

The Surface Areas of Amorphous Mixed Oxides and Their Relation to Potentiometric Titration

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The surface areas of amorphous mixed oxides of silica with alumina, ferric oxide, and titania have been measured by adsorption of ethylene glycol, water, and nitrogen. Surface areas from ethylene glycol adsorption give improbably high values. Isotherms of water adsorption indicate microporosity and estimates of the external surface area from water adsorption are similar to areas from nitrogen adsorption. An estimate of surface areas from potentiometric titration curves is made and compared to the areas from the other measurements. The area determined by titration falls between the areas from water and nitrogen adsorption. It is concluded that the most meaningful estimation of surface areas of hydrous amorphous oxides is obtained by considering an external surface area measured by nitrogen adsorption and an internal pore volume obtained from analysis of the water adsorption isotherm.

INTRODUCTION

Amorphous materials generally have large surface areas in the range 50–1000 m²/g, have a considerable pore structure which is frequently microporous (1–3), and contain appreciable quantities of water which are both adsorbed onto the surface and incorporated into the structure. These characteristics make the meaning of the term "surface area" difficult to specify except under well-defined conditions. Assignment of a specific surface area to amorphous materials should be related to the purpose for which the surface area is to be used and will depend on the method used for the area determination to a greater extent than for crystalline minerals. There is a considerable literature on the surface properties of amorphous oxides, but much of it considers the surface area to be well defined, rather than a major source of uncertainty (4–6). The surface areas of synthetic amorphous oxides have been measured by a variety of methods, including adsorption of water (7), nitrogen (4, 8), and polystyrene (9), and examina-

tion by electron microscopy (10) and low-angle X-ray diffraction (11, 12). Surface areas estimated from electron microscopy have generally provided little information, both because of the lack of any identifiable primary particles and the porous nature of the material. These methods have also been used on natural amorphous silico-aluminas (13) that occur in soils, often termed "allophane"; in addition, the adsorption of glycerol, ethylene glycol, ethylene glycol monoethyl ether (1, 14), and long chain organic molecules (15) have been used. Often there is little agreement between the different methods.

A distinction can be drawn between samples that have been prepared entirely at low temperature and those that have been subjected to calcination. The former samples, which usually include allophane, tend to be microporous (1–3) and to show areas from water adsorption that are greater than those by nitrogen adsorption (3, 16). Calcined samples on, the other hand, are rarely considered to be microporous (17), generally

have large nitrogen surface areas (8, 17, 18), and show evidence of hydrophobicity (7, 19) in that the area by water adsorption is considerably less than that from nitrogen adsorption. Little comparative data has been published on the surface areas of amorphous materials prepared from sodium silicate and the metal salts of Al, Fe, or Ti, although this is both a common method of preparation (11, 20, 21) and a closer approximation to the soil situation (21, 22) than cohydrolysis of the alkoxides. The BET N_2 area of the natural amorphous silico-alumina allophane has usually been found to be less than the H_2O area (14, 15) or the ethylene glycol area (1, 14).

The present study was carried out in conjunction with potentiometric titration experiments on binary amorphous oxides of silicon with aluminium, iron, or titanium, prepared at low temperature from sodium silicate and the metal salt. The study was aimed at determining the surface area that is relevant to an analysis of the potentiometric titration curves of these oxides and similar natural amorphous materials obtained in aqueous suspension. It was thought that the use of polar absorbates such as H_2O and ethylene glycol would give a better estimate of the titratable surface area than N_2 adsorption due to the porosity and high water content of the material. The surface areas obtained by these three methods were compared to the surface area estimated from titration curves on the assumption that the maximum charge uptake at high electrolyte concentration on these oxides would be similar on an area basis to a reference amorphous oxide.

MATERIALS AND METHODS

Preparation of the Samples

Samples were precipitated from 1 M Na_2SiO_3 and 1 M $Al(NO_3)_3$, 1 M $Fe(NO_3)_3$, or $TiCl_4$. Sodium silicate was prepared by dissolving equivalent amounts of dry SiO_2 (Merck, extra pure) in (A.R.) NaOH. Tita-

nium tetrachloride was prepared from (S.L.R.) $TiCl_4$ (1), redistilled six times, and diluted to 1 M.

Five hundred milliliters of 1 M Na_2SiO_3 (aq) and 500 ml of the required concentration of metal salt were mixed simultaneously using a two-channel constant flow Ismatec pump flowing at 180 ml/hr into a 2-liter plastic beaker initially containing 100 ml of deionized water. The system was magnetically stirred and held at a constant pH of 7 throughout the precipitation by the dropwise addition of NaOH or HNO_3 . The reaction was carried out at $20 \pm 2^\circ C$. After addition of the reagents, the mixture was stirred for a further 0.5 hr, freeze dried to facilitate washing, then washed by centrifugation to a supernatant specific conductivity of less than $30 \mu mho cm^{-1}$, and freeze dried again. These procedures were used to obtain a homogeneous product which was noncrystalline. Both X-ray and electron diffraction indicated that the products, including the end members, were amorphous. The dry weight of samples was considered to be the weight after drying to a constant weight in a dessicator over P_2O_5 that had been evacuated by water pump at $20^\circ C$.

Surface Area Determination

Unless specified otherwise, nitrogen adsorption isotherms were determined using a BET apparatus after outgassing at $80^\circ C$ and 10^{-6} Torr until no rise in pressure occurred when the sample was isolated. This usually took about 10 hr. Preliminary tests indicated no change in measured surface area whether the samples were outgassed at 20 or $80^\circ C$. The surface area of the N_2 molecule was taken to be 16.2 \AA^2 .

Water adsorption measurements were carried out in duplicate on approximately 0.2 g of P_2O_5 dried sample. The sample was then placed in a dessicator over saturated calcium bromide at 19% relative humidity, evacuated in the same way, and allowed to stand in a constant temperature room at 20

$\pm 2^\circ\text{C}$ until it reached constant weight, when a monolayer was assumed to have been formed (13). Adsorption and desorption isotherms were similarly obtained using saturated solutions of ZnCl_2 (11%), CaBr_2 (19%), MgCl_2 (33%), $\text{Ca}(\text{NO}_3)_2$ (56%), NaCl (79%), and K_2SO_4 (98%) (23).

Water adsorption isotherms were also obtained by an adsorption apparatus built in this department by Perry (24). The vapor pressure was regulated by varying the temperature of various salt solutions and was measured with an oil manometer. The samples were pelleted and placed in aluminum buckets hung on quartz spirals, the extension of the spiral as the samples adsorbed more water being measured by a cathetometer. The area of the H_2O molecule was assumed to be 10.8 \AA^2 .

Ethylene glycol adsorption was determined using the dynamic method of Rawson (25) in which the surface area of the sample is determined relative to an internal standard of known surface area. Wyoming bentonite with a specific surface area of $775 \text{ m}^2/\text{g}$ was used as the internal standard, although in a later experiment amorphous iron oxide with an area of $250 \text{ m}^2/\text{g}$ was used as the standard. The surface area by equilibrium desorption of ethylene glycol was also measured using the method of Bower and Goetzen (31).

Surface area by potentiometric titration. One hundred milligrams of sample dried over P_2O_5 was dispersed ultrasonically in 25 ml of 1, 0.1, or 0.01 N NaNO_3 and titrated with 0.100 N NaOH or 0.100 N HNO_3 using a Radiometer automatic titrator. The system was flushed with CO_2 -free high purity nitrogen for 24 hr before titration and continuously during the titration. The titration speed used was 3 hr per pH unit. All titration curves were done in duplicate. The slope of the 1 N titration curve was measured at pH 7 and compared to the slope of a reference material, which was chosen to be amorphous iron oxide for reasons discussed later.

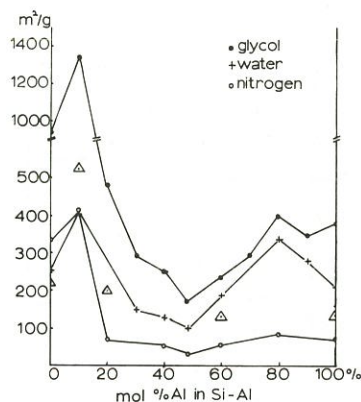


FIG. 1. Surface area of silico-aluminas by adsorption of nitrogen, water, and ethylene glycol as a function of composition. Triangulated points refer to the ethylene glycol surface area using amorphous iron oxide as the internal standard.

RESULTS AND DISCUSSION

The surface areas obtained by adsorption of N_2 using the BET method, H_2O at 19% relative humidity, and ethylene glycol by Rawson's method are shown for mixed oxides of SiAl , SiFe , and SiTi , in Figs. 1–3. In every case the surface area from adsorption of glycol is considerably higher than the area determined from H_2O or N_2 adsorption and, with the exception of silica and iron oxide, the H_2O adsorption areas are greater than those by N_2 adsorption. The occurrence of H_2O areas greater than N_2 areas for low temperature amorphous solids has previously been reported for $\text{Cr}(\text{OH})_3$ (26), $\text{Al}_2\text{O}_3\text{--TiO}_2$ (17), $\text{SiO}_2\text{--Al}_2\text{O}_3$ (16), and the natural amorphous silico-alumina allophane (1, 14). The smaller surface area of H_2O compared to N_2 on silica has been frequently reported (27, 28) and has been attributed to the hydrophobicity of the siloxane bonds on the SiO_2 surface. Surface area estimates based on the number of OH groups on the SiO_2 surface (29, 30) give better agreement with the N_2 surface area, and it is likely that a reappraisal of the cross-sectional area of the H_2O molecule based on the density of OH groups on the surface would lead to agreement between the N_2

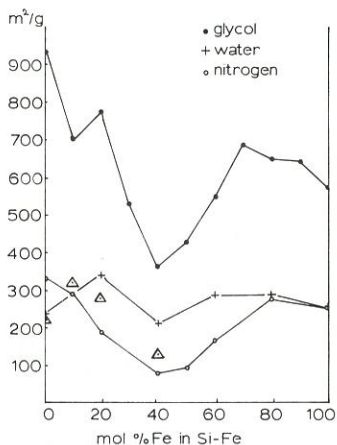


FIG. 2. Surface area of silico-ferric oxides by adsorption of nitrogen, water, and ethylene glycol. Triangulated points refer to the ethylene glycol surface area using amorphous iron oxide as the internal standard.

and H_2O areas. Comparative ethylene glycol areas have been studied on allophane only (1, 14) in which adsorption of glycol gives areas similar to adsorption of other polar molecules such as glycerol and water.

Glycol Surface Areas

Since it is unlikely that surface areas as high as $1340 \text{ m}^2/\text{g}$ are true surface areas, the glycol surface area method has been examined more closely. First, the use of bentonite, a crystalline expanding lattice mineral, as an internal standard involves the considerable assumption that the time required to form a monolayer on bentonite is the same as on the amorphous oxides. To examine this assumption, amorphous iron oxide was used as the internal standard, it being assumed that the surface area of $250 \text{ m}^2/\text{g}$, given by both N_2 and H_2O adsorption, is correct. The results, shown as triangles in Figs. 1 and 2, follow the same trend that is observed with the bentonite standard, but there was no evidence of monolayer coverage from the pressure-time plot of the adsorption (not shown), nor was the reproducibility good. Although this did not establish whether or not multilayer

adsorption on the oxides results from the use of the bentonite standard, glycol adsorption using the iron oxide standard did show that distinct monolayer coverage of glycol by this method does not occur on amorphous oxides. Second, the method uses ethylene glycol at or near its saturation vapor pressure. For many materials this appears unimportant as the method is a kinetic not an equilibrium one, but for amorphous oxides the fact that no definite monolayer is detected means that a lower vapor pressure should be used. This modification would, however, undermine the principle of the method.

A method using the lower vapor pressure in an equilibrium situation has been developed by Bower and Goetzen (31) who used an ethylene glycol-calcium chloride solvate for desorbing glycol from a sample wet with glycol. This method was applied to two samples, SiAl 90-10 and SiAl 50-50, the surface areas being found to be 1040 and $88 \text{ m}^2/\text{g}$, respectively. Although the area for SiAl 50-50 is in good agreement with the H_2O area, the result for SiAl 90-10 is still so high as to cast doubt on this method. It is probable that although a still lower vapor pressure may result in monolayer adsorption, both Rawson and Bower and Goetzen's method

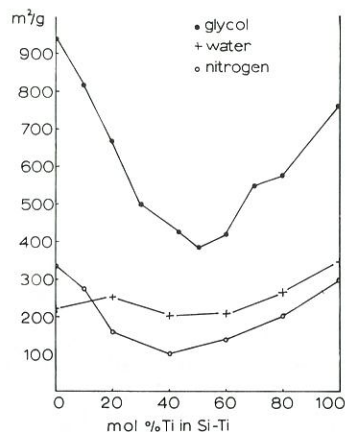


FIG. 3. Surface area of silico-titanias by adsorption of nitrogen, water, and ethylene glycol as a function of composition.

should be used with caution on amorphous materials.

N_2 and H_2O Surface Areas

It is well known that the effects of pumping, heating, and grinding on amorphous oxides prior to adsorption can seriously alter the structure and surface area of the sample (3, 8, 26). Consequently, two preliminary experiments were conducted to examine the effect of outgassing conditions on N_2 and H_2O adsorption. First, the BET N_2 surface area of a typical sample was determined under outgassing conditions varying from 5 min of pumping at 20°C up to 60 hr of pumping during which the temperature was slowly raised to 175°C. The N_2 surface area remained unchanged throughout with a coefficient of variation of 10%. In a second experiment the H_2O surface area was measured on several samples after outgassing over P_2O_5 and a water pump in a desiccator. The samples were then degassed at 20°C for 30 hr at 10^{-5} torr and the H_2O area was remeasured. The results again indicated no change in area, although the reproducibility was not as good as for N_2 adsorption. The difference between the H_2O and the N_2

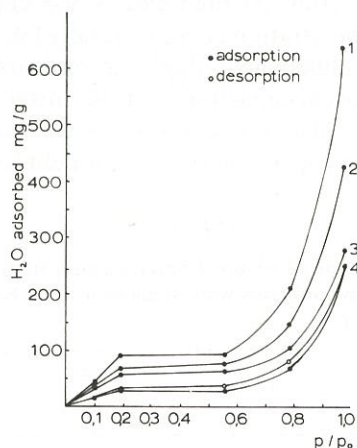


FIG. 4. Water adsorption isotherms from adsorption in a desiccator over saturated salt solution. (1) SiAl 100-0, (2) SiTi 0-100, (3) SiFe 0-100, (4) SiAl 50-50. Isotherms (1), (2), and (3) were reversible.

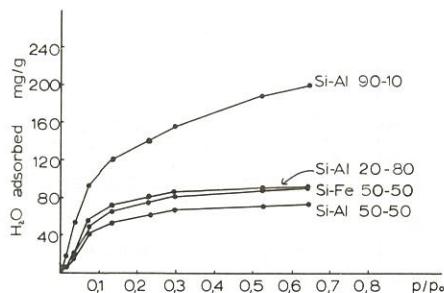


FIG. 5. Water adsorption isotherms at low pressure using the continuous adsorption apparatus of Perry (25).

areas is therefore not due to any change in structure prior to adsorption, and somehow nitrogen is being excluded from areas accessible to water molecules. To examine this difference in greater detail, water adsorption at different relative humidities was examined.

Water adsorption isotherms determined by adsorption in a desiccator over saturated solutions of constant relative humidity are shown in Fig. 4. They indicate first that the samples are probably microporous because of the plateau in the mid-range of the isotherm (32), and second that there is either activated or restricted entry into these micropores because of the sigmoidal shape of the low pressure region of the isotherm. This low pressure region of the adsorption isotherm was reexamined using the more accurate water adsorption technique. The results, shown in Fig. 5, reinforce the conclusions from the more primitive isotherms in Fig. 4 in that they reproduce both the sigmoidal shape at low pressure and the plateau in the mid-range of the isotherm. It was noted that the adsorption of H_2O on SiAl 50-50 increased considerably between the time of doing the isotherms shown in Figs. 4 and 5 (approximately 12 months). This effect did not occur for the other samples. The results of Fig. 5 have been replotted as t curves using the universal water adsorption curve of Hagymassy *et al.* (36) and are shown in Fig. 6. A nonmicroporous absorbent would be expected to show a

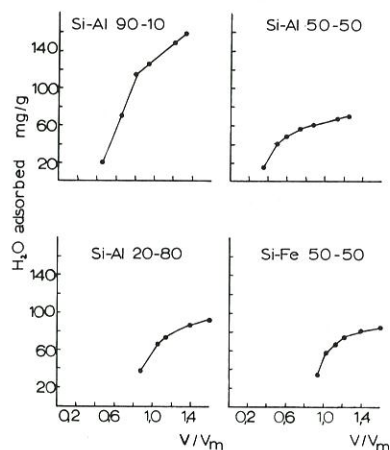


FIG. 6. t plots of the water adsorption isotherms from Fig. 5. Slopes of the upper straight line section of each graph expressed as surface area were: SiAl 90-10, $300 \text{ m}^2/\text{g} \pm 5\%$; SiAl 50-50, $87 \text{ m}^2/\text{g} \pm 5\%$; SiAl 20-80, $100 \text{ m}^2/\text{g} \pm 25\%$; SiFe 50-50, $80 \text{ m}^2/\text{g} \pm 25\%$.

straight line plot through the origin, the slope of which is proportional to the surface area. A microporous solid would normally be expected to show a steeply curved portion at low pressure, then a straight line whose intercept on the y axis is proportional to the microporous area. The unusual behavior at low pressures suggests activated adsorption which has been well documented for CO_2 adsorption on coal (33-35) and has been observed for water vapor adsorption on Portland cement by Brunauer (28), but this is not considered further here. The slope of the straight line part of the t plot is believed (32) to represent the external or non-microporous area of the sample, and the difference between this and the BET area is the area occupied by micropores. However, the presence of microporosity in the samples means that the assignment of a constant cross-sectional area to the water molecule is no longer valid, the surface areas being overestimated when using the BET theory.

To test the hypothesis that the N_2 molecule is unable to penetrate the micropores, the N_2 area can be compared to the external area from H_2O adsorption. The results, pre-

sented in Table I, show that the two areas are in broad agreement, and analysis of two plots of complete nitrogen adsorption isotherms on SiAl 50-50 and SiFe 50-50 (not shown) using the universal t curve of Lip-pens *et al.* (37) did not indicate any microporosity. The inability of nitrogen to penetrate into most of the micropores accessible to water molecules, although it is perhaps capable of entering part of the microporous region, is well known for expanding clay minerals. Aomine (14), in reporting the same effect for allophane samples, concludes that aggregation of very fine particles produces the regions that are inaccessible to N_2 . Our results and other results obtained in this laboratory from a microprobe examination of these samples agree with Aomine's conclusion and would also suggest that these aggregates persist in suspension (Pyman and Posner, submitted for publication).

Surface Area from Titration

The estimation of the surface area from titration curves was based on the assumption that the slope of the curves at high electrolyte concentration would be the same for all amorphous oxides that are similar in preparation and properties to some reference material. At high electrolyte concentration the titration curve generally becomes a straight line whose slope is proportional to the electrical capacitance of the surface (38) and thus also proportional to the surface area. The capacitance is not thought to vary

TABLE I

Comparison of External Surface Areas from Water Adsorption Isotherms with Areas from BET Nitrogen Adsorption

Sample	Total H_2O area (m^2/g)	External H_2O area (m^2/g)	Total N_2 area (m^2/g)
SiAl 90-10	515	300	416
SiAl 50:50	230	87	54
SiAl 20:80	212	100	86
SiFe 50:50	222	80	94

much among similar oxides. (39). However, rather than estimate the capacitance from first principles which involves making assumptions about the surface, a reference material has been used for calibrating the uptake on amorphous oxide surfaces. The reference material was chosen to be amorphous iron oxide for several reasons. First, the H_2O and N_2 surface areas are the same, suggesting that the surface is neither hydrophobic nor microporous. Second, titration of iron oxide is much simpler than silica or alumina since there is no dissolution of the surface, and third, another iron oxide prepared by a different method with an N_2 area of $138 \text{ m}^2/\text{g}$ and an H_2O area of $350 \text{ m}^2/\text{g}$ had exactly the same charge uptake as the reference amorphous oxide, providing that the H_2O area was used. This latter fact was considered to be evidence in favor both of the use of iron oxide as a reference material and of the preferred use of the H_2O area for titration curve analysis. The slopes of the titration curves of both the samples and the reference iron oxide were measured at pH 7 and the area was calculated relative to the $250 \text{ m}^2/\text{g}$ of the iron oxide. This pH represents a compromise between the slope near the points of zero charge, which are all

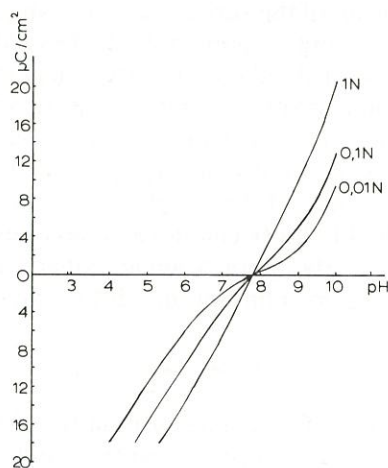


FIG. 7. Potentiometric titration curves of amorphous ferric oxide, SiFe 0-100, in NaNO_3 . Units of charge are microcoulombs per cm^2 .

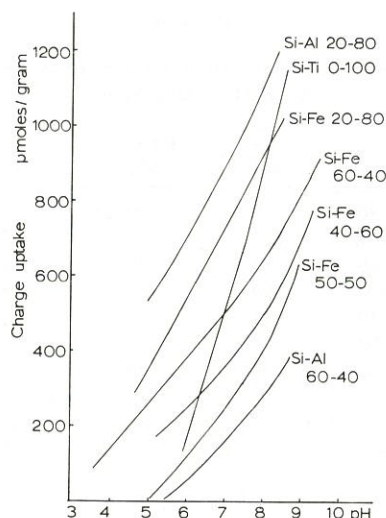


FIG. 8. Potentiometric titration curves in 1N NaNO_3 . The charge uptake has been arbitrarily set for each curve.

known to be low, and the onset of dissolution of Si and Al, which begins above pH 8. For the reference iron oxide the slope was linear over the whole of the titration range.

This is an approximate procedure in estimating surface area, for three reasons. First, the slope of the titration curve is known to vary with titration conditions and, in general, is not fully reversible. Second, at the higher pHs the slope becomes steeper due to dissolution of the surface. Finally, the assumption that the slope is similar for all amorphous oxides similarly prepared is one that will be judged by internal consistency rather than from "a priori" reasoning. However, the use of a standardized technique should increase the validity of this method and provide the most direct estimation of the titratable surface area.

The complete titration curves for the iron oxide standard and the titration curves in 1N NaNO_3 for four samples are shown in Figs. 7 and 8, respectively. The surface areas calculated from these slopes are compared to the N_2 and H_2O areas in Table II. The errors from reproducibility and curva-

TABLE II
Comparison of Titration Surface Areas with
N₂, H₂O Surface Areas

Sample	N ₂ area (m ² /g)	H ₂ O area (m ² /g)	Titration area (m ² /g) ^a
SiFe 60-40	78	230	150
SiFe 20-80	277	290	223
SiAl 60-40	53	130	124
SiTi 0-100	299	358	340
SiFe 50-50	94	260	150
SiFe 40-60	91	290	145
SiAl 20-80	86	340	211

^a The titration surface area refers to the slope of the titration curve at pH 7.

ture on these slopes can reach $\pm 15\%$, depending on the linearity of the slope. For the two samples where N₂ and H₂O areas are similar, SiFe 20-80 and SiTi 0-100, the titration areas are in broad agreement. This is an indication of the assumption in this method that the charge uptake of amorphous oxides at high electrolyte concentration is similar on an area basis and allows further distinctions between N₂ and H₂O areas to be made with greater confidence.

For the samples that differ considerably in their N₂ and H₂O areas, the titration area falls between the N₂ and H₂O areas. In view of the conclusion already reached that N₂ measures only the external surface area, it is expected that the titration area should exceed the N₂ area. However, it was also expected that the titration area would agree with the H₂O area. That this is not the case except for one sample, SiAl 60-40, could be due to two factors. First, as already mentioned, the presence of microporosity from the water adsorption isotherms means that it is not strictly valid to use a BET plot to estimate surface area. Areas obtained in this way are overestimated. Second, measurement of the slopes of the titration curves at pH 7 may give an underestimate of the surface area. This is because the maximum charge uptake on these oxides is developed at pH values greater than 7 at which dis-

solution of the surface is also occurring. For this reason it is impossible to use the slope of the titration curve for surface area estimation at high pH values. Consequently, although it could be said that the surface area of the sample lies somewhere between the titration and the H₂O areas, such an area is too imprecise to be used for interpreting the titration curves and has very limited meaning in view of the hydrated and microporous nature of the sample. A better description of the surface area would be to quote only the external surface area and to express the remaining internal area as a pore volume. Both areas can be obtained from a plot of the water adsorption isotherms, and the external area can also be measured by the N₂ area. The expression of internal area as pore volume is an accepted procedure in detailed analysis of the surfaces of the microporous solids (32), although generally N₂ adsorption is used. The use of water adsorption for such analyses is not as well established as N₂ due to its more complex interaction with the surface and consequent difficulty in interpreting the isotherms (40). It is used here because conventional adsorbates such as N₂ and CO₂ (unpublished data) do not indicate the full extent of the internal surface area.

Division of the surface area into an external area and a pore volume has consequences for the theoretical treatment of adsorption and titration data. Analysis of the titration curves would have to be carried out in two sections, adsorption onto the external surface of the sample where a full diffuse double layer can develop and adsorption into the pore volume, where there would be no room for any diffuse layer.

SUMMARY

The use of glycol adsorption for the surface area of amorphous oxides is not satisfactory for although it reveals trends in surface areas that are also revealed by other methods of surface area measurement, the

point of monolayer adsorption is not distinct and the values for the surface area obtained are too high by up to 300%. The contrast between this behavior of synthetic silico-aluminas and the generally good agreement between water and glycol adsorption on allophanes indicates that there may be a difference in morphology between the synthetic and the natural silico-aluminas.

The low value of the nitrogen area, the reversible nitrogen isotherms, and analysis of the isotherms by t plots demonstrate that nitrogen does not reveal any micropores. The larger H_2O areas might suggest either multilayer adsorption of water, entry into pores inaccessible to nitrogen either by virtue of size or polarity, or some mechanism such as activated entry that is specific to water. The characteristics of the water isotherms have ruled out multilayer adsorption, but analysis of the isotherms by the use of Brunauer's universal t curve shows up considerable microporosity. The extent of the nonmicroporous area from water adsorption agrees approximately with the nitrogen area, reinforcing the suggestion that nitrogen measures the external surface only. However, the presence of microporosity undermines the assignment of a specific surface area, as the water molecule will no longer have a constant-cross sectional area. The effect of this will be for the calculated water area to be an overestimate of the true water area. The possibility of an adsorption mechanism specific to water such as has been found on amorphous oxide gels (26) is being further investigated.

The use of titration curves to estimate the surface area in aqueous suspension has shown itself to be internally consistent against samples with similar water and nitrogen areas. This is to be expected if the electrical capacitances of amorphous oxides differ little from each other. When applied to samples whose water and nitrogen areas differ considerably, the titratable surface area is less than the area from water adsorption, but considerably greater than the nitrogen

surface area. Since the titration surface area as mentioned here is likely to be an underestimate, due to the slope of the titration curve being measured at too low a pH, and the water area is likely to be an overestimate due to microporosity, the surface area in aqueous suspension should lie between these two areas. However, the best description of the surface area should result from expressing the total surface area in terms of an external surface area, as measured by N_2 adsorption, and a micropore volume, determined from an analysis of the water adsorption isotherms.

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REFERENCES

1. Paterson, E., *Clay Min.* **12**, 1 (1977).
2. Rosseaux, J. M., and Warkentin, B. P., *Soil Sci. Soc. Amer. Proc.* **40**, 446 (1976).
3. Aldcroft, D., Bye, G. C., Robinson, J. G., and Sing, K. S. W., *J. Appl. Chem.* **18**, 301 (1968).
4. De Kimpe, C., Gastuche, M. C., and Brindley, G. W., *Amer. Min.* **46**, 1370 (1961).
5. Herbillon, A. J., and Tran Vinh, An J., *J. Soil Sci.* **20**, 223 (1969).
6. Tadros, Th. F., and Lyklema, J., *J. Electroanal. Chem. Interfac. Electrochem.* **17**, 267 (1968).
7. Murayama, H., and Meguro, K., *Bull. Chem. Soc. Japan* **43**, 2385 (1970).
8. Fripiat, J., "Clays Clay Min. 12th Nat. Cong.," p. 327, 1963.
9. Eltekori, Yu A., "Proc. Int. Symp. on Surf. Area Determination," p. 295, 1969.
10. Schlaffer, W. G., Morgan, C. Z., and Wilson, J. N., *J. Phys. Chem.* **61**, 714 (1961).
11. Elkin, P. B., Shull, C. G., and Roess, L. C., *Ind. Eng. Chem.* **37**, 327 (1945).
12. Renouprez, A., "Proc. Int. Symp. on Surf. Area Determination," p. 361, 1969.
13. Quirk, J. P., *Soil Sci.* **80**, 423 (1955).
14. Aomine, S., and Otsuka, H., *Trans. 9th Int. Congr. Soil Sci.* **1**, 731 (1968).
15. Greenland, D. J., and Quirk, J. P., "Int. Soil Conf. N. Z. Commissions IV and V," p. 3, 1962.
16. Cornell, R. M., Ph.D. Thesis, Univ. West. Australia, p. 181, 1974.

17. Clark, A., Holm, V. C. F., and Blackburn, D. M., *J. Catal.* **1**, 244 (1962).
18. Sato, M., Aonuma, T., and Shiba, T., *3rd Cong. Catal.* **1**, 396 (1964).
19. Hosaka, H., and Meguro, K., *Bull. Chem. Soc. Japan* **44**, 1252 (1971).
20. Milliken, T. H., Mills, G. A., and Oblad, A. G., *Disc. Faraday Soc.* **8**, 279 (1950).
21. Mattson, S., *Soil Sci.* **30**, 459 (1930).
22. De Kimpe, C., Gastuche, M. C., and Brindley, G. W., *Amer. Min.* **49**, 1 (1964).
23. Winston, P. W., and Bates, D. H., *Ecology* **41**, 232 (1960).
24. Perry, R. J., Ph.D. Thesis, Univ. West. Australia, p. 39ff, 1977.
25. Rawson, R. A. G., *J. Soil Sci.* **20**, 325 (1969).
26. Baker, F. S., Carruthers, J. D., Day, R. E., Sing, K. S. W., and Stryker, L. J., *Faraday Disc.* **52**, 173 (1971).
27. Young, G. J., *J. Colloid Interface Sci.* **13**, 67, (1958).
28. Brunauer, S., "Proc. Int. Symp. on Surf. Area Determination," p. 63, 1969.
29. Morimoto, T., Nagao, M., and Imai, T., *Bull. Chem. Soc. Japan* **44**, 1282 (1971).
30. Zhuravlev, L. T., and Kiselev, A. V., "Proc. Int. Symp. on Surf. Area Determination," p. 155, 1969.
31. Bower, C. A., and Goetzen, J. O., *Soil Sci.* **87**, 289 (1959).
32. Gregg, S. J., and Sing, K. S. W., "Adsorption, Surface Area and Porosity," 367 pp. Academic Press, New York, 1967.
33. Walker, D. L., and Kini, K. A., *Fuel (London)* **44**, 453 (1965).
34. Anderson, R. B., Hofer, L. J. E., and Bayer, J., *Fuel (London)* **41**, 559 (1965).
35. Nandi, S. P., and Walker, P. L., *Fuel (London)* **43**, 385 (1964).
36. Hagymassy, J., Brunauer, S., and Mikhail, R. S. H., *J. Colloid Interface Sci.* **29**, 485 (1969).
37. Lippens, B. C., Linsen, B. G., and De Boer, J. H., *J. Catal.* **3**, 32 (1964).
38. Bowden, J. W., Posner, A. M., and Quirk, J. P., *Aust. J. Soil Res.* **15**, 121 (1977).
39. Bowden, J. W., Ph.D. Thesis, Univ. West. Australia, p. 154, 1973.
40. Carruthers, J. D., Payne, D. A., Sing, K. S. W., and Stryker, L. J., *J. Colloid Interface Sci.* **36**, 205 (1971).