Powder Surface Area Comparison BET and Acorn Area

By David Fairhurst, Ph.D.

The importance of measuring the surface area of powdered materials is well established. Powder surface area affects many important aspects of product performance and is often, along with particle size, considered to be a routine characterization method. Indeed, manufacturers often include surface area data on material specification sheets and certificates of analysis.

There are number of techniques, both chemical and physical, for measuring the surface area of powders (1). These include gas adsorption, adsorption from solution and estimation from particle size distribution data. Gas adsorption is currently the most widely used method for finely divided and porous solids and the most common form of this technique is the BET method (2, 3). In this method nitrogen (N_2) gas 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 initially degassed to drive off any material adsorbed on the particle surface (sample conditioning). This requires a source of liquid N_2 to maintain the proper sample temperature; and is a critical experimental requirement (4). The entire process takes several hours. Adsorption from solution (titration) is often non-routine since it requires the availability of a suitable solute (that will specifically adsorb onto the adsorbent surface) and the means to detect changes in solute concentration. This entails sensitive instrumentation and skilled operation. Calculation of surface area from particle size data is only possible if the material in question is spherical and monodisperse. Particle shape, surface irregularities and porosity will inevitably lead to results significantly less than the true value (5).

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 (6). The Acorn Area takes advantage of the fact that liquid 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 dispersed in a liquid 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 dynamic light scattering, where the raw intensity data has to be deconvoluted by means of complex algorithms, here the relaxation time is converted into the absolute surface area by means of a straightforward calculation.

The basic assumption of monolayer coverage of fluid on the particle surface applies for NMR relaxation just as it does in BET gas adsorption and titration methods. The Acorn Area measures concentrated dispersions directly and requires no dilution, sample pretreatment or temperature control. It is inherently

XiGo Nanotools 704 Ginesi Drive, Suite 15 Morganville, NJ 07751
(732) 536-9070 fax: (732) 536-9072 www.xigonanotools.com

Page | 1

a much simpler measurement technique; and as little as 0.1ml of sample is needed.

To calculate the surface area from the measured relaxation time, the following formula is used:

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

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

R_b is the relaxation rate constant for the free or bulk solvent

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:

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

The surface area can then be calculated from:

$$\text{Surface Area} = R_{sp} \, R_b / K_a \, \psi_p$$
(3)

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).

Validation of the Acorn AreA technique

Klebosol® 30HB25K (Rohm & Haas) is a nanoparticulate silica slurry used in the electronics industry as a polishing compound for silicon wafers. The silica particles are spherical, the dispersion is highly monodisperse, and is supplied as a 30% slurry.

The surface area of these particles was determined from titration (by the manufacturer) to be **120** m^2/gm. Independent estimation of the surface area from the measured mean particle size (diameter) as determined by dynamic light

scattering was **123** m^2/gm. Direct measurement using the Acorn Area gave **121**m^2/gm.

Clearly the NMR relaxation technique can precisely determine the surface area of a well-characterized suspension with values that are in accord with independent techniques.

Comparison of Surface Area Data

It is well known and accepted that the measurement of the size of broadly distributed asymmetric particles by different sizing techniques will result in different mean sizes, polydispersity and distribution (7). The differences arise from the sensitivity of each technique in the detection of the various size fractions and the method of deconvoluting the raw data.

A similar situation occurs when comparing surface area by NMR relaxation and gas adsorption. The NMR technique used in the Acorn Area differs from gas adsorption in that the sample is measured in the dispersed, "wetted" state in a liquid. Thus, *a priori*, it should not be expected that the two techniques should necessarily give the same value for the total surface area.

However, molecules of water (H_2O) and nitrogen (N_2) possess roughly the same size. Thus, if a material is efficiently wetted by the fluid and the particles are well dispersed, then the surface area calculated assuming a monolayer adsorption coverage of water molecules should be in reasonable agreement with a surface area obtained from a monolayer coverage of N_2 molecules. However, the correct wetting and dispersing of powders is not a trivial exercise (7,8).

To test how the NMR technique compares against the traditional measurement using BET (N_2) gas adsorption, we took 4 samples of dry powders (two silica powders, a zeolite and a carbon black) covering a wide range of surface area and hydrophilicity. They were:

1. A mesoporous silica, TMPS-4, supplied by Taiyo Kagaku. The prefix "4" refers to the nominal pore diameter of 4nm.

2. An amorphous fumed silica, AEROSIL 200, from Degussa that has a nominal surface area of 200 ± 25 m^{2}g^{-1} (manufacturer's literature).

3. A zeolite, JRC Z5-25H, supplied by the Japanese Research Council that is used as a reference material. The material has a pore access diameter of 0.5nm.

4. An active Carbon, Lot#3845, from Tokai Carbon Co.

An aqueous suspension of each powder was prepared at approximately 12.5wt% using proprietary surfactant/dispersant solutions developed at XiGo and the

wetted surface area measured using a single point determination of the stock suspension. The surface area value shown (together with the standard deviation and coefficient of variation) in Table 1 is an average of three samplings of the stock suspension each run three times. The BET surface area was measured only once using a BELSorp Model 28SA-36.

Although the wetted surface area will obviously depend on the fluid and how well the powder has been dispersed, the agreement between the mean surface area values measured using BET (N_2) gas adsorption for the dry powder and by the Acorn Area for wet suspensions of the same materials is excellent. The difference is that each of the BET measurements required extensive sample conditioning prior measurement (degassing at ca 400°C for a minimum of 4 hours) prior to measurement. In contrast, the total measurement time (including the dispersing stage and all repeats) using the Acorn Area took less than 10 minutes.

TABLE 1

Method	BET (N_2)	Acorn AreA
Sample State	Dry powder	Wet suspension
Material	Surface Area (m^2g^{-1})	Surface Area (m^2g^{-1})
Mesoporous Silica PowderTMPS-4	942	932 (SD:2, CV: 0.02)
Zeolite JRC Z5-25H	413	425 (SD:11, CV: 0.03)
Fumed Silica Aerosil 200 (0410)	196	195 (SD:10, CV: 0.05)
Active Carbon #3845	53	56 (SD:3, CV: 0.05)

REFERENCES

1. G.D. Parfitt and K.S.W. Sing (eds), "Characterization of Powder Surfaces", Academic Press, London, 1976.
2. S. J. Gregg and K.S.W. Sing, "Adsorption, Surface Area and Porosity", 2nd Edition, Academic Press, London, 1982.
3. S. Lowell and J. E. Shields, "Powder Surface Area and Porosity", Chapman & Hall, London, 1984.
4. K.S.W. Sing, "The Use of Gas Adsorption for the Characterization of Porous Solids", *Colloids and Surfaces*, 38 113 (1989).
5. T. Allen, "Particle Size Measurement", Chapman & Hall, 4th Edition, New York, 1990.
6. US Patent, 7,417,426, August 26, 2008.
7. A.Jillavenkatesa, S. J. Dapkunas and Lien-Sien. H. Lum, "Particle Size Characterization", Special Publication 960-1, NIST, 2001.
8. G. D. Parfitt (ed), "Dispersion of Powders in Liquids", Applied Science Publishers, 3rd edition, London, 1981.
9. D. Fairhurst and R. W. Lee, Drug Delivery Technology, Vol 8, No. 8, September (2008).