# Responds to the Referees

## Referee #1

The manuscript by Du et al. entitled 'The design and characterization of a High-Performance Single-Particle Aerosol Mass Spectrometer (HP-SPAMS)' describes the development and improvement of single particle mass spectrometry in the inlet system, higher detection efficiency and hit rate, and greatly improved mass resolution in the analyzer. The results shown here impressively demonstrate the possibilities of this technology and clearly show advantages and actual scientific questions, which will be addressed here.

However, questions remain and should be discussed and improved before publication. Overall, this manuscript should be accepted for publication after improvements focused on the specific comments below.

More general comments:

- Add spot sizes for ionization and sizing lasers.

**Answer:** Thank you for your suggestion, the description of the laser spot size " Two beams of continuous-wave Nd:YAG (532 nm) laser (500 mW, LaserWave, LWGL532 nm-500 mW) spaced orthogonally 6 cm apart were focused by a plano-convex lens (PLCX-25.4-51.5-C-532, CVI Laser Optics) into a 300 μm-sized spot at the first focus of the ellipsoidal mirror, respectively. Scattered light is produced as the particles pass through the laser beam and is focused by the ellipsoidal mirror to the photomultiplier tube (PMT, H10721-110, Hamamatsu) for detection. " and " HP-SPAMS uses a diode-pumped Nd: YAG 266 nm (100 Hz, 9 ns pulse width, Centurion Plus, Quantel) that is focused by a UV fused silica plano-convex lens (f=175 mm, SPX026, Newport Corporation) into a 300 μm square uniform spot at the center of the ion source " has been added.

- Add energies of ionization lasers of SPAMS and HP-SPAMS because it highly influences the hitrate.

**Answer:** Thanks, both HP-SPAMS and SPAMS operate at laser energies of about 0.5 mJ/pulse during the experiments, and it has been added in Section 2.3.

- Define 'hitrate' (' of mass specs in relation to # at PMT2 ??)

**Answer:** I'm sorry if the definition of hit rate confused you. The hit rate is defined as the ratio of the number of particles with mass spectra to the number of sizing particles, where the number of sizing particles refers to the number of particles accurately measured by the sizing system at the time the ionizing laser can be emission.

- The detection efficiency is given in % -> in relation to what? How is the higher repetition rate of the newer system， and its timing electronics taken into account?

**Answer:** (1) Sorry for not defining this detection efficiency well, it may be more acceptable to use the scattering efficiency. The scattering efficiency of particle is defined as the ratio of the response pulse count of the photomultiplier tube to the total number of injected particles, in which the total number of injected particles can be obtained from the particle concentration and the injection flow rate. Taking the 960 nm PSL as an example, the number of particles detected by CPC is shown in Figure S1, and the average number concentration is 8.8 particles/cm$^3$. For HP-SPAMS, the average number of particles detected by the two laser beams is 64.9 (particles/s) and (62.2 particles/s), and the scattering efficiency is 96.3% and 92.3%, respectively, according to the following equation. Therefore, the scattering efficiency is calculated with the normalization of the inlet flow already.

$$\text{Scattering efficiency} = \frac{response\ pulse\ by\ instrument}{CPC\ concentration \times inlet\ flow \times time} \qquad \text{(equation 1)}$$

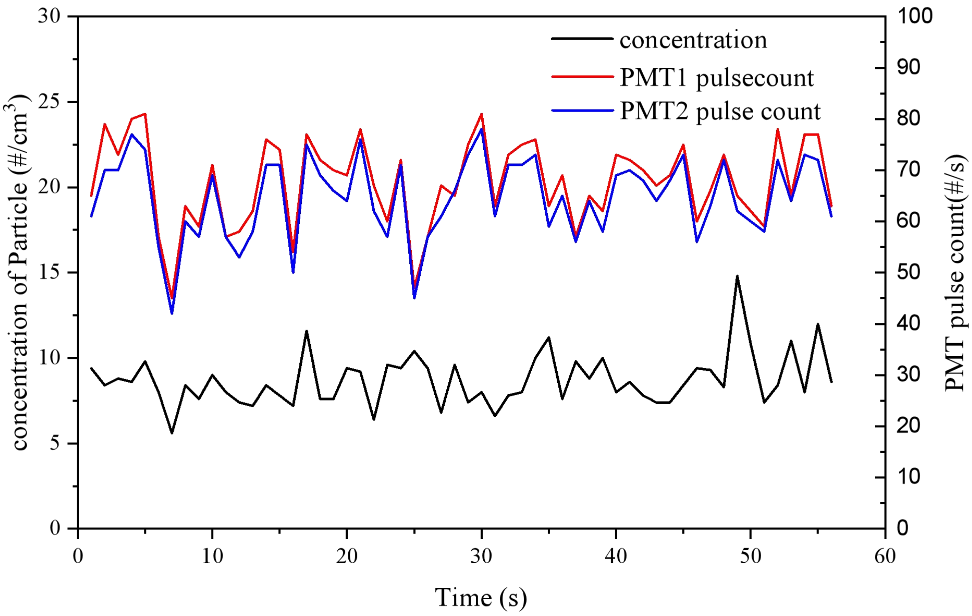



Figure S1: Concentration of 960 nm PSL for CPC detection and pulse counting for HP-SPAMS.

(2) The maximum frequency is the laser output frequency of 100Hz, which has been judged logically on the timing card and can meet the maximum 500/s trigger.

(3) The new timing card uses a serial port (baud rate 115200) which can transmit 11520 bytes a second and does not transmit the complete waveform of the PMT in the data transmission. On the one hand, only the pulse counts of individual PMTs are counted, and on the other hand, only the time-of-flight information (4 bytes) of the measured particles is transmitted to the host computer after judging the exact particles by a certain logic. Therefore, it is possible to meet the requirements.

- Figure 4: PMT2 is of course always lower in signal number and therefore detection efficiency, why is the detection efficiency in (d) with all errorbars the same as for PMT1? This should at least show a difference due to the divergence of the particle beam.

Answer: Thanks for your reminding. I think this may be explained by: (1) for dioctyl sebacate (DOS, density 0.90 g/cm$^3$, shape factor = 1), the divergence of the lens is smaller for spherical particles; (2) the density of the DOS particles used in Figure 4d is 0.9 g/cm3, which is smaller than the standard PSL (1.05 g/cm3). Therefore, the geometry of the particles with the same aerodynamic diameter will be larger ( $d_{va} = d_p \frac{\rho_p}{\chi \rho_0}$, ***see Alla Zelenyuk 2011*** ) and the intensity of scattered light will be enhanced, which may be the reason why the errorbar of HP-PMT1 and HP-PMT2 of DOS are similar. Especially for DOS particles of 400-1000 nm particle size, the pulse counts of HP-PMT1 and HP-PMT2 are almost the same, so the errorbar of this particle size is almost the same.

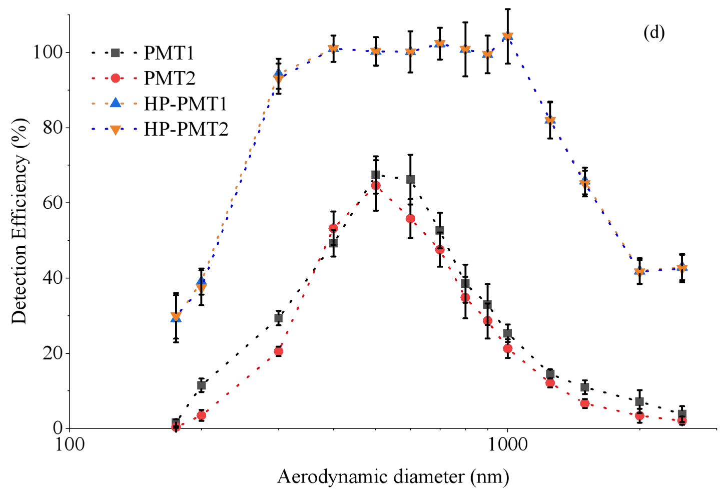



Figure S2: Scattering efficiency of HP-SPAMS and SPAMS for DOS

- Figure 4: Please add data from CPC for better understanding of the detection efficincy and normalize to to sample volume, so that the two systems can be better compared.

**Answer:** Thank you for your suggestions. Here the detection efficiency (has been changed to scattering efficiency) is already normalized, see equation 1. We have used the measured concentrations of CPC in the calculation of the efficiency and normalized them. And the method of calculation we have also added in the manuscript.

- Figure 6: please also add a plot as the third one for the (non-HP) SPAMS.

**Answer:** We are very sorry that (non-HP) SPAMS uses an old timing card, which does not have the function to record the pulse counts of photomultiplier tubes, so we cannot show the data of this part. Although the SPAMS data are missing, this does not affect the analysis of the correlation between the scattering counts of HP-SPAMS and $PM_{2.5}$. As a supplement, the number of sizing particles and hitting particles are recorded for SPMAS and HP-SPAMS (Figure S3).

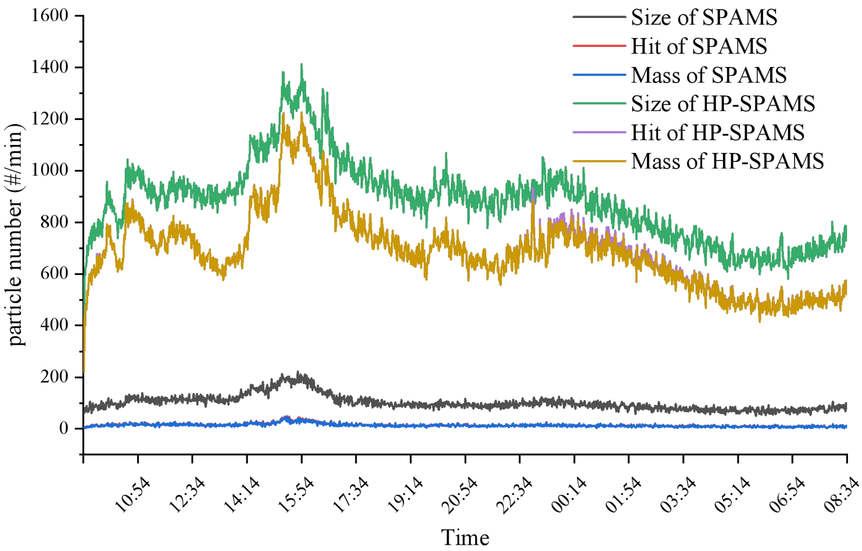



Figure S3: The number of sizing particles and hitting particles of SPMAS and HP-SPAMS. Size particle is the particle accurately measured by the sizing system and emitted by the ionizing laser. Hit particle is the number of particles with a spectrum after laser emission. Mass particle is a particle that is present in both positive and negative mass spectra.

- Figure 7: right side y-axis update to #/time (24 h ??)
- Figure 7: normalize to sample flow (ml/ccm^3 -> like SMPS)

**Answer:**(1) Thank you for your suggestion, we have modified it.

(2) Here we have normalized to show the average concentrations detected by both instruments under 24h hourly collection as shown in Figure S4. As can be seen from the figure, the difference in the number concentrations detected by HP-SPAMS and SPAMS is reduced after normalizing the flow rate, but HP-SPAMS still has an enhancement in the whole particle size range, especially in the small particle size range.

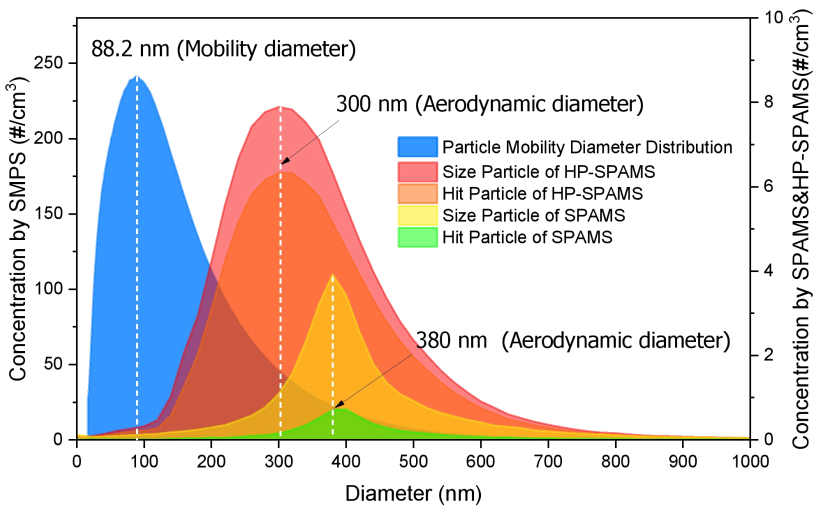



Figure S4: Particle size distribution of SPMS, HP-SPAMS and SPAMS detection during 24 hours. The peak particle sizes of the three instruments were 88.2 nm, 300 nm, and 380 nm, respectively.

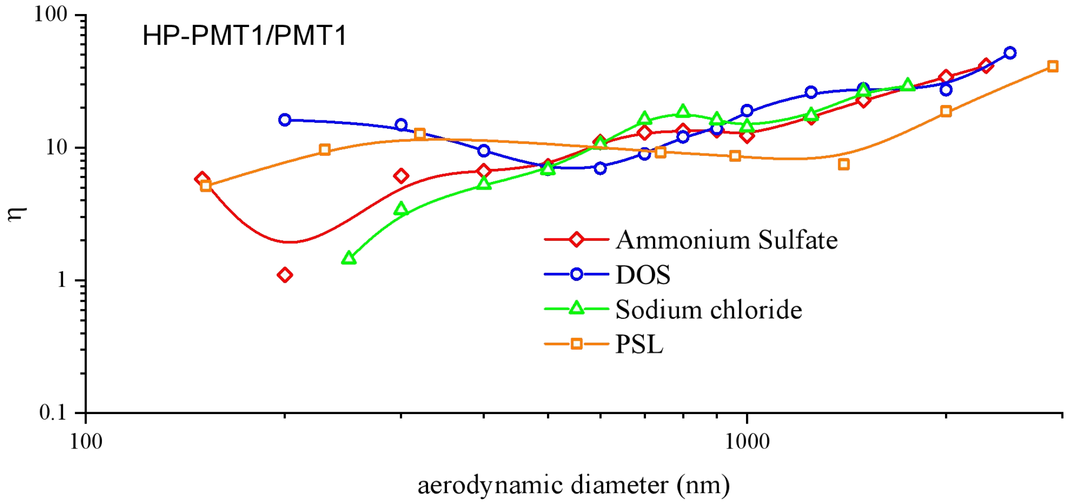
The number of sizing particles measured by the two instruments was 1,281,846 and 146,600, respectively. The number of comparisons hit particles was 1002141 (78.2 % hit rate) and 20,943 (14.3 % hit rate).

Line 95: Why is this size used? Is there the possibility to use also even larger sized orifice with higher flows and even more particles? Is the flow through the aerodynamic lens also higher or is it the same as in the older version?

**Answer:** (1) With a size in the range of 0.18-0.22 mm, combined with a virtual concentration device, it is possible to increase the total inlet flow rate of the instrument and to ensure that the pressure at the front of the aerodynamic lens remains in the range of 1.8-2.2 Torr ;(2) Using a higher pumping speed and a larger bore, more particles can be obtained, but not endlessly, as it will be limited by the sizing system; (3) The aperture of the aerodynamic lens has been improved, but the flow through is still about 100mL/min (at standard conditions).

Line 176: Not in every case the number of particles is 10 times as high, for NaCl particles the difference is sometimes only about one third. Furthermore, as shown in Figure 4, the difference is size and particle type dependent. Please revise formulation more precisely and elaborate.

**Answer:** Thank you for correcting our mistake, where it is true that not all particles meet the 10 times efficiency (see Figure S5). As can be seen from the graph, the number of particles detected differs by a factor of 1-40 for different particle size ranges. And the multiplier increase is different for different types of particles. Here we modify it to "the number of particles detected by the HP-SPAMS sizing system could be greatly increased, and it is related to the particle size and the type of the particles."



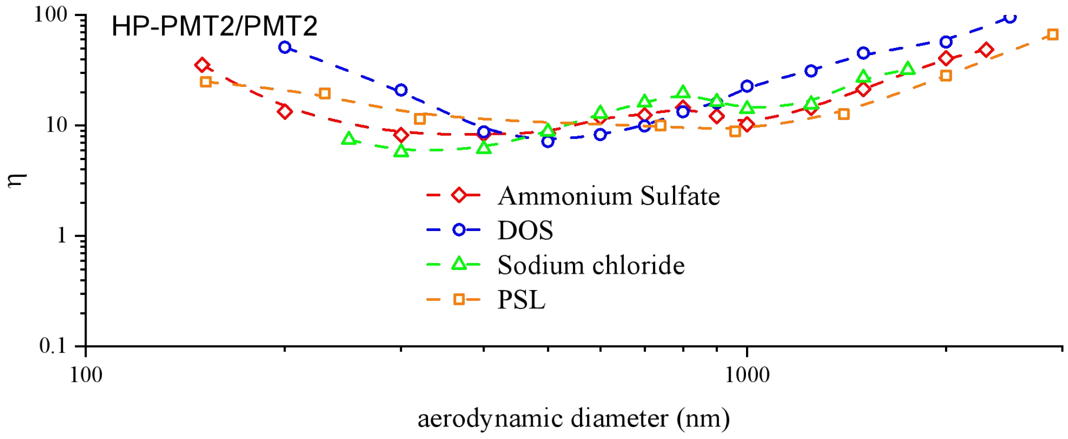



Figure S5: The ratio of pulse counts detected by HP-SPAMS and SPAMS in the simultaneous injection condition.

Line 183: Compared to what number? PMT2 or CPC? Please add information on count number of CPC 1/ccm^3

**Answer:** Here it may refer to line 181. We intended the comparison to be between the particle size distributions measured by HP-SPAMS and SPAMS to show that SPAMS has a small number of acquisitions in the large particle size segment and is not statistically significant. Here we has deleted the " (see later comparing the number of particles in air samples)" to avoid ambiguity.

Line 183/184: Both are decreasing with smaller particle sizes, please revise formulation more precisely and elaborate.

**Answer:** Thank you for your suggestion, here is modified to "As seen from Figure 5, the hit rate of HP-SPAMS for PSLs could be maintained in the range of 200-3000 nm from 80 % to 100 % for PSLs, while the SPAMS was within 20 %. In the range of 100 to 500 nm, the hit rate of both instruments decreases with smaller particle size".

Line 209: Should be: ...SMPS, HP-SPAMS, and SPAMS respectivley... change word order

**Answer:** Thanks. It has been corrected from"The peak particle sizes of the three instruments were 88.2 nm, 300 nm, and 380 nm, for SMPS, SPAMS, and HP-SPAMS, respectively" to "The peak particle sizes of the three instruments were 88.2 nm, 300 nm, and 380 nm, for SMPS, HP-SPAMS, and SPAMS, respectively".

Line 210: This is a total value not taking into account the sample flow rate, please add normalized values.

**Answer:** Thank you for your suggestion, we added a normalized average data. Here is modified to "…the number of sizing particles measured by the two instruments was 1,281,846 (2.8 particle per milliliter on average) and 146,600 (1.02 particle per milliliter on average)…"

All in all, the first paragraph in the results section (lines 159 - 194) is very confusing and should be fundamentally revised. The comparisons with the previous and older measurement system are misleading in this form, since no laser energies and spot sizes are given and the results have not been normalized. This will make the difference between the systems considerably smaller, nevertheless this is a very good and useful improvement of the technology.

**Answer:** Thank you very much for your suggestions. We have made changes to this, in summary: (1) redefining the detection (scattering) efficiency and hit rate to make these concepts and expressions clearer. (2) Normalized the presentation of these data, such as scattering efficiency, particle concentration, etc., to allow better comparison between instruments. (3) Some descriptive errors are corrected.

## Referee #2

Review of Du et al., The design and characterization of a high-performance single-particle aerosol mass spectrometer (HP-SPAMS)

This manuscript is, as the title implies, a technical description of a single particle mass spectrometer. This is a commercial instrument, but the description is primarily technical and does not feel too much like an advertisement. It falls reasonably into the type of paper that describes the performance of a commercial instrument.

The technical specifications are in some respects quite impressive. This instrument is, for example, significantly better than the ATOFMS sold some years ago in the US by TSI, Inc. The writing is good and the references are balanced. The manuscript should be publishable with minor revisions.

1) One general change that would benefit the manuscript is to do fewer comparisons to the previous SPAMS instrument developed by the same group and emphasize absolute performance more. The authors are justifiably proud of their improvements, but the eventual paper should be presented for a general audience of all users of single particle mass spectrometers, not just those who own an older instrument developed/sold by the same authors. An example of something to de-emphasize or delete: “the number of lead-containing particles is 145 times higher than that detected by SPAMS” (abstract). An example of something to emphasize more: the comparison in Figure 4 of the detection efficiency of various kinds of particles, presumable due to spherical or non-spherical shapes. This is a very useful comparison between types of particles. These are just examples: there are probably dozens of places in the manuscript where the comparisons to the older SPAMS could be reduced. A few are OK, but only a few.

**Answer:** Thank you for your suggestion. We have also noticed this problem and have added comparative descriptions with ATOFMS, LAAPTOF, as well as reduced some comparative descriptions with older instruments, in order to better demonstrate the absolute performance of the instruments. In detail, we have made the following changes to the manuscript:

(1) Revise the abstract section "For the analysis of individual particles, the HP-SPAMS's improved resolution helps distinguish between most organic fragment ions and metal ions and facilitates the analysis of complex aerosol particles" to " For the analysis of individual particles, HP-SPAMS achieves an average mass spectral resolution of 2500 at m/z 208, which helps distinguish between most organic fragment ions and metal ions and facilitates the analysis of complex aerosol particles."

Delete " for example, HP-SPAMS can completely differentiate the isotopes of lead elements and the number of lead-containing particles is 145 times higher than that detected by SPAMS. " In the abstract.

(2) Delete " The repetition frequency of the laser was increased 5 times compared to 20 Hz in SPAMS, which could reduce the "busy time" of the laser and improve the temporal resolution. " in Section 2.2.

(3) Add "This is due to the fact that for irregular particles there is a force perpendicular to the direction of gas motion, while for spherical particles this force is zero, resulting in greater dispersion of non-spherical particles after passing through the lens system. (Liu et al., 1995)"in section 3.1.

(4) Delete"… and this correlation was significantly higher than that of SPAMS results." in section 3.1.

(5) Delete" … indicating that HP-SPAMS improved the total number of detected particles by 47.8 times compared to SPAMS."

(6) Added description of resolution compared to other instruments (LAAPTOF and A-ATOFMS). Change "It can also be seen from Figure 8 that the resolution of HP-SPAMS using exponential pulse delay extraction is, on average, 2-3 times better than that of the DC-extraction SPAMS, and the average resolution is up to 2500 (Full Width at Half Maximum) at m/z 208. This resolution is better than that of instruments of the same type such as LAAPTOF (600) and A-ATOFMS (1072)." to" It can also be seen from Figure 8 that the resolution of HP-SPAMS using exponential pulse delay extraction is, on average, 2-3 times better than that of the DC-extraction SPAMS, and the average resolution is up to 2500 (Full Width at Half Maximum) at m/z 208. This resolution is better than that of instruments of the same type such as LAAPTOF (600) and A-ATOFMS (1072)" in Section 3.2.

(7) Delete" This meant a difference of about 145 times between each other." and" In addition, the 7955 lead-containing particles detected by HP-SPAMS could be further analyzed in time series for changes in the concentration, which is not possible using SPAMS at low concentrations. Thus, the improved instrument performance of HP-SPAMS relative to SPAMS could better characterize particles, especially in low-concentration environments" in Section 3.2.

2) One important technical detail that is missing is a list of the spot sizes of the detection and ionization lasers. One cannot interpret the performance of the aerodynamic lens without knowing how big of a target is provided by the detection lasers beams. And one needs the ionization laser spot size to know the fluence available to ionize particles.

**Answer:** Thank you for your suggestion, we have added the spot size in Section 2.1 and Section 2.2. " Two beams of continuous-wave Nd:YAG (532 nm) laser (500 mW, LaserWave, LWGL532 nm-500 mW) spaced orthogonally 6 cm apart were focused by a plano-convex lens (PLCX-25.4-51.5-C-532, CVI Laser Optics) into a 300 μm-sized spot at the first focus of the ellipsoidal mirror, respectively. Scattered light is produced as the particles pass through the laser beam and is focused by the ellipsoidal mirror to the photomultiplier tube (PMT, H10721-110, Hamamatsu) for detection. " and " HP-SPAMS uses a diode-pumped Nd: YAG 266 nm (100 Hz, 9 ns pulse width, Centurion Plus, Quantel) that is focused by a UV fused silica plano-convex lens (f=175 mm, SPX026, Newport Corporation) into a 300 μm square uniform spot at the center of the ion source. "

3) I found the discussion of the aerodynamic concentrator incorporated into the aerodynamic focusing inlet to be confusing. Maybe because it is incorporated into the inlet, it was never clear to me what the baseline was for its performance. In the abstract it says that it “enables concentration… but a factor of 3-5 times”. Compared to what? And then in section 3.1 I was not clear in the discussion of detection efficiency what the maximum detection efficiency should be. Should it be 100%? Or perhaps the maximum should be 300 to 500%, because the best possible performance would be 100%, but the concentrator would then multiply that by 3 to 5? I think a clear definition of how the baseline is defined would solve these. By the way, incorporating the aerosol concentrator into the inlet instead of having a separate concentrator upstream looks like a clever idea with several advantages.

**Answer:** Thank you very much for your suggestion, we have made the following changes to this:

（1） Change “enables concentration… but a factor of 3-5 times” to “The combination of an aerodynamic particle concentrator (APC) system and a wide range of aerodynamic lenses (ADLs) enables the concentration of particles in the 100-5000 nm range. Using APC increases the instrument inlet flow by a factor of 3-5”.

（2） We have changed “detection efficiency” to “scattering efficiency”. The scattering efficiency of particle is defined as the ratio of the response pulse count of the photomultiplier tube to the total number of injected particles, in which the total number of injected particles can be obtained from the particle concentration (from CPC) and the injection flow rate. Therefore, the scattering efficiency is the result obtained after normalizing the inlet flow and the maximum scattering efficiency value is 100%.

4) It would be interesting to see a few spectra on a logarithmic scale, perhaps in supplemental material, to see the dynamic range from the high range/low range digitization and whether or not that induces any artifacts.

**Answer:** Thanks to your suggestion, we have shown the example data in logarithmic scale in the supplemental material Figure S6. It is worth noting that since there is a zero value in the original intensity, therefore, the intensity is overall biased by 0. 1 mV when plotting this graph. From Fig. S6(a) and Fig. S6(b), it can be seen that the maximum data acquisition range can reach 20V ($K^+$), and the smallest signal can be acquired to 0.004V. Fig. S6(c) shows that this is a standard EC containing particle, and from Fig. S(d), which is displayed in logarithmic scale, it can be seen that this EC particle still contains a very small amount of OC.

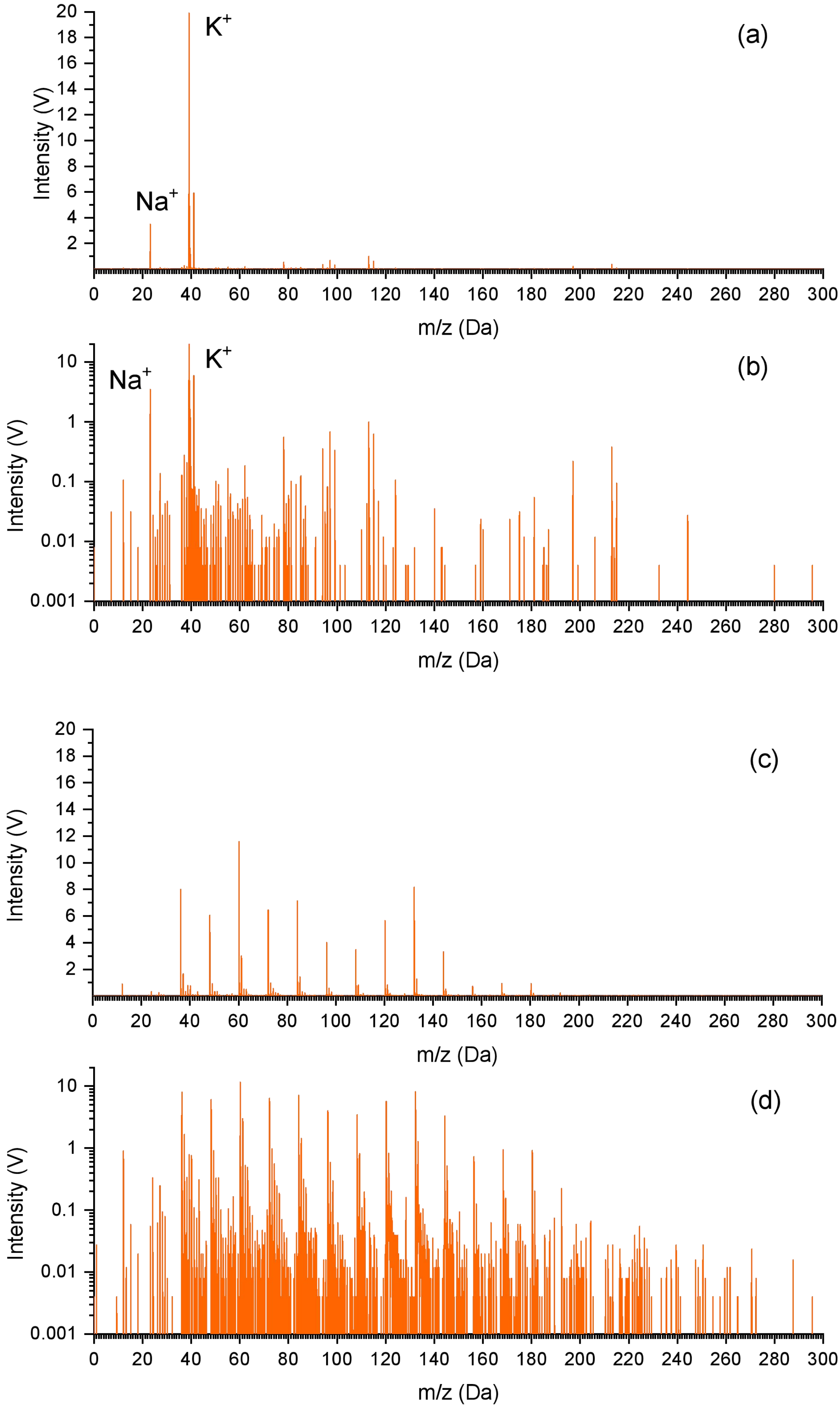



Figure S6: Example particles of mass spectra in linear scale and logarithmic scale (a)&b Na-K containing particles; (c)&(d) EC containing particle.

5) Near line 104, the pressure would be helpful as well as the orifice diameters. I think the symbol/line labels in Figure 5 may be incorrect.

**Answer:** Thank you for your suggestions:

(1) We have added "The aerodynamic inlet pressure is in the range of 2.0 ± 0.2 Torr and the exit nozzle size is 3 mm." in Section 2.1.

(2) we have exchanged the "Hit rate of HP-SPAMS (PSLs)" with "Hit rate of SPAMS(PSLs)" in legend.