

1 Piezoelectric Crystal Microbalance measurements of enthalpy 2 of sublimation of C2-C9 Dicarboxylic acids

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8 Abstract

9 We present here a novel experimental setup able to measure the enthalpy of sublimation of a given
10 compound by means of Piezoelectric Crystal Microbalances (PCM). The PCM sensors have been
11 already used for space measurements, such as detection of organic and non-organic volatile species
12 and refractory materials in planetary environments. **In the atmospherics' Earth applications, PCMs
13 can be also used in order to obtain some physical-chemical processes concerning the Volatile
14 Organic Compounds (VOC) present in atmospheric environments. Experimental setup has been
15 developed and tested on Dicarboxylic acids.** In this work, a temperature controlled effusion cell was
16 used to sublime VOC, creating a molecular flux that was collimated onto a cold PCM. The VOC
17 re-condensed onto the PCM quartz crystal allowing the determination of the deposition rate. From
18 the measurements of deposition rates, it **has been** possible to infer the enthalpy of sublimation of
19 Adipic acid, i.e. ΔH_{sub} : $141.6 \pm 0.8 \text{ kJ mol}^{-1}$, Succinic acid, i.e. $113.3 \pm 1.3 \text{ kJ mol}^{-1}$, Oxalic acid, i.e.
20 $62.5 \pm 3.1 \text{ kJ mol}^{-1}$ and Azelaic acid, i.e. $124.2 \pm 1.2 \text{ kJ mol}^{-1}$. The results obtained show an accuracy
21 of 1 percent for Succinic, Adipic, Azelaic and within 5 percent for Oxalic acid and are in very good
22 agreement with previous works (within 6 percent for Adipic, Succinic and Oxalic acids and within
23 11 percent or larger for Azelaic acid).

24 1. Introduction

25 A large number of aerosol species is present in atmosphere and many physical-chemical processes
26 occur to create/destroy compounds, **so that** monitoring and characterizing some of them is a tricky
27 task.

28 The primary atmospheric aerosol is composed of particles coming from processes such as rocks
29 erosion and fire and from anthropogenic processes (such as the fossil fuels combustion or by the
30 industrial activity). Volatile organic compounds (VOC) in primary aerosol can generate the

1 secondary organic aerosol (SOA) composed of fine particles, *i.e.* lower than 1-2 μ m, (Salzen and
2 Schlünzen, 1999) from photo-oxidation reactions with compounds in Earth's atmosphere, in
3 particular hydroxyl radical, ozone and nitrate radical. For example, hydrocarbons are enriched
4 carboxyl (-COOH), carbonyl (-CO) or hydroxyl (-OH) functional groups and are transformed in
5 ketones or carboxylic acid after several reactions.

6 Because of the wide number of VOC transformation processes it is crucial to know the chemical-
7 physical properties (*i.e.* enthalpy, entropy, free energy) in order to characterize the organic fraction
8 of the atmospheric aerosol. In detail, specific substances (*markers*) or class of substances should be
9 identified in order to provide some information on the atmospheric aerosol sources, *e.g.* evaluating
10 the transformation degree of the organic compound and their release by primary sources
11 (Pietrogrande et al., 2014). Carbohydrates and Dicarboxylic acids with low molecular weight (*these*
12 *latter* subclass of carboxylic acids) are among the most important groups of molecules identified in
13 the atmospheric aerosol. It could be useful to consider these substances as molecular tracers
14 ("markers") providing information on the aerosol origin (biogenic or anthropogenic), *i.e.* on the
15 emission source and on the processes that the organic substances undergo in the atmosphere.
16 Dicarboxylic acids are present in various concentrations in different terrestrial environments, *e.g.*
17 marine, rural, urban (Kawamura et al. 2005, Yu and Fraser 2004, Limbeck et al. 2001), and their
18 formation in atmosphere is likely due to photochemical reactions in gaseous phase involving VOC
19 (in particular aliphatic and aromatic hydrocarbons) of biogenic and anthropogenic origin. In
20 particular, they play an important role on physical-chemical reactions involving aerosol particles,
21 that may be gathered in agglomerates (sub-micron sized), and represent an important component of
22 the atmospheric aerosol particles, both in remote and urban areas (Rohrl and Lammel, 2001). The
23 Oxalic acid is the most abundant Dicarboxylic acid in the tropospheric aerosol and comprises 41-67
24 percent of the total diacids (Sorooshian et al., 2006, Kawamura and Keplan, 1983) whereas the
25 Succinic and Malonic acids are less abundant and reach peaks of 4-8.7 percent during the summer
26 (Kawamura and Ikushima, 1993). Adipic and Succinic acids have been identified in laboratory
27 studies as SOA products (reaction of O₃ and cyclohexene, Hatakeyama et al., 1985). The Adipic
28 acid is related to N₂O emission, a greenhouse gas that causes stratospheric ozone depletion (US
29 EPA, 2013) whereas the Succinic acid origins probably from biogenic sources, and is an important
30 compound in biochemistry due to its role in the citric acid cycle (Krebs cycle). The Azelaic acid is
31 considered a photon-induced oxidation's product, deriving from biogenic unsaturated fatty acid,
32 presenting one or more double bond in their chain (Kawamura and Keplan, 1983). Succinic and
33 Oxalic acids had been proven to be part of the organic materials that contribute to form
34 condensation nuclei of atmospheric clouds (Kerminen et al. 2000, Prenni et al. 2001) and it has

1 been suggested that the ratio between Oxalic and Succinic acid is a good marker of the atmospheric
2 aerosol oxidation state. On the other hand, Adipic-Azelaic ratio could be an indicator of
3 anthropogenic sources, considering that Adipic acid derives from cycle-hexane's oxidation
4 (Kawamura and Ikushima, 1993).

5 In order to characterize the Dicarboxylic acids different methods are used, based on measurement of
6 the evaporation rates and calculation of the enthalpy of sublimation/evaporation, e.g. Thermal
7 Desorption Particle Beam Mass Spectrometry (TPTD) method (Chattopadhyay and Ziemann 2007),
8 Knudsen Effusion Mass-loss (da Silva et al.2001), Knudsen Effusion Mass Spectrometry(KEMS)
9 (Booth et al. 2009), Tandem Differential Mobility Analyzer (TDMA) technique (Bilde et al. 2003)
10 and effusion method (Davies and Thomas, 1960, Granovskaya, 1948). Discrepancies between
11 results obtained by the different methodologies were found to be up to two orders of magnitude,
12 and this makes the acids characterization even more difficult.

13 In this study low molecular weight Dicarboxylic acids (carbon chains from C₂ to C₉, see Fig.1) were
14 analyzed by means of a new experimental set-up, based on Piezoelectric Crystal Microbalances
15 (PCM) commonly used to detect mass variations, density, viscosity, absorption/desorption
16 processes, by means of transformation of mass change into fundamental resonance frequency
17 variation. The PCM oscillation frequency goes as $1/m$, being m the mass deposited on the
18 microbalance, as stated by the Sauerbrey equation (Sauerbrey, 1959). Therefore, in principle it is
19 possible to measure VOC sublimation or deposition on the crystal surface by changing the PCM
20 temperature: the mass variation during the sublimation process will give the amount of the volatile
21 component, while the physical properties of some atmospherically relevant compound can be
22 inferred in the chosen temperatures range (Salo et al., 2010). A compound can be characterized more
23 precisely by retrieving its enthalpy of sublimation: this is possible by measuring the sample
24 deposition rates on the PCM at different temperatures (see Section 5).

25 Piezoelectric crystal microbalances (PCM) have been recently used in space applications and
26 technology environments, as in industrial and biomedical fields (Palomba et al.,2002, Wood et al.,
27 1998, Freedman et al., 2008, Effiong et al., 2011,Lutfi Yola et al., 2014).

28 The TG-Lab facility, located in IAPS-INAF, is a dedicated facility to study feasibility, development
29 and calibration of TGA sensors optimise

30 d for space measurements. One of the TG-Lab projects concerns VISTA (Volatile In Situ
31 Thermogravimeter Analyser), a sensor developed for the Marco Polo-R mission (Palomba et al.,
32 2015, Barucci et al., 2011) and studied for other ESA Cosmic Vision missions, addressed to Venus

1 atmosphere (Wilson et al. 2011), Titan low atmosphere (Longobardo et al., 2013) and sub-surface of
2 Europa (Gowen et al., 2011).

3 In this work, PCM is cooled down to -72°C by means of a cold sink whereas the sample is
4 positioned in an effusion cell and heated up to sublimation. The setup is placed in vacuum in order
5 to avoid water vapour condensation and to facilitate the sublimation process (occurring between
6 25°C and 80°C), whereas the cooled crystal works as mass attractor for VOC's molecules. This
7 configuration allowed to measure the deposition rate of the VOC samples on the PCM at different
8 temperatures and to infer the corresponding enthalpy of sublimation. First attempts to measure
9 enthalpy of sublimation by means of PCM were performed by Dirri et al. (2012) and were focusing
10 on upgrading the thermal contact between PCM and the cold sink, by increasing the difference
11 between sensor effusion cell temperature and the PCM, improving the efficiency of the PCM as
12 mass attractor. This made it possible to measure deposition fluxes even at two close temperatures
13 (e.g. $\Delta T=5^{\circ}\text{C}$). However, in the Dirri et al. (2012) experiment a very small frequency variation (3
14 kHz) was observed, due to the low deposition of acid molecules (Adipic acid), and the retrieved
15 enthalpies of sublimation were different from previous works **by about 20 percent** (Chattopadhyay,
16 2007). In this work our accuracy has been improved as described in **Section 2**.

17 **Section 2 describes the experimental setup while the theoretical background and the thermodynamic**
18 **relation considered for data analysis are explained in Section 3. The measurement procedure is**
19 **explained in Section 4 whereas the results are described in Section 5. Finally, Section 6 is devoted**
20 **to conclusions.**

21

22 **2. Set-up operation and composition**

23 **2.1 PCM and effusion cell**

24 A Piezoelectric Crystal Microbalance (resonance frequency of 10 MHz) has been used to monitor
25 the transition phase (solid \rightarrow gas) of some Dicarboxylic acids in a controlled environment in order to
26 obtain their enthalpy of sublimation.

27 The microbalance is composed of a quartz crystal having a diameter of 14 mm and a thickness of
28 0.2 mm. The electrode, the sensible area of the crystal, is located in the **central part** and has a
29 diameter of 4 mm (Fig.1). The microbalance is connected to its **Proximity Electronics** (PE),
30 including a frequency counter and an oscillation circuit, powered by USB-PC input.

FIGURE 1

In order to use the microbalance as an efficient mass attractor, the quartz crystal should be cooled with respect to the surrounding environment and in addition the VOC molecular flux should be focused onto the crystal. The PCM cooling is performed by means of a conductive connection to a copper plate in thermal contact with a coil containing liquid nitrogen. Finally, the PCM is enclosed in a metal case, acting as thermal shield and avoiding the PCM heating by irradiation of internal wall of the vacuum chamber, which are at ambient temperature (see Fig.2).

In order to maximize the VOC flux, the microbalance has been placed in front of the effusion cell. This configuration strongly improves the flux collimation, increasing the amount of the collected molecules. The metal case has a temperature similar or even slightly smaller of the crystal and if the effusion cell is too far away from the PCM, the molecular flux could condense preferably on the metal case rather than the crystal, lowering the deposition rate too much (Fig. 2, *Left*). Moreover, reaching lower PCM **temperatures** (i.e. -72°C instead of -25°C of the first attempt) by improving the thermal contact with PCM and cold sink, we were able to increase the incident **flow of molecules** on the microbalance (avoiding molecules dispersion in the surrounding environment). **A previous calibration performed with Adipic acid sample, has been performed at $T_{\text{PCM}} = -72^{\circ}\text{C}$ and at 10^{-6} mbar. The effusion cell has been heated from 30°C to 75°C . This first test have experimentally determined that the distance between PCM and effusion cell allowing the larger flux onto the PCM crystal is 2 cm. At higher distance, the fluxes are too low and the monitoring of the sublimation process is not reliable.**

Then PCM and effusion cell are placed in a *sublimation micro-chamber*, i.e. a controlled environment of cylindrical form (located inside the vacuum chamber) made of insulating material (Teflon), which further minimises thermal dispersion and avoids VOC's loss into the microbalance surrounding area (Fig. 2, *Right*). The effusion cell is inserted in a hole in the cylinder's base.

In this experiment the PCM is cooled down to -72°C while the acid sample is placed in a small cylinder case (effusion cell) **6 mm wide and 10 mm deep**. This configuration allows to monitor the VOC's deposition rates from about 10^{-13} $\text{molcm}^{-2}\text{s}^{-1}$ up to 10^{-10} $\text{molcm}^{-2}\text{s}^{-1}$, two orders of magnitude better than the first setup version discussed in Dirri et al. (2012). The sample is heated from room temperature (i.e. 25°C - 30°C) up to **high temperatures** (i.e. 75°C - 80°C) by means a heater of $20\ \Omega$ (resistance) in thermal contact with the effusion cell. In Fig.3 a schematic representation of the set-up is shown.

FIGURE 2

FIGURE 3

2.2 Vacuum System and Data Acquisition System

The whole set-up is placed in a vacuum chamber in order to facilitate the transition phase, to avoid the simultaneous condensation on the PCM of other molecules present in the atmosphere at ambient pressure (mainly H₂O) and to avoid convective heat exchange with the atmosphere which would affect PCM and effusion cell temperature. The Vacuum System (Fig. 4) is composed by a Rotative pump (CF29PR-Alcatel Society), Turbo Pump (1602450-Elettrotrava Society) and a chamber (90 litres), all of them assembled by the Vacuum Centre Representative (CRV S.r.l., Rome, Italy). Rotative Pump can drive the system down to 10⁻² mbar whereas the Turbo Pump can lower the pressure down to 10⁻⁶ - 10⁻⁷ mbar. Pressure is measured using the TC1 sensor (Varian) up to 10⁻² mbar and the IG sensor (Varian) or Ionization Gauge up to 10⁻⁶ - 10⁻⁷ mbar. During data acquisition the pressure of the system is maintained constant during each experiment (fixed values between 3.5×10⁻⁶ mbar and 8×10⁻⁷ mbar).

FIGURE 4

The temperatures of copper plate, metal case, resistance and effusion cell, have been continuously monitored with platinum sensors (PT100, dimensions of 7.6×7.6×0.7 mm), whose resistance changes linearly with temperature. Temperature controls of the effusion cell (heating system from 25°C to 110°C) and of the copper plate (cooling system, set to -90°C and stable within 0.2 °C) have been driven by a Proportional-Integral-Derivative system (PID), which allows a temperature stability of typically ±0.5 °C and managed by means the LabView (2010) software (PC1). The **frequencies** has been acquired by means of the Eureka electronic box powered by a USB of PC2, controlled by the software provided by Bioelectronics and Advanced Genomic Engineering (BioAge S.r.l., Lamezia Terme, Italy).

3. Theoretical approach and thermodynamic relation

During the experiment, the sublimation process has been monitored and the enthalpy of sublimation, **i.e. the enthalpy change accompanying the conversion to one mole of solid substance directly into vapour phase at a given temperature (Tyagi, 2006), has been inferred for four different crystalline pure acids.** At 25°C and low pressure (10⁻⁶ mbar) it is possible already to observe the sublimation of some **acids** (See Sec. 5), due to their high volatility.

1 The Clausius-Clapeyron relation characterizes a phase transition, since allows us to infer the vapor
 2 pressure at each temperature T and the enthalpy variation from vapor pressure at two different
 3 temperatures:

$$4 \quad \frac{dp}{dt} = \frac{\Delta H}{T\Delta V} \quad (1)$$

5 being ΔH the specific latent heat of the process (sublimation, vaporization, or fusion), p the vapor
 6 pressure and ΔV the difference between volumes of gaseous and solid/liquid
 7 (sublimation/vaporization) phase, respectively. If the products are in gaseous phase and at
 8 temperatures much smaller than their critical one, they can be approximated as ideal gases, i.e. $\Delta V \sim$
 9 $V_{\text{gas}} = RT/p$. Replacing in the Eq. (1), we have the differential form:

$$10 \quad \frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} \quad (2)$$

11 **In order to characterize a pure substance**, the thermogravimetry can be used to determine the vapor
 12 pressure, by recurring at Langmuir equation for free kinetic sublimation/evaporation in vacuum
 13 (Langmuir, 1913):

$$14 \quad p = \frac{\sqrt{2\pi R}}{\alpha} \times \frac{dm}{dt} \times \sqrt{\frac{T}{Mi}} \quad (3)$$

15 where p is the vapor pressure of the gas, dm/dt is mass loss rate per unit area (**the area of the PCM's**
 16 **electrode**) is the deposition rate experimentally measured, **Mi the molecular weight**, R the gas
 17 constant, T the absolute temperature and α the vaporization coefficient, assumed to be 1 in vacuum
 18 environment (Price, 2001). Replacing Eq. (3) in Eq. (2), it is possible to obtain the enthalpy of
 19 sublimation (multiplied **by** a constant) as slope of the curve $\ln(dm/dt)T^{1/2}$ versus T^{-1}

$$20 \quad \ln \frac{dm}{dt} T^{1/2} = \ln C - \frac{\Delta H}{RT} \quad (4)$$

21 **where C is the term $(2\pi R/\alpha Mi)^{1/2}$ that remains constant during all the measurement.** The enthalpy of
 22 sublimation/evaporation can be also obtained by means of the Van't Hoff relation (Benson, 1968),
 23 i.e. by measuring at two different **temperatures** T_1 and T_2 and the respective rate constants k_1 and
 24 k_2 (**the deposition rates on the PCM**):

$$25 \quad \Delta H = R \left[\left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \left(\frac{k_1 \sqrt{T_1}}{k_2 \sqrt{T_2}} \right) \right] \quad (5)$$

1 Then, the Van't Hoff relation (Eq.5) is used to monitor the enthalpy variation step by step in the
2 considered temperature interval in order to monitor the state functions (e.g. Enthalpy, Gibbs energy,
3 and Entropy) in a transition phase. According to this relation, for an endothermic process (i.e. $T_1 > T_2$
4 and $\Delta H > 0$), as those considered in this work, we have $k_1 > k_2$, i.e. temperature is directly proportional
5 to rate constant. Indeed, the increasing temperature corresponds to an increasing of the deposition
6 rate which should be constant for a fixed temperature set-point.

8 4. Experimental activity

9 4.1 Selection of Dicarboxylic acids

10 The Dicarboxylic acid chemical formula is $HOOC(CH_2)_{n-2}COOH$ where n is the number of carbon
11 atoms. The considered samples are acids in small grains in white crystalline form (odorless solid)
12 with a purity degree of 99 percent. Considering the sublimation point of these acids and the
13 temperature range available by our setup (from 25°C to 80°C), the studies were focused on acids
14 with n between 2 and 9 carbon number: Oxalic ($n=2$), Succinic ($n=4$), Adipic ($n=6$) and Azelaic
15 ($n=9$) acids. Adipic acid was provided by Sigma Aldrich S.r.l., Succinic acid by Institute of
16 Translational Pharmacology (ITF-CNR, Rome, Italy) while Azelaic and Oxalic were kindly
17 provided by University of Rome, La Sapienza (Department of Chemistry). Some structural and
18 thermodynamic characteristics of the acids utilized in this work are shown in Tab. 1.

19 TABLE 1

20 21 4.2 Measurement procedure

22 In order to measure the enthalpy of sublimation, PCM has been used as mass attractor for the
23 volatile molecules inside the teflon micro-chamber. Firstly, the crystal in thermal contact with a
24 copper plate has been cooled down to -72°C (constant temperature during the heating cycle).

25 Then, each sample (13-20 mg) has been placed in effusion cell and at a later stage has been heated
26 by a resistance in a range of temperature from 25-30°C to 75-80°C. The stabilization of VOC's
27 molecular flow at each heating temperatures has been obtained by keeping the temperature constant
28 for 30 minutes, while a good distinction between two successive flows at two different temperatures
29 has been possible by adopting temperature steps of 5°C. The PCM frequency and temperature have
30 been measured every two seconds. Then, deposition rates have been measured at each temperature
31 set point in $\text{mol cm}^{-2} \text{s}^{-1}$.

1 Finally, in order to infer the enthalpy of sublimation in a well-defined temperature range (from 25-
2 30°C to 75-80°C), different couples of temperatures (T_1 and T_2) have been considered for data
3 analysis. By applying the Van't Hoff relation (Eq.5) to each couple of T_1 and T_2 and considering the
4 related deposition rates k_1 and k_2 , measured in Hz s^{-1} , ΔH_{sub} has been inferred. The parameters of
5 heating cycles of different acids, i.e. initial mass, pressure, expected enthalpy of sublimation,
6 temperature range, stabilization time at each temperature, are listed in Tab. 2.

7 TABLE 2

8 Our set-up and measurement procedure is similar to Albyn (2001). Thus similarly to him, we can
9 predict that a temperature stability of $\pm 0.5^\circ\text{C}$ (temperature control on effusion cell), should produce
10 an error on the enthalpy of sublimation of about ± 7 percent. This value would be a good starting
11 point for the organic compounds analyzed in this work. This value is mainly related to the
12 temperature instability of the sample heating and the efficiency of the deposition process (Albyn,
13 2001).

14 At 30°C with the PCM at -72°C , the Succinic and Oxalic acids already show higher sublimation
15 rates than Adipic and Azelaic acids. Thus, the enthalpy of sublimation has been calculated
16 considering a maximum temperature of 55°C for Oxalic and Succinic, lower than those used for
17 Adipic acid, i.e. 70°C , and Azelaic, i.e. 60°C (see Table 3). Besides, the retrieval of the enthalpy of
18 sublimation can be considered reliable as long as T_2 is quite distinct ($\geq 5^\circ\text{C}$) from the temperature
19 limit, T_L (Table 2) where the flows of molecules are not reliable. Choosing $T_2 \sim T_L$, a slope change
20 of deposition curve is expected due to the phase transition or due to the introduction of a new
21 physical-chemical process.

22

23 5. Data analysis and results

24 Deposition rates df/dt in Hz s^{-1} have been measured with a sampling rate of 10 seconds. A PCM
25 frequency decrease has been observed at increasing temperature due to the larger VOC deposition.

26 The rates in Hz s^{-1} have been multiplied for the PCM sensitivity ($4.4 \text{ ng cm}^{-2} \text{ Hz}^{-1}$) and converted in
27 $\text{g cm}^{-2} \text{ s}^{-1}$. Then, they have been divided by the substance molecular weight and converted in mol
28 $\text{cm}^{-2} \text{ s}^{-1}$ (Tab. 3). Finally, the enthalpy of sublimation and its error have been expressed in kJ mol^{-1}
29 (Tab. 3). The uncertainty on temperatures and deposition rates have been calculated as standard
30 deviation of the mean, due to the Gaussian distribution of measured values.

1 Thus, in order to monitor enthalpy variation over the whole temperature range considered, a good
2 choice for T_2 could be a temperature not close to T_L (i.e. from 60°C to 70°C for Adipic acid, from
3 50°C to 60°C for Azelaic acid and from 45°C to 55°C for Succinic acid). Our results were
4 compared with previous works (Tab.4) using a similar effusion method and theoretical approach
5 (i.e. Albyn 2001, Booth et al. 2009, R. da Silva et al. 2001) and with works analyzing the same
6 Dicarboxylic acids used in our study (Chattopadhyay et al. 2007, Bilde et al. 2003).

7 The weight average values (ΔH_{sub}) obtained in this work are reported in Tab.4. These results have
8 been obtained with the *weight function*: $\omega_i=(1/\sigma^2_i)$ where the i index express the number of data
9 obtained listed in Tab.3. Thus, ΔH_{sub} can be calculated as $[(\sum_i \omega_i \Delta H_i)/(\sum_i \omega_i)]$.

10

11 **5.1 Oxalic acid (C₂)**

12 A total frequency variation of 13 kHz has been observed for the Oxalic acid in the whole
13 temperature range monitored (Fig.5, *Blue curve*): from 25 to 65°C, corresponding to a mass
14 deposition of 9.3µg. This compound (with short carbon chain, C₂) showed a high volatility even at
15 low temperature confirmed by the moderately high deposition rate measured already at 25°C. The
16 deposition rate curve shows a continuous increase up to 60°C, with a constant slope (Fig. 5, *Blue*
17 *curve*). The enthalpy of sublimation has been obtained in the temperature range from 25 up to 55°C
18 (Tab.3), due to the instability of the sublimation flows at temperatures larger than 60°C. Moreover,
19 a best agreement is obtained when the difference between T_1 and T_2 is between 15°C and 25°C
20 (within 9 % compared with the literature values, Tab.3).

21 The Oxalic acid presents in its molecular structure two water molecules (dihydrate, monocline
22 structure) which loses at about 100°C and 1 bar. In this dehydration reaction, its molecular structure
23 changes from monocline to rhombic crystals and becomes anhydrous (Bahl, 2007). In our
24 experiment, we considered a monocline dehydrate Oxalic acid and the obtained enthalpy results
25 (Tab.4) differ than previous works, relative to the anhydrous form (Booth et al., 2009). On the
26 contrary, our results, i.e. $62.5 \pm 3.5 \text{ kJmol}^{-1}$ (Tab.4), agree within 5.5 percent with values, relative to
27 dehydrate Oxalic acid (De Wit et al., 1983, Granovskaya, 1948), as it should be. Indeed, as verified
28 by de Wit at al. (1983), a difference for the sublimation enthalpy values between the two anhydrous
29 forms (beta and alpha, obtained by means vacuum sublimation) and the dehydrate state (this
30 work) happens, due to the two water molecules desorption from Oxalic acid structure.

31

1 **5.2 Succinic acid (C₄)**

2 In the Succinic acid case, the frequency decreases of 10.6 kHz in the whole temperature range
3 monitored (i.e. from 30°C to 75°C), corresponding to 5.9 µg. The measured deposition rates are
4 shown in Fig. 5 (*Orange curve*). During the sublimation process, at temperature larger than 60°C,
5 the deposition rate oscillates around a medium value (Fig.5, *Orange curve*). The enthalpy of
6 sublimation has been obtained in the temperature range from 30 to 55°C (Tab.3) because of the
7 instability of the flow of molecules from 60°C. Probably, a new chemical-physical process should
8 be occurred at these temperatures. The results at 75°C have been excluded due to the high
9 temperature oscillations occurred.

10 Succinic acid (with short carbon chain, C₄) shows a smaller deposition rates than the Oxalic acid,
11 even if it strongly sublimates already at 25°C. Deposition rate curve shows an increase up to 60°C
12 and a slope change beyond this temperature. The Succinic acid tends to lose easily one water
13 molecule, becoming succinic anhydride. A good temperature range to monitor enthalpy variation is
14 30°C-55°C, far away from the point where Succinic acid changes its structure (~137°C)(Vanderzee
15 and Westrum, 1970). In this range, the average enthalpy of sublimation measured is 113.3±1.3
16 kJmol⁻¹, in agreement within 5 percent with the previous works (Chattopadhyay and Ziemann,
17 2007, Davies and Thomas, 1960, Tab.4). Considering the vacuum environment and an upper
18 temperature larger than 55°C, the retrieved enthalpy may be not reliable for the transformation
19 (initial phase) of Succinic acid crystalline form (monocline/triclinic prisms) into cyclic anhydride, a
20 ring structure (pyramidal crystal) losing one water molecule (Orchin et al., 2005, Vanderzee and
21 Westrum, 1970).

22 **FIGURE 5**

23

24 **5.3 Adipic acid (C₆)**

25 In the case of Adipic acid (long carbon chain, C₆), a total frequency decrease of 28 kHz in the
26 whole temperature range monitored (i.e. from 30°C to 75°C, Fig. 6, *Black curve*) corresponding to a
27 15.5 µg, has been observed. A considerable frequency variation is observed above 50°C, due to the
28 high volatility of the acid at these temperatures. This acid sublimates at low pressure without a
29 decomposition and only at 230-250°C changes its molecular structure becoming cyclopentanone
30 plus H₂O and CO₂. As a matter of fact, at temperatures smaller than 50°C, the variation of
31 deposition rates of Adipic acids are only 1.5% and 27% of that measured for Oxalic and Succinic

1 acid, respectively: this is due to the better stability of its carbon chain at these temperatures. The
2 enthalpy of sublimation of Adipic acid has been obtained in the temperature range from 40 to 70°C.
3 The data acquired at 75°C have been excluded to the analysis due to the high temperature
4 oscillations, which produce unstable deposition rates. The deposition rates at 30 and 35°C have
5 been also excluded because of the low flows of molecules. At these temperatures, the Adipic acid
6 flows are two order of magnitude lower than the Oxalic and Succinic acids.

8 **5.4 Azelaic acid (C₉)**

9 Azelaic acid shows a larger frequency variation than Succinic and Oxalic acid, with a total
10 frequency decrease in the whole temperature range monitored (from 35 to 80°C, Fig. 6 *Red curve*)
11 of 21 kHz corresponding to 11.6µg. Azelaic acid presents a very slow sublimation up to 35°C and
12 reaches the maximum deposition rate at 75°C (whereas at 80°C deposition rate begins to decrease).
13 The enthalpy of sublimation has been obtained in the temperature range from 35 to 60°C (Tab.3).
14 The enthalpies of sublimation at temperatures higher than 60°C have not been considered reliable
15 due a decrease of the deposition rates.

16 **FIGURE 6**

17 This compound starts to decay at 360°C (at atmospheric pressure) but in our experiment the
18 deposition curve shows a slope variation at 80°C and a instability on the deposition flow from 65 to
19 80°C (*not used for the analysis*). The reasons for that should be studied in more detail and the
20 temperature range should be increased in order to monitor enthalpy variation at larger temperatures.
21 Probably, monitoring a wider temperature range for the two other acids (Oxalic and Adipic) we
22 could observe the same trend.

23 **TABLE 3**

24 **25 5.5 Discussion and comparison of obtained results**

26 As listed in Tab.3, when the temperature oscillations are within $\pm 0.5^\circ\text{C}$ the errors does not exceed 5
27 kJ mol^{-1} whereas when the temperatures oscillations are larger than $\pm 0.5^\circ\text{C}$, the errors on the
28 enthalpy of sublimation are larger than 8 kJ mol^{-1} (Adipic and Succinic acids). In Table 4, are listed
29 the temperatures range used and enthalpies results obtained in this study: an high accuracy has been
30 obtained for Succinic, Adipic and Azelaic, i.e. within 1 percent and within 5 percent for Oxalic

1 acid. Thus, in order to demonstrate the high quality of our method and the validity of our results, the
2 enthalpies of sublimation have been compared with the results obtained by previous works. In the
3 comparison we will take into account the different boundary conditions (initial temperatures and
4 working pressures) of among the different procedures (Tab.4): TDMA (Bilde et al., 2003), Knudsen
5 mass loss (Silva et al., 1999), KEMS (Booth et al. 2009), TDPB (Chattopadhyay and Ziemann,
6 2007), effusion method, EM (Davies and Thomas, 1960, Granovskaya, 1948), E-1559 Method B
7 (Albyn, 2001).

8 9 TABLE 4

10 The values of enthalpy of sublimation obtained in our experiments for Succinic and Adipic acids
11 are within 5 percent of the enthalpies values reported by Chattopadhyay and Ziemann (2007), who
12 present a Temperature Programmed Thermal Desorption method (TPTD) where the particles were
13 collected at -50°C in vacuum chamber. Successively, by means of a heating process ($2^{\circ}\text{C min}^{-1}$), the
14 vapour pressure and evaporation rates of submicron particles were measured. This method use a
15 modified Langmuir equation and Clausius-Clapeyron equation, similar to our theoretical approach.
16

17 Our results are quite lower than those measured by Bilde et al. (2003) (within 9 percent for the
18 Adipic acid), who demonstrate the capability of Tandem Differential Mobility Analyser technique
19 (TDMA) to measure the vapour pressures of submicron aerosol particles at solid-state structure. The
20 results of evaporation rates, over the temperature range $17-41^{\circ}\text{C}$ were measured. In TDMA
21 technique the major source of error was based on the sensitivity analysis (a conservative uncertainty
22 and systematic errors were considered on vapor pressures). A different method was used by Booth
23 et al. (2009), who directly measured the steady state vapour pressure using Knudsen Mass Loss
24 Effusion Spectrometer (KEMS) method with solid sample. In Booth et al. (2009), the working
25 pressure and heating method of the sample were similar to ours: temperature step of 5°C
26 considering 10 minutes of stabilization time. The obtained enthalpy for Adipic and Succinic acids
27 are smaller than those measured in this work and larger one for the Oxalic acid. However, it should
28 be noted that their measurements are affected by a large uncertainty, in particular the errors
29 obtained for Oxalic acid (19 kJ mol^{-1}) are the result of the variation in the three calibration
30 compounds used for that determination whereas the high error on the Adipic acid (26 kJ mol^{-1}) is
31 the result of low pressures, resulting in decreased signal noise ratio. Regarding the Oxalic acid, as
32 discussed above, it is highlighted that these authors measured the value of the α -orthorhombic
33 anhydrous form and a difference from our results is expected. This difference is evident in de Wit et

1 al. (1983) results, where the analysis of dehydrate and anhydrous form (prepared by a prolonged
2 evacuation of the hydrate substance and vacuum sublimation) of the Oxalic acid has been
3 performed. The enthalpy of sublimation of Oxalic acid, as listed in Tab.4, agrees within 5.5 percent
4 with the average value obtained from the dehydrated results (de Wit et al., 1983, Granovskaya,
5 1948). Instead, Ribeiro da Silva et al. (1999, 2001), who presents a Knudsen Mass Loss Effusion, a
6 method similar to Booth et al.(2009) in order to study the vapor pressures of crystalline
7 Dicarboxylic acids at much higher temperatures. The vapor pressures were calculated with
8 Langmuir equation whereas the enthalpy of sublimation at the mean temperature was derived by
9 Clausius-Clapeyron equation. Ribeiro da Silva et al.(1999) results show larger values than ours
10 (Tab. 4): 32 kJ mol⁻¹ for Azelaic acid (R. da Silva et al., 1999) and 10 kJ mol⁻¹ for Succinic acid (R.
11 da Silva et al., 2001). As stated by Bilde et al. (2015) the enthalpy of sublimation values between
12 the different experimental methods can differ of tens of kilojoules per mole. Davies and Thomas
13 (1960), who measured heats and entropy of sublimation by means of Effusion Method at 1.013 bar
14 pressure, are in agreement with our values (within 9.5 percent for the Adipic acid and within 4
15 percent for the Succinic acid). Albyn (2001) used two different 15 MHz microbalances cooled at -
16 42°C in vacuum chamber to measure the deposition rates of Adipic acid from 25 to 60°C. The
17 enthalpy of sublimation measured by Albyn is 121±8 kJ mol⁻¹ and shows a difference of 20 kJ mol⁻¹
18 compared with our result (Tab.4). This is probably due to the different setup and measurement
19 procedure, i.e. the microbalance's temperature of -42°C instead of -72°C (this work) and the
20 distance between the sensing crystal and the sample of 20 cm instead of 2 cm (this work). The
21 constant error of 8 kJ mol⁻¹, obtained with a temperature stability of ±0.5°C on the effusion cell
22 (Albyn, 2001), could be due to the re-evaporation of a minor portion of the deposited material. In
23 this work, when the temperature stability is within ±0.5°C, the error does not exceed 5 kJ mol⁻¹
24 (Tab. 3, Oxalic, Succinic and Adipic acid). This improvement in the accuracy could be due to our
25 increased gas flow of Adipic molecules.

26 Thus, main differences observed among the various examined works and enthalpy results are
27 probably due to different temperature and pressures considered in the experiments and different
28 forms of the sample (e.g. solid or aerosol), that produced different evaporation rates and different
29 vapour pressures at each monitored temperature.

30 In our procedure the efficiency of deposition process was improved when the difference between
31 PCM surface's and effusion cell's temperature increased, and molecules flux was focused directly
32 on PCM crystal (Dirri et al., 2012). In this way, we were able to discern deposition rate at different
33 temperatures. Data analysis has been performed excluding the set point with high temperature

1 oscillations (Adipic and Succinic acids) which affects the deposition rates trend and the low flows
2 of molecules at lower temperatures (e.g. 30-35°C, Adipic acid case). As listed in Tab.3, a
3 temperature stability of $\pm 0.5^\circ\text{C}$ on the effusion cell causing errors on the enthalpies of sublimation
4 lower than 4 percent for Oxalic, Adipic and Succinic acids (a better accuracy compared with Albyn,
5 2001) whereas when the temperature stability is larger than $\pm 0.5^\circ\text{C}$, the corresponding errors are
6 larger than 10 percent. Thus, for each compound we obtained several measurement of the enthalpy
7 of sublimation (individually having a worst accuracy, Tab.3) that allows to retrieve the weigh
8 average value for the enthalpy of sublimation where the weight function: $\omega_i = (1/\sigma_i^2)$ has been used.
9 The weight average values show a better accuracy compared with the single enthalpy measurement,
10 i.e. an accuracy within 1 percent for Succinic, Adipic and Azelaic acids and within 5 percent for
11 Oxalic acid (Tab.4). In Fig.7 the enthalpy of sublimation of four Dicarboxylic acids analyzed in this
12 work are compared with previous studies. The behaviors of the enthalpies of sublimation are very
13 similar and increase as the carbon chain number of the substance increases. Indeed, the substances
14 with a short carbon chain (Oxalic and Succinic acid) show a lower enthalpy of sublimation
15 compared with the substances with a higher carbon chain (Adipic and Azelaic acids), which require
16 a higher temperature to reach the complete sublimation (larger than 60°C). Furthermore, as reported
17 by other studies (Booth et al. 2009, Bilde et al. 2003, Bilde et al. 2015), the Dicarboxylic acid with
18 an odd number of carbon atoms have a lower sublimation enthalpies compared with Dicarboxylic
19 acids having an even number of atoms. This behavior is based principally on the solid-state
20 crystalline structure of the acids. In this work, the enthalpy alternation between the odd and even
21 carbon chain Dicarboxylic acid ($>C_5$) has been confirmed for two compounds: the enthalpy of
22 sublimation of Adipic acid (C_6) is higher than the sublimation enthalpy of Azelaic acid (C_9) of 17 kJ
23 mol^{-1} (Fig.7). The alternation in the enthalpy of sublimation it has been also confirmed by Bilde at
24 al. (2003) results, which included the Adipic and Azelaic acids. As explained by Booth et al.
25 (2009), the behavior of the enthalpy alternation is not always clear and it is not possible to say
26 firmly that this effect was observed in their work.

27
28
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FIGURE 7

6. Conclusions and future perspective

29 A new experimental set-up has been developed in order to characterize the C2-C9 Dicarboxylic
30 acids (i.e. Oxalic, Succinic, Adipic and Azelaic acid), compounds present in atmospheric aerosols,
31 over the temperature range of 25°C - 80°C . The capability of our instrumental setup to monitor the
32 sublimation process in vacuum condition (10^{-6}mbar) has been tested successfully. The measurement
33 procedure is relatively simple and requires about 6 hours for a single experiment (cooling the PCM,

1 heating the sample and follow the process **continuously**). Then, the deposition rates of Dicarboxylic
2 acids have been measured and their sublimation enthalpies have been obtained **in the temperature**
3 **range from 25 to 70°C**. The results were compared with the other techniques (KEMS, TDMA, EM,
4 TDPD, **E-1559 Method B**).

5 This experimental set-up, based on Piezoelectric Crystal Microbalance technology, provides many
6 advantages over other methods: it is lightweight, with a better accuracy and requires a smaller
7 amount of materials for the analysis.

8 **The values of the enthalpy of sublimation obtained in this study (Tab.4) for Succinic and Adipic**
9 **acid are in agreement within 5 percent with the average enthalpy obtained by previous works**
10 **(Chattopadhyay and Ziemann, 2007, Davies and Thomas 1960, Bilde et al., 2003, R. da Silva et al.,**
11 **2001, Albyn 2001, Booth et al., 2009). The results for the Oxalic acid are in good agreement (within**
12 **6 percent) with the enthalpy average value from Granovskaya (1948) and de Wit et al.(1983)**
13 **whereas the enthalpy of sublimation of Azelaic acid is in agreement within 11% with Bilde et al.**
14 **(2003).**

15 **In addition, our results show a good accuracy if we consider the values obtained with an accurate**
16 **temperature control (within $\pm 0.5^\circ\text{C}$): the accuracy on the enthalpy of sublimation are within 1**
17 **percent for Succinic, Adipic and Azelaic and within 5 percent for Oxalic acid. Contrarily, the**
18 **accuracy worsens (and results are less reliable) when T_1 approaches T_2 (Azelaic acid) or at higher**
19 **temperatures (larger than 60°C) where the temperature oscillations cause the instability of the acid's**
20 **flow (e.g. Adipic and Succinic acids).**

21 Thus, by means of our measurement procedure and comparing the results with previous works
22 (Bilde et al. 2003, Davies and Thomas 1960, Ribeiro da Silva et al., 1999) we have been able to
23 obtain a best accuracy on the enthalpy of sublimation results, as listed in Tab.4. **In particular, the**
24 **accuracy may be refined by improving the temperature control system, in order to extend the**
25 **temperature range monitored and to obtain a better accuracy at each set point (lower than $\pm 0.5^\circ\text{C}$).**
26 To work at lower temperatures would be useful especially for Oxalic and Azelaic acids and this
27 would allow to monitor solid \rightarrow gas phase and to obtain more information about other phase
28 transitions (gas \leftrightarrow liquid, solid \leftrightarrow liquid). On the other hand, the extension at larger temperatures,
29 which can be simply obtained by changing the resistive element, would make it possible to study
30 also less volatile compounds, such as some Carboxylic Acids or Polycyclic Aromatic Hydrocarbons
31 (PAH).

32

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- 23
- 24
- 25 Table 1. Thermodynamic properties of the compounds used in experiments at ambient pressure. In
26 particular, the Oxalic and Succinic acids have a high solubility in water, and are the most present in
27 submicron terrestrial aerosol. (^aAfeedy, H.Y., NIST 1998; ^b*CRC Handbook of Physical Properties
28 of Organic Chemicals*; ^cCAS Data Base List - Chemical Book, ^dCalculated for 30 °C in Davies and
29 Thomas).

Name	Oxalic(C ₂)	Succinic(C ₄)	Adipic(C ₆)	Azelaic(C ₉)
Chemical formula ^a	C ₂ H ₂ O ₄	C ₄ H ₆ O ₄	C ₆ H ₁₀ O ₄	C ₉ H ₁₆ O ₄
Molecular weight ^a	90.03	118.0880	146.1412	188.2209

Water solubility (mg/l) at 25°C	^b 2.2×10 ⁵	^b 8.3×10 ⁴	^b 3.2×10 ²	^c 2.28×10 ³
Vapour Pressure (torr)	^c <10 ⁻²	^d 6.9×10 ⁻⁷	^d 1.5×10 ⁻⁷	^c 2×10 ⁻⁶
ΔH _{sub} (kJmol ⁻¹) ^a	93-98	118-123	129,3	156-159
ΔH _{fus} (kJ mol ⁻¹) ^a	--	32,9	34,8	32,6
T _{fusion} (°C) ^a	189.5	188	152.1	110

1
2

3 Table 2. Parameters of the experiments involving the different Dicarboxylic acids. λ_{Start} and $\lambda_{Sublimated}$
4 are the initial mass and the sublimated mass of the sample measured before and after the heating
5 process with an electronic balance. Pressure is stable in the range of 10⁻⁶ - 10⁻⁷ mbar. T_L is the limit
6 temperature, i.e. the temperature above which a slope change of deposition curve is expected.
7 T_{Monitored} is the temperature interval where the effusion cell was heated. Δt_{Stabilization} is the time
8 interval where the frequency and temperature data have been recorded and used for the analysis.
9 ΔH_{Literature} is the average value obtained from the in literature values (for Oxalic acid, only the
10 enthalpy of dehydrates form have been considered) which using different methods (see Tab.4).

Name	Oxalic(C ₂)	Succinic(C ₄)	Adipic(C ₆)	Azelaic(C ₉)
λ _{Start} (mg)	20± 0,5	13.0±0.5	13.0±0.5	19± 0,5
P _{work} (mbar)	3,5 × 10 ⁻⁶	6,5 × 10 ⁻⁶	5,5 × 10 ⁻⁶	8 × 10 ⁻⁷
T _L (°C)	55	55	70	60
T _{Monitored} (°C)	25 to 65	30 to 75	30 to 75	25 to 80
Δt _{Stabilization} (min)	30	30	30	20
ΔH _{Literature}	<u>59.2</u>	<u>118.2</u>	<u>134</u>	148.9
λ _{Sublimated} (mg)	3	1	4	3

11

12 Table 3. Enthalpy of sublimation calculated from acid deposition rates measured in our experiment.
13 Considering the Succinic acid (bold highlighted values), when T₂ approaches T_L, the calculated
14 enthalpy deviates from the previous work values whereas the temperature oscillations larger than
15 ±0.5°C produce an error ≥8 kJ mol⁻¹ on the enthalpy of sublimation (underlined values). Oxalic and
16 Succinic acids (weak lattice energies at low temperature) sublime at smaller temperatures, in the
17 range 25/30-55°C where the sublimation process was monitored. Otherwise, Adipic and Azelaic
18 acid sublime at larger temperatures. The temperature range is wide enough to calculate the

- 1 enthalpy of sublimation but should be extended if the intent is to monitor the complete sublimation
- 2 process (in particular for Adipic acid, $T \geq 75^\circ\text{C}$).

Acid	$T_1 \pm \sigma_{T1} (^\circ\text{C})$	$T_2 \pm \sigma_{T2} (^\circ\text{C})$	$k_1 (\text{mol cm}^{-2} \text{s}^{-1})$	$k_2 (\text{mol cm}^{-2} \text{s}^{-1})$	$\Delta H_{\text{sub}} \pm \sigma_{\Delta H} (\text{kJ mol}^{-1})$	
Oxalic	24.772±0.111	44.969±0.002	6.56×10^{-12}	3.01×10^{-11}	60.67±1.31	
	29.843±0.105	44.969±0.002	9.15×10^{-12}	3.01×10^{-11}	64.35±0.64	
	34.964±0.015	44.969±0.002	1.52×10^{-11}	3.01×10^{-11}	56.85±0.93	
	24.772±0.111	49.962±0.075	6.56×10^{-12}	4.59×10^{-11}	63.15±1.34	
	29.843±0.105	49.962±0.075	9.15×10^{-12}	4.59×10^{-11}	66.65±0.84	
	34.964±0.015	49.962±0.075	1.52×10^{-11}	4.59×10^{-11}	62.40±1.07	
	24.772±0.111	54.952±0.059	6.56×10^{-12}	6.04×10^{-11}	61.06±1.07	
	29.843±0.105	54.952±0.059	9.15×10^{-12}	6.04×10^{-11}	63.44±0.60	
	34.964±0.015	54.952±0.059	1.52×10^{-11}	6.04×10^{-11}	59.32±0.73	
	Succinic	34.85±0.02	45.42±0.68	1.59×10^{-12}	7.22×10^{-12}	117.93±4.36
		39.90±0.04	45.42±0.68	3.31×10^{-12}	7.22×10^{-12}	<u>118.45±7.97</u>
		34.85±0.02	50.22±0.02	1.59×10^{-12}	1.35×10^{-11}	116.61±3.32
39.90±0.04		50.22±0.02	3.31×10^{-12}	1.35×10^{-11}	116.21±3.41	
29.98±0.02		54.64±0.02	8.01×10^{-13}	2.17×10^{-11}	111.88±4.15	
34.85±0.02		54.64±0.02	1.59×10^{-12}	2.17×10^{-11}	112.17±2.66	
39.90±0.04		54.64±0.02	3.31×10^{-12}	2.17×10^{-11}	110.27±2.47	
45.42±0.68		54.64±0.02	7.22×10^{-12}	2.17×10^{-11}	<u>105.14±11.75</u>	
50.22±0.02		54.64±0.02	1.35×10^{-12}	2.17×10^{-11}	<u>95.73±3.47</u>	
Adipic		39.84±0.04	59.65±0.05	1.10×10^{-12}	2.60×10^{-11}	139.58±3.69
		49.82±0.04	59.65±0.05	5.47×10^{-12}	2.60×10^{-11}	142.90±3.06
		39.84±0.04	64.93±0.04	1.10×10^{-12}	5.78×10^{-11}	140.26±1.22
	49.82±0.04	64.93±0.04	5.47×10^{-12}	5.78×10^{-11}	142.95±1.86	
	55.01±0.68	64.93±0.04	1.25×10^{-11}	5.78×10^{-11}	<u>143.54±13.90</u>	
	59.65±0.05	64.93±0.04	2.59×10^{-11}	5.78×10^{-11}	142.99±4.98	
	39.84±0.04	70.01±0.03	1.10×10^{-12}	1.20×10^{-10}	140.15±2.29	
	49.82±0.04	70.01±0.03	5.47×10^{-12}	1.20×10^{-10}	142.14±1.22	
	55.01±0.68	70.01±0.03	1.25×10^{-11}	1.20×10^{-10}	<u>142.24±9.01</u>	
	59.65±0.05	70.01±0.03	2.59×10^{-11}	1.20×10^{-10}	141.34±2.18	
	Azelaic	34.95±0.22	50.16±0.02	6.94×10^{-13}	6.09×10^{-12}	119.59±6.91
		40.13±0.26	50.16±0.02	1.48×10^{-12}	6.09×10^{-12}	120.24±8.27
45.26±0.48		50.16±0.02	2.98×10^{-12}	6.09×10^{-12}	<u>126.42±20.11</u>	
40.13±0.26		55.14±0.27	1.48×10^{-12}	1.29×10^{-11}	124.70±8.06	
45.26±0.48		55.14±0.27	2.98×10^{-12}	1.29×10^{-11}	<u>130.25±14.03</u>	
50.16±0.02		55.14±0.27	6.09×10^{-12}	1.29×10^{-11}	<u>134.14±11.74</u>	
45.26±0.48		60.04±0.02	2.99×10^{-12}	2.48×10^{-11}	127.81±6.72	
50.16±0.02		60.04±0.02	6.09×10^{-12}	2.48×10^{-11}	128.53±1.86	
55.14±0.27		60.04±0.02	1.29×10^{-11}	2.48×10^{-11}	<u>122.65±10.71</u>	

1

2 Table 4. Comparison of enthalpy of sublimation of Dicarboxylic acids retrieved by different
 3 techniques (1=Booth et al. 2009, 2=Granovskaya 1948, 3=Chattopadhyay and Ziemann 2007,
 4 4=Bilde et al. 2003, 5=Davies and Thomas 1960, 6a=Ribeiro da Silva et al., 1999, 6b= Ribeiro da
 5 Silva et al., 2001, 7=de Wit et al., 1983, 8=Albyn, 2001). $\Delta T(^{\circ}\text{C})$ is the temperature range used to
 6 calculate the enthalpy of sublimation. The enthalpy values and corresponding errors reported for
 7 this work have been calculated as the weighted average. The anhydrous (A) and dehydrate (deh)
 8 forms of the Oxalic acid have been treated and the results for the enthalpy of sublimation have been
 9 reported.

Compound	$P_{\text{work}}(\text{mbar})$	$\Delta T(^{\circ}\text{C})$	$\Delta H_{\text{sub}}(\text{kJ mol}^{-1})$	Reference
Oxalic	10^{-6}	25/55	^(deh) 62.5±3.1	This work
	10^{-6}	30/60	^(A) 75.0±19.0	1
	--	20/50	^(deh) 61.8	2
	--	-22/54	^(deh) 56.5	7
	--	37/62	^(A) 98.5	7
Succinic	10^{-6}	30/55	113.3±1.3	This work
	10^{-6}	30/60	93.0±6.0	1
	10^{-8}	7/29	119.5	3
	10^3	17/41	138.0±11.0	4
	10^3	99/128	117.5±3.3	5
	10^{-7}	87/102	123.2±1.6	6b
Adipic	10^{-6}	40/70	141.6±0.8	This work
	10^{-6}	30/60	119.0±26.0	1
	10^{-8}	12/34	146.2	3
	10^3	17/41	154.4±6.0	4
	10^3	86/133	129.2±1.0	5
	10^{-7}	25/60	121.0±8.0	8
Azelaic	10^{-7}	35/60	124.2±1.2	This work
	10^{-8}	21/38	138	3
	10^3	17/41	153±24	4
	10^{-7}	95/113	155.8±1.6	6a

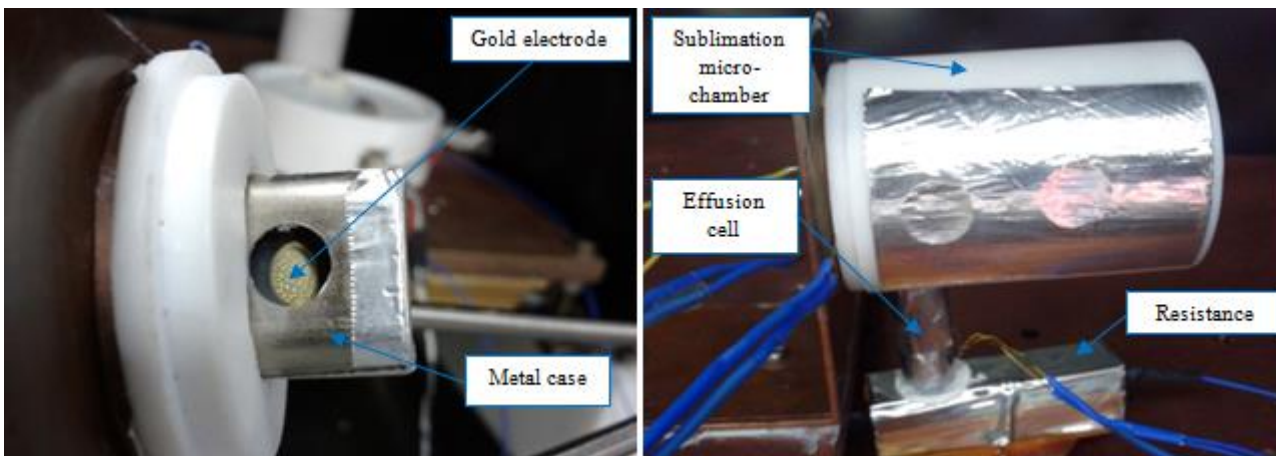
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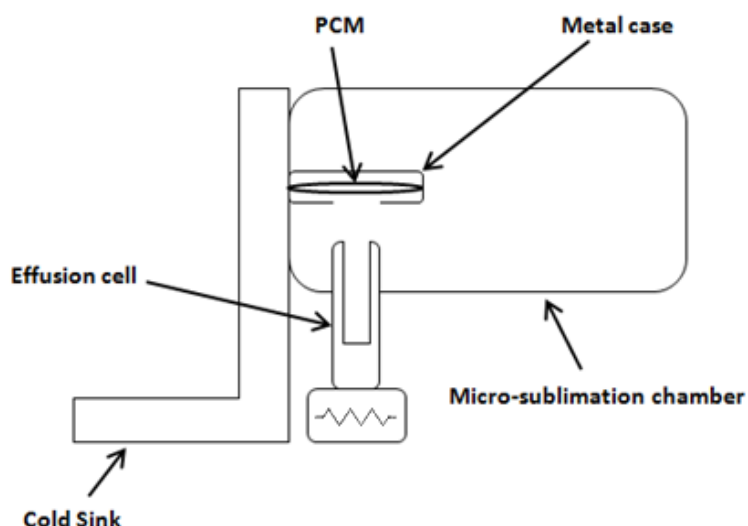
2 Figure 1. Piezoelectric Crystal Microbalance: quartz crystal (transparent plate) and gold electrode in
 3 the centre. On the right side and left side are presents the contact points for the proximity electronic.

4



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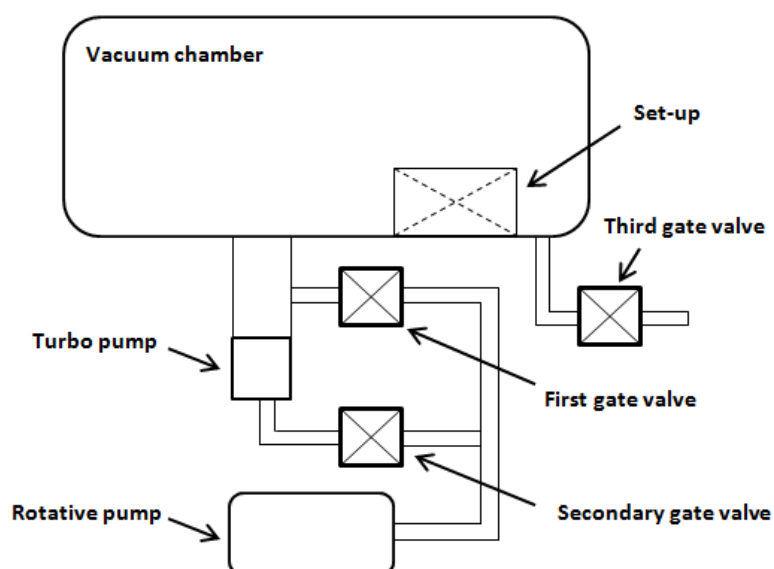
6 Figure 2. Pictures of the experimental setup. *Left*: PCM inserted in the metal case. VOC molecules
 7 deposited on the PCM's electrode are visible and correspond to the white spots on the crystal area.
 8 *Right*: the sublimation micro-chamber containing the PCM and the outgassing material. It is made
 9 of insulating material (Teflon) in order to limit sublimation and thermal dispersion. The contacts are
 10 instead made of grease vacuum.



1

2 Figure 3. Schematic representation of the experimental setup. The sample is placed in the effusion
 3 cell and heated by a resistance. PCM (cooled by a cold sink) is positioned in a metal case perforated
 4 in the center to allow the VOC deposition. The deposition rates are monitored by PCM frequency
 5 whereas the sample temperature is monitored (5°C for each step) by a resistance temperature with
 6 PT100 sensor (see section 4.2). In order to avoid flux dispersion, PCM and effusion cell are located
 7 in an isolated micro-chamber and the whole set-up is placed in a vacuum chamber. The resistance is
 8 separated by cold sink in order to obtain a first sublimation step from 25°C-30°C.

9

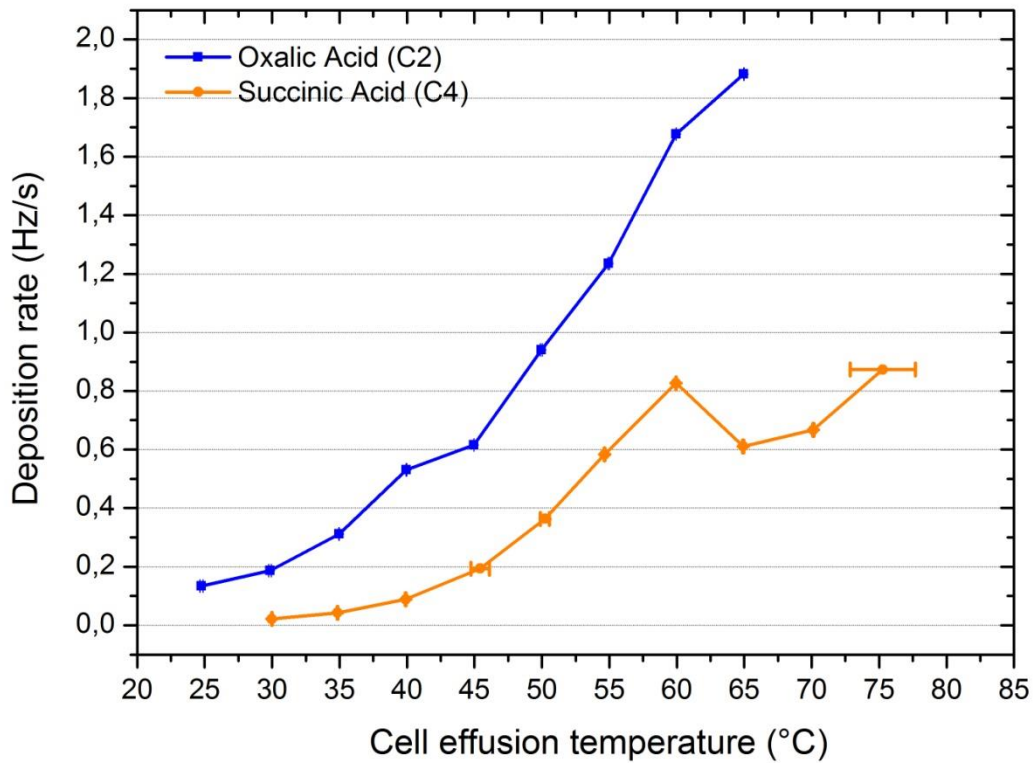


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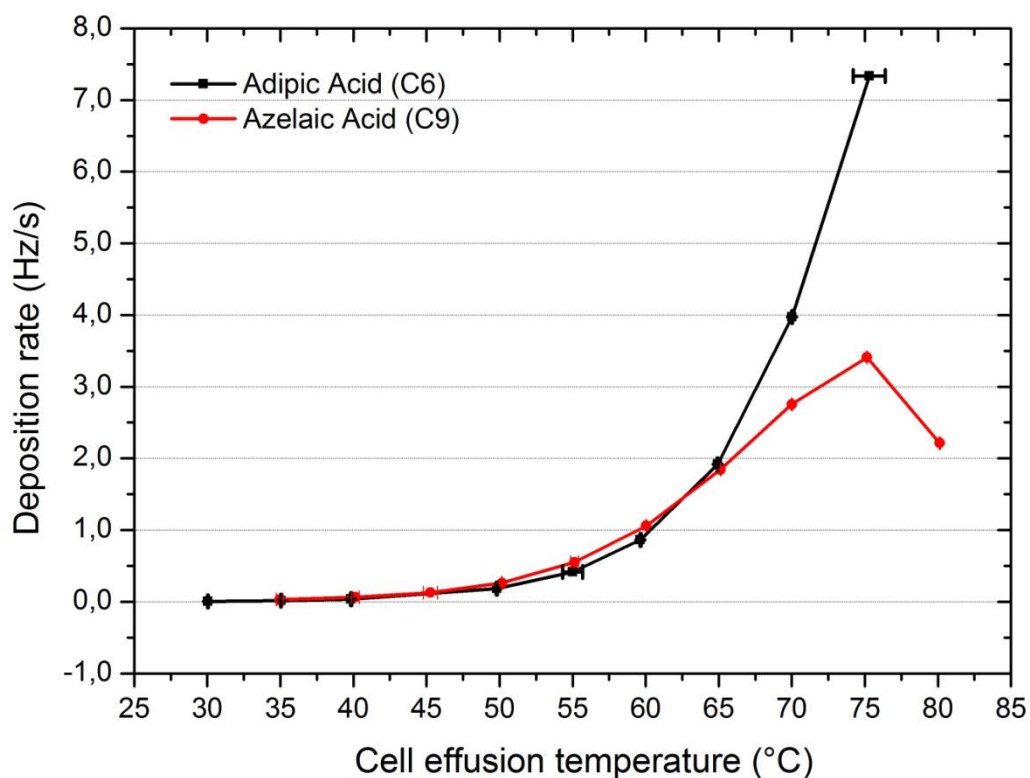
12 Figure 4. The Vacuum System, composed by a Rotative pump, Turbo pump and a Vacuum
 13 Chamber. Each pump is managed by an electro-valve: in the initial phase, the first valve (Rotative)

1 is opened whereas the second valve is closed (Turbo); in the next phase (at pressure of 10^{-2} mbar)
2 the first valve is closed whereas the second valve is opened (down to 10^{-6} mbar). The third valve is
3 used to apply the re-entry in air at the end of each experiment.



4
5 Figure 5. *Blue curve*: deposition rate curve of Oxalic acid with temperature steps of 5°C , each
6 lasting 30 minutes. The deposition linearly increases with temperature, up to 60°C . *Orange curve*:
7 Deposition rate curve of Succinic acid. Deposition rate increases with temperature up to 60°C ,
8 whereas at larger temperatures tends to oscillate around an average value of 0.75 Hz s^{-1} , due to the
9 steadiness of the sublimation flux.

10

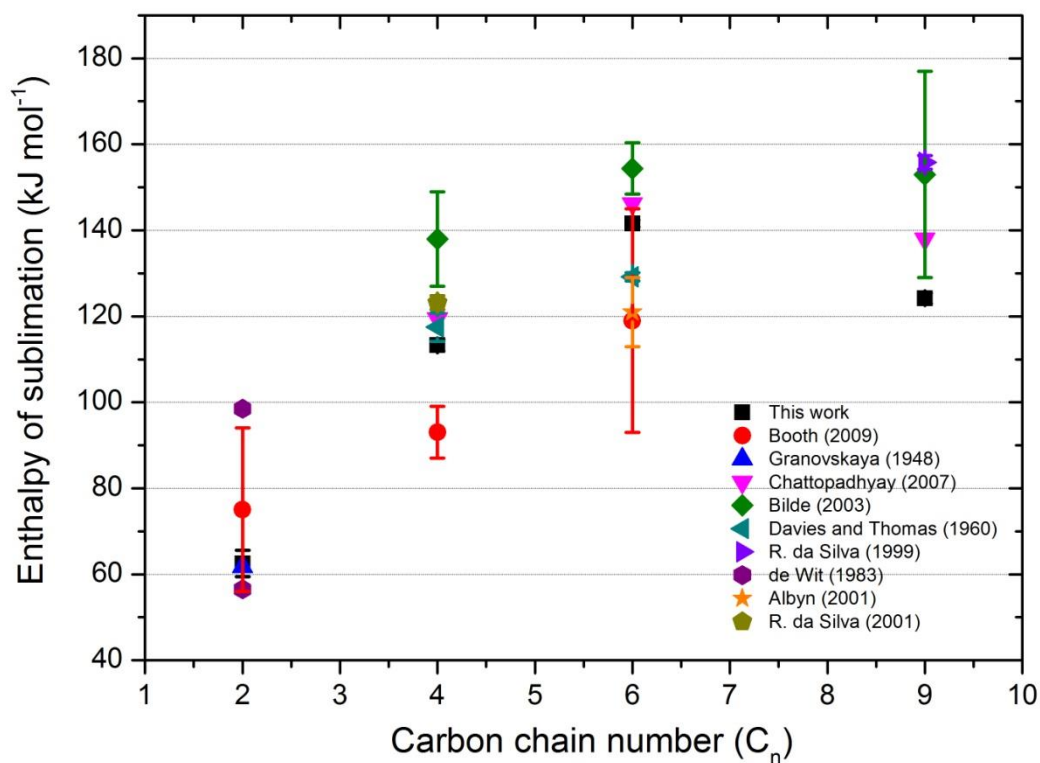


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2 Figure 6. *Black curve*: Deposition rate curve of Adipic acid shows an increase up to 75°C without
 3 decrease at larger temperature (an oscillation around an average value would be observed at even
 4 larger temperatures). *Red curve*: Deposition rate curve of Azelaic acid: molecules flux is small at
 5 low temperature as for Adipic acid case and contrarily to Oxalic and Succinic acids that show an
 6 high sublimation rates at these low temperature, i.e. 25°C-30°C(weak intermolecular forces).

7

8



1

2 Figure 7. Comparison between the enthalpies of sublimation obtained with various methods and
 3 different compounds (C₂, Oxalic acid; C₄, Succinic acid; C₆, Adipic acid and C₉, Azelaic acid,
 4 weight average values). Different experiment conditions (temperature monitored and work pressure,
 5 Tab.4) lead to diverging results: Booth et al. (2009), Chattopadhyay and Ziemann (2007), R. da
 6 Silva et al. (1999) in vacuum environments, Bilde et al. (2003), Davies and Thomas (1960) at
 7 atmospheric pressure. For Oxalic acid are plotted the results for anhydrous and dehydrate forms (de
 8 Wit et al., 1983 and Booth et al., 2009).

9

10