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Micro-thermogravimetry for planetary in-situ measurements

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Abstract

The thermogravimetry technique has a wide set of applications, from Space mission to chemical and biological fields.
In the present work, we verified the capability of a micro-thermogravimeter to reach high temperatures in order to measure organics and water desorption in planetary regolith analogs. In addition, we applied thermogravimetry to monitor sublimation, and to measure the corresponding enthalpy of sublimation, of dicarboxylic acids, present in Earth's atmosphere and also used in industrial field.

1. Introduction

Thermogravimetric analysis (TGA) is a technique used to monitor processes involving volatile compounds, such as deposition/sublimation and absorption/desorption. For example, sublimation process are monitored for pharmaceutical and industrial applications, in order to determine the fate of various material in atmospheric environment [1,2].
In planetary missions, μ–TGA would be useful to measure water and organics content in the asteroid regolith/dust [3], as well as to monitor outgassing contamination [4].
The thermogravimeter core is a Piezoelectric Crystal Microbalance, whose oscillation frequency linearly depends on the mass deposited on it, according to the Sauerbrey equation [5]:

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

The PCM temperature can be increased by, an appropriate heater, in order to allow sublimation/desorption of the most volatile component of the analyzed sample. Mass and composition of the volatile can be inferred by the frequency change and by desorption temperature, respectively. Moreover, the volatile compounds can be characterized by a physical-chemical parameter which can be obtained by thermogravimetric analysis, i.e. the enthalpy of sublimation/evaporation [6].

2. Planetary applications of TGA: the VISTA project

The work here presented has been performed in the framework of the VISTA (Volatile In Situ Thermogravimetry Analyser) project.
VISTA is a micro-thermogravimeter, equipped with built-in heater and built-in temperature sensor on a $GaPO_4$ crystal surface. It has been selected in the payload of the ESA MarcoPoloR mission study [7], but also other applications have been studied, e.g. on Europa and Ganimede [8] and on Mars [9].
Depending on the planetary environment, the thermogravimeter can reach the following goals: measurement of volatile amounts, e.g. water, organics, in planetary/asteroidal regolith and detection of cometary-like activity of asteroids (MarcoPoloR mission); measurement of dust and ice settling rate, water content in dust and humidity (Mars); characterization of organic species by measuring its enthalpy of sublimation, in order to monitor the evolution of atmospheric aerosol (Earth's environment).
In the analysis of a regolith sample (MarcoPolo-R), temperatures of 50-160 °C should be reached to allow the desorption of *physically adsorbed water* whereas, at temperatures of 250-300°C, the *organic* decomposition and *surface-bound water* desorption are expected [3].
The VISTA instrument is able to perform this analysis with a very low power budget (as well as to have very small mass, i.e. 25 grams, and volume, i.e. <10cm^3, requirements) As a matter of fact, only 0.29W are required to obtain a ΔT_v~185°C in vacuum and ΔT_a~100°C in air, whereas to obtain a ΔT=250°C in vacuum only 0.43W are needed.

3. Enthalpy of sublimation measurement

The enthalpy of sublimation has been measured for five dicarboxylic acids, i.e. Adipic, Succinic, Oxalic, Azelaic and Suberic acid. These substances are present in Earth's atmospheric aerosols at varying concentrations and are used in industrial fields as precursor of final product of reaction.

In our experiment, PCM and effusion cell (with acid sample) are positioned in a teflon cylindrical case: PCM is cooled down to -72°C by means a cold finger whereas the sample is heated up to its sublimation (Fig. 1).

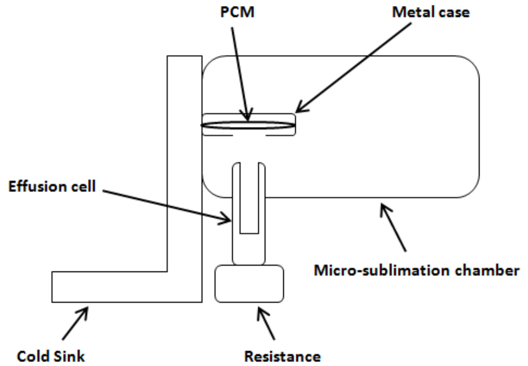

Figure 1: Schematic representation of the set-up.

The whole set-up is placed in vacuum chamber (10^{-6} mbar) in order to facilitate the sublimation process. By heating the sample (from 25 to 80°C), it was possible to measure the condensation rates, k_1 and k_2, at two different temperatures, T_1 and T_2, and to calculate enthalpy of sublimation ΔH, with Van't Hoff relation [10]:

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

being R, the gas constant. A decrease of PCM frequency was observed at increasing temperature due to the molecules condensation on the crystal surface. A comparison between the condensation rate curves of acids are shown in Figure 2.

Our results are in agreement with literature [11,12,13] within 15% for Succinic, Adipic, Suberic and Azelaic acid whereas, Oxalic acid results shows a slight disagreement (Tab. 1) due to high volatility of this substance at low pressure. Therefore, the temperatures interval monitored should be extended at T<25°C.

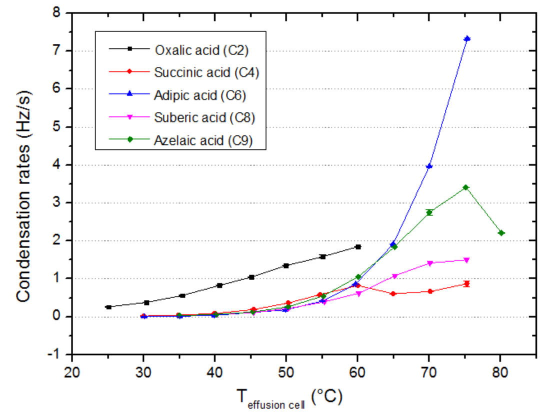

Figure 2: Condensation rate vs. sample temperature of five dicarboxylic acids.

Acid sample	*ΔH*$_{sub}$ *(kJ/mol) This work*	*ΔH*$_{sub}$ *(kJ/mol) Reference*
Oxalic	53.1±0.3	75.0±19.0
Succinic	110.2±1.5	119.5
Adipic	139.2±0.4	146.2
Azelaic	123.3±1.2	138
Suberic	106.6±13	101±10

Table 1: measured enthalpy of sublimation (weighted average), compared with literature values.

These results demonstrate the capability of our thermogravimeter to characterize each compound trough the enthalpy of sublimation measurements. In the future, it is planned to characterize other compounds interesting for studies in industry, planetary and space environments.

References

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