

Response to Referee 1

We sincerely thank the valuable comments and suggestions from Referee 1. We accept the majority of the suggestions and extensively revise the manuscript accordingly. Here we provide point-by-point replies to all the comments.

Reviewer 1

This study describe a standard-free mass calibration algorithm used for the detailed chemical characterization of individual particles by single particle mass spectrometers. Their algorithm allows to improve mass accuracy by a factor of 20. In addition, it makes it possible to differentiate adjacent ions with similar m/z (difference of 0.05 Th) and to identify trace ions that were poorly studied in the litterature. Overall, the results of this article may help to improve our knowledge of atmospheric chemistry. However, some of the passages are difficult to read and the English should be revised. Some of the comments and suggested English corrections are listed below.

Abstract

1. Instead of using the terms "tentatively calibrated", I would recommend saying "precalibrated" or "initially calibrated" to better emphasise the provisional aspect. The same applies to the rest of the paper

Response: We sincerely thank the referee's suggestion and replaced *tentatively calibrated* to *initially calibrated* in the revised manuscript.

2. L23 – 24 : Change

« With maximum conformity, the optimal calibrated spectrum was obtained. »

With

« The optimum calibrated spectrum was obtained with maximum conformity. ».

Response: We accept the referee's suggestion and revised in our manuscript accordingly.

Introduction

1. L42 – 43 : « The transformation could be described using mathematical functions (Kozhinov et al., 2013; Kolarova et al., 2017; Lou et al., 2010). ». This is not essential to understand, considering the following sentence.

Response: We sincerely thank the reviewer for this comment. However, to the best of our knowledge, the mathematical functions value a word to explanation as the background knowledge of mass calibration of mass spectra, in case of potential confusion between different calibration methods. Therefore, we decide to keep this sentence in the manuscript.

2. L65 – 76 : Too much information for the introduction. Try to be concise and just present the study's plan.

3. L75 – 76 : « The improved understanding of particle composition was also proved by increased spectra entropy from an information theory perspective. ». This sentence comes out of nowhere.

Response: We thank the reviewer for this suggestion. We have revised our introduction and present our study's plan as follows:

Here, we present a calibration algorithm that eliminates the need for internal, external, or assumed calibrants for single-particle mass spectra. We first developed a calibration theory, in which the traits possessed by accurate mass spectra were concluded. After that, a value function was established to quantitatively assess the quality of calibration. Calibration was successfully applied to more than 98% of the total 12 million SPMS spectra of ambient aerosols with an average mass resolution of 2000, and the bilateral mass deviation range was limited to ~ 0.05 Th on average. With the improved mass accuracy (~ 500 ppm), the detailed chemical composition of single particles was revealed. The improved understanding of detailed chemical composition was also proved by increased spectra entropy from an information theory perspective.

Methodology

1. L150 – 151 : Change

« encompassing a large amount of the chemical species and distribution patterns of high occurrence in ambient aerosols »

with

« and includes a large number of chemical species and distribution patterns commonly found in ambient aerosols. »

Response: We accepted the referee's suggestion and revised our manuscript accordingly.

2. L163 – 164 : Change

« is suitable for the implementation of the algorithm, because of the absence of interference when calibrating different mass spectra spontaneously. »

With

« is suitable for implementing the algorithm because there is no interference in the spontaneous calibration of different mass spectra. »

Response: We accepted the referee's suggestion and revised our manuscript accordingly.

3. L165 : Change

« only ~ 12 hours was consumed. »

With

« only ~ 12 hours consumed. »

Response: We accepted the referee's suggestion and revised our manuscript accordingly.

Results and discussions

1. L177 : Replace « correctness » with « accuracy »

Response: We accepted the referee's suggestion and revised our manuscript accordingly.

2. L206 – 207 : Change

« with an accuracy of ~500 ppm (Fig. 4), whereas their presence is difficult to determine in the raw spectra, and thus these species were poorly studied before. »

With

« with a precision of ~500 ppm (Fig. 4), although their presence is difficult to detect in the raw spectra and has therefore been little studied in the literature. »

Response: We accepted the referee's suggestion and revised our manuscript accordingly.

3. L 254 – 255 : Change

« Principally, mass spectra are comprised of peak information. With our algorithm, calibration of adjacent m/z is achieved, thereby preserving crucial peak information. »

With

« Principally, mass spectra are made up of peak information. Our algorithm achieves calibration of adjacent m/z, thereby preserving critical peak information. »

Response: We accepted the referee's suggestion and revised our manuscript accordingly.

4. Part 3.3 should be better explained as the Shannon entropy comes out of nowhere and is not explained.

Response: We sincerely thank the reviewer for the advice. We have revised the description of Shannon entropy which we believe could help the reader's comprehension.

Principally, mass spectra are information that is made up of peaks. According to information theory, the information content in any mass spectrum could be quantified by Shannon entropy (Shannon, 1948).

Conclusions and implications

1. L275 : add « ppm » at « ~1000 »

Response: We thank the reviewer for this suggestion. However, in L275, ~1000 is used to describe mass resolution, therefore, it is appropriate to be dimensionless here, since *ppm* is conventionally a metric of accuracy.