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Measuring enthalpy of sublimation of volatiles by means of micro-thermogravimetry: the case of Dicarboxylic acids

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Abstract

VISTA (Volatile In Situ Thermogravimetry Analyser) is a thermogravimeter currently under study for the proposed mission MarcoPolo-R [1,2]. In the framework of this project, we developed a set-up to measure the enthalpy of sublimation ΔH of three dicarboxylic acids, i.e. adipic, succinic and oxalic. The obtained results are in good agreement with literature, and this demonstrates the capability of our device to perform this kind of measurements.

1. Introduction

Dicarboxylic acids are present in planetary atmospheric aerosols, as well as in different environments (marine, rural, urban), at varying concentrations. They originate from photo-oxidation of biogenic and anthropogenic compounds but details about their formation are still debated [3].

The VISTA instrument, , selected for the M3 Marco Polo-R mission currently under study, is based on μ-Thermogravimetric Analysis (TGA), a widely used to investigate deposition/sublimation and absorption/desorption processes of volatile compounds in different environments. The core of the μ-TGA is a Piezoelectric Crystal Microbalance (PCM), which converts mass in frequency variations, as stated by the Sauerbrey equation [4]:

$$\Delta f \propto \frac{f_0^2}{A}\Delta m$$

Once the material is deposited onto the sensor it is possible to measure the amount of weight change as a function of increasing temperature due to the release of more volatile species or to decomposition of organic material. This measurement gives the volatile content inside the analyzed sample, while its composition can be inferred by desorption temperature. The enthalpy of sublimation and the temperature of desorption/adsorption processes are two fundamentals parameters to identify a compound.

In this work, we show the development of a measurement set up equipped with a VISTA breadboard to infer the enthalpy of sublimation of various compounds. In particular, enthalpy was measured for three dicarboxylic acids, i.e. adipic, succinic and oxalic.

2. Experimental set-up & measurements

The PCM and the acid sample are positioned in a teflon cylindrical case, which is connected directly to a copper support, in thermal contact with the coil of liquid nitrogen (Fig.1). The whole setup is placed inside a vacuum chamber.

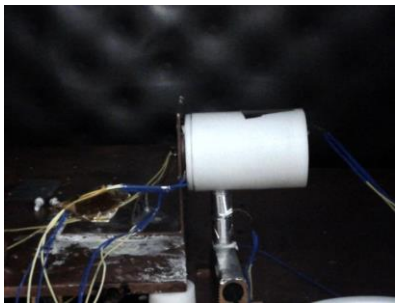

Figure 1. Cylindrical case and becker containing the dicarboxylic acid.

Then, the sample is heated to favor its sublimation, while the PCM is cooled down to -72°C by a cold finger, in order to allow the deposition of the gas

molecules produced by the sublimation process (Fig.2). According to the Van't Hoff relation [5] (where R is the gas constant)

$$\Delta H = R(\frac{T_2 T_1}{T_2 - T_1}) \ln(\frac{R_2}{R_1})$$

By measuring the rates of deposition on the PCM: R_1 and R_2 at two different sample temperatures T_1 and T_2, it would be possible to infer the enthalpy of sublimation ΔH of the analysed sample, whose values are reported in the literature. Temperature steps of 5°C are applied and measurements are taken for 30 minutes at each temperature.

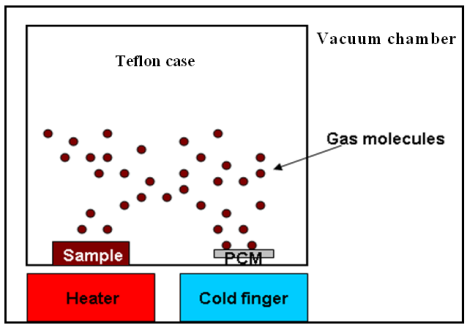

Figure 2. PCM and sample in the vacuum chamber.

Preliminary tests have been performed in order to study the stability of the PCM frequency and its performance with the pressure and the temperature [1]. In this calibration phase it has been verified that the PCM frequency goes as the cube of the temperature and linearly with pressure.
The frequency tends to stabilize if the PCM temperature and the system pressure are constant.

3. Results

A substantial decrease of the PCM frequency has been observed at increasing temperature, due to larger deposition of acid molecules.
The trend of the deposition rate with temperature confirm a linear increasing in time (Fig. 3)

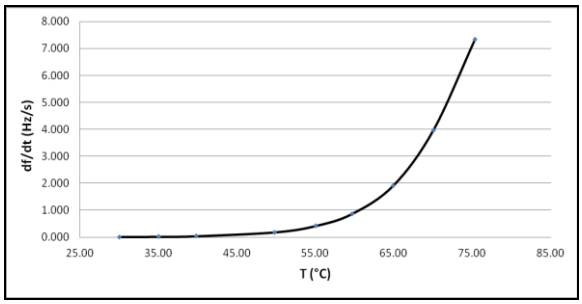

Fig.3. Deposition rate of the adipic acid

The obtained results, compared with the value predicted in literature [6-9] at 298.15 K can be seen in Table 1:

Acid	*ΔHμ-TGA (kJ/mol)*	*ΔHref (kJ/mol)*
Adipic	133,34 ± 10,94	132,55 ± 1,66
Succinic	115,31 ± 7,66	114,37 ± 2,38
Oxalic	72,71 ± 0,86	93,70 ± 1,30

Table 1. Obtained enthalpies of sublimation, compared with literature value.

The agreement is very good for the adipic and the succinic acid. On the contrary, for the oxalic acid, we found slight disagreement. This is probably due to a PCM frequency instability observed during the experiment. For this reason, a new experiment is planned for this acid.
Our results demonstrated the full capability of the thermogravimetry (and of the VISTA breadboard) to perform enthalpy of sublimation of various acids. In the future we plan to apply this technique to other acids and volatiles compounds of planetary interest.

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