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Measuring enthalpy of sublimation of volatiles by means of micro-thermogravimetry for the study of water and organic in planetary environments

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Abstract. In this work, we present a new experimental set up to infer the enthalpy of sublimation for a known specie of dicarboxylic acid, i.e. adipic acid. This type of acids, with various concentrations are present in different environments (e.g. marine, rural, urban). The experiment is performed in the framework of the VISTA (Volatile In Situ Thermogravimetry Analyser) project, an instrument currently under study for the ESA Cosmic Vision proposed mission MarcoPolo-R. The enthalpy of sublimation of adipic acid was measured by means of micro-thermogravimetric analysis (μ-TGA), a widely used technique to investigate condensation/sublimation and absorption/desorption processes of volatile compounds. The measurements were performed with a 10 MHz temperature controlled piezoelectric crystal microbalance (PCM), placed in a vacuum chamber (10^{-6} mbar). The obtained enthalpy of sublimation is (123 ± 16) $kJ \times mol^{-1}$, a value in good agreement with literature within 10%. This result (connected to the deposition rate curve, from 30° to 75°C), demonstrates the capability of our device to perform this kind of measurements.

Key words. Enthalpy of sublimation – Micro-thermogravimetric analysis – Adipic acid – PCM

1. Introduction

Micro-thermogravimetric analysis (μ-TGA) is a technique used to study volatile compounds in any environment. The core of the -TGA is a Piezoelectric Crystal Microbalance (PCM), which converts mass in frequency variations, as stated by the Sauerbrey equation (Sauerbrey 1959). The PCM temperature can be increased by means of an appropriate heater, in order to allow the most volatile component of the analysed sample to desorbs. The abundance of the volatile component will be given by the mass variation during the desorption process (Fig. 1) , whereas its composition can be inferred by the sublimation temperature (Olin & Sem 1971), (Zinzi et al. 2011). Micro-thermogravimetric analysis can be applied to planetary in-situ missions in order to detect the possible presence of water and organics, that

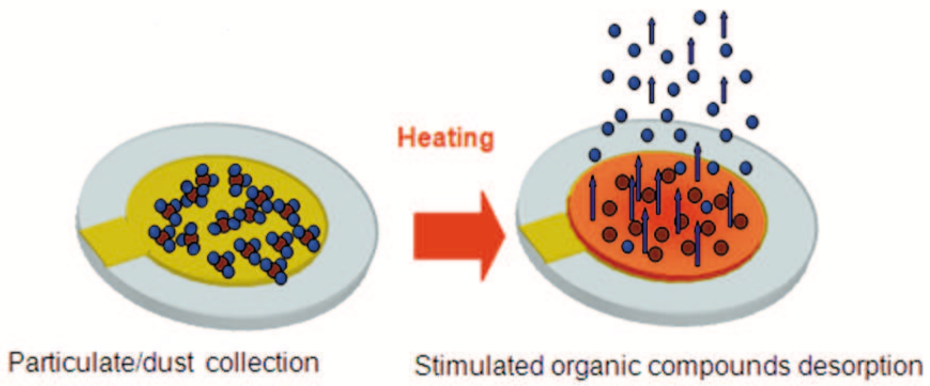

Fig. 1. TGA: volatiles desorption

can be linked to the habitability of the planetary body. However, identification of the desorbed compound can be a tricky task, because different volatile species can have similar desorption temperatures. Therefore, it is necessary to characterise the compound by measuring other thermal properties, such as the enthalpy of sublimation/evaporation ΔH, which is the amount of energy absorbed or released during a chemical-physical process. In the section 2 we described the VISTA project with the scientific objectives whereas the theory and experimental set-up are explained in detail in the section 3 and 4. The results and discussion about the preliminary tests are reported in the section 5 and in the section 6 we give some conclusions and future work.

2. VISTA project

VISTA (In Situ Volatile Thermogravimeter Analyser) is a micro-thermogravimeter developed by a consortium of Italian institutes, which is under study for Phase A of the MarcoPolo-R (M3-ESA Cosmic Vision) mission (Barucci et al. 2011), (Palomba et al. 2013) and was studied for the Marco Polo and Jupiter Icy moon Explorer (respectively M2 and L2 ESA Cosmic Vision) missions, too. The MarcoPoloR mission proposes the study of a primitive asteroid with the bulk sample return to Earth. Laboratory tests will be conducted on the returned samples in order to study the origin of planetary materials, to identify and analyze the organic and volatile substances in a primitive asteroid as well as to understand the geomorphology, the dynamics and the evolution of a binary NEA. The specific applications of the VISTA instrument depend on the planetary environment under study. In the Marco PoloR scenario, VISTA is able to measure water and organic content in the asteroid regolith and the possible cometary-l ike activity of the asteroid (detecting emitted gas and dust). Whereas the first goal can be reached by heating the VISTA PCM, to accomplish the second purpose the PCM should be maintained at low temperature to enable passive collection of dust and gas molecules. The main advantages of the VISTA instrument are its low mass (25 g, a sensor), low volume (about 10 cm^3) and low power required (170 mW to obtain $\Delta T \approx 60K$ in vacuum), as well as the small amount of material required for the analysis (less than 1 mg).

3. Theory

The enthalpy variation, ΔH, or heat of reaction, is the amount of energy absorbed or released by a thermodynamic reaction and is given by the difference between energy of the reactants and energy of the products. In a physical-chemical process, where either reactant or product is in gaseous phase, it is possible to obtain the enthalpy of the process from the Clausius-Clapeyron equation, i.e.

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2} \tag{1}$$

where P is the vapor pressure. If the reaction takes place in an environment at constant pressure, it is possible to use the Van't Hoff relation (or Van't Hoff isobar) that expresses the linear variation of the equilibrium constant (or rate constant k), which indicates the ratio between the products and reactants concentrations of the reaction, as a temperature function:

$$\frac{dlnk}{dT} = \frac{P\Delta H}{RT^2} \tag{2}$$

where R is the gas constant. In order to know the enthalpy variation, the Van't Hoff equation (Benson 1968) is generally applied considering two different temperatures T_1 and T_2 and the respective rate constant k_1 and k_2:

$$\ln(\frac{k_2}{k_1}) = \frac{\Delta H}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{3}$$

Furthermore we can derive the ΔH of the reaction (melting, evaporation, sublimation, condensation), if we know rate constants at two definite temperatures, at least.

4. Experimental activity

The PCM and the dicarboxylic acid sample are positioned in a teflon cylindrical case (in order to limit the thermal dispersion), which is connected directly to a copper support, in thermal contact with the coil of liquid nitrogen that cools the PCM (Fig. 2). The whole setup is placed inside a vacuum chamber (internal pressure of 10^{-6} mbar). A mass of adipic acid (i.e. 10 ± 2 mg) is placed into a becker connected to a resistance, which heats the sample for Joule effect up to its sublimation. On the contrary, the PCM is cooled down to -74°C by a cold finger, in order to allow the deposition of the gas molecules produced by the sublimation process (Fig. 3). By extrapolating ΔH from the Eq. 3, we obtain:

$$\Delta H = R(\frac{T_2 T_1}{T_2 - T_1})ln(\frac{k_2}{k_1}) \tag{4}$$

By measuring the deposition rates of acid on the PCM k_1 and k_2 at two different sample temperatures T_1 and T_2 (not close to the sublimation point), it would be possible to infer the enthalpy of sublimation ΔH of the analysed sample, whose values are reported in the literature (Albyn 2004), (Albyn 2001). We started from an acid temperature of 30°C, and then we applied a stepwise temperature increase (ΔT=5°C). The system is maintained at each temperature for about 30 minutes, in order to allow the stabilization of the deposition rate.

5. Results and discussion

5.1. Deposition rate curve

A substantial decrease in the PCM frequency has been observed at increasing temperature, due to larger deposition of acid molecules. The difference between the starting frequency at that measured at 75°C is about 3 KHz. The behavior of the deposition rate (Hz/sec) with temperature confirm a linear increasing growth (from 45°C to 75°C) in time (Fig. 4). At low temperatures (i.e. 30°-35°C) we are quite far from the sublimation point, hence deposition rate are too small to give a retrieval of enthalpy of sublimation with good accuracy. Otherwise, the deposition rate reaches its peak near the sublimation point, that is at 80°C. However, when we approach the sublimation point, the frequency rate starts to decrease, due to the lack of the acid solid phase.

5.2. Enthalpy of sublimation

The obtained results, compared with the value predicted in literature can be seen in Table 1. For what exposed in the sub-section 5.1, the T_2 temperature should be chosen neither too

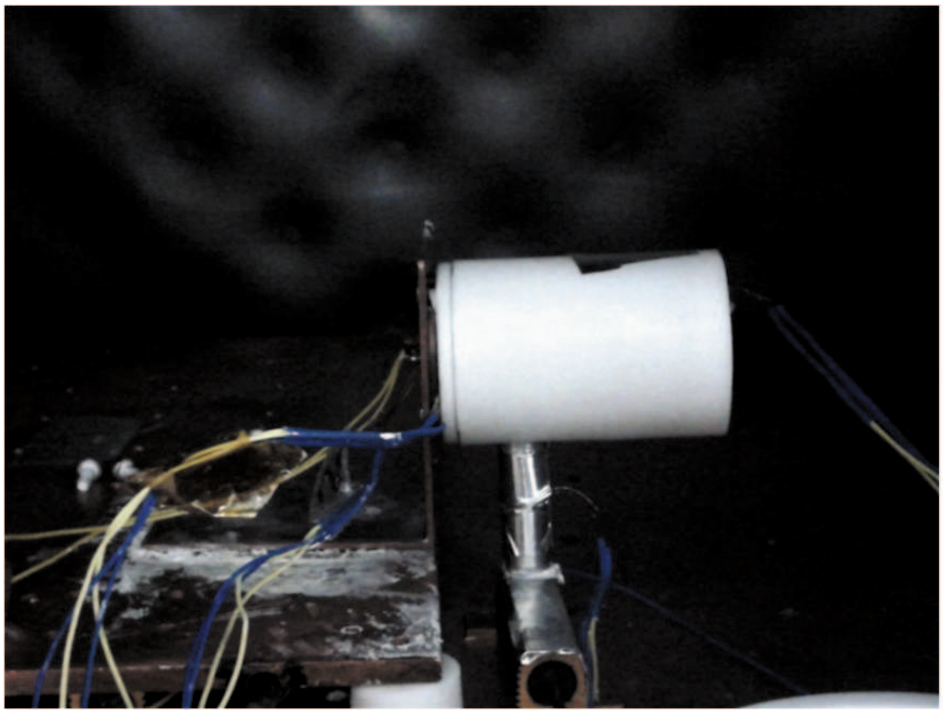

Fig. 2. Cylindrical case and becker with adipic acid.

Table 1. Enthalpy of sublimation calculated from adipic acid deposition measurements

T_1 (°C)	T_2 (°C)	k_1 $(moles/cm^2 \times s)$	k_2 $(moles/cm^2 \times s)$	ΔH $(kJ \times mol^{-1})$	σ_H $(kJ \times mol^{-1})$	Δ (%)
45	65	2.69×10^{-13}	9.95×10^{-12}	123.09	15.94	94
50	65	1.46×10^{-12}	9.95×10^{-12}	116.19	6.33	89
55	65	2.98×10^{-12}	9.95×10^{-12}	108.11	9.73	83
60	65	5.31×10^{-12}	9.95×10^{-12}	112.39	16.06	86

close or too far from the sublimation point. We thought that 65°C is a good compromise between the two requirements. The deposition rates (k_1 and k_2) are measured in hertz per second (Hz/s) and, converted in $mol/cm^2 \times s$, by taking into account the PCM sensitivity and the acid molecular weight. The enthalpy of sublimation and its error are measured in kJ/mol while Δ variable is the percentage of calculated enthalpy compared to literature value (131 kJ/mol (Albyn 2004), Albyn 2001). The exact agreement between the calculated enthalpy and reference value may not always be achieved and a decision on the accuracy for the measurements must be made. A range for acceptable error in the calculated enthalpy of sublimation could be e.g. ±15%. Our results are in agreement with the literature values within this threshold as long as T_1 and T_2 are neither too close neither too far from the

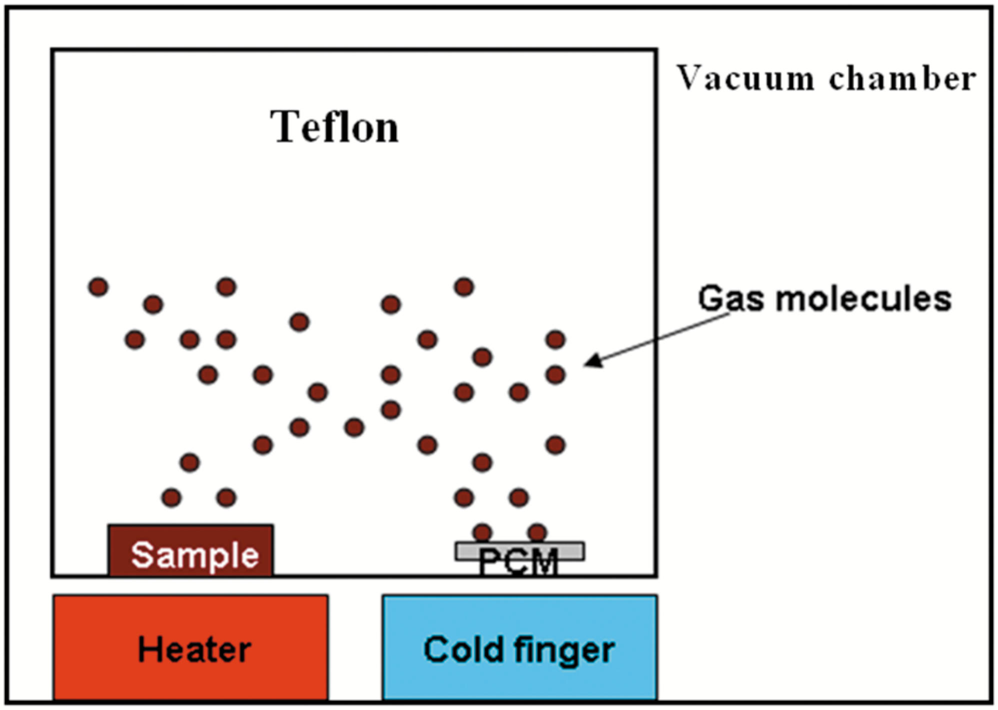

Fig. 3. The whole set-up, composed by PCM and the sample located in a teflon cylindrical case, is placed in a vacuum chamber. The sample is heated, in order to favour sublimation and deposition of acid molecules on the PCM, cooled by liquid nitrogen.

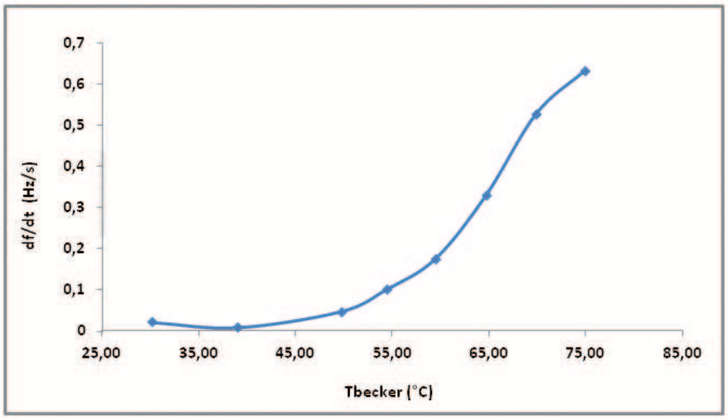

Fig. 4. Deposition rate of the adipic acid on the PCM as function of acid temperature.

sublimation: when this occurs, the errors on the enthalpy of sublimation are higher than 10 kJ/mol.

6. Conclusion

As we seen in Table 1, the results of the calculated enthalpies are in agreement within 15% with the literature value. However, an improvement of the measurement set-up is in progress in order to improve the accuracy of this result. For example, by increasing the time for each temperature step and by diminishing the distance sample-PCM, it is possible to increase the deposition rate of adipic acid molecules, increasing the signal-to-noise ratio and hence reducing the uncertainty on the measurement. However, the exposed results already show the good performance of PCM as mass sensor to measure the enthalpy of sublimation of a known species at different temperatures as well as the full capability of our device (and of the VISTA breadboard) to perform these kind of measurements (μ-TGA). In the future we plan to apply this technique to other acids and volatiles compounds of planetary interest.

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