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Atmospheric Measurement Techniques Discussions

Interactive comment on "Statistical precision of the intensities retrieved from constrained fitting of overlapping peaks in high-resolution mass spectra" *by* M. J. Cubison et al.

Anonymous Referee #2

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The paper by Cubison et al. addresses the estimation of the statistical precision of peak intensities obtained upon deconvolution of two overlapping Gaussian peaks. Such statistical precision depends on several factors, among which this study considers only the m/Q calibration and the noise in the measurement distribution.
The general idea of the paper is useful to the atmospheric science communty given the increasing popularity of high resolution mass spectrometers but the paper is not publishable in the present form and needs major revisions.
The result section should be condensed, avoiding unecessary and redundant figures, focusing on meaningful points, and providing quantitative data to support the conclu-

sions. Many considerations are only supported by qualitative graphical observations and therefore may not be rubust. Examples: Section 3.2, Fig. S3-S7.
Generally speaking the paper should be presented employing a more "ready to use" approach, otherwise its usefullness for the audience would be limited. A more straightforward way to estimate the statistical precision of retrieved peak intensities (taking in input suitable parameters from constrained fitting) should be provided.

Specific comments:
- 12623, 8: give a definition for iToF space, although the meaning is generally understandable from the context
- 12623, 11: the mass resolving power should be m/Δm =(t/ Δt)/2=2000/2=1000
- 12623,16-23: the equation from which the calibration parameters are determinde should explicitly be provided. Moreover the way the perturbation on m/Q values is applied should be better explained
- 12624,1-2: even in modern aquisition systems, for low intensity peaks (e.g. for recorded at high m/Q values in ToF spectra) sometimes the baseline noise and the peak intensity are comparable
- 12625, 14: "The precision" should probably be substituted by "The uncertainty"
- 12625, 18: "1000" instead of "4000".
- 12624, 21-12625,25: σ is used to express SDs (e.g. for σ_A) or normalized precision (e.g. for σ_N). Please be consistent.
- 12626: in this section a quantitative determination of σ_C depending on the two peak intensities (and/or other suitable parameters) should be provided.
- 12629, 16: mass resolving powers should be half (and not double) of TOF resolving power reported in Fig. 3
- 12630: the reason why m/Q calibration errors affect estimation of ion intensities should be better explained. It is because peak positions are constrained in the fits? In this case, why an error in peak position does not affect estimated peak intensity appreciably in the case of "counting-error regime"? Is it because the considered

calibration errors are small? The authors should make an effort to quantify their claims (e.g. define “appreciable increase in the precision”)
- 12630: A definition of X_d should be provided. When is a value of σ_I defined to diverge from the counting-error limit?
- 12630: The considerations on the parameters from which X_d is independent should be more schematic or in a dedicated sub-section. Moreover, conclusions arising from graphical consideration (S3, S4, S5, S6, and S7) could be more straightforwardly motivated by quantitatively assessing the impact of each parameter on X_d and eliminating redundant figures.
- 12632, 6-19: a clear parameterisation of the dependence of σ_I and X_d on I_p, R_I, W, δ_t should be provided. The way it is presented in the paper is not effective.
- Supplementary material: it should be presented in a more convenient way. E.g. I have problems figuring out which figure is S1.

Technical corrections:
- 12619, 6 and 12619, 26: the reference Titzmann et al. 2010 is misspelled
- 12621, 22: “of” is not needed

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 12617, 2014.