AN AUTOMATED ADSORPTION ISOTHERM DEVICE

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ABSTRACT A device is described for the automated determination of the water adsorption isotherms of biological materials. The vapor pressure and weight of the adsorbate are measured directly with appropriate transducers, and equilibrium is defined on the basis of constant pressure. The accuracy of the device, determined on two samples with well-known water binding properties, is ±5%. Automation is achieved by electronic control.

INTRODUCTION

The determination of the gas adsorption properties of materials has long been a useful way to study the surface of such adsorbents. In particular, from a biological point of view, the adsorption isotherms of water bound to macromolecules and larger cellular structures have been of special interest (1–3). Usually some description of the adsorbing surface is possible and water binding is defined in terms of thermodynamic parameters such as enthalpy, etc.

The actual determination of the adsorption isotherm in the case where water is the adsorbate has been, in general, a somewhat tedious, time-consuming affair. Weighed amounts of adsorbent have been exposed to different humidities maintained in closed containers by the use of various saturated salt solutions. The uncertainty of knowing when equilibrium is reached usually results in allowing lengthy equilibration times.

In this paper, we describe an apparatus which uses electronic circuitry to monitor the approach to equilibrium and a sample holder designed to decrease equilibration time. The device consists of an adsorption chamber containing a pressure transducer and a weight transducer so that at any time, the vapor pressure and the total weight of adsorbent and water adsorbed may be measured. The electronic controller determines equilibrium conditions and permits addition or removal of water from the chamber.

ADSORPTION CHAMBER

The chamber, illustrated in Fig. 1, consists of two parts, both made of 7440 Pyrex glass, which can be fitted together using a rubber "O-ring" and a clamp. The chamber is cylindrical in shape and has a volume of approximately 230 cm^3. Inside the lower part is mounted a weight transducer with a range of 10 g (Type FTA A, Schaevitz Engineering, Pennsauken, N.J.). Electrical connections to the outside are made via Kovar leads through the wall of the chamber. The upper half of the chamber is attached to a metal

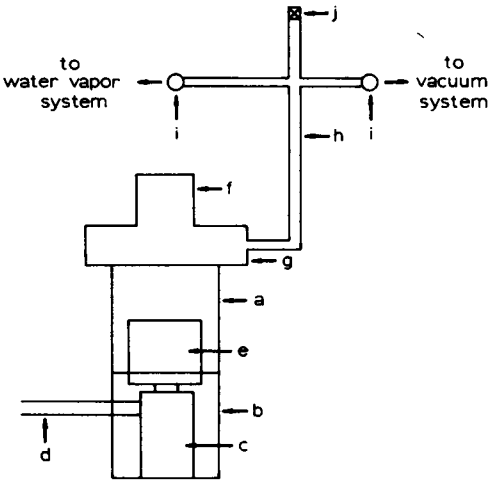

FIGURE 1 Diagram of the adsorption chamber showing *a*, upper half; *b*, lower half; *c*, weight transducer; *d*, electrical leads enclosed in rubber tubing; *e*, sample holder; *f*, pressure transducer; *g*, housing containing glass to metal seal; *h*, metal tubing, *i*, solenoid valves; and *j*, manual valve.

housing containing a pressure transducer (Type PTA 3, Schaevitz Engineering) with a range of 0–50 mm Hg. Both transducers are operated with signal conditioning modules (SCM-025, Schaevitz Engineering) which have circuitry to compensate for temperature changes in the transducers. The metal housing is connected to a vacuum system and to a container of water (liquid and vapor in equilibrium) via metal tubing and two separate solenoid valves (no. 8262C90 VH, Automatic Switch Company, Florham Park, N.J.). During the course of an experiment the chamber and water vapor container are immersed in a water bath maintained to within ±0.1°C.

ELECTRONIC CONTROLLING UNIT

The main task of this unit is to monitor constantly the pressure transducer output voltage, so that a "constant pressure" equilibrium can be detected. The reader is referred to Fig. 2, the control system block diagram. Normally, a run begins with a fully hydrated sample in thermal equilibrium with water vapor. A "manual start" command activates the electronic clock (K303, K210) (Digital Electronics Corporation, Maynard, Mass.) and sets the unit into the desorption or "down" mode. The clock is used to increment the controller logic through a repetitious cycle until equilibrium is reached. The clock frequency is adjustable from 1 ms to 48 s and is selected to obtain desired measuring resolution. In the "down" mode, the vacuum system valve is opened for a preset time which is manually adjustable from 3 s to 40 min. When the valve has closed, the clock pulses cycle the sample and hold (S&H) circuits (Model SHA III, Analog Devices, Cambridge, Mass.) in chronological sequence with each S&H storing a pressure related voltage. At the first clock pulse, S&H 1 samples the voltage, V_p, and stores its value. S&H 2 samples the voltage, V_p, at the second clock pulse, and S&H 3

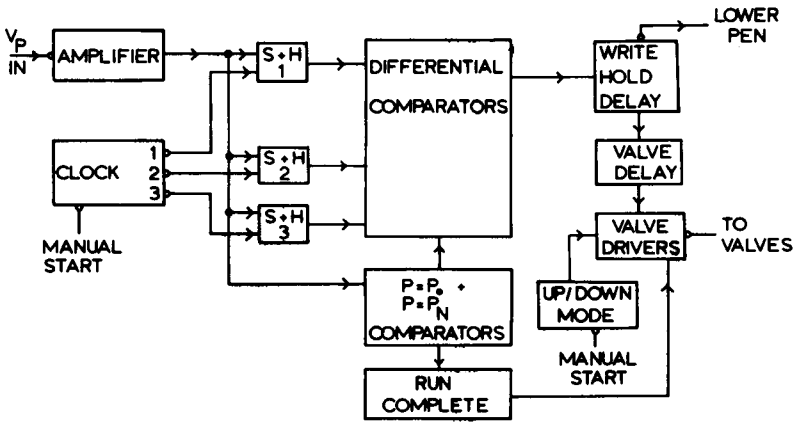

FIGURE 2 Electronic control system block diagram. The arrows indicate the direction of major information flow.

at the third pulse. At this point the differential comparator (Lutronix Consulting Services, Berlin, Conn.) is used to compare, in pairs, the S&H stored voltages. If the differences between all three voltages are within a preset, minimal range, an equilibrium condition is assumed and the clock is inhibited for data taking. If not, S&H is reactivated by clock pulse no. 4 to store another voltage, and so on, until all three S&H circuits store similar voltages. At equilibrium, the "write hold," (K303, K614; Digital Electronics) is activated to lower a pen on an X-Y recorder and record voltages corresponding to the equilibrium vapor pressure (Y) and the weight (X). After the data are recorded, an appropriate valve is opened for a given time (via K614; Digital Electronics) (vacuum system valve in the desorption mode; water vapor system valve in the adsorption mode), and the clock is restarted to repeat the cycle. In addition to equilibrium tests, the pressure-related voltages are also compared with preset voltages P_0 and P_N. When the equilibrium pressure voltage equals P_N, a system mode transfer is automatically made from "down" (desorption) to "up" (adsorption). When the equilibrium pressure equals p_0, the run is complete and terminated by inhibiting the clock.

ADSORPTION ISOTHERM SAMPLES

Samples are dissolved in either chloroform or water. Weighed Pyrex wool sheets (2.5 cm square) are soaked in these suspensions and then dried to constant weight. The sheets with sample are then attached to a metal holder and placed inside the sorption chamber where they are screwed in place on the weight transducer. Usually four sheets, each containing 150–200 mg of sample, were employed.

The water binding capacity of the Pyrex wool sheets was examined *in situ* at two temperatures (20° and 34°). It was found that they adsorbed only a few milligrams of water at most—approximately the error limits of the weight measurement.

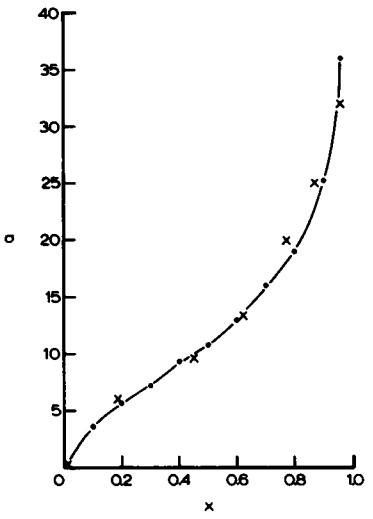

FIGURE 3

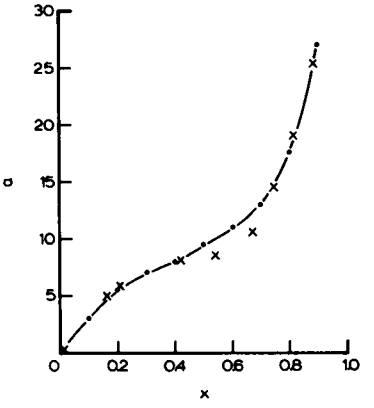

FIGURE 4

FIGURE 3 Comparison of the desorption isotherm of egg albumin obtained using the automated device (X—X) with the literature values (•—•) of Bull (2). Hydration *a*, grams water per 100 g adsorbent, is plotted vs. the relative vapor pressure.

FIGURE 4 Comparison of the desorption isotherm of egg lecithin obtained using the automated device (X—X) with literature values (•—•) of Elworthy (3). The abscissa and ordinate are as in Fig. 3.

CALIBRATION AND ACCURACY

The weight and pressure transducers were calibrated against known weights and an oil-filled manometer, respectively, at several temperatures between 5° and 50°C. There was no measurable hysteresis in either transducer. (The output voltages were measured with a digital voltmeter accurate to one part in a thousand.) There was no measurable effect of temperature on the slopes calculated from plots of output voltage vs. calibration weight or pressure. Regression analysis of these plots indicated that the 99% confidence interval of the pressure measurements was ±1% of the slope and ±4% for the weight measurements. The latter was a larger error because only a part of the total range of the weight transducer was used and this part was amplified electrically.

To test the accuracy of the whole device, two samples were prepared and their isotherms determined. They were egg lecithin and ovalbumin, whose water binding properties had been investigated by others (2, 3). Equilibration times measured in this apparatus were found to be no more than 4 h despite the large samples required (500 mg to 1 g) probably because of the large surface area afforded the water vapor due to the Pyrex wool sheets. A comparison of isotherms measured with this device with literature data is to be found in Figs. 3 and 4. They show that the accuracy of the automated unit is ±5%. All hysteresis effects were smaller than this error.

It is believed that the overall error could be easily decreased by the use of a more sensitive and stable weight transducer. Despite efforts to keep the signal conditioning modules at constant temperature, there was a significant drift problem resulting in the error limits above. Substitution of a pressure transducer with a different range should permit use of this apparatus with gases other than water vapor.

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