**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 #1

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Cubison et al provide a theoretical piece on the achievable precision of least square retrievals of the intensities of unresolved peaks in time of flight mass-spectra. While the retrieved intensities are sensitive to a number of parameters, the authors focus on the uncertainty in mass scale calibration and counting statistics. In principle this work is publishable and of good service to an increasing community of TOF users in the field of atmospheric sciences.

While the general structure and most Figures are useful, the manuscript is poorly written (insufficient/sloppy, complicated and/or ambiguous explanations) and cannot be published without a major make over. In addition there are many odd sentences, so

thorough proofreading by English native speakers is required as well.

Another major point is that the authors should try to further reduce their results to distill the essence of their work. For example, Figures 5 and 6 are largely redundant and could be combined. The same holds for Fig 7a&c and Fig 7b&d, respectively. There are a number of Figures in the supplementary section, which, in my opinion, are not needed. In the spirit of community service it would be useful to provide a tool (short script or even spreadsheet) allowing users to estimate the precision of their modeled peaks (input parameters mass and modeled intensities of parent and child, resolution).

See below some specific comments as example (Note that there are many more issues than I have pointed out.):

12621,20-22: incomplete sentence

12623, 7-9: The sentence 'It is chosen. . .' is very confusing and refers to several unexplained facts: which are the peak parameters? What is the iTOF space? How is m/Q transferred to iTOF (give equation!) and wherefrom comes the non-linearity?

12623, 21-23: The sentence 'This perturbation was applied consistently to both fitted peaks for a given fit, but varied from one fit iteration to the next.' does not make sense.

12625,4-5: The sentence 'δt the separation of the discrete data points in iToF space' is hardly understandable.

12625, 14: odd sentence: 'The precision arising from counting error is unavoidable'

In Table 1 I miss sigma_A and sigma_t (section 3.1)

Figure 1: I don't understand what is displayed in the insert of Figure 1. Needs better explanation in the Figure caption.

12629,14-16: The given numbers do not seem to agree with Fig 3. The ppm precisions should compare to resolutions of 1000, 2000, 4000, and 8000.

Fig S5: give peak intensities in decimal powers

12632,20 – 12633,4: Even after carefully reading this graph three times, I don't understand the idea behind this.

Supplementary information:

The supplementary information is presented in a very inconvenient format and should be compiled into one pdf.

S1. The manuscript refers to S1a which is not labeled in the Figure. Furthermore, I do have problems connecting the caption text to what is shown on the Figure. This clearly needs improvement: What is displayed on x and y? What on the main chart and insert, respectively? What is the difference between the different datasets displayed?.

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

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