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A quartz micro balance for measuring the kinetics of guest uptake from the vapour

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Abstract

The design of a multiple probe quartz microbalance (QMB) for the study of guest-uptake in inclusion compounds is reported. The kinetics of inclusion of 1,3-dioxolane by 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene is reported as an example of the use of this apparatus in the study of guest uptake from the vapour, under controlled temperature and pressure. © 1997 Elsevier Science B.V.

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1. Introduction

In recent years, there has been great interest in developing chemical sensors based on oscillating quartz crystals [1,2]. These sensors have possible applications in measuring concentrations for medical purposes, as well as industrial process control. They are often employed as 'chemical noses' to detect very small amounts of odorant [3]. Saunders et al. [4] have obtained 'kinetic signatures' of six different surface coatings when exposed to one of the eighteen different odorants. This method has been recently extended to chiral molecular recognition from a solution, where the quartz crystal was coated with a dipeptide host compound [5]. Jane and Shih [6] developed a quartz crystal electrode, coated with a crown ether, as a detector of either cations or anions in ion chromatography.

The method is based on the mass-frequency dependence of an oscillating quartz crystal according to the formula:

$$\Delta f = -kf_0^2\Delta m$$

where f_0 is the frequency of the unloaded crystal and k is a constant specific to each crystal. The frequency of the oscillation decreases with increasing mass of the crystal and this can be exploited to weigh very small quantities of the organic compound coating the surface. A detection limit of 1 ng, using 9 MHz quartz crystals, has been reported [1].

An oscillating quartz crystal can be made into a quartz microbalance (QMB) by coating it with a suitable host compound (H) which in turn reacts with targeted guest compound (G) according to the following equation:

$$H_{(\mathrm{s},\alpha)} + nG_{(\mathrm{g})} \rightarrow HG_{n(\mathrm{s},\beta)}$$

When the host compound, in the non-porous α-phase, is exposed to a guest vapour a phase change

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takes place and the inclusion compound in the β-phase is formed. This change in phase can be monitored by using X-ray powder diffraction. The gain in mass of the quartz crystal results in a decrease in oscillation frequency which can be monitored as a function of time, thus enabling the kinetics of reaction to be measured.

Most of the references to the use of QMBs in the literature refer to their use as chemical sensors. We are reporting the design of a multiple probe QMB system for the investigation of the isothermal kinetics of guest sorption of very small samples. Often the hosts under investigation are specialised compounds which are not commercially available, and the limited availability of the host compounds dictates the types of experiments which can be carried out. The kinetics of desorption of inclusion compounds can be studied on a conventional TG using sample sizes ranging between 2–5 mg. In order to study the formation of inclusion compounds, the host has to be placed in a saturated guest atmosphere. Siedel et al. [7] recently reported guest uptake studies carried out on a conventional simultaneous TG–DSC. Due to the corrosive nature of some guest vapours this is not always feasible. A levitation balance [8], previously designed for this purpose requires sample masses of 300–500 mg of host compound. The QMB system reported here was hence developed to study very small samples (100–500 µg).

2. Description of apparatus

The QMB apparatus, shown in Fig. 1, consists of a glass cell which can be evacuated and whose internal pressure can be monitored, using a pressure transducer with a stainless steel diaphragm. There is an inlet for the guest vapour which is injected via a rubber septum. The cell was placed in a thermostatted cupboard, and the temperature was controlled within 0.1 K using a PID controller. The cell contains three quartz crystal probes. Each probe, shown in Fig. 2, comprises a 10 MHz quartz crystal which has been mounted in a socket on a glass cone, with a crystal oscillator circuit secured inside the cone. Each cone was sealed with a silicone sealant.

An electronic circuit, shown in Fig. 3, monitors the change in frequency of a given crystal and the signal is fed to a microcomputer which displays the change in frequency against time. The QMB circuit consists of a 10 MHz reference quartz oscillator located inside the main instrument case and the three probes in the reaction cell. The quartz crystal oscillator is very compact and consists of a commercially available eight pin integrated circuit. The circuit requires a 5 V power supply, a 0.01 µF supply decoupling

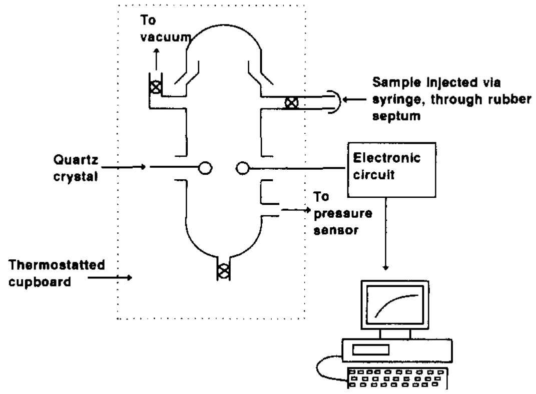


Fig. 1. Schematic diagram showing the principal features of the QMB system.

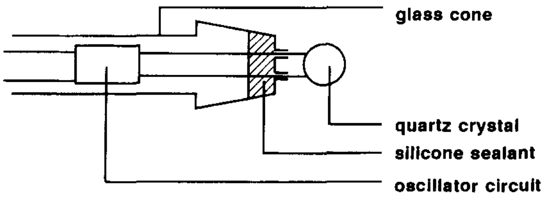


Fig. 2. Schematic diagram of the quartz crystal probe.

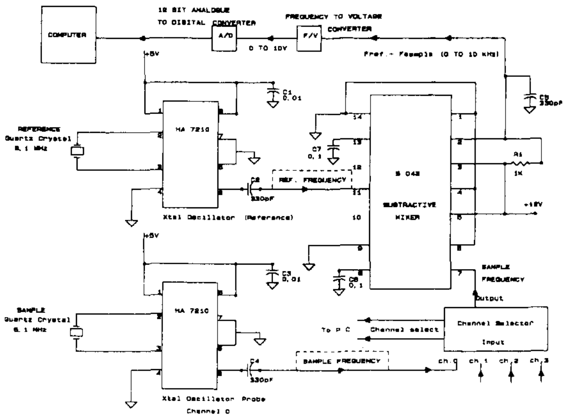


Fig. 3. Crystal oscillator and mixer circuit.

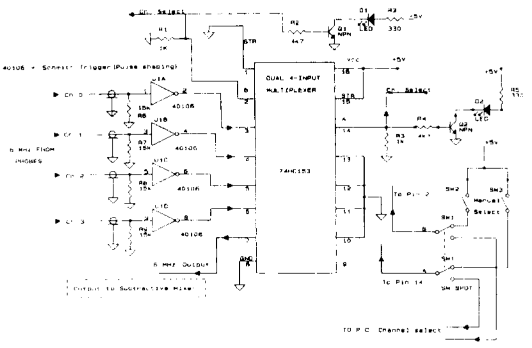


Fig. 4. Channel selector circuit.

capacitor and the appropriate pin connections as shown in Fig. 4. The quartz crystal determines the frequency of oscillations and the circuit can be configured to oscillate between 10 kHz and 10 MHz.

The software controls the Channel Selector which sequentially scans the frequencies of the probe oscillators in the reaction cell and feeds the frequency (F_s) into a subtractive mixer, which subtracts the frequency of the reference oscillator (F_r) from each incoming probe oscillator frequency. The difference ($F_s - F_r$) is fed to a frequency to voltage converter (F/V), which produces an output of 1 V for every kHz of difference frequency, with a maximum output voltage of 10 V (10 kHz). The difference frequency vs. time data are displayed via a real time graphic interface and captured into a data file, which can easily be analysed using any commercially available spread sheet package.

3. Experimental

3.1. Coating and conditioning

The quartz crystals were coated with the α-phase of the appropriate host compounds. An even coating was obtained by dipping the quartz crystal into a concentrated solution of the host compound in diethyl ether. Upon evaporation of the solvent a coating of the unstable diethyl ether inclusion compound remained on the surface of the quartz crystal. This coating procedure was repeated until a sufficient coating (100–500 μg) was obtained. The quartz crystal was left at atmospheric pressure overnight, so that the diethyl ether could desorb, yielding the non-porous α-phase of the host. It is imperative to allow the evaporation and desorption to take place slowly, at room temperature and atmospheric pressure, in order to obtain a uniformly coated crystal.

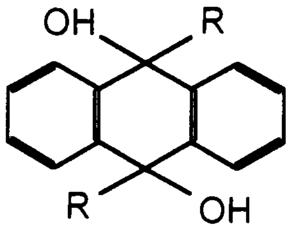
It was found that the rate of the sorption reaction increased, with repeated cycles, due to surface damage increasing the host surface area. Based on these results the host compounds were conditioned prior to kinetic studies, by repeating sorption–desorption cycles until the rate of reaction remained constant, under fixed conditions of temperature and vapour pressure of the guest.

3.2. Calibration

One probe was left uncoated in the reaction cell to monitor the response of the quartz crystal due to changes in temperature and pressure, while the other two quartz crystals were incrementally coated with the host compound under investigation. A series of Δf vs. Δm data were obtained at room temperature and the existence of a linear relationship between mass and frequency was confirmed. The mass-frequency dependence was also confirmed at other temperatures.

4. Application

The host 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (see Scheme 1) forms a 1 : 1 inclusion compound with 1,3-dioxolane. We have used the QMB system to study the kinetics of enclatration by exposing the non-porous α-phase of the host compound to the dioxolane vapour and measuring the mass gain with time, at various temperatures and vapour pressures of dioxolane. The α-time curves at various temperatures, for the injection of fixed volume of 1,3-dioxolane are shown in Fig. 5. An



Scheme 1.

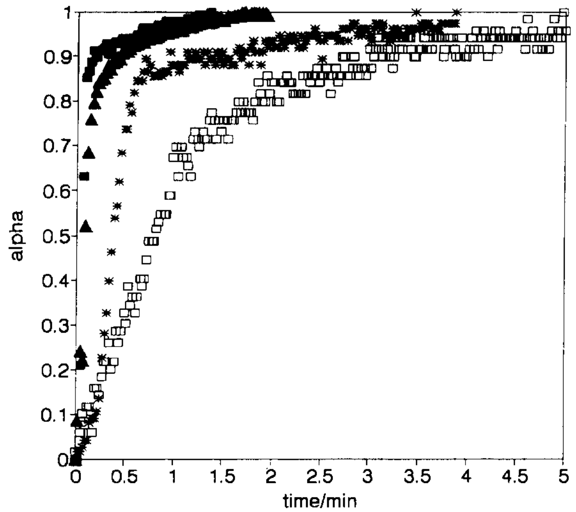


Fig. 5. α vs. time curves for the addition of 118 mmHg of 1,3-dioxolane. ■ – 303 K, ▲ – 308 K, * – 313 K and □ – 318 K.

excess of guest was injected (typically ten times more than stoichiometric amounts) to ensure that the partial pressure of guest does not decrease with increased extent of reaction. The guest absorption reactions reached completion within a few minutes, since such small host samples were used (typically 500 μg). The observed rate of absorption, for a given number of moles of guest vapour, decreases with an increase in temperature, and therefore the reaction displays apparent anti-Arrhenius behaviour.

This phenomenon was first observed by Barbour, Caira and Nassimbeni [9] for the reaction of this host with acetone vapour. They proposed an empirical rate law:

$$\ln(1-\alpha) = k_f \frac{(P-P_0)}{P_0} t$$

where $k_{obs} = k_f(P-P_0)/P_0$, k_f is the rate constant for the (forward) inclusion reaction and P_0 is a threshold pressure, below which the absorption reaction will not take place. The α-time curves at 313 K, and at various vapour pressures of the dioxolane guest are shown in Fig. 6. They fit the Prout–Tompkins mechanism for sigmoidal curves:

$$\ln[\alpha/(1-\alpha)] = k_{obs}t.$$

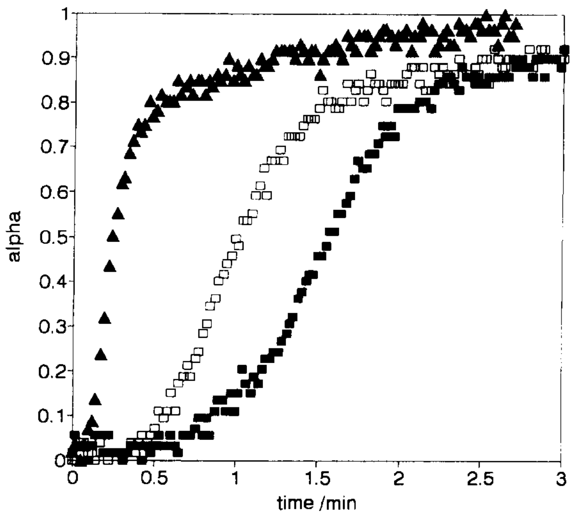


Fig. 6. α vs. time curves obtained at 313 K and (a) 120 mmHg, (b) 97 mmHg and (c) 82mm Hg of 1,3-dioxolane. ■ – 82 mmHg, □ – 97 mmHg and ▲ – 120 mmHg.

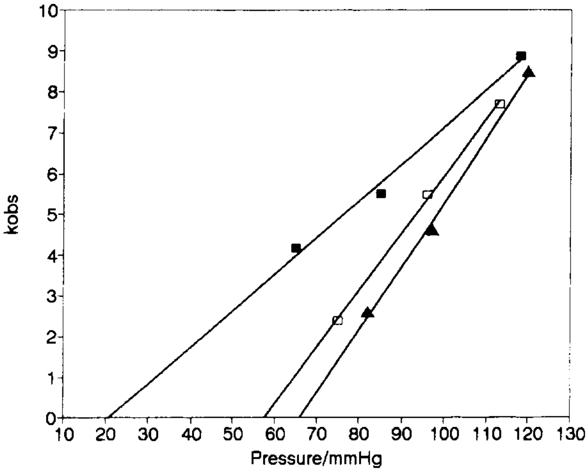


Fig. 7. A plot of k_{obs} vs. p P(1,3-dioxolane). ■ 303 K, □ – 308 K and ▲ – 313 K.

From a plot of k_{obs} vs. the pressure of the guest, yielding a straight line, for each temperature, the threshold pressure, P_0 and the rate constant, k_f can be obtained. In Fig. 7 these curves are shown for three different temperatures, 303, 308 and 313 K. The results summarised in Table 1, confirm the existence of a threshold pressure, P_0, below which the absorption reaction does not takes place. This has also been confirmed experimentally. Using this treatment, the rate constants k_f do increase with increasing temperature and a plot of $\ln k_f$ vs. $1/T$ approximated linearity.

Table 1

Temperature (K)	P_0 (mmHg)	k_f (min^{-1}) (from slope)	k_f (min^{-1}) (from intercept)
303	21	1.9(1)	1.9(4)
308	58	8.1(2)	8.1(1)
313	66	10.6(2)	10.4(3)

An activation energy of 1.4(5) × 10^2 kJ mol^{-1} was obtained for the inclusion reaction.

5. Conclusions

A multiple probe QMB was designed for the simultaneous investigation of sorption reactions between various host compounds and the same guest vapour. This apparatus has been successfully used to study the kinetics of formation of a 1 : 1 inclusion compound between 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene and 1,3-dioxolane.

The advantages of this system are:

- Each crystal requires very small quantities of host compound (approximately 100–500 μg).
- With multiple crystals, one can simultaneously test the selectivity of several host compounds for a given guest.
- In many cases it will be possible to study the reverse reaction, by raising the temperature and pumping out the cell.
- Real-time graphical display of the change in frequency and pressure.

The major disadvantage of this apparatus is that the QMB uses such small samples that it is not possible to monitor the *X*-ray diffraction patterns of the material. In case where bulk analyses of the samples are required the levitation balance designed for the study of guest uptake in controlled atmospheres [8] still has to be used. Another disadvantage of using such small samples is that the signal to noise ratio is fairly low. This system is ideal for preliminary investigations. One can easily establish whether a given host includes the guest under investigation, without using much sample. The instrument could be extended to measuring analytes in solutions. This will require special coating techniques of the host on the quartz crystal to ensure durability.

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