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APPARATUS FOR THE ACCURATE  
DETERMINATION OF THE ISOTHERMS  
FOR WATER VAPOUR SORPTION IN FOODS

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CONTENTS

	page
1. Introduction . . . . .	1
2. Construction . . . . .	2
3. Principle of operation . . . . .	4
4. Accuracy of results . . . . .	5
5. Conclusion . . . . .	8
6. References . . . . .	9

I. INTRODUCTION

The isotherm for water vapour sorption (abbreviated: isotherm) of a material represents the relation between its water content and its wateractivity ( $a_w$  or 0.01·erh) at constant temperature.

Isotherms are very important characteristics of all hygroscopic materials that are to be preserved and stored. Especially for foods and other biological materials knowledge of the isotherm is a main prerequisite for processes such as drying, mixing, packing and storage. Moreover isotherms are of theoretical importance: after assumption of a model for the sorption mechanism, physical and thermodynamic quantities can be calculated from the isotherm.

One problem in interpreting isotherms for biological materials is that hysteresis occurs between desorption-equilibrium (drying) and resorption-equilibrium (moistening). The size of this effect may be considerable. So there is an influence of the history of the material on its hygroscopic properties. In order to estimate these effects an accurate method is necessary.

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As has been shown by MULTON (1973) accurate estimation of isotherms is far from easy. Measurements of isotherms on the same tapioca starch material at 13 different laboratories gave a wide range of results. The maximum differences were even 20% in equilibrium relative humidities and 4% in moisture content on dry basis, given in absolute values.

GÁL (1967) gave an excellent and comprehensive review of the methods for determining water vapour sorption isotherms. Gravimetric methods are most widely used. From Gál's review it is clear that the most modern methods employ a precision balance in a carefully controlled atmosphere in the absence of air.

After comparison of several methods and preliminary experiments with a prototype, we decided to build an instrument basically consisting of six quartz spring balances each suspended within its own glass chamber. In these chambers the inert gas pressure can be reduced to a chosen value (minimum  $10^{-6}$ Torr). Also temperature and water vapour pressure can be controlled continuously. MCBAIN and BAKR (1926) were the first to apply the quartz spring balance technique for sorption measurements. With our apparatus 6 different isotherms can be determined simultaneously. The samples can be weighed at any moment without disturbing the sorption process. The water vapour pressure in the separate chambers can be controlled continuously between water activities of ca. 0.03 and 1.0. The upper limit of the temperature range in which the isotherms are estimated is restricted because condensation of water vapour must be prevented within those parts of the equipment that are not temperature controlled.

## 2. CONSTRUCTION

The sorption apparatus is schematically represented in Fig. 1, where only one of the six parallel columns has been drawn<sup>2</sup>. Fig. 2 is a photograph of the apparatus.

The sample, usually about ca. 100 mg dry material is placed in an aluminium foil cup (diameter 30 mm) in a phosphor bronze sample holder. The weight of the sample holder plus cup is about 100 mg. The sample holder is suspended from a quartz spring (Quartz et Silice, den Haag) with the following specifications:

1. maximum load 500 mg
2. sensitivity 1 mm/mg
3. spring diameter 19 mm
4. number of turns 146
5. thickness of quartz thread 0.22 mm
6. length at maximum load 1000 mm
7. length without load 500 mm

<sup>2</sup> A composite drawing (scale 1:5) indicating the position of the complete apparatus relative to its frame is obtainable from the authors on request.

The quartz spring is in a vertical double walled water jacketed pyrex glass column with internal diameter 60 mm, external diameter 90 mm, length (ball joints excluded) 1150 mm, length of water jacket 900 mm. The high vacuum ball joints (Pulles & Hanique, Eindhoven) at top and bottom of the column are made of pyrex glass, sealed with Apiezon L grease and both parts are pressed together with pinches<sup>3</sup>. After the upper ball joint has been removed the quartz spring can be put into or removed from the inside of the column with a tacker fixed over the column. In the lower part of the column is a reference point with which all readings with the cathetometer are compared.

In Fig. 1 all parts left of the glass/metal transition pipe are made of pyrex glass; the valves are high vacuum tight, sealed with Apiezon T grease, have hollow plugs with borings 25 mm  $\varnothing$  which are not interchangeable. The internal diameter of the T-piece is 30 mm. All glass parts are fixed to a steel frame by means of pinches which permit some flexibility.

As an isotherm measurement is done in static vacuum and this determination can take several months, there must be hardly any leakage of air into the apparatus. Experiments have shown that the rate of increase in pressure due to leakage of air into a column is less than  $5 \cdot 10^{-5}$  Torr per 24 hours provided the valve between T-piece and glass/metal transition pipe is closed.

The temperature controlled water bath (Tamson TXK9/10Q, Zoetermeer) underneath the column can be cooled to  $-10^{\circ}\text{C}$  with standard refrigeration equipment. The bath contains a glass flask with a water vapour source (distilled water or saturated LiCl-solution).

The glass/metal transition pipe (Pulles & Hanique) consists essentially of pyrex glass and stainless steel (Leybold-Heraeus, Woerden) interconnected by four glass rings with succeeding coefficients of thermal expansion.

All parts to the right of the glass/metal transition pipe are made of metal, principally stainless steel, interconnected by flanges (Leybold-Heraeus) and fixed to a steel frame. Each flange sleeve consists of a stainless steel centre ring connected to a Vitilan packing ring. These rings are pressed together by pinches.

The expansion pipe (Leybold-Heraeus) is made of Tombak, internal diameter 32 mm, length 100 mm. The collecting manifold, internal diameter 70 mm, length 150 cm is made of stainless steel 304 (AISI) argon-arc welded with backing and connected with the six column-units.

A stainless steel water cooled barrier (LEYBOLD-HERAEUS, 1971, NW 65 LF, no. 22625) prevents oil vapour from the diffusion pump penetrating into the column-parts of the apparatus.

The oil diffusion pump (Leybold-Heraeus, 1971, Leybodiff 170 L, no. 22620) contains about 35 cm<sup>3</sup> oil (LH, DC 705) and has a working range of  $10^{-3}$  to  $10^{-6}$  Torr and a capacity of 90 dm<sup>3</sup> per second at  $10^{-5}$  Torr. The minimum attainable absolute pressure in the closed system at the suction side of the diffusion pump is  $10^{-6}$  Torr. This pump is equipped with a water flow monitor, which is a safety device to prevent damage from a cooling water failure.

<sup>3</sup> Ball joints were chosen because of their easy removal after several months static vacuum.

The vacuum pump (Edwards Speedivac ED 100, supplied by A. de Jong TH, Rotterdam) is a two stage rotary pump with swept volume 100 dm<sup>3</sup>/min and ultimate vacuum of 2.10<sup>-3</sup>Torr (without gas ballast), belt driven by a 3 phase 0.25 kW electric motor.

Between the rotary and the diffusion pump a Secuvac safety valve (Leybold-Heraeus, NW 20 KF, no. 27302) is fitted, which closes when the electric current fails and so prevents air from penetrating into the vacuum system. At the same time air is automatically admitted to the rotary pump thus preventing oil from the pump entering the vacuum system.

An oil mist filter (Edwards, OMF 200) is fitted at the outlet side of the vacuum pump.

The absolute pressures in the top part of one column and at the inlet and outlet sides of the diffusion pump are measured by three sensors TR 201 (Leybold-Heraeus, no. 16202), each connected to the electronic unit TM 203 (no. 16259) with ranges of 10<sup>-1</sup> to 760 Torr and 10<sup>-3</sup> to 10<sup>-1</sup> Torr. The operation is based on measurement of the electric voltage supply to a resistance wire controlled at constant temperature. Removal of heat from the resistance wire and electric power supply to the wire compensate each other. So both depend on the absolute pressure in the same way. Moreover the pressure at the suction side of the diffusion pump can be measured by a sensor IE 36 (Leybold-Heraeus, no. 16348) range 10<sup>-8</sup> to 10<sup>-2</sup>Torr connected to an Ionivac IM 30 (Leybold-Heraeus, no. 16350) electronic unit. Measurement is based on ionization of gas molecules.

The elongation of the quartz spring, giving the weight of the sample, is measured with a cathetometer (The Precision Tool and Instrument Co. Ltd., supplied by Tamson, Zoetermeer) of the following specifications:

1. span 0–53 cm.
2. 1 division = 0.5 mm.
3. 1 division on nonius = 0.01 mm.
4. measuring distance 90 cm – ∞ without auxiliary lens.  
40 cm – 90 cm with auxiliary lens.

Proir to each reading the lens system is levelled, with a spirit-level.

The temperatures of the water in the baths as well as those at the inlet and outlet of the columns can be measured by electrically isolated copper/constantan thermocouples against a common cold junction in melting ice. The thermoelectric tension to be measured is compensated by a continuously variable counter voltage source (Knick, type S 2, supplied by van Oortmerssen N.V., den Haag) accuracy better than ± 0.1 % of the chosen voltage range.

### 3. PRINCIPLE OF OPERATION

After the sample has been suspended from the spring in the column, the system is evacuated because the time necessary for equilibration is very much less if air is absent (max. pressure ca. 0.5 Torr).

Before and/or after measurement of the water vapour sorption isotherm the dry weight of the sample is determined by drying at ambient temperature until constant weight at an absolute pressure of ca.  $10^{-6}$  Torr at minimum.

For isotherm measurement the sample is equilibrated with water vapour of known pressure. The water vapour pressure is held constant with well known water vapour sources, kept at constant temperature. A change in water vapour pressure corresponds to a change in moisture content of the sample material causing a change in the length of the quartz spring.

During isotherm estimation the temperature in the sample chamber is kept constant.

#### 4. ACCURACY OF RESULTS

For determination of water vapour sorption isotherms, it is necessary to control water vapour pressure ( $p$ ) and the sample temperature. After equilibrium has been attained, the water content of the sample must be measured and compared with the weight of the dry material in the sample. Hence the accuracy of the estimation is determined by the accuracies of the estimation of:

1. water vapour pressure
2. saturated water vapour pressure at the temperature of the sample
3. weight of the moist sample
4. weight of the dry sample

##### 4.1 *Water vapour pressure*

Water vapour pressures are adjusted by controlling the temperature of saturated LiCl-solutions in the range  $0.4 < p < 1.5$  Torr and  $2.0 < p < 6.8$  Torr and of distilled water above  $p = 2.5$  Torr. According to YOUNG (1967) the range  $1.5 < p < 2.0$  Torr should be avoided when using LiCl because of the transition  $\text{LiCl} \cdot 2\text{H}_2\text{O} \rightarrow \text{LiCl} \cdot \text{H}_2\text{O}$  at  $18.8^\circ\text{C}$ . When using saturated LiCl-solution the inaccuracy in the water vapour pressure is caused by inaccuracies:

1. in the data of YOUNG (1967) for LiCl.
2. in measurement of temperature of the solution
3. in the table of water vapour pressures from PERRY (1941).

When using distilled water as a water vapour source inaccuracies are introduced by:

1. measurement of water temperature
2. using the water vapour pressure table of PERRY (1941).

The accuracy of Young's data is not known. However, in the range  $2.5 < p < 6.8$  Torr both  $\text{LiCl} \cdot \text{H}_2\text{O}$  and water can be used as water vapour sources. The results of experiments with LiCl did not systematically deviate from those with water.

Temperature of the water vapour source is based on temperature measurement in the controlling bath. Because of the temperature control there are fast periodic (ca. one minute) temperature fluctuations of the order of  $\pm 0.01^\circ\text{C}$  in

the bath: the water vapour sources are believed to be unable to follow these fluctuations. Moreover, measurements showed that there are long term (several hours) shifts in temperature level of the order of  $\pm 0.025^\circ\text{C}$  which the water vapour source can follow well. These shifts are due to external factors. These long term temperature fluctuations are incorporated in the temperature adjustment of the water vapour source and consequently into corresponding variations in the vapour pressures. These are believed to be followed by the sample only partially because equilibrium is established slowly.

Each of the thermocouples was tested at random with a calibrated quartz thermometer (Hewlett-Packard, type 2801 A), absolute inaccuracy less than  $\pm 0.02^\circ\text{C}$ . The results show that the systematic deviations in temperature measurement did not exceed  $\pm 0.05^\circ\text{C}$ . Perry's water vapour pressure table gives values for water vapour pressures rounded to 0.001 Torr. It is assumed that the last decimal that is given is significant and that therefore errors in this table are negligible.

#### 4.2. Saturated water vapour pressure at the temperature of the sample

Here the same holds as for the measurement of the water vapour source temperature: the inaccuracy will not exceed  $0.05^\circ\text{C}$ . Another source of error may be introduced because the sample temperature can deviate from the temperature of the water in the jacket in 2 ways:

1. as the sample is suspended in an atmosphere of very low pressure it is thermally well insulated. Consequently heat transfer by radiation from outside the column to the sample may alter the sample temperature to some extent. It has been found that there is an influence of radiation from ordinary light sources (e.g. a 200 W bulb about 2 m above the sample) on the sample weight depending on the moisture content. The influence ranged from 0.2% moisture by weight at  $a_w = 0.60$  to 25% by weight at  $a_w = 1.00$  for a freeze-dried rice starch sample. A radiation shield of cardboard with aluminium foil and substitution of the 200 W bulb by a 40 W TL-tube, colour 16 at the sample height, eliminated these influences completely.

2. sorption and desorption of water vapour are accompanied by heat effects: on sorbing water vapour the sample will warm up and on desorbing water vapour the sample will cool down. We only have a general idea to what extent these effects occur but it is clear that when sorbing (desorbing) water vapour the temperature change of the sample will always be limited indirectly by the limiting water vapour pressure of the immediate surrounding atmosphere. In the final equilibrium state the temperatures of sample and waterjacket must be equal. However, it has been found (DOWNES et al, 1958; VAN DEN BERG et al, in press) that the final equilibrium moisture content may be influenced somewhat by the previous temperature/time history of the sample. If we assume maximum uncertainties in temperature measurement of  $\pm 0.05^\circ\text{C}$  the corresponding errors in the water activity can be calculated for a sample temperature of  $20^\circ\text{C}$ . The results are shown in Table 1.

TABLE 1. Calculated maximum errors in water activity, plus or minus.

LiCl			H <sub>2</sub> O				
0.10	0.20	0.30	0.30	0.50	0.70	0.90	1.00
0.0006	0.0012	0.0018	0.0020	0.0032	0.0044	0.0056	0.0062

### 4.3. Weight of the moist sample

Sample weights are derived from cathetometer readings. To eliminate vertical displacements of column and cathetometer to each other, readings are compared with a reference point fixed in the lower part of the column. Possible systematic errors in the measurements caused by non linearity in the scale of the cathetometer and of the characteristic behaviour of the quartz spring are eliminated by calibration. In this way also effects caused by refraction of light rays and turning of the spring around its axis under variable load, are eliminated. Calibration is performed at atmospheric pressure and at constant temperature with the aid of standards weights with maximum inaccuracies of  $5 \cdot 10^{-3}$  mg. With the computerized Least Squares Method the most probable calibration curve was calculated for each spring. It was found to be sufficient to repeat the calibration once a year. Reproducibility was perfect.

Using the standard weights, two sets of ten comparable readings were obtained before and after a usage period of two years. Within these two sets the maximum deviation was 0.08 mm and the algebraic mean of the differences was  $-0.001$  mm indicating that there is no systematic change in the characteristic behaviour of the springs during a period of two years.

As the spring is suspended from a point in the column above the water jacket, ambient temperature variations might influence the results. However, warming up to  $50^{\circ}\text{C}$  this part of the column showed that these influences do not exceed  $\pm 0.02$  mm under actual conditions. The influence of the actual ambient temperature fluctuations of  $\pm 4^{\circ}\text{C}$  on the thermal expansion of the scale of the cathetometer is negligible.

It was found that the most important source of error is the accidental error in the readings of the spring and the reference point. To test the reproducibility 10 independent observations (sample reading minus reference reading) were made. The results are:

maximum deviation from mean reading  $\pm 0.08$  mm  
 mean deviation  $\pm 0.04$  mm  
 standard deviation  $\pm 0.05$  mm

The standard deviation is defined by

$$s = \frac{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2}}{n - 1}, \quad \text{in which}$$

$x_i$  = value of  $i$  th reading

$\bar{x}$  = mean value of readings

$n$  = total number of observations

#### 4.4 Weight of the dry sample

After equilibration at an absolute pressure of  $10^{-6}$  Torr, the dry samples were weighed in the same way as described above for the moist sample. From this it follows that both determinations have the same accuracy. In calculating the dry and wet weights of the sample, a correction of 0.26 mm is made for the effect of buoyancy of each spring, sample holder and sample dish. No correction is made for the buoyancy of the standard weights used for calibration of the springs at atmospheric pressure. This correction is proportional to the mass of the standard weights and in this way influences the weight of the moisture and the weight of the dry sample by the same factor and therefore leads to no error in the calculated moisture content. Percentage moisture content on dry basis (d.b.) is, as usual, calculated by:

$$w = \frac{\text{weight moist sample} - \text{weight dry sample}}{\text{weight dry sample}} \cdot 100$$

The uncertainty in  $w$  is mainly determined by the error in the numerator of the above expression. Although the maximum possible error in the quantity of water is twice the maximum deviation in the wet or dry weight, the mean deviation and the standard deviation are about the same as for the individual determination and are independent of moisture content. Based on the above mentioned results we can estimate for:

mean deviation in moisture content  $\pm 0.04\%$   
standard deviation in moisture content  $\pm 0.05\%$

From another set of 30 independent observations obtained by simulation of the water sorption process by 100 mg sample with the aid of standard weights, 'water contents' were calculated both from the cathetometer readings and from the standard weights. The results obtained are:

maximum deviation  $\pm 0.10\%$  by weight  
mean deviation  $\pm 0.026\%$  by weight  
standard deviation  $\pm 0.025\%$  by weight

We think that the real errors in the measurements of the moisture contents of 100 mg samples are of the above mentioned magnitude, especially after skill has been acquired in handling the apparatus (e.g. cathetometer readings).

## 5. CONCLUSION

With the apparatus described in this article it is possible to determine very accurately isotherms for water vapour sorption. The maximum error in the measurement of the temperatures of the sample and the water vapour source amounts to  $\pm 0.05^\circ\text{C}$ . From this it follows that the maximum error in the water activity increases with increasing water activity with a maximum error of  $\pm 0.0062$  at a water activity approaching unity.

The maximum possible error in the determination of the water content of a

100 mg sample amounts to  $\pm 0.1\%$  by weight on dry basis, being independent of water content.

#### SUMMARY

A detailed description is given of an apparatus for the simultaneous accurate determination of six different water vapour sorption isotherms. The operation is based on establishing constant water vapour pressures and measuring the corresponding equilibrium water contents in the samples without disturbing the equilibrium conditions.

The maximum error in the adjustment of water activity increases with increasing water activity and reaches its maximum value of  $\pm 0.0062$  for water activities approaching unity. The maximum error in the determination of the equilibrium moisture content of 100 mg sample amounts to  $\pm 0.1\%$  by weight on dry basis.

#### ACKNOWLEDGEMENT

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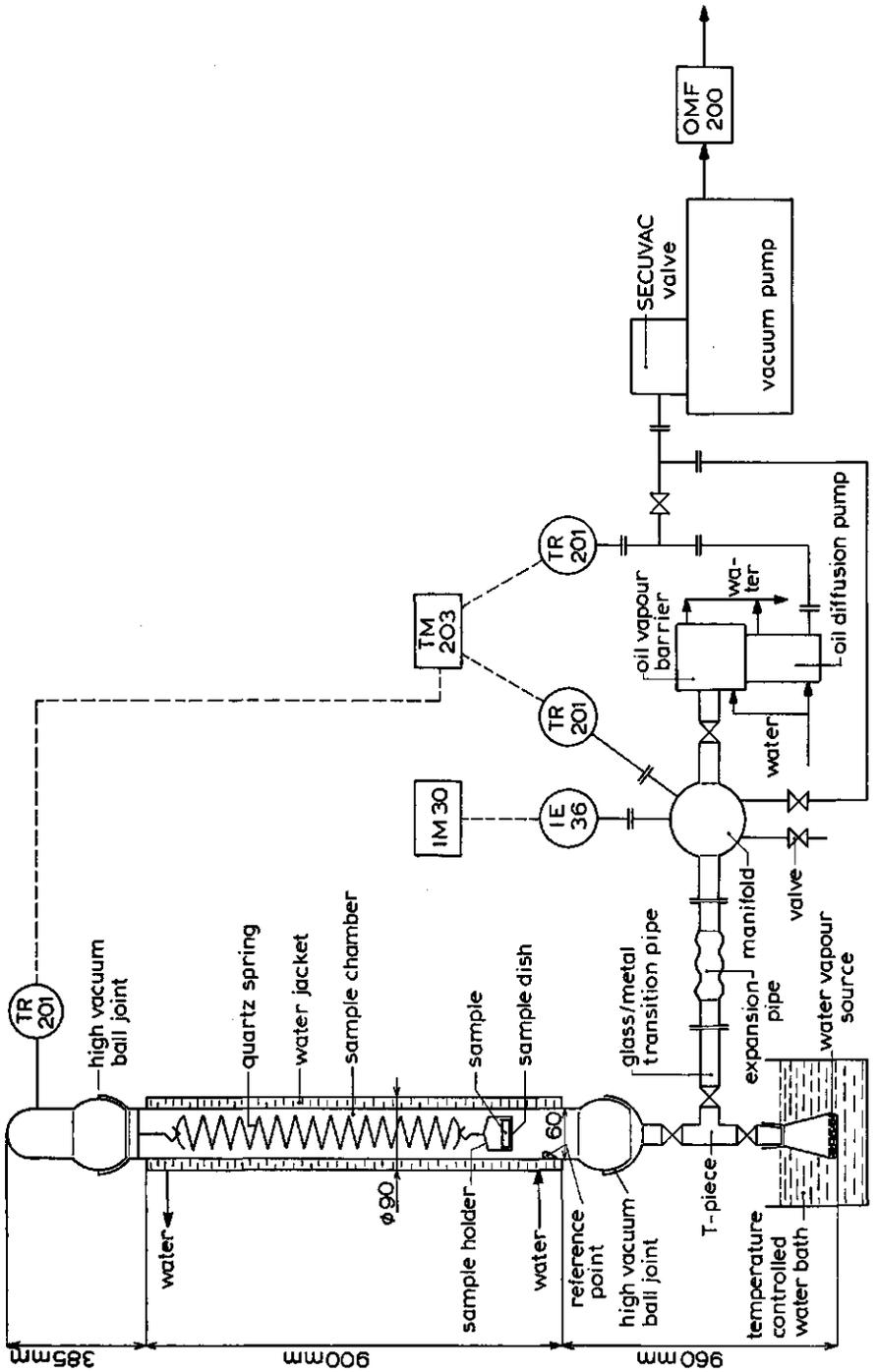


Fig. 1. Schematic representation of sorption apparatus.

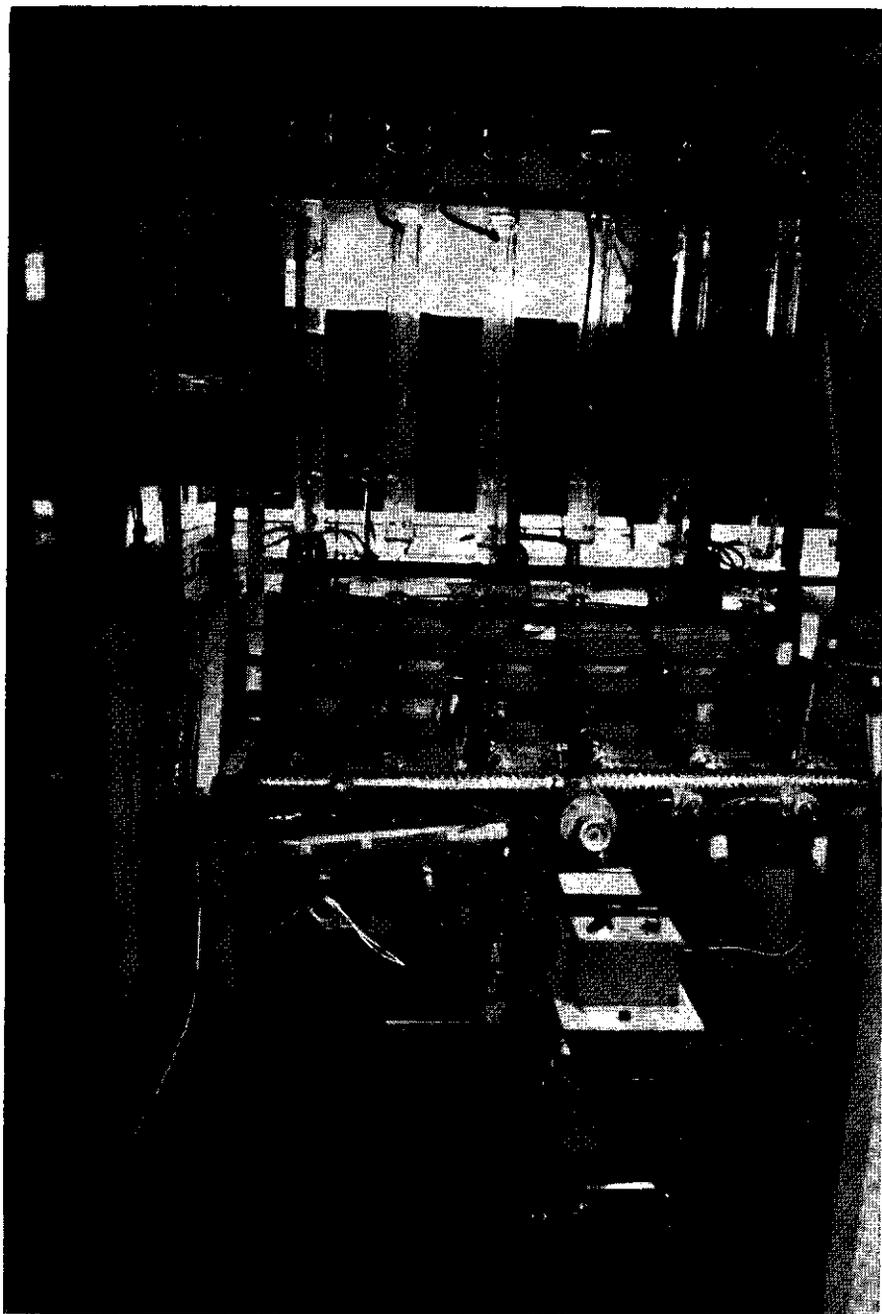


FIG. 2. Photograph of sorption apparatus.