Response to Referee 2

We sincerely thank referee 2 for the valuable comments, and we have extensively revised our manuscript according to these suggestions. Below we list our point-by-point replies to the comments and the descriptions of the changes we made in the revised manuscript.

Referee 2

This manuscript describes a mass calibration algorithm applied to single-particle mass spectra obtained using the HP-SPAMS (Hexin Instrument Co.).

This work is quite similar to the manuscript by Zhu et al. (2020, Atmos. Meas. Tech.), which the authors claim is "sufficient for calibration" (Lines 149-150). Yet, the current manuscript is lacking many details, including how their work differs from and improves upon Zhu et al., who also claim similar mass accuracy.

Response:

We thank the referee for this comment. Below we firstly summarized three helpful truths about mass calibration, which we believe could help the reader's understanding before we explain the difference between our current algorithm with our previous work, i.e., Zhu et al. (2020, Atmos. Meas. Tech.).

a) The coefficients in the linear function (Eq 4. with $v = 1$) are required to be determined.

b) The coefficients in the function account for the correctness of calibration.

c) Different calibration algorithm adopts different approach to determine the coefficients.

$$m/z_{\mathrm{c}} = \sum_{j=0}^{v} a_j \left(m/z_{\mathrm{r}} \right)^j \tag{4}$$

In our previous method, the mass calibration is based on assumed calibrants. Since no calibrants (standard chemicals) are physically added to the aerosol particles in SPMS measurement. For instance, in the mass spectrum to be calibrated, peaks around 24 Th is assumed to be exactly 23.98 Th (Mg^+), and the assumed exact value serves as presumed internal calibrant for determining the calibration coefficients. However, because such assumptions require empirical assignment of exact values to a portion of measured peaks in each mass spectrum, the method is limited when dealing with ambient particles. As discussed in our introduction section (Lines 57-64):

> *Previous studies attempted to avoid the addition of standard chemicals for calibrating the SPMS spectra, by assuming the exact m/z of certain peaks in the raw spectrum (Chudinov et al., 2019; Zhu et al., 2020). For instance, if a peak was observed between 23.50 Th and 24.49 Th in the raw spectrum, it was empirically assumed to be Mg^+ (23.98 Th), without considering other possibilities such as C_2^+ (24.00 Th) within the same range. Logically, the exact m/z could only be obtained after the mass calibration, implying that the rationality of the assumption could not be proved during the calibration process. Additionally, chemicals in the assumptions were used to serve as calibrants, although standard chemicals were not physically added. Therefore, the calibration approach in previous studies was empirical and could be subject to unreliability (Chudinov et al., 2019; Zhu et al., 2020).*

Instead, in our current algorithm, no such assumption is needed because all possible coefficients are tested. The quality of each possible calibration is quantified by the value function (a function quantifying the calibration quality by accessing characteristic ion patterns), which makes the current algorithm much more universal. As a comparison, while previous work could only calibrate <40% ambient particles, the current algorithm is suitable for >98% ambient particles. Further, the accuracy we proposed (~500 ppm) corresponds to a bilateral mass deviation < 0.025 Th at ~50 Th, which is 2 times more accurate than our previous result (~0.1 Th).

In addition, the description of "sufficient for calibration" is used for the linear function (Eq 4. with $v = 1$), rather than the calibration method proposed by Zhu et al. (2020, Atmos. Meas. Tech.), since our full description in Lines 149-150 is

> *For the current resolution of the SPMS, **a linear function** is sufficient for calibration (let $v = 1$) (Chudinov et al., 2019; Zhu et al., 2020; Gobom et al., 2002).*

Further, Zhu et al. include evidence of identifying nearby peaks (< 0.1 m/z), within the same mass spectra. Yet, in the current manuscript's abstract, the authors state "a twentyfold improvement in mass accuracy, from ~10,000 ppm (integer) to ~500 ppm (2 decimal places) was achieved", which seems misleading when compared to Zhu et al.

Response:

We would like to clarify some widely accepted conventions in mass spectrometry. When referring to the mass-to-charge ratio (*m/z*), the unit should be Th (Thomson), Da (Dalton), or atomic mass unit (amu). If we use m to represent *m/z* for brevity, mass accuracy could be defined as[1–4]:

> "In mass spectrometry, mass accuracy refers to the nearness of a measured *m/z* ratio with the "true" *m/z* value for an ion of interest. Mass accuracy is often reported as a parts-per-million (ppm) relative error value, which can be calculated as:"

$$mass\ accuracy = \frac{m_{\text{measured}} - m_{\text{true}}}{m_{\text{true}}} \times 10^6 \qquad (R1)$$

Therefore, our expression of mass accuracy as "…~500 ppm…" is proper. In addition, the accuracy we proposed (~500 ppm) corresponding to a bilateral mass deviation < 0.025 Th at ~50 Th, which is 2-times more accurate than our previous result (~0.1 Th) in Zhu et al. (2020, Atmos. Meas. Tech.).

It is also unclear why the intended journal for the current manuscript is ACP, since the manuscript focuses on method development (new calibration algorithm) for a specific instrument rather than new atmospheric science results.

Response:

The scope of the ACP Technical note is provided below:

> "Technical notes are peer-reviewed publications that report new developments, significant advances, or novel aspects of experimental and theoretical methods and techniques that are relevant for scientific investigations within the scope of the journal. These can also include developments or assessments of new or improved emission inventories, or the development of numerical algorithms for the interpretation of atmospheric data (such as statistical methods and

machine learning) …"

(https://www.atmospheric-chemistry-and-physics.net/about/manuscript_types.html)

Please note that single particle mass spectrometry is an important apparatus for studying the chemical and physical properties of aerosols. We have developed a standard-free mass calibration algorithm for detailed chemical analysis in the mass spectra of individual particles, which fits into the scope of ACP Technical Note "development of numerical algorithms for the interpretation of atmospheric data". Further, our algorithm could be implemented in other mass spectrometers in environmental research by extending the prototype database, since the calibration theory we proposed is not restricted to single particle mass spectrometry.

Further, the assessment of the accuracy of the author's approach is unclear without running lab standards to check their claims (only ambient particles were measured).

Response:

We sincerely thank the referee for this suggestion. Nevertheless, running lab standards is unnecessary in checking the validity of our algorithm, because our standard-free calibration algorithm is based on a database (prototype) containing theoretical information (exact m/z, isotopic fragmentation, etc.) about hundreds of chemicals (please refer to Table 1 for some examples), which means peaks in the lab standards will be exactly calibrated to the corresponding theoretical m/z values and thus is not helpful in proving the validity of our algorithm. In addition, in the real world, the chemical components of particles are complex and thus not predictable, it is required to develop a novel approach for checking the validity of calibration when dealing with ambient particles.

Table 1. Three types of traits in the prototype database for calibration.

Trait type	Criterion [a]	Related ions
Isotopic distribution (fraction) of ions [b]	$p(\sim6.015\ Th): p(\sim7.015\ Th) \approx 0.082: 1$	*Possibly $^6Li^+$, $^7Li^+$*
	$p(\sim11.999\ Th): p(\sim13.003\ Th) \approx 1: 0.011$	*Possibly $^{12}C^+$, $^{13}C^+$*
	$p(\sim17.026\ Th): p(\sim18.023\ Th) \approx 1: 0.004$	*Possibly NH_3^+*
	$p(\sim23.984\ Th): p(\sim24.985\ Th): p(\sim25.982\ Th) \approx 1: 0.127: 0.140$	*Possibly $^{24}Mg^+$, $^{25}Mg^+$, $^{26}Mg^+$*
	$p(\sim28.030\ Th): p(\sim29.034\ Th) \approx 1: 0.021$	*Possibly $C_2H_4^+$*
	$p(\sim29.013\ Th): p(\sim30.010\ Th) \approx 1: 0.007$	*Possibly N_2H^+*
	$p(\sim31.018\ Th): p(\sim32.021\ Th) \approx 1: 0.011$	*Possibly CH_3O^+*
	$p(\sim35.999\ Th): p(\sim37.003\ Th) \approx 1: 0.032$	*Possibly C_3^+*
	$p(\sim38.015\ Th): p(\sim39.018\ Th) \approx 1: 0.032$	*Possibly $C_3H_2^+$*
	$p(\sim38.963\ Th): p(\sim40.961\ Th) \approx 1: 0.072$	*Possibly $^{39}K^+$, $^{41}K^+$*
	$p(\sim39.962\ Th): p(\sim43.955\ Th) \approx 1: 0.022$	*Possibly $^{40}Ca^+$, $^{44}Ca^+$*
	$p(\sim57.935\ Th): p(\sim59.930\ Th): p(\sim61.928\ Th) \approx 1: 0.385: 0.05$	*Possibly $^{58}Ni^+$, $^{60}Ni^+$, $^{62}Ni^+$*

	$p(\sim125.859\ Th): p(\sim127.857\ Th): p(\sim129.855\ Th)$ $\approx 1: 0.889: 0.120$	Possibly $^{126}Cu_2^+$, $^{128}Cu_2^+$, $^{130}Cu_2^+$
	$p(\sim197.967\ Th): p(\sim198.968\ Th): p(\sim199.968\ Th): p(\sim200.970\ Th): p(\sim201.971\ Th):$ $p(\sim203.973\ Th) \approx 0.334: 0.565: 0.774: 0.441: 1: 0.23007$	Possibly $^{198}Hg^+$, $^{199}Hg^+$, $^{220}Hg^+$, $^{201}Hg^+$, $^{202}Hg^+$, $^{204}Hg^+$
	$p(\sim205.974\ Th): p(\sim206.976\ Th): p(\sim207.977\ Th) \approx 0.460: 0.422: 1$	Possibly $^{206}Pb^+$, $^{207}Pb^+$, $^{208}Pb^+$
Chemical distribution patterns [c]	$\sim50.95\ Th$ & $\sim66.95\ Th$	Possibly V^+ / VO^+
	$\sim47.948\ Th$ & $\sim63.943\ Th$	Possibly Ti^+ / TiO^+
	$\sim n*11.999\ Th, n = 2, 3, 4, 5, ...$	Possibly $C_n, n = 2, 3, 4, 5, ...$
	W^+ distribution & WO^+ distribution	Possibly W^+, WO^+
	Pb^+ distribution & PbO^+ distribution	Possibly Pb^+ / PbO^+
	$\sim(n*1.007 + m*11.999)\ Th, n, m = 1, 2, 3, ...$	Possibly $C_nH_m, n, m = 1, 2, 3, ...$
Isolate ions [d]	$\sim7.015\ Th$ exists	Certainly $^7Li^+$
	$\sim11.999\ Th$ exists	Certainly ^{12}C
	$\sim-1.008\ Th$ exists	Certainly $^1H^-$
	$\sim-12.001\ Th$ exists	Certainly $^{12}C^-$

a. The peak area at specific m/z is denoted p(m/z).

b. Once the isotopic pattern is matched, the criterion of trait corresponding to it could be satisfied. However, the behavior of the tentatively calibrated spectrum on the entire prototype database should be checked using the value function before determining whether one trait is truly positive. Thus, a weight was assigned to each trait for quantification of the matching process. In addition, isotopic fraction may vary in different aerosol particles of different sources, such that an error range (5% in our calibration) was considered in practice.

c. The listed pairs of species may or may not coexist in a spectrum, with the weight assigned to each trait corresponding to the number of ions involved.

d. Isolate ions are far from adjacent ions ($\Delta m/z > \sim1\ Th$) with no other ions confusing their determination.

Therefore, we developed the calibration algorithm in which the validity of calibration could be

checked by a purely mathematical approach. Before we refer to the mathematical approach, we would like to summarize our calibration and the corresponding validation checking approach (Section 2.2.) as the following steps:

a) Choose a proper calibration function (Eq.4), specify the corresponding coefficient space (a set of all possible calibration coefficients) by observing a large number of spectra, build a prototype database that contains information about characteristic ion fragments (Table 1);

b) Try all possible choices of coefficients in the coefficient space, generate all possible calibrated spectra;

c) Calculate the *value* of each calibrated spectrum by the value function, the optimal calibration corresponds to the maximum *value* because, with maximum value, characteristic ion fragments in the prototype database are fully matched. If a maximum *value* does not exist, i.e., *value* = 0 for every calibrated spectrum, the calibration failed, otherwise the calibration is valid. Note that if we extend the prototype database and make it contain more characteristic ion fragments, the calibration failure rate will decrease.

Specifically, in Lines 123-131, we detailly proposed the method for checking the optimal calibration.

As the value function is defined, the quality of a tentatively calibration is quantifiable, because the optimal calibration attempt generates the maximum value. If none of the θ allows a spectrum possessing a value > 0, the spectrum cannot be calibrated until the prototype is expanded to include additional traits. However, how the value is distributed in the θ space is unknown, which means an advanced optimization algorithm is not currently suitable for optimizing θ. Thus, the obtainment of θopt requires a thorough search in the entire θ space. Therefore, every possible θ in θ space should be traversed and tested to generate a St (Fig. 1). In our iterative search for θopt in θ space, the step size of iteration is set to be sufficiently small (at least comparable to the resolving ability of the MS) to ensure thorough exploration of the θ space for reaching the global optimum. In other words, the step size ensures the calibration converges toward the optimal solution and was determined by the resolution of the mass spectrometer used.

And we have already checked the validity of our calibration algorithm, as described in Lines 166-167:

The calibration failure rate was less than 2% of the total spectra (value = 0), primarily due to the absence of corresponding traits in the prototype database for calibration. The high success rate (> 98%) reflects the universality of the algorithm.

There are also problems, described below, regarding misleading claims by the authors.

The authors state on Lines 208-209 that "the isotopic distribution and the accurate m/z values in Fig. 4 jointly imply the validity of our calibration." However, Figure 4 focuses on metals with isotopes separated by ~1 amu, for which the "improved" mass accuracy is not necessary.

Response:

We thank the reviewer for the comment. However, mass **accuracy** is used to describe the error between the exact m/z and the measured m/z, it is not related to the **separation** of peaks of isotopes

(Eq. R1). The ability to separate peaks is quantified by another term named **resolution**, which is related to the resolving ability of the instrument. The definition of mass resolution is[1–4]

> "The resolving power, that is, the ability to differentiate two masses, is given by the resolution R, defined as the nominal mass divided by the difference between two masses that can be separated:

$$mass\ resolution = \frac{m}{\Delta m} \qquad (R2)$$

> where Δm is the mass difference between two resolved peaks and m is the nominal mass at which the peak occurs."

Seemingly, the referee is asking for high resolution rather than high accuracy (our focus). In Figure 4, the accuracy is reflected by the *m/z* values (shown as the label upon each peak) of the peaks of each isotope, rather than the spacing between different isotopic peaks.

In Figure 5a, the authors zoom in on the averaged mass spectrum of particles that were determined to contain both CaOH+ and C3H5O+, but without viewing the remainder of the mass spectrum (to look for the co-presence of Ca+ and other oxygenated organics, for example), the reader is not able to evaluate whether the co-identification of these two different ions is accurate, as stated on Lines 221-222. It would be informative to view the calibrated individual particle mass spectrum, rather than an averaged mass spectrum of >1k particles.

Response:

We thank the referee and accept this suggestion. In the revised Figure 5a, we labeled all major peaks with the calibrated *m/z* values, which we believe could help the reader's evaluation and understanding. Nevertheless, the determination of $CaOH^+$ and $C_3H_5O^+$ is based on the accurate *m/z* values. Theoretically, the peak at *m/z* = 57.05 Th is $C_3H_5O^+$, and the peak at *m/z* = 56.95 Th is $CaOH^+$ under the mass accuracy of ~500 ppm. We checked the coexistance of $CaOH^+$ and $C_3H_5O^+$ in each single-particle mass spectrum, and obtained thousands of spectra that contains both $CaOH^+$ and $C_3H_5O^+$. These spectra are then directly averaged to plot the averaged spectrum. Therefore, the averaged spectrum is as informative as the spectrum of individual particles in showing the coexistance of $CaOH^+$ and $C_3H_5O^+$.

Most of the text in Section 3.2 ("Determination of adjacent ions in single particles") focuses on distinguishing V+ and C4H3+ (0.05 Th). However, in the text and Figure 5 parts b & c, the authors report these ions did not co-exist within the same particles. Therefore, the goal of separating 0.05 Th adjacent ions within mass spectra of single particles (i.e. within the same particle, i.e. the same mass spectrum) is not achieved by this example. Therefore, the concluding sentence about this particular analysis (quoted here) is inaccurate: "…the successful determination of adjacent ions also validates our calibration algorithm." In addition, this makes the following statement at the end of introduction (Lines 72-73) also inaccurate: "For instance, two adjacent ions in tracing ship emissions, V+ (50.95 Th) and C4H3+ (51.00 Th), were isolated and analyzed for the first time at the single-particle level." The authors are presumably also referring to this in the abstract with the misleading statement: "The improved mass accuracy validated the determination of adjacent ions with m/z difference ~0.05 Th."

Response:

We thank the referee for this comment. In the revised manuscript, we change the topic of Section 3.2 from *Determination of adjacent ions in single particles* to *Determination of ions with close m/z value* in case of misunderstanding (here, "close ions" referring to ions with <0.5 Th difference in exact m/z between each other), since the goal of mass calibration is improving mass accuracy, i.e. aligning the *m/z* of peaks to its theoretical values, rather than separating adjacent ions in single-particle mass spectra (Eq. R1 and Eq. R2). Therefore, the coexistence of V^+ (*m/z* = 50.95 Th) and $C_4H_3^+$ (*m/z* = 51.00 Th) is irrelevant in proving the accuracy improvement.

In other words, according to the definition of mass accuracy, we are dealing with the problem below in the V^+ and $C_4H_3^+$ case in Section 3.2:

> A peak around 51 Th is detected in the raw spectrum, whether it is V^+ (*m/z* = 50.95 Th) or $C_4H_3^+$ (*m/z* = 51.00 Th) is unknown. We should calibrate the spectrum to get the accurate *m/z* value, and then determine whether this peak is V^+ or $C_4H_3^+$.

Since our calibration algorithm achieved the mass accuracy of ~500 ppm, the actual *m/z* value of a peak near 51 Th is determined within ±0.025 Th mass error. Therefore, after the calibration, we can confidently make the decision whether this peak corresponds to V^+ (*m/z* = 50.95 Th) or $C_4H_3^+$ (*m/z* = 51.00 Th). Further, although in our V^+ or $C_4H_3^+$ case, the coexistence of two m/z-values-similar ions is not observed, we have already provided another pair of m/z-value-similar ions, i.e., the case of $CaOH^+$ and $C_3H_5O^+$ in Section 3.2.

Theoretically, the ions with close *m/z* values in single particles are not restricted to pairs. There is also a possibility of 3 or more chemical species that possess a similar *m/z* value, and with our calibration algorithm, the correct species can be determined within 500-ppm accuracy.

Further, it is stated that "distinguishing V+ and C4H3+ in spectra is crucial in shipping aerosol research". Why is this, since organics have been previously shown (through single-particle measurements) to co-exist in shipping particles? Figure 5b also shows the presence of m/z 37 (unlabeled, but presumably C2H+) in the V-containing particles. Given the significant fragmentation of the original hydrocarbon compounds upon ionization, it is unclear what differentiating C4H3+ and C2H+ tells the reader, and this aspect is not discussed.

Response:

1. Previous studies proved the validity of using V^+ as the tracer of ship-emitted particles, while $C_4H_3^+$ is not a tracer of such particles .[5–7] Therefore, to identify shipping particles in ambient air using SPMS spectra, it is important to accurately identify the V^+ signal in each single-particle mass spectrum. While V^+ corresponds to *m/z* = 50.95 Th, the organic fragment $C_4H_3^+$ corresponds to *m/z* = 51.00 Th. The mass difference between these two species is ~0.05 Th, which requires ~500 ppm accuracy to distinguish them, otherwise there will could be an overestimation of shipping-emission particles. In previous studies, the SPMS has only integral-level accuracy, which means both 50.95 Th and 51.00 Th are considered to be 51 Th. Note that, no evidence in previous studies shows it is necessary for V^+ and $C_4H_3^+$ species to co-exist in individual particles, previous studies only proposed the possibility of organic fragments to coexist with V^+. Further, we have already permitted the co-presence of V^+ and $C_4H_3^+$ signals in

individual particles since their co-presence is not theoretically prevented. Nevertheless, we did not observe such co-presence in our ambient measurement, as stated in Lines 229-230:

> *The co-presence of V+ and C4H3+ signal in a single particle is theoretically permitted, though such a scenario was not observed in our database.*

2. Therefore, if the peak around 51 Th is not calibrated to determine whether it is V^+ or $C_4H_3^+$, as in previous studies, it is easy to overestimate the V^+ containing particles (i.e. ship-emitted particles):

> Case of overestimation: some particles only contain a 51.00 Th signal, which corresponds to $C_4H_3^+$, as observed in our result in Section 3.2. Without our calibration, these peaks would be considered as 51 Th (integral level accuracy), however, V^+ is also 51 Th under integral-level accuracy. Therefore, these $C_4H_3^+$-containing particles will be misidentified as V^+, and an overestimation of shipping particles occurs.

Furthermore, the overestimation underestimation will confuse subsequent works such as mechanism revealment and source apportionment.

In addition, in our manuscript, we have already distinguished the two particle groups (V^+ or $C_4H_3^+$-containing particles). The number of V^+-containing particles is 296,259, while there are also 105,477 $C_4H_3^+$-containing particles (do not contain V^+). Without our calibration, these $C_4H_3^+$-containing particles will be misidentified as V^+-containing particles, which will induce ~30% overestimation of shipping emission particles.

Lines 69 & 157 claim "successful" calibration, when I couldn't find an explanation of how that was evaluated. This seems challenging for ambient particles with unknown composition. There needs to be discussion of how "successful calibration" was assessed, rather than simply a statement of "success". Further, for the authors to back up their claims it would be useful for the authors to make lab standards of mixtures of compounds producing ions that are close to one another (such as the hypothetical ion pairs in Table S1) to test experimentally whether they have sufficient resolution and accuracy to separate the ions within an individual mass spectrum.

Response:

We thank the reviewer for the comment. To the best of our knowledge, this comment is equivalent to the comment "Further, the assessment of the accuracy of the author's approach is unclear without running lab standards to check their claims (only ambient particles were measured)" above. Therefore, here we only provide general explanations.

1. The approach the referee suggested "…. producing ions that are close to one another…" could only prove the resolving ability of the mass spectrometer (Eq. R2), while it is not suitable for proving the accuracy (Eq. R1). Further, the proof of mass resolution is already done by Du et al. (2022).

2. Further, aerosol generated by the mixture of standard chemicals contains only specific components that are added to the mixture. If such aerosols are measured by SPMS and their mass spectra are subsequently calibrated, the validity of the calibration is only checked on the specific aerosol type with specific components (lab standards). However, in the real world, the

chemical components of particles are complex and not predictable, so the validity of the calibration algorithm remains unsure on different particles, regardless the algorithm works well on the lab standards.

3. As described above, the validity of the calibration algorithm should be checked through a more universal approach, and we have already proposed such an approach in our manuscript.

The authors state, on Lines 112-114 (with a similar statement on Lines 147-149), "The coefficients of Eq. (4) are restricted within a specific range, partially because of the constrained initial position deviation of the particles and the size of the laser spot (Text S1, Fig. S1)." However, no information is provided in Text S1 or Fig S1 (general instrument schematic) about this "initial position deviation" or laser spot size, so the reader is not able to evaluate or understand this statement.

Response:

We thank the referee for this comment. However, in our Text S1, we have already provided the information required by the referee:

The initial positions of ions before flight in the TOF-MS are deviated resulting from the focusing limit of AFL,(Dienes, 2003) leading to shifts in the flight path and the accelerating potential from the designed parameters (Fig. 1b), and consequently, a drift in the flight time and the corresponding m/z.(Wang et al., 2010) Since the deviation is uncertain for each particle, specific coefficients are required in the calibration function for individual particles.(Chen et al., 2020; Clemen et al., 2020) Moreover, studies have shown that the inhomogeneity of ionizing laser could also influence the mass measurement.(Wenzel and Prather, 2004)

The reason for the mass deviation is related to instrument construction, which is out of the research scope of this study. Therefore, we only provide some potential reasons for this deviation. Nevertheless, though the causes of mass deviation are not our focus, we have already analyzed the range of mass deviation through a statistical approach (Line 143-145).

Section 2.1: Since the calibration of mass spectra from a specific single-particle mass spectrometer (the HP-SPAMS) is the focus of this manuscript, it is critical to include information about the instrument in the main text methods, rather than only in the SI text. Text S1 should be moved to the main text. Even the instrument name is missing here in the main text. Since the authors are presenting ambient particle data, it is also crucial that the authors provide additional sampling information, beyond only the location and month of sampling (e.g., dates, sampling inlet information, etc).

Response:

We thank the referee for this advice and agree to move some details from the SI to the main text, such as the detailed sampling date and the instrumentation. The revised description of Lines 79-80 is provided below:

A sampling campaign was conducted at Southern University of Science and Technology (SUSTech) located in urban Shenzhen, China (22.604°N, 114.006°E, 100 m above sea level) from April 2, 2021, to April 30, 2021. TOF spectra of 12,371,204 individual particles were continuously collected using an SPMS (HP-SPAMS, Hexin Instrument Co., Ltd.) with detailed

instrumental information provided in Text S1 (Zhai et al., 2023). Briefly, aerosols are focused using an aerodynamic focus lens (AFL) to form a particle beam. Particles in the beam are then sequentially ionized by laser desorption/ionization (LDI) technique. The resulting ions fly under the force of accelerating potential in a TOF-MS. Time-of-flight data are obtained by calculating raw m/z with predetermined parameters of the TOF-MS, e.g., length of flight path and voltage of the accelerating potential. In our HP-SPAMS, the delayed extraction technique is implemented, which improves the mass resolution from 500 to 2000. The improved resolution provided the foundation for achieving ~500 ppm mass accuracy by calibration.

The Du et al (2022) reference corresponds to an EGUSphere pre-print that does not appear to have resulted in a publication. It is inappropriate to cite this manuscript.

Response:

We thank the referee for this comment. The preprint (Du et al (2022)) we cited is recently available online at Atmospheric Measurement Techniques (https://doi.org/10.5194/amt-17-1037-2024), and we have changed the reference to this published version in our reference list.

Additional comments:

The authors state in the abstract (Lines 25-26) that "atmospheric trace ions that were poorly studied before are successfully specified". This phrasing could easily confuse a reader, as "atmospheric ions" typically refers to gas-phase ions, rather than ions produced from particle ionization during measurement, which is what I believe the authors are referring to here.

Response:

We thank the referee and accept the suggestion. In the revised manuscript, we have changed the expression "atmospheric trace ions" to "particulate trace elements" in case of potential confusion.

Lines 208: The authors refer to the isotopic distributions of metal ions are showing "validity of our calibration". However, while the spacing of the isotopes were assigned in the calibration, I did not find any report of isotopic ratios that would further aid in assessment of the accuracy of the assignments.

Response:

We thank the reviewer for the comment. Examples of isotopic ratios have been provided in Table 1 named *isotopic distribution (fraction) of ions*. Actually, in our calibration, the isotopic ratios serve as criteria in assessing the calibration quality by the value function and are considered to be satisfied within an error range of 5%. This point is implied in Lines 97-107:

A tentatively calibrated spectrum is created by substituting θ into Eq. (1). Among all θ in θ space, there exists only one optimal θ, denote θopt, that yields the accurate spectrum. An indicator is required to determine whether a specific θ is optimal. In our algorithm, the indicator is a value function. The value function assesses the quality of calibration by analyzing the traits that the calibrated spectrum possesses, and could potentially guide the search for the θopt. Traits are characteristics that distinguish accurate spectra from inaccurate ones. The value function is defined in Eq. (2) and (3), where wi represents the weight assigned to each trait and is the number of m/z involved in the specific trait, n represents the total number of

traits, St is the tentatively calibrated spectrum, Ti is the ith trait in a database named prototype, and match is a function for determining the presence of Ti in each spectrum. The method for the selection of traits is provided in detail in Text S2. A searching range of m/z comparable to the resolution is used in match. Generally, there exist 3 types of traits, and examples of the traits are given in Table 1 for atmospheric aerosol research. All the traits are collected in a database named prototype, and the congruence of each trait in the prototype should be tested with St as shown in Eq. (3).

Nevertheless, we now add the following description about using the isotopic ratios in our revised manuscript to help the reader's understanding (Lines 108-109):

Specifically, in the traits typed "isotopic distribution (fraction) of ions", both the isotopic ratios and the exact m/z serve as conditions for trait matching in our calibration.

Line 243: It is stated that the mass spectra (shown in Figure b & c) are the result of "averaging millions of particles". Please provide actual numerical values for each group of particles, and clarify if these millions were all obtained during the time period shown in Figure 5d.

Response:

We thank the referee for this suggestion. We have added the specific details about the particle groups and modified our description in Lines 228-229 as:

Two distinct groups of mass spectra were isolated from our 10-million database of single-particle mass spectra, each containing 296,259 and 105,477 mass spectra with signals at 50.95 Th (V^+) or 51.00 Th ($C_4H_3^+$), respectively.

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