Interactive comment on "Piezoelectric crystal microbalance measurements of enthalpy of sublimation of C_2–C_9 dicarboxylic acids" by F. Dirri et al.

Anonymous Referee #1

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General comments

The manuscript presents a novel approach to measure enthalpy of sublimation of different organic compounds. It is generally well written and the conclusions are reached, after being clearly summarized in the abstract. However the sections devoted to the data analysis are quite confusing, with different values reported in tables, figures and text and with some sentences not clearly supported by the data themselves. For this reason I suggest the publication of this work after the authors will address the issues reported in the "Specific comments" section below.

Specific comments Page 7128 Lines 20/21: It is not clear to me what "weight average values" means in this case.

Page 7129 Line 4: Please define the "fine" word in quantitative terms.

Page 7138 Line 6/7: In the text the authors say that for Succinic and Oxalic acids there was a narrower temperature range. However from Table 3 the following temperature ranges are retrieved: âA˘ c Oxalic: 24.772 –> 54.952 ´ ◦C ; DT = 30.18 ◦C âA˘ c Succinic: ´ 34.85 –> 54.64 ◦C; DT = 19.79 ◦C âA˘ c Adipic: 39.84 –> 75.30 ´ ◦C; DT = 35.46 ◦C âA˘ c´ Azelaic: 34.95 –> 60.04 ◦C; DT = 25.09 ◦C Therefore DT for Oxalic acid is broader than Azelaic and the sentence seems to be incorrect. Maybe the authors are referring to lower maximum temperatures used. But also in this case the maximum temperature is sensibly different only for Adipic acid, since there are less than 6 ◦C of difference among Succinic (54.64 ◦C) and Azelaic (60.04 ◦C) cases. The sentence must be better constrained. Line 14/15: Here the authors link the frequency decrease only to larger VOC deposition. But it is also stated that a temperature variation is measured: does this imply some change in frequency? For example in Zinzi et al. (2011) it is clear shown that changing the temperature the frequency of the PCM varies in a non-linear form (Fig. 4 of that paper) as theorized by Salt et al. (1987). Line 16/17: Did the authors perform a parallel check on the mass loss by measuring it also by means of "classic" balances (e.g., before and after the process)? Or they only relied on the PCM sensitivity? In this case how much is this value reliable? What is its error? And is there any reference to be added?

Pages 7139-7141: Sections 5.1-5.4 During all these sections the data are very diffi- cult to understand. In particular Table 3, that is also referred as the reference for the measurements made by the authors, does not reflect what is both viewed in Figs. 4-5, where results are graphically displayed, and described in the text. In the table the temperature ranges are (in ◦C and rounded here for the sake of simplicity) [25, 55], [35,55], [40, 75], [35, 60] for Oxalic, Succinic, Adipic and Azelaic acids respectively. On the contrary Figs. 4-5 show, for the same compounds: [25, 65], [30,

75], [30, 75], [35, 80]. Moreover in Table 4 the following ranges are reported for this work: Oxalic [25, 60], Succinic [30, 75], Adipic [30, 75], Azelaic [25, 80]. Again different from both Table 3 and Figs. 4-5. What are the temperature ranges used? Furthermore, what is the "weighted average mean" used? What are the weights used?

Section 5.1: "choosing T1 quite lower than T2 value a best agreement in obtained, whereas when T1 approaches T2 the agreement is worse". This sentence seems not to be supported by data presented in Table 3. By looking at the following table with data rearranged from Table 3 it seems that the "central" (out of the set of 3 – highlighted in red) measurement is always the best. : T2-T1 (rounded to first decimal) [◦C] Measure – Literature [%] 20.2 -11.30% 15.1 -5.92% 10.0 -16.89% 25.2 -7.68% 20.1 -2.56% 15.0 -8.77% 30.2 -10.73% 25.1 -7.25% 20.0 -13.27%

Section 5.3: The final sentence, regarding the last two measurements in Table 3 relative to Adipic acid, seems to be incorrect, as the values of enthalpies shown (133.28 and 128.05 kJ/mol) are only 3 and 7 % lower than the 137.2 kJ/mol shown in Table 2 as reference. Furthermore, the large error bars make them completely in agreement with the reference value.

Technical corrections Page 7128 Lines 10/12: It could preferable to reword the sentence as follows: "Acids of both biogenic and anthropogenic origin with low molecular weight are among the components of organic fraction of particulate matter in the atmosphere." Line 22: Results are summarized for Adipic, Succinic and Oxalic acid, but not for Azelaic. Line 25: Substitute "therefore" with "so that". Page 7129 Line 7: The groups are carboxyl and hydroxyl, not carboxylic and hydroxides. Line 16: In the parenthesis please add "these latter" before subclass, as I guess that only dicarboxylic acids are subclass of carboxylic acids. Line 17: Change "acid" with "acids". Line 21: Change "with various" with "in various". Line 25: Since you already stated that these acids are present in urban environments change "In addition" with "In particular". Line 29: acid –> acids (after "Succinic and Malonic") Page 7130 Line 1/2: Put the Hatakeyama reference inside the parenthesis of "reaction of O3 with cyclohexene". Line 15: Delete "that is" before "commonly". Line 23/24: Please insert some reference to characterization by means of enthalpy. Page 7131 Line 1: Reword the sentence as: "The TG-Lab facility, located in IAPS-INAF, is dedicated to. . ." Line 22: "prediction of 20%" –> "prediction by 20%". Page 7132 Line 10: "acid sublimation, due to the their high volatility". Change acid –> acids or their –> its Page 7133 Line 1: Please provide a reference for the sentence. Line 9: Substitute "for" with "by" and it could be of interest to specify the constant physical mean. Line 14: "temperature" –> "temperatures". Line 21: Please reword the last sentence as "temperature is directly proportional to rate constant". Page 7134 Line 7: "central area" –> "central part" Line 8: "proximity electronic" –> "proximity electronics" Line 26: "PCM temperature" –> "PCM temperatures" Page 7135 Line 1: "molecule flow" –> "flow of molecules". Line 9: "wide 6 mm and deep 10 mm" –> "6 mm wide and 10 mm deep". Page 7136 Line 8: "frequencies"' –> "frequencies" Page 7142 Line 10: add "and" between "method" and "shows". Page 7143 Line 8: Why "minute by minute"? Maybe "continuously" is more appropriate.

Interactive comment on "Piezoelectric crystal microbalance measurements of enthalpy of sublimation of C_2–C_9 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).