A Technique for the Measurement of the Water Adsorption of Small Amounts of Hygroscopic Materials. Water Adsorption Isotherm of Polyglycine

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A technique for the measurement of the adsorption of water vapour by films of hygroscopic materials is described. The basis of the technique is the use of a resonating quartz crystal which is coated with the material to be investigated. The resonant frequency of the quartz crystal is lowered when mass is added to the crystal, and the adsorption of water vapour is followed by measuring the change in frequency of the crystal. The response of the quartz crystal to mass has been determined and other factors affecting the frequency of the crystals have been investigated. Finally the water adsorption isotherm of polyglycine has been determined at 31·5°C and compared with data in the literature.

THE use of resonating quartz crystals to measure small masses has been known for some time. Instruments using these crystals are available commercially for the measurement of rate of vacuum deposition of metals. Coated quartz crystals have also been used for the detection and estimation of gases in the atmosphere[1]. As far as the author is aware this is the first time that this technique has been used to measure water adsorption isotherms.

The details of the technique are given in the experimental section. Briefly, the advantages of this technique over conventional beam balance techniques are the sensitivity of the method – masses of the order of nanograms can be measured; and the freedom of the technique from such environmental factors as levelling and electrostatic interference.

The main disadvantage of the technique is that the substance whose adsorption isotherm is to be obtained must be evenly distributed and adhered on the quartz crystal. This is usually achieved by dissolving the substance in a solvent, spreading the resulting solution on the quartz crystal, and evaporating off the solvent to leave an even film of solid.

THEORY

The natural frequency of a quartz resonator plate excited to thickness shear vibration is extremely sensitive to changes in the quartz environment. For example, the frequency will change if the plate is coated with a film of foreign material; if it is heated (or cooled); or if the gas pressure around the quartz plate is changed. Depending on the angle the quartz plate makes with the crystallographic axis of the quartz, plates can be prepared which are either predominantly mass or predominantly temperature sensitive. The frequency of plates cut at 35° to the crystallographic axis (AT plates[3]) is very sensitive to mass, whereas the frequency changes due to changes in temperature and gas pressure are very small (see experimental section). For

AT cut plates the mass of the added material is proportional to the corresponding frequency change[2]. The constant of proportionality can be calculated from the natural frequency of the quartz resonator, thus eliminating any empirical determinations.

The thickness shear vibration of a quartz plate is a standing transverse wave. For the fundamental mode, the thickness of the plate, d, is equal to half the wavelength. Thus the natural frequency f is given by

$$f=V_{tr}/2d=N/d \tag{1}$$

where V_{tr} is the velocity of propagation of the transverse wave in the direction of the plate thickness and N is the frequency constant. The velocity of propagation, and thus N, is, in the case of quartz, dependent on the crystallographic direction. For AT cut plates[4] the frequency constant $N=1\,670$ kHz mm.

Differentiating equation (1) gives

$$\Delta f/f=-\Delta d/d \tag{2}$$

where Δf is the change in frequency caused by the small change in thickness Δd, and since

$$\Delta d=\Delta m_q/A\rho_q \tag{3}$$

where m_q, A and ρ_q are the mass, the area and the density of the quartz plate, respectively.

$$\Delta f/f=-\Delta m_q/A\rho_q d \tag{4}$$

However, the surface quartz layers affect the natural frequency only because of their inert mass[2], and consequently a thin film of foreign material on the plate affects the natural frequency of the plate in the same way as a layer of the quartz plate of equal mass. That is, Δm_q can be replaced by Δm where Δm is the mass of the added film,

$$\Delta f/f=-\Delta m/A\rho_q d \tag{5}$$

Introducing the frequency constant $N=fd$

$$\Delta f=-f^2\Delta m/A\rho_q N \tag{6}$$

$$\Delta f=-C_f\Delta m/A \tag{7}$$

where C_f is the sensitivity for mass determination and is equal to $f^2/N\rho_q$.

For the AT cut quartz crystals used in this work, the fundamental frequency of oscillation is 6 MHz and using the values $N=1\,670$ kHz mm and $\rho_q=2{\cdot}65$ g cm^{-3} for quartz,

$$C_f=8{\cdot}13\times10^7\ \text{Hz cm}^2\ \text{g}^{-1}$$

or a change in the frequency of 1 Hz corresponds to a mass change of approximately 20 ng.

EXPERIMENTAL

The apparatus shown schematically in *Figure 1*, consists of the crystal controlled oscillator circuit and power supply which excite the quartz crys-

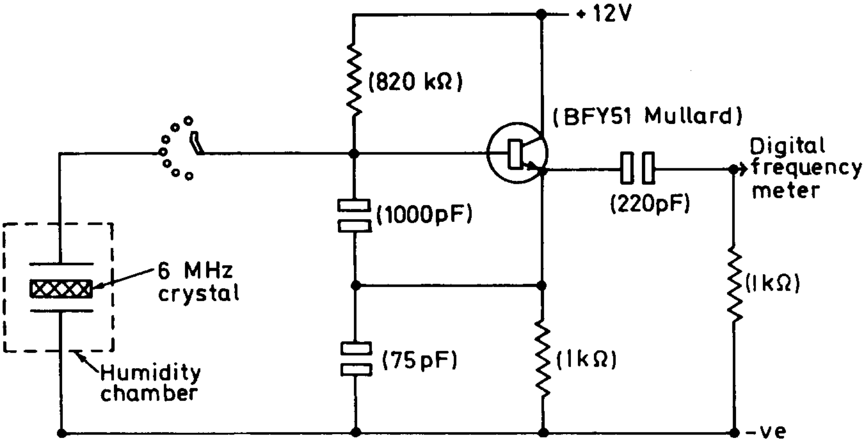

Figure 1—Schematic diagram of the apparatus, showing oscillator circuit, quartz crystal and humidity chamber

tal; the resonating quartz crystal onto which the films are cast; the constant temperature/humidity chamber in which the crystals are placed; and the frequency measuring device which indicates the frequency of the resonating crystal.

The oscillator circuit is shown in *Figure 1.* The 12 V power supply is provided by two 9 V Ever-Ready PP10 power packs connected to the circuit through a 30 kΩ potential divider. The quartz crystals are 6 MHz AT quartz blanks from Standard Telephones and Cables Ltd and measure approximately 13 × 13 × 0·25 mm. The anti-nodal region is confined to the centre of each of the two largest faces, and most of this mass sensitive area is covered with two gold electrodes, one on each side, which are vacuum deposited onto the quartz crystal. The gold covers about 20% of the total quartz crystal surface and films are cast onto this gold/quartz surface. The crystal is secured at two corners in a crystal clip (Marconi B114) which is plugged into a PTFE socket (Marconi), and this assembly is soldered to two silver wires which are sealed into a B19/34 Quickfit convertor with Araldite. This then forms the stopper for a series of conical 500 ml B34 flat bottomed flasks, which act as humidity chambers.

A constant temperature air enclosure is provided for the oscillator circuit and the constant humidity chambers. This is a large wooden insulated box (15 × 24 × 27 in) (381 × 610 × 686 mm) the temperature of which is controlled to ±0·1 degC by means of a contact thermometer, a 100 W light bulb and two small circulating fans. Constant partial pressures of water vapour are provided[5] in the 500 ml flat bottomed flasks using the following systems at 31·5 ± 0·1 °C:

GPR Phosphorus pentoxide (vacuum, 5×10^{-2} mmHg — 0 % relative humidity
GPR Lithium chloride (satd. soln) — 11·7% relative humidity
AR Magnesium chloride (satd. soln) — 31·6% relative humidity
AR Sodium chloride (satd. soln) — 75·0% relative humidity
AR Potassium nitrate (satd. soln) — 92·0% relative humidity
Triple distilled water —100 % relative humidity.

The frequency measuring device is a 100 MHz digital frequency meter (Racal type 801R) which displays frequency to 1 Hz (sampling time 1 s) or to 0·1 Hz (sampling time 10 s). Between the oscillator circuit and the digital frequency meter there is a six-position switch. Six quartz crystals are connected to this switch and the frequency of each can be determined in turn. Since it is not necessary to monitor the frequency of an individual crystal continuously (except in kinetic experiments) it is possible to have six adsorption experiments in progress at the same time.

Experimental procedure for measuring adsorption

The film whose water adsorption isotherm is to be determined is cast on all six sides of the gold plated quartz crystal. This is done by immersing the whole crystal in a solution of the polymer and then evaporating off the solvent. Electrical contact is maintained by casting the film over the supporting clips so that the clips are in electrical contact with the gold electrodes. Because only the anti-nodal area of the quartz plate is affected by mass, the position of the clips is not critical.

The mass of dry film on the quartz crystal is determined by measuring the difference in frequency between the uncoated crystal and the coated crystal, both measurements being carried out in the vacuum flask containing phosphorus pentoxide. The coated crystal is then transferred to the 500 ml flask containing saturated lithium chloride solution. At equilibrium the frequency is noted and the coated crystal is then transferred in turn to each of the other chambers in order of increasing relative humidity. In this way the water adsorption of several different masses of film from zero to several micrograms is determined.

There are two sources of error in this work. The first, which is always ±1 Hz, arises from reading the frequency. As a percentage this error varies with film thickness and can range from ±2·5% for very thin films at low humidities (where the uptake of water is small) to ±0·05% for thicker films at high humidities. However, accuracy can be improved at low humidities by using thicker films, and in this work errors due to frequency reading at 11·7% relative humidity are less than 0·5%. The second error arises from the variation of relative humidity with temperature. The temperature of the humidity chambers is 31·5±0·1°C, and over this temperature range the percentage change in humidity is less than 0·05% for all the saturated salt solutions used[5].

RESULTS

The change in frequency on adding known masses to the quartz crystal has been determined for a range of materials. Graphs have been plotted of added mass against change in frequency, for masses greater than 10 μg. Straight lines through the origin are obtained in every case. From the slope of the line and the area, A, of the crystal (1·595 cm^2), C_f the sensitivity for mass determinations has been calculated using equation (7). *Table 1* shows the materials used, the value of C_f for each material, and the loading at which deviation from linearity of Δf versus Δm occurs.

Polyglycine was deposited from 0·1% dichloroacetic acid solution and the silicone oil from 0·4% trichlorethylene solution. The mass of these

Table 1

Material	$C_f \times 10^{-7}$ *(Hz cm² g⁻¹)*	*Added mass above which deviations from linearity occur (μg)*
Polyglycine	7·99	300
Silicone oil (MS 200)	7·72	100
Copper	8·36	500

solvent-free films was determined by weighing the coated crystals on a Cahn RG electrobalance. The mass of copper deposited from copper sulphate/sulphuric acid solution was determined from the current and the time of deposition.

The agreement between the experimentally determined and the calculated values of C_f are very good considering the difficulty in spreading even films over the quartz crystal. It does appear therefore that the frequency of the quartz crystal is affected only by the mass of the added material in the ranges indicated.

The effect of temperature and pressure on the frequency of the quartz crystal has been determined. The coefficient $\Delta f/\Delta T$ over the range 30-33 °C is 0·5 Hz degC^{-1}. The uncertainty in frequency measurements due to fluctuations in temperature of the thermostat is therefore 0·1 Hz.

On transferring the quartz crystal from vacuum (5×10^{-2} mmHg) to dry air at atmospheric pressure the frequency change was between +3 and +4 Hz. This compares with values of +2·7 Hz and +3·9 Hz for argon and neon respectively[6]. Consequently in this work a correction of +4 Hz has been added to all frequency measurements made in vacuum, in order to convert them to a standard pressure of 760 mmHg.

From the above considerations it can be stated that if the temperature and pressure of the environment enclosing a coated AT cut quartz crystal are controlled, any frequency changes are due to changes in mass of the coated crystal.

Water adsorption of polyglycine

Polyglycine (supplied by Dr M. Bradbury, Portsmouth Polytechnic) of an undetermined molecular weight, was dissolved in dichloroacetic acid (1% w/v), and deposited on the quartz crystal by solvent evaporation. Trapped solvent was removed by soaking in water for 10 min and drying in an oven at 102 °C.

The infra-red spectrum of films of polyglycine, deposited on a silver chloride plate from dichloroacetic acid, was recorded on a Perkin-Elmer 225 grating spectrophotometer. *Table 2* shows some of the bands obtained at room temperature and, for comparison, bands for samples of polyglycine (I) and (II), also at room temperature[7]. There is no evidence of Amide I, II and V bands at 1 640, 1 550 and 750 cm^{-1} respectively, which are characteristic of polyglycine (II). The films as deposited in this work thus appear to be predominantly in the extended polyglycine (I) configuration.

The experimental procedure outlined in the previous section was followed. Because of the very thin films of polyglycine used in this work equilibrium

Table 2. Comparison of IR data of a film of polyglycine on a silver chloride plate with samples of polyglycine (I) and (II)

Assignment	*Wavenumbers* (*cm*$^{-1}$)		
	Polyglycine film on AgCl	*Sample of polyglycine (I)*	*Sample of polyglycine (II)*
Amide A	3 295	3 295	3 290
Amide B	3 070	3 075	3 090
CH_2 stretch	2 925	2 920	2 977
		2 850	2 935
			2 850
			2 805
Amide I	1 628	1 624	1 640
Amide II	1 522	1 520	1 550
CH_2 bend	1 431	1 432	1 414
Amide V	701	708	750

at any relative humidity is usually reached within 12 h. After 12 h at any relative humidity no detectable weight changes were noted over a period of two weeks. Three quartz crystals and a range of thicknesses of polyglycine films were used. *Figure 2* shows the total uptake of water (in μg) by the quartz crystal plus film for different masses (in μg) of film at several relative

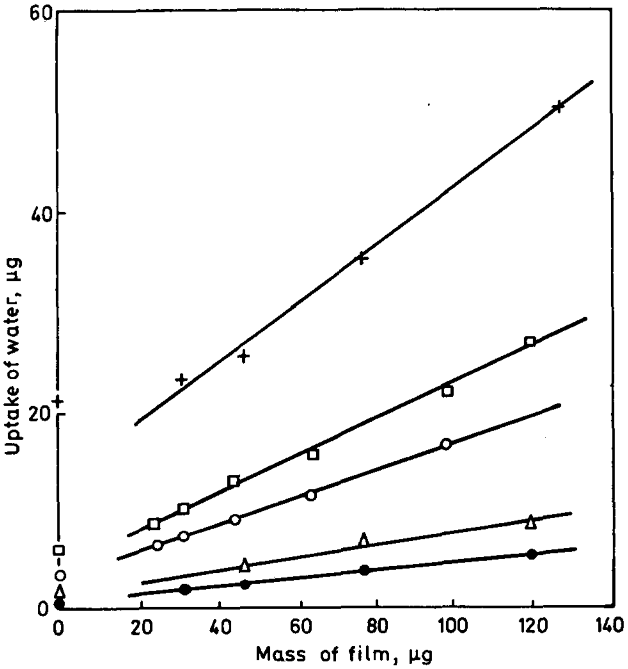

Figure 2—Uptake of water vapour by crystal plus polyglycine film versus mass of polyglycine film.
+, 100%; □, 92·0%; ○, 75·0%; △, 31·6%; ●, 11·7% relative humidity.
The points on the vertical axis correspond to the water adsorption of the uncoated quartz crystal

humidities. The linearity of the graphs indicates that the whole mass of polyglycine film is available to water vapour at all relative humidities. The intercepts on the uptake of water axis correspond to the adsorption of water by the crystal itself at each humidity. These intercepts calculated by the method of least squares, however, do not correspond to the measured adsorption of water by the quartz crystal, the measured values invariably being greater than the values indicated by the intercepts. This may be due to an interaction between the polyglycine and the gold plated quartz crystal whereby some of the water adsorption sites of the crystal are blocked.

The slopes of the graphs of *Figure 2* corresponding to the uptake of water per unit mass of polyglycine together with the adsorption expressed in moles of water per mole of glycine are given in *Table 3*. Also for comparison in *Table 3* are given the results of Mellon, Korn and Hoover[8] on the adsorption of water by the methyl ester of polyglycine at 30°C using a conventional balance.

Table 3. Uptake of water by polyglycine

Relative humidity (%)	*Slope of graph of uptake versus mass* ($\mu g\ H_2O / \mu g$ *polyglycine*)	*Molecules of water per mole glycine* *This work*	*Ref. 8*
11·7	0·0355	0·112	0·110
31·6	0·0628	0·199	0·209
75·0	0·1336	0·423	0·431
92·0	0·1843	0·584	0·592
100	0·2850	0·903	

The agreement between the two sets of results is very good. As expected the very slight differences in the polyglycine samples used had no effect on the water adsorption. The value for the uptake of water by polyglycine at 100% relative humidity indicates that, at this humidity, approximately one water molecule is associated with each peptide group.

CONCLUSIONS

The quartz crystal technique of measuring water adsorption has been shown to be reliable and simple to use. The technique is extremely mass sensitive (less than 0·5 mg of polyglycine was required for this work) which makes it a useful technique for materials which are difficult to obtain in large quantities.

The technique can also be used to measure the kinetics of water adsorption and desorption, because the frequency of the crystal and the corresponding mass changes of the coated crystal can be monitored continuously.

Because of the simple shape of the quartz crystal and the method of measuring the water adsorption of films of polymer it is possible to study the effect of secondary structure on water adsorption. Polymer films may either be deposition from solution (the solvent determining the configuration of the polymer), or multiple layers of polymer may be built up on the crystal by immersion and withdrawal through oriented polymers spread on a Langmuir trough.

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