

## Titration Surface Area Method Comments

Wet titration methods have been used for many years in numerous industries for the determination of the surface area of dispersions; in general, they are non-routine and time consuming and can have poor sensitivity/selectivity. However, the main problem is that they are not *primary* methods (i.e. based on first principles) and it is generally accepted that, in determination of surface area, the results from any secondary method must be treated with caution (1).

### **Surface Area from Colloid Titration (Potentiometric and Conductimetric)**

Potentiometric and conductimetric titration of colloidal dispersions is well established for the determination of the *point-of-zero charge* (PZC) of oxides (2). However, the determination of a *surface area* of a colloidal suspension from such methods is an *empirical* exercise. The colloid in question is titrated with either acid, or base, and the change in pH monitored. Unfortunately, the pH titration method requires standardization and, typically, a BET area, obtained from N<sub>2</sub> gas adsorption on a dried powder sample, is used to estimate the area occupied by a surface hydroxyl.

More seriously, and of critical import in any potentiometric titration, however, is the assumption that the surface potential is given by the Nernst equation. Unfortunately, it is not valid for any colloidal oxide-solution interface (3). It is also assumed that there is no *specific* adsorption of any of the ions present and no chemical alteration of the solid (no impurities).

### **Sears number**

The Sears Number is often used as a measure of the specific surface area of silica (and, sometimes, other metal oxide) suspensions. It is based on a pH titration method that essentially provides the total concentration of hydroxyl groups (4) from which the material surface area is then deduced. Given the assumptions used in the determination of, and the number of experimental measurements (and calculations) needed to obtain a value for, the S-number it is not surprising that the S-number methodology can result in fairly insensitive data.

First, as mentioned above, the pH titration method requires standardization. Second, the sensitivity of the S-number to surface area depends on the accuracy of measuring the difference between the mass of dry silica (obtained from the dried weight of the dispersion) and the total mass of the silica and bound water. Third, this latter value is obtained from the volume fraction that is, in turn, calculated from a viscosity measurement using the Mooney Equation which is, itself, based on a number of assumptions (5), *viz* (i) the particles have to be non-porous, (ii) the suspension must contain no aggregates and (iii) charge (electro-viscous) effects are minimized. For the

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titration, the pH of the silica suspensions is reduced to pH2. This is close to the iso-electric point (IEP) of silicon dioxide (6) meaning that the particles will have little, or no, charge stabilization against possible aggregation. Fourth, generally, a Brookfield-type device is used to measure viscosity. In spite of their widespread use, when used with particulate suspensions (and, especially concentrates) rotational viscometers provide non-viscometric flow and non-zero shear conditions and, often, no temperature control. Such conditions can render the data obtained virtually unusable. Fifth, conversion of the S-number to a surface area value requires knowing the thickness of the bound water layer, the calculation of which is model dependent, unless some completely independent method (such as neutron scattering!) is available. It has been estimated (7, 8) that there is approximately one bound layer of water at the surface of silica. This calculation assumes that 2 bound water molecules are present per reacted water molecule (condensed as surface hydroxyls) – a gross oversimplification. Thus, it is usual/necessary to use a “calibration” curve.

### ***Adsorption from Solution***

In theory, solution adsorption seems to offer a versatile method that can be used for the determination of specific surface of porous and non-porous solids. A variety of adsorbents have been employed from dye molecules to surfactant ions and polymers. For example, CTAB (cetyl trimethyl ammonium bromide), a quaternary amine that is cationic (positively charged) in aqueous solution, has been used to determine the surface area of silica particles (9) and iodine (from potassium iodide solution) has been used with Carbon Black particles (10).

While the experimental measurement of adsorption from solution is relatively straightforward, unfortunately because of a variety of factors, the interpretation of the experimental data is usually more complicated than with gas adsorption (1). It is assumed that the adsorption of one component (the solvent) is negligible compared to that of the other (the solute); the choice of solvent is, therefore, a critical factor. The true site area of the adsorbed solute molecule is uncertain, the possibility of solvation of the adsorbed species is usually not taken into account, the reversibility of adsorption is rarely tested, the exact orientation of the adsorbed molecules is nearly always in some doubt.....etc, etc.

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### Conclusion

In determination of surface area, the results from any secondary method, (i.e. one not based on first principles) must be treated with caution (1). It is usually necessary to calibrate the method by the determination of the specific surface of a representative sample by means of a more reliable method such as N<sub>2</sub> gas adsorption. Unfortunately, it has long been accepted that any procedure which requires a dry sample (such as BET or Knudsen flow of a gas at low pressure) may give a surface area value which, for all its accuracy, has little relation to the effective area in solution (11). Further, N<sub>2</sub> is fairly agnostic in terms of its ability to adsorb at a surface (whether porous or non-porous). In contrast, the adsorption of water vapor onto surfaces is, however, complex (12) and, in the literature, comparisons between BET-water and BET-N<sub>2</sub> surface areas present a very confused picture; in many cases the BET-water data shows considerably higher surface area values because of multilayer formation and also, in porous materials, capillary condensation. This is because there is a high degree of specificity in the interaction of water with solid surfaces (13).

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