Interactive comment on “Design and construction of a simple Knudsen Effusion Mass Spectrometer (KEMS) system for vapour pressure measurements of low volatility organics” by A. M. Booth et al.

Anonymous Referee #2

Received and published: 12 May 2009

Review of “Design and construction of a simple Knudsen Effusion Mass Spectrometer (KEMS) system for vapour pressure measurements of low volatility organics” by Booth et al.

In this work a new Knudsen Effusion Mass Spectrometer (KEMS) has been build. The KEMS method is an established method in other fields of science but has not been applied before for studies of atmospherically relevant substances. There is a strong need for measurements of thermodynamic properties of semi-volatile organic molecules of atmospheric relevance and the proposed method complements existing
methods nicely.

Using the new instrument the authors have measured vapor pressures of a series of di-carboxylic acids and compared with available literature data.

The manuscript certainly merits publication; however a number of issues must be addressed first.

In the interactive discussion good comments have already been given. In addition the following issues should be addressed.

In general, the text can be significantly improved by more precise formulations and additional literature references, some suggestions are given below.

1) A short discussion of solid state versus sub-cooled liquid state vapor pressures and methods to come from one to the other could be given in the introduction. It should be made clear that the presented method provides solid state vapor pressures.

2) In the introduction it says that simple hydrocarbons are not of interest to atmospheric community – I would suggest to say “are of less interest”.

3) First line in section 2 is a repetition and can be deleted.

4) No description of the sample preparation is given– this should be done: the purity and provider of the used chemical should be given. Also it should be described how the sample was prepared and handled and it should be explained how much sample was used.

5) a reference to the Quadstar software package should be provided

6) An example of the data obtained are given in the last figure. It would seem more natural to present and discuss an example of data (Figure 7) early in the paper (as Figure 4)

7) The role and importance of the hole size should be better explained and the relevant
equation(s) given

8) Page 898, line 22 – please discuss the uncertainties – is the agreement using different references satisfactorily?

9) Page 899, line 15 and Table 4, caption: the text is unclear. Why is suddenly malonic acid mentioned as a reference, what does it mean “with SEM detection”? How were the errors given in Table 4 determined? In Table 4 it says that the variation for the oxalic acid is largely due to the use of 3 different calibration compounds – please explain and justify in the text – was the average used? The vapor pressure variation for adipic acid is also high?

10) In the discussion the authors write that their method tend to give higher values compared to the TDMA method – this does not seem right to me – it is only the case for succinic and malonic acid as far as I can see – for glutaric and adipic acid the KEMS method gives lower vapor pressures?

11) Why does the evaporation of some sample “inadvertently” explain the lower vapor pressure obtained by Cappa et al. 2007?

12) References: I suggest the authors go carefully through the manuscript and check that they include the relevant references. Below some suggestions:

Page 894, line 25: Johnson et al. is only concerning aromatic hydrocarbons – some reference to other types of hydrocarbons would be appropriate

Page 895, line 1 – please give some references illustrating that some estimation methods give erroneous results

Page 895 Line 18: the authors site Cappa et al. 2007 for the TPD method – they should also site Chattopadhyay and Ziemann 2005.

SOA compounds are likely to have vapor pressures upwards of 10^-4 Pa – please provide some references for this statement
The authors should use the name of the first author when citing literature, for example: Ravishankara -> Cappa et al. 2007

In the conclusion references to TDMA type measurements on aqueous mixtures should be given (e.g. Riipinen et al. 2006).

13) Notation– use consistent notation in equations and in the text and explain – e.g. page 898: dH₀ (in equation) and dH in text. Notation in abstract should correspond to notation in text

14) Figure 4: In Vapor pressure – please explain better and use same notation as in equations, also give the unit of vapor pressure. In the caption an open symbol is given, in the figure a closed symbol.

15) The authors write that the technique could be improved by increasing the sensitivity of the mass spectrometer – what is it now? – and how large an improvement is reasonable to expect?

Technical:

Page 894, line 25: sentence not complete “hydrocarbons” missing after oxygenated

Page 895 Line 15: they have --> these vapor pressures . . . would sound better

Page 901: dicarboxylics -> dicarboxylic acids Page 897: no “.” after cell

Some References:


Riipinen, K. E. J. Lehtinen, B. Svenningsson, M. Bilde, A. Gaman, M. Kulmala Atmospheric Research 2006, 82, 579-590.