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STUDY OF SORPTION PROPERTIES AND STRUCTURE OF PORASILS OVER A WIDE TEMPERATURE RANGE

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SUMMARY

Various types of Porasils used in gas chromatography have been studied over a wide temperature range and their sorption properties and changes in structure have been followed. Adsorption isotherms of benzene were measured on Porasils that were thermally pre-treated from 100° to 1000° and their specific surface areas were calculated. The adsorption isotherms had concave shapes in all instances. At pre-treatment temperatures above 700°, a pronounced decrease in the amount adsorbed per gram of the adsorbent occurred. Only Porasil F yielded identical results over the whole range of pre-treatment temperatures. Porasil A and D exhibited irreversible changes at temperatures above 700°. In this region, emanometric and X-ray analyses, porosimetric analysis and grain size measurements were carried out, and microscopic photographs were taken. The results show that Porasil pre-treated at temperatures of 900–1000° meets the requirements for an ideal support better than thermally untreated silica gels of low surface area.

INTRODUCTION

Silica gel is used in various chromatographic systems, either in gas–solid systems, in liquid chromatography, in ion-exchange chromatography, or as a support for gas–liquid chromatography. A number of papers^{1–14} have been devoted to its analytical applications, theoretical studies and various pre-treatment techniques.

The chemical structure of the surface of silica gel has not yet been clarified satisfactorily^{7,8,11–20}. However, there are no substantial differences in opinion on the type of bonding of water to the silica surface. The majority of authors agree on two models and differentiate between physically bound water, which can be removed within a temperature range of 25–120°, and water bound by hydrogen bonds, which is desorbed at temperatures of 120–180°, or water simultaneously bound physically and by hydrogen bonds, which is liberated at temperatures of about 200°^{7,21,22}.

In a previous paper²³, the sorption properties of various types of Porasil, activated at a temperature of 100°, were studied. It follows from the results of differential thermal analysis, given in this paper, that even at temperatures above 200° some loss of water occurs, which may considerably affect the properties of these materials

as adsorbents or supports in gas-liquid chromatography. In the pre-treatment methods used so far, Porasil and other types of silica gel were mostly activated at temperatures of about 250°, where the physically bound water was removed but not all of the water bound in the micropores. As adsorption proceeds reversibly in this temperature region, deactivation of the material and consequently substantial and irreproducible changes in its surface may occur under commonly used experimental conditions. Far better properties as a support may be expected with silica gel ignited at a temperature above 600°, where the micropores are closed and the specific surface area decreases^{7,13,20}. In order to be able to assess more satisfactorily the use of the silica gels pre-treated in this way as supports, it was necessary to measure the dependence of the basic sorption characteristics on the pre-treatment temperature, and especially in the temperature range where irreversible changes occur.

EXPERIMENTAL

The measurements were carried out on Porasil A, D and F, produced by Waters Ass., Framingham, Mass., U.S.A. Samples of the sorbents studied were ignited in an electrical resistance furnace in a platinum crucible. The temperature was adjusted with a variable transformer and controlled with a platinum/rhodium thermocouple. After the required temperature had been established, the sample was ignited for 4 h and, after being transferred into the column, was activated *in situ* at 200° for a further 5 h. The adsorption isotherms were measured at a temperature of 70° and the heats of adsorption from 60° to 80° in approximately 5° steps.

Benzene (p.a.) and *n*-hexane (p.a.) from Lachema, Brno, Czechoslovakia, were used as sorbates. The adsorption isotherms were measured by frontal techniques on a modified Fractovap Model C instrument (Carlo Erba, Milan, Italy) equipped with a thermal conductivity detector. The instrument was suitable for isothermal work and enabled the temperature to be maintained to within $\pm 0.1^\circ$. Hydrogen saturated with benzene vapour was used as the carrier gas at a flow-rate of 1.5–2.5 cm/sec. The heats of adsorption were measured on the Fractovap Model C instrument with a flame ionization detector. The other operating parameters were identical with those used for the measurement of the isotherms. In both instances, Hamilton syringes with volumes of 1, 5 and 50 μ l were used for sampling.

RESULTS AND DISCUSSION

Changes in the sorption properties of Porasil A, D and F over a wide temperature range

Benzene adsorption isotherms on Porasil A, D and F. By the frontal chromatographic technique, the benzene adsorption isotherms on Porasil A, D and F were obtained at a temperature of 70°. All three types of Porasil were thermally pre-treated at temperatures of 100–1000° at 100° intervals. The adsorption isotherms obtained on Porasil A and D are shown in Figs. 1 and 2, respectively. On Porasil F, the differences among the amounts adsorbed at various activation temperatures were very small and overlapped each other. Therefore, the maximum relative measuring error for both variables was calculated. The magnitude of this error involves the whole interval of the measured isotherms. The adsorption isotherm obtained by calculation of the averages of both variables is shown in Fig. 3, together with the maximum relative er-

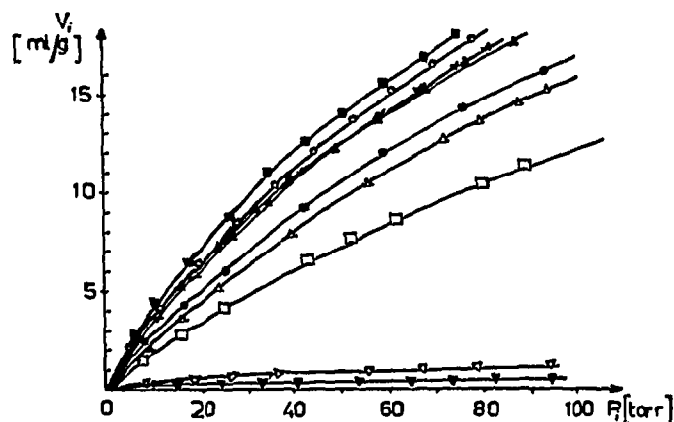


Fig. 1. Adsorption isotherms for benzene on Porasil A pre-treated at different temperatures: ■, 100°; ▲, 200°; ○, 406°; +, 508°; ●, 600°; △, 700°; □, 800°; ▽, 900°; ▼, 1010°.

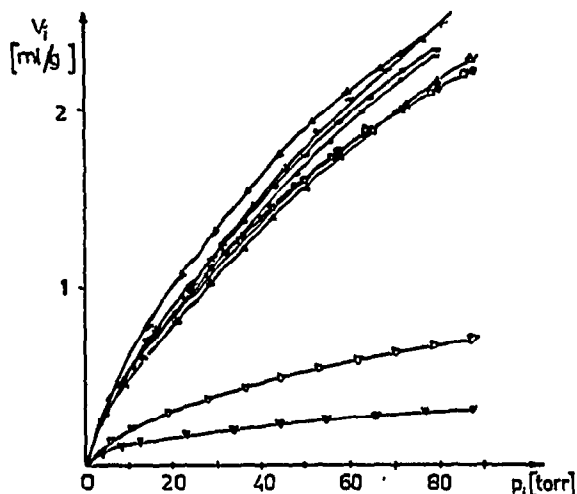


Fig. 2. Adsorption isotherms for benzene on Porasil D pre-treated at different temperatures: ■, 100°; ▲, 200°; ○, 402°; +, 506°; ●, 580°; △, 700°; □, 810°; ▽, 910°; ▼, 1000°.

rors of both variables. All the isotherms obtained were plotted in the BET co-ordinates and the specific surface areas calculated. The changes in the specific surface areas due to the thermal pre-treatment of the sorbent are given in Table I. From these results, the specific isotherms were then calculated (Figs. 4 and 5).

The benzene adsorption isotherms on all three Porasilis (Figs. 1-3) have a concave shape. The shape of the isotherms on Porasil A and D is markedly affected by opening and closing of the micropores. In Porasil A, which is a narrow-pore material, there are micropores with diameters smaller than 7 Å, most of which are opened only at temperatures above 300°. As capillary condensation occurs in these pores, the isotherms obtained after thermal pre-treatment of the material at 406° and 508° in a region of higher partial pressures (30-40 Torr) have a markedly steeper shape than

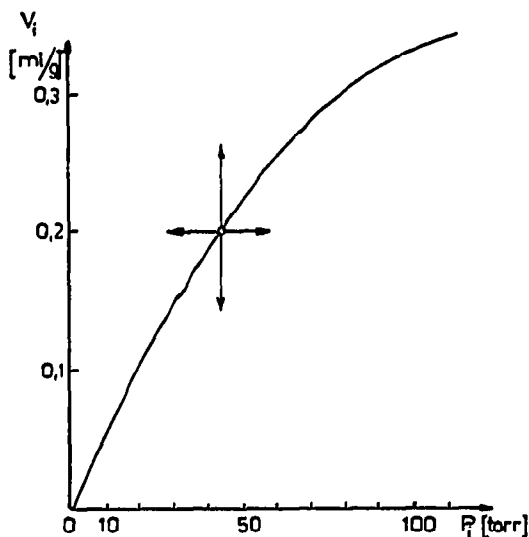


Fig. 3. Adsorption isotherm for benzene on Porasil F measured with the maximum relative errors $\varepsilon_{V_i} = \pm 0.268$ and $\varepsilon_{P_i} = \pm 0.314$.

the isotherms of the materials with micropores that are still unopened (at 200°) or already closed (700°). These results are in agreement with those of Nichols and Thorp¹³, who demonstrated micropore closing by porosimetric analysis on a narrow-pore silica gel at 660°.

With Porasil D, a sorbent with a medium pore size, capillary condensation occurs after thermal pre-treatment at 506°, 580° and 700°, for partial pressures of 20–30 Torr. At these temperatures, the pores begin to narrow and capillary condensation again participates in the overall sorption effect.

It can be seen from the dependence of the specific surface area on the pre-treatment temperature for both Porasils (Table I) that the specific surface areas of

TABLE I

SPECIFIC SURFACE AREAS (S) OF PORASIL A, D AND F PRE-TREATED AT DIFFERENT TEMPERATURES

Porasil A		Porasil D		Porasil F	
Temperature (°C)	S (m^2/g)	Temperature (°C)	S (m^2/g)	Temperature (°C)	S (m^2/g)
100	211.5	100	23.1	100	1.72
200	209.7	200	26.9	200	2.14
406	232.4	402	28.1	405	1.69
508	220.3	506	29.7	490	1.63
600	203.6	580	29.3	600	1.89
700	188.7	700	26.7	705	1.55
800	156.9	810	23.2	810	2.06
900	11.1	910	6.85	900	1.90
1010	4.56	1000	2.84	1010	1.77

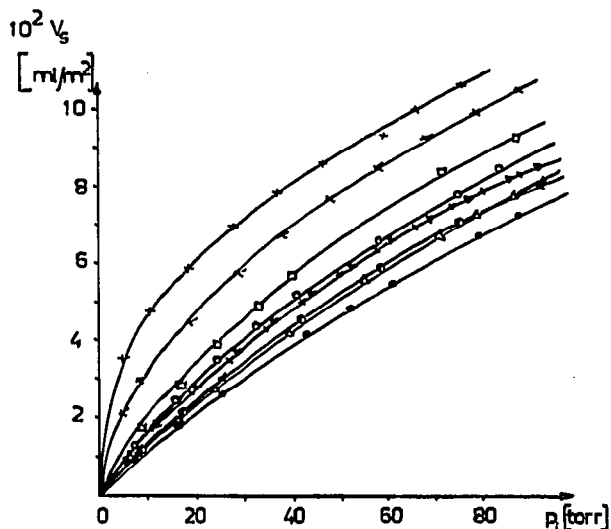


Fig. 4. Specific isotherms for benzene on Porasil A pre-treated at different temperatures: \square , 100° ; \circ , 200° ; \blacktriangledown , 406° ; \blacksquare , 508° ; \triangle , 600° ; \odot , 700° ; \bullet , 800° ; \times , 900° ; $+$, 1010° .

Porasil A after thermal pre-treatment at 100° and 200° are almost identical; however, the appropriate adsorption isotherms also indicate that a change in the surface occurs, probably caused by desorption of the last residues of water bound to the sorbent surface. Water bound in the micropores is desorbed only in the temperature range 200 – 400° . Accordingly, Porasil A has the largest specific surface area at temperatures of about 400° , where the maximum number of micropores are probably uncovered. The contribution from capillary condensation to the overall sorption process

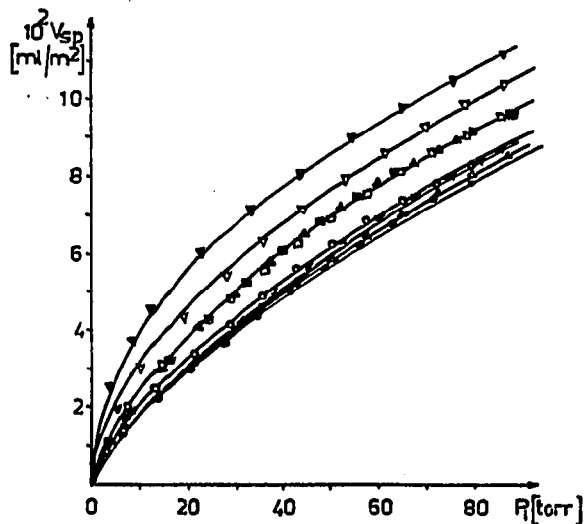


Fig. 5. Specific isotherms for benzene on Porasil D pre-treated at different temperatures: \blacksquare , 100° ; \blacktriangle , 200° ; \circ , 402° ; $+$, 506° ; \bullet , 580° ; \triangle , 700° ; \square , 810° ; ∇ , 910° ; \blacktriangledown , 1000° .

is also greatest within this region. The decrease in the specific surface area with a further increase in the temperature of pre-treatment of the material can be explained by the initiation of dehydroxylation of the silanol groups. While the shapes of the specific isotherms for pre-treatment temperatures of 406° and 508° are almost identical (which also confirms that the characters of the sorption on the surface are identical), at a pre-treatment temperature of 600° the micropore effect decreases and it disappears completely at a temperature of 700°. The specific surface area of the material pre-treated at a temperature of 600° decreased to a value close to the specific surface area of the materials pre-treated at 100° and 200°. On further increase in the pre-treatment temperature, gradual surface dehydroxylation and the formation of siloxane groups occur.

With Porasil D, an increase in the specific surface area occurs after thermal pre-treatment at 200°, which can be explained by the uncovering of new silanol groups in the pores that were still blocked by water at 100°. After thermal pre-treatment at 402°, a further increase in the specific surface area can be observed, due to uncovering of the maximum number of micropores. At pre-treatment temperatures of 506° and 580°, the specific surface areas attain almost identical maximum values. With materials pre-treated at these temperatures, capillary condensation in the micropores, which were narrowed by the thermal treatment, occurs to a marked extent. The effect of capillary condensation is also confirmed by the shape of the adsorption and specific isotherms. After thermal pre-treatment at 700°, a decrease in the specific surface area again occurs, owing to a decrease in the number of silanol groups and the formation of siloxane groups. Capillary condensation participates in the sorption process to the same extent as with materials pre-treated at a temperature of 580°; the shape of both specific isotherms are almost identical. Complete closing of the micropores takes place at 800°, when the surface area decreases to a value almost identical with that for Porasil D activated at 100°. The shapes of the adsorption and specific isotherms are also virtually identical.

At pre-treatment temperatures above 800°, a sudden decrease in the specific surface area was observed with Porasil A and D (see Table I). The amounts sorbed per unit surface area increase markedly (see Figs. 4 and 5). At a temperature of 1000°, a further decrease in the specific surface area by more than one half occurs, accompanied by a further increase in the amounts sorbed per unit surface area.

Very small changes in the shape of the adsorption isotherms on Porasil F, and also changes in the specific surface area at various activation temperatures, indicate that this adsorbent does not change its chemical or physical character on thermal pre-treatment.

Heats of adsorption of benzene on Porasil A, D, and F. The heats of adsorption were measured chiefly with regard to determination of the extent of dehydroxylation of the silica gel surface in the region 600–1000° (Fig. 6).

On Porasil A, benzene has the highest heat of adsorption at 200° within the temperature range studied, which indicates that the surface is fully hydroxylated. The heat of adsorption for a pre-treatment temperature of 600° is higher than that for 700–900°, which indicates that dehydroxylation is not completed at 600°. A similar dependence was found with Porasil D.

The heats of adsorption of benzene on Porasil F remain almost unchanged over the whole temperature range, in contrast with Porasils A and D.

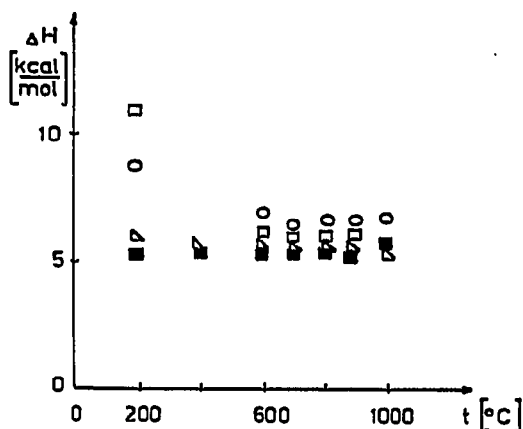


Fig. 6. Heats of adsorption for benzene on Porasil A, D and F at various pre-treatment temperatures: □, Porasil A; ○, Porasil D; △, Porasil F; ■, *n*-hexane on Porasil F.

In order to be able to find the extent of dehydroxylation of the surfaces of all three types of Porasil, the heats of adsorption of *n*-hexane were measured, as this is a sorbate which cannot specifically react with surface hydroxyl groups. While the heats of adsorption of benzene and *n*-hexane on Porasil A and D are virtually identical, except at activation temperatures above 600°, those of both sorbates on Porasil F are identical over the whole of the temperature range studied.

The adsorption energy is therefore the same in all instances in the region above 600°, even if the adsorption and specific isotherms differ. Hence it can be assumed that the adsorption centres no longer change qualitatively and that the change in the adsorption properties is caused by deeper structural changes in the material.

Physical changes in Porasil A and D at pre-treatment temperatures above 800°

In the temperature region where surface dehydroxylation is virtually complete, the changes in the sorption properties can be explained only by a basic change in the structure.

TABLE II

PARTICLE DIAMETERS OF PORASIL A AND D UNTREATED AND PRE-TREATED AT DIFFERENT TEMPERATURES

Porasil A		Porasil D	
Temperature (°C)	Particle diameter (mm)	Temperature (°C)	Particle diameter (mm)
—	0.15–0.20	—	0.17–0.20
600	0.15–0.20	580	0.17–0.20
800	0.15–0.20	810	0.17–0.20
900	0.12–0.15	910	0.15–0.17
1010	0.11–0.12	1010	0.13–0.16

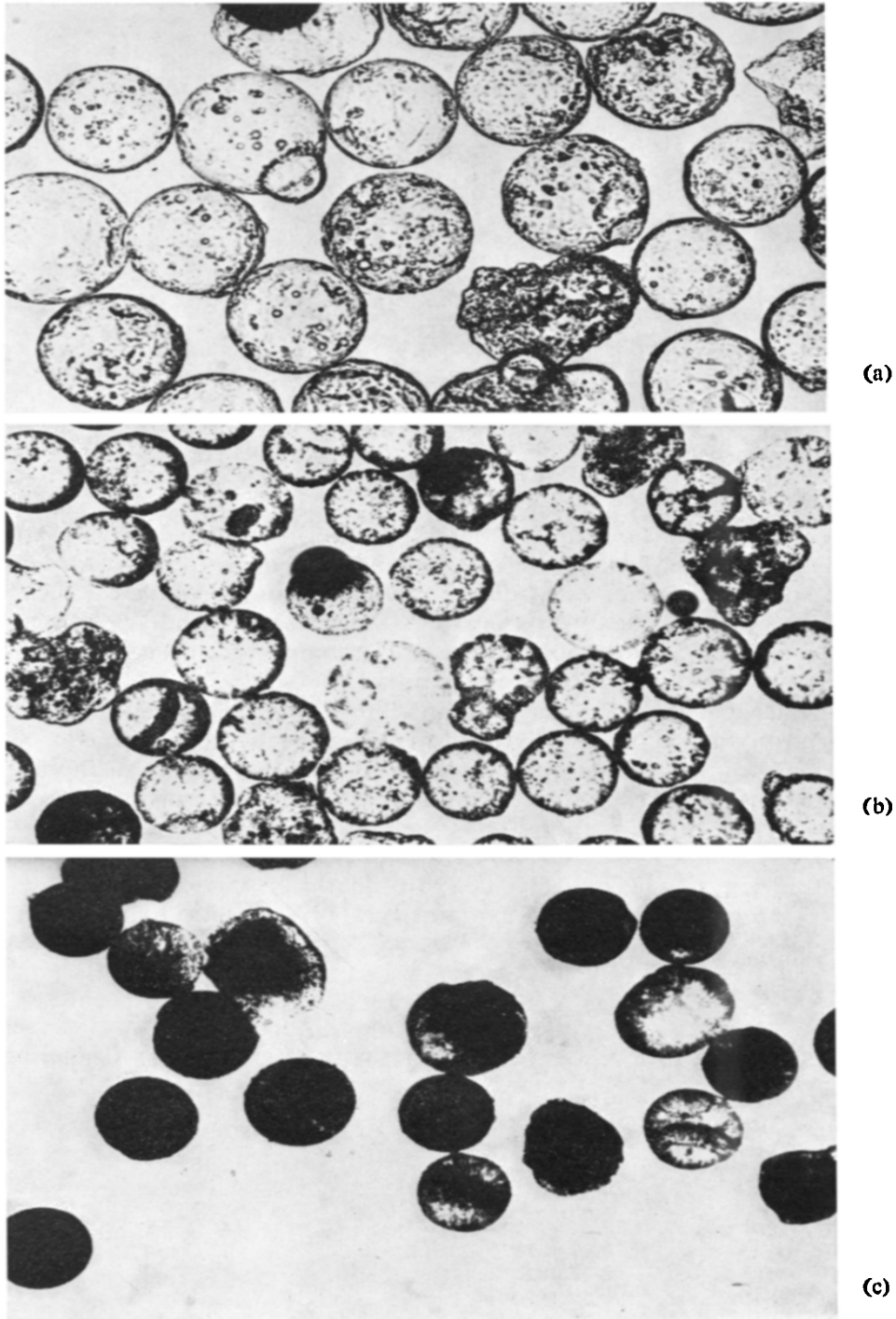


Fig. 7. Microphotographs of Porasil A at $100\times$ magnification after pre-treatment at temperatures of (a) 100° , (b) 900° and (c) 1010° .

In order to be able to find the character of these changes, X-ray analysis of Porasil A and D samples, pre-treated at temperatures of 100°, 800°, 900° and 1000°, was carried out, and also emanometric analysis and porosimetric analysis of Porasil D, and microscopic measurement of particle diameter.

The microscopic measurements showed a volume contraction, beginning at 800° and continuing up to 1000°. The results of the particle diameter measurements are given in Table II.

For the sake of lucidity, microphotographs in a light beam were taken, from which the change in the size of the particles, and also a change in their appearance or transparency, is evident (see Fig. 7).

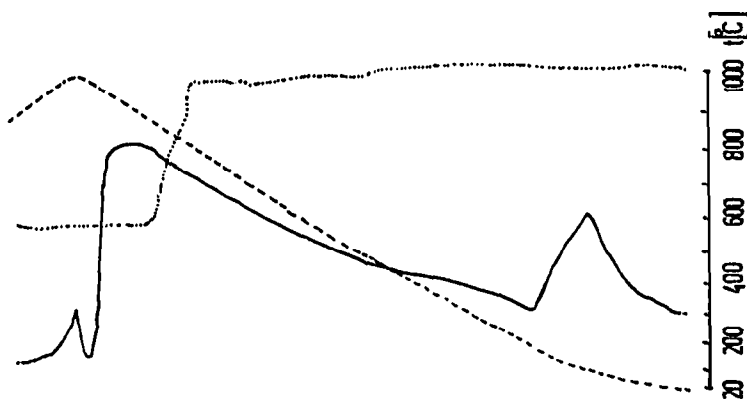


Fig. 8. The emanometric analysis of Porasil A: ———, emanometric recording; - - -, thermometer recording; ·····, dilatometer recording.

The emanometric analysis of Porasil A (see Fig. 8) indicates that most of the physically bound water is desorbed from Porasil A at 100°. An increase in the slope at about 400° indicates uncovering of the micropores. At about 900°, crystallization begins, which causes a sharp change in the emanation properties of the adsorbent. The peak at 1000° is caused by initiation of cooling of the material.

With Porasil D, crystallization begins at a lower temperature and is accompanied by a smaller volume contraction than with Porasil A. After cooling the sample in the atmosphere, repeated analyses showed that the amount of physically bound water desorbed at about 100° was many times lower than with the original sample.

Porosimetric analysis was carried out with an original Porasil D sample and a sample pre-treated at a temperature of 1000°. It is evident (see Fig. 9) that the thermally pre-treated Porasil D has a narrower pore spectrum and a lower overall pore volume. The radius of the most characteristic pores increased to 3800–4000 Å, *i.e.*, approximately ten times. In addition to these pores, pores with larger radii exist on the surface of the pre-treated sample, which cannot markedly affect the sorption process. It is obvious from the results of the porosimetric measurements that pre-treatment at 1000° causes deep and permanent textural changes (the measurements were carried out 5 months after the thermal pre-treatment of the sample).

Further, X-ray analyses of Porasil A and D samples were performed. The re-

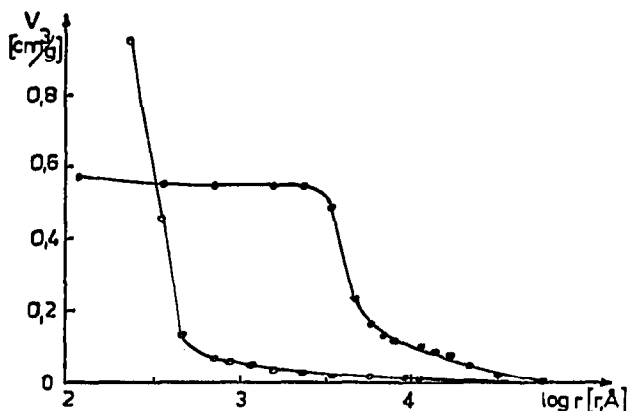


Fig. 9. The porosimetric analysis of Porasil D, untreated (○) and pre-treated at 1000° (●).

sults for Porasil A are shown in Fig. 10. It is evident that the material pre-treated at 800° is still amorphous, at 900° partial crystallization has occurred, and at 1010° it is entirely crystalline. The crystalline structure is identical with that of α -cristoballite.

The X-ray analysis results for Porasil D are virtually the same. However, partial crystallization occurs at a pre-treatment temperature of 800°.

It follows from all the measurements performed that the sudden change in the sorption properties in the pre-treatment temperature interval of 800–1000° is caused by the basic structural and textural changes in Porasil A and D.

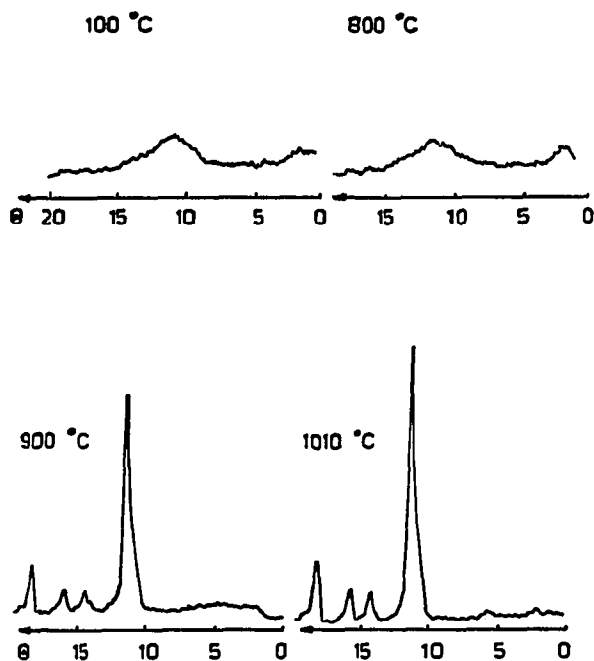


Fig. 10. The X-ray analysis of Porasil A after pre-treatment at various temperatures.

From the point of view of the use of Porasil A and D for chromatographic purposes, the materials thermally pre-treated at 800–1000° meet the requirements for an ideal support for gas-liquid chromatography better than thermally untreated silica gels of low-surface area. The main advantage is their small specific surface area, the absence of micropores, almost homogeneous particle size, increased mechanical strength, an exactly defined structure and an unchanging texture in any temperature range, and the virtual absence of physically bound water. According to preliminary experiments with the pre-treated materials, both Porasil A and D pre-treated at 1000° and Porasil F, whose structure is independent of thermal pre-treatment, functioned well as supports. As an example, elution curves of methanol, using the materials studied coated with a Carbowax 1500 monolayer, are shown in Fig. 11. A marked

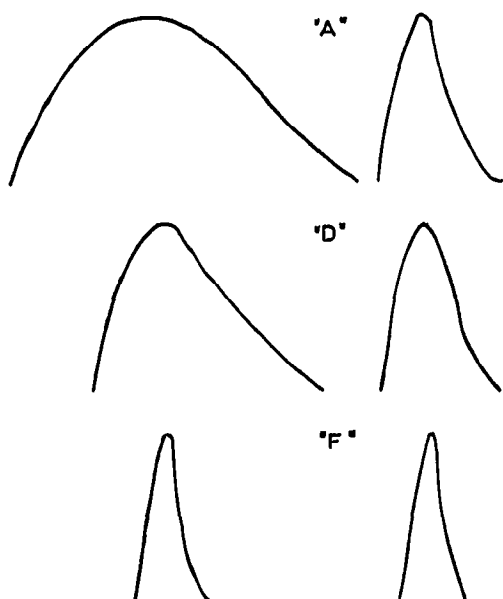


Fig. 11. Peak shapes of methanol on Porasil A, D and F (untreated on the left, pre-treated at 1000° on the right).

decrease in the asymmetry of the elution curve using thermally pre-treated Porasil A and D is evident. Analogous observations have also been made for a series of other alcohols. A more detailed investigation of the analytical use of the pre-treated Porasils as supports in gas chromatography is at present being carried out.

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