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ASTROBIOLOGY

VISTA: A μ-Thermogravimeter for Investigation of Volatile Compounds in Planetary Environments

Ernesto Palomba[1] · Andrea Longobardo[1] · Fabrizio Dirri[1] · Emiliano Zampetti[2] · David Biondi[1] · Bortolino Saggin[3] · Andrea Bearzotti[2] · Antonella Macagnano[2]

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Abstract This paper presents the VISTA (Volatile In Situ Thermogravimetry Analyser) instrument, conceived to perform planetary in-situ measurements. VISTA can detect and quantify the presence of volatile compounds of astrobiological interest, such as water and organics, in planetary samples. These measurements can be particularly relevant when performed on primitive asteroids or comets, or on targets of potential astrobiological interest such as Mars or Jupiter's satellite Europa. VISTA is based on a micro-thermogravimetry technique, widely used in different environments to study absorption and sublimation processes. The instrument core is a piezoelectric crystal microbalance, whose frequency variations are affected by variations of the mass of the deposited sample, due to chemical processes such as sublimation, condensation or absorption/desorption. The low mass (i.e. 40 g), the low volume (less than 10 cm^3) and the low power (less than 1 W) required makes this kind of instrument very suitable for space missions. This paper discusses the planetary applications of VISTA, and shows the calibration operations performed on the breadboard, as well as the performance tests which demonstrate the capability of the breadboard to characterize volatile compounds of planetary interests.

Keywords Thermogravimetric analysis · Planetary in-situ measurements · Organics detection · Space instrumentation

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✉ Ernesto Palomba
ernesto.palomba@iaps.inaf.it

[1] IAPS-INAF, via Fosso del Cavaliere 100, 00133 Rome, Italy

[2] IIA-CNR, Rome, Italy

[3] Politecnico di Milano, Milan, Italy

Introduction

The search for life and for biosignatures in the Solar System is one of the most important scientific topics indicated by all space agencies. The goal of this research is two-fold: from one side there is the search for extraterrestrial life, from the other side the understanding of mechanisms which caused the origin of life on the Earth.

Primitive asteroids, i.e. those less evolved since the Solar System's formation, contain organic material, and further may have played an important role in the delivery of organics to the prebiotic Earth. Some asteroids present hydrothermally altered materials, indicating the past presence of liquid water (e.g. Webster et al. 1988). Furthermore, primitive asteroids represent interesting targets in the search for organic compounds that may have seeded extraterrestrial life. Comets are also rich in organics and contain abundant water ice, which can also be in liquid form if core melting occurred (Berger et al. 2011).

Evidence for the presence of liquid water in the past on Mars has been suggested by orbiter and rover measurements (e.g. Klein 1979). Jupiter's satellite Europa also is potentially habitable since it appears to have a liquid water ocean under its icy surface (Carr et al. 1998).

Furthermore, detection and measurement of the amount of water and organics on planetary surfaces can give important information about the formation and evolution of these bodies and of the Solar System. How water and organics were delivered and processed on the Earth and other planets is a first step to understand the origin of life.

The VISTA Instrument

Basic Principles

VISTA (Volatile In Situ Thermogravimeter Analyser) is a μ-thermogravimeter system, developed by a consortium of Italian institutes, which aims to perform planetary in situ measurements.

Thermogravimetric analysis (TGA) is a widely used technique to investigate condensation/sublimation and absorption/desorption processes in different environments (Wood et al. 1996; Serpaggi et al. 1999; Stalport et al. 2005; Zinzi et al. 2011). The core of the VISTA μ-thermogravimeter is a Piezoelectric Crystal Microbalance (PCM), whose oscillation frequency varies as the inverse of the mass deposited on it, according to the Sauerbrey equation (Sauerbrey 1959):

$$\Delta f = -K_0 f^2 \frac{\Delta \mathrm{m}}{A_0}, \tag{1}$$

where f and Δf are the PCM resonant frequency and frequency variation, respectively, Δm is the variation of the mass deposited on the crystal, A_0 is the sensor area and K_0 is a constant dependent on the piezoelectric material.

PCM sensors have been often applied in space to monitor dust flux and volatile outgassing (e.g. Palomba et al. 2002; Wood et al. 1996; Mckeown 1998).

In a μ-thermogravimeter, the PCM's temperature can be increased by means of an appropriate heater. When this occurs, the sample deposited on the microbalance surface is reduced in mass as the sample is heated at specific temperatures, resulting in a frequency change.

The mass variation (shown in Fig. 1, for the case of Calcium Oxalate Monohydrate) can be obtained by applying the Sauerbrey equation (Eq. 1), and the sequential reaction steps for release of H_2O, CO and CO_2 can be inferred from the temperature associated with the frequency variation.

Instrument Concept

VISTA is based on a lab-on-chip miniaturised sensor philosophy (Fig. 2), since it has very small mass/volume and power requirements and needs a quite small amount of material for the analysis, i.e. less than 1 mg.

The VISTA head sensor consists of a PCM and the related proximity electronics (PE). The main innovation introduced by VISTA concerns the special design of the PCM, equipped with two built-in resistors, placed on the opposite faces on the crystal, acting as heater and temperature sensor, respectively (Fig. 2). The main advantage of this configuration is the possibility to measure the actual temperature of the PCM sensing crystal. This is possible by calibrating the temperature sensor resistance as a function of the crystal temperature.

Moreover, the presence of the built-in heater reduces the power needed to reach a required temperature. The crystal heating is obtained by supplying power to the built-in heater. This power is dissipated by the Joule effect and causes the temperature increase inside the sensor area. The power needed to reach a certain temperature is further reduced if the thermistor acts as additional heater in parallel with the other resistor, since the total resistance in this case is halved.

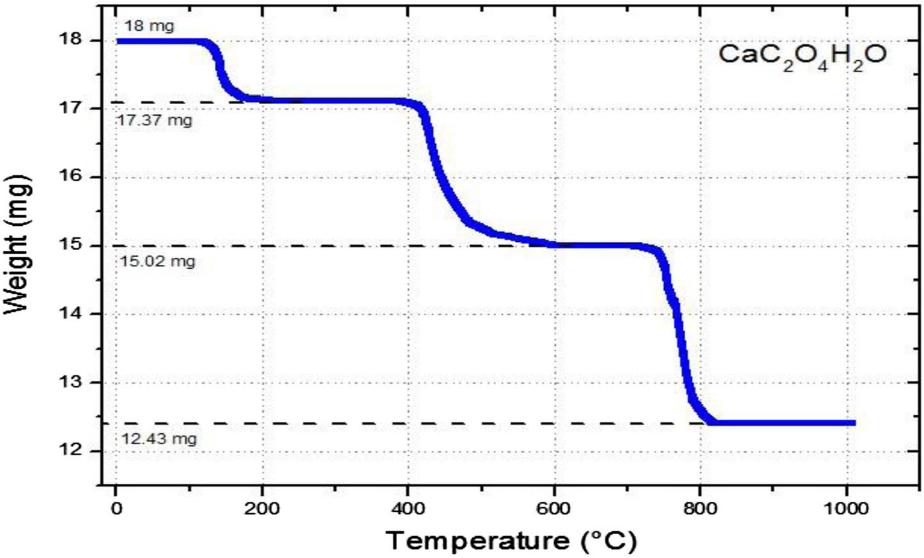

Fig. 1 Thermal decomposition of Calcium Oxalate Monohydrate (CaC_2O_4-H_2O) obtained by heating the sample from room temperature up to 1000 °C. On vertical axis the mass fraction remaining is reported while the mass after each loss are shown by the *dotted lines*. Thermal decomposition occurs in three distinct steps (180 °C, 500 °C and 750 °C) where most of volatiles are produced. By means of frequency variation it is possible to obtain the mass changes (associated with the sequential loss of H_2O, CO and CO_2) at their respective decomposition temperatures

Fig. 2 Picture of a crystal used for VISTA, produced at the IIA-CNR Facility Center. The central area is occupied by the electrode, the sensitive area of the crystal. The Omega-shape element surrounding the electrode is a built-in resistor acting either as heater or temperature sensor. This configuration, i.e. electrode surrounded by built-in resistor, is replicated on the opposite face of the crystal

The technical characteristics of the VISTA sensor hosted in the MarcoPolo-R scientific payload are summarised in Table 1.

VISTA Applications

The specific applications of VISTA depend on the planetary environment under study, but the main goal is usually related to water and organics detection in dust or aerosols. These measurements have a relevant scientific interest, since they are related to habitability of planets and satellites. VISTA has been studied for three ESA mission designs: Marco Polo, MarcoPolo-R and JUICE (JUpiter and ICy moons Explorer).

Marco Polo and MarcoPolo-R aim to return a sample from a primitive asteroid (Barucci et al. 2011). The VISTA purpose was to detect the possible cometary-like activity of the asteroid (VISTA1), i.e. emission of dust and ice from the surface, to monitor the touchdown operations, by measuring the dust raised in this procedure, and to measure water and organic content in the asteroid regolith (VISTA2). Cometary-like activity can be detected by measuring the dust grains

Table 1 Technical characteristics of the VISTA sensor head part of the MarcoPolo-R scientific payload

VISTA technical characteristics	
Mass (g)	40
Volume (mm^3)	24x24x20
Resonance Frequency (MHz)	5.8
Accuracy (Hz)	4
Sampling rate (s^{-1})	5
Sensitivity (ng/Hz)	0.4
Saturation mass (mg)	~10
Crystal Diameter (mm)	14
Thickness (mm)	0.2

and ice particles emitted from the asteroid during the spacecraft approach. The touchdown operations are monitored by measuring the dust raised by the sampling procedures. Water and organics content are measured by heating the regolith deposited on the crystal up to 570 K in order to allow their desorption.

In February 2013, the ESA Payload Review Committee selected VISTA2 as part of the MarcoPolo-R scientific payload.

In the case of JUICE, VISTA has been studied in combination with a Penetrator (Gowen et al. 2011), in order to perform in-situ measurements on the surfaces of Europa and Ganymede, such as investigating composition of non-ice materials, detection of clathrate hydrates and organics.

VISTA can find application on other planetary in-situ missions:

- On a Mars mission, VISTA can measure the dust and ice settling rate on the surface, the water content in the dust (by heating up to 300 K) and the water frost point (Palomba et al. 2011). The latter is obtained by cooling the crystal until ice frosts on the sensor area. The water frost point is related to the partial pressure of the water vapour and, by combining this information with the actual pressure of the Martian atmosphere, it is possible to infer the humidity of the atmospheric environment;
- In a lunar mission, it would detect water ice (sublimating at 160 K) and measure the water and organic content (by heating the PCM up to 570 K) in the lunar regolith in polar regions (Longobardo et al. 2013);
- In a Venus mission, VISTA could give insights about the cloud aerosols, by measuring the dew point of condensable species and the composition of refractory components, thought to lose mass between 300 K and 400 K (Wilson et al. 2012)
- In a Titan mission, it can provide information about the satellite habitability conditions, by inferring the composition and the amount of organics in the atmospheric cloud particles, as well as by measuring the methane dew point (Mitri et al. 2013)

Sublimation/desorption points could help to characterize the volatile compound in combination with calorimetry measurements, such as measurement of enthalpy of sublimation (sub-section 4.2).

Tests

Functional Tests

The power budget required by the VISTA breadboard to perform TGA cycles has been measured both in air and in vacuum. To obtain a ΔT of 60 °C about 0.5 W are needed in air (Fig. 3). This value is one order of magnitude lower in vacuum (the test has been performed in low vacuum, i.e. at 10^{-6} mbar), about 50 mW (Fig. 3).

PCM frequency can change not only due to mass deposition/release but also to variation of environmental parameters, such as temperature and pressure. In order to disentangle frequency variations due to mass deposition and to environmental parameters, the breadboard sensor has been calibrated by measuring the frequency as a function of temperature and pressure. According to literature predictions (Salt 1987), the frequency-temperature curve follows a third degree polynomial (Fig. 4, left). The PCM frequency increases at decreasing pressure,

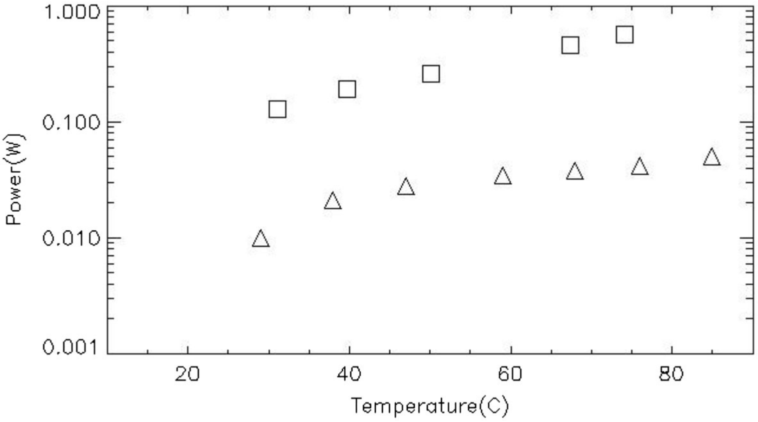

Fig. 3 Applied power to the PCM as function of its actual temperature in a test performed in air (*squares*) and in a vacuum chamber held a pressure of 10^{-6} mbar (*triangles*)

due to the water vapour depletion in the working environment (Fig. 4, right). Finally, the PCM frequency temporal stability has been verified.

Performance Tests

To verify the capability of our device to perform TGA cycles, we performed a hydration-dehydration experiment on a clay mineral sample, i.e. illite.

The experiment consists of four steps (Zinzi et al. 2011): a) hydration by means of a Controlled Hydration Chamber; b) stop hydration; c) dehydration by heating the crystal up to 50 °C by means of the built-in heater; d) heater turning off. If the instrument is able to perform thermal cycles, the frequency at the origin and at the end of the experiment should be the same, because this means that the amount of water absorbed during hydration is consistent with that released during dehydration. In addition, we are able to infer the amount of absorbed/desorbed water by frequency variations measured during the hydration and dehydration processes, respectively.

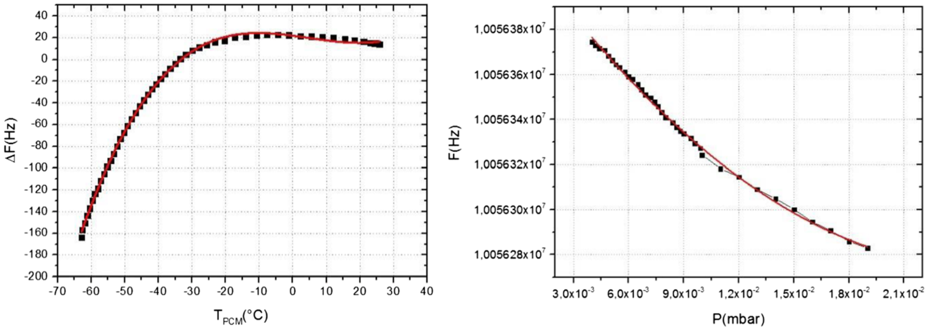

Fig. 4 Functional tests on the VISTA breadboard, performed in a vacuum chamber. *Squares* are the experimental points (for clarity, only one point is shown for each seven measurements) while the *red curve* is the best fit, obtained by means of least squares method. *Left*: PCM frequency as function of PCM temperature. The R^2 of the fit is 0.99. *Right*: PCM frequency as function of the environment pressure

PCM frequency was monitored throughout the whole experiment (Fig. 5). The frequency measured at the start and at the end of the experiment coincided, whereas the frequency variation observed during hydration/dehydration was consistent with an amount of absorbed/desorbed water of 3 %. The inferred water abundance has been measured also by techniques other than μ-TGA (i.e. laboratory balance), demonstrating the reliability of our device in performing μTGA measurements.

Another important test performed on the VISTA breadboard concerns calorimetry measurements, in particular the characterization of a volatile compound, by measuring its enthalpy of sublimation.

Calorimetry application (using PCM) is usually employed in different research fields in order to characterize the physical-chemical properties of materials in the terrestrial atmosphere and for industrial application (Ashcroft 1970; Glukhova et al. 1985; Torres et al. 1994; Freedman et al. 2008).

In this specific application of VISTA, it is possible to decrease the PCM's temperature down to −50 °C in order to measure the heat of transformation of a sample subjected to a temperature variation in a controlled environment. In this case, the PCM is used as mass attractor for sample molecules under a chemical-physical process. A sublimation process has also been investigated by heating a pure compound in a sublimation micro-chamber in vacuum (Dirri et al. (2014) Measuring enthalpy of sublimation of volatiles by means of micro-thermogravimetry, unpublished). It has also been possible to characterize some volatile compounds by measuring deposition rates on the microbalance surface (obtaining the typical sublimation curve for each sample, Fig. 6) and the enthalpy of sublimation, by applying the Van't Hoff relation (Benson 1968). The results are in agreement with literature within 10 %. This makes it possible to constrain the composition of a mixture of compounds having different enthalpies of sublimation.

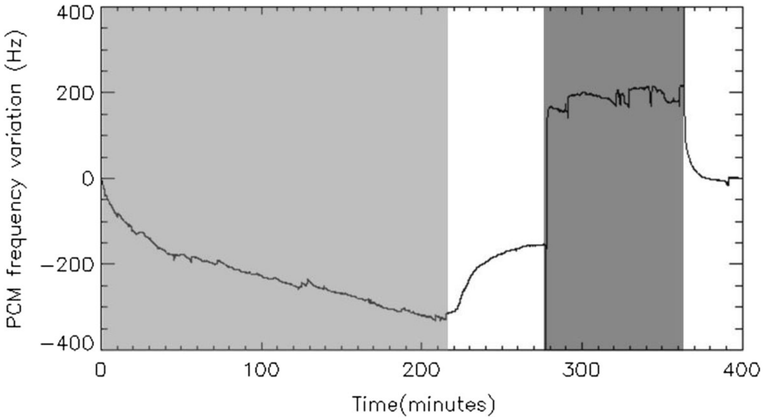

Fig. 5 Hydration and dehydration experiment performed on a clay mineral sample (i.e. illite) deposited on a PCM. The hydration is obtained by placing the PCM in a Controlled Hydration Chamber (at room temperature and 80 % relative humidity), resulting in a weight gain and a PCM frequency decrease (step a - light shadowing in the plot). When the hydration is stopped (minute 214), the sample is over-saturated with water, and hence releases water molecules: this causes a PCM frequency increase up to an equilibrium (step b - no shadowing between minutes 214 and 277). Then the PCM is quickly heated up to 50 °C by means of the integrated heater, causing a frequency increase at minute 277 (due to the temperature increase). The PCM is kept at that temperature for more than one hour, favoring the desorption of water from clay (step c - dark shadowing). Finally, the heater is turned off (step d – no shadowing in the last part of the graph). The PCM frequency then decreases (due to the temperature change) and stabilizes at the frequency value measured at *time* = 0

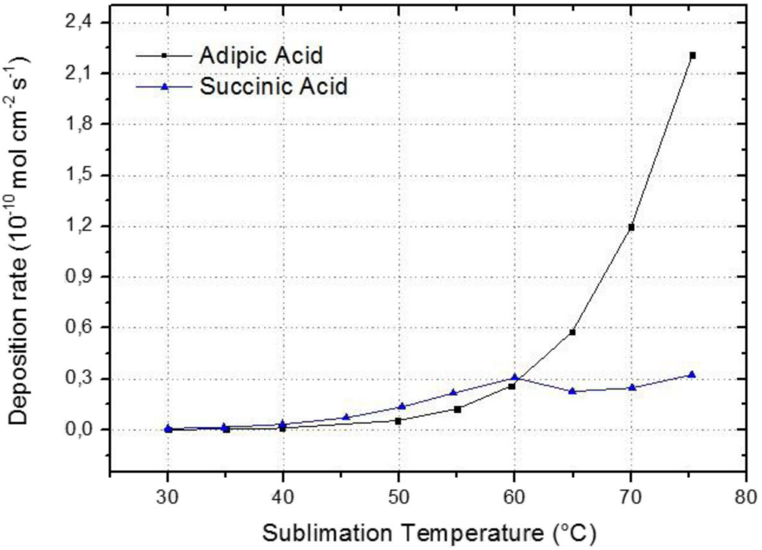

Fig. 6 Typical sublimation of two pure organic samples, i.e. Adipic and Succinic acid (Dirri et al (2014) Measuring enthalpy of sublimation of volatiles by means of micro-thermogravimetry, unpublished)

Two different behaviors are observed between 30 °C and 75 °C. Up to 60 °C the deposition rate increases in both cases. At greater temperature, the behavior is dependent on the molecular structure of the sample (Dirri et al (2014) Measuring enthalpy of sublimation of volatiles by means of micro-thermogravimetry, unpublished). The curve slope and the deposition rates at temperatures lower than the sublimation points allow inference of the sublimation enthalpy. A mixture of two compounds would be characterized by intermediate curves.

Conclusions

The VISTA micro-thermogravimeter has been designed to perform planetary in-situ measurements, providing insights into features as diverse as dust infall rates and the nature of volatile compounds, in particular water and organic content in planetary regolith and detection of water ice (Longobardo et al. 2013). Getting reliable TGA data with enthalpy of sublimation would be an important advance in understanding volatile mineralogy and the availability of volatiles for possible biological systems.

A breadboard of the VISTA instrument has been characterized to check its functionality against environmental parameters, such as pressure and temperature, as well as to investigate signal stability over time. These calibrations are essential to obtain the correct interpretation of the PCM frequency change due to mass deposition or release.

Performance tests applied on the same breadboard have demonstrated the capability of VISTA for detecting the absorption/desorption of water molecules from a clay sample, retrieving the thermal release profile and the amount of the volatile fraction contained in the analyzed samples. In addition to the abundance, the VISTA instrument has been able to retrieve the enthalpy of sublimation of analyzed volatiles, and this measurement can help in characterizing volatile compounds.

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