SENSING OF ORGANIC VAPOR ADSORPTION ON GOLD USING A TEMPERATURE INSENSITIVE MICROBALANCE

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Abstract

The adsorption of organic vapor molecules onto the gold electrode surface of a dual mode 10MHz 3rd overtone SC-cut quartz microbalance (QCM) was investigated. Using this dual mode QCM, the separation of mass and temperature change can be made in real time, with resolutions of 56 pg and better than 0.01K, respectively. The QCM experiments were performed in a UV/Ozone chamber so that the gold electrodes could be maintained in a clean state. Organic vapors or liquids (e.g., benzene, hexane, methanol, ethanol, isopropanol, or butanol) were injected into the chamber while the two modes of the dual mode QCM were monitored and the mass-frequency and temperature changes were extracted. This paper demonstrates the ability of the sensor to determine in a matter of seconds, sub-ppm (ppm=parts per million) gas concentrations of benzene and hexane while operating in an elevated temperature environment without any temperature stabilization. In addition, the mass changes for a series of adsorbed methanol, ethanol, isopropanol, and butanol were found to be proportional to molecular weights.

Introduction

Quartz crystal oscillators are some of the most widely used acoustic devices with a long history of development as sensors of temperature, stress, acceleration, viscosity, mass, and are universally used to measure time [1-5]. Due to the effects of mass loading, the quartz crystal microbalance (QCM) works as a sensor of mass, with a capability of sensing considerably less than a single molecular layer of adsorbed material. Most QCM's utilize AT-cut, which has a temperature coefficient of 0 ppm/K at room temperature. Though working well at the specified design temperature, as the temperature deviates from this "turnover temperature" (usually near room temperature), the temperature coefficient of frequency increases, which makes the temperature induced mass sensing errors also increase. Depending on the application, precise temperature regulation may be necessary to eliminate temperature change effects. For example, a QCM typically used for film thickness monitoring in a thin film deposition system is cooled by circulated water. Temperature control, however, imposes increased power, size, and complexity requirements. Moreover, temperature control has its own limitations, e.g., due to thermal gradients among the temperature sensor, heater (or cooling means), and the resonator. Temperature control is not always practical in certain applications.

We have demonstrated a temperature insensitive quartz microbalance (QCM) technique [6], which employs dual mode frequencies, the fundamental mode and 3rd overtone, to discriminate between mass change effects and temperature change effects. This technique requires neither temperature control nor an independent temperature sensor, only the resonator itself. Dual mode excitation of SC-cut resonators can be used for highly accurate self-temperature sensing over wide temperature ranges. SC-cut resonators derive their "SC" designation from the fact that the cut is "stress compensated". This property also results in thermal-transient compensation. These unique properties of the SC-cut allowed for the development of a temperature compensated microbalance. Detailed discussion of the method of separating temperature and mass effects can be found in Ref. [6]; and is not reproduced here.

Experiments

The resonator used in the experiments was a plano-convex SC-cut 10 MHz 3rd overtone (3.3 MHz fundamental mode) resonator developed for a microcomputer compensated crystal oscillator (MCXO) [7]. The diameters of the plate and gold electrode were 14 mm and 5.0 mm, respectively, and the plate contour was 3 diopters. The resonator frequencies were measured using a dual mode crystal oscillator (DMXO), which was originally developed for an MCXO, then modified for an opened resonator. A resonator in a vacuum-sealed metal can was calibrated for temperature effects in a temperature controlled chamber, in which temperature
was ramped from 10°C to 85°C in steps of 4°C. At each temperature step the oven was held for 30 minutes after reaching the target temperature. This was to ensure that the resonator and the quartz thermometer (used to measure the oven temperature) were as close to the same temperature as possible. Fig. 1 shows the fundamental (or c1) mode \( f_{c1} \) and the 3rd (or c3) overtone \( f_{c3} \) versus the beat frequency \( f_b \) (defined by \( f_b = 3f_{c1} - f_{c3} \)). It can be seen that both the \( f_{c1} \) and \( f_{c3} \) curves are nonlinear, with the \( f_{c3} \) having a turnover at room temperature, so \( f_{c1} \) or \( f_{c3} \) alone would not be useful for measuring temperature when mass change is present or visa versa. The beat frequency (0.166 MHz), on the other hand, decreases monotonically and nearly linearly as temperature increases. The slope of the beat frequency was about 91 ppm/K or 15 Hz/K.

By using two counters controlled by a personal computer, both frequencies were simultaneously measured with 0.1 sec gate time and 0.06 sec dead time for data transfer and calculation. The hysteresis of the DMXO with the unopened resonator was measured to be 1.5 x 10^-4. Allan deviation [8] of the DMXO with the opened resonator was obtained to be 2.2 x 10^-10 and 2.3 x 10^-10 for \( f_{c1} \) and \( f_{c3} \), respectively, at uncontrolled laboratory ambient temperature. The peak to peak noise of the mass frequency (or the resolution) of the DMXO with the opened resonator was 2 ppb (parts per billion).

Since the QCM was exposed to air, the gold electrode surfaces were quickly contaminated by hydrocarbons existing in the ambient air. Such organic contamination could be removed to a monolayer level using an UV-ozone cleaning chamber. The UV/O3 chamber was a commercially available model and its volume was \(-2.7 \times 10^{-1}\) cm³. When the unit is turned on, the mercury lamp emits UV primarily at 185nm and 254nm. The 185nm radiation produces ozone from oxygen in the air and the UV and ozone work in concert to clean the gold electrode surfaces [9]. The resonator's temperature rose as a result of the UV photon flux (~30 mW), the transfer of heat from the lamp to the chamber air, and the exothermic reactions occurring in the chamber and at the surface. Typically the maximum temperature was 65°C.

When the UV lamp was turned off, immediate temperature drop induced transient effects as 0.1–0.2 ppm changes of the mass frequency and contamination began to collect on the surface. After 30 minutes from the point the lamp was turned off, the surface contamination from the ambient completely blocked the sensing of injected organic vapor. The same amount of vapor could be easily detected if the UV lamp was left on continually cleaning the surface. To circumvent problems of surface contamination and the effects of the thermal transient, the UV lamp was kept on during the injection experiments. This procedure introduces some questions about the possibility of sensing UV-ozone decomposed molecules in the vapor, rather than intact sample molecules. Nevertheless, whatever was adsorbed, different injected molecules produced different responses, and, qualitatively, the responses varied with the molecular weights, which suggests that, with further development, one may be able to obtain not only high sensitivity but also selectivity. With better contamination control a clean sensor surface would be maintained for a longer time and experiments could be performed with the UV lamp off.

**Results and Discussion**

Fig. 2 shows the results for consecutive benzene vapor injections of 0.3 ml and 0.6 ml. Figs. 2(a)(b) are the raw data of \( f_{c1} \) and \( f_{c3} \), respectively. Note that from the raw data it is not clear when the benzene was injected. In Fig. 2(c), however, by applying the algorithm that separates mass and temperature effects, the two benzene peaks from the injections are clearly identifiable. The units of mass frequency changes are shown in ppm.

In Fig. 2(d) the temperature is shown to be about 62.6°C with a precision on the order of thousandths of a degree. The majority of the frequency changes in Fig. 2(a) and Fig. 2(b) are due to temperature. When sensing small mass change, small drifts in temperature, which are unavoidable, can obscure the measurement of mass. The advantage of the SC-cut QCM in removing this effect is obvious here. Note that the temperature was far above the temperature that would be required for an AT-cut QCM to work properly without temperature control.

In Fig. 2(c) adsorption occurred in less than a half second. The adsorbed molecules were completely removed within about 5 minutes. This removal occurred in part by the UV-ozone cleaning process, but also by the lowering of the benzene vapor pressure due vapor phase UV-ozone reaction and by leakage out from the chamber as the chamber was not hermetically sealed. In a short time the clean surface was regenerated and this allowed for consecutive injections. The 0.3 ml benzene vapor was equivalent to a maximum of 1.3 ppm (by volume) benzene in the chamber. The mass frequency change for 0.3 ml injection was 13 ppb, which is six times greater than the balance's resolution of 2 ppb. The sensitivity is on the order of \((2/13) \times 1.3 \text{ ppm} = 0.2 \text{ ppm (by volume)}\) for benzene vapor. The microbalance with an unmodified gold surface is a better detector for benzene than the human nose, which has the odor detection threshold for benzene vapor of 1.5 ppm (by volume) [10]. In addition, the detection occurs instantly.
Fig. 3 shows the results for three consecutive hexane vapor injections of 0.6 ml, 0.4 ml, and 0.6 ml. Figs. 3(a)(b) are the raw data of \( f_c \) and \( f_c3 \), respectively. In the raw data the injection points are identifiable. In Fig. 3(c), applying the separation algorithm of mass and temperature effects increased the signal to noise. As in the benzene case, the adsorption happened very quickly, but the adsorbed molecules were also completely removed in 2 minutes, which was faster than that of benzene. The 0.4 ml hexane vapor was equivalent to a maximum of 3.7 ppm (by volume) hexane in the chamber. The mass frequency change for 0.4 ml injection was 44 ppb, which is 22 times greater than the balance's resolution of 2 ppb. The sensitivity is on the order of \( (2/44) \times 3.7 \text{ ppm} = 0.17 \text{ ppm} \) (by volume) for hexane vapor. The balance thus has a detection limit of about 0.13% that of the 150 ppm (by volume) odor detection threshold for hexane vapor. Again the detection happens very rapidly on the clean gold surface. Also shown is Fig. 3(d), the temperature was about 55.8°C.

Fig. 4 shows the result of the injection of 0.01 ml of liquid methanol, ethanol, propanol, and butanol. Each liquid was injected into the chamber some distance away from the actual resonator and the liquid vaporized in the warm chamber. The adsorption of the alcohols was less than for benzene and hexane, so small liquid samples were used instead of vapors in order to increase the partial pressure of the vapors. The increased noise compared to the benzene and hexane experiments was due to the airflow in the chamber. The previous two experiments were performed with the resonator housed in a metal can with only the top electrode surface exposed to the lamp. This was to minimize air turbulence effects. The trade-off was that the exposed surface only was cleaned. In an effort to clean the both surfaces (i.e. to double the sensing area), the fully exposed resonator without the can was put in a position perpendicular to the lamp for the alcohol experiment. This caused the resonator to be more susceptible to the airflow. It is seen that the mass frequency changes are approximately proportional to the molecular weights of the alcohols.

The thickness of a 10 MHz 3rd overtone resonator is ~0.53 mm. This, with the density of quartz (2.65g/cm³), gives an areal density of ~0.14g/cm². The microbalance has a sensitivity of ~140 ng/cm²-ppm. The measurement resolution of 2 ppb represents 280 pg/cm². Since the electrode area was about 0.2 cm², the mass resolving ability is on the order of 56 pg (assuming a simple thin film model). This sensitivity can also be considered in terms of monolayers. When large quantities of hexane liquid were injected into the chamber with a fully exposed resonator (data not shown), the frequency mass change approached a saturation value of about 1.85 ppm. This change equates to 259 ng/cm² or 1.8×10¹⁵ molecules/cm² considering both electrodes and 0.9×10¹⁵/cm² for each electrode. The 280 pg/cm² resolution equates to about 1×10¹² hexane molecules on each gold electrode surface.

### Summary and Conclusions

A microbalance utilizing dual mode excitation of an SC-cut resonator, has been demonstrated to sense concentrations of benzene and hexane below 1 ppm (by volume), by separating mass from temperature effects. The method improves the accuracy of a microbalance, especially when operating over wide temperature ranges. The method also eliminates the need for controlling the microbalance temperature. A mass change resolution of 56 pg has been demonstrated at elevated temperatures and under uncontrolled transient temperature conditions.

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### References


Fig. 1: Frequency changes as a function of beat frequency for a dual mode SC-cut resonator oscillator.

Fig. 2: Benzene vapor injection: (a) c1 mode, (b) c3 mode, (c) mass frequency changes, and (d) temperature.

Fig. 3: Hexane vapor injection: (a) c1 mode, (b) c3 mode, (c) mass frequency changes, and (d) temperature.

Fig. 4: Methanol, ethanol, isopropanol, and butanol injections.