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Atmospheric Measurement Techniques Discussions

Interactive comment on "Three-dimensional factorization of size-resolved organic aerosol mass spectra from Mexico City" *by* I. M. Ulbrich et al.

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This paper presents the application of two 3D factorisation techniques to an AMS dataset. This is a very timely and relevant paper, given the fact that no-one has published an analysis technique such as this before. While many important papers have been published using 2D factorisation, these have intrinsically been limited to the integrated mass concentrations with no size-resolved information being delivered (although I am aware of people attempting this on a few occasions). While there is no great scientific insights provided in this instance, the work has the potential to be of

high significance if applied to other datasets. Overall, the paper is very thorough and certainly appears to be very diligently prepared. I have no hesitation in recommending this be published in AMT. I would ask, however, that the authors take the following (mainly technical) comments under consideration first:

General comments:

The error model as presented will not be completely sufficient for the 3-vector data model because it does not include particle counting statistics. This is not included in the 2D TOF-AMS error model for PMF because it is a multiplicative error in m/z space, however it will have an effect in PToF space if the aerosol is polydisperse (even if it is monodisperse, there will still be a smaller effect due to chopper broadening). Successive samples of a given aerosol will produce differently shaped distributions if the number of particles within a sample is small. However, this is unlikely to be an issue in a high signal environment such as Mexico City and is likely to be insignificant compared to the problems associated with 'real' changes in particle size with time. Given how much work would be involved in putting this in the error model, I am not asking the authors to include it. However, it should be mentioned as a caveat for the sake of someone attempting to repeat this work in a low signal environment. Note that this will not affect the vector-matrix model, as this treats the PToF points independently so random variations in the size distribution caused by particle counting statistics will not be discernible from 'real' variations.

I feel a little uneasy about how the beta parameter is being used to constrain the factors present. The difference in vaporisation times (which, to be fair, the authors point out on several occasions) presents a physical reason why the factor profiles from MS and PToF modes might not be expected to agree. Furthermore, the level of disagreement may vary factor to factor, so hence different levels of relaxation may be appropriate for different factors (although I accept that implementing and testing this would be a little much to ask for this paper). The discussion of the choice of beta to be 0.06 on pages 4592-3 justifies it empirically, but I would be more comfortable if the authors could

provide some more discussion in this section on the competing physical or statistical effects that would dictate the optimal value of this parameter, if only on a conceptual level. This will be invaluable to anyone attempting to repeat this work on other datasets because my gut tells me the optimal value is not likely to be the same.

The figure captions are, in general, a little on the long side. I would suggest the authors revise them for brevity and rely on the body text to convey some of the more technical concepts.

Sections 1 and 2 of the supplementary material are informative, but most of it does not seem to be relevant to the work presented here (the 2D work in particular seems a little out of place, given 2D factorisation of AMS data is already well established). Unless the authors can provide more context, I don't see why these sections are necessary.

Specific comments:

P4563, L4: The comment about being applicable to other techniques is not really adequately supported (see later). I would suggest removing or toning down this comment.

P4571: The authors are slightly incorrect in their discussion of PToF vs IToF times. IToF is the time taken to transit between the orthogonal extraction region and the detector, however all the data collected on an individual mass spectrum is organised according to the time of the extractor pulse, which is fixed in PToF space, so therefore IToF in itself will not cause any artefacts at all on the PToF distribution. However, what could potentially cause a problem is the time delay between ionisation and transport to the orthogonal extraction region. This is not measured and could, in principle, vary according to m/z ratio. This should be discussed.

P4579, L5: It is worth pointing out that the PToF distributions of the gases in the AMS have been found to roughly follow Boltzman distributions according to the kinetic velocities of the gas molecules (ch. 2 in: "Chemical Kinetics and Microphysics of Atmospheric Aerosols", James Morris, Ph.D. Thesis Boston College, 2002). This will cause

the CO2 molecules to arrive slightly later on average than the nitrogen molecules.

P4585, L23: The authors need to expand on what they mean by "too small" and what they are comparing them to.

P4598: One line of discussion notably absent here is whether the authors think that there is any 'real' variation in the mass spectral profile of factors taking place (BBOA, for instance, is known to vary according to fuel, burn conditions and atmospheric processing). This may be part of the cause for the variability and ambiguity in the solutions.

P4604-5: While it is tempting to think that this technique will be directly applicable to other aerosol mass spectrometric techniques, many of the examples cited will carry with them their own inherent issues that should not be trivialised. For instance, the GC/MS-FID will have the problem of column bleed, which could potentially play havoc with the data model presented here. Also, the AMS thermal denuder data will need to be binned and normalised to be put on a 3D data scheme, which will need to be taken account of in the error model. While 3D factorisation no doubt has great potential here, I'm a little concerned that the authors are perhaps a little too bullish about its chances of success.

Fig. 1: I find this figure a little bewildering. Given that b) and c) were not ultimately used and are not analogous to existing 2D factorisations of AMS data, I would strongly urge the authors remove these parts.

Fig. 2: The concept described in this figure has been in existence since the advent of the TOF-AMS and as such, I don't consider this figure necessary.

Figs. 7&8: Was the data smoothed before or after factorisation?

S12, L298: The average fraction should be stated

Technical comments:

P4565, L28: "only a few researchers" seems an odd choice of words given the three

lines of references that follow the sentence. Consider revising.

P4568, L5: Technically, it is “mass spectral profile” rather than “chemical composition”

P4571, L12: The standard calibration function used with the AMS (eqn. 9 in Allan et al., 2003) has a much more complex relationship than a simple inverse square root dependence.

P4573, L23: Allan et al. (2003) did present a method to calculate precision of PToF data in terms of a detection limit, although this would not necessarily be best suited to this application.

P4575, L19: The lower particle duty cycle will only affect precision when using the 3-vector model (see general points). The lower duty cycle is not necessarily the more important source of noise in PToF-resolved data; a potentially more significant cause is because the data is distributed through a larger number of channels. Compared to MS mode, less averaging takes place, so the electronic and background ion noise will be greater. The smoothing, in effect, partly reverses this.

P4599, L22: Surely this is also as a result of the non-negativity constraint on the data? Also, was the data used in the tracer method still smoothed?

P4602, L11: Recommend using something more descriptive than ‘spiky’.

Figs. 7-9: If the size distributions have been normalised, the quantity should not be described as dM/dlogdva, as this risks confusion with the non-normalised data.

Fig. 9: dM/dlogdva should have the units μg/mˆ3 in the non-normalised image plot. The normalised distributions should be dimensionless.

Supplement figures: The axis labels should be checked in light of the two points above.

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