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Publisher's version / Version de l'éditeur:

<https://doi.org/10.4224/20338201>

Internal Report (National Research Council of Canada. Division of Building Research), 1957-10-01

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NATIONAL RESEARCH COUNCIL OF CANADA
DIVISION OF BUILDING RESEARCH

MOISTURE ADSORPTION MEASUREMENTS

by
C.E. Mossman

Report No. 133
of the
Division of Building Research

Ottawa
October 1957

PREFACE

The objectives of a program of study of water vapour adsorption by porous solids, and of the accompanying dimensional changes have already been given in DBR Report No. 126 which presented the results of a literature survey. The apparatus which was devised and constructed for the experimental phase of the project is now described. Data are given for a limited number of samples of clay, concrete and plaster, on which measurements of surface area, adsorption and length change have been made.

Ottawa
October 1957

N.B. Hutcheon
Assistant Director

MOISTURE ADSORPTION MEASUREMENTS

by

C.E. Mossman

PART 1 - APPARATUS

The high-vacuum apparatus to be described here was designed for the purpose of studying the effect of variations in relative humidity upon the dimensional stability of different building materials.

It was necessary, therefore, to provide for the measurement of any dimensional change taking place in the samples, as well as the water-vapour adsorption isotherms. In addition, it was considered desirable to obtain nitrogen adsorption data for the same samples, so that the surface area available to water molecules could be compared with that measured by the adsorption of nitrogen at liquid air temperature.

Description

Figure 1 is a schematic diagram of the high-vacuum apparatus and Fig. 2 is a photograph of the apparatus.

The pumping system consists of a two-stage water-cooled oil-diffusion pump protected from the rest of the apparatus by a liquid air trap (No. 1) and backed by an oil-sealed vacuum pump. The degree of evacuation in the apparatus can be determined by means of a McLeod gauge, which reads two ranges of pressures, from 0.001 micron to 25 microns and from 0.05 mm Hg to 1.10 mm Hg.

The main part of the apparatus includes a 5-liter nitrogen storage bulb, a source of water vapour, the sample tubes and manometers. The nitrogen gas, obtained from a commercial cylinder, is first purified by passage through a liquid air trap. The water-vapour pressure is generated from the water or ice in bulb a or bulb b. Bulb a is used for the lowest pressure, that of water at the temperature of dry ice in ethylene glycol (-15°C), and for saturation pressure (p_0) at room temperature (73°F). Bulb b is immersed in a glycol bath, the temperature of which can be set anywhere in the range from -22°F to 71°F , by means of a series of "red-top" thermoregulators. This temperature is measured with a thermocouple-recorder arrangement, and can be controlled to $\pm 0.02^{\circ}\text{F}$.

Three samples of material can be tested simultaneously. Two are suspended from calibrated helical quartz springs in sample tubes A and B, and the changes in weight are observed by measuring the length changes of the springs with a cathetometer. The sensitivity of the springs used in the present work has varied from 18.98 cm/gm to 30.87 cm/gm while the cathetometer readings are accurate to 0.01 mm. The third sample, used for the dimensional change measurements, is placed in tube C. A Tuckerman optical extensometer is mounted on the sample, and readings of the length change can be made through the flat glass top of the sample tube by an auto-collimator. The smallest movement measurable is $\frac{1}{200,000}$ cm.

The laboratory is controlled at a constant temperature of 73°F ($\pm 2^\circ$), which eliminates the necessity of placing the sample tubes in a thermostat for the water adsorption measurements. For the nitrogen adsorption measurements, which should be carried out at liquid air temperature (-195°C), the lower parts of sample tubes A and B are placed in large Dewar flasks, which are then kept filled with liquid air. In this way, the samples in the tubes are immersed well below the level of the liquid air.

Two U-tube manometers are used to measure adsorbate vapour pressures: a mercury manometer is used for the higher nitrogen pressures and; a manometer filled with Octoil - S (and protected with spray traps) is used for the water vapour pressures.

The stop-cocks and ground-glass joints are lubricated with Apiezon T high vacuum grease.

Procedure

In some of the early experiments, the samples to be suspended from the quartz spirals were placed in special quartz buckets. However, these were very easily tipped when raising the lower part of the sample tube into position, and there was also the danger of losing part of the sample by air entrainment during evacuation. By using long narrow bags of 2-mill polythene for holding the samples these difficulties were overcome. These bags were suspended from a length of platinum wire hooked on to the bottom hook of the quartz spiral. Since the cathetometer readings were usually of the position of the bottom hook, the platinum wire served as an extension for lowering the samples into the Dewars for the nitrogen measurements, while the hooks remained visible above the tops of the Dewars.

One disadvantage of using polythene containers is that samples cannot be heated to speed up the process of evacuation. This is not too important, however, in the present measurements where there may be danger of altering the surface structure of the samples by heating.

The load capacity of the quartz spirals was either 2 or 3 gm so that the samples to be used in the gravimetric measurements were of the order of 1 gm in weight. These samples could be in either pulverized or solid form. The sample used for dimensional change measurements had to be in the form of a solid wafer with a flat surface. The extensometer is mounted on this sample and held in place by a light rubber band. Before placing both in sample tube C, the extensometer is adjusted so that the light image is visible on the auto-collimator scale. The samples are weighed before being attached to the quartz spirals; they are then placed in the sample tubes and the initial position of some reference point on the spirals (usually the bottom hook) is noted before beginning evacuation.

The vacuum pump alone is used, with the liquid air trap (No. 1) until the pressure in the system is reduced to approximately 0.1 micron Hg; then it is used in conjunction with the diffusion pump. A vacuum of less than 10^{-6} mm Hg can be obtained quickly (in less than thirty minutes) provided there are no leaks. While the pumping is in progress, the glass walls of the apparatus can be heated with a Bunsen flame to help drive off any adsorbed gases, though it should be emphasized that great care must be exercised in this heating. The samples themselves cannot be heated, however, because of the polythene containers.

Evacuation is considered complete when the samples stop losing weight. The pressure in the system should not rise appreciably when the main part of the apparatus is shut off from the pumps; if there is a considerable increase in pressure a poorly seated stop-cock or ground-glass connection may be at fault. This trouble usually can be located by shutting off the different sections after evacuation and then opening them in turn to the manometers. Possible pin-holes in the glass can be found by testing with a high-frequency spark-coil. After evacuation has been satisfactorily completed, the main part of the system is shut off from the manifold and the adsorption measurements can be started.

For nitrogen adsorption, gas is transferred from the cylinder to liquid air trap No. 2, where it is frozen and later allowed to expand into the N₂ storage bulb. Two large Dewars, in which the lower parts of sample tubes A and B have been set, are filled with liquid air so that the samples are at liquid air temperature for the N₂ sorption measurements. A quantity of N₂ is then admitted to the adsorption system from the storage bulb until approximately the desired pressure is indicated by the Hg manometer. Equilibrium is reached when the pressure no longer decreases and no further change in quartz-spiral length can be observed. This pressure reading and the spiral extension are recorded. Time required for equilibrium may vary from 15 minutes or half an hour at the lower pressures to 2 or 3 hours at the higher pressures. Further additions of N₂ give measurements of weight change at a

series of pressures, saturation pressure (p_o) being taken as 760 mm Hg. Starting from saturation pressure, the desorption isotherm is obtained by pumping off successive quantities of N_2 and again measuring the change in spiral length corresponding to each pressure value. Knowing the calibration of the quartz spirals, the cathetometer readings can be readily translated to weight of gas adsorbed or, as usually expressed, the volume of gas adsorbed per gram of sample at S.T.P. The isotherms are then plotted as V (cm^3/gm) vs p/p_o .

In the water-vapour adsorption measurements, the vapour-pressure is varied by altering the temperature of the water (or ice) in either bulb a or bulb b. At each vapour pressure (read on the oil manometer) the extension of the quartz spirals and the linear change as indicated by the extensometer are recorded. The samples are at room temperature which is constant at $73^\circ F$, and saturation pressure is the vapour pressure of the water in bulb a, measured at room temperature. It was found that "lagging" the sample tubes with cardboard cylinders filled with glass wool helped to prevent moisture condensation on the glass and the spirals at high relative pressures. For desorption, the vapour pressure is reduced by lowering the temperature of the adsorbate source.

The time required for equilibrium varied from 20 minutes to 1 or 2 hours for adsorption measurements, although for certain materials a longer desorption time was necessary. Dimensional equilibrium was often found to take a longer time than adsorption, although an average time of 2 hours was usually sufficient.

General

The adsorption data can be used to calculate values of surface area for the different samples. For this purpose, the linear form of the B.E.T. equation can be used for relative pressures between 0.05 and 0.40:

$$\frac{p}{W(p_o - p)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \cdot p/p_o$$

Here W is the weight of gas or vapour adsorbed at pressure p ; W_m is the weight required to cover the surface with a monomolecular layer and p_o is the saturation pressure. C is related to the energy of adsorption. When $\frac{p}{W(p_o - p)}$ is plotted against p/p_o , W_m can be calculated from values of the slope $\left(\frac{C - 1}{W_m C}\right)$ and intercept $\left(\frac{1}{W_m C}\right)$.

This value can be easily converted into the number of molecules per gram, and knowing the area occupied by one molecule (from the density of liquefied adsorbate), a simple multiplication yields the total surface area of adsorbent available to the adsorbate used.

Adsorption data also can be used to obtain information about the pore structure of the adsorbent which in turn, can be correlated with results of the dimensional change measurements.

In the present apparatus, it is impossible to measure dimensional change and adsorption on the same sample unless sample tube C is detached and weighed at each pressure. There is probably very little error introduced by using two samples from the same piece of material, provided the material is relatively homogeneous. Also, since sample tube C cannot be placed conveniently in a Dewar flask at liquid air temperature, it has been impossible to follow any dimensional change taking place during the nitrogen adsorption measurements. Since the purpose of these measurements has been merely to obtain N_2 surface areas for comparison with those measured by water-vapour sorption, this is not really a drawback. It may be possible, in future, to design a type of extensometer which can be mounted on the samples in tubes A and B without disturbing the gravimetric measurements.

PART 2 - RESULTS

1. NITROGEN SORPTION ON CLAY SAMPLES

These N_2 adsorption measurements were made chiefly for checking the reliability of the new high vacuum apparatus by comparing the B.E.T. surface area results for two clays with values reported by other workers for the same type of material.

(a) Montmorillonite - This clay mineral was supplied in a powdered form (air-dried), and after being weighed and placed in the apparatus and evacuated at room-temperature, the N_2 sorption measurements were begun without treating the samples further. Complete adsorption - desorption isotherms were determined for several samples of montmorillonite.

No hysteresis was observed, and a typical sorption curve for one sample is shown in Fig. 3. The data for this measurement are given in Table 1, and the corresponding B.E.T. plot is shown in Fig. 4. Values of surface area calculated for four different samples were 11.2, 10.5, 11.0 and 7.0 m^2/gm .

Mooney, Keenan and Wood (2) give a value of 26.9 m^2/gm for the surface area of natural, homogeneous, montmorillonite. The difference between their higher value and the present values could easily be accounted for by the difference in particle size. For example, Mooney et al used screened samples (200 mesh) in which X-ray diffraction revealed no impurities in observable quantities. The present sample of Bentonite was not screened and was dried in vacuum at room temperature, while the screened samples were dried in vacuum at 70°C, so that the results are not strictly comparable.

(b) Illite - The illite was supplied in rough lumps of the naturally occurring mineral. Before use, it was pulverized with a mortar and pestle, but was not screened according to particle size. Like the montmorillonite, the samples were evacuated in the apparatus at room temperature prior to the adsorption measurements.

Complete isotherms were not measured for the illite samples since the B.E.T. equation is only linear up to a relative pressure of approximately 0.40. Again the adsorption was reversible in this region and satisfactory agreement was found between the data for two samples for which surface area values of 49.6 and 52.3 m²/gm were obtained. One of the B.E.T. plots for this clay is given in Fig. 5.

Mooney et al reported surface area values ranging from 39.2 to 90.4 m²/gm, depending upon the particle size and exchangeable cation in the illite sample used. Therefore, the results obtained in the present measurements can be considered satisfactory and of the correct order. Also the temperature of the samples in the high vacuum apparatus may be slightly above -195°C because of the size of the sample tubes immersed in the Dewar flasks containing the liquid air.

The temperature control for the water vapour source was not in working order when the clays were being studied and so, no water-vapour isotherms were obtained. However, data reported by Mooney et al and other workers (1, 4) indicate that the water-vapour surface areas are many times greater than the areas available for adsorption of the nitrogen molecule, especially for montmorillonite which has a large internal surface due to its plate-like structure.

2. MOISTURE SORPTION ON CONCRETE

The concrete used was a two-year old specimen of the following proportions: 1: 2.25: 3.07 with Arnprior sand and Ottawa Valley crushed limestone as coarse aggregate with a maximum size of one-half inch. The water-cement ratio was 0.47 and the concrete had no slump. Belleville cement was used.

Before measuring water-vapour isotherms for the concrete samples, an attempt was made to obtain N₂ sorption data for the purpose of comparing the internal surface areas accessible to N₂ and H₂O vapour molecules. Unfortunately, the samples did not adsorb any measurable quantity at liquid air temperature, so that this measurement had to be abandoned.

Three complete water-vapour adsorption - desorption cycles were determined for two samples of pulverized concrete. The results for one sample are plotted in Fig. 6 and may prove difficult to interpret without making further measurements.

The adsorption of water-vapour appeared to cause no permanent alteration in the composition of the material since the original dry weight of the sample remained unchanged even after several cycles. The wide hysteresis loops, extending to zero relative pressure, probably can not be explained by the usual mechanism of capillary condensation, in which case hysteresis occurs only after a reversible portion of the isotherm has been completed (usually above $p = 0.4 P_0$). It is possible that the non-reversibility of the concrete isotherms may be related to the manner in which pores, which are somewhat larger than those in which condensation would take place, are filled and emptied.

The second and third adsorption curves appear to coincide except at saturation pressure, while the desorption data obtained at the lower relative pressures lie on the same curve. These latter values have been used in the B.E.T. plot (Fig. 7), for calculating the surface area of the concrete. Values of 42 and 44 m^2/gm were obtained for the two samples.

It will be noticed that the amount of water adsorbed at saturation pressure increased with each successive cycle. This was not found to be the case by Powers and Brownyard (3) for wafers of neat cement. It has been suggested that the present results may be due to the fact that the concrete was in the form of a powder which, although loosely packed originally, became more compacted with each desorption, producing an increasing number of smaller pores. Then, even if there was no capillary condensation but only layer adsorption, more water would be held in many small pores than in the fewer large pores initially present. Similar measurements on a solid piece of the same concrete specimen would be desirable in order to test the possible validity of this explanation.

During the adsorption measurements a series of dimensional change measurements was carried out on a solid sample of the concrete. The results for one of the sorption cycles are shown in Fig. 8, while Fig. 9 shows the relation between the dimensional change and the corresponding moisture content of the sample.

3. MOISTURE SORPTION ON PLASTER

As in the case of concrete, it was found impossible to measure N_2 sorption on plaster. Water-vapour adsorption data have been obtained for three different samples of plaster and simultaneous dimensional change measurements were made on two of these samples.

Initially it was hoped that plaster samples could be formed having pore characteristics sufficiently different to affect their moisture-sorbing properties. The samples used in the present measurements are therefore described:

Sample No. 1: Composition was plaster of paris: water 2:1 (by weight); mixed to uniform consistency, formed in wax molds and allowed to set at room temperature.

Sample F: Composition was plaster of paris: water - 10:7; mixed until blended (approximately 40 seconds), placed in a wax mold, covered with a layer of water and left overnight. Allowing this sample to set under water should eliminate the usual compaction on setting due to moisture suction in the pores, so that any compaction which occurs should be due solely to crystal growth.

Sample Nos. 2 and 3 (both from the same specimen): Composition was plaster of paris: water - 2:1; mixed for 2 minutes then placed in a water bath at 70°C in a thin rubber membrane for 1 hour. Then the temperature was raised to 90°C and the samples left in the bath over a week-end.

Unlike the concrete and clay samples, which could be evacuated to dryness prior to the first sorption run in approximately 24 hours, up to 12 days of pumping at less than 10^{-6} mm Hg pressure was necessary to remove all the adsorbed gases and moisture from sample Nos. 1 and F (Fig. 10), and one week for sample Nos. 2 and 3. The dimensional change (contraction) of sample F during this period is shown in Fig. 11, the greater the contraction taking place the drier became the plaster. Similar behaviour was later observed for sample No. 2, although the total contraction was very much smaller.

Results of the water-vapour adsorption measurements on sample Nos. 1 and F are plotted in Fig. 12. Figure 13 gives the corresponding dimensional change for sample F. It proved impossible to determine a desorption curve for these samples as the plaster appeared to hold the adsorbed water so strongly that it could only be removed by evacuating the system. However, after pumping, the samples returned to their original dry weight, and a second adsorption run reproduced the results of the first satisfactorily.

The B.E.T. plots for these samples are given in Fig. 14. These do not appear to be linear over the usual pressure range, although a more linear plot could possibly be obtained by using a more complex form of the equation. Approximate values of surface area were calculated to be $134 \text{ m}^2/\text{gm}$ and $149 \text{ m}^2/\text{gm}$ for sample Nos. 1 and F respectively. Figure 15 shows the results of dimensional change measurements on sample No. 2. The B.E.T. surface area of this sample was found to be $172 \text{ m}^2/\text{gm}$.

It will be noticed that the surface areas of the plaster samples were roughly three times as large as for concrete. The maximum dimensional change for concrete was approximately 0.04 per cent, for plaster sample No. 2 it was 0.18 per cent while plaster sample F showed almost a 1 per cent change at high relative humidities.

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3. Powers, T.C., and T.L. Brownyard, Studies of the physical properties of hardened portland cement paste. Part 7 - permeability and absorptivity, (Proc. Am. Concrete Inst., Vol. 43, 1947, p.865). Bulletin No. 22, Portland Cement Assoc., Chicago, 1948.
4. Quirk, J.P., Significance of surface areas calculated from water vapour sorption isotherm by use of B.E.T. equation. Soil Science, Vol. 80, p.423-30, 1955.

APPENDIX I

B.E.T. Calculations

1. Measure \underline{V} , the amount of adsorbate sorbed for relative pressures varying from 0.05 to 0.40.

$$\frac{P}{V (P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P_0}$$

This B.E.T. equation may be written as:

$$\frac{1}{\underline{V}} \cdot \frac{x}{1-x} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot x$$

where $x = p/p_0$. \underline{V} is expressed as mg adsorbed per gram of sample (as weighed after initial evacuation).

2. If $\frac{1}{\underline{V}} \cdot \frac{x}{1-x}$ is plotted against x , the slope of the (linear) graph = $\frac{C-1}{V_m C}$ and the intercept = $\frac{1}{V_m C}$.

3. V_m , the amount of adsorbate necessary to complete one monolayer can then be calculated.

4. If V_m is expressed as $\frac{\text{mg}}{\text{g}}$ it can be converted into molecules by first changing into $\frac{\text{cc}}{\text{gm}}$ (STP):

$$V_m \times 0.800 \text{ (for } N_2 \text{ as adsorbate)}$$

$$V_m \times 1.245 \text{ (for } H_2O \text{ as adsorbate)}$$

$$\text{then } V_m \left(\frac{\text{molecules}}{\text{gm}} \right) = \frac{6.06 \times 10^{23}}{2.24 \times 10^4} \times V_m \left(\frac{\text{cc}}{\text{gm}} \right)$$

5. Knowing the area occupied by one molecule of adsorbate, a simple multiplication gives the total surface area of adsorbent available to the gas or vapour used.

Values used for area of one molecule are:

$$(15.8 \text{ \AA}^2 \quad (15.8 \times 10^{-20} \text{ m}^2) \text{ for } N_2$$

$$\text{and } 10.8 \text{ \AA}^2 \quad (10.8 \times 10^{-20} \text{ m}^2) \text{ for } H_2O.$$

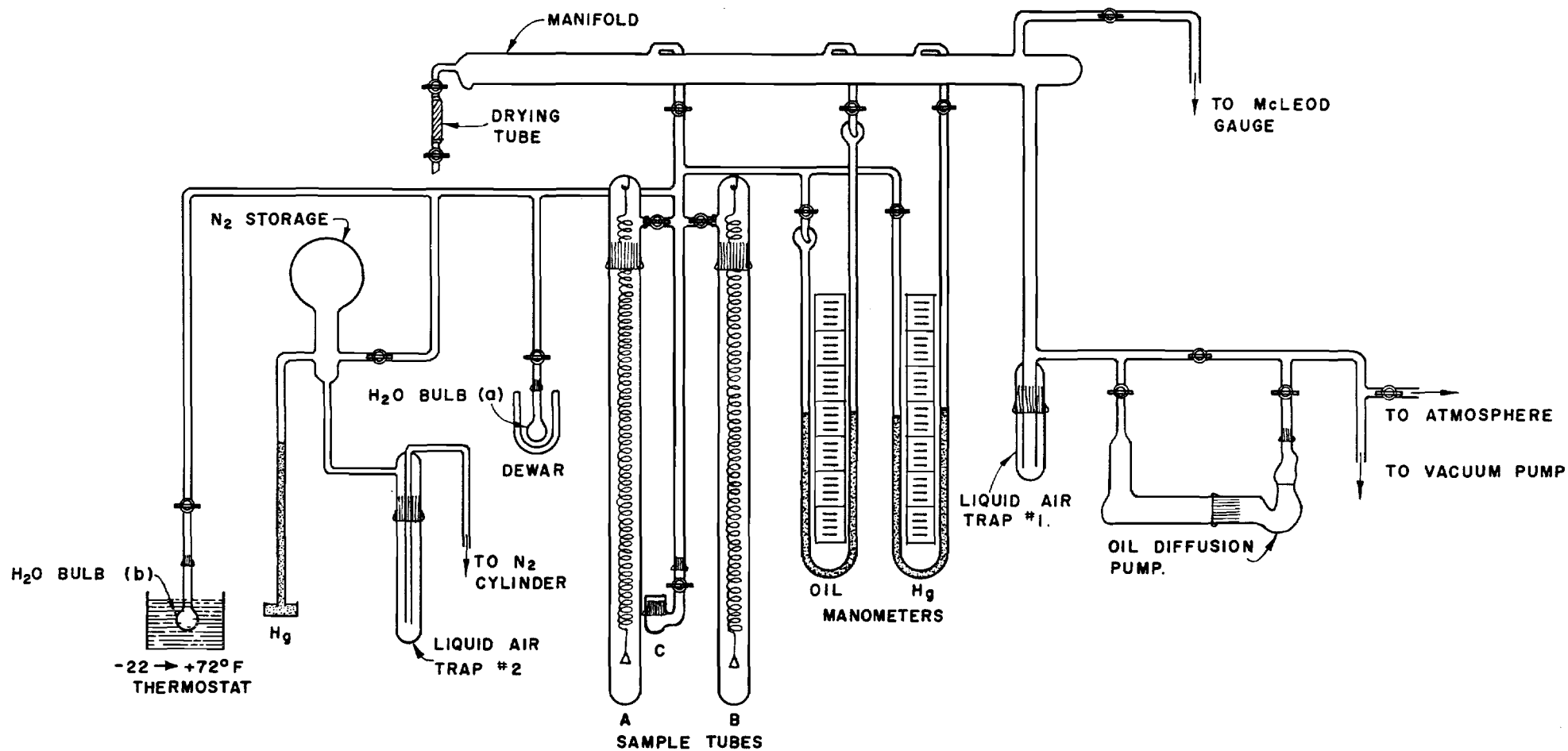
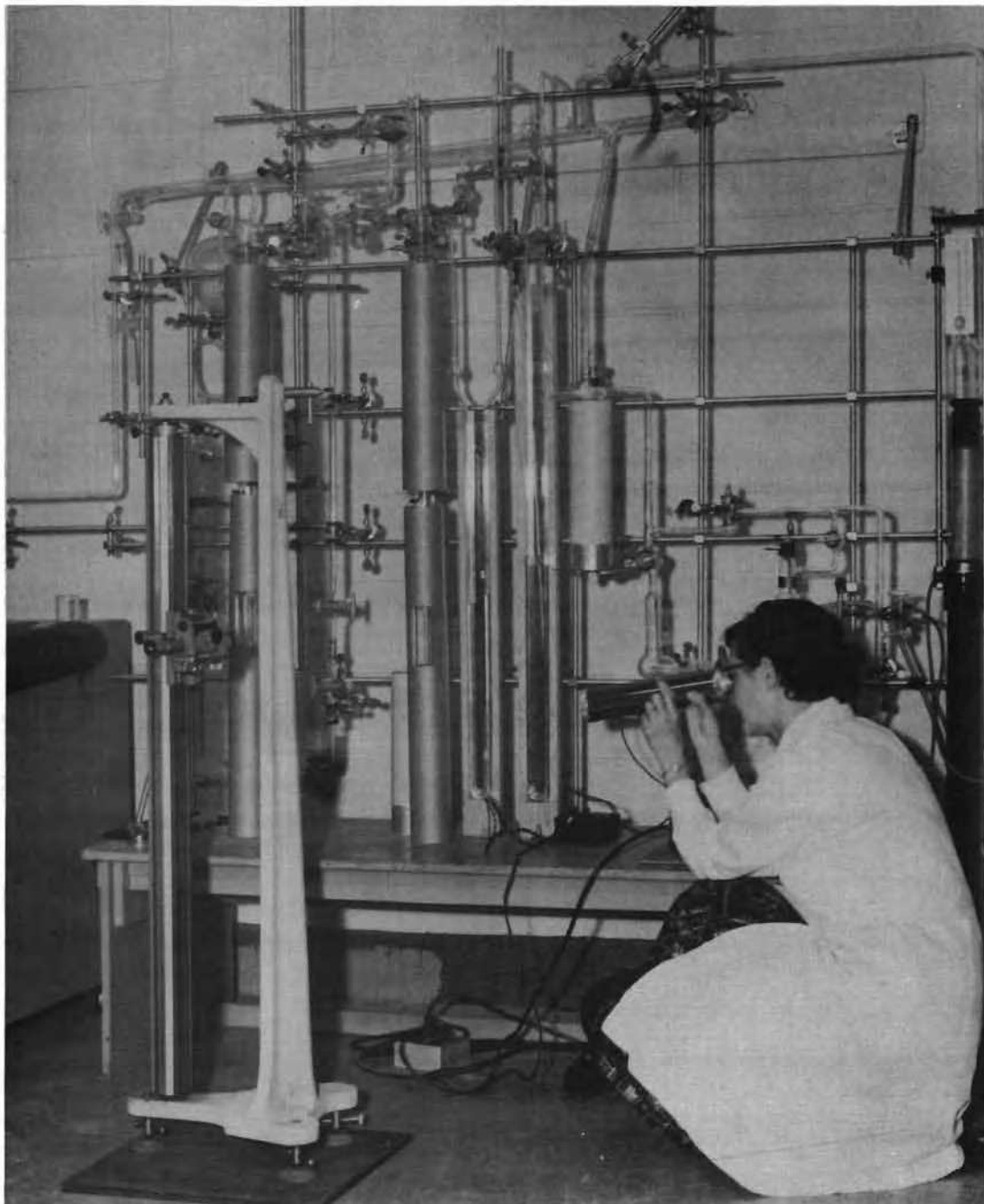


FIGURE 1
HIGH VACUUM ADSORPTION APPARATUS

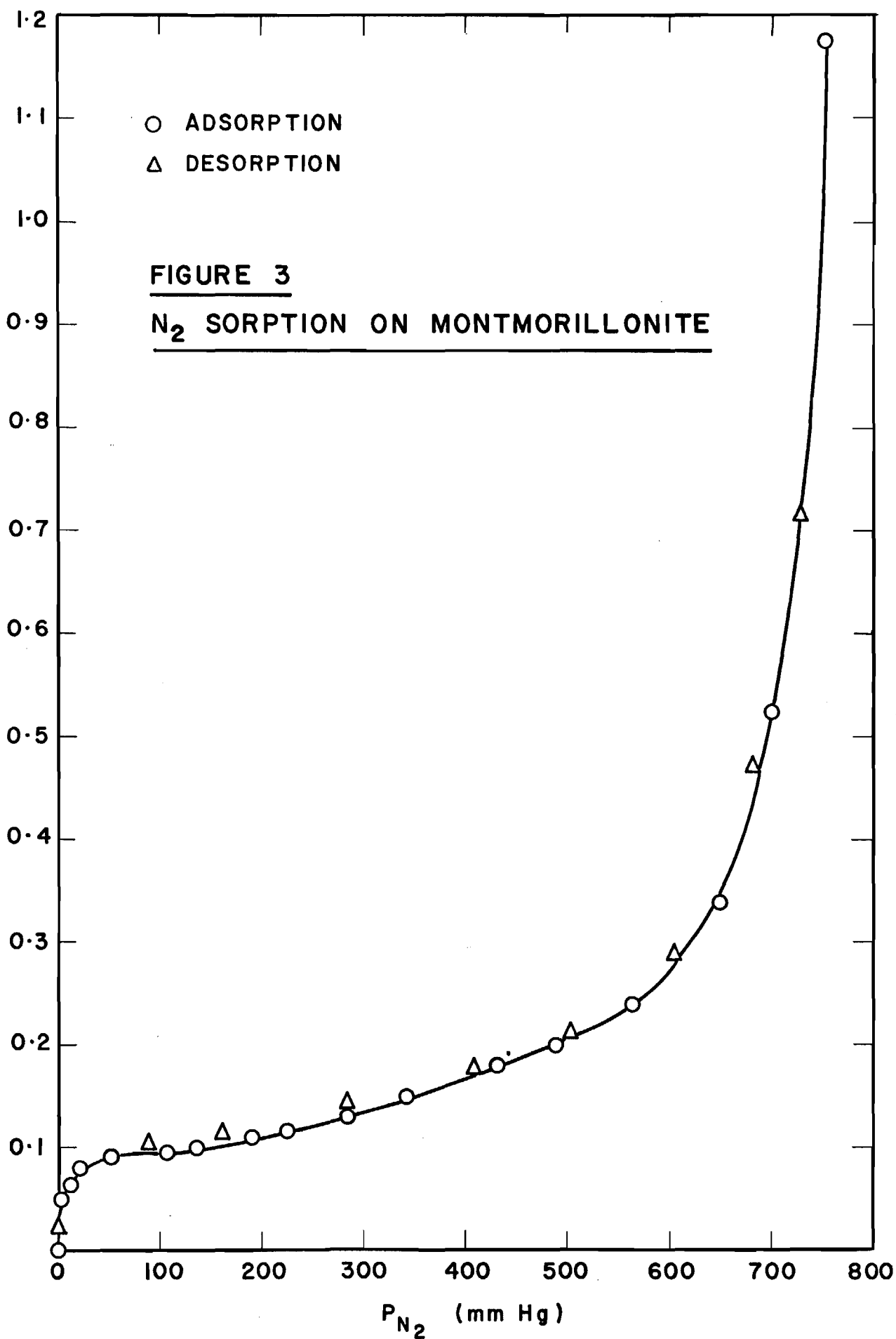


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Figure 2 The high-vacuum apparatus

$w = \text{EXTENSION} \times 29.6 \frac{\text{mg}}{\text{g}}$

SPIRAL EXTENSION (CM)



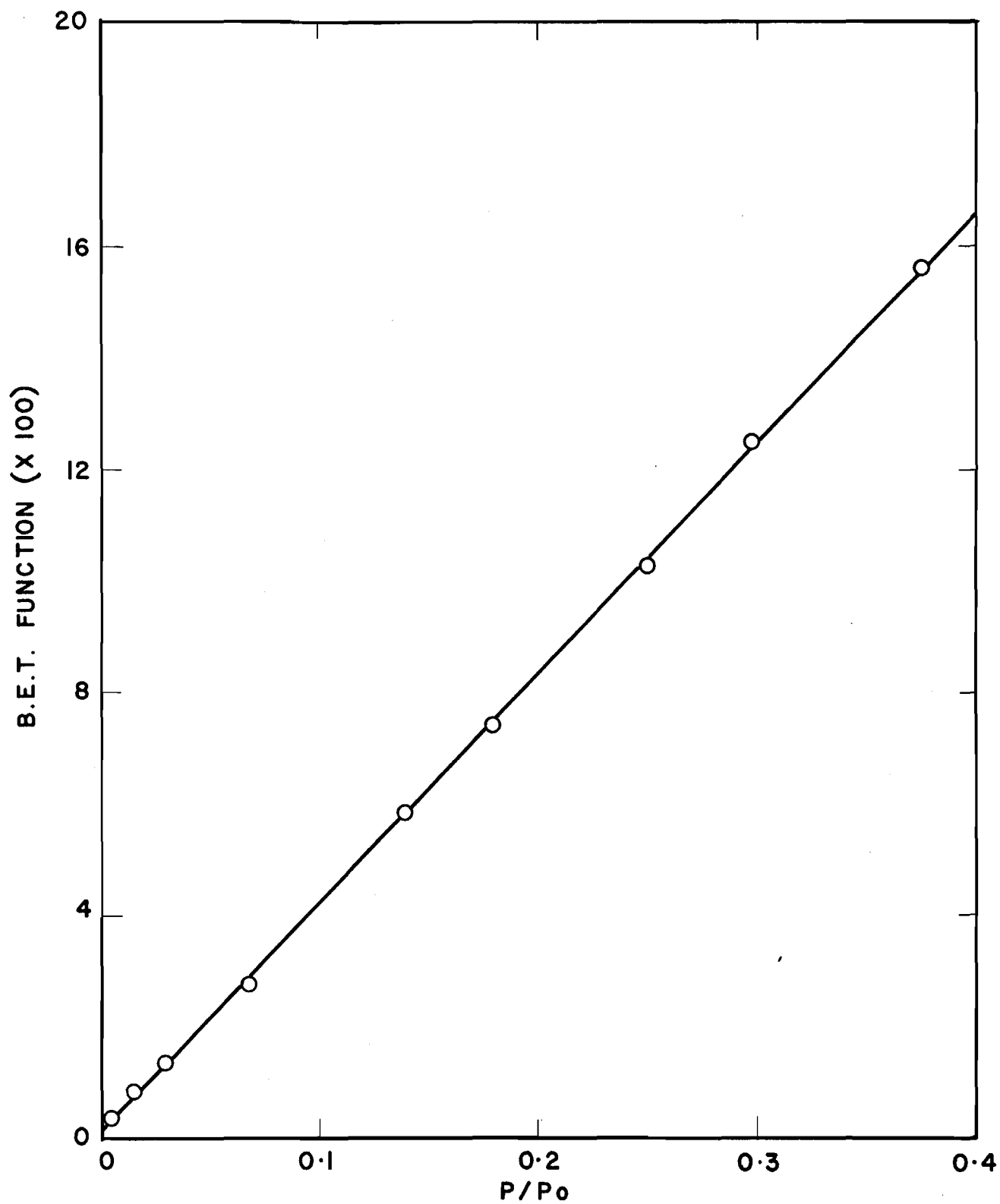


FIGURE 4

B.E.T. PLOT FOR N₂ ON MONTMORILLONITE

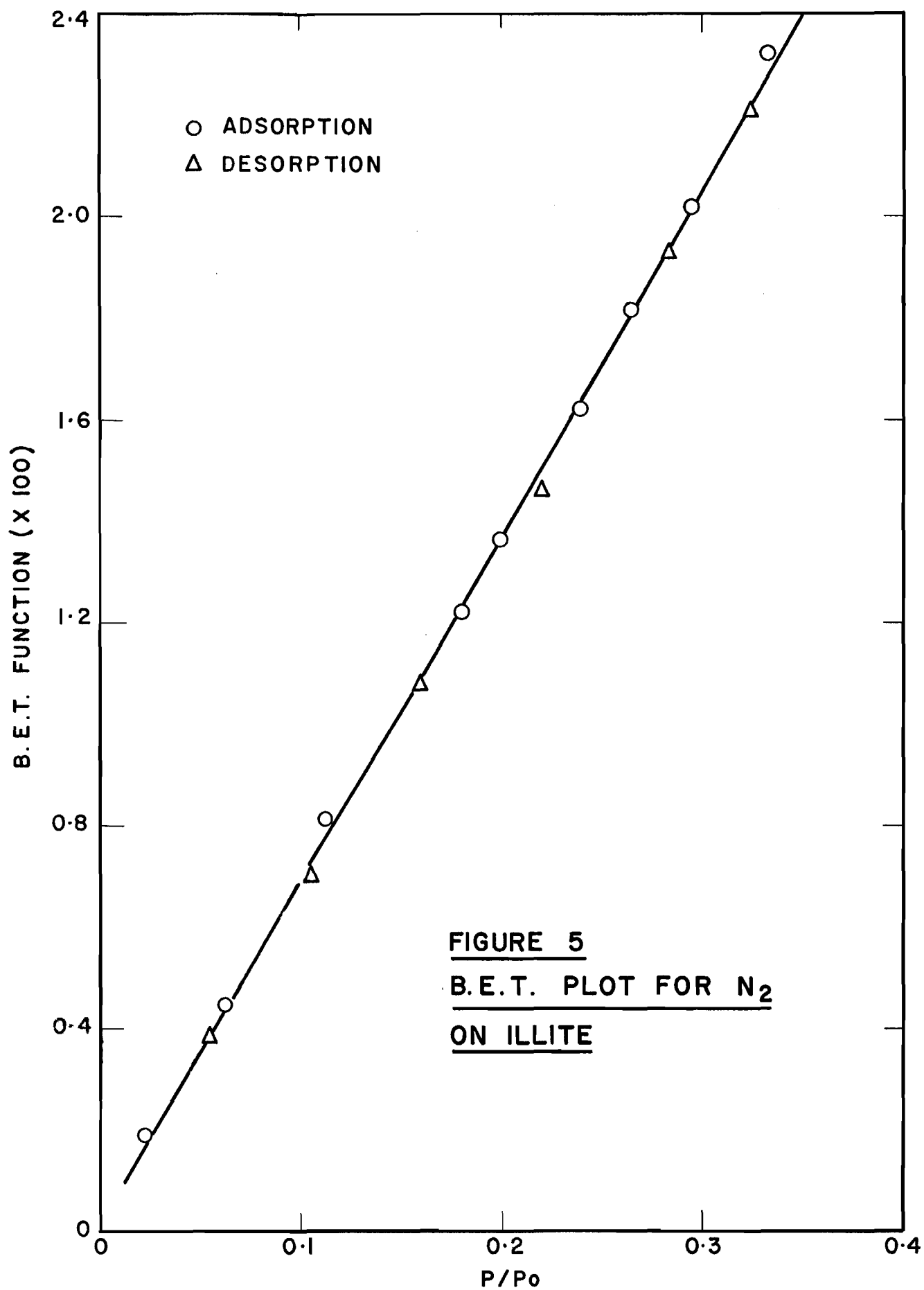


FIGURE 5
B.E.T. PLOT FOR N_2
ON ILLITE

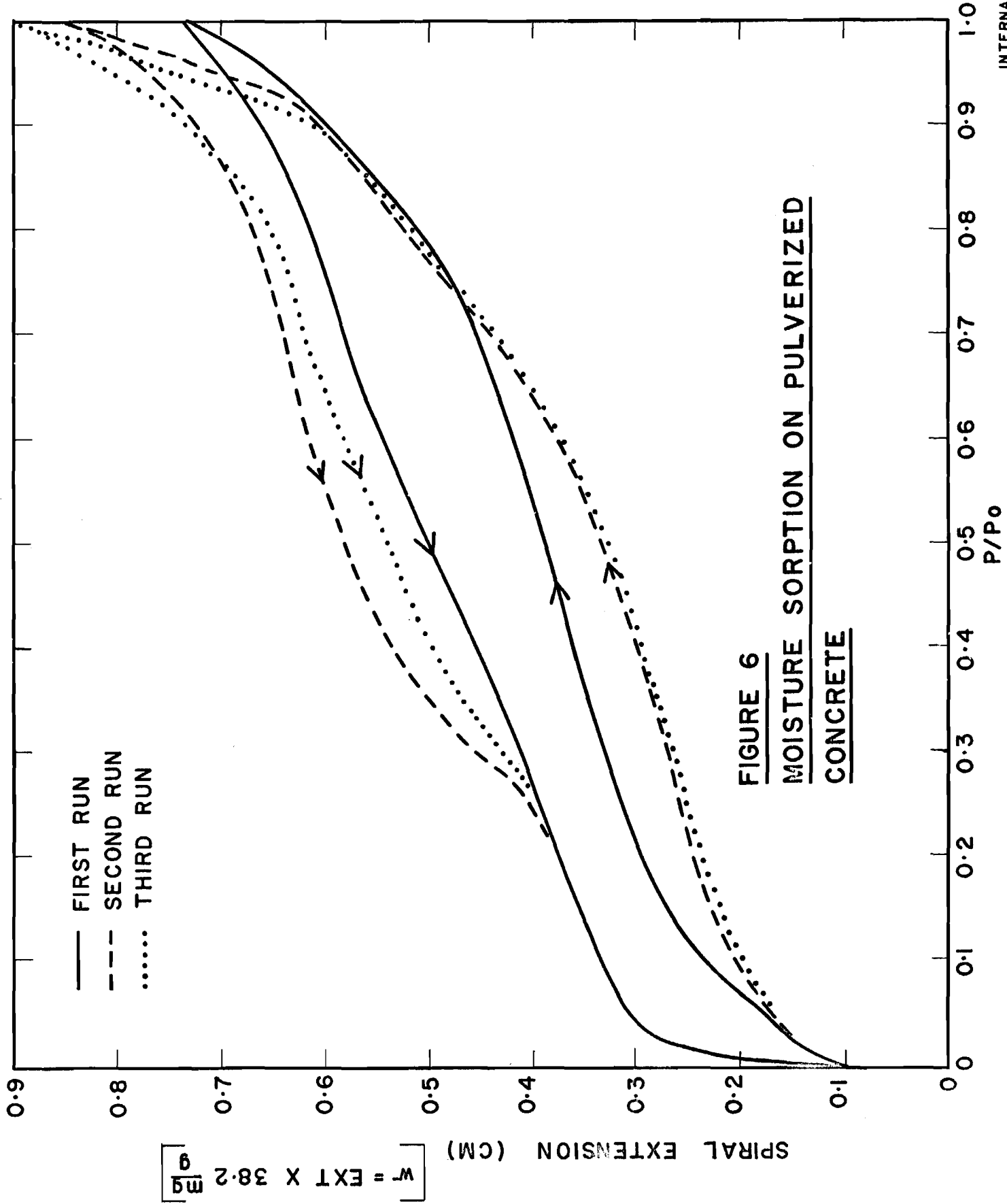


FIGURE 6
 MOISTURE SORPTION ON PULVERIZED
 CONCRETE

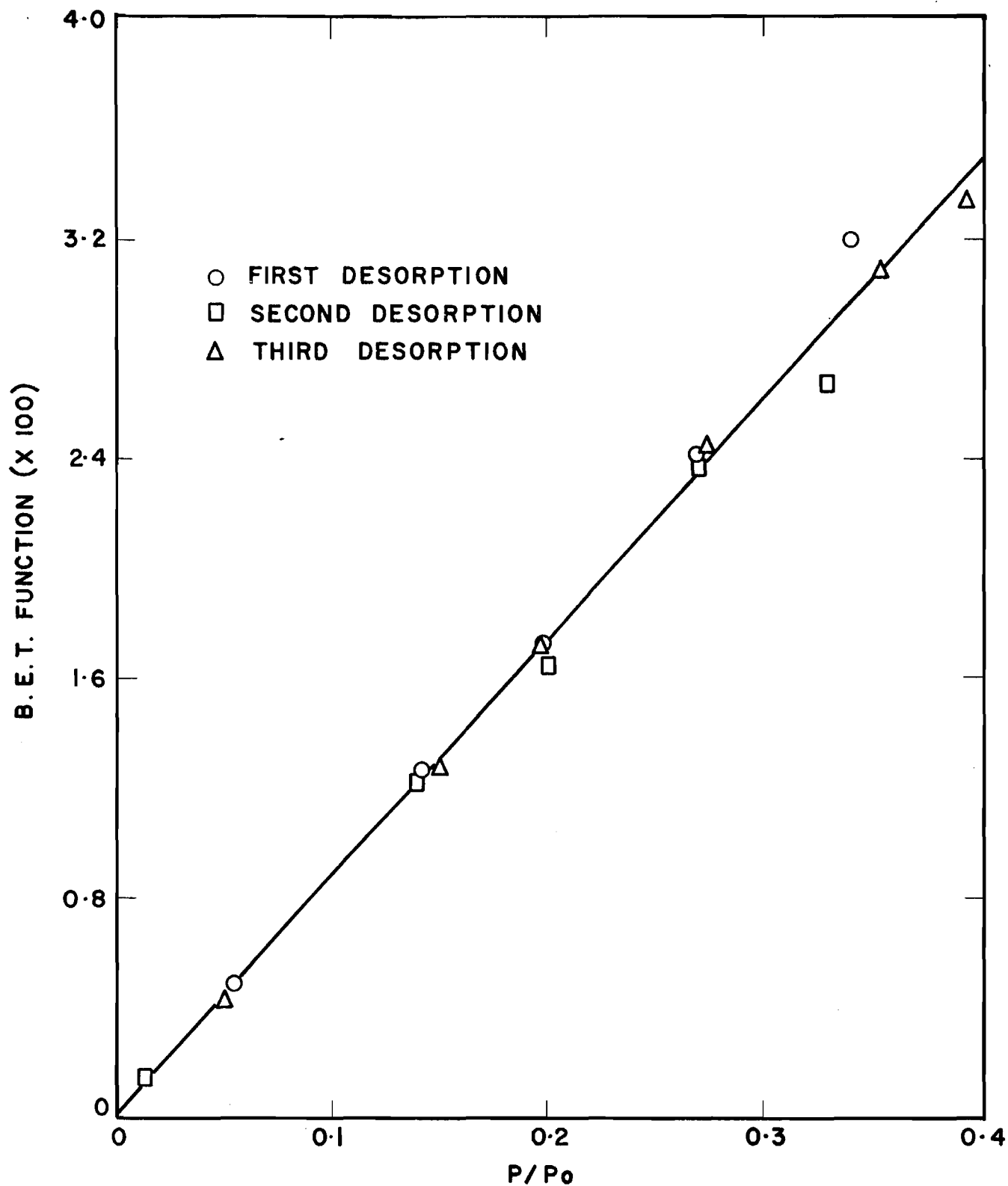
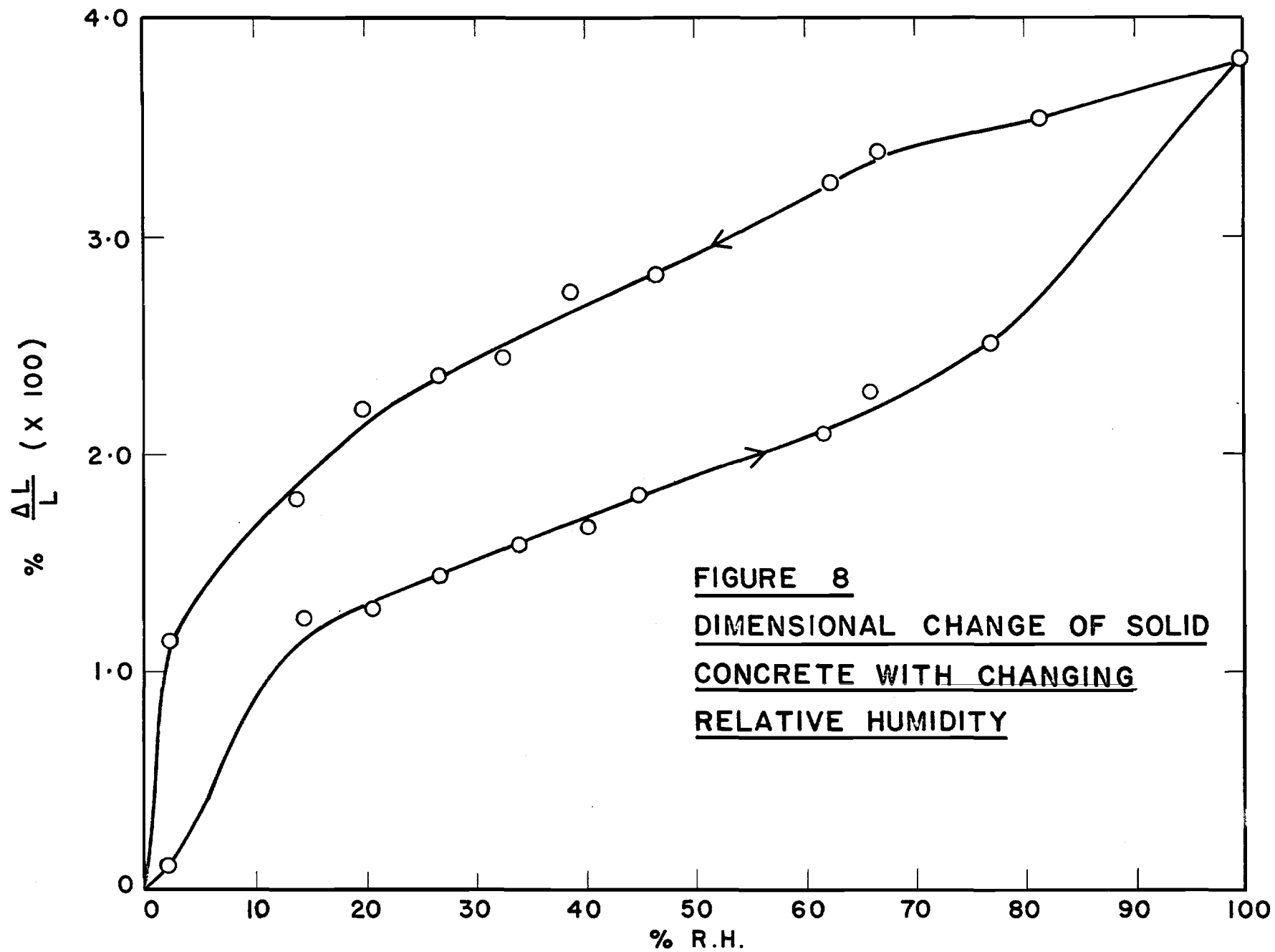
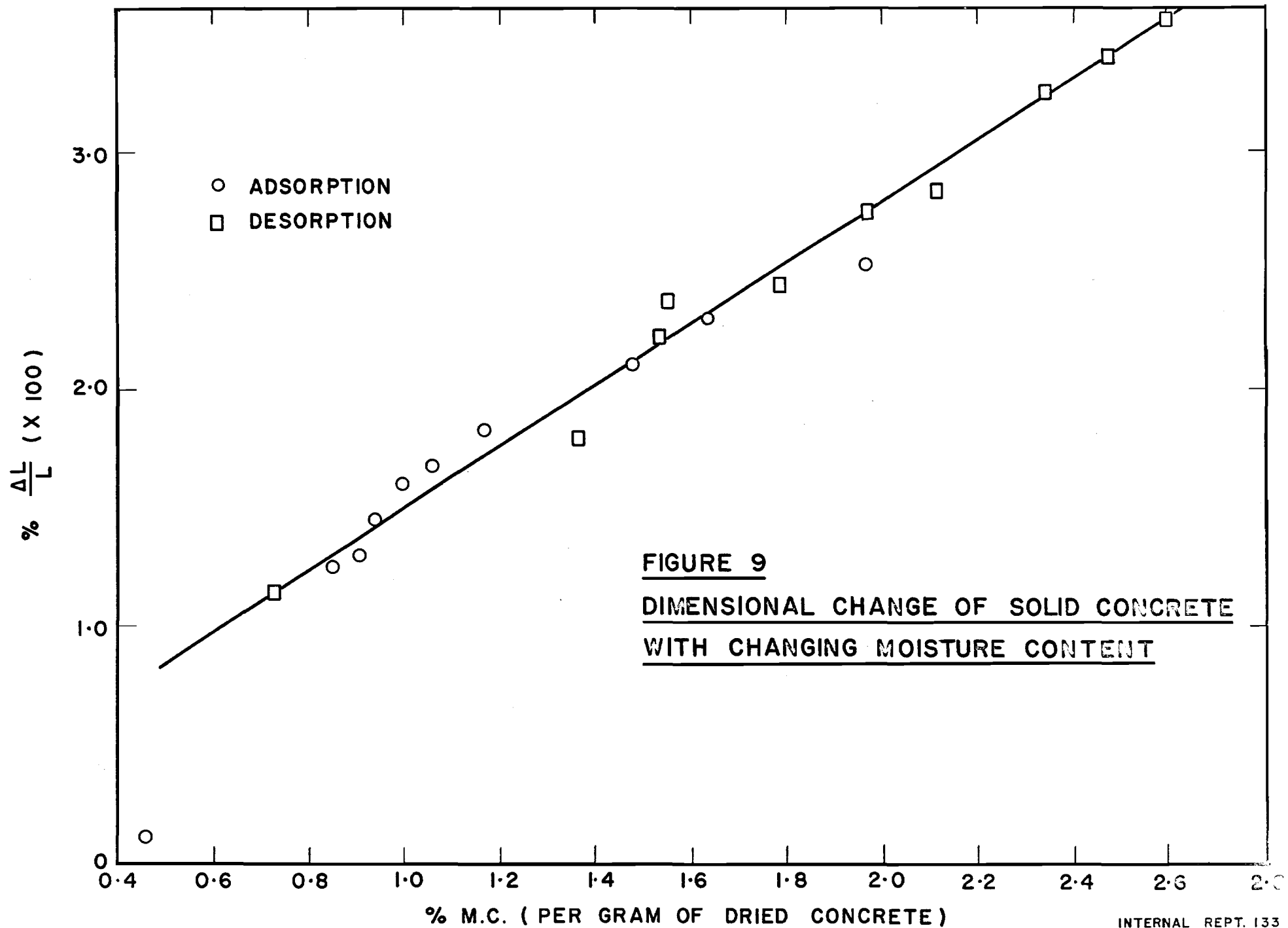


FIGURE 7

B.E.T. PLOT FOR WATER VAPOR IN PULVERIZED
CONCRETE





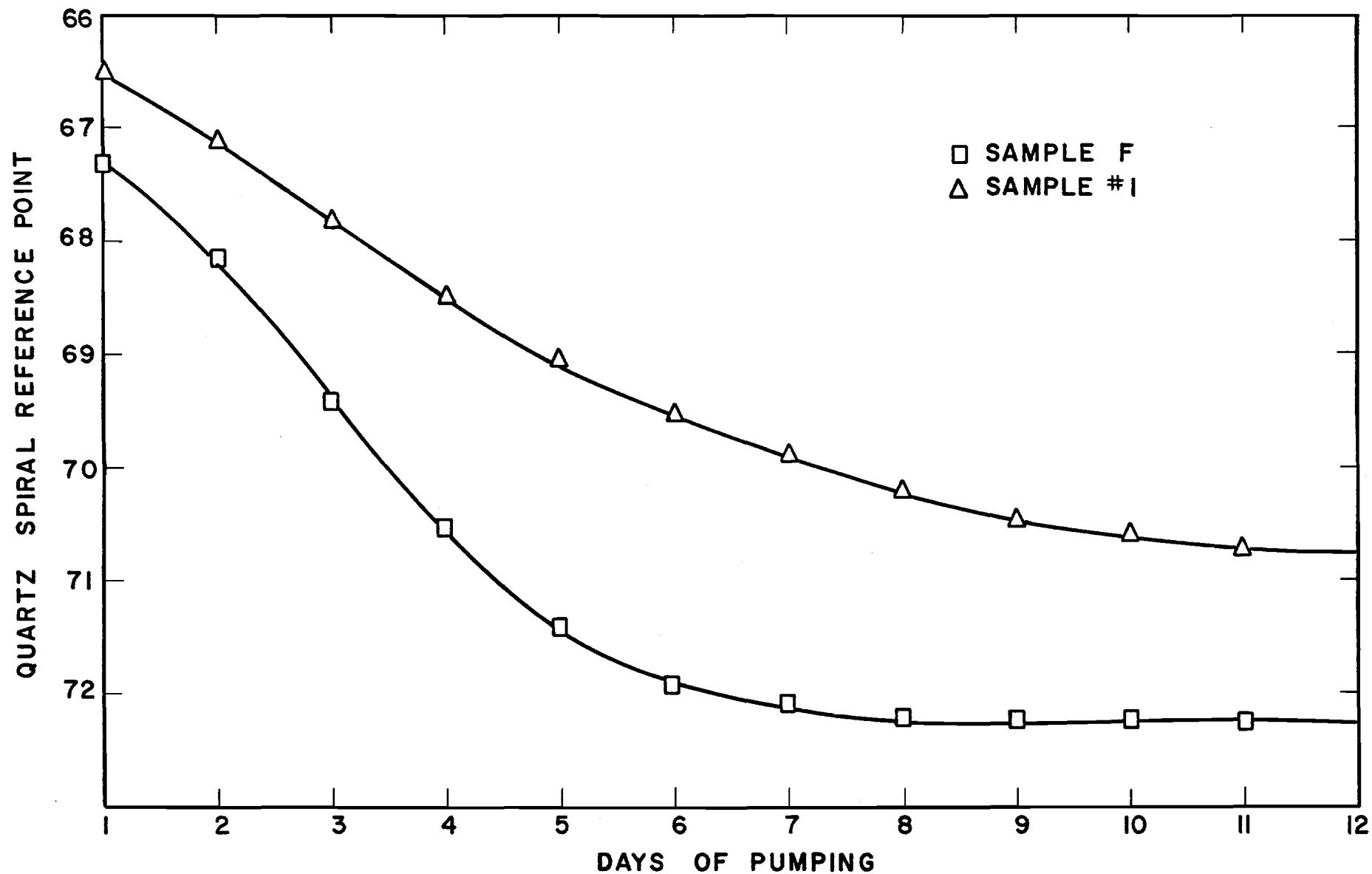


FIGURE 10

REMOVAL OF H₂O FROM PLASTER SAMPLES BY EVACUATING

AT 10⁻⁶ mm Hg

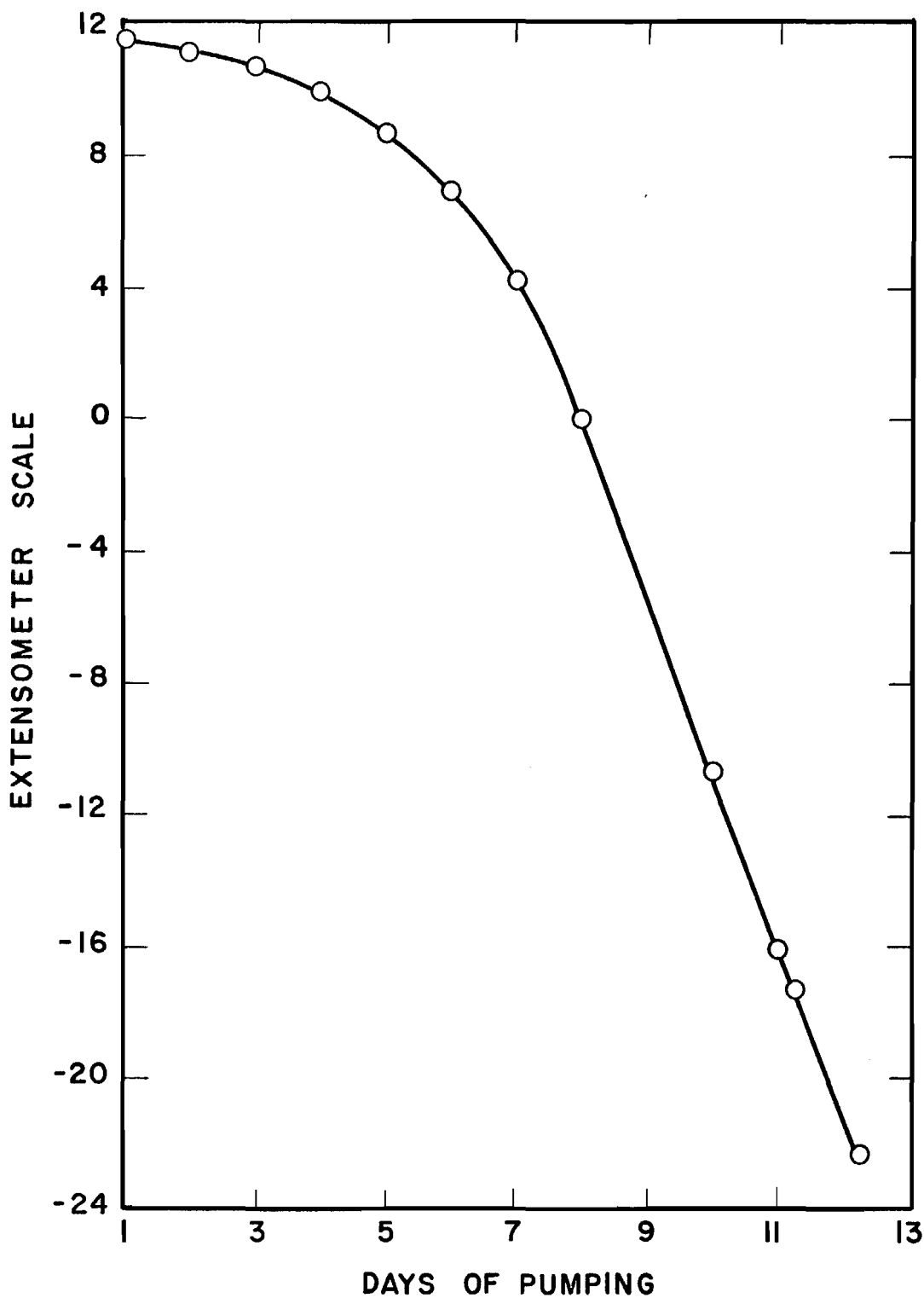
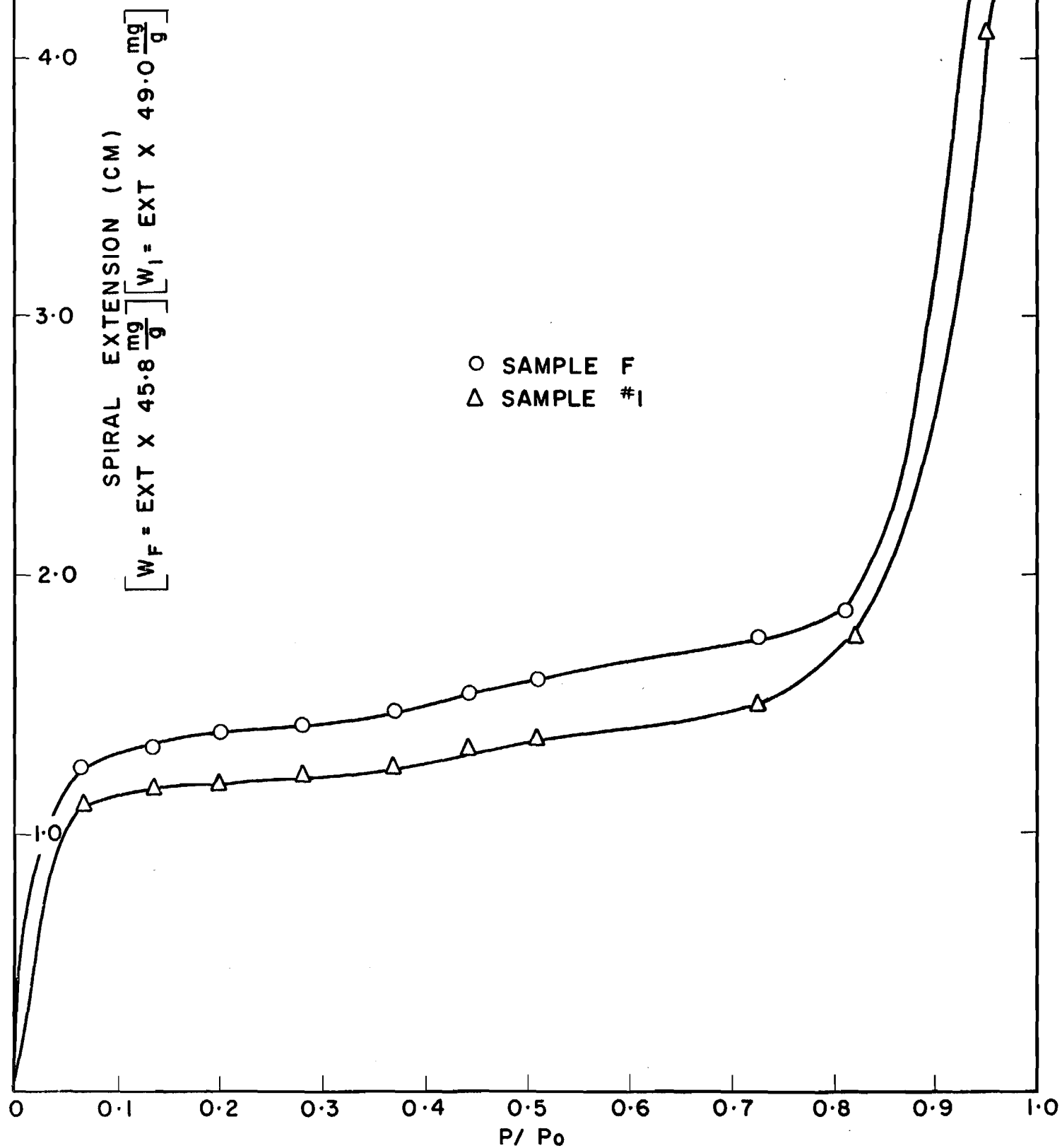


FIGURE II
DIMENSIONAL CHANGE IN PLASTER SAMPLE F
DURING EVACUATION

FIGURE 12
WATER VAPOR SORPTION ON PLASTER



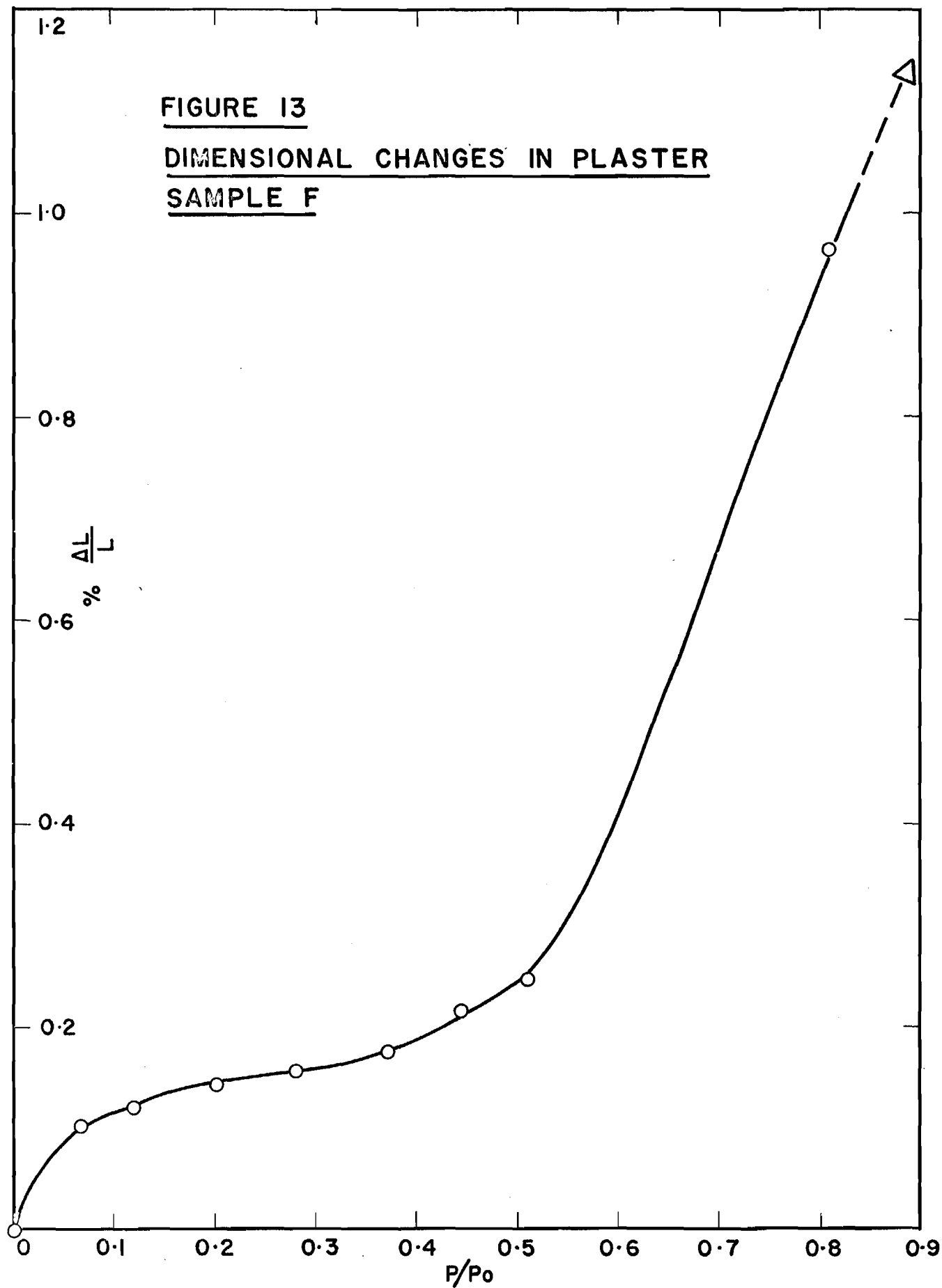
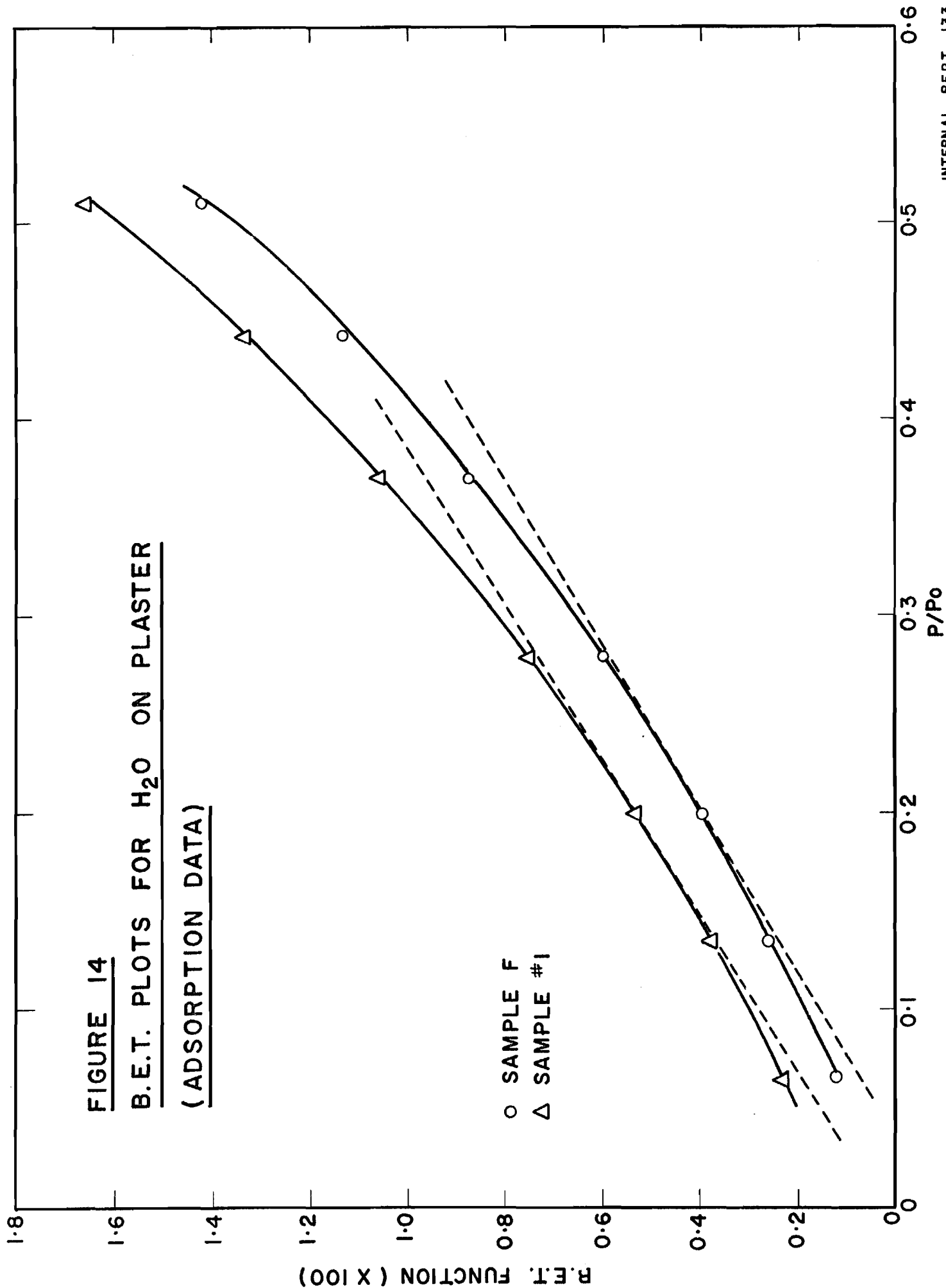


FIGURE 14
B.E.T. PLOTS FOR H₂O ON PLASTER
(ADSORPTION DATA)



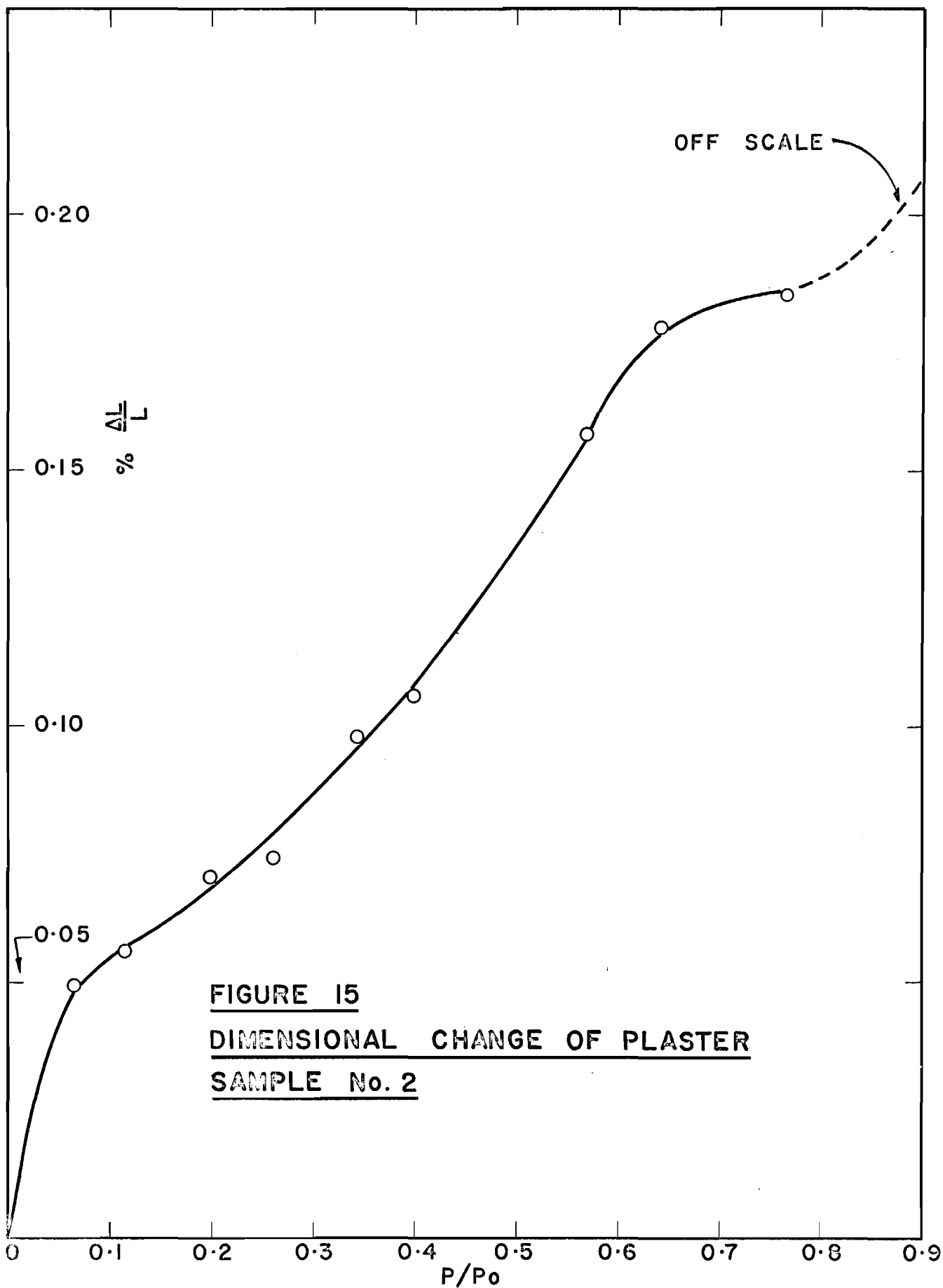


FIGURE 15
DIMENSIONAL CHANGE OF PLASTER
SAMPLE No. 2