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Atmospheric Measurement Techniques Discussions

Interactive comment on "Orbitool: A software tool for analyzing online Orbitrap mass spectrometry data" *by* Runlong Cai et al.

Anonymous Referee #3

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General comments:

The authors present the application of a novel software solution (open source) for analyzing Thermo Fisher raw mass spectrometry files, which are not designed for online monitoring. This is of great value for the atmospheric science community, which increasingly applies Orbitrap technology for atmospheric applications. The paper certainly fits into the scope of AMT.

However, the paper requires quite some language editing and needs to explain some approaches more in detail. I am surprised that the major benefit of a HR-MS is not shown: the capability to resolve isobaric species.

Furthermore, the authors should comment on the data acquisition of the Orbitrap,

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Discussion paper

which pre-filters data and should only record signals that are not attributed to (electronic) noise. Otherwise, the reader might be confused by the extensive effort of distinguishing noise from signal.

The term “identification [of compounds]” is used in this manuscript quite often, but it rather describes the attribution of a molecular formula to a measured mass. An accurate mass measurement (incl. isotopic pattern) can only help in determining the sum formula, not the identification of compounds! For the correct use of “molecular identification” see Noziere et al., Chem. Rev., 2015. Therefore, the abstract needs rewriting, since the terms “identification” and “separation” are discussed in a wrong context.

Since Orbitool is GUI-based software, some words about installation instruction on the website can be helpful for researchers which are not familiar with Python, but still are willing to use the software.

Overall, the manuscript fits into AMT very well, the work is important for the community, but the paper needs additional information, major rewriting and some corrections, as partly listed under the following comments.

Specific comments:

p.2 l.8: Do you really mean “noise”? IUPAC definition of noise: “The random fluctuations occurring in a signal that are inherent in the combination of instrument and method.” Maybe your analysis just discards noise with a more strict filter than the XCalibur acquisition software (which to my knowledge already applies a noise-filter during data acquisition)?

p.2 l.9: The presented work does not show ozonolysis of monoterpenes, as atmospheric scientists would think of. You tested ozonolysis of orange peel emissions. These emissions contain monoterpenes, but not exclusively.

p.2 l.13: “Identification of unknown species” is not in line with the molecular identifica-

tion defined by Noziere et al. – it is rather “sum formula attribution” than “identification”.

p.2 l.15: In this case, do not use the term “separate” in order to avoid misunderstanding with chromatographic separation techniques.

p.5 l.10: TofTools also requires the background data between all nominal masses, which are not recorded by XCalibur.

p.6 l.7: Before describing how data are handled with Orbitool, it should be described how data are recorded (E.g. experimental setup, ion source settings, data acquisition settings (scan rate, pre-averaging, use of a lock-mass, centroid mode, profile mode?), etc.).

p.7, l.9: I do not understand what the numbers of the mass defect range ([0.5, 0.8]) intend to express. What is the center of your mass defect and what is the isolation width. This does not become clear.

p.8, l.22: The concept of the lock mass is that the mass accuracy is stable for long time-series, making additional mass calibrations obsolete.

p.9, l.9-16: For ion signals which are > 1e6 molecules cm-3, the isotopic pattern can be used to verify / falsify sum formulas by calculating an isotopic pattern matching score. Is this feature possible with Orbitool?

p.11, l.16: Additionally to the mass defect plot, other visualizations might be also informative, such as the aromaticity index or the Kendrick mass defect.

p.11, l.22: Again, I do not understand the mass defect range of [0.5, 0.8] as a filter for determining the noise level. Does this rather broad range of 0.5 amu requires only one main ion signal within this range? My experience, is that in such a large mass range on can usually find more than five-to-ten different (baseline-separated) ion signals. I think the text needs a more detailed explanation.

p.12, l.10-12: “... number of peaks after noise reduction with the 50th percentile is

insensitive to the averaging time." –> I cannot see this in the data: After 5 min averaging time the number of peaks converges to ∼1000, after 30 min to ∼1300, and after 60 min to ∼2000. Hence, your reasoning appears questionable.

Figure 4: Can you also demonstrate the Orbitrap technology really has an advantage over ToF-MS by resolving several gas-phase signals on one nominal mass? My experience is that with NO3-CIMS (using ToF) of monoterpene ozonolysis peaks are already well fitted, and show little evidence for isobaric interference. A zoom in on the x-scale of both experiments would be worth to show.

Technical corrections:

Consider to minimize the use of "greatly" (used in p.2 l. 8, l. 13)

p.2 l.3: "wildly-used"? I think you rather intended to say "widely-used"

p.2 l.6: maintaining –> improving?

p.2 l.14: consider: . . . ambient gas-phase measurements in urban Shanghai.

p.3 l. 2: produce . . . into the atmosphere? Needs rephrasing. E.g. Biogenic and anthropogenic sources emit a wide variety of VOCs into the atmosphere.

p.4. l. 22-23: What do you mean with ". . .overcome the interference of noise and accumulate signals."?

p.8. l.20: It is m/z which is determined, not the mass.

Figure 5: blue and purple are very hard to distinguish from each other.

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