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Atmospheric Measurement Techniques Discussions

Interactive comment on "Aerosol quantification with the Aerodyne Aerosol Mass Spectrometer: detection limits and ionizer background effects" *by* F. Drewnick et al.

Anonymous Referee #2

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Review of Drewnick et al.

This paper presents a detailed study on the detection limits of the main species detected with the AMS, comparing two versions of the instrument and the influence of several parameters. If this was a 'one-of-a-kind' instrument, such a paper would probably be overkill. However the AMS is rapidly becoming very popular in atmospheric science with of the order of 100 instruments being used at present by many groups around the world. Such a detailed analysis of the factors influencing the AMS detection limits thus has the potential to be useful to many scientists. The paper is clear and well written. I recommend publication in AMT after the following issues are addressed.

- P171 L7-11: here strangely the detection limits reported by Takegawa et al. (2005) are mentioned first, and later it is said that 'Bahreini et al. (2003) ... again determined...' Clearly the Bahreini paper was the first among those quoted to report AMS detection limits, and the text should be rewritten to reflect this.

- P173 L3: many AMS aerodynamic lenses have some transmission beyond 1 um, e.g. ˜60% in Fig. 9 in Jayne et al. (2000) and ˜50% in Figure A1 in Takegawa et al. (2008), who also show significant transmission at 1.2 um. A more appropriate value for negligible transmission is probably 1.5 or 2 microns.

- P175, L9: it is not a given that the noise will produce a normally distributed error curve. For example ion counts produce Poisson-distributed noise (Allan et al., 2003b, as discussed later in the paper), for which the normal approximation breaks down at low ion counts (high m/z or short averaging times).

- P177 Equation 4: one effect that is not considered here is that the noise at some m/z's does increase in the beam open position, even if no particles are present. This is true at m/z's that have a contribution for air molecules, such as m/z 16 from O+ or m/z 44 from CO2+. Also in the ToF-AMS the abundant air ions (N2+ and O2+) can lead to some electronic ringing and some 'dead microchannels', and are scattered by the grids in the instrument creating tails that extend for several m/z and that contribute significant noise. For example m/z 29 has much additional noise for this reason in the open beam position which is not present in the closed beam position, which can make the quantification of this ion difficult under low aerosol concentration conditions. The scattered ions extend to very high m/z, and can be a significant fraction of the noise at high m/z that have little aerosol signal (but may still have peaks of interest). Although these effects are likely not large since the DLs determined with this method compare well with those determined with a filter, they may explain why the filter DLs are larger for ammonium (due to the O+ effect) and organics (due to e.g. 29 and 44). This should be mentioned in the paper and the DL estimated from equation 4 should be qualified as a lower limit.

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Another reason why these detection limits are a lower limit is because they assume that the molecules from particle species are infinitely dispersed in the gas phase, when in reality they are quantized in large clumps (the particles). This is also a limitation of the filter and statistical DL estimates, but should be mentioned here since this paper is discussion DLs in such detail. The averaging time limitations imposed by particle counting statistics are documented and discussed in Table 1 of Bahreini et al. (2003) and Table 1 of DeCarlo et al. (2006) and the paper could refer to those.

- P180 L7: the reasons for the differences between the detection limits of the various AMSs and the link to the ion duty cycles were discussed (albeit in less detail) by DeCarlo et al. (2006), and this should be acknowledged here.

- P184 L8-9: there are other reasons why the cross-sensitivity of the ToF-AMS is higher than for the Q-AMS. Quadrupoles are much better than TOFs at rejecting the influence of adjacent m/z's. This is typically ~1 part-per-million for good quadrupoles while TOFs suffer from tails over several m/z at the part-per-thousand level and scattered ions as discussed above.

- P185 L20-30: another effect which is not mentioned here is that a fraction of less volatile particles can bounce from the AMS vaporizer (e.g. Huffman et al. 2005) and will then land on various surfaces around the ionizer and chamber. Molecules will desorb more slowly from these particles, contributing to the effect discussed here, and I suggest that this is mentioned as well. This may also play a role or even dominate the effect discussed later in section 3.2.3.

- P186 L2: a better way to analyze these data would be to fit the sum of multiple exponentials to such data, which would provide more accurate time constant and perhaps reveal additional subtleties on the background decays.

- P188 L25: it would be worth showing the similar figure to Fig 5 for the ToF-AMS, as Fig 5b.

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- P189 L5: the wording 'arbitrarily low values' does not appear appropriate. E.g. I doubt that averaging would allow the detection of an aerosol species with a concentration of 1 fg/m3 since other effects would eventually pose a limit.

- P189 L7: there is no need to assume something here, the authors can easily recalculate the detection limit vs. averaging time for organics without including the m/z's that have air and water interferences, and establish whether their hypothesis about the non-zero intercepts is accurate or not. It is also possible that the residual is caused by summing electronic noise across many m/z's for organics.

- P189 L16: another option to reduce detection limits in the Q-AMS is to scan a smaller range of m/z, e.g. up to m/z 200 instead of 300.

- P189 L28: I disagree with this statement. The detection limit calculated with equation (4) does increase when the chopper open/closed ratio is increased. However this is likely incorrect for the real detection limit that would need to take into account particle counting statistics (equation (4) does not).

- P192 L11: is I2 sticky? It is a non-polar species with high vapor pressure, so this is somewhat surprising. Perhaps other iodine species may be responsible for the observed effects? Also this species had not been mentioned before in the manuscript.

- P197, Table 1: this table would be more readable if the DLs were given in ng m-3 and not ug m-3.

- P198, Table 2: are these constants the time for the DL to decay to 1/e of the DL under high concentration conditions? Or for the excess DL under high concentration conditions (the difference between the DL and the baseline DL under clean conditions)? E.g. in Fig 4 the baseline DL is only 4 times the high concentration DL, and this distinction is significant.

- General comment: a method to estimate PAH concentrations from AMS spectra has been recently published (Dzepina et al., 2007), who also reported detection limits for

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these species. The authors of this paper are also active in this area. With very little additional space the detection limits for the PAHs calculated in this way could be added to Table 1 and briefly discussed, which would be an interesting addition to the paper.

- General comment: a brief discussion or perhaps a table comparing the DLs determined here with those reported by the previous publications cited would be useful.

Minor items, Grammar, etc.

- P170 L23-24: please spell out the acronyms for the versions of the AMS

- P171 L1: 'its' should be 'their'

- P171 L29: the term 'procedures' here suggest that this is something that is done by the instrument operator. A better word would be 'processes', since these are occurring without operator intervention.

- P172 L7: suggest changing 'the reduction of m/z' to 'the reduction of the number of m/z'

- P172 L14-15: the sentence starting with 'While' repeats much of the information in the previous sentence.

- P173 L10: for ambient studies the AMS vaporizer is run at a standard temperature of 600C, although some groups still use an older standard of 550C. The vaporizer itself can be operated at colder temperatures, down to 200C in steady state and up to at least 800C. In this context, the sentence in the paper is incorrect and ambiguous.

- P173 L18: suggest replacing 'includes' with 'contains'

- P173 L22: 'quantitatively reach the vaporizer' can be confusing since some particles can be lost between the chopper and the vaporizer due to shape effects or poor alignment (e.g. Huffman et al., 2005). Suggest rewording.

- P174 L3-4: suggest writing 'is typically scanned' and 'is typically acquired'

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- P174 Equation 1: the CE of the AMS is omitted from this equation. This can increase the detection limits, for example during many ambient studies, and should be included in the equation.

- P175 L26: it would be best to list these citations in chronological order.

- P175 L23: suggest writing 'is only 0.3% (under the Gaussian assumption).'

- P176 L11: suggest replacing 'of' with 'to'

- P176 L21: 'lower' should be 'higher' here.

- P177 L22: 'background ion' should be 'background species' here as the background is constituted of neutral molecules (which are ionized by the detection system).

- P178 L25: suggest replacing 'control' with 'monitor'

- P179 L5: suggest replacing 'with the AMS' with 'with our AMSs' as instruments do vary and newer instruments often benefit from design improvements.

- P180 L10: the duty cycle of the chopper is more typically 45% or so due to the dead time needed to change positions every few seconds.

- P181 L24: 'then' should be 'than'

- P182 L5: it is worth mentioning that filaments that do not contain tungsten are available, which would be of interest if the tungsten m/z were of high interest for e.g. an organic aerosol laboratory experiment.

- P185 L15: some information in this paragraph appears repetitious with previous passages of the paper, and could perhaps be shortened.

- P190 L17: 'semi-urban' is unclear. Perhaps 'suburban'? Or 'regionally-influenced urban'?

- P191 L3-6: for clarity I suggest rewording as 'However, it must be noted that while the organics detection limits and precision are improved using this method the uncertain-

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ties (accuracy) ...'

- P201, caption of Fig 3: the averaging time corresponding to the DLs shown should be mentioned here. Similarly for the caption of Fig. 6.

- P203 Fig 5: it is very hard to see the evolution of the DLs for nitrate, sulfate, and chloride, they should be multiplied by an appropriate number for graphing purposes, or perhaps shown in a log scale instead.

- P204 Fig 6: there are some strange jumps up and down in the DL when the m/z's are sorted according to SNR for the ToF-AMS. What is the explanation for these? Perhaps this should be mentioned in the figure caption.

References

Dzepina et al. Detection of Particle-Phase Polycyclic Aromatic Hydrocarbons in Mexico City using an Aerosol Mass Spectrometer. International Journal of Mass Spectrometry, 263, 152-170, 2007

Huffman et al. Design, Modeling, Optimization, and Experimental Tests of a Particle Beam Width Probe for the Aerodyne Aerosol Mass Spectrometer. Aerosol Science and Technology, 39, 1143-1163, 2005.

Takegawa et al. Performance of an Aerodyne Aerosol Mass Spectrometer (AMS) during Intensive Campaigns in China in the Summer of 2006. Aerosol Sci. Technol., in press.

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 169, 2008.