NETSUSOKUTEI 10(2) 48–52 (1983)

Design and Testing of a Calorimeter for Studies of Water Vapor Sorption on Biological Materials

Kisook Kim, Teruyuki Fujita, and Seiich Hagiwara*

(Received July 23, 1982)

A gas adsorption calorimeter has been remodelled for use in studies of water vapor sorption on biological materials.

Major modifications on a sorption vessel and a water vapor delivery system were made on a commercially available calorimeter. The time constant of the calorimeter response is 2 min and the heat effect sensitivity is about 0.12 μV/μW.

Test experiments which include electrical calibration and measurements of water vapor sorption on potato starch indicate that the calorimeter is available for studies on the physical properties of water in biological materials.

1. Introduction

The state of water in biological materials plays an important role in their function and structure[1]. Most foods are derived from biological materials and physical properties of water in foods closely relate to the quality of foods[2] and their preservation.

Thus far, studies on properties of water in biological materials have been investigated by using sorption isotherm[3,4], DSC[5] and NMR[6,7] etc. but calorimetric measurement of the heat of water vapor sorption has been rarely carried out. It may be due to the fact that the amount of water vapor sorbed on biological materials is large when compared with those of other gases, and it takes long period to establish the sorption equilibrium. In addition, it is difficult to determine the exact amount sorbed in the sample since water vapor is also adsorbed on the inner surface of the sorption assembly including the branched glass tube and sorption vessels.

Design and testing of a sorption calorimeter modified to meet these conditions are described in this paper. The main purpose of the instrument is to provide a convenient analytical tool for studying the state of water in biological materials. In connection with the testing of the instrument, measurements have been made on the heat of sorption of water vapor on potato starch.

The Institute of Applied Microbiology, University of Tokyo, Bunkyo-ku, Tokyo 113, and *Tokyo Riko Co., Ltd, Tokyo

2. Experimental

2.1 Calorimeter

The calorimeter for studies of water vapor sorption has been modified from the gas adsorption calorimeter (MPC-11, Tokyo Riko Co.,) of which construction was based upon the design of earlier calorimetric equipment[8] (GAC-2, Tokyo Riko Co.,). The sorption block of the calorimeter is shown in Fig. 1. The major modification of the calorimeter involved the design of a sorption vessel and the substitution of a gas delivery system for a water storage bottle which supplies water vapor and is placed in the heat sink. The sorption block was placed in the thermostated bath which regulates the temperature of the heat sink within ±0.005°C. The thermopile plate which was used is a semiconductor thermoelectric module with a temperature sensitivity of about 30 mV/°C.

Fig. 2 shows the sketch of the modified sorption assembly. The sorption assembly is fixed to the underside of the lid of the heat sink. It is constructed of a glass tube, sorption vessels and a water storage bottle. The water storage bottle is made of glass with a working volume of 25 cm^3

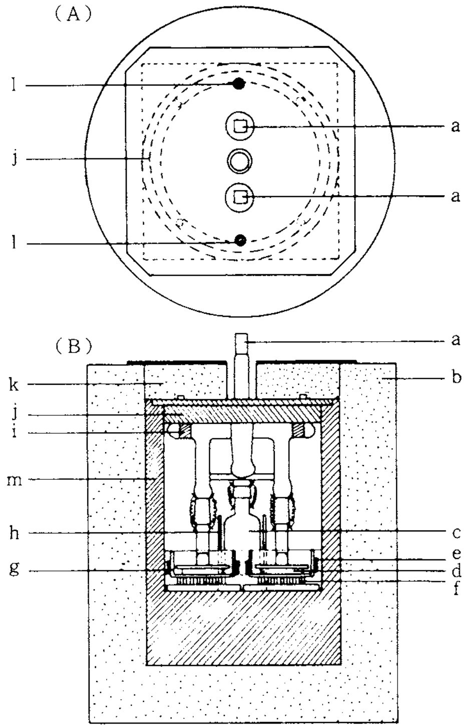

Fig. 1. Sorption block of the calorimeter.
(A) top view, (B) cross section;
a) stopcock, b) insulation, c) water storage bottle, d) sorption vessel, e) heater, f) thermopile plate, g) vessel holder, h) water storage bottle holder, i) glass tube supporter, j) aluminium lid of heat sink, k) insulation lid, l) screw, m) heat sink.

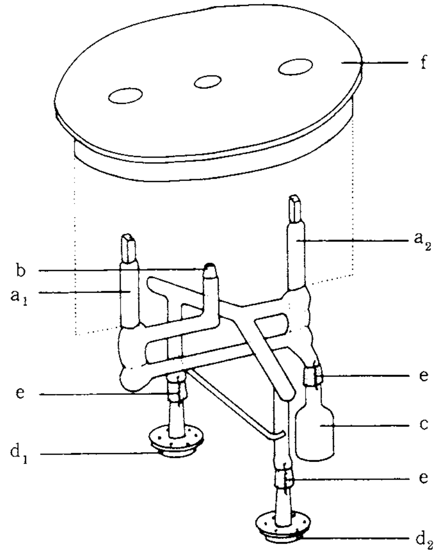

Fig. 2. Sketch of the sorption assembly.
a_1) stopcock which connects a water storage bottle to a connecter (b), a_2) stopcock which connects a water storage bottle to two vessels, b) connecter to a vacuum line, c) water storage bottle, d_1) reference vessel, d_2) sample vessel, e) connecting wire spring, f) aluminium lid of heat sink.

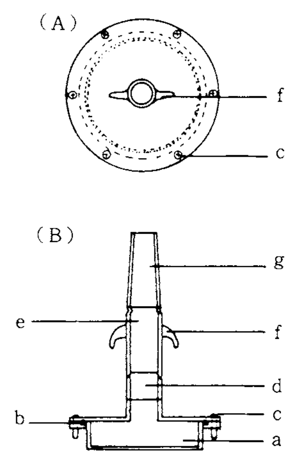

Fig. 3. Sorption vessel.
(A) top view, (B) cross section;
a) vessel, b) O-ring, c) bolt, d) Kovar tube, e) glass tube, f) hook, g) taper joint.

and is usually filled with 10 cm^3 of water. It is connected to the glass tube by a taper joint and supplies the water vapor in place of a gas delivery system placed outside the calorimeter.

Fig. 3 shows the sorption vessel which is made of stainless steel with a working volume of 7 cm^3. The vessels are closed with bolts and an O-ring to make it easy to open for operation. The vessels are attached to the glass tube with a taper joint and fixed by means of springs.

2.2 Procedure

Test material used in this experiment was potato starch (Practical Grade, Wako Pure Chemical Ind. Ltd.) without further purification.

Prior to the sorption experiments, samples were dehydrated in a vacuum in a desiccator containing P_2O_5 for a day and the water content was determined. Samples thus prepared were placed on a pan made of aluminium foil. The same pan without sample was put in the reference vessel. Since the weight of the aluminium pan is less than that of the samples, small changes in the weight of the samples could be determined. Weighing was reproducible to within 0.1 mg.

Prior to evacuation, the vessels and a glass stopper were connected to the glass tube and evacuated for the desired time. During evacuation the water storage bottle was replaced by the glass stopper and the two stopcocks were opened. After evacuation, the stopcocks were closed and the glass stopper was replaced with the water storage bottle.

After a small amount of paraffin oil was put into the holder to facilitate heat exchange, the assembly was placed in the proper position in the heat sink. After temperature equilibration, about 2 h, the sorption experiment was started by opening the stopcock which connects the sorption vessel to the water storage bottle.

When sorption was terminated, determination of the quantity of water vapor sorbed was made by weighing the samples and measuring water content before and after the calorimetric experiment. The water content was measured as the weight decrease after heating for 5 h at 105°C under atmospheric pressure in the air and expressed as the ratio of weight to dry matter.

3. Results and discussion

3.1 Electrical calibration

The electrical calibration data were obtained by electrical heating at a known power for different periods. The results are shown in Fig. 4. A calibration heater is wrapped around the outer surface of the vessel holder. The experiments were made on 100 mg of potato starch. Results shows that

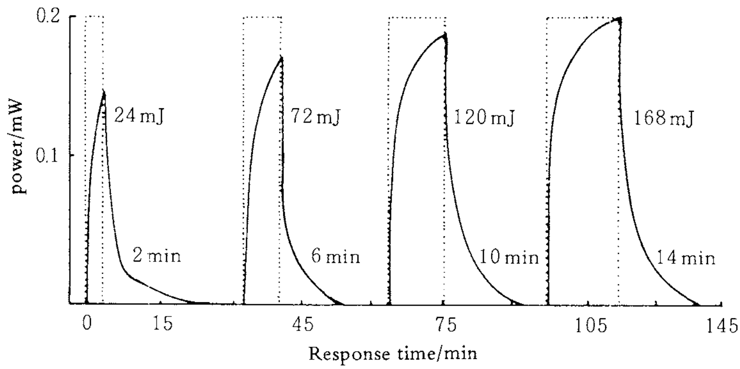

Fig. 4. Calorimetric records given by a constant power heating for different periods.
—— observed curve; ----- heat input.

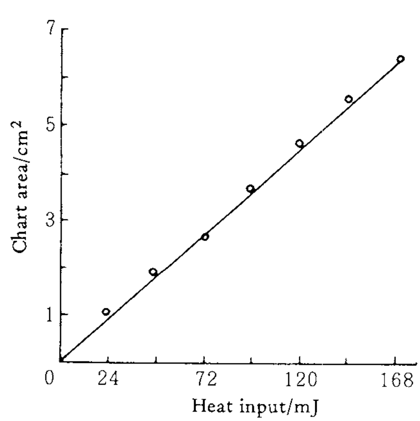

Fig. 5. Relationship between the chart area and the heat input.

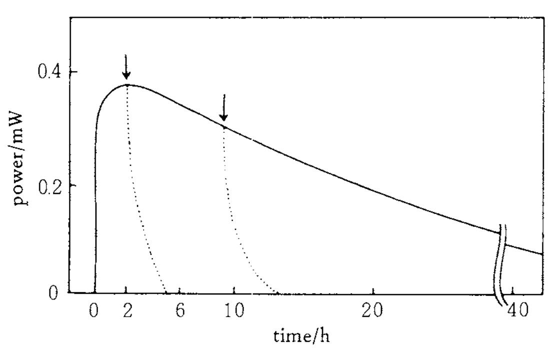

Fig. 6. Heat production curve of water vapor sorption on potato starch at 30°C.
—— continuous sorption curve;
----- sorption curve when sorption was stopped at the time marked by the arrow, resultant water contents after 2 h and 9 h were 3.30% and 6.53% respectively.

the thermal lag of the instrument affects the time course of the record. The rising part of the recorded curve is approximately exponential with a time constant of 2 min.

As shown in Fig. 5 the relationship between the chart areas under the calorimetric records and the heat input is linear. From the results of repeated calibration experiments, the sensitivity of the calorimeter for slow heat effect was about 0.12 μV/μW. The drift of a base line during a 24 h period was less than ± 0.5 μV.

3.2 Performance of the calorimeter

The performance of the calorimeter was tested by measuring the heat of water vapor sorption on 100 mg of potato starch. Fig. 6 shows a typical heat production curve of water vapor sorption on potato starch at 30°C. The maximum heat production occurred approximately after 2 h and then gradually decreased. It did not return to the base line even after more than 40 h (—— curve). Therefore, the heat of sorption on samples having various water contents was measured by closing the stopcock at the appropriate time. In Fig. 6, the sorption was interrupted by closing the stopcock after 2 h and 9 h then the heat production decreased exponentially (---- curve).

The integral heat of sorption on potato starch with various water contents was estimated from the chart area under the heat production curve by using the above method (Fig. 7).

Fig. 8 showed the differential heat of water vapor sorption on potato starch ($-\Delta H$) calculated from the slope of the plotted curve in Fig. 7. The slope was estimated from the increment of the integral heat for water content of 1% taken from 0.5% of either side of the desired point. The curve of differential heat of sorption obtained in this study has the similar pattern to that estimated by the temperature dependence of sorption isotherm of starch[9]. As shown in Fig. 8, the molar differential heat of sorption for the potato starch with a water content of 12% and above is almost equal to the heat of vaporization of pure water (43.8 kJ/mol), while it increases with decreasing water contents in the range below 12%, suggesting that water molecules in this range are bound to the potato starch with larger amounts of interaction energe as compared with those in the bulk liquid state.

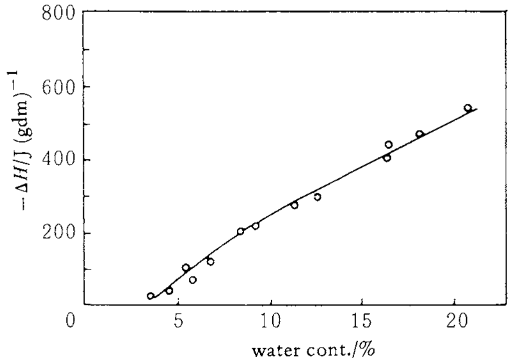

Fig. 7. Relationship between integral heat of sorption and water content of potato starch at 30°C.
gdm here is gram of dry matter.

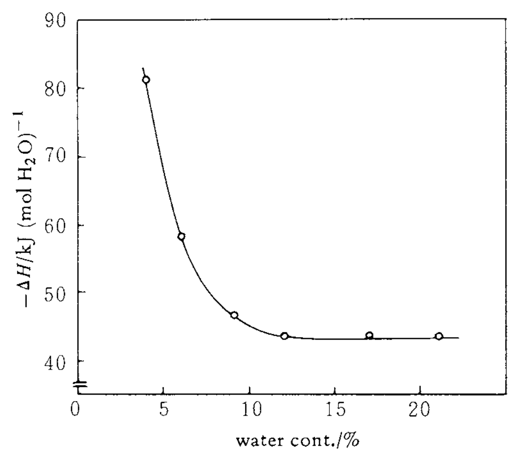

Fig. 8. Molar differential heat of water vapor sorption on potato starch at 30°C.

The devices adapted to the calorimeter offer a convenient method for measuring the heat of sorption and provide information about the physical properties of water in biological materials for both analytical and thermodynamic studies.

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