collision. More rapid splashes exhibit a fascinating structure of their own, but have lost the intriguing ring bulge that occurs in this low-speed range.

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Chromatographic Silica Gel: Surface Area Determined by Adsorption

Abstract. *The surface area of silicic acid, a form of silica gel, has been determined by adsorption of methanol from a benzene solvent. The method is straightforward, uses inexpensive apparatus, and should be applicable to other particulate adsorbents.*

Surface areas of particulate solids are usually determined by the BET procedure (*1*), which involves gas adsorption at cryogenic temperatures; the apparatus is delicate and expensive, and requires a skilled operator for reliably accurate results. In an effort to simplify determinations of area and to avoid the complicated BET apparatus, Nelsen and Eggertsen (*2*) devised a continuous-flow method that is based on changes in thermal conductivity exhibited by a gaseous adsorbate stream as it is passed over the solid at cryogenic temperatures; their approach provided good agreement with standard BET determinations. Later, Roth and Elwood (*3*) adapted a gas chromatograph to this continuous-flow method. A commercial instrument that measures surface area and pore volume, and whose design is based on the Nelsen-Eggertsen concept, is on the market.

Table 1. Adsorbate-adsorbent relations that allow calculations of surface area from alcohol adsorption data. Areas per molecule based on the assumption of spherical shape. N_o, Avogadro number.

Solute	Alcohol				Area per:	
		Adsorbed				
	Conc. in supernatant (vol. % in benzene)	On SiO_2		Molecules (N_o) (moles $\times 10^{20}$)	Molecule (Å^2)	Gram of SiO_2 (m^2)
		(Moles $\times 10^{-3}$)/g	Gram/gram			
Methanol	0.90	4.50	0.145	27.1	19.9	540
Ethanol	1.00	3.10	0.144	18.6	25.5	474
1-Propanol	0.95	2.43	0.145	14.5	30.2	438
2-Propanol	0.90	2.41	0.146	14.6	30.8	450
1-Butanol	0.80	1.98	0.147	11.9	34.4	409

After Frankel *et al.* (*4*) developed a liquid-chromatographic system based on methanol-benzene–silicic acid (SiO_2), we evaluated the parameters essential to the system (*5*). In an attempt to determine chromatographic mechanisms that influence separations of lipid materials on silicic acid, we turned to evaluation of solvent systems other than methanol-benzene (*6*). From a third investigation and the two immediately preceding we established the validity of the general chromatographic formula that Frankel *et al.* (*4*) had found empirically to be useful for lipid materials. Indeed their empirical formula is based on a solvent-adsorbent combination wherein methanol is adsorbed on the silica to a level of concentration representative of monolayer coverage. Under these conditions, lipid materials during fractionation received efficient competition from methanol for active sites on the silica, and therefore eluted as sharp peaks exhibiting quantitatively useful resolution within practical time limits.

Figure 1 shows typically Langmuir-type adsorption isotherms for five aliphatic alcohols adsorbed on 50 g of silicic acid from 100 ml of benzene. Each alcohol was added to the adsorbent at concentrations of 4, 8, 16, 32, and 50 percent by weight. Relative concentrations of adsorbed and unadsorbed methanol were determined from an ordinary calibration plot of solution refractive index versus known alcohol concentration (*6*). Solution compositions were converted to mole percentages for isotherm plots. Extrapolation of the linear portions of these isotherms enabled determination of each isotherm "knee"—a point at which the alcohol adsorbate is conventionally assumed to exist on the silica surface as a monolayer (*7*). Table 1 lists, among other data, solute-solvent relations pertinent to the isotherms.

It seemed likely that methanol adsorption on silica might be a means of determining surface area. If one assumes that alcohols are spherical molecules, and on the basis of knowledge of the molecular weight and density of each, one can calculate the cross-sectional area of one molecule.

The last five columns of Table 1 contain necessary information for relating solute cross section with the true area covered by the alcohol adsorbed at monolayer concentration; Fig. 2 graphically depicts this relation. Deviation of the plot from infinite slope (vertical) is a measure of the error introduced by assumption that the alcohols are spherical molecules. Obviously they are not; if they were simply spheres of increasing size, each would be sterically adsorbed to an extent proportional to its radius. For example, butanol has twice the carbon content of ethanol and thus about twice the assumed circular cross section; SiO_2 should therefore adsorb only half as much butanol as ethanol. The data point for butanol would lie directly below that for ethanol, since a circle representative of one butanol molecule could cover twice the area of one for ethanol. Since butanol does not lie below ethanol, an assumption of sphericity becomes in greater error as the

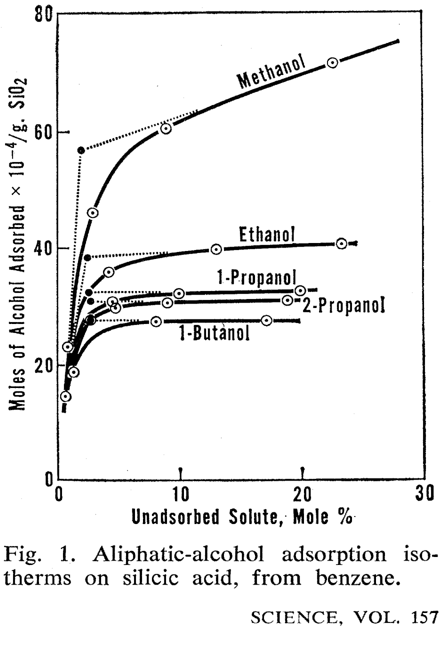

Fig. 1. Aliphatic-alcohol adsorption isotherms on silicic acid, from benzene.

molecular weights of alcohols increase. Such an assumption for methanol is not in serious error since the supplier of the silicic acid has quoted its BET area at 540 to 640 m^2/g (Table 2).

Using a continuous-flow method similar to that of Nelsen and Eggertsen, we obtained values of 540 to 630 m^2/g that depended on the extent of adsorbent activity. Our methanol-adsorption data indicate 540 m^2/g (Table 1, last column; Table 2, third column). It is likely that the batch measured in these experiments was of the lower activity (540 m^2/g).

Competitive adsorption offered from the benzene solvent becomes greater as steric factors begin to reduce adsorption of higher alcohols. A less-polar solvent, such as pentane, would minimize this competitive effect, allow somewhat more alcohol to be adsorbed, and increase the values determined for the adsorbent area by shifting the data points up and away from the ordinate.

The third, fourth, and fifth columns of Table 1 show that adsorption of monofunctional aliphatic alcohols on silicic acid, from a benzene solvent, is sterically controlled. As the carbon number increases, the apparent affinity of silicic acid for the alcohol decreases (Fig. 1). Only methanol, and to a lesser extent ethanol, can adsorb on the silica at concentrations exceeding a monolayer; in higher alcohols increased size of the hydrophobic alkyl substituent effectively shields the SiO_2 surface and thus prevents multilayer formation by decreasing the availability of alcoholic-hydrogen atoms to which further layers can be adsorbed (*8*). Adsorption is also influenced by inductive electrical effects, but, within the unsubstituted aliphatic-alcohol series, steric effects predominate; electrical considerations will be treated elsewhere.

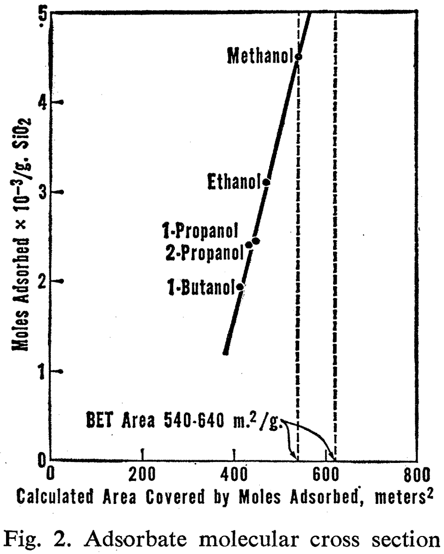

Fig. 2. Adsorbate molecular cross section versus moles of alcohol adsorbed per gram of silicic acid. BET range depends on adsorbent activity.

Table 2. Methanol-adsorption and continuous-flow surface areas of silicic acid activated at two different temperatures. Supplier's area for silicic acid, 540 to 640 m^2/g (adsorbent activity not specified). TGA, thermogravimetric analysis.

SiO_2 activation, 1 hour (°C)	Surface area (m^2/g)			
	By continuous flow	By methanol adsorption	By continuous flow after TGA	Represented by water lost (calc.)
110	540	540		
500	630		640	11

Hockey (*8*) has stated that there are approximately 4.6 active silanol groups per 100 Å^2 of silica surface to which polar materials may hydrogen-bond. The calculated cross-sectional area of methanol (19.9 Å^2) indicates that our assumption of monolayer coverage by a spherical molecule is not too unreasonable ($100\ \text{Å}^2/19.9\ \text{Å}^2 = 5.03$) and lends support to the general validity of measurements of area by liquid-solid adsorption.

Molecular scale models and scaled coordinate paper clearly show that the area data in Table 1 are in good agreement with molecular geometry. At monolayer concentrations, even though alcohol molecules are adsorbed on all active sites, molecular populations are too low to offer side support to their alkyl chains. At much higher concentrations, alkyl groups are forced to stand erect by virtue of crowding. However, models indicate that at monolayer concentrations, when all sites are occupied, the alkyl moieties lack this side support. As their chains bend, adsorbed molecules exert a "sphere of influence" whose size depends on the length of the alkyl residue. Models also support our contention that, in this adsorbent-adsorbate system, 1-propanol has a larger sphere of influence than has 2-propanol. The longer alkyl side chain of 1-propanol can effectively cover a greater area when it is rotated about the adsorbed hydroxylic oxygen atom in a plane parallel to the adsorbent surface.

Our continuous-flow determinations of 540 to 630 m^2/g depended on whether the SiO_2 was activated at 100° or 500°C. Thermogravimetric analysis of chromatographic-grade (630-m^2/g) silica indicated a weight loss of approximately 11.5 percent between 25° and 860°C; this loss, usually attributed to adsorbed water (*7–9*), represents a surface increase of about 11 m^2/g based on area measurements of the water molecule. A portion of SiO_2, previously subjected to thermogravimetric analysis and again measured by the continuous-flow method, exhibited an area of 640 m^2/g (Table 2), which corresponds almost exactly to the expected increase of 11 m^2/g based on loss of adsorbed water. Because measurements of surface area depend on amounts of adsorbed water, our experimental results of 540 to 640 m^2/g, determined at different levels of adsorbent activity, appear to agree excellently with the supplier's BET determination.

A most important discovery is that adsorption of methanol offers a simple means of estimating areas without resort to complex and expensive apparatus. Our findings are derived from preliminary experiments with laboratory solvents that had not been dried or otherwise purified. Further purification or another choice of solvent would probably shift the value of 540 m^2/g, determined by methanol adsorption, nearer to the values of 575 to 630 m^2/g established by the continuous-flow method. In any event 540 m^2/g is within the range of the supplier's analysis.

Alcohol adsorption is a promising method for measuring surface area, especially since little equipment and operating skill are required. The technique is certainly appropriate for a first approximation of surface area, and it should be applicable to any particulate solid possessing affinity for physically small and polar adsorbates about which information on cross-sectional area is determinable.

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