



# Piezoelectric crystal microbalance measurements of enthalpy of sublimation of C<sub>2</sub>–C<sub>9</sub> dicarboxylic acids

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Received: 18 May 2015 – Published in Atmos. Meas. Tech. Discuss.: 10 July 2015

Revised: 17 November 2015 – Accepted: 13 December 2015 – Published: 26 February 2016

**Abstract.** We present here a novel experimental set-up that is able to measure the enthalpy of sublimation of a given compound by means of piezoelectric crystal microbalances (PCMs). The PCM sensors have already been used for space measurements, such as for the detection of organic and non-organic volatile species and refractory materials in planetary environments. In Earth atmospheric applications, PCMs can be also used to obtain some physical–chemical processes concerning the volatile organic compounds (VOCs) present in atmospheric environments. The experimental set-up has been developed and tested on dicarboxylic acids. In this work, a temperature-controlled effusion cell was used to sublime VOC, creating a molecular flux that was collimated onto a cold PCM. The VOC recondensed onto the PCM quartz crystal, allowing the determination of the deposition rate. From the measurements of deposition rates, it has been possible to infer the enthalpy of sublimation of adipic acid, i.e.  $\Delta H_{\text{sub}} : 141.6 \pm 0.8 \text{ kJ mol}^{-1}$ , succinic acid, i.e.  $113.3 \pm 1.3 \text{ kJ mol}^{-1}$ , oxalic acid, i.e.  $62.5 \pm 3.1 \text{ kJ mol}^{-1}$ , and azelaic acid, i.e.  $124.2 \pm 1.2 \text{ kJ mol}^{-1}$ . The results obtained show an accuracy of 1 % for succinic, adipic, and azelaic acid and within 5 % for oxalic acid and are in very good agreement with previous works (within 6 % for adipic, succinic, and oxalic acid and within 11 % or larger for azelaic acid).

## 1 Introduction

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

The primary atmospheric aerosol is composed of particles coming from processes such as rock erosion and fires, and from anthropogenic processes (such as fossil fuel combustion or industrial activity). Volatile organic compounds (VOCs) in primary aerosol can generate secondary organic aerosol (SOA) composed of fine particles, i.e. lower than 1–2  $\mu\text{m}$ , (Salzen and Schlünzen, 1999) from photo-oxidation reactions with compounds in Earth's atmosphere, in particular hydroxyl radicals, ozone, and nitrate radicals. For example, hydrocarbons are enriched with carboxyl (–COOH), carbonyl (–CO), or hydroxyl (–OH) functional groups and are transformed into ketones or carboxylic acid after several reactions.

Because of the wide number of VOC transformation processes it is crucial to know the chemical–physical properties (i.e. enthalpy, entropy, free energy) in order to characterize the organic fraction of the atmospheric aerosol. In detail, specific substances (markers) or a class of substances should be identified in order to provide some information on the atmospheric aerosol sources, e.g. evaluating the transformation degree of the organic compound and their release by primary sources (Pietrogrande et al., 2014). Carbohydrates and dicarboxylic acids with low molecular weight (the latter are a subclass of carboxylic acids) are among the most important groups of molecules identified in the atmospheric aerosol. It could be useful to consider these substances as

molecular tracers (“markers”) that provide information on the aerosol origin (biogenic or anthropogenic), i.e. on the emission source and on the processes that the organic substances undergo in the atmosphere. Dicarboxylic acids are present in various concentrations in different terrestrial environments, e.g. marine, rural, and urban (Kawamura et al., 2005; Yu and Fraser, 2004; Limbeck et al., 2001), and their formation in the atmosphere is likely due to photochemical reactions in the gaseous phase involving VOCs (in particular aliphatic and aromatic hydrocarbons) of biogenic and anthropogenic origin. In particular, they play an important role on physical–chemical reactions involving aerosol particles that may be gathered in agglomerates (submicron-sized), and represent an important component of the atmospheric aerosol particles, both in remote and urban areas (Rohrl and Lammel, 2001). Oxalic acid is the most abundant dicarboxylic acid in the tropospheric aerosol and comprises 41–67 % of the total diacids (Sorooshian et al., 2006; Kawamura and Keplán, 1983), whereas the succinic and malonic acids are less abundant and reach peaks of 4–8.7 % during the summer (Kawamura and Ikushima, 1993). Adipic and succinic acids have been identified in laboratory studies as SOA products (reaction of O<sub>3</sub> and cyclohexane; Hatakeyama et al., 1985). The adipic acid is related to the emission of N<sub>2</sub>O, a greenhouse gas that causes stratospheric ozone depletion (US EPA, 2013), whereas the succinic acid probably originates from biogenic sources, and is an important compound in biochemistry due to its role in the citric acid cycle (Krebs cycle). The azelaic acid is considered a photon-induced oxidation product, deriving from biogenic unsaturated fatty acids, presenting one or more double bond in their chain (Kawamura and Keplán, 1983). Succinic and oxalic acids had been proven to be part of the organic materials that contribute to form condensation nuclei of atmospheric clouds (Kerminen et al., 2000; Prenni et al., 2001), and it has been suggested that the ratio between oxalic and succinic acid is a good marker of the atmospheric aerosol oxidation state. On the other hand, the adipic : azelaic ratio could be an indicator of anthropogenic sources, considering that adipic acid derives from cyclohexane’s oxidation (Kawamura and Ikushima, 1993).

In order to characterize the dicarboxylic acids, different methods are used, based on the measurement of the evaporation rates and calculation of the enthalpy of sublimation/evaporation, e.g. the thermal desorption particle beam mass spectrometry (TDPBMS) method (Chattopadhyay and Ziemann, 2007), the Knudsen effusion mass-loss method (Ribeiro da Silva et al., 2001), Knudsen effusion mass spectrometry (KEMS) (Booth et al., 2009), the tandem differential mobility analyser (TDMA) technique (Bilde et al., 2003), and the effusion method (Davies and Thomas, 1960; Granovskaya, 1948). Discrepancies between results obtained by the different methodologies were found to be up to 2 orders of magnitude, and this makes the acids’ characterization even more difficult.

In this study, low molecular weight dicarboxylic acids (carbon chains from C<sub>2</sub> to C<sub>9</sub>; see Fig. 1) were analysed by means of a new experimental set-up, based on piezoelectric crystal microbalances (PCMs) commonly used to detect mass variations, density, viscosity, and absorption/desorption processes, by means of transformation of mass change into fundamental resonance frequency variation. The PCM oscillation frequency is  $1/m$ ,  $m$  being the mass deposited on the microbalance, as stated by the Sauerbrey equation (Sauerbrey, 1959). Therefore, in principle it is possible to measure VOC sublimation or deposition on the crystal surface by changing the PCM temperature. The mass variation during the sublimation process will give the amount of the volatile component, while the physical properties of some atmospherically relevant compounds can be inferred in the chosen temperatures range (Salo et al., 2010). A compound can be characterized more precisely by retrieving its enthalpy of sublimation; this is possible by measuring the sample deposition rates on the PCM at different temperatures (see Sect. 5).

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

The TG Lab facility, located in IAPS-INAF, is a dedicated facility to study the feasibility, development, and calibration of TGA sensors optimized for space measurements. One of the TG Lab projects concerns VISTA (Volatile In Situ Thermogravimetry Analyser), a sensor developed for the Marco Polo-R mission (Palomba et al., 2015; Barucci et al., 2011) and studied for other ESA Cosmic Vision missions, aimed at the Venus atmosphere (Wilson et al., 2011), Titan low atmosphere (Longobardo et al., 2013), and the sub-surface of Europe (Gowen et al., 2011).

In this work, a PCM is cooled down to  $-72^{\circ}\text{C}$  by means of a cold sink, whereas the sample is positioned in an effusion cell and heated up to sublimation. The set-up is placed in a vacuum in order to avoid water vapour condensation and to facilitate the sublimation process (occurring between 25 and  $80^{\circ}\text{C}$ ), whereas the cooled crystal works as mass attractor for VOC’s molecules. This configuration allowed the deposition rate of the VOC samples on the PCM to be measured at different temperatures and the corresponding enthalpy of sublimation to be inferred. First attempts to measure enthalpy of sublimation by means of PCM were performed by Dirri et al. (2012) and were focusing on upgrading the thermal contact between PCM and the cold sink, by increasing the difference between sensor effusion cell temperature and the PCM, improving the efficiency of the PCM as mass attractor. This made it possible to measure deposition fluxes even at two close temperatures (e.g.  $\Delta T = 5^{\circ}\text{C}$ ). However, in the Dirri et al. (2012) experiment a very small frequency variation (3 kHz) was observed, due to the low deposition of acid molecules (adipic acid), and the retrieved enthalpies of sublimation were different from previous works by about 20 %



**Figure 1.** Piezoelectric crystal microbalance: quartz crystal (transparent plate) and gold electrode in the centre. On the right side and left side are the contact points for the proximity electronics.

(Chattopadhyay, 2007). In this work our accuracy has been improved as described in Sect. 2.

Section 2 describes the experimental set-up, while the theoretical background and the thermodynamic relation considered for data analysis are explained in Sect. 3. The measurement procedure is explained in Sect. 4, whereas the results are described in Sect. 5. Finally, Sect. 6 is devoted to conclusions.

## 2 Set-up operation and composition

### 2.1 PCM and effusion cell

A piezoelectric crystal microbalance (resonance frequency of 10 MHz) has been used to monitor the transition phase (solid  $\rightarrow$  gas) of some dicarboxylic acids in a controlled environment in order to obtain their enthalpy of sublimation.

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

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 on 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 a thermal shield and avoiding the PCM heating by irradiation of the internal wall of the vacuum chamber, which is at ambient temperature (see Fig. 2).

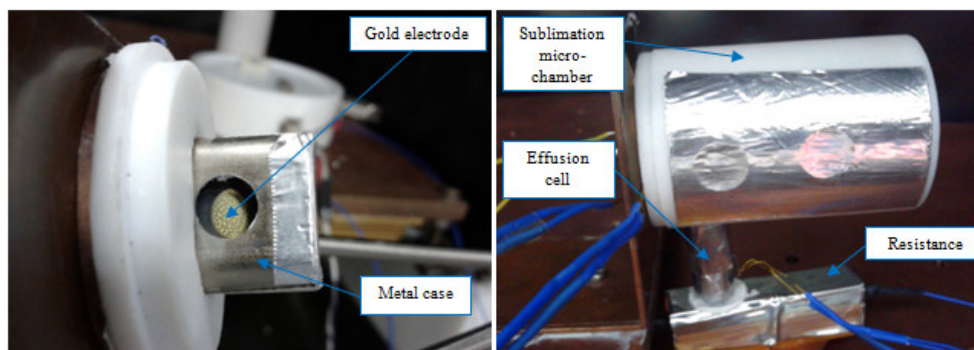
In order to maximize the VOC flux, the microbalance has been placed in front of the effusion cell. This configuration strongly improves the flux collimation, increasing the amount of the collected molecules. The metal case has a temperature similar or even slightly smaller than the crystal and if the effusion cell is too far away from the PCM, the molecular flux could more likely condense on the metal case rather than the crystal, lowering the deposition rate too much (Fig. 2, left). Moreover, reaching lower PCM temperatures (i.e.  $-72^\circ\text{C}$  instead of  $-25^\circ\text{C}$  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 the 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 to  $75^\circ\text{C}$ . This first test has experimentally determined that the distance between the PCM and the effusion cell allowing the larger flux onto the PCM crystal is 2 cm. At higher distances, the fluxes are too low and the monitoring of the sublimation process is not reliable.

Then the 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 minimizes thermal dispersion and avoids the VOC's loss into the microbalance surrounding area (Fig. 2, right). The effusion cell is inserted into a hole in the cylinder's base.

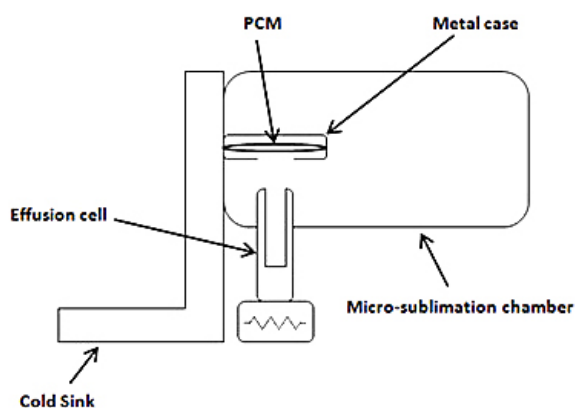
In this experiment the PCM is cooled down to  $-72^\circ\text{C}$ , while the acid sample is placed in a small cylinder case (effusion cell) 6 mm wide and 10 mm deep. This configuration allows the VOC's deposition rates to be monitored from about  $10^{-13}$  mol cm $^{-2}$  s $^{-1}$  up to  $10^{-10}$  mol cm $^{-2}$  s $^{-1}$ , 2 orders of magnitude better than the first set-up version discussed in Dirri et al. (2012). The sample is heated from room temperature (i.e.  $25\text{--}30^\circ\text{C}$ ) up to high temperatures (i.e.  $75\text{--}80^\circ\text{C}$ ) 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.

### 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  $\text{H}_2\text{O}$ ) and to avoid convective heat exchange with the atmosphere, which would affect PCM and effusion cell temperature. The vacuum system (Fig. 4) is composed of a rotative pump (CF29PR-Alcatel Society), a turbo pump (1602450-Elettrovacua Society), and a chamber (90 L), all of them assembled by the Vacuum Centre Representative (CRV S.r.l., Rome, Italy). A rotative pump can drive the system down to  $10^{-2}$  mbar, whereas the turbo pump can lower the pressure down to  $10^{-6}\text{--}10^{-7}$  mbar. Pressure is measured using the TC1 sen-



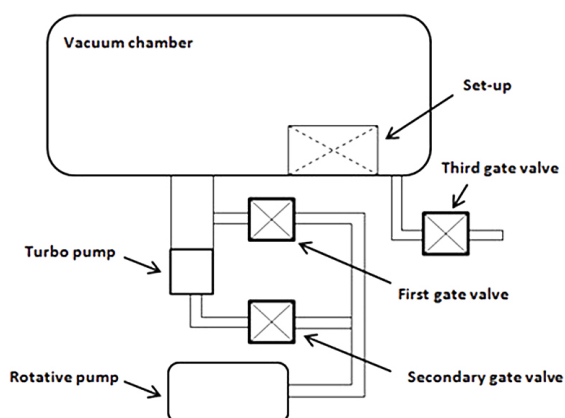
**Figure 2.** Pictures of the experimental set-up. Left: PCM inserted in the metal case. VOC molecules deposited on the PCM's electrode are visible and correspond to the white spots on the crystal area. Right: the sublimation micro-chamber containing the PCM and the outgassing material. It is made of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



**Figure 3.** Schematic representation of the experimental set-up. The sample is placed in the effusion cell and heated by a resistance. A PCM (cooled by a cold sink) is positioned in a metal case perforated in the centre to allow the VOC deposition. The deposition rates are monitored by PCM frequency, whereas the sample temperature is monitored ( $5^{\circ}\text{C}$  for each step) by a resistance temperature with PT100 sensor (see Sect. 4.2). In order to avoid flux dispersion, the PCM and effusion cell are located in an isolated micro-chamber and the whole set-up is placed in a vacuum chamber. The resistance is separated by a cold sink in order to obtain a first sublimation step from  $25$  to  $30^{\circ}\text{C}$ .

sor (Varian) up to  $10^{-2}$  mbar and the ionization gauge (IG) sensor (Varian) up to  $10^{-6}$ – $10^{-7}$  mbar. During data acquisition the pressure of the system is maintained constant during each experiment (fixed values between  $3.5 \times 10^{-6}$  mbar and  $8 \times 10^{-7}$  mbar).

The temperatures of the copper plate, metal case, resistance, and effusion cell have been continuously monitored with platinum sensors (PT100, dimensions of  $7.6 \times 7.6 \times 0.7$  mm), whose resistance changes linearly with temperature. Temperature controls of the effusion cell (heating system from  $25$  to  $110^{\circ}\text{C}$ ) and of the copper plate (cooling system, set to  $-90^{\circ}\text{C}$  and stable within  $0.2^{\circ}\text{C}$ ) have been



**Figure 4.** The vacuum system, composed of a rotative pump, turbo pump, and a vacuum chamber. Each pump is managed by an electro-valve: in the initial phase, the first valve (rotative) is opened, whereas the second valve is closed (turbo); in the next phase (at pressure of  $10^{-2}$  mbar) the first valve is closed, whereas the second valve is opened (down to  $10^{-6}$  mbar). The third valve is used to apply the re-entry in air at the end of each experiment.

driven by a proportional–integral–derivative system (PID), which allows a temperature stability of typically  $\pm 0.5^{\circ}\text{C}$  and is managed by means of LabVIEW 2010 software (PC1). The frequencies have 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 1 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 already possible to observe the sublimation of some acids (see Sect. 5), due to their high volatility.

The Clausius–Clapeyron relation characterizes a phase transition, since it allows us to infer the vapour pressure at each temperature  $T$  and the enthalpy variation from vapour pressure at two different temperatures:

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

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

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

In order to characterize a pure substance, thermogravimetry can be used to determine the vapour pressure, using the Langmuir equation for free kinetic sublimation/evaporation in a vacuum (Langmuir, 1913):

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

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

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

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

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

Then, the Van 't Hoff relation (Eq. 5) is used to monitor the enthalpy variation step by step in the considered temperature interval in order to monitor the state functions (e.g. enthalpy,

Gibbs energy, and entropy) in a transition phase. According to this relation, for an endothermic process (i.e.  $T_1 > T_2$  and  $\Delta H > 0$ ), as the processes considered in this work, we have  $k_1 > k_2$ ; i.e. temperature is directly proportional to rate constant. Indeed, the increasing temperature corresponds to an increase of the deposition rate which should be constant for a fixed temperature set point.

## 4 Experimental activity

### 4.1 Selection of dicarboxylic acids

The dicarboxylic acid chemical formula is  $\text{HOOC}(\text{CH}_2)_{n-2}\text{COOH}$  where  $n$  is the number of carbon atoms. The considered samples are acids in small grains in white crystalline form (odourless solid) with a purity degree of 99 %. Considering the sublimation point of these acids and the temperature range available by our set-up (from 25 to 80 °C), the studies were focused on acids with  $n$  between 2 and 9 carbon number: oxalic ( $n = 2$ ), succinic ( $n = 4$ ), adipic ( $n = 6$ ), and azelaic ( $n = 9$ ) acids. Adipic acid was provided by Sigma Aldrich S.r.l., succinic acid by Institute of Translational Pharmacology (ITF-CNR, Rome, Italy), while azelaic and oxalic acids were kindly provided by the University of Rome, La Sapienza (Department of Chemistry). Some structural and thermodynamic characteristics of the acids utilized in this work are shown in Table 1.

### 4.2 Measurement procedure

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

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

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



**Table 1.** Thermodynamic properties of the compounds used in experiments at ambient pressure. In particular, the oxalic and succinic acids have a high solubility in water, and are the most present in submicron terrestrial aerosol.

Name	Oxalic (C <sub>2</sub> )	Succinic (C <sub>4</sub> )	Adipic (C <sub>6</sub> )	Azelaic (C <sub>9</sub> )
Chemical formula <sup>a</sup>	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>
Molecular weight <sup>a</sup>	90.03	118.0880	146.1412	188.2209
Water solubility (mg L <sup>-1</sup> ) at 25 °C	<sup>b</sup> 2.2 × 10 <sup>5</sup>	<sup>b</sup> 8.3 × 10 <sup>4</sup>	<sup>b</sup> 3.2 × 10 <sup>2</sup>	<sup>c</sup> 2.28 × 10 <sup>3</sup>
Vapour pressure (torr)	<sup>c</sup> <10 <sup>-2</sup>	<sup>d</sup> 6.9 × 10 <sup>-7</sup>	<sup>d</sup> 1.5 × 10 <sup>-7</sup>	<sup>c</sup> 2 × 10 <sup>-6</sup>
ΔH <sub>sub</sub> (kJ mol <sup>-1</sup> ) <sup>a</sup>	93–98	118–123	129.3	156–159
ΔH <sub>fus</sub> (kJ mol <sup>-1</sup> ) <sup>a</sup>	–	32.9	34.8	32.6
T <sub>fusion</sub> (°C) <sup>a</sup>	189.5	188	152.1	110

<sup>a</sup> NIST (Afeedy et al., 1998); <sup>b</sup> CRC Handbook of Physical Properties of Organic Chemicals; <sup>c</sup> CAS DataBase List – Chemical Book, <sup>d</sup> Calculated for 30 °C in Davies and Thomas, 1960.

**Table 2.** Parameters of the experiments involving the different dicarboxylic acids. λ<sub>Start</sub> and λ<sub>Sublimated</sub> are the initial mass and the sublimated mass of the sample measured before and after the heating process with an electronic balance. Pressure is stable in the range of 10<sup>-6</sup>–10<sup>-7</sup> mbar. T<sub>L</sub> is the limit temperature, i.e. the temperature above which a slope change of deposition curve is expected. T<sub>Monitored</sub> is the temperature interval where the effusion cell was heated. Δt<sub>Stabilization</sub> is the time interval where the frequency and temperature data were recorded and used for the analysis. ΔH<sub>Literature</sub> is the average value obtained from the values in literature (for oxalic acid, only the enthalpy of hydrates form have been considered) which use different methods (see Table 4).

Name	Oxalic (C <sub>2</sub> )	Succinic (C <sub>4</sub> )	Adipic (C <sub>6</sub> )	Azelaic (C <sub>9</sub> )
λ <sub>Start</sub> (mg)	20 ± 0.5	13.0 ± 0.5	13.0 ± 0.5	19 ± 0.5
P <sub>work</sub> (mbar)	3.5 × 10 <sup>-6</sup>	6.5 × 10 <sup>-6</sup>	5.5 × 10 <sup>-6</sup>	8 × 10 <sup>-7</sup>
T <sub>L</sub> (°C)	55	55	70	60
T <sub>Monitored</sub> (°C)	25 to 65	30 to 75	30 to 75	25 to 80
Δt <sub>Stabilization</sub> (min)	30	30	30	20
ΔH <sub>Literature</sub> (kJ mol <sup>-1</sup> )	59.2	118.2	134	148.9
λ <sub>Sublimated</sub> (mg)	3	1	4	3

Our set-up and measurement procedure is similar to Albyn (2001). Thus similarly to him, we can predict that a temperature stability of ±0.5 °C (temperature control on effusion cell) should produce an error on the enthalpy of sublimation of about ±7 %. This value would be a good starting point for the organic compounds analysed in this work. This value is mainly related to the temperature instability of the sample heating and the efficiency of the deposition process (Albyn, 2001).

At 30 °C with the PCM at -72 °C, the succinic and oxalic acids already show higher sublimation rates than adipic and azelaic acids. Thus, the enthalpy of sublimation has been calculated considering a maximum temperature of 55 °C for oxalic and succinic, lower than those used for adipic acid, i.e. 70 °C, and azelaic, i.e. 60 °C (see Table 3). Besides, the retrieval of the enthalpy of sublimation can be considered reliable as long as T<sub>2</sub> is quite distinct (≥ 5 °C) from the temperature limit, T<sub>L</sub> (Table 2), where the flows of molecules are not reliable. Choosing T<sub>2</sub> ~ T<sub>L</sub>, a slope change of deposition curve is expected due to the phase transition or due to the introduction of a new physical–chemical process.

## 5 Data analysis and results

Deposition rates  $df/dt$  in Hz s<sup>-1</sup> were measured with a sampling rate of 10 s. A PCM frequency decrease was observed at increasing temperature due to the larger VOC deposition.

The rates in Hz s<sup>-1</sup> were multiplied for the PCM sensitivity (4.4 ng cm<sup>-2</sup> Hz<sup>-1</sup>) and converted into g cm<sup>-2</sup> s<sup>-1</sup>. Then, they were divided by the substance molecular weight and converted into mol cm<sup>-2</sup> s<sup>-1</sup> (Table 3). Finally, the enthalpy of sublimation and its error were expressed in kJ mol<sup>-1</sup> (Table 3). The uncertainty of temperatures and deposition rates has been calculated as standard deviation of the mean, due to the Gaussian distribution of measured values.

Thus, in order to monitor enthalpy variation over the whole temperature range considered, a good choice for T<sub>2</sub> could be a temperature not close to T<sub>L</sub> (i.e. from 60 to 70 °C for adipic acid, from 50 to 60 °C for azelaic acid, and from 45 to 55 °C for succinic acid). Our results were compared with previous works (Table 4) that use a similar effusion method and theoretical approach (i.e. Albyn 2001; Booth et al., 2009; Ribeiro da Silva et al., 2001) and with works that analyse the same dicarboxylic acids used in our study (Chattopadhyay et al., 2007; Bilde et al., 2003).

The weight average values ( $\Delta H_{\text{sub}}$ ) obtained in this work are reported in Table 4. These results have been obtained with the weight function:  $\omega_i = (1/\sigma_i^2)$ , where the  $i$  index expresses the number of data obtained listed in Table 3. Thus,  $\Delta H_{\text{sub}}$  can be calculated as  $[(\sum_i \omega_i \Delta H_i)/(\sum_i \omega_i)]$ .

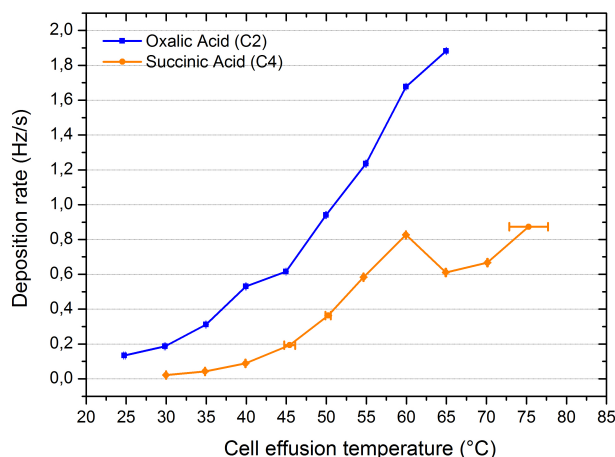
### 5.1 Oxalic acid (C<sub>2</sub>)

A total frequency variation of 13 kHz has been observed for the oxalic acid in the whole temperature range monitored (Fig. 5, blue curve): from 25 to 65 °C, corresponding to a mass deposition of 9.3 µg. This compound (with short carbon chain, C<sub>2</sub>) showed a high volatility even at low temperatures, confirmed by the moderately high deposition rate measured already at 25 °C. The deposition rate curve shows a continuous increase up to 60 °C, with a constant slope (Fig. 5, blue curve). The enthalpy of sublimation has been obtained in the temperature range from 25 up to 55 °C (Table 3), due to the instability of the sublimation flows at temperatures larger than 60 °C. Moreover, a best agreement is obtained when the difference between  $T_1$  and  $T_2$  is between 15 and 25 °C (within 9 % compared with the literature values, Table 3).

The oxalic acid presents in its molecular structure two water molecules (dihydrate, monocline structure) which are lost at about 100 °C and 1 bar. In this dehydration reaction, its molecular structure changes from monocline to rhombic crystals and becomes anhydrous (Bahl and Bahl, 2010). In our experiment, we considered a monocline dehydrate oxalic acid and the obtained enthalpy results (Table 4) differ to previous works, relative to the anhydrous form (Booth et al., 2009). On the contrary, our results, i.e.  $62.5 \pm 3.5 \text{ kJ mol}^{-1}$  (Table 4), agree within 5.5 % with values, relative to dehydrate oxalic acid (de Wit et al., 1983; Granovskaya, 1948), as it should be. Indeed, as verified by de Wit et al. (1983), a difference for the sublimation enthalpy values between the two anhydrous forms (beta and alpha, obtained by means vacuum sublimation) and the dehydrate state (this work) happens due to the two water molecules' desorption from oxalic acid structure.

### 5.2 Succinic acid (C<sub>4</sub>)

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



**Figure 5.** Blue curve: deposition rate curve of oxalic acid with temperature steps of 5 °C, each lasting 30 min. The deposition linearly increases with temperature, up to 60 °C. Orange curve: deposition rate curve of succinic acid. The deposition rate increases with temperature up to 60 °C, whereas at larger temperatures, it tends to oscillate around an average value of  $0.75 \text{ Hz s}^{-1}$ , due to the steadiness of the sublimation flux.

Succinic acid (with a short carbon chain, C<sub>4</sub>) shows a smaller deposition rate than the oxalic acid, even if it already strongly sublimates at 25 °C. The deposition rate curve shows an increase up to 60 °C and a slope change beyond this temperature. The succinic acid tends to lose one water molecule easily, becoming succinic anhydride. A good temperature range to monitor enthalpy variation is 30–55 °C, far away from the point where succinic acid changes its structure ( $\sim 137 \text{ °C}$ ) (Vanderzee and Westrum, 1970). In this range, the average enthalpy of sublimation measured is  $113.3 \pm 1.3 \text{ kJ mol}^{-1}$ , in agreement within 5 % with the previous works (Chattopadhyay and Ziemann, 2007; Davies and Thomas, 1960; Table 4). Considering the vacuum environment and an upper temperature larger than 55 °C, the retrieved enthalpy may not be reliable for the transformation (initial phase) of succinic acid crystalline form (monocline/triclinic prisms) into cyclic anhydride, a ring structure (pyramidal crystal), losing one water molecule (Orchin et al., 2005; Vanderzee and Westrum, 1970).

### 5.3 Adipic acid (C<sub>6</sub>)

In the case of adipic acid (long carbon chain, C<sub>6</sub>), a total frequency decrease of 28 kHz in the whole temperature range monitored (i.e. from 30 to 75 °C, Fig. 6, black curve) corresponding to 15.5 µg has been observed. A considerable frequency variation is observed above 50 °C, due to the high volatility of the acid at these temperatures. This acid sublimates at low pressure without a decomposition and only at 230–250 °C changes its molecular structure, becoming cyclopentanone plus H<sub>2</sub>O and CO<sub>2</sub>. As a matter of fact, at temperatures lower than 50 °C, the variation of deposition rates

**Table 3.** Enthalpy of sublimation calculated from acid deposition rates measured in our experiment. Considering the succinic acid (bold highlighted values), when  $T_2$  approaches  $T_L$ , the calculated enthalpy deviates from the values in previous works, whereas the temperature oscillations larger than  $\pm 0.5^\circ\text{C}$  produce an error  $\geq 8\text{ kJ mol}^{-1}$  on the enthalpy of sublimation (italic values). Oxalic and succinic acids (weak lattice energies at low temperature) sublimate at smaller temperatures, in the range  $25/30\text{--}55^\circ\text{C}$  where the sublimation process was monitored. Otherwise, adipic and azelaic acid sublimate at larger temperatures. The temperature range is wide enough to calculate the enthalpy of sublimation but should be extended if the intent is to monitor the complete sublimation 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 $\pm$ 0.111	44.969 $\pm$ 0.002	6.56 $\times$ 10 <sup>-12</sup>	3.01 $\times$ 10 <sup>-11</sup>	60.67 $\pm$ 1.31	
	29.843 $\pm$ 0.105	44.969 $\pm$ 0.002	9.15 $\times$ 10 <sup>-12</sup>	3.01 $\times$ 10 <sup>-11</sup>	64.35 $\pm$ 0.64	
	34.964 $\pm$ 0.015	44.969 $\pm$ 0.002	1.52 $\times$ 10 <sup>-11</sup>	3.01 $\times$ 10 <sup>-11</sup>	56.85 $\pm$ 0.93	
	24.772 $\pm$ 0.111	49.962 $\pm$ 0.075	6.56 $\times$ 10 <sup>-12</sup>	4.59 $\times$ 10 <sup>-11</sup>	63.15 $\pm$ 1.34	
	29.843 $\pm$ 0.105	49.962 $\pm$ 0.075	9.15 $\times$ 10 <sup>-12</sup>	4.59 $\times$ 10 <sup>-11</sup>	66.65 $\pm$ 0.84	
	34.964 $\pm$ 0.015	49.962 $\pm$ 0.075	1.52 $\times$ 10 <sup>-11</sup>	4.59 $\times$ 10 <sup>-11</sup>	62.40 $\pm$ 1.07	
	24.772 $\pm$ 0.111	54.952 $\pm$ 0.059	6.56 $\times$ 10 <sup>-12</sup>	6.04 $\times$ 10 <sup>-11</sup>	61.06 $\pm$ 1.07	
	29.843 $\pm$ 0.105	54.952 $\pm$ 0.059	9.15 $\times$ 10 <sup>-12</sup>	6.04 $\times$ 10 <sup>-11</sup>	63.44 $\pm$ 0.60	
	34.964 $\pm$ 0.015	54.952 $\pm$ 0.059	1.52 $\times$ 10 <sup>-11</sup>	6.04 $\times$ 10 <sup>-11</sup>	59.32 $\pm$ 0.73	
	Succinic	34.85 $\pm$ 0.02	45.42 $\pm$ 0.68	1.59 $\times$ 10 <sup>-12</sup>	7.22 $\times$ 10 <sup>-12</sup>	117.93 $\pm$ 4.36
		39.90 $\pm$ 0.04	45.42 $\pm$ 0.68	3.31 $\times$ 10 <sup>-12</sup>	7.22 $\times$ 10 <sup>-12</sup>	<i>118.45 <math>\pm</math> 7.97</i>
		34.85 $\pm$ 0.02	50.22 $\pm$ 0.02	1.59 $\times$ 10 <sup>-12</sup>	1.35 $\times$ 10 <sup>-11</sup>	116.61 $\pm$ 3.32
39.90 $\pm$ 0.04		50.22 $\pm$ 0.02	3.31 $\times$ 10 <sup>-12</sup>	1.35 $\times$ 10 <sup>-11</sup>	116.21 $\pm$ 3.41	
29.98 $\pm$ 0.02		54.64 $\pm$ 0.02	8.01 $\times$ 10 <sup>-13</sup>	2.17 $\times$ 10 <sup>-11</sup>	111.88 $\pm$ 4.15	
34.85 $\pm$ 0.02		54.64 $\pm$ 0.02	1.59 $\times$ 10 <sup>-12</sup>	2.17 $\times$ 10 <sup>-11</sup>	112.17 $\pm$ 2.66	
39.90 $\pm$ 0.04		54.64 $\pm$ 0.02	3.31 $\times$ 10 <sup>-12</sup>	2.17 $\times$ 10 <sup>-11</sup>	110.27 $\pm$ 2.47	
45.42 $\pm$ 0.68		54.64 $\pm$ 0.02	7.22 $\times$ 10 <sup>-12</sup>	2.17 $\times$ 10 <sup>-11</sup>	<b><i>105.14 <math>\pm</math> 11.75</i></b>	
50.22 $\pm$ 0.02		54.64 $\pm$ 0.02	1.35 $\times$ 10 <sup>-12</sup>	2.17 $\times$ 10 <sup>-11</sup>	<b><i>95.73 <math>\pm</math> 3.47</i></b>	
Adipic		39.84 $\pm$ 0.04	59.65 $\pm$ 0.05	1.10 $\times$ 10 <sup>-12</sup>	2.60 $\times$ 10 <sup>-11</sup>	139.58 $\pm$ 3.69
		49.82 $\pm$ 0.04	59.65 $\pm$ 0.05	5.47 $\times$ 10 <sup>-12</sup>	2.60 $\times$ 10 <sup>-11</sup>	142.90 $\pm$ 3.06
		39.84 $\pm$ 0.04	64.93 $\pm$ 0.04	1.10 $\times$ 10 <sup>-12</sup>	5.78 $\times$ 10 <sup>-11</sup>	140.26 $\pm$ 1.22
	49.82 $\pm$ 0.04	64.93 $\pm$ 0.04	5.47 $\times$ 10 <sup>-12</sup>	5.78 $\times$ 10 <sup>-11</sup>	142.95 $\pm$ 1.86	
	55.01 $\pm$ 0.68	64.93 $\pm$ 0.04	1.25 $\times$ 10 <sup>-11</sup>	5.78 $\times$ 10 <sup>-11</sup>	<i>143.54 <math>\pm</math> 13.90</i>	
	59.65 $\pm$ 0.05	64.93 $\pm$ 0.04	2.59 $\times$ 10 <sup>-11</sup>	5.78 $\times$ 10 <sup>-11</sup>	142.99 $\pm$ 4.98	
	39.84 $\pm$ 0.04	70.01 $\pm$ 0.03	1.10 $\times$ 10 <sup>-12</sup>	1.20 $\times$ 10 <sup>-10</sup>	140.15 $\pm$ 2.29	
	49.82 $\pm$ 0.04	70.01 $\pm$ 0.03	5.47 $\times$ 10 <sup>-12</sup>	1.20 $\times$ 10 <sup>-10</sup>	142.14 $\pm$ 1.22	
	55.01 $\pm$ 0.68	70.01 $\pm$ 0.03	1.25 $\times$ 10 <sup>-11</sup>	1.20 $\times$ 10 <sup>-10</sup>	<i>142.24 <math>\pm</math> 9.01</i>	
	59.65 $\pm$ 0.05	70.01 $\pm$ 0.03	2.59 $\times$ 10 <sup>-11</sup>	1.20 $\times$ 10 <sup>-10</sup>	141.34 $\pm$ 2.18	
	Azelaic	34.95 $\pm$ 0.22	50.16 $\pm$ 0.02	6.94 $\times$ 10 <sup>-13</sup>	6.09 $\times$ 10 <sup>-12</sup>	119.59 $\pm$ 6.91
		40.13 $\pm$ 0.26	50.16 $\pm$ 0.02	1.48 $\times$ 10 <sup>-12</sup>	6.09 $\times$ 10 <sup>-12</sup>	120.24 $\pm$ 8.27
45.26 $\pm$ 0.48		50.16 $\pm$ 0.02	2.98 $\times$ 10 <sup>-12</sup>	6.09 $\times$ 10 <sup>-12</sup>	<i>126.42 <math>\pm</math> 20.11</i>	
40.13 $\pm$ 0.26		55.14 $\pm$ 0.27	1.48 $\times$ 10 <sup>-12</sup>	1.29 $\times$ 10 <sup>-11</sup>	124.70 $\pm$ 8.06	
45.26 $\pm$ 0.48		55.14 $\pm$ 0.27	2.98 $\times$ 10 <sup>-12</sup>	1.29 $\times$ 10 <sup>-11</sup>	<i>130.25 <math>\pm</math> 14.03</i>	
50.16 $\pm$ 0.02		55.14 $\pm$ 0.27	6.09 $\times$ 10 <sup>-12</sup>	1.29 $\times$ 10 <sup>-11</sup>	<i>134.14 <math>\pm</math> 11.74</i>	
45.26 $\pm$ 0.48		60.04 $\pm$ 0.02	2.99 $\times$ 10 <sup>-12</sup>	2.48 $\times$ 10 <sup>-11</sup>	127.81 $\pm$ 6.72	
50.16 $\pm$ 0.02		60.04 $\pm$ 0.02	6.09 $\times$ 10 <sup>-12</sup>	2.48 $\times$ 10 <sup>-11</sup>	128.53 $\pm$ 1.86	
55.14 $\pm$ 0.27		60.04 $\pm$ 0.02	1.29 $\times$ 10 <sup>-11</sup>	2.48 $\times$ 10 <sup>-11</sup>	<i>122.65 <math>\pm</math> 10.71</i>	



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

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

of adipic acids is only 1.5 and 27 % of that measured for oxalic and succinic acid, respectively; this is due to the better stability of its carbon chain at these temperatures. The enthalpy of sublimation of adipic acid has been obtained in the temperature range from 40 to 70  $^{\circ}\text{C}$ . The data acquired at 75  $^{\circ}\text{C}$  have been excluded from the analysis due to the high temperature oscillations which produce unstable deposition rates. The deposition rates at 30 and 35  $^{\circ}\text{C}$  have been also excluded because of the low flows of molecules. At these temperatures, the adipic acid flows are 2 orders of magnitude lower than the oxalic and succinic acids.

#### 5.4 Azelaic acid ( $\text{C}_9$ )

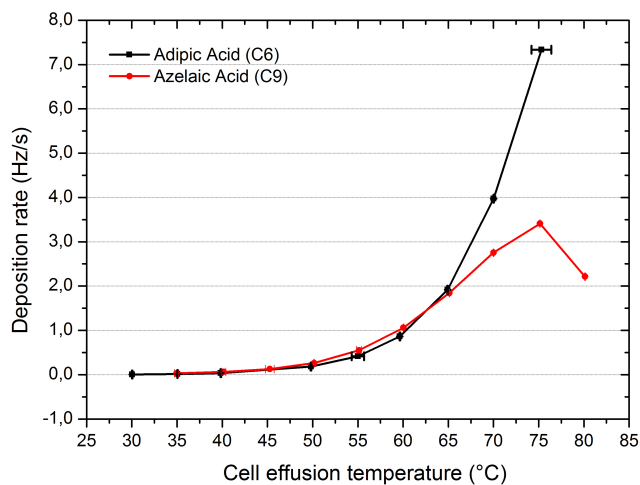
Azelaic acid shows a larger frequency variation than succinic and oxalic acid, with a total frequency decrease in the whole temperature range monitored (from 35 to 80  $^{\circ}\text{C}$ , Fig. 6, red curve) of 21 kHz corresponding to 11.6  $\mu\text{g}$ . Azelaic acid presents a very slow sublimation up to 35  $^{\circ}\text{C}$  and reaches the maximum deposition rate at 75  $^{\circ}\text{C}$  (whereas at 80  $^{\circ}\text{C}$ , the deposition rate begins to decrease). The enthalpy of sublimation has been obtained in the temperature range from 35 to 60  $^{\circ}\text{C}$  (Table 3). The enthalpies of sublimation at tempera-

tures higher than 60  $^{\circ}\text{C}$  have not been considered reliable due to a decrease of the deposition rates.

This compound starts to decay at 360  $^{\circ}\text{C}$  (at atmospheric pressure) but in our experiment, the deposition curve shows a slope variation at 80  $^{\circ}\text{C}$  and a instability of the deposition flow from 65 to 80  $^{\circ}\text{C}$  (not used for the analysis). The reasons for that should be studied in more detail and the temperature range should be increased in order to monitor enthalpy variation at larger temperatures. Probably, monitoring a wider temperature range for the two other acids (oxalic and adipic) we could observe the same trend.

#### 5.5 Discussion and comparison of obtained results

As listed in Table 3, when the temperature oscillations are within  $\pm 0.5$   $^{\circ}\text{C}$ , the errors do not exceed 5  $\text{kJ mol}^{-1}$ , whereas when the temperatures oscillations are larger than  $\pm 0.5$   $^{\circ}\text{C}$ , the errors on the enthalpy of sublimation are larger than 8  $\text{kJ mol}^{-1}$  (adipic and succinic acids). In Table 4, the temperature range used is listed, as well as enthalpy results obtained in this study. A high accuracy has been obtained for succinic, adipic, and azelaic acid, i.e. within 1 % and within 5 % for oxalic acid. Thus, in order to demonstrate the high



**Figure 6.** Black curve: deposition rate curve of adipic acid shows an increase up to 75 °C without a decrease at higher temperature (an oscillation around an average value would be observed at even larger temperatures). Red curve: deposition rate curve of azelaic acid: molecules flux is small at low temperature as for the adipic acid case and contrarily to oxalic and succinic acids that show high sublimation rates at these low temperature, i.e. 25–30 °C (weak intermolecular forces).

quality of our method and the validity of our results, the enthalpies of sublimation have been compared with the results obtained by previous works. In the comparison, we will take into account the different boundary conditions (initial temperatures and working pressures) of the different procedures (Table 4): TDMA (Bilde et al., 2003), Knudsen mass loss (Ribeiro da Silva et al., 1999), KEMS (Booth et al., 2009), TDPBMS (Chattopadhyay and Ziemann, 2007), the effusion method, EM (Davies and Thomas, 1960; Granovskaya, 1948), and E-1559 Method B (Albyn, 2001).

The values of enthalpy of sublimation obtained in our experiments for succinic and adipic acids are within 5 % of the enthalpy values reported by Chattopadhyay and Ziemann (2007), who present a temperature programmed thermal desorption method (TDPBMS) where the particles were collected at  $-50^{\circ}\text{C}$  in a vacuum chamber. Successively, by means of a heating process ( $2^{\circ}\text{C min}^{-1}$ ), the vapour pressure and evaporation rates of submicron particles were measured. This method use a modified Langmuir equation and the Clausius–Clapeyron equation, similar to our theoretical approach.

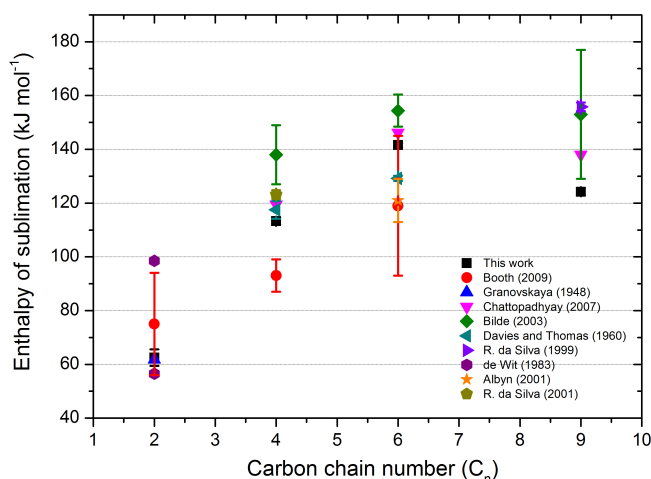
Our results are quite low compared to those measured by Bilde et al. (2003) (within 9 % for the adipic acid), who demonstrate the capability of the tandem differential mobility analyser (TDMA) technique to measure the vapour pressures of submicron aerosol particles at solid-state structure. The results of evaporation rates were measured over the temperature range 17–41 °C. In the TDMA technique, the major source of error was based on the sensitivity analysis

(a conservative uncertainty and systematic errors were considered on vapour pressures). A different method was used by Booth et al. (2009), who directly measured the steady-state vapour pressure using the Knudsen effusion mass spectrometry (KEMS) method with a solid sample. In Booth et al. (2009), the working pressure and heating method of the sample was similar to ours: there was a temperature step of 5 °C considering 10 min of stabilization time. The enthalpy obtained for adipic and succinic acids is smaller than that measured in this work and is larger than that for the oxalic acid. However, it should be noted that their measurements are affected by a large uncertainty; in particular, the errors obtained for oxalic acid ( $19\text{ kJ mol}^{-1}$ ) are the result of the variation in the three calibration compounds used for that determination, whereas the high error on the adipic acid ( $26\text{ kJ mol}^{-1}$ ) is the result of low pressures, resulting in decreased signal-to-noise ratio. Regarding the oxalic acid, as discussed above, it is highlighted that these authors measured the value of the  $\alpha$ -orthorhombic anhydrous form and a difference from our results is expected. This difference is evident in de Wit et al. (1983) results, where the analysis of the hydrate and anhydrous form (prepared by a prolonged evacuation of the hydrate substance and vacuum sublimation) of the oxalic acid has been performed. The enthalpy of sublimation of oxalic acid, as listed in Table 4, agrees within 5.5 % of the average value obtained from the dehydrated results (de Wit et al., 1983; Granovskaya, 1948). Instead, Ribeiro da Silva et al. (1999, 2001) present Knudsen mass-loss effusion, a method similar to Booth et al. (2009) in order to study the vapour pressures of crystalline dicarboxylic acids at much higher temperatures. The vapour pressures were calculated with a Langmuir equation, whereas the enthalpy of sublimation at the mean temperature was derived by the Clausius–Clapeyron equation. Ribeiro da Silva et al. (1999) results show larger values than ours (Table 4):  $32\text{ kJ mol}^{-1}$  for azelaic acid (Ribeiro da Silva et al., 1999) and  $10\text{ kJ mol}^{-1}$  for succinic acid (Ribeiro da Silva et al., 2001). As stated by Bilde et al. (2015) the enthalpy of sublimation values between the different experimental methods can differ by tens of kilojoules per mole. The results of Davies and Thomas (1960), who measured heat and entropy of sublimation by means of the effusion method at 1.013 bar pressure, are in agreement with our values (within 9.5 % for adipic acid and within 4 % for succinic acid). Albyn (2001) used two different 15 MHz microbalances cooled at  $-42^{\circ}\text{C}$  in a vacuum chamber to measure the deposition rates of adipic acid from 25 to 60 °C. The enthalpy of sublimation measured by Albyn is  $121 \pm 8\text{ kJ mol}^{-1}$  and shows a difference of  $20\text{ kJ mol}^{-1}$  compared to our result (Table 4). This is probably due to the different set-up and measurement procedure, i.e. the microbalance's temperature of  $-42^{\circ}\text{C}$  instead of  $-72^{\circ}\text{C}$  (this work) and the distance between the sensing crystal and the sample of 20 cm instead of 2 cm (this work). The constant error of  $8\text{ kJ mol}^{-1}$ , obtained with a temperature stability of  $\pm 0.5^{\circ}\text{C}$  on the effusion cell (Albyn, 2001), could

be due to the re-evaporation of a minor portion of the deposited material. In this work, when the temperature stability is within  $\pm 0.5$  °C, the error does not exceed  $5 \text{ kJ mol}^{-1}$  (Table 3, oxalic, succinic, and adipic acid). This improvement in the accuracy could be due to our increased gas flow of adipic molecules.

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

In our procedure the efficiency of the deposition process was improved when the difference between PCM surface's and effusion cell's temperature increased, and molecule flux was focused directly on the PCM crystal (Dirri et al., 2012). In this way, we were able to discern the deposition rate at different temperatures. Data analysis has been performed excluding the set point with high temperature oscillations (adipic and succinic acids) which affects the deposition rates trend and the low flows of molecules at lower temperatures (e.g. 30–35 °C, adipic acid case). As listed in Table 3, a temperature stability of  $\pm 0.5$  °C on the effusion cell causes errors on the enthalpies of sublimation lower than 4 % for oxalic, adipic, and succinic acids (a better accuracy compared with Albyn, 2001), whereas when the temperature stability is larger than  $\pm 0.5$  °C, the corresponding errors are larger than 10 %. Thus, for each compound, we obtained several measurements of the enthalpy of sublimation (individually having a worse accuracy, Table 3) that allows the weight average value to be retrieved for the enthalpy of sublimation where the weight function,  $\omega_i = (1/\sigma_i^2)$ , has been used. The weight average values show a better accuracy compared with the single enthalpy measurement, i.e. an accuracy of within 1 % for succinic, adipic, and azelaic acids and within 5 % for oxalic acid (Table 4). In Fig. 7 the enthalpy of sublimation of four dicarboxylic acids analysed in this work is compared with previous studies. The behaviours of the enthalpies of sublimation are very similar and increase as the carbon chain number of the substance increases. Indeed, the substances with a short carbon chain (oxalic and succinic acid) show a lower enthalpy of sublimation compared with the substances with a higher carbon chain (adipic and azelaic acids), which require a higher temperature to reach complete sublimation (larger than 60 °C). Furthermore, as reported by other studies (Booth et al., 2009; Bilde et al., 2003, 2015), the dicarboxylic acid, with an odd number of carbon atoms, has a lower sublimation enthalpy compared with dicarboxylic acids that have an even number of atoms. This behaviour is based principally on the solid-state crystalline structure of the acids. In this work, the enthalpy alternation between the odd and even carbon chain dicarboxylic acid ( $> C_5$ ) has been confirmed for two compounds: the enthalpy of sublimation of adipic acid ( $C_6$ ) is higher than the sublimation enthalpy of azelaic acid ( $C_9$ ) of  $17 \text{ kJ mol}^{-1}$  (Fig. 7). The alternation in the enthalpy



**Figure 7.** Comparison between the enthalpies of sublimation obtained with various methods and different compounds ( $C_2$ , oxalic acid;  $C_4$ , succinic acid;  $C_6$ , adipic acid and  $C_9$ , azelaic acid, weight average values). Different experiment conditions (temperature monitored and work pressure, Table 4) lead to diverging results: Booth et al. (2009), Chattopadhyay and Ziemann (2007), and Ribeiro da Silva et al. (1999) in vacuum environments, and Bilde et al. (2003) and Davies and Thomas (1960) at atmospheric pressure. For oxalic acid, the results for anhydrous and dehydrate forms are plotted (de Wit et al., 1983; Booth et al., 2009).

of sublimation has also been confirmed by the results of Bilde et al. (2003), which included the adipic and azelaic acids. As explained by Booth et al. (2009), the behaviour of the enthalpy alternation is not always clear and it is not possible to say firmly that this effect was observed in their work.

## 6 Conclusions and future perspective

A new experimental set-up has been developed in order to characterize the  $C_2$ – $C_9$  dicarboxylic acid (i.e. oxalic, succinic, adipic, and azelaic acid) compounds present in atmospheric aerosols, over the temperature range of 25–80 °C. The capability of our instrumental set-up to monitor the sublimation process in vacuum condition ( $10^{-6}$  mbar) has been tested successfully. The measurement procedure is relatively simple and requires about 6 h for a single experiment (cooling the PCM, heating the sample, and monitoring the process continuously). Then, the deposition rates of dicarboxylic acids were measured and their sublimation enthalpies were obtained in the temperature range from 25 to 70 °C. The results were compared with other techniques (KEMS, TDMA, EM, TDPBMS, and E-1559 Method B).

This experimental set-up, based on piezoelectric crystal microbalance technology, provides many advantages over other methods: it is lightweight, with a better accuracy and requires a smaller amount of materials for the analysis.

The values of the enthalpy of sublimation obtained in this study (Table 4) for succinic and adipic acid are in agreement within 5 % of the average enthalpy obtained by previous works (Chattopadhyay and Ziemann, 2007; Davies and Thomas 1960; Bilde et al., 2003; Ribeiro da Silva et al., 2001; Albyn 2001; Booth et al., 2009). The results for the oxalic acid are in good agreement (within 6 %) with the enthalpy average value from Granovskaya (1948) and de Wit et al. (1983), whereas the enthalpy of sublimation of azelaic acid is in agreement within 11 % of the results of Bilde et al. (2003).

In addition, our results show a good accuracy if we consider the values obtained with an accurate temperature control (within  $\pm 0.5$  °C); the accuracy of the enthalpy of sublimation is within 1 % for succinic, adipic, and azelaic acids and within 5 % for oxalic acid. Contrarily, the accuracy worsens (and results are less reliable) when  $T_1$  approaches  $T_2$  (azelaic acid) or at higher temperatures (larger than 60 °C) where the temperature oscillations cause the instability of the acid's flow (e.g. adipic and succinic acids).

Thus, by means of our measurement procedure and comparing the results with previous works (Bilde et al., 2003; Davies and Thomas 1960; Ribeiro da Silva et al., 1999) we have been able to obtain a best accuracy of the enthalpy of sublimation results, as listed in Table 4. In particular, the accuracy may be refined by improving the temperature control system, in order to extend the temperature range monitored and to obtain a better accuracy at each set point (lower than  $\pm 0.5$  °C). Working at lower temperatures would be useful, especially for oxalic and azelaic acids, and this would allow solid  $\rightarrow$  gas phase to be monitored and more information about other phase transitions (gas  $\leftrightarrow$  liquid, solid  $\leftrightarrow$  liquid) to be obtained. However, the extension at higher temperatures, which can be simply obtained by changing the resistive element, would also make it possible to study less volatile compounds, such as some carboxylic acids or polycyclic aromatic hydrocarbons (PAH).

*Acknowledgements.* The authors thank Angelo Boccacini (IAPS-INAF) and David Biondi (IAPS-INAF) for their technical support, Yeghis Keheyan (Department of Chemistry, la Sapienza) and the Institute of Translational Pharmacology (ITF-CNR, Italy) for providing the substances used in the experiments. We also thank the BioAge S.r.l. for the concession to use the Eureka instrument and software for the frequencies acquisition data.

Edited by: H. Herrmann

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