A New Method to Determine Relative Surface Area by Gas Chromatography. I

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Two kinds of methods have been employed to determine the surface area of an adsorbent, the common B.E.T. static method, and the B.E.T. flow method* using gas chromatography.

During the investigation of the relation between the sample size and the peak shape, using the same column packing in gas chromatography we found that the displacement point from monolayer- to multilayer-adsorption appeared in the change in peak shape. Therefore, the relative surface area of adsorbent per gram was calculated from the sample size at the displacement point. By this procedure, we determined the relative surface area of a copper complex compound, $Cu(Py)_2(NO_3)_2$.** The results obtained will be discussed.

When this method can be used, the surface area can be more easily determined compared with the results obtained with the methods mentioned above.

The Estimation of Relative Surface Area

In general, the relation between the sample size and the retention time can be described

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* For example, F. M. Nelson and F. T. Eggertsen, *Anal. Chem.*, **30**, 1387 (1958).

** This substance has been found to be a new adsorbent for the analysis of hydrocarbons in gas chromatography by L. B. Rogers and A. G. Altenau (*Anal. Chem.*, **35**, 915 (1953)).

as follows: When a Langmuir-type adsorption isotherm is established, it is observed that the larger the sample size, the shorter the retention time. In the case of an anti-Langmuir-type adsorption isotherm, the larger the sample, the longer the retention time. The shapes of the peak in both cases are shown in Fig. 1.

When the two types of adsorption isotherms are combined, the second type of B.E.T. adsorption isotherm will be obtained, as Fig. 2 shows. This expectation was realized in our experiments. When the sample size is small, the peak shape is symmetrical. As the sample size is increased, however, the peak shape acquires a sharp front and a diffuse tail, and a defect at the front side of the peak top; then it obtains a diffuse front and a sharp tail. That the peak begins to have a defect at the front side of the top indicates the point of the displacement from monolayer- to multilayer-adsorption. This point corresponds to the B-point of the B.E.T. II-type adsorption isotherm.

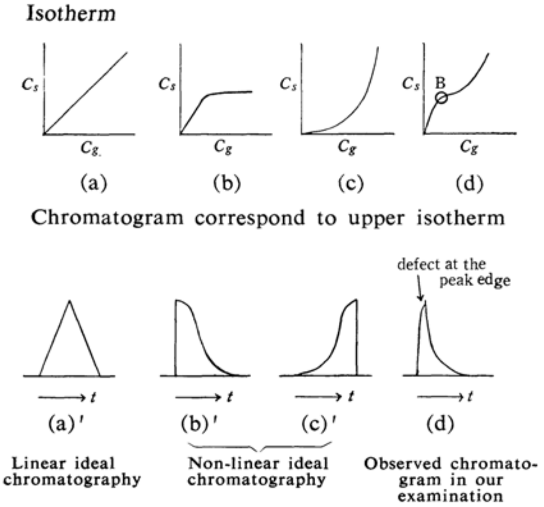

Fig. 1. The relation between peak shapes and the adsorption isotherms.

C_s Concentration in stationary phase
C_g Concentration in moving phase
t Time

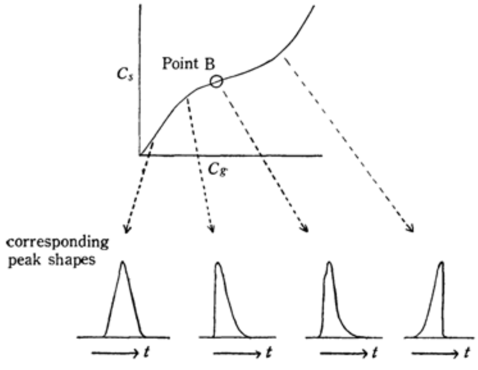

Fig. 2. The second type of B.E.T. adsorption isotherm and corresponding peak shapes.

C_s Concentration in stationary phase
C_g Concentration in moving phase
t Time

Therefore, the relative surface area of the adsorbent covered with a monolayer of an adsorbate at the displacement point may be calculated by Eq. 1.

$$S=\frac{V}{V_m}\cdot N_A\cdot s \qquad (1)$$

where

S: the surface area of the adsorbent (cm^2)
V: the volume of the adsorbate which forms the monolayer (cc.)
N_A: Avogadro's number
s: the surface area that was occupied by one molecule of the adsorbate (cm^2)
V_m: the molecular volume (cc.)

Provided the sample is adsorbed in the form of the closest packing of the face-centered cubic lattice on the adsorbent, the surface area (s) is expressed as follows:[1]

$$s=\frac{6}{\sqrt{3}}\left(\frac{M}{4\sqrt{2}N_A\cdot D}\right)^{2/3} \qquad (2)$$

where

D: the density of the adsorbate at the adsorbed temperature
M: the molecular weight

The surface area must be reduced to that per gram of the adsorbent, so the authors assumed the next Eq. 3:

$$S_g=\frac{S}{W\cdot\frac{w}{\left(\frac{a\cdot L}{F}\right)}}=S\left(\frac{1}{W}\cdot\frac{a}{w\cdot F}\cdot L\right) \qquad (3)$$

where

S_g: the surface area per gram of the adsorbent (cm^2/g.)
W: the weight of the adsorbent (g.)
F: the flow rate of the carrier gas (cc./min.)
L: the column length (cm.)
a: the cross section area of the column (cm^2)
w: the peak width

and the term (aL/F) means the time required for the carrier gas to pass through the column.

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[1] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 1553 (1937).

Apparatus and Materials

A Yanagimoto gas chromatograph GCG-2 was employed.

The detector used was of the thermal-conductivity type with a tungsten filament. The column was made of U-shaped stainless steel and was 2 m. long and 5 mm. in inside diameter. The flow rate of the carrier gas was measured by a soap-film flow meter.

Di-pyridine-copper nitrate $Cu(Py)_2(NO_3)_2$, used as an adsorbent, was prepared through $Cu(Py)_4(NO_3)_2$ according of Pfeiffer's method.[2] The blue-violet crystals of $Cu(Py)_4(NO_3)_2$ were sorted with a 32—48 mesh and then heated at 100°C for six hours to give a light blue dipyridine salt.

The change from tetrapyridine salt to dipyridine salt was observed at 70—83°C by means of the differential thermal analysis of pyridine copper salt, and the identity of the dipyridine salt produced was confirmed by the quantitative analysis of pyridine, that is, by the measurement of the weight change of the sample and by the ultraviolet absorption spectrometric method.*

Results

Benzene, carbon tetrachloride, cyclohexane and *n*-hexane were used as adsorbates.

The heats of the adsorption of these substances on $Cu(Py)_2(NO_3)_2$ were found to be 8.4, 8.1, 8.4 and 8.0 kcal./mol. respectively, in the temperature range from 30 to 60°C,[3] suggesting the physical adsorption.

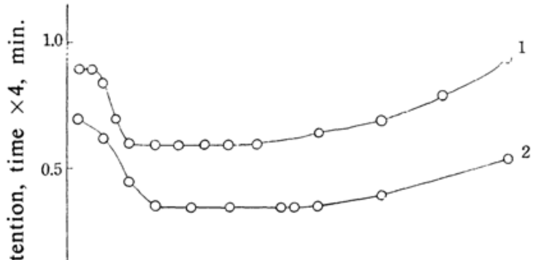

Fig. 3. The change of retention times with increasing sample sizes.

1 Benzene
2 Carbon tetrachloride
cell current 150 mamp, column inlet pressure 0.2 kg./cm², cell temp. 100°C, carrier gas H_2, 57.7 cc./min., inlet temp. 118°C, column temp. 50°C, adsorbent $Cu(Py)_2(NO_3)_2$, 32—48 mesh 29.3 g.

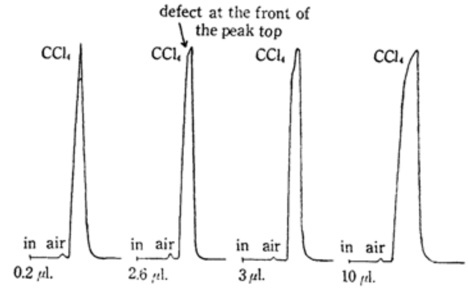

Fig. 4. The change of peak shapes with increasing sample sizes.

cell current 150 mamp., column inlet pressure 0.2 kg./cm², cell temp. 80°C, inlet temp. 118°C, carrier gas H_2, 41.7 cc./min. (22.5°C), adsorbent $Cu(Py)_2(NO_3)_2$ 32—48 mesh 29.3 g., column temp. 48°C

The relation between the sample size and the retention time in the cases of benzene and carbon tetrachloride is shown in Fig. 3, while the change in peak shape in the case of carbon tetrachloride is shown in Fig. 4.

The displacement point from monolayer- to multilayer-adsorption may be affected by the flow rate of the carrier gas, the column temperature and the properties of the adsorbate.

First, the relation between the flow rate of the carrier gas and the displacement point was examined.

When the flow rate was increased up to 60 cc./min., the peak width became narrow, but the displacement point of the peak shape showed no change. On the other hand, the flow rate was decreased less than 20 cc./min., the peak changed to a symmetrical shape under the influence of axial dispersion,[4,5] and the displacement point could not be found. Therefore, the experiments were carried out in the flow rate range from 20 to 60 cc./min.

Next, the relation between the sample size at the displacement point and the column temperature was investigated. In the case of cyclohexane, the sample size was found to be 1.4 μl. when the temperature was below 50°C, while the sample size was as large as double that when the temperature rose above 50°C, as is shown in Table I. The results suggest that the relative surface area may be calculated as too large when the temperature rises above 50°C it also calls into question the assumption that the sample molecules are adsorbed in the

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[2] P. Pfeiffer and V. Pimmer, *Z. anorg. Chem.*, **48**, 98 (1906).

* This method was discovered by Dr. Isao Masuda.

[3] Y. Kuge and Y. Yoshikawa, *Sci. Rep. Osaka Univ.*, **12**, 9 (1963).

[4] G. Houghton, *J. Phys. Chem.*, **67**, 84 (1963).

[5] R. D. Oldenkamp and G. Houghton, ibid., **67**, 597 (1963).

TABLE I. THE CORRELATION OF SAMPLE SIZE WITH THE TEMPERATURE AT THE DISPLCEMENT POINT

Adsorbate : cyclohexane

Column temp. °C	Flow rate cc./min.	Sample size μl.
32	57.7	1.4
46	55.6	1.4
50.5	56.6	2.4

the form of the closest packing of the face-centered cubic lattice at a higher temperature.

At about the boiling points of adsorbates (near 80°C), the peak changed to a symmetrical shape and the displacement point was hardly observed. The range of the temperature applicable for the determination of the relative surface area by this method has not yet been generalized.

With such precautions, the relative surface area of adsorbents was calculated, according to Eq. 3, on the basis of the results obtained when the column temperature was 50°C and the flow rate of the carrier gas was 60 cc./min. The values obtained are listed in Table II.

As Table II shows, the values of the relative surface area were found to be nearly equal for planer and for spherical molecules, such as benzene, carbon tetrachloride and cyclohexane, while a larger value was found for chain molecules such as n-hexane. Similar results have been obtained by the ordinary B.E.T. static method.

TALE II. THE RELATIVE SURFACE AREA OF 29.3 g. OF $Cu(Py)_2(NO_3)_2$ FOR SEVERAL ADSORBATES

Adsorbate	Sample size μl.	$s\times10^{16}$ cm^2	Relative surface area m^2/g.	Shape of molecule
Benzene	2.7	30.6	1.75	Planar
Carbon tetrachloride	2.6	33.1	1.68	Spherical
Cyclohexane	2.5	34.9	1.50	Planar
n-Hexane	5.7	38.7	3.44	Chain

In this report, we have used the term "relative surface area" instead of "surface area" because the values obtained have not been compared to those obtained by the ordinary B.E.T. method.

The determination of the absolute surface area by static and dynamic B.E.T. methods using gas chromatography is now under way.

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