AN APPROACH TO THE DEVELOPMENT OF A SIMPLE AND RAPID GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF SURFACE AREA

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SUMMARY

The potentialities of organic adsorbates for a simpler and more rapid gas–solid chromatographic method for determining surface area have been explored. It has been observed that the logarithm of the surface area of adsorbents varies linearly with the slope of the universal straight line obtained by plotting retention times *versus* the number of carbon atoms of a selected group of *n*-paraffins. Using this as a calibration plot, the surface areas of sixteen solids of different chemical compositions have been determined. The advantages of this method over existing gas chromatographic methods and the methods of BRUNAUER *et al.*[1] have been discussed. A strong influence of the nature of carrier gas on the position of the slope–surface area plot has been observed.

INTRODUCTION

There is considerable scope for a rapid method of determination of surface area, particularly in the evaluation and comparison of the performance and activities of adsorbents and solid catalysts. The classical method of BRUNAUER, EMMETT AND TELLER (B.E.T.)[1], although accurate and standard, is slow, cumbersome and suffers from other inherent disadvantages. The use of gas chromatography (GC) has been considered as a promising solution[2-12]. NELSON AND EGGERTSEN[2] first used GC in a dynamic flow method, which was followed with slight modifications by a number of workers[3-11]. This method was based on the direct measurement of the amount of adsorbed or desorbed nitrogen instead of recording the pressure–volume changes, other experimental and computational procedures remaining essentially the same as in the B.E.T. method. The next refinement of the GC method by KUGE AND YOSHIKAWA[13] consisted in the direct determination of the amount of an adsorbate required for monolayer coverage, from the changes in peak shape with sample size.

The most radical refinement in recent years involves the use of organic compounds[13-24] as adsorbates. The major advantages inherent in this modification include

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TABLE I

DESCRIPTION OF COLUMNS, OPERATING CONDITIONS, PROPERTIES OF ADSORBENTS AND SLOPE VALUES WITH NITROGEN CARRIER GAS

Column: 2 ft. × 1/8 in. copper tube.

No. of column	Column inlet pressure (p.s.i.)	Carrier gas flow-rate at column outlet (ml/min)	Adsorbent		Surface area (m²/g)			Slope value
			Type	Mesh size	B.E.T. method	Literature value	Slope method	
I	30	52.7	Porasil-A	100–150	—	250–500	425	0.41
2	30	46.1	Porasil-C	100–150	125	50–100	—	0.29
3	30	38.8	Porasil-D	100–150	—	25–45	68	0.23
4	30	33.5	Porasil-E	100–150	—	10–20	17	0.09
5	14	11.3	Porasil E	100–150	—	10–20	17	0.09
6	36	49.2	Porasil E	100–150	—	10–20	18	0.10
7	30	12.3	SiO_2, standard	100–150	375	—	—	0.40
8	30	27.2	SiO_2, standard, heated at 950°	100–150	291	—	—	0.36
9	30	3.6	SiO_2, coated with 12% Cu, heated at 950°	100–150	24	—	—	0.13
10	30	23.0	SiO_2, batch II	100–150	—	—	320	0.38
11	30	9.2	SiO_2, batch II, HF-treated	100–150	—	—	28	0.14
12	30	9.2	SiO_2, batch II, HF-treated	70–100	—	—	20	0.11
13	24	6.8	SiO_2, batch II, HF-treated	70–100	—	—	25	0.13
14	16	5.4	SiO_2, batch II, HF-treated	70–100	—	—	19	0.10
15	40	21.7	SiO_2, batch II, HF-treated	70–100	—	—	25	0.13
16	30	36.9	Chromosorb P	100–150	—	4–8	10	0.06

TABLE II

DESCRIPTION OF COLUMNS, OPERATING CONDITIONS, PROPERTIES OF ADSORBENTS AND SLOPE VALUES WITH ARGON CARRIER GAS

No. of column	Column inlet pressure (p.s.i.)	Carrier gas flow-rate at column outlet (ml/min)	Column dimensions	Adsorbent		Surface area, B.E.T. method (m²/g)	Slope value
				Type	Mesh size		
I	37.5	19.6	3 ft. × 1/8 in.	Al_2O_3	70–100	152.4	0.35
2	37.5	46.1	3 ft. × 1/8 in.	Al_2O_3, heated at 950°	70–100	44.4	0.26
3	70.0	11.9	3 ft. × 1/8 in.	Al_2O_3, coated with 11% (w/w) of Cu, heated at 950°	70–100	7.15	0.115
4	26.0	10.4	2 ft. × 1/8 in.	Al_2O_3, coated with 11% (w/w) of Cu as $Cu(NH_3)_4SO_4$, heated at 950°	70–100	11.4	0.155
5	7.0	5.9	5 ft. × 1/8 in.	SiO_2, coated with 24% (w/w) of Na_2SO_4	60–80	1.5	0.002

a wider choice of carrier gas besides helium; elimination of the mandatory and tedious procedures in the B.E.T. method of prior degassing of the sample and the maintainance of cryogenic temperatures; choice of ultrasensitive detectors such as ionization detectors in addition to the thermal conductivity detectors that for so long have been used exclusively in surface area studies; use of extremely small amounts of adsorbates for solids having a very short linear portion of the adsorption isotherm; determination of very low surface areas with better precision; application of higher adsorption temperatures; and relative insensitivity towards small variations of particle size, flow-rate of carrier gas, etc.

The adsorbate[8] should be selected so as to permit its completely reversible adsorption on the solid surface and its GC properties should be wholly determined by the whole of the surface of the solid sample. According to KISELEV[25], the adsorption behaviour of the n-paraffins is strictly non-selective for all solids that differ in the electron density distribution of atoms exposed on the pore surface. In the proposed method, we advocate the use of the spherically symmetrical and non-reactive n-paraffins as adsorbates, and a parameter derived from the GC retention properties of a number of, rather than a single, n-paraffin as the basis of the calculation of surface area.

EXPERIMENTAL

All the experiments were carried out in a Varian Aerograph 600D gas chromatograph with a flame ionization detector, with nitrogen as the carrier gas for the adsorbents in Table I and argon for those in Table II. A number of adsorbents were investigated; the Porasils were obtained from Waters Associates, U.S.A., and the silicas[26] and modified aluminas[27] were prepared in this laboratory. The surface areas of one Porasil, three silica adsorbents and all the aluminas were determined by the B.E.T. method. The GC results were collected from triplicate runs. The temperature gradient of the column oven was about 1° and an adsorption temperature of 100° was maintained. A description of the columns and adsorbents used in this study is given in Tables I and II.

RESULTS AND DISCUSSION

The last column in Table I gives experimental values of the slopes measured from the plots of the logarithm of retention times (from a given column maintained at constant temperature and carrier gas flow-rate) against the number of carbon atoms of a selected set of three or more n-paraffins. This choice was based on the symmetry of the eluted peaks, sufficient difference in retention times and linearity of the slope plots. It was observed that these conditions are satisfied by those n-paraffins whose molecular dimensions are commensurate with the average pore diameter of the adsorbent used. For example, the two silica adsorbents in columns 7 and 8 of Table I were found to give symmetrical peaks and linear slope plots with n-paraffins that contained a maximum of six carbon atoms, significant tailing being observed with n-heptane at 100°. Similarly, the silica adsorbent with a surface area of 24 m²/g eluted methane to n-butane with no or little difference in retention times. It was also observed that the range of n-paraffins suitable for an adsorbent is extended with the

adsorption temperature. The gas hold-up correction was not made, because both the dead volume of the apparatus and the free gas space of these small columns, packed with relatively fine particles, were considered to be negligible. Moreover, this correction will not significantly alter the order of accuracy of the surface area results as claimed in this investigation. The observed variations in the slope values were less than ±0.01 for the Porasils and about ±0.02 for the other adsorbents.

Of all organic compounds, the n-paraffins, by virtue of their symmetrical distribution of electron density, have the least possibility of retention on solids by forces other than adsorption. The usual effects of chemical reaction or irreversible adsorption on the solid surfaces used in this work were not observed in the peaks of the n-paraffins under the conditions used.

By plotting the logarithm of the B.E.T. surface area against the slope values for the Porasils and silica supports in columns Nos. 2, 7, 8 and 9, a straight line was obtained, as shown in Fig. 1, A. Using this as a standard calibration plot, the surface areas of other adsorbents were calculated from the corresponding slopes and are given in Table I. The surface areas thus found for Porasil A and Porasil E are within the range of values reported in the manufacturer's literature.

The surface area of Porasil D measured from Fig. 1, A, was found to be 68 m²/g, which is outside the range of values reported in the manufacturer's literature. This value may not be incorrect when compared with the fact that Porasil C was also found
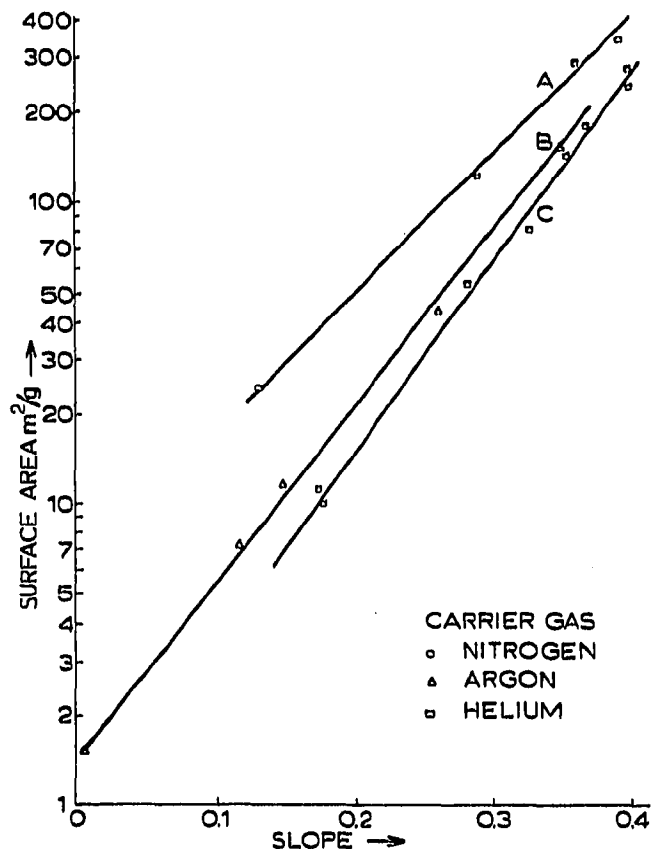

Fig. 1. A linear plot of the logarithm of specific surface area against the slope, determined from retention data of n-paraffins on adsorbents. Plots A and B represent the present experimental data and plot C was drawn from the data of O'BRIEN[20].

to have a B.E.T. surface area of 125 m²/g, compared with the literature range of 50–100 m²/g. The difference in the surface area of Chromosorb P as determined by the slope method (Fig. 1, A) and the reported maximum value of 8 m²/g may be due to experimental error or dissimilarities in the pore structures of Chromosorb P and silica gels or Porasils.

The validity of the slope method has been further corroborated by Fig. 1, B, where a good fit was obtained between the slope values of the corresponding n-paraffins and the logarithm of the B.E.T. surface area for five adsorbents prepared by thermal and salt modifications of silica[26] and alumina[27]. As argon was used as the carrier gas, this calibration plot is different from Fig. 1, A, which also shows a strong effect of carrier gas on the slope method.

It appears that the applicability of the slope method and the accuracy of the results will be better for adsorbents with approximately similar pore structures. It may be mentioned that the slope values calculated from the retention data of n-paraffins and the surface areas of a number of organic polymer beads[28] do not seem to have any correlation. The reason may be that even without a coated stationary liquid, the organic polymer beads behave simultaneously both as an adsorbent and as a partition medium.

Another probable limitation of the slope method is that when the ratio of the diameters of the average pore and of the adsorbate molecule falls below about 10, molecular sieving action begins and thus the linearity of the logarithm of slope against surface area plot may no longer apply.

The data of O'BRIEN[20] for modified aluminas and silica–aluminas were analysed and more than 50% of them were found to give a linear plot (Fig. 1, C), the remainder fitting on this straight line when an average error of ±0.03 is assumed in the reported slope values. This correction is not unlikely, because we also obtained a variation of ±0.02 in the slope values.

It has also been found that the surface areas of the adsorbents studied in this investigation do not give a linear variation with retention volume or relative retention volume of any n-paraffin. Moreover, for practical purposes, a linear calibration plot such as that in Fig. 1 is always preferred to non-linear standard curves. The adsorption temperature in the proposed slope method can be varied to suit the experimental accuracy and convenience, e.g., by decreasing the elution times of the corresponding n-paraffins from a strong adsorbent by using higher temperatures, or increasing the retention times of n-paraffins by using lower column temperatures for a weak adsorbent. This is an added advantage over the B.E.T. method, in which the area occupied by the adsorbate molecule on the adsorbent surface may vary with temperature[13,14].

A strong influence of the nature of the carrier gas was noted in the slope–surface area plots in Fig. 1, A, B and C, where the carrier gases were nitrogen, argon and helium, respectively. The nature of the carrier gas affects retention behaviour much more strongly in GSC as compared with GLC. Fig. 1,B was constructed from the data of an earlier publication[27] of this laboratory and gives additional support to the principle of the linear relationship between the logarithm of the surface areas of solids and the slope of the corresponding n-paraffins—a hypothesis first proposed in this paper.

Regarding other variables of the proposed slope method, such as flow-rate of the carrier gas and particle size of the solids and of solids of similar surface area but of different surface structure, etc., further study is necessary. In other words, there is

scope for refinement of this proposed method before its universal adoption. It is also believed that further study with a large number of adsorbents will improve our understanding of the physics of pore surfaces.

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