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Atmospheric Measurement Techniques Discussions

Interactive comment on "Piezoelectric crystal microbalance measurements of enthalpy of sublimation of C₂–C₉ dicarboxylic acids" *by* F. Dirri et al.

Anonymous Referee #2

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This works presents a new innovative technique for measuring enthalpies of vaporization of low volatile organic molecules. The method is based on a piezoelectric crystal microbalance method previously used for space applications. Vapor pressures and transition enthalpies of low-volatile organic molecules are important thermodynamic parameters in atmospheric science. Large unresolved differences between thermodynamic data reported from different techniques and laboratories do however exist. The topic of the manuscript is thus timely and relevant. Unfortunately, the article is difficult to follow and I have a number of concerns. In particular, the theoretical background and the experimental technique should be explained more clearly and in larger detail.

It is not clear to me what the major uncertainties in the method are and how the 10% error bar is obtained. In the discussion section the authors should improve on the way they cite the literature. There are some inconsistencies in notation and numbers between text, table and figures (as pointed out by reviewer 1). The structure of the manuscript could be made clearer as suggested below and the language should be improved throughout.

I would like to point the attention of the authors to a recent article in Chemical Reviews addressing vapor pressure and enthalpies of low volatile atmospheric organic molecules and dicarboxylic acids in particular (reference given below), this I think might be useful in the discussion section.

I recommend major revisions.

Some major comments Abstract: The abstract should describe the method and the results. It is in my opinion not relevant to discuss characteristics of the laboratory where the experiments are performed in the abstract (line 5-6). Also the discussion on the dicarboxylic acids belong in the introduction and not the abstract (line 10-14). Introduction: The description of dicarboxylic acids and why they are important is repeated in different versions in abstract, introduction, theoretical approach, and experimental sections. These sections should be merged and presented in the introduction only.

Theoretical approach The text is hard to follow. Several details are missing and some of the text I found confusing: "The enthalpy of sublimation can be seen as . . .— is this not the definition of enthalpy – why is it written in this way? "constituting condensation nuclei for clouds formation. Therefore, xxx "? It is possible to determine vapor pressure by thermogravimetry – but this is not related to cloud formation. . .., m is mass loss rate per unit area — unit area of what? M is molecular weight of the studied molecule. Maybe it would be useful to add an indices i for the molecule. Equation (4): explain what C is. Equation 5: explain what k1 and k2 are. "i.e. temperature increase is related to rate constant increase" – this should be explained and expanded upon.

It would help I think, if the experimental setup was presented before the theory section.

Setup operation and composition: “preliminary calibrations” – this should be explained – which molecule was used for calibration?

Experimental activity What does it mean that samples were provided by e.g. University of Rome – was it a commercial sample or was it synthesized there?’

Measurement procedure: It is not clear what the different temperatures, steps, T1 and T2 etc. are – where they are in the system, when they are measured etc.. The parameters in Table 2 should be clearly explained. “an uncertainty of 10 “ on the retrieved enthalpy of sublimation could be sufficient to provide a good accuracy for our measurements” – how is the uncertainty of 10 % obtained, is it based only on the temperature stability? What is meant by could be sufficient”

Data analysis and results I am wondering: is it not possible also to infer vapor pressures at 298 K from the experimental data? This would be useful for comparison with other studies. The authors have chosen to test the method by studying the vapor pressure of dicarboxylic acids and compare with values in the literature. The authors have chosen to compare with some, but not all of the available literature data. This might be justified, but if so, it is not clear from the text why. As the authors point out, literature values differ by orders of magnitude. As mentioned above I would like to point the attention of the authors to a recent review article in Chemical Reviews summarizing state of the art knowledge on vapor pressures and heat of vaporization of dicarboxylic acids that might be useful in the discussion. The authors should check carefully the references they cite: eg. line 16 p. 7142 “is due to the presence of unevaporated water within the aerosol particles”. This statement is not quite correct as written here. The error reported in that study is based on a sensitivity analysis. It is true however that a potential effect of remaining water in in dried aerosols (as used in TDMA systems) has been suggested as an explanation for differences between different studies. Again I refer to the review paper. Another example: Table 1: The article by Prenni et al is focused on cloud droplet

formation and it seems strange to use it as a reference for vapor pressures. It should be cited in the motivation part of the introduction instead. Regarding succinic acid I miss a reference for the statement that succinic acid will lose a water molecules above 60C. There are inconsistencies between notation and numbers (e.g. temperatures) given in the text, different tables and figures. Table 2: It is not clear what the different parameters in the table are. In the text M is used for molecular weight but in the tables it is a mass?

Reference "Saturation vapor pressures and transition enthalpies of low-volatility organic molecules of atmospheric relevance: from dicarboxylic acids to complex mixtures." Bilde, M., K. Barsanti, M. Booth, C. D. Cappa, N. M. Donahue, E. U. Emanuelsson, G. McFiggans, U. K. Krieger, C. Marcolli, D. Topping, P. Ziemann, M. Barley, S. Clegg, B. Dennis-Smither, M. Hallquist, A. M. Hallquist, A. Khlystov, M. Kulmala, D. Mogensen, C. J. Percival, F. Pope, J. P. Reid, M. A. V. Ribeiro da Silva, T. Rosenoern, K. Salo, V. P. Soonsin, T. Yli-Juuti, N. L. Prisle, J. Pagels, J. Rarey, A. A. Zardini and I. Riipinen. Chemical reviews 115(10): 4115-4156 (2015).

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