CHROM. 8889

APPLICATION OF INVERSE GAS CHROMATOGRAPHY TO THE DETERMINATION OF THE SURFACE AREA OF MACROPOROUS AND MESOPOROUS ADSORBENTS

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(Received October 7th, 1975)

SUMMARY

The gas phase chromatographic methods described for determining the surface area of porous materials can be applied to hydroxylated adsorbents such as silica gels, activated aluminas and oxides and to materials coated with hydroxylated liquids. These determinations are not based on the area occupied by a volatile sorbate in a monolayer according to the chromatographic variation of the BET method, but are based on the measurement of the area of a stationary phase monolayer by inverse gas chromatography.

The application of one of the methods to macroporous materials leads to determinations that are probably more accurate and certainly more precise than any other previously described. The results give some insight into the physical state and the site occupied by "stationary phases" in porous media.

INTRODUCTION

The BET method for the determination of the surface area of porous materials can be applied to almost any type of surface, except those with very low surface energy, and gives rapid and relatively precise determinations. One of its variations takes advantage of the so-called "gas chromatographic" determination of part of an adsorption isotherm, according to the method of Nelsen and Eggertsen[1], which has been improved by many workers[2]. Nitrogen is usually used as a volatile sorbate. The value and the versatility of these techniques for routine measurements are undisputed.

However, BET determinations are based on more or less disputable assumptions or approximations and a somewhat arbitrary evaluation of the adsorbate molecular area, and therefore they can be questioned from the point of view of accuracy and precision. In routine measurements on adsorbents and catalysts, disagreements are frequent and consequently there is a need for the development of methods that are completely independent of the BET hypothesis and do not require very specialized and expensive apparatus.

Our recent studies on the physical state of stationary phases on the surface of supports by inverse gas chromatography[3–6] led us to develop such a technique, which

can be applied to hydroxylated surfaces, particularly to silica and alumina adsorbents. The aim of this paper is to describe these new methods for the determination of surface areas, and the favourable case of macroporous supports is emphasized.

PRINCIPLE OF THE DETERMINATION OF SURFACE AREA BY INVERSE GAS CHROMATOGRAPHY

In general, we utilize the actual formation of a monolayer of stationary phase and not just the calculation of the amount of a volatile sorbate that would be necessary for the completion of such a layer, as is the practice in all BET methods, whether chromatographic or not.

All the methods we propose for hydroxylated surfaces are based on the experimentally observed distribution of the stationary phase between two phases, a monolayer and a bulk material, characterized by completely different properties. This model is inconsistent with the widely prevalent concept of the multilayer, the properties of which would change progressively from the adsorbent surface, as we found[7] for a normal alkane layer on the non-hydroxylated surface of graphite.

Method based on the discontinuity in chromatographic properties corresponding to the formation of a monolayer of stationary phase for increasingly charged columns

This method was described recently[2] and has been applied to silica and glycol surfaces on siliceous supports.

We measure the retention volume by unit mass of the support (V_s) of an arbitrary solute at a determined temperature for a series of columns characterized by a load in mass of stationary phase per unit mass of support (τ). We plot V_s/τ as a function of $1/\tau$. Thus we obtain a graph consisting of two straight lines, intersecting at the critical load τ_c which corresponds to the formation of a monolayer (Fig. 1).
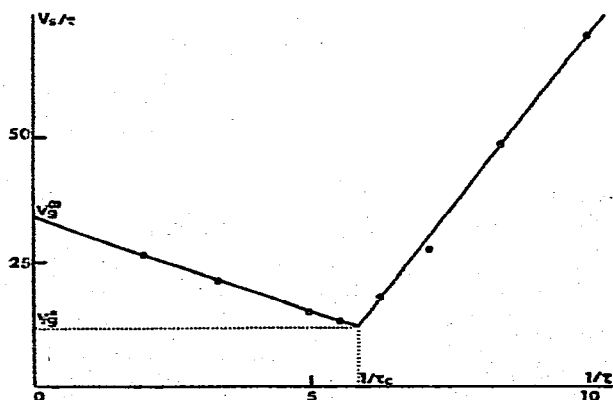

Fig. 1. Variation of V_s/τ with $1/\tau$ for *n*-pentane as solute and octadecanol as stationary phase on Spherosil X OB 075 (87 m²/g) as support at 58°.

The line on the left intersects the ordinate at a limiting value of V_s/τ that is often denoted by V_g^∞. It is, in fact, the true specific retention volume per gram of stationary phase, V_g. This extrapolation has become a classical means of eliminating the influence of adsorption phenomena at interfaces[8].

The value on the ordinate of the point of intersection of the two lines is the retention volume due to adsorption on the compact monolayer, $V_g{}^*$, relative to unit mass of the film. For a long-chain fatty stationary phase, $V_g{}^*$ is much lower than V_g, because the external part of the film consists of large CH_3 groups of very low polarity and very low surface energy. However, in general, $V_g{}^*$ may be larger than V_g, as we shall show.

In any case, on the left of the intersection of the two lines there is an excess of bulk material in the presence of a compact film, while on the right there is a non-compact monolayer, the retention of which increases when its density decreases as a consequence of the increasing influence of the underlying surface*.

The specific surface area, S, can easily be calculated from the critical load by the equation[2]

$$S = \frac{\tau_c N A}{M_f} \tag{1}$$

where N is Avogadro's number, M_f the molecular weight of the stationary phase and A the molecular area of the compact film at the arbitrarily chosen temperature. As with BET measurements, determination of the surface area using eqn. 1 does not obviate the partly arbitrary choice of a molecular area for the film, but there are two obvious advantages: (1) a pure monolayer can be laid on the surface with any desirable approximation; (2) studies we have made by inverse gas chromatography on long-chain fatty stationary phases on the surfaces of silica, glycol and water substrates[2,4,6,9,10] have indicated very similar properties of the films, in particular in a sort of surface solid, the so-called "condensed" state. Also, all of our experiments on "condensed" octadecanol films at the melting temperature of this material (58°) on various macro-porous substrates of silica, glycerol and water have always given a molecular area very close to 21.0 Å² by use of eqn. 1 and careful BET surface measurements.

Thus we are led to assume that condensed films of octadecanol on different hydroxylated substrates are identical. Their molecular area is imposed by the cross-section of the fatty chain itself. On the contrary, small molecules, such as nitrogen, are completely immersed in the force field of the adsorbing surface and it is possible to assume that they occupy a varying area from one adsorbent to another. Such a possibility has already been attributed as the consequence of localized adsorption[11].

The molecular area of a fatty alcohol in the condensed state can easily be determined by direct area measurements on the surface of the trough of a Langmuir film balance. If lower values of about 19–20 Å², corresponding to a phase obtained by surface compression, are disregarded, values of about 21 Å² have always been found[12], in spite of the possible influence of solubility in the bulk substrate, which is excluded in chromatographic columns. In such condensed phases, fatty chains are slightly tilted from the perpendicular to the surface.

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* The linear character of this part of the diagram has no theoretical basis. It cannot be extended far from the intersection point.

It is possible to determine surface areas by means of non-condensed films. In this case, the molecular area is determined by eqn. 1 from previous surface area measurements. Nevertheless, in order to carry out this method, at least four column preparations are needed, so that except for calibration purposes, its practical application would be much too time consuming. Since our first paper was published[2], we have developed a much easier variant of our inverse gas chromatographic technique.

Determination of the increase in the retention of a solute resulting from the melting of a small excess of bulk material

In this technique we use only one chromatographic column, in which a slight excess of bulk stationary phase is in equilibrium with the film on the support. An increase in the retention volume of the test solute by melting of the stationary phase allows the measurement of this excess. By difference between the total load of the stationary phase and the load corresponding to the excess of bulk material, it is easy to calculate τ_c, the critical load corresponding to the formation of a compact film. The surface area of the support can be deduced from τ_c as above. In fact, the result is more precise if the excess of bulk material is small. Therefore, a preliminary experiment may be necessary in order to obtain a first approximate determination.

For many reasons[4] and chiefly because of the capillary decrease of the melting point[13,14], the retention volume begins to increase at temperatures well below the normal melting temperature of the stationary phase, T_f. Thus an extrapolation of the linear parts of the log V_s versus $1/T$ diagram is necessary for the determination of

$$\Delta V_s = V_{s2} - V_{s1} \tag{2}$$

as shown in Fig. 2.

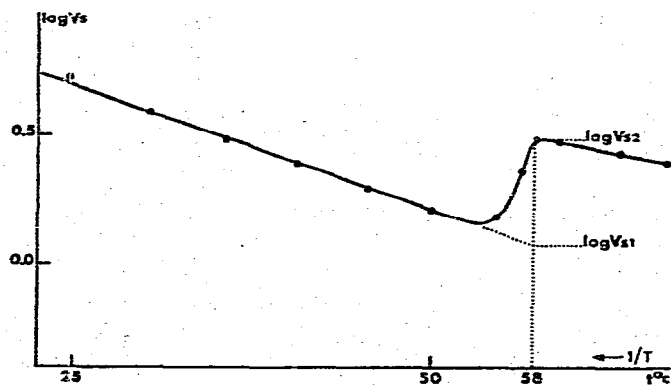
Fig. 2. Variation of log V_s, with $1/T$ for *n*-octane as solute and 2.70% of octadecanol as stationary phase on Spherosil X OC 005 (11.08 m²/g) ($\tau_c = 2.36\%$).

In practice, the load of the stationary phase, τ, would be 10–20% higher than the τ_c value obtained from eqn. 5 (see below). Theoretically, only one measurement at the melting point and two measurements below it would be sufficient. Nevertheless, it is recommended that four different temperatures below and four temperatures

above the melting point should be used. Good estimates of V_{s2} and V_{s1} are obtained by the least-squares method. The load of bulk material is given by

$$\tau_b = \frac{\Delta V_s}{V_g} \tag{3}$$

$$\tau_c = \tau - \tau_b \tag{4}$$

If A is expressed in $\mathring{A}^2$ and τ_c in %, the surface area (m²/g) is given by

$$S = \frac{60.6\tau_c A}{M_f} \tag{5}$$

If V_g is unknown, it can easily be determined by the same type of experiment on a silanized support. We have shown[6] and we shall confirm that the usual stationary phases do not give films in such hydrophobic materials and that they are exclusively in the state of a capillary condensate. Thus the melting transition in this instance has to be attributed to the whole of the deposited material:

$$V_g = \frac{(\Delta V_s)_{silan.}}{\tau} \tag{6}$$

The determination of surface areas by the adsorption of fatty compounds from solutions was proposed many years ago[15], but there are difficulties in the application of these liquid phase techniques. Firstly the interpretation of a liquid phase isotherm is just as difficult as for a gas phase isotherm in most instances. In general, a compact film cannot be in equilibrium with an excess of pure solvent, except for apolar solvents and very polar sorbates[16], but the very low solubility of these "solutes" is the origin of experimental difficulties. Secondly, construction of the liquid phase adsorption isotherm is hampered by the setting up of equilibrium and analytical problems that are specific to each sorbate. There are no such difficulties in our inverse gas chromatographic method.

Determination of surface area by a single measurement of retention volume

If the members of a particular type of adsorbent can be considered to be always alike, single measurements of retention volume for a particular solute at a determined temperature give relative evaluations of the surface areas in the columns. This idea was proposed soon after the advent of gas chromatography by workers such as Cremer[17]. Unfortunately, the practical application of this idea is very difficult for most adsorbents, because the retention depends critically on the degree of activation of these adsorbents, *i.e.*, on the elimination of all impurities, particularly water. In any case, it is very improbable that two adsorbents would have very different surface areas but identical surface structures.

However, we propose to apply the above idea after coating the adsorbent with a convenient organic monolayer. We shall see that approximate measurements are possible in this way with a very simple chromatograph.

EXPERIMENTAL

Experiments were performed with a very simple chromatograph described in previous paper[2]. We shall discuss only a few experimental aspects of the work here.

Materials

Spherosils (very pure silica gels in bead form) were obtained from Rhône Progil (Paris, France). We are indebted to Pechiney-Ugine Kuhlman (Research Center, Pierre Benite, France) for samples of α-alumina and for the determination of their textural characteristics.

Dibutyl sulphone and benzophenone were "pure" products from Eastman-Kodak (Rochester, N.Y., U.S.A.) and Fluka (Buchs, Switzerland), respectively. We used C_5–C_6 n-alkanes as solutes.

Preparation of adsorbents

Except for the silanized supports, all of the adsorbents were activated for 24 h at 150° in air. Under these conditions, all of the silicas of large surface area lose about a monolayer of water ($A = 20$ Å^2). It was confirmed that coating of these adsorbents with dibutyl sulphone without special precautions and filling of the column in the air did not result in a large uptake of water.

BET surface areas

All of the measurements were made by the dynamic method described recently[2]. We are indebted for these determinations to M. Perrin of the Institut de Recherches sur la Catalyse. The results were corrected to take into account the loss of water during the activation of the adsorbent.

Calculations

The retention volume by unit mass of the support (V_s) is calculated by the equation

$$V_s = \frac{d'_R}{U} \cdot F_M \cdot j \cdot \frac{273.2}{T_M} \left(1 - \frac{f_M}{p_0}\right) \frac{1}{W_s} \tag{7}$$

where the subscript M refers to the soap-film flow meter, W_s is the weight of support in the column and the other symbols have the usual significance[18].

RESULTS AND DISCUSSION

Macroporous materials

For these materials, the use of a long-chain fatty alcohol such as octadecanol as the stationary phase is advisable. These compounds have a very low volatility at their melting point. They give condensed monolayers of 21 Å^2 on all hydroxylated surfaces and give rise to large chromatographic transitions at their melting point.

In a previous paper[2], we reported the agreement between the BET evaluations of the surface areas of silica, Chromosorb and glycol and the results of our first time-consuming method by inverse gas chromatography. In Table I, BET measurements are compared with results of the method proposed here for the determination of surface areas by measurement of the increase in the retention volume at the melting point of the stationary phase for differents silicas and aluminas.

The precision of such determinations was established by three independent measurements (three coatings) using Spherosil X OC 005. The surface areas determined were 11.08, 11.05 and 11.12 m^2/g, giving a variability ($s/\bar{x}$) with 95% probability of 1.3%.

TABLE I

COMPARISON OF THE DETERMINATION OF SURFACE AREAS (m^2/g) BY BET MEASUREMENTS AND BY THE PROPOSED METHOD WITH OCTADECANOL AS STATIONARY PHASE

Method	Chromosorb P	Spherosil		"Exal" α-alumina		
		X OC 005	X OB 015	Sample 1	Sample 2	Sample 3
BET	3.6	11.1	26.2	6.5	14.5	28
This work	3.60	11.08	25.5	7.04	14.4	27.6

We applied this method to materials of very low surface area, such as Chromosorb G (0.41 m^2/g). We had to increase the retention volumes by using longer columns and less volatile hydrocarbons as solutes.

Mesoporous materials

Condensed films of octadecanol consist of 25 Å long chains almost perpendicular to the adsorbing surface. The curvature of the surface makes it impossible to form such well shaped films if the pore diameter is less than 200 Å (ref. 4). At the expense of some experimental difficulties, we have been able to extend the application of our techniques to pores in the range 60–200 Å by using a fatty compound with much shorter chains. We chose a highly polar compound, with a relatively high melting point (46°) for a small molecule, and giving very stable and well ordered films, namely dibutyl sulphone.

On a silica gel of known surface area, after determination with octadecanol, the molecular area of dibutyl sulphone was found to be 42.8 Å². For two fatty chains per molecule, this value corresponds to a "condensed" state.

Table II shows a comparison of BET measurements on macroporous and mesoporous adsorbents with the results obtained for these materials by our inverse chromatographic method.

TABLE II

COMPARISON OF THE DETERMINATION OF SURFACE AREAS BY BET MEASUREMENTS AND BY THE PROPOSED METHOD WITH DIBUTYL SULPHONE AS THE STATIONARY PHASE

Property	Chromosorb P	Spherosil		"Exal" α-alumina
		X OC 005	X OA 200	
Mean pore diameter (Å)	10 000	3000	150	ca. 2000[*]
Surface area (m^2/g) (BET method)	3.6	11.1	162.5	28
Surface area (m^2/g) (this work)	3.58	11.08[**]	162.8	26.2

[*] With a considerable population of pores of about 200 Å.
[**] Used to determine the molecular area of dibutyl sulphone after octadecanol measurements.

The lower precision with dibutyl sulphone arises from the very high retention on the film itself at a temperature lower than the melting point. This fact, which is connected with the high polarity of this small molecule, results in a relatively small increase in the retention volume at the melting point.

In addition, measurement of this melting transition is made difficult by the capillary decrease of the melting point in narrow pores[13,14]. Therefore, the transition is smoothed and shifted towards lower temperatures (Fig. 3). Also cooling the column in an ice-bath before the experiment is advisable, in order to prevent supercooling of the liquid phase in mesoporous materials.
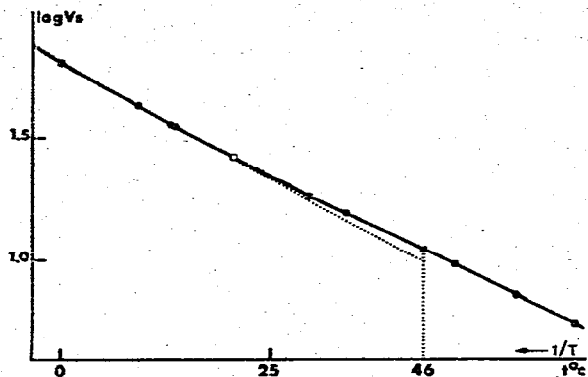

Fig. 3. Variation of log V_s with $1/T$ for n-pentane as solute and 15.93 % of dibutyl sulphone as stationary phase on Spherosil X OA 200 (162.8 m^2/g) ($\tau_c = 11.2$ %).

For more microporous materials such as Spherosil X OA 400 of 80 Å mean pore diameter, supercooling cannot be avoided. However, plotting V_s/τ versus $1/\tau$ according to our first method can be used to determine the critical load, τ_c.

At the expense of these time-consuming experiments, we obtained for this Spherosil a surface area of 442 m^2/g, which can be compared with the value of 469 m^2/g resulting from BET measurements. It is not impossible that part of the surface in the smallest pores might be inaccessible to the stationary phase or hidden from the solute by plugs of stationary phase.

Use of a non-fatty stationary phase

Some experiments were carried out with the aromatic compound benzophenone. The increase in the retention volume of heptane at the melting point of the stationary phase (49°) gives approximately the same type of curve as in our experiments on dibutyl sulphone in the case of Chromosorb P, which is a very microporous material.

On the other hand, with slightly less macroporous materials (Spherosil X OC 005 of 3,000 Å pore diameter), supercooling makes the application of the melting method extremely difficult. In this instance, the application of our first method leads to a V_s/τ versus $1/\tau$ plot that does not differ from those obtained with dibutyl sulphone. These experiments on Spherosil X OC 005 lead to a surface area of 12 m^2/g, in agreement with octadecanol measurements if a molecular area of 45 Å^2 is taken for the stationary phase after measurements on Chromosorb P.

In spite of the lack of practical interest of these experiments with benzo-phenone, they indicate the possibility of generalizing the use of our techniques to new kinds of porous solids by using low-molecular-weight compounds as film-forming materials.

Determination of surface area by a single measurement of retention volume

We have already shown[6] that retention volumes of hydrocarbons per unit surface area on condensed films of long-chain fatty alcohols are only slightly de-pendent on the nature of the underlying macroporous support. However, experience has shown many exceptions, for example for Chromosorbs W and G and acid-washed materials. Much better results have been obtained with dibutyl sulphone films, which are more stable and less influenced by curvature of the pores and surface hetero-geneities.

During the determination of a surface area according to the proposed method, values of V_s at a particular temperature (e.g., $0°$) can be obtained in order to give a simple comparison of different supports. Thus, using the specific surface area of Spherosil X OC 005 as a reference, we obtained the results given in Table III for different materials. The results obtained by the previous method are also reported.

TABLE III

DETERMINATION OF SURFACE AREAS BY A SINGLE MEASUREMENT OF RETENTION VOLUME COMPARED WITH RESULTS OF A MORE ELABORATE METHOD

Surface area	Spherosil		Chromosorb P	"Exal" α-alumina
	X OC 005	X OA 200		
Approximate (m²/g)	11.08	155	4.2	24.9
Precise method (m²/g)	11.08	162.8	3.60	26.2

By precise determinations using the melting transition of the stationary phase, consideration of the V_s value at one temperature (for a compact film with a slight excess of bulk material) allows a sort of "cross-checking" of the result. An approxi-mate determination by this principle could be obtained rapidly by means of a very simple chromatograph equipped with an ice-bath as a thermostat.

Determination of V_g by using a silanized Chromosorb

As we have shown for alkanes, esters and fatty alcohols[4–5], dibutyl sulphone and benzophenone similarly do not wet a silanized Chromosorb. In particular, the lack of a film results from the compatibility of eqns. 3 and 6 when they are applied to the same stationary phase.

In addition, in Table IV we have compared retention volumes by unit mass of the same Chromosorb P, DMCS treated, at $46°$, for n-octane as solute and three dif-ferent stationary phases below their melting points. It is striking that these retention volumes are very similar in spite of the very different chromatographic properties of these phases (see the specific retention volumes, V_g, of these substances). In fact, the common V_s value at $46°$ is merely the retention volume due to adsorption on the bare silanized Chromosorb.

TABLE IV

COMPARISON OF THE RETENTION VOLUMES OF n-OCTANE AT 46° ON THE SAME
CHROMOSORB P DMCS COVERED WITH THREE DIFFERENT STATIONARY PHASES

Property	Stationary phase		
	Octadecanol	Dibutyl sulphone	Benzophenone
Melting point (°C)	58	46	49
V_s	1.91	1.77	1.75
V_g	915*	291	332*

* Extrapolated.

Distribution of the stationary phase between a film and a monolayer

Except on silanized supports, all of our stationary phases are distributed between a film and a capillary condensate, in agreement with an idea first proposed by Giddings[19] and quoted by many workers. However, the semi-quantitative model of Giddings, in which the thickness of a multilayer is connected with the radius of the largest filled pore, proved to be incorrect in all of the experiments of this study.

The monolayer character of the film seems to be a rather general property, at least for pure monomeric molecules on hydroxylated substrates. The film and bulk material have very distinct properties. This situation can be explained by the highly orientated character of the first layer on contact of the active support. This orientation favours the "autophoby" of the stationary phase (i.e., the non-wetting of the film by its own bulk liquid) and its "suction" by the smallest pores. In agreement with the ideas of Fox et al.[20], autophoby is not exclusive to fatty compounds.

It is noteworthy that the prevailing capillary location of most of the stationary phases can be deduced from the good agreement between the experimental pore size distribution and BET surface area measurements on coated supports made by Berezkin et al.[21].

Supercooling of the stationary phases

Supercooling of stationary phases in pores is a severe effect, especially for molecules with bulky ring structures such as benzophenone. In fact, capillary liquid, distributed in many partly filled small pores, forms a large number of completely independent phases between which the propagation of crystallization is impossible. We consider that overcooling phenomena have been largely responsible for masking the problem of the chromatographic retention of stationary phases below their melting points.

CONCLUSION

The inverse gas chromatographic method proposed in this paper can be applied to the determination of the surface areas of macroporous and mesoporous hydroxylated materials, and particularly to industrial adsorbents and catalysts.

Evaluation of an excess of bulk stationary phase in equilibrium with a monolayer, by increasing the retention volume of a solute at the melting point, leads to a determination that is at least as accurate as and certainly more precise than any BET

measurement. For macroporous adsorbents, the use of a long-chain fatty alcohol as the stationary phase is advisable.

If the adsorbent has pores of less than 200 Å, the same method can be applied with a short-chain highly polar stationary phase such as dibutyl sulphone. For pores of 60–80 Å, results can be obtained by a very time-consuming method. A relative method for the determination of surface area by a single measurement of retention volume after coating the surface with a monolayer has already given encouraging results.

Certain conclusions have been drawn from the results of this study regarding the lack of wettability of silanized supports, the absence of a multilayer on other substrates and the severe supercooling of certain phases in the small pores.

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