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Interactive comment on “Piezoelectric crystal microbalance measurements of enthalpy of sublimation of C₂–C₉ 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.

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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: ΔT Oxalic: 24.772 \rightarrow 54.952 $^{\circ}\text{C}$; $\text{DT} = 30.18$ $^{\circ}\text{C}$ ΔT Succinic: 34.85 \rightarrow 54.64 $^{\circ}\text{C}$; $\text{DT} = 19.79$ $^{\circ}\text{C}$ ΔT Adipic: 39.84 \rightarrow 75.30 $^{\circ}\text{C}$; $\text{DT} = 35.46$ $^{\circ}\text{C}$ ΔT Azelaic: 34.95 \rightarrow 60.04 $^{\circ}\text{C}$; $\text{DT} = 25.09$ $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ of difference among Succinic (54.64 $^{\circ}\text{C}$) and Azelaic (60.04 $^{\circ}\text{C}$) 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 difficult 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 $^{\circ}\text{C}$ and rounded here for the sake of simplicity) [25, 55], [35,

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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”

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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 Atmos. Meas. Tech. Discuss., 8, 7127, 2015.

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