technol., 26, 544-559, https://doi.org/10.1080/02786829708965452, 1997.

Vu, K. T., Dingle, J. H., Bahreini, R., Reddy, P. J., Apel, E. C., Campos, T. L., DiGangi, J. P., Diskin, G. S., Fried, A., Herndon, S. C., Hills, A. J., Hornbrook, R. S., Huey, G., Kaser, L., Montzka, D. D., Nowak, J. B., Pusede, S. E., Richter, D., Roscioli, J. R., Sachse, G. W., Shertz, S., Stell, M., Tanner, D., Tyndall, G. S., Walega, J., Weibring, P., Weinheimer, A. J., Pfister, G., and Flocke, F.: Impacts of the Denver

Cyclone on regional air quality and aerosol formation in the Colorado Front Range during FRAPPÉ 2014, Atmos. Chem. Phys., 16, 12039-12058, https://doi.org/10.5194/acp-16-12039-2016, 2016.

Xu, W., Croteau, P., Williams, L., Canagaratna, M., Onasch, T., Cross, E., Zhang, X., Robinson, W., Worsnop, D., and Jayne, J.: Laboratory characterization of an aerosol chemical speciation monitor with PM2.5 measurement capability, Aerosol Sci. Technol., 51, 69-83, https://doi.org/10.1080/02786826.2016.1241859, 2017.

Zhang, X., Smith, K. A., Worsnop, D. R., Jimenez, J., Jayne, J. T., and Kolb, C. E.: A Numerical Characterization of Particle Beam Collimation by an Aerodynamic Lens-Nozzle System: Part I. An Individual Lens or Nozzle, Aerosol Sci. Technol., 36, 617-631, https://doi.org/10.1080/02786820252883856, 2002.