

Interactive comment on “FATES: A Flexible Analysis Toolkit for the Exploration of Single Particle Mass Spectrometer Data” by Camille M. Sultana et al.

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Response to Comment 1: To keep the paper clear and concise, specific examples and instructions for changing the data formats are not detailed in the paper. However, an extensive FATES manual has been developed and is now included as a supplement to the paper. Where appropriate, references to specific sections of the manual are made throughout the entirety of the paper to guide the intended users of the program.

Also FATES has now been successfully implemented with three distinct SPMS datasets: ATOFMS (operated in Dr. Kim Prather’s lab at the University of California, San Diego), ALABAMA (operated in Dr. Johannes Schneider’s lab at the Max Planck Institute for Chemistry), and commercial TSI-ATOFMS (operated in a number of labora-

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ories world-wide). Data files for these SPMSs have completely different organizations and structures and store a variety of variables that are not all shared between the datasets. However, the inconsistencies in the variables recorded within each dataset provided no barrier to implementation within FATES due to the toolkits designed flexibility.

Response to Comment 2: Unfortunately due to both the qualitative and inconsistent nature of SPMS spectra, developing “standard” criteria for creating robust particle types is well beyond the scope of this paper and is realistically not feasible across an unbounded set of particle types and a range of different instruments. First, it is important to note that the generation of single particle mass spectra will be heavily influenced not only by particle composition but also by SPMS instrumental design and operation. Different desorption and ionization laser wavelengths and powers, single-step versus two-step ionization methods, single polarity versus dual polarity acquisition, and the pre-processing functions for baseline determination, noise reduction, and peak picking algorithms will all influence the collected data. Furthermore, discussions on accurate methods to identify particle types not only span a range of mathematical and grouping techniques (Giorio et al., 2012; Gross et al., 2010; Murphy et al., 2003; Rebotier and Prather, 2007; Zelenyuk et al., 2008a), but also are usually specific to a narrow set of particles or even a single type (Pratt and Prather, 2009; Silva et al., 1999; Silva and Prather, 2000; Zawadowicz et al., 2016), and may also be instrument dependent (Hinz et al., 2006). Because of this setting, some sort of standard clustering threshold (whether using ART-2a, K-means, or a clustering algorithm of choice) will almost certainly leave some particle types split across multiple clusters and some clusters composed of multiple particle types (Murphy et al., 2003; Phares et al., 2001; Rebotier and Prather, 2007; Wenzel and Prather, 2004; Zelenyuk et al., 2008a). This reality means SPMS analysis on external aerosol populations will almost always require some form of expert knowledge and further analysis beyond initial algorithmic grouping, as specified in almost all field study publications (e.g. Dall’Osto and Harrison, 2006; Pratt and Prather, 2009; Qin et al., 2012). The various visual interfaces provided in FATES

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were built to facilitate the flexibility needed to properly create and shape particle types and allow to more thoroughly and freely investigate both ungrouped datasets and initial groupings generated by various algorithms. Below we detail some of the specific hurdles to generating these specific recommendations from the reviewer.

As mentioned in the paper, it has been frequently demonstrated that the mass spectra generated via laser desorption/ionization (LDI) show wide particle to particle variation even for particles of identical chemical composition (e.g. Gross et al., 2000; Wenzel and Prather, 2004; Zelenyuk et al., 2008). This variation is exacerbated by variations in particle size (Reinard and Johnston, 2008; Zelenyuk et al., 2008a), inconsistency in laser fluence experienced by the particles (Steele et al., 2005; Wenzel and Prather, 2004), or spatial chemical heterogeneity within particles (Cahill et al., 2015; Cai et al., 2006; Zelenyuk et al., 2008b). Gross et al. (2000) show that for 1 μm particles composed of 2,4- dihydroxybenzoic acid and ionized by an inhomogeneous laser, ART-2a generated 15-20 clusters even for very low vigilance factors (0.2-0.6), well below the threshold for initial clustering which is usually utilized for field study datasets (~ 0.7 - 0.8) where there is a need to separate spectra from actually distinct particle types (e.g. Dall'Osto and Harrison, 2006; Pratt and Prather, 2009; Qin and Prather, 2006). These problems in spectra variation are intensified for particle types where all particles are of similar composition, but within each particle there is spatial heterogeneity in the chemical makeup, such as “core-shell” morphologies. For example, Zelenyuk et al. (2008b) showed that 146 nm NaCl particles, coated in a 59 nm shell of dioctyl phthalate (DOP) can generate mass spectra with 100% contribution from DOP ions to 85% contribution from NaCl ions at a constant laser power of 0.38 J/cm². Algorithmic analysis of these mass spectra would divide these results into an array of distinct particle types, despite the existence of only a single particle population. A wide array of particle types can exhibit chemical spatial heterogeneity, such as effloresced sea spray aerosols and particles which have undergone secondary processing (e.g. reaction with nitric acid, condensation of gas phase organic species, etc.). We have detailed just a few of the many examples in the SPMS literature, where particles with identical chemical compo-

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sition generate widely disparate mass spectra.

Analysis of SPMS datasets is also made more difficult by the fact that a combination of matrix effects (Hinz and Spengler, 2007; Nash et al., 2006; Sullivan and Prather, 2005) and differences in ionization efficiency (Bhave et al., 2002; Ge et al., 1998; Gross et al., 2000; Hinz and Spengler, 2007; Spencer and Prather, 2006) result in non-quantitative mass spectra. As such, mass spectra can have large relative contributions from minor components of the particle composition and major components of a particle may only contribute negligibly to the mass spectra. This can result in distinct particle types having very similar mass spectra (Murphy et al., 2003; Silva et al., 1999; Zawadowicz et al., 2016). For example, one area of ongoing discussion is the accurate identification and discrimination between aerosolized dust and cells, because both types often share major ion markers (potassium, phosphate, organic nitrogen) with only frequently much smaller ion markers, such as silicates and aluminum, distinguishing between the two (Ault et al., 2011; Creamean et al., 2013, 2014; Holecek et al., 2007; Pratt et al., 2009; Zawadowicz et al., 2016).

The array of SPMS designs and the non-quantitative nature of SPMS mass spectra combined with the wide particle-to-particle mass spectral variation for particles even of similar particle composition, demands flexible data analysis techniques. This is already noted briefly in the paper and the concept will be very familiar to SPMS users. The authors know of no algorithmic methods or associated thresholds utilizing mass spectral information that have been shown to both reliably separate distinct particle types across a large range of chemical compositions and also maintain single particle types within a single cluster. We now emphasize at the end of section 4.1 that this is still an area of active research and discussion in the SPMS field and provide a number of references on the topic. However as stated previously this topic is well beyond the scope of this paper to discuss. A promising potential technique for creating accurate particle types from SPMS datasets is the use of discontinuities in common particle data, such as particle size as discussed by Zelenyuk et al. (2008b), but could also be

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extended to values such as total ion intensity. Because this technique is not dependent on specific ion markers, it has the potential to be effective for a broad range of particle types, but is yet to be fully explored. In addition the technique as described by Zelenyuk et al. (2008b) still requires user input to subjectively identify discontinuities. This work by Zelenyuk et al. (2008b) was already briefly referenced at the end of section 4.1, but the discussion has now been expanded slightly to highlight the potential of the “discontinuity technique.”

Response to L95: FATES has been tested for compatibility with MATLAB 2016b and is compatible. The text has been changed to reflect this.

Response to L109: The first instance of ‘id’ has now been changed to ‘identifier (ID)’. All further instances of ‘id’ have been changed to ID.

Response to Section 2.2: A table has now been included to summarize the various run times. While FATES has been updated to be able to import and utilize ALABAMA and TSI-ATOFMS data, we have not included run times beyond study creation. All run times outside of “study creation” will be comparable across SPMS datasets. All SPMS datasets are held in the same FATES data architecture, so data retrieval and analysis is controlled by the size of the data to be retrieved and the FATES data architecture itself. It should be noted that the datasets provided by other laboratories (ALABAMA and TSI-ATOFMS) were only provided to perform proof-of-concept. As such we were only given small amounts of data: 10,000 hit particles from ALABAMA and 68,400 particles for the TSI-ATOFMS. The run times to initiate study creation for these test datasets are included in Table 2 and discussed briefly in Section 2.2. In addition section 2.2 has been reorganized slightly to make it easier to follow.

Response to L318: Please see the response to comment 2. In addition, we would like to emphasize that FATES is a toolkit, and is not a technique. The FATES toolkit allows users to organize SPMS datasets in MATLAB in a standardized architecture regardless of specific SPMS instrumentation. This allows datasets to be easily shared

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between labs and that continuity can be maintained within labs even as improvements and additional functionalities to individual SPMS datasets are made. FATES is an open-source toolkit, meaning that users have easy access to all code associated with FATES. Therefore, users may modify scripts if needed for their individual lab's purposes but also there is complete transparency for how the data is imported, stored, processed, and analyzed. FATES has been designed to minimize memory demands and computational time required for processing importing, storing, recalling, and analyzing particle and spectral data. Once an SPMS dataset is stored as a FATES study users can apply a virtually unlimited set of analysis techniques utilizing native MATLAB functions. In addition within the FATES toolkit there are a set of visual interactive data analysis tools have also been provided, which can act as a complement to script and algorithmic-based analysis techniques. In summary, FATES is a toolkit intended to enable knowledge discovery from complex SPMS datasets. However, as discussed extensively in the reply to comment #2, laying out "rules" for the wide array of available analyses is well beyond the scope of this paper.

In addition, the visual tools provided in FATES can also be utilized in exploration of datasets consisting of a single particle type. Many papers have been published detailing the effects of laser power (Steele et al., 2005; Wenzel and Prather, 2004), size (Reinard and Johnston, 2008; Zelenyuk et al., 2008a), water content (Neubauer et al., 1997, 1998), and spatial chemical heterogeneity (e.g. Gross et al., 2000; Wenzel and Prather, 2004; Zelenyuk et al., 2008) on laboratory-generated uniform particle populations. In these cases, because the user is not attempting to create distinct particle types, but rather understand the influences of particle and experimental characteristics on the mass spectra generated where algorithmic grouping utilizing mass spectra is largely unnecessary or even inappropriate. In these cases there is no "satisfactory" result, because the goal is not to create or identify particle types, but to more amor- phously understand multivariate influences on mass spectral generation.

Response to Section 4.4: As with many aspects of SPMS data analysis, there are

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not standard procedures for mass calibration across SPMS designs, and attempts to create standards are somewhat fraught by the mass spectral particle-to-particle variation. While not discussed extensively in the literature, the time of flight of specific m/z will vary depending on the laser fluence experienced by the particle, the location of the particle in the ionization/extraction region of the mass spectrometer, and also the degree to which the particle's chemical components absorb the ionizing radiation. This means that with even careful creation of calibration parameters, there is still often variance in calculated m/z values for what should be identical ion peaks. We are only familiar with the standards used for calibration used in the Kim Prather lab at UCSD, which still result in imperfect calibrations for some particles due to the reasons detailed above. Other laboratories likely have different standards, and it is not unlikely that best practices would vary between instrumental designs. The paper has been modified to gently suggest the methods utilized in Kim Prather's lab at UCSD, but we are hesitant to label such as "standards".

Response to Figures: The annotations on the figures have been enlarged. In addition the resolution of the figures have been greatly increased to allow closer examination.

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