

Interactive comment on “Secondary organic material formed by methylglyoxal in aqueous aerosol mimics – Part 2: Product identification using Aerosol-CIMS” by N. Sareen et al.

Anonymous Referee #1

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This paper presents mass-spectrometric measurements of mixtures containing methylglyoxal with ammonium sulfate (AS) and sodium chloride (NaCl) solutions. Methylglyoxal is of significant interest to the tropospheric chemistry community due its potential to contribute to secondary organic aerosol (SOA) formation.

The goal of the paper is to address the influence of the salts NaCl and AS on condensed phase methylglyoxal reaction products. However, without a methylglyoxal control experiment it is not clearly demonstrated that the compounds observed do not already exist in the starting material. This work, as presented, cannot be reviewed due to this flaw in methodology as described in more detail below:

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1. Purity of the methylglyoxal solution: The manuscript notes that the solutions had a pH of 2 (p. 15570) and the companion paper states that the methylglyoxal solution itself also had a pH of 2. This indicates that other compounds, e.g. pyruvic acid-the oxidation product of methylglyoxal, were also present.

2. The data should be presented in the context of control experiments and a progression of additives. It would be useful to include each of the reagents individually as controls, and include experiments that are performed using permutations of ions (i.e. ammonium chloride and sodium sulphate), with attention to ionic strength of these solutions, to demonstrate the effect of each ion.

3. With the exception of nitrogen containing compounds there is insufficient evidence for an effect of AS or NaCl on methylglyoxal:

m/z 217, 271, 273, 275 and 289 in figure 3 comprise most of the m/z discussed in the manuscript. These m/z appear to be related to m/z 109, 163, 165, 167 and 181 in figure 5. The patterns are very similar, except for slight intensity differences. The assignment, expressed as C₃H₆O₃ (I-/H₃O⁺), C₆H₈O₄ (I-/H₃O⁺), C₆H₁₀O₄ (I-/H₃O⁺), C₆H₁₂O₄ (I-/H₃O⁺), C₆H₁₀O₅ (I-/H₃O⁺), which is one of the possibilities given in the paper, can explain this pattern.

Compared to the differences observed in figure 3, the intensity differences observed between the AS and NaCl solutions for the above m/z in figure 5 are very small. Thus from figure 5 one cannot conclude that there is a specific effect of AS versus NaCl, except for the nitrogen containing compounds (m/z 125.9 and 143.8 in fig. 5). This raises the concern that the intensity differences observed between the two solutions (and thus an inferred difference in reactivity between AS and NaCl in figure 3) are caused by a difference in ionization efficiency (e.g., the compounds in question do not get ionized efficiently by I- in presence of Cl-). The above m/z exist in both salt solutions and without a methylglyoxal control experiment it is difficult to conclude that the salts have influenced their formation.

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4. The companion paper clearly demonstrates an effect of AS on the optical properties. However, the carriers of this signal could be present at low concentration and/or unrelated to many of the m/z discussed in this manuscript.

This review does not conclude that the discussed compounds are not reaction products and that salts, in particular, AS have no effect, but rather that it is not possible to draw conclusions without the appropriate control experiments. The subject of this study is of significant interest and the paper should thus be resubmitted after addressing the concerns raised here.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15567, 2009.

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