Thermal Analysis of Nanogram Quantities Using a Micromechanical Cantilever Sensor

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ABSTRACT
Thermal analytical techniques, such as thermogravimetry, are routinely used for forensic and material analysis, and typically require sample masses of a few milligrams. Tracking the resonance frequency of a micromechanical cantilever sensor as a function of temperature permits tiny changes of the actuated sensor mass to be determined. Such changes can arise from an additional sample which is placed on the cantilever sensor. A piezoresistive cantilevers can be operated as microbalance by determining its resonance vibration amplitude. The electrical current through the piezoresistive layer produces an electrical power dissipation, which directly heats the micromechanical device. The presented micromechanical thermogravimetry technique has a mass resolution which is in the picogram range. This is demonstrated in quantitative analysis of a dehydration, a desorption, and a decomposition reaction of nanogram materials.

INTRODUCTION
The characterization of nanogram quantities of samples is very important in analytical chemistry and physics. Thermal analytical techniques such as thermogravimetry (TG), are routinely used for forensic and material analysis (1). However, using standard commercial tools, sample masses of a few milligrams are required. Sometimes this quantity is not available or cannot be synthesized. The use of micro-electro-mechanical system (MEMS) devices allows to measure a variety of different signals (2). One characteristic of MEMS devices is their short response times. Furthermore, these sensors are made by Si-technology allowing to manufacture hundreds of individual functional elements on a single chip and several tens of these on a wafer. In addition, on-chip circuitry such as electronic amplifiers and data processing elements can be integrated. One example is the parallelization of scanning force microscope type sensors for high density data storage (3). Here, the heating of individual tips can be used for thermo-mechanical writing of pits. Microhotplate platforms were fabricated to study thermally dependent desorption and are used as gas detectors (4).
Calorimetric analysis based on a micromechanical bimetallic sensor principle was performed to study the heat evolution of catalytic reactions (5) and to analyze the heat associated with phase transitions (6,7). Humidity sensing was reported by using zeolites which were attached to the apex of a cantilever (8). Here the resonance frequency changes upon mass increase owing to water adsorption were detected. In this manuscript the application of an in-situ heated, resonating cantilever to study mass changes will be discussed. To illustrate the potential of micromechanical thermogravimetry (MMTG) some experimental results are exemplarily summarized in this article (9,10,11). Recently, special designed cantilevers have been developed for this specific application (12).

EXPERIMENTAL

The operational set-up of the MMTG including the electronical apparatus is schematically illustrated in Fig. 1. The sensor (S) consists of two flexible, 2-4 µm thick beams carrying a rigid platform (PF). The other end of the cantilever is supported by a Si chip. Samples A are placed in the middle of the cantilever platform for MMTG analysis. A piezoresistive layer (PR) is integrated into the top side of the sensor forming an electrical path through the cantilever. Electrical bond connections are made from a chip housing to the Si chip Al bond pads (BP). The whole chip is mounted on a 5 × 5 mm² piezo-electric actuator (PA). The PA is connected to a frequency generator (FG). This arrangement is placed into a glass container (not shown) which can be continuously flushed by a gas.

![Fig. 1. A schematic setup of the MMTG in side (A) and in top view (B) which also includes the electronic external components. (C) shows a scanning electron micrograph of a sensor in side view holding a single zeolite crystal.](image)
Different sensors can be fixed on the PA and contacted to the electronic circuit. Changes in the resistance of the PR-layer, $R_{PR} + \Delta R_{PR}(z)$, are measured via a Wheatstone bridge with reference resistors $R_{ref}$. The electrical bridge circuit was balanced for each sensor individually by a resistor-potentiometer combination ($R + \Delta R$). A lock-in technique was used to determine the sensor resonance amplitude in dependence of the computer controlled FG frequency. The lock-in output signal is recorded via a 12-bit data acquisition board in the computer. The FG frequency is computer-controlled to maintain the maximum cantilever vibrating amplitude.

The applied bridge voltage $V_{WB}$ produces an electrical power dissipation $P_{PR}$ of approximately $0.25 \times V_{WB}^2 R_{PR}^{-1}$, which heats the cantilever sensor. In the MMTG experiments $V_{WB}$ is ramped under computer control, producing an increase in temperature $T$ at the rigid platform where the sample is placed. Finite element simulations have revealed a good temperature uniformity (12). Reference heating and cooling cycle experiments performed without samples have revealed that $R_{PR}$ remains constant at room temperature for at least 10 cycles. Thermal response times are in the millisecond range indicating that a thermal steady state can be achieved on a similar time scale. The electrical resistance of the PR-layer is also dependent on the temperature. We took this $R_{PR}$ value to monitor the temperature of the cantilever sensor. The cantilever’s resonance frequency $F$ is given by

$$F = \frac{1}{2\pi} \sqrt{\frac{K}{m}},$$

where $K$ is the cantilever spring constant, and $m$ is the effective actuated mass. For varying sensor temperatures the frequency change is given by

$$\frac{1}{F} \frac{dF}{dT} = \frac{1}{2K} \frac{dK}{dT} - \frac{1}{2m} \frac{dm}{dT}.$$

Consequently, tracking the resonance frequency as a function of $T$ permits changes of the total sensor mass to be determined. Such changes may arise from a sample mass $m_s$ which is placed on the platform (Fig. 1), resulting in a total actuated mass $m = m_s + m_a$, where $m_s$ is the effective cantilever mass. The used sensors can hold masses from several hundreds of nanograms down to the picogram range. The zeolite sample which is shown in Fig. 1C has a mass of approx. 150 ng. A detailed description how the absolute sample mass can be calculated from sensor’s resonance frequency change can be found in (9). However, the temperature dependence of $K$ leads also to changes in resonance frequency. This can be corrected by recording both, the resonance frequency during the heating and during the cooling of the sample-cantilever sensor (9). In the case there is a negligible mass change during cooling, the difference of both curves allows to calculate the pure mass change in the heating cycle.

RESULTS AND DISCUSSION

As a first experimental study, MMTG data of the dehydration reaction of CuSO$_4 \cdot$ 5H$_2$O is presented in Fig. 2A. The thermally induced resonance
frequency shift owing to H₂O mass loss of the CuSO₄ · 5H₂O sample is plotted versus sensor temperature. The frequency steps observed at (I) 50-60 °C and (II) 170-220 °C correspond to two dehydration reactions respectively. The scale bar indicates the corresponding mass change which was determined by

\[ m_\Delta - m'_\Delta = \frac{K}{4\pi^2} \left( \frac{1}{F'^2} - \frac{1}{F_{in}^2} \right), \]

where \( m'_\Delta \) is the remaining sample mass undergoing a mass change upon heating, \( F' \) is the resonance frequency of the heated sensor and \( F_{in} \) is the resonance frequency including the sample at the initial starting temperature. In addition, the calculated relative weight loss is indicated at the right side of the plot of Fig. 2A.

**Fig. 2.** Examples of MMTG measurements: (A) A dehydration reaction of 420 ± 20 ng of CuSO₄ · 4H₂O (B) desorption of PNA from Silicalite-1-zeolite and (C) thermal decomposition of 5.88 ng (top) and 4.687 ng (bottom) of CaC₂O₄ · H₂O under a CO₂ atmosphere and in vacuum. (D) shows a measurement of a volcanic Palagonite sample.

In a second experiment, zeolites are used as porous crystalline structures. These materials offer high adsorption capacity and their channel system can be loaded with ‘guest’ molecules. Such host–guest interactions of Silicalite-1 zeolites loaded with dye molecules p-Nitroaniline (PNA) can be characterized by thermal analysis. Theoretically, a fully loaded silicalite-1 zeolite would correspond to 4 PNA molecules per unit cell (13) and would result in a weight loss of 9%. In our experiment a 80 x 25 x 30 µm³ PNA loaded zeolite was mounted at the cantilevers apex (Fig 1C). The sample mass loading was estimated to be 148 ± 8
ng. During heating a weight loss of 11.7 ± 0.1 ng was measured in a temperature range between 150 °C and 250 °C (Fig. 2B). This mass loss corresponds to a loss of 7.7 ± 0.5 weight %. The minimum detected mass change during the experiment was 6.5 pg (10,11). For comparison a standard TG analysis was performed on similarly prepared crystals of Silicalite-1-PNA having a total sample mass of 7.11 mg. This agglomerate consists of approx. 50000 individual crystals. The obtained mass loss of 8.0 ± 0.4 weight % is in excellent agreement with the above presented MMTG analysis of one single crystal.

Third, thermal decomposition of calcium oxalate monohydrate CaC₂O₄ ⋅ H₂O was measured in vacuum and under a CO₂ atmosphere (Fig. 2C) (14). At 200 °C the crystal water dehydrates (I), the atmosphere is here of minor influence. At about 500 °C the decomposition reactions starts for both experiments. Under CO₂ atmosphere (Fig 2C - top) the decomposition step II which corresponds to the formation of CaCO₃ and CO can be measured. Here 0.65 ng calcium carbonate are produced. Up to a temperature of 700°C the complete decomposition was not observed. Under vacuum conditions the decomposition of calcium carbonate into CaO and CO₂ (III) was observed at a temperature of about 500°C. Both reaction steps II and III were resolved in the MMTG measurements as one step (Fig 2C - bottom). In the latter case a total mass loss to about 62% was calculated. In particular, these MMTG-experiments show that picogram mass resolution can be obtained under various atmospheric conditions as well as under different pressures (14).

Launch is one of the highest cost factors for space-based systems and is directly related to mass. Any reduction in mass, volume and power requirements is desirable and will have a significant effect on cost. Here, micro- and nanotechnology are considered an excellent means (15). A MMTG study of Palagonite, a pale yellow-brown, hydrated basaltic glass, which has a similar composition as material from the planet Mars (16) was performed. The resulting MMTG data is plotted in Fig. 2D. Both, the heating (h) and the cooling curve (c) are shown. Reference experiments using standard TG reveal a similar characteristic. However, we don’t know details of the temperature induced mass loss in the Palagonite experiment.

CONCLUSIONS

MMTG performed with micromechanical cantilevers offers a way to analyze very small sample mass. Samples can be individually selected and analyzed. This offers a way to study individually tailored small samples. A comparison between standard TG and MMTG is given in Tab. 1. We found that some key parameters are by 3 orders of magnitude better for a MMTG setup.

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<th>standard TG</th>
<th>MMTG</th>
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<tr>
<td>sample mass</td>
<td>mg</td>
<td>ng</td>
</tr>
<tr>
<td>mass resolution</td>
<td>µg</td>
<td>pg</td>
</tr>
<tr>
<td>heating rate</td>
<td>10⁴ K/min</td>
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Tab. 1. A comparison of TG and MMTG tool parameters.
Furthermore, the MMTG technique can be parallelized by using arrays of cantilevers (17). This might allow an application for combinatorial material analysis or as disposable MMTG sensors.

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