Journal of Chromatography, 518 (1990) 319–328
Elsevier Science Publishers B.V., Amsterdam

CHROM. 22 676

Tracer pulse chromatographic method for the determination of nitrogen BET isotherms and surface areas

HENGCHANG SONG, JOSEPH R. STRUBINGER and JON F. PARCHER*
Department of Chemistry, University of Mississippi, University, MS 38677 (U.S.A.)
(Received March 28th, 1990)

ABSTRACT

A new method for the determination of surface areas and nitrogen isotherms at 77 K has been developed. The method utilizes mass spectrometric tracer pulse chromatography with $^{15}N_2$ as the isotopic probe. The technique was used to measure the BET surface area of silica, chemically bonded silica, graphitized carbon black, glass beads and diatomaceous earth chromatographic adsorbents. The results were compared with the surface areas measured by volumetric methods for 5-μm silica and 5-μm C_{18}-bonded silica. The agreement was within the experimental error of the two experimental techniques.

In addition, the total surface areas of three packed high-performance liquid chromatography columns were determined *in situ* without unpacking or disturbing the column in any way. It was shown that the measured total surface area agreed within 10% with the specific surface area times the packing weight for a column packed with 5-μm silica particles.

The method is fast, accurate and simple. The primary experimental data are retention times, rather than peak areas, and the method is applicable to any vapor or inert gas adsorbate. The major disadvantages are the requirements for a mass-selective detector and labeled isotopic solute probes.

INTRODUCTION

In 1958, Nelsen and Eggertsen [1] proposed a continuous-flow, thermal desorption chromatographic method for the determination of BET isotherms and surface areas from nitrogen adsorption at 77 K. This method was improved and developed to provide the basis for commercial instrumentation commonly used today. In addition to this thermal desorption method, at least three other chromatographic procedures have been used for the measurement of solid surface areas. Frontal, tracer pulse and elution chromatography have all been used to determine the adsorption isotherms of inert gases or other probe solutes on solid surfaces. The surface areas could be calculated from the isotherm by fitting the data to an adsorption model, such as that of Brunauer, Emmett and Teller [2].

Two other chromatographic techniques for the determination of surface areas are based on the "Point B" method [3] for the estimation of the monolayer capacity of an adsorbent. Kuge and Yoshikawa [4] developed an elution method for measuring the monolayer capacity of type II and IV adsorbents. The method is based on the formation of a shoulder or other anomaly in the shape of the elution peak when the sample size of the eluted probe solute is sufficient to cover the adsorbent surface with a monolayer of the solute. A second, rather unique type of single-point method was

0021-9673/90/$03.50

developed by Serpinet [5]. In this method several columns with different liquid loadings were required, and the monolayer capacity was determined from the breakpoint in a plot of the retention volume of a probe solute versus the reciprocal of the liquid loading. The plots showed two linear regions corresponding to adsorption on the liquid-modified adsorbent and partition into the liquid coated on the adsorbent. The breakpoint in the plot indicated the transition from one mechanism to the other which presumably occurred at the point of complete surface coverage. This method has the advantage of being independent of any adsorption model; however, it also requires the preparation of multiple columns with a range of liquid loadings.

All of these chromatographic methods for the determination of isotherms and surface areas have been extensively reviewed in several monographs [6–8]. The commonly cited advantages of chromatographic methods compared to the classical gravimetric and volumetric methods are speed, simplicity and low maintenance requirements. The latter advantage arises because the methods do not require high vacuum, and commercial gas chromatography (GC) instrumentation is adequate for all of the chromatographic techniques.

More recently, mass spectrometric tracer pulse chromatography [9] has been used to determine the adsorption isotherms of organic vapors on chromatographic adsorbents [10,11]. The same technique has also been used to measure binary isotherms [12,13] to study the interactions between adsorbates in the condensed, two-dimensional adsorbed phase.

This technique, however, has not been used to study the adsorption of inert gases at low temperatures, although the method is theoretically applicable for such systems. The possible advantages of the tracer pulse procedures over the other chromatographic methods for BET surface area measurements would be that (i) the primary measured data are retention times rather than peak areas, (ii) the system remains isothermal rather than alternating between adsorption at 77 K and desorption at 300 K, (iii) the system is isocratic so there is no "sorption effect", (iv) only one packed column is required and (v) a full isotherm can be determined rather than a single point. The thermal desorption method of Nelsen and Eggertsen [1] is popular, but suffers from the need for frequent detector calibration and sample blanks required to correct for the flow-rate and baseline disturbances caused by the thermal excursions.

The primary objectives of the present work were to investigate the application of tracer pulse chromatography to the determination of nitrogen isotherms at 77 K and to determine the feasibility and accuracy of the method for the measurement of surface areas and pore-size distributions.

EXPERIMENTAL

Instrumentation

A schematic diagram of the instrument is shown in Fig. 1. The GC–mass spectrometric (MS) system was a Hewlett-Packard 5995, and the only major modification of the instrument was the incorporation of very precise flow regulators and pressure sensors. The flow controllers were Matheson Model 8202 regulators with Model 8102 flow sensors (0–50 ml STP[a]/min). The pressure transducers were Setra

---

[a] STP = Standard temperature and pressure.

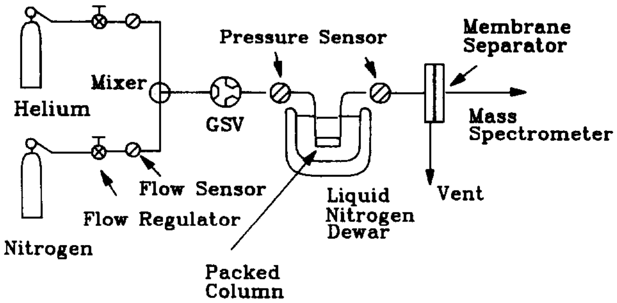

Fig. 1. Schematic diagram of the instrumentation. GSV = Gas-sampling valve.

Model 204 (0–100 p.s.i.g.). The flow regulators were controlled from a microcomputer via a digital-to-analog converter with an output of 0–5 V d.c. The pressure transducers were monitored through an analog-to-digital converter with an input range of 0–5 V d.c. Precise control of the mixed flow of gases was a critical factor in the precision of the apparatus. The probe solutes were injected with a pneumatically controlled gas-sampling valve which was actuated via the RS-232 port of the computer.

Columns

The columns were packed in metal tubing of various dimensions determined by the specific surface area of the adsorbents. The materials studied included silica, chemically bonded silica, graphitized carbon black, glass beads and diatomaceous earth adsorbents. A complete description of the chromatographic columns is given in Table I.

In addition, three packed HPLC columns were used for *in situ* determination of the total surface area of the stationary phase. The commercial columns were Models 2060250 (5-μm silica) and 2060210 (5-μm C_{18}-bonded silica) (SGE), 150 mm × 2 mm I.D. The weight of packing material in these columns was not determined, although the weights were probably in the range 0.4–0.6 g. A third column was packed in the laboratory with 0.205 g of C_{18}-bonded silica (SGE) in a stainless-steel tube 100 mm × 2 mm I.D.

TABLE I

DESCRIPTION OF CHROMATOGRAPHIC COLUMNS AND ADSORBENTS

Adsorbent material	Particle size (μm)	Column dimensions (mm)	Packing weight (mg)
Carbopack A	180–250	100 × 3	150.0
Carbopack B	180–250	60 × 3	44.1
Carbopack C	150–180	400 × 3	831.3
Silica	5	50 × 3	49.1
C_{18}-Bonded silica	5	50 × 3	75.4
Diol-bonded silica	5	50 × 3	40.3
Cyano-bonded silica	5	50 × 3	59.6
Glass beads	180–250	400 × 6.4	9320
Chromosorb P	180–250	300 × 3	304.2

All of the columns were conditioned prior to the isotherm measurements. The conditioning strategy varied with the type of adsorbent. In general, the procedure involved temperature programming from 30 to 100–150°C with the temperature maintained at the upper temperature until no effluent was monitored by the mass spectrometer. The use of MS in the scan mode to sense the type and quantity of outgassing effluent allowed the use of variable conditioning procedures for each type and batch of adsorbent.

Procedure

The flow-rates and mixing ratios of He and N_2 were set and allowed to stabilize for 5–10 min. A mixture of Ne, Ar and $^{15}N_2$ was injected via the gas-sampling valve at the same time the MS system was activated. The MS system was operated in a "selected ion monitor" mode to detect m/e values of 20, 30 and 40 and ignore the N_2 background at m/e 28. The nitrogen probe solute was 98.8% $^{15}N_2$ (MSD Isotopes, Montreal, Canada).

The use of labeled nitrogen introduces the possibility of an "isotipe effect" on the retention of $^{15}N_2$ compared with $^{14}N_2$. In an attempt to determine the magnitude of this effect, a sample containing natural and labeled nitrogen along with neon was injected into a silica column at 77 K with pure helium as the carrier gas. The experiment showed that there was an isotope effect of about 1.05. That is, the ratio of the retention times of the unlabeled and labeled solute was approximately 1.05. This correction factor was used to adjust all of the reported data.

Calculations

The amount of nitrogen adsorbed, Γ_j (μmol/g), was calculated from the retention times of neon, t_0, and the isotopic nitrogen probe, $t_{R,i}$ (min), by the relation:

$$\Gamma_j = (t_{R,i} - t_0)\left(\frac{P_r F_c Y_j}{R T_r W_s}\right) \tag{1}$$

where F_c is the flow-rate, P_r and T_r are the pressure and temperature for which the flow regulators were calibrated, *i.e.*, ambient conditions, Y_j is the mole fraction of nitrogen in the carrier gas, W_s is the weight of the solid adsorbent in the column and R is the molar gas constant.

The surface areas of the adsorbents were determined from the calculated monolayer capacity, V_m, obtained from linear regression of the BET equation in the form:

$$\frac{P_j}{\Gamma_j(P_j^0 - P_j)} = \left(\frac{1}{CV_m}\right) + \frac{C-1}{CV_m}\left(\frac{P_j}{P_j^0}\right) \tag{2}$$

where P_j and P_j^0 are the pressure of nitrogen in the column and the vapor pressure of liquid nitrogen at the column temperature, and C is an empirical parameter which is related to the heat of adsorption and the shape of the isotherm in the region of monolayer formation.

RESULTS AND DISCUSSION

One of the major problems in the determination of adsorption isotherms by a chromatographic or any other method is the accurate determination of the void volume of the column or apparatus. This measurement is particularly critical with chromatographic methods for gas–solid adsorption at very low temperatures and/or high pressures. The commonly used probes, such as air or methane, were not useful because they were significantly adsorbed under the conditions used in this study. The "hypothetical perfect gas" perturbation method of Kobayashi and co-workers [14,15], which is commonly used for chromatographic isotherm measurements, was also inapplicable in the present study because of the significant retention of argon and the higher inert gases. However, it was found that, although the retention time of argon and the other inert gases varied with the amount of N_2 adsorbed, the retention time of neon was independent of surface coverage with nitrogen. This effect is shown in Fig. 2. The constant retention times of neon indicated that neon, like helium, was not adsorbed on the solid and could serve as an accurate probe for the determination of t_0.

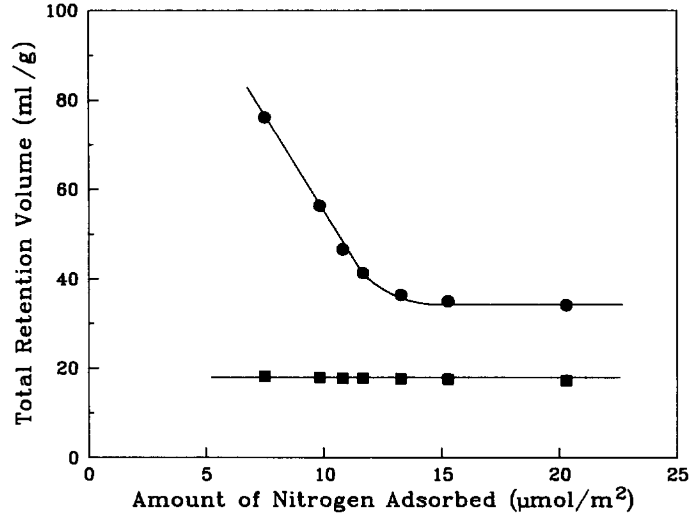

Fig. 2. Retention times of eluted samples of argon and neon with different amounts of nitrogen adsorbed on the surface of Carbopack C. ● = Argon; ■ = neon.

Another potential problem in the proposed experiment is the possible adsorption of nitrogen on the walls of the column and connecting tubing. This effect would be particularly significant for low surface area adsorbents. To check the magnitude of this effect, the solutes were injected into an empty column at 77 K at several flow-rates. It was observed that the three solutes, Ne, Ar and $^{15}N_2$ all eluted concurrently. Thus the amount of nitrogen adsorbed in the instrumental apparatus was less than the lowest limit for the experimental measurement.

The tracer pulse experimental procedure was used to measure the isotherm of nitrogen on 5-μm silica gel at 77 K. The full isotherm was obtained by using three

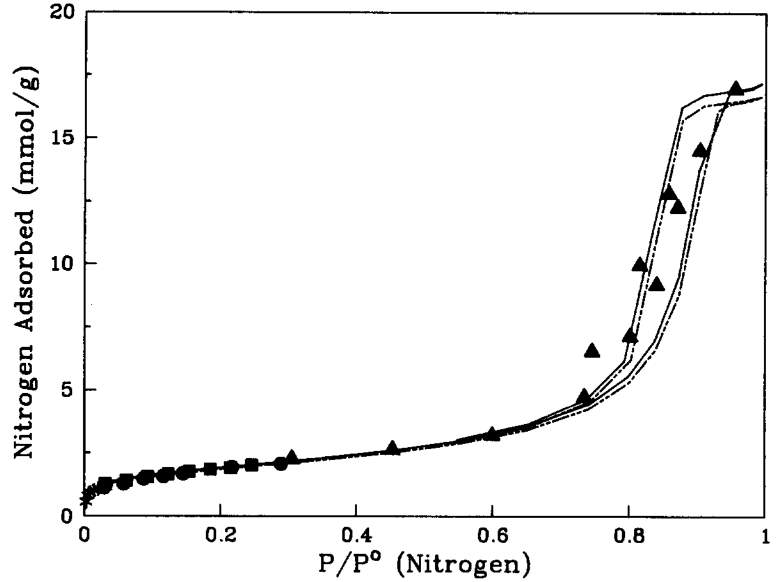

Fig. 3. Experimentally measured adsorption isotherms of nitrogen on 5-μm silica. * = 2% N_2 in He; ●, ■ = 20% N_2 (duplicate experiments); ▲ = 100% N_2; — - - - — = volumetric data (duplicate experiments) [16].

different compositions of the He + N_2 carrier gases. Tanks with compositions of 2, 20 and 100% N_2 were used to cover the low, intermediate and high ranges of P/P^0 required for the full isotherm. Within each range, smaller incremental changes in composition were controlled by variation of the ratio of flows through the two flow controllers. The range required for the BET analysis, $0.05 \leqslant P/P^0 \leqslant 0.35$, could be studied with only a single tank containing 20% N_2. The measured isotherm is shown in Fig. 3. The lines in the figure show the duplicate isotherms measured by the classical, volumetric method [16]. The agreement with the volumetric data is excellent at relative pressures of less than 0.7. Above this pressure, the mesoporous-silica adsorbent shows a hysteresis loop which the chromatographic method could not follow accurately because of the significant pressure drop across the column. Fig. 4 shows the BET plot for the measured isotherm in the applicable range of P/P^0. In both cases, the agreement between the volumetric (static) and chromatographic data were within the experimental uncertainty of either method. The BET surface areas were determined for all of the absorbents listed in Table I. The results of this analysis are given in Table II.

One of the potential applications of this technique is the determination of the total surface areas of packed GC, high-performance liquid chromatography (HPLC) or supercritical fluid chromatography columns *in situ* without disturbing the column packing in any way. This application would be significant for high-efficiency columns packed with very small particles, *i.e.*, < 10 μm, because of the difficulty of packing and weighing these particles. The pressure drop across the columns was large due to the very small particle size. However, the viscosity of the helium and nitrogen mixtures was also diminished at 77 K, so a reasonable flow-rate could be obtained without an excessive pressure drop across the column. Typically with commercial packed (5-μm)

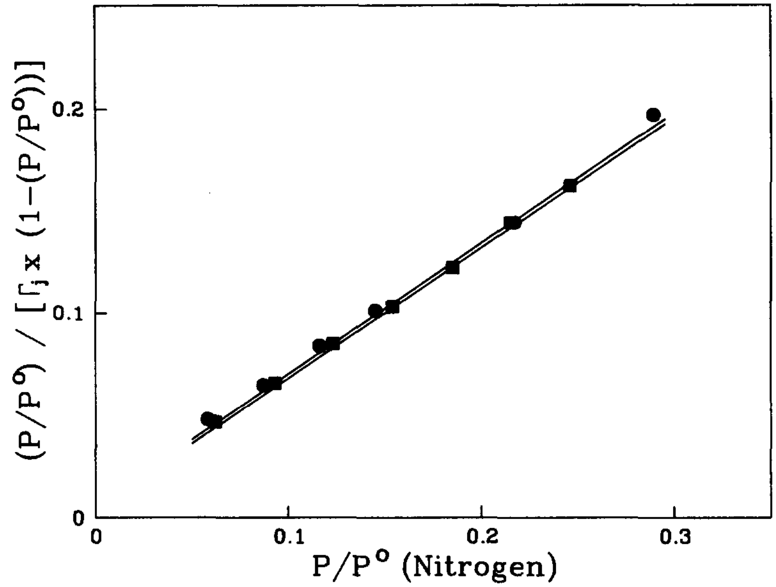

Fig. 4. BET plots for 5-μm silica. ●, ■ = this work (duplicate experiments); ——— = volumetric data [16].

columns a head pressure of 30 p.s.i. gave a flow-rate in the order of 10 ml/min at 77 K. The results for the total surface areas in the two commercial columns were 34 m^2 and 42 m^2 for the C_{18} and silica columns, respectively.

The surface area of the stationary phase in the laboratory-packed column was measured *in situ* at several flow-rates to determine the influence of the column pressure drop on the measured surface areas. The specific surface area was also measured for the packing material alone. The results of both experiments are given in Table III.

TABLE II

LINEAR REGRESSION DATA FOR VARIOUS CHROMATOGRAPHIC ADSORBENTS

Adsorbent	Linear regression results		Surface areas (m^2/g)	
	V_m (μmol/g)	C	This work	Volumetric
Carbopack A	124	280	12.0	15 [17]
Carbopack B	834	150	80.4	100 [17]
Carbopack C	94.8	341	9.1	9 [17]
Silica	1530	108	147.8	155.4 [16] 150.9 [16]
C_{18}-Bonded silica	974	26	93.9	89.7 [16] 97.6 [16]
Diol-bonded silica	2500	56	241.0	
Cyano-bonded silica	1158	40	111.6	
Glass beads	0.90	29	0.09	0.01–0.1
Chromosorb P	56.1	27	5.4	

TABLE III

COMPARISON OF SPECIFIC AND TOTAL SURFACE AREAS FOR A C_{18}-BONDED SILICA HPLC COLUMN

(Specific surface area) × (packing weight) = (93.9 m^2/g) (0.205 g) = 19.2 m^2

Carrier gas flow-rate (ml/min)	Inlet pressure (p.s.i.)	Compressibility correction factor, j	Measured total surface area (m^2)
3.5	20.6	0.81	22.4
5.5	24.0	0.74	22.6
10.5	30.3	0.62	21.2
20.4	40.3	0.49	20.6

The two measurements agreed within about 10%. However, there appears to be a slight, but systematic, dependence of the calculated isotherms and surface areas on the flow-rate and/or the pressure drop across the column. The *in situ* isotherm method for packed HPLC columns can only provide an average of the amount of nitrogen adsorbed because of the significant difference between the partial pressure of N_2, and consequently the amount of N_2 adsorbed, at the inlet and outlet of the column. These pressures may differ by a factor 2–3 (Table II). This effect would be most deleterious in the regions of the isotherm where $(\partial\Gamma/\partial P)$ is large, *i.e.*, at very low pressures. In the relative pressure range of 0.05–0.35, which is the range where eqn. 2 is valid, the effect of pressure drop is not as critical. The use of an average pressure, *e.g.*, P_{out}/j, produced linear BET plots and acceptable surface areas. Fig. 5 shows the BET data for the experiments described in Table III along with the results from the volumetric

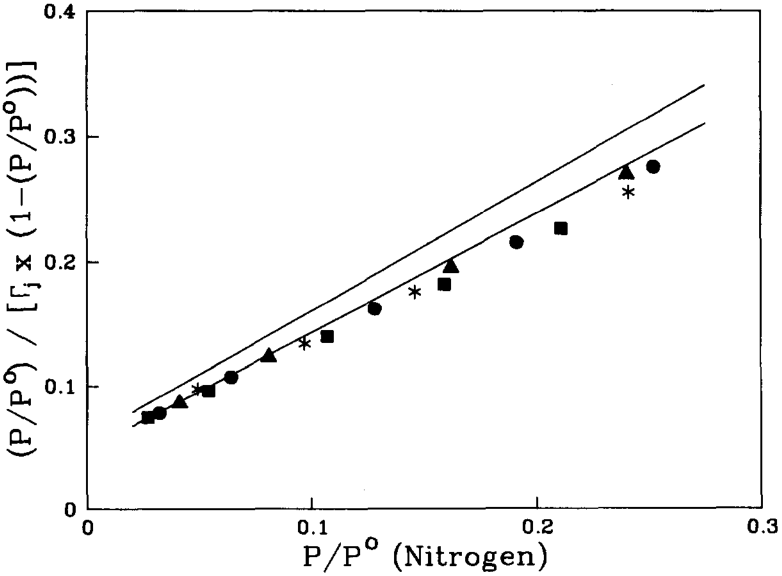

Fig. 5. BET plots for C_{18}-bonded silica. $*$, ●, ▲, ■ = this work (each different symbol in the figure corresponds to a row in Table II); ——— = volumetric data [16].

measurements [16]. The variations caused by the significant pressure drop in the *in situ* experiments are less than the repeatability of the volumetric procedure.

The tracer pulse method for the determination of BET isotherms requires a mass-specific detector to measure the retention time of an isotopically labeled tracer of the adsorbable component of the gas. The requirements for the MS system are, however, minimal, and the simplest instruments, such as the mass-specific detector or ion trap detector are adequate for the isotherm measurements described above. The required isotopes can be expensive or difficult to prepare, although this is not the case for the $^{15}N_2$ probes used in this study. The method suffers from all of the disadvantages inherent in the BET model [3]; however, the experimental technique is not limited to N_2 as the adsorbate. Other solutes and perhaps other adsorption models could be used for the surface areas calculations.

The flow-through systems used for all chromatographic techniques have the advantage that equilibrium is established rapidly, but the disadvantage is that the inlet of the column must be at a higher pressure than the outlet. This means that the measured isotherm data are always some type of "average" although this effect does not appear to significantly influence the surface-area measurements as shown in Table III and Fig. 5. However, this effect can be minimized by the use of low flow-rates, short columns, or coarse particles.

One disadvantage of the tracer pulse method, as well as any other chromatographic method, is that it is inherently a "batch process". This disadvantage is partially off-set by the slightly reduced experiment time per sample. The primary experimental datum is the retention time of the $^{15}N_2$ probe. This retention time was typically in the range 2–20 min, and the equilibration time for a gas-phase composition change was 5–10 minutes. A complete BET plot requires at least 5 data points. The estimated time for a complete BET surface-area measurement by this technique would be 0.5–2 h. This time can be reduced by minimizing the retention time of the probe solute. Volumetric measurements require 10–20 h for a full (50 point) isotherm, or about 1–2 h for a 5-point surface-area measurement.

The method is easily automated with a computer-controlled GC–MS system and gas-sampling valve. The only actions required are periodic injections and adjustments of the flow-rates.

CONCLUSIONS

Mass spectrometric tracer pulse chromatography can be used to measure the adsorption isotherms of nitrogen on solid adsorbents. If the measurements are carried out at 77 K, the adsorption data in the range $0.05 \leqslant P/P^0 \leqslant 0.35$ can be fit to the BET model to determine the surface area of solid adsorbents. The method has been applied to a variety of different adsorbent types with surface areas from 0.09 to 240 m^2/g.

The method is comparable in accuracy and reproducibility with the static volumetric methods. Commercially available, simple GC–MS systems are adequate for the instrumentation, and the MS can serve to monitor the outgassing effluent to minimize the preparation time and to ensure that the outgassing process has been completed.

The method is fast, accurate, and simple. The major disadvantages are the need for a GC–MS system and isotopically labeled solutes. The method is not limited to a particular adsorbate or temperature, and the adsorption isotherms of two or more adsorbates can be measured simultaneously.

The variation of the retention volume of one probe, such as argon, can also be determined as a function of the surface coverage by another adsorbate, such as nitrogen. This phenomenon is illustrated in Fig. 1. If this type of experiment can be used to determine the monolayer capacity of an adsorbent, it would lead to a surface area measurement technique that, like Serpinet's [5] method, would not require a theoretical model for interpretation of the data.

ACKNOWLEDGEMENTS

Acknowledgements are made to the National Science Foundation for support of this research and to Dr. Terry Berger (Hewlett-Packard Co.) for donation of the chemically bonded silica adsorbents.

REFERENCES

1 F. M. Nelsen and F. T. Eggertsen, *Anal. Chem.*, 30 (1958) 1387.
2 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
3 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982, Ch. 2.
4 Y. Kuge and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 38 (1965) 948.
5 J. Serpinet, *J. Chromatogr.*, 119 (1976) 483.
6 A. V. Kiselev and Y. I. Yaskin, *Gas-Adsorption Chromatography*, Plenum, New York, 1969, Ch. IV.
7 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley-Interscience, New York, 1979, Ch. 10.
8 R. J. Laub and R. L. Pecsok, *Physicochemical Applications of Gas Chromatography*, Wiley-Interscience, New York, 1978, Ch. 7.
9 J. F. Parcher and M. I. Selim, *Anal. Chem.*, 51 (1979) 2154.
10 P. J. Lin and J. F. Parcher, *J. Colloid Interface Sci.*, 91 (1983) 76.
11 K. J. Hyver and J. F. Parcher, *Anal. Chem.*, 56 (1984) 274.
12 J. F. Parcher and P. J. Lin, *Anal. Chem.*, 53 (1981) 1889.
13 J. F. Parcher and K. J. Hyver, *J. Chromatogr.*, 302 (1984) 195.
14 S. Masukawa and R. Kobayashi, *J. Gas Chromatogr.*, 6 (1968) 257.
15 Y. Hori and R. Kobayashi, *J. Chem. Phys.*, 54 (1971) 1226.
16 Micromeritics, Inc., Atlanta, GA, personal communication, 1989.
17 *Bulletin 738A*, Supelco, Inc., Bellefonte, PA, 1976.