



EGUsphere, author comment AC1
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Reply on RC1

Antonis Dragoneas et al.

Author comment on "The realization of autonomous, aircraft-based, real-time aerosol mass spectrometry in the upper troposphere and lower stratosphere" by Antonis Dragoneas et al., EGU Sphere, <https://doi.org/10.5194/egusphere-2022-33-AC1>, 2022

Dear Referee 1,

thank you for your overall positive feedback, as well as your suggestions and detailed comments.

As a general remark, it is worth mentioning that some of the technical details and performance characteristics addressed by these comments are discussed in the companion paper (Hünig et al., 2022). Below, we are addressing and providing answers to all of your comments.

Suggested additions:

1)

Referee comment: *For both the single particle and thermal desorption mass spectrometers, please list some dimensions and voltages. The energy of the ions is especially important since it affects detection at the MCP. The electric field across the ion source is also important for understanding the ionization processes. Simply calling it an Ionwerks spectrometer is not sufficient.*

Answer: Regarding the physical characteristics of the mass spectrometers, the ERICA-LAMS bipolar mass spectrometer measures 250 x 667 x 90 mm; the longest dimension (667 mm) is equally distributed to the positive and negative ion-flight chambers, wherein the ions follow a V-shaped trajectory. The dimensions of the ERICA-AMS mass spectrometer (including the ionization chamber) are 300 x 290 x 130 mm. Also, detailed information about the ERICA-LAMS dimensions and voltages are given on p. 190 (Fig. 90, Table 19) in the PhD thesis of Hünig (2021). Similarly, the respective information for the ERICA-AMS is given on p. 191 (Fig. 91, Table 20) of the same thesis.

The ion impact energy for the ERICA-AMS is approximately 2800 eV and, noteworthy, the detection is strongly influenced by the electron avalanche, which is determined by the voltage across the MCP stack (about 2000 V). The ion source itself is designed to primarily be field-free. The geometry of the ion extraction field is similar to those of other commercial Aerodyne AMS instruments (Drewnick et al., 2005), but its exact dimensions are unknown to us. Nevertheless, the ionization process is rather dependent on the acceleration and energy of the incident electrons, which is 70 eV, as mentioned in Line

135.

Changes: The dimensions of the ERICA-LAMS and the ERICA-AMS have been added to the text, together with the description given above. We suggest not specifying the voltage settings in this paper, but rather referring to the PhD thesis of (Hünig, 2021), wherein this information is given in detail.

2)

Referee comment: *In a bipolar mass spectrometer, one or both detectors must be floating at high voltage. Please describe in detail how the signals are coupled to ground and what preamplifiers are used.*

Answer: Both units (for anions and cations) are identical and decoupled from ground using one high voltage capacitor (100 pF, 7 kV) each. The preamplifiers are manufactured by Tofwerk AG, they are AC-coupled, their bandwidth is 3 kHz to 1.8 GHz and their gain is 21 db.

Changes: This information has been added to the text.

3)

Referee comment: *Describe the spot size for the ionization laser. A 10 mJ pulse has very different implications depending on how tightly it is focused.*

Answer: The ablation laser characteristics are discussed in Section 3.2.1 of Hünig et al. (2022). The spot diameter is approximately 250 μm .

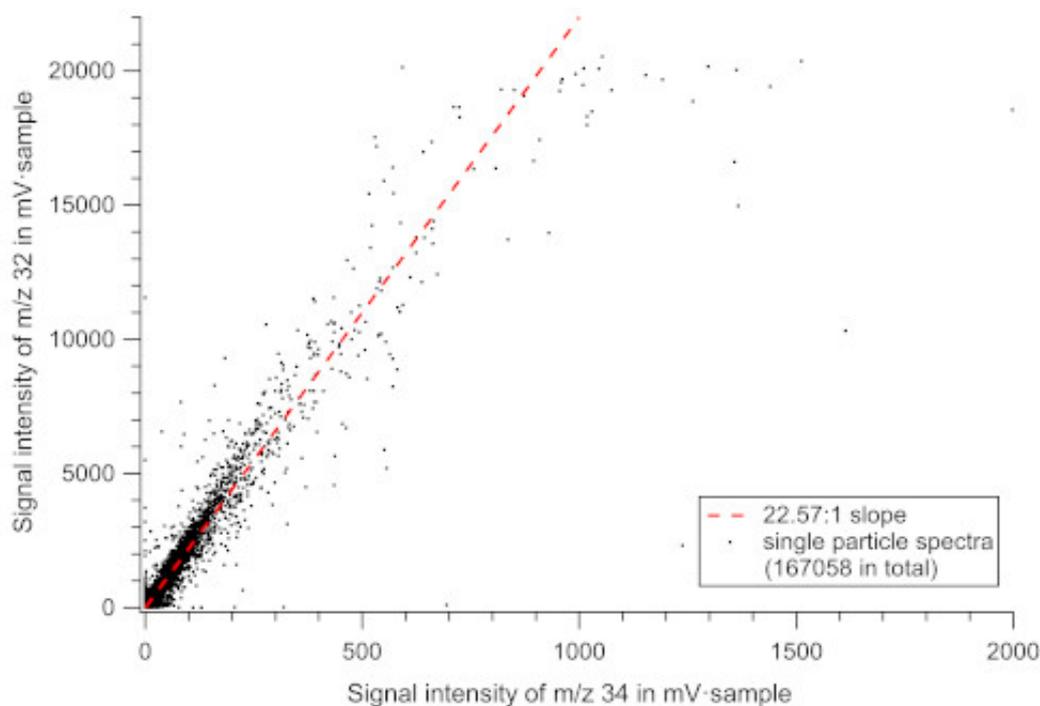
Changes: This piece of information has been added to the text.

4)

Referee comment: *What fraction of laser shots in the single particle instrument result in spectra? Is this a function of particle size?*

Answer: The fraction of laser shots which results in single-particle spectra is discussed in Section 3.2.3 of Hünig et al. (2022) and the size-dependence of it is illustrated in Fig. 8 of the same publication. This fraction, also referred to as "hit rate", can exceed 50% for particle sizes around 250 nm, while it typically ranged from 10% to 30% for the particles collected during the aircraft deployments of the instrument.

Changes: A relevant sentence regarding the hit rate, together with a reference to Hünig et al. (2022), have been added to the text.



5)

Referee comment: *It might be helpful to show an isotope ratio plot as a diagnostic of the linearity of the single particle spectrometer. ^{41}K versus ^{39}K , ^{54}Fe and ^{56}Fe , or ^{32}S and ^{34}S would be possibilities. There are other contributions to the peaks but a scatter plot will show a locus of points along the isotope ratio.*

Answer: To demonstrate the linearity of the ERICA-LAMS, we have added a plot of m/z 32 versus m/z 34 to the Supplement, as per your suggestion, which is shown above. The dashed red line indicates the ratio of the naturally occurring abundance of the two isotopes of sulfur.

Changes: A sentence regarding the linearity of the instrument with a reference to this figure has been added to the text. The figure has been added to the Supplement.

6)

Referee comment: *What detection limits were achieved for the thermal desorption (AMS) spectrometer?*

Answer: The ERICA-AMS detection limits are discussed in detail in Section 3.3.4 of Hünig et al. (2022). More specifically, Table 1 of this paper, gives the detection limits for chloride, ammonium, nitrate, organics, and sulfate.

Changes: Since this information is provided by the companion paper Hünig et al. (2022) and extends beyond the scope of the work presented here, we suggest making no changes in this case.

Technical comments:

a)

Referee comments: *Line 61: The strong statement about quantitation is not true. SPMS instruments can be quantitative both for types of particles and components within particles:*

Cornwell et al., Direct Online Mass Spectrometry Measurements of Ice Nucleating Particles at a California Coastal Site, JGR, 2019.

Cziczo, et al., Ablation, Flux, and Atmospheric Implications of Meteors Inferred from Stratospheric Aerosol, Science 291, 1772 (2001);

Froyd et al., 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, 2019

Qin et al., Comparison of Two Methods for Obtaining Quantitative Mass Concentrations from Aerosol Time-of-Flight Mass Spectrometry Measurements, Anal. Chem. 2006, 78, 6169-6178

Answer: Although a strong statement may not be apt in this case, we still think that the basic idea behind that statement is true: SPMS methods are generally incapable of providing quantitative aerosol concentrations without applying scaling provided by independent external measurements.

We believe that the cited publications under your comment support this statement. In some of these publications, the authors even explicitly state that SPMS is not capable of providing quantitative information. In some of these papers, as well as in a large number of other SPMS publications, fractional contributions of individual aerosol types to the total aerosol are determined, often as a function of particle size. However, as stated in some of the cited papers, this approach is limited by the fact that particle detection and ablation / ionization can depend on the type of particles, due to their different particle shapes and optical properties. Such effects even limit these semi-quantitative capabilities of SPMS, i.e. the determination of fractional contributions of different particle types.

Quantitative determination of components within particles, i.e. the measurement of concentrations of chemical components within the particles or within the aerosol, is further limited due to the generally particle-size-dependent and often particle-type-dependent detection of particles and the LDI ionization process that produces absolute and relative ion signal intensities, which can strongly depend on the particle matrix. Also, this is stated in several of the publications, cited by the reviewer. The presented approaches to calculate absolute concentrations of different particle types, all rely on the use of external size distribution measurements, combined with assumptions about the composition of individual particle types. Using this approach, indeed, some quantitative information can be indirectly extracted from the SPMS measurements.

Changes: To make clearer that SPMS cannot deliver quantitative measurements by itself, while it can contribute (together with other measurements) to the calculation of quantitative data, we re-worded the statement in line 61: "*Most importantly, a number of studies have shown that the use of simultaneous vaporization and ionization, as it happens with LDI, results in strongly matrix-dependent ion signals, which constitutes the main reason why SPMS does not intrinsically provide quantitative measurements (Reilly et al., 2000; Allen et al., 2000)*".

b)

Referee comment: *Line 72: It is worthwhile to mention that a bipolar SPMS has been flown at lower altitudes: Pratt et al., Anal. Chem. 2009, 81, 1792–1800, Development and*

Changes: We have added the following sentence to the text: "However, at least one bipolar SMPS instrument has been demonstrated to operate aboard an aircraft, albeit at much lower altitudes (Pratt et al., 2009)".

c)

Referee comment: *Line 105: Please mention the model of the PMT.*

Answer: The model of both PMTs used in the instrument is H1021-210, manufactured by Hamamatsu Photonics K.K. Japan. These products are PMT modules featuring an embedded high-voltage supply; their gains are externally controlled by two separate low-voltage signals.

Changes: This information has been added to the text.

d)

Referee comment: *Line 131. Having the motor outside is potentially much cleaner than the motor inside the vacuum. Is the organic background in the AMS region lower than in a stock Aerodyne AMS?*

Answer: Indeed, the reason of using a magnetically-coupled shaft is to substantially reduce contamination, especially due to the proximity of the shutter to the ionization region of the ERICA-AMS. As a side note, it is worth mentioning that the organic background of any AMS instrument deployed for aircraft measurements is largely depended on the pumping time elapsed prior to the onset of measurements. This is due to the fact that all aircraft instruments are typically powered down and only turned on a few hours before each take-off. Different pumping times yield different vacuum levels, which in turn, result in different organic backgrounds. As also discussed above (answer 6), the detection limits of the ERICA-AMS for the StratoClim measurements are given in Section 3.3.4, in the companion paper by Hünig et al. (2022). The value for organics was 500 ng/m³ for measurement cycles of 10 s, which corresponds to approximately 290 ng/m³ for a 30-second average. Although better values have been reported for Aerodyne AMS instruments deployed for aircraft measurements, i.e. 70 to 140 ng/m³ (Schmale et al., 2010), and 110 ng/m³ (Schulz et al., 2018), a direct comparison cannot be easily made, as the pre-flight pumping times may differ.

Changes: The sentence "*The shutter is driven by an external servo motor via a magnetically-coupled feedthrough rated for ultra-high vacuum*" has been changed to: "*Due to the proximity of the shutter the ionization region of the ERICA-AMS and to avoid contamination, a servo motor has been installed outside the vacuum chamber and connected to the shutter via a magnetically-coupled feedthrough rated for ultra-high vacuum*". We suggest omitting any reference to the organic background due to the reasons discussed in the answer above.

e)

Referee comment: *Line 145. An AMS has previously been flown on a stratospheric balloon. Although not built by Aerodyne, it was an AMS: it included an aerodynamic lens, vaporizer, shutter for the particle beam, and a mass spectrometer. Schreiner et al., A mass spectrometer system for analysis of polar stratospheric aerosols, Review of Scientific Instruments 73, 446 (2002); <https://doi.org/10.1126/science.290.5497.1756>.*

Changes: We have added the following statement to the Introduction, circa Line 79 (not

Section 1): "In addition, instruments employing the TD-EI technique have been used for high-altitude balloon-borne measurements (Voigt et al., 2000)"

f)

Referee comment: *Line 178: I found the discussion of changing pressure confusing – the instrument is in a pressure vessel, only talked about later. Readers will think the electronics are exposed to changing pressure.*

Answer: That sentence refers to the instrument compartments (bays) of the aircraft. To avoid confusion, we have slightly rephrased that sentence.

Changes: Sentenced rephrased to: *"Moreover, the technical specifications and limitations of the aircraft were taken into consideration; such parameters are the lack of pressurized instrument compartments, the absence of an instrument operator on board, the electrical supply limitations, and the high speed of the platform".*

g)

Referee comment: *Circa line 220: Given the radiative cooling, it is surprising that the instrument couldn't just stay fairly indefinitely in low power mode with a modest external fan blowing on the pressure chamber rather than a dedicated air conditioning unit. Radiative cooling with a 10 to 20C temperature difference is hundreds of watts.*

Answer: We can confirm that your assumption on radiative cooling holds true; as an example, for a temperature difference of 20 K (i.e. pressure vessel temperature = 40 °C, cowling surface temperature = 20 °C) and an emissivity of 0.8 for painted aluminium, the radiative cooling is approximately 470 W. However, as stated in Line 362, the power consumption of the instrument in Low-Power Mode is about 600 W while the ambient temperature on ground was even exceeding 30 °C during pre-flight operations. The ambient temperature can be seen in Fig. 7. For these reasons, the use of an external air-conditioning unit has been deemed necessary.

Changes: We suggest making no changes in this case.

h)

Referee comment: *Line 665: I am convinced the gold is from contamination; you don't need to mention space debris.*

Changes: We have removed the statement regarding space debris.

i)

Referee comment: *Section 4.4 first paragraph: You can probably reduce the number of times the same references are cited in successive sentences.*

Changes: The double citation has been removed.

j)

Referee comment: *Figure 4: I think Figure 4 belongs in supplemental.*

Answer: Regarding your comment on Fig. 4, we suggest keeping it in the main manuscript rather than moving it to the supplement. The main reason is that it illustrates all units (sub-systems) which are described in the text, while it clearly shows the signals

exchanged between them, making easier for the reader to understand the operation of the entire system.

Changes: We suggest making no changes in this case.

k)

Referee comment: *What supplemental material is there is appropriate and appreciated. One could also consider a digital file of the spectra shown in the figures in the manuscript.*

Changes: The files with the spectral data shown in all relevant figures will be made available online, as per your request.

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