Silica Surface Area with the Acorn Area™

By David Fairhurst

Silica is a mineral of general composition SiO_2; it is the most common of all materials and occurs naturally in different forms including minerals such as quartz, sand and flint; many clays and rocks are largely composed of small silica crystals. Man-made silicas differ markedly from most of the natural silicas in that commercial materials can have enormously greater specific surfaces - dessicant silica gel, for example, can have a specific surface several million times greater than its apparent geometrical surface. Factors such as surface area, pore volume/size and particle size are, to some extent, independently controllable and it is this which makes the amorphous silicas important commercially; a good review of the characterization of the surface of silicas exists (1).

The commercial uses of silica are many and varied. They include ablative protective coatings (it is extremely hard - Mohs hardness 7 - and resists temperatures to 2800°F), rubber compounding (reinforcement) and as a filler in plastics (it gives a plasticizing action that aids in extrusion), as a thickening agent for industrial greases and cosmetic formulations. In pharmaceuticals it is used as an anticaking agent in tableting of active pharmaceutical agents (API). Silica is also used to coagulate oil slicks on water so that they can be harvested and burned off.

Colloidal silica sols (where the particle size is <1um and, in many cases <50nm) are a special case (2). These materials are also used in the making of molded ceramics, for treating textiles (to increase the coefficient of friction and give uniformly high-strength yarns) and as flatting agents in paints; the extremely small particle size makes them invaluable for use in clear lacquers and varnishes.

While it is evident that as the particle size of a material is reduced the surface area increases (as $1/d^2$), what may be less obvious, as mentioned earlier, is the exceptionally large surface area-to-volume ratio per given mass for the particles involved. This is an essential characteristic common to all colloidal dispersions. It matters little what the particle shape is - the surface area per mass of any colloid is orders of magnitude larger than it is for particles of even only a few micrometers in size. This huge increase in surface area dramatically effects not just adsorption of chemicals and other moieties onto the particle surface but also the interaction between particles and, importantly from a commercial perspective, system properties such as suspension rheology, coating and adhesion. Thus, the surface area of any colloidal silica is a vital metric in quantifying the performance of the material. Further, colloidal silicas are intrinsically wet suspensions of particles so it is essential that the surface area be measured directly on these materials as supplied.

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The Acorn AreA™

The Acorn AreA™ is a new instrument using a patented technique based on NMR relaxation to determine the wetted surface area of suspensions of particulate materials such as colloidal silicas (3). The Acorn AreA™ takes advantage of the fact that liquid that is bound to a particle surface has a much lower relaxation time than the free or bulk liquid. Thus a sample with a high surface area will have a lower total relaxation time than a low surface area sample because there should be more of the fluid bound to the surface. Unlike, the measurement of particle size by, for example DLS, where the raw intensity data has to be deconvoluted by means of complex algorithms, here the relaxation time can be converted into the absolute surface area by means of a straightforward calculation. However, as in the BET gas adsorption method, there is a basic assumption of monolayer coverage of fluid onto the particle surface.

The most common method of surface area determination is nitrogen (N_2) gas adsorption (4, 5). In this method N_2 is adsorbed on a sample kept at liquid N_2 temperature at a series of different pressures, This method is useful only for dry powders and requires that the sample be degassed to drive off any adsorbed material (sample conditioning); this requires a source of liquid N_2 to maintain the proper sample temperature; and this is also a critical experimental requirement (6). In contrast, the Acorn AreA™ measures suspensions directly and requires no sample pretreatment or temperature control. It is inherently a much simpler measurement technique; and as little as 0.1mL of sample is needed.

The formula for calculating the surface area from the measured NMR relaxation time is:

$$R_{av} = \psi_p \, S \, L \, \rho_p \, (R_s - R_b) + R_b \tag{1}$$

where R_{av} is the average spin relaxation rate constant, ψ_p is the particle volume to liquid volume ratio, S is the total surface area per unit weight, L is the surface layer thickness of liquid, ρ_b is the bulk particle density, R_s is the relaxation rate constant for the bound solvent and R_b is the relaxation rate constant for the free or bulk solvent.

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Using a standard reference material we can define a constant, $K_a = L \, \rho_b \, (R_s - R_b)$ so that the equation 1 reduces to:

$$R_{av} = K_a \, S \, \psi_p + R_b \qquad\qquad\qquad (2)$$

The surface area can then be calculated from:

$$SA \ = \ R_{sp} \, R_b / \, K_a \, \psi_p$$

where, $R_{sp} = R_{av}/R_b \ - \ 1$

A more precise method is to use the slope of a plot R_{sp} as a function of different volume ratios, ψ_p (i.e. concentrations).

Results of Surface Area Measurements

To demonstrate the wide applicability of the Acorn Area to the measurement of the surface area of colloidal silicas, we chose two proprietary materials that differ by almost one order of magnitude in particle size and distribution (PSD). The particles in both materials are spherical (Figure 1). Prior to the surface area analysis, the PSD of each sample was measured using X-ray disc centrifugation, a technique ideally suited to oxide materials (7).

The first material is LUDOX TM50 from W.R. Grace. This is a monodisperse, nanosized colloidal silica suspension that is supplied as a 50 wt% slurry. LUDOX TM50 is typically used to pre-treat metal surfaces for corrosion control (resistance). The material is basic (through incorporation of a small amount of alkali during manufacture). It is also is considered to be highly anionic (negatively charged); the zeta potential, which is a measure of the surface charge (8) was determined by electrophoretic light scattering (ELS) to be -38mV. The mean particle size of the Ludox TM-50 was determined to be 20nm (diameter) with a narrow PSD (Figure 2a); the polydispersity index (the ratio of D_v:D_n) was 1.05. Since the PSD is narrow then the calculation of the surface area from the mean particle size is reasonable; the estimated surface area was 128 m^2/g^{-1}.

The sample was measured as a function of concentration *viz* 50 wt% (as supplied), 25wt%, 12.5wt% and 2.5wt%. All dilutions were made using DI H_2O. The results of the relaxation measurements using the Acorn AreA are shown in Figure 3a below. The relaxation times (in milliseconds) varied as expected; the more dilute sample has less available surface area and the relaxation should be larger and hence R_{sp} smaller. The mean Surface Area, as calculated from the slope of the plot of R_{sp} vs. Volume Ratio, ψ_p, is 122$m^2 \, g^{-1}$.

The second material is a larger-sized, monodisperse silica from NanoGIANT. This material was supplied as an 8wt% slurry; it was also found to

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be anionic with a mean zeta potential of -34mV. The mean particle size was 254nm diameter with a very narrow size distribution (Figure 2b) - a PDI of 1.02. The NanoGIANT material had an estimated surface area of 12 m^2/g. Again, the relaxation time was measured as function of serial dilution with DI H_2O (Figure 3b) from which the Surface Area was calculated to be $14m^2g^{-1}$.

All measurement data are summarized in Table 1.

TABLE 1

Material	Particle Size	Zeta Potential	Surface Area	
	(nm)	(mV)	(m^2g^{-1})	
			Estimated	Measured
LUDOX TM50	20	-38	**128**	**122**
			(85-210)*	(SD:4.7, CV:0.04)
NanoGIANT	220	-34	**12**	**14**
			(10-15)*	(SD:1.7,CV:0.12)

* SA values calculated using 90th and 10th percentiles of the PSD

The agreement between estimated and measured mean surface area values for both the LUDOX TM50 and the NanoGIANT materials is excellent.

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