The Fastest Technique for Determination of Envelope Surface Area and Average Particle Size of Ceramic Powders

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The technique described here calculates the envelope surface area and average particle size of powders using the flow rate through the sample at a given differential pressure. As opposed to the Brunauer, Emmett, and Teller (BET) technique which normally uses liquid nitrogen and requires a significant amount of time, the Envelope Surface Area Analyzer (ESA) uses compressed air at room temperature and yields data within a few minutes.. The BET technique gives total surface area including that within the particles, while the ESA gives the surface area on the exterior of the particles. The ESA surface area is used to calculate the average particle size.

Introduction

Recently, PMI finished development of an automated instrument for determination of the envelope surface area of powders from their gas permeability. The technique is based on theoretical and experimental work from several sources including Carman [1], Kraus, Gerard, Ross, John W., and Girifalco, L. A. [2], and Emmett, P. H. [3]. The equipment is ideal for quality control and development, as it is a fast, easy to use, and reproducible for determining the exterior surface area and the average particle size of a sample. The average particle size is the diameter of spheres of equivalent exterior surface area. For spherical sample particles, the ESA results compare well with the real particle diameter. Specific surface area obtained with ESA on particles with no internal voids compares well with that obtained with BET.

Theoretical Background

Carman first suggested in 1937 [1] the use of liquid permeability and the Kozeny equation, equation (1), for measurement of the surface area of powders. Experimental work through the 40's and 50's proved that the concept gave reproducible values for both specific surface area and average particle size in comparison to nitrogen adsorption method. In the 50's, gas permeability was developed as an alternative to liquid permeability. Because the gas permeability method left the sample physically unaltered as a result of the test, the method became the preferred one. However, it was quickly found that the use of gasses at low pressures required a modification of the Kozeny equation to account for molecular or slip flow. This additional term is equivalent to the Knudsen flow equation. Equation (2) gives this combined equation. For samples of very small capillary size, such as a packed powder bed, the molecular or slip flow cannot be ignored even at the atmospheric pressure. Using equation (2), the specific surface area of

a sample can be calculated. From the specific surface area, a value for the average particle size can be calculated. Equation (3) shows how the specific surface area can be used to calculate a mean diameter by assuming spherical particle shape. Using these equations, the average particle size of a sample can be determined from the gas permeability.

$$(1) \quad \frac{Ql}{\Delta Pa} = \frac{\varepsilon^3}{k(1-\varepsilon)^2 S_v^2 \eta}$$

Q = volume flow at the average pressure
l = thickness of the powder bed
ΔP = differential pressure across the sample bed
a = cross sectional surface area of the powder bed
ε = porosity of powder bed = void volume/ total volume
k = aspect factor, taken to be 5.
S_v = Surface Area per unit volume of the solid
η = viscosity of the gas

$$(2) \quad \frac{Ql}{\Delta Pa} = \frac{\varepsilon^3}{k(1-\varepsilon)^2 S_v^2 \eta} + \frac{z\varepsilon^2 \pi}{(1-\varepsilon) S_v \sqrt{2\pi\rho \overline{P}}}$$

z = constant, taken to be 48π/13
ρ = density of the gas at the average pressure
$\overline{P}$ = mean pressure of gas in sample

$$(3) \quad d = \frac{6}{S_o \rho} \quad \textit{spherical approximation}$$

d = average particle diameter
S_o = specific surface area, surface area of sample/ mass of sample
ρ = true density of material

Method of Operation

The ESA is based on the gas permeability technology developed by PMI. Figure 1 shows the instrument and the computer with the control software. The test monitors the gas flow through the sample as a function of the differential pressure across the sample. The pressure is accurately controlled and increased in small steps. The differential pressure and flow at each step is allowed to stabilize before the data for that point is taken so as to assure a steady state reading. To insure a sufficient average, the test is designed to take data at several differential pressures. The method is completely automated, requiring only the initial input of the sample parameters such as sample mass and absolute density. The

test from initial weighing to the removal of the sample chamber can be accomplished in less than 15 minutes, much faster than the 60 minutes needed for a BET analysis. Also, the ESA method, unlike the BET method, does not require any special gasses or cryogenic liquids. The data is analyzed using PMI analysis software. The results are provided automatically at the end of each test and can be reviewed at any future point. A wide range of sample surface areas, from 0.1 to 10 m^2/g can be tested.

Figure 1: Envelope Surface Area Analyzer

Results

Three types of samples were tested. The first two samples, A and B, are magnesium stearate powders; the next two, C and D, are glass bubbles and the others are alumina powders. The three types of samples were also tested using BET for comparison of BET data with those of ESA. The BET results for the magnesium stearate samples used nitrogen adsorption while the glass bubbles used krypton. A comparison of the two methods is presented in Table 1. This table shows that there is a very good comparison between the BET and ESA results. Table 2 shows the reproducibility of the ESA method. Here again the results mainly were reproducible to within a couple of percent. Figure 2 shows typical results for samples C and D.

Table 1: Comparison Between BET and ESA Methods

Sample	ESA Surface Area	ESA Particle Size	BET Surface Area	BET Particle Size
A	11.13 m^2/g	0.43 microns	12.16 m^2/g	0.39 microns
B	6.97 m^2/g	0.69 microns	7.13 m^2/g	0.67 microns
C	0.89 m^2/g	14.82 microns	0.915 m^2/g	14.38 microns
D	1.76 m^2/g	22.25 microns	1.91 m^2/g	20.53 microns

Table 2: Reproducibility of ESA Method

Sample	ESA Particle Size	Percent Deviation
A	0.43 ± 0.04 microns	9.3%
B	0.69 ± 0.01 microns	1.4%
C	14.82 ± 0.2 microns	1.3%
D	22.25 ± 0.5 microns	2.2%

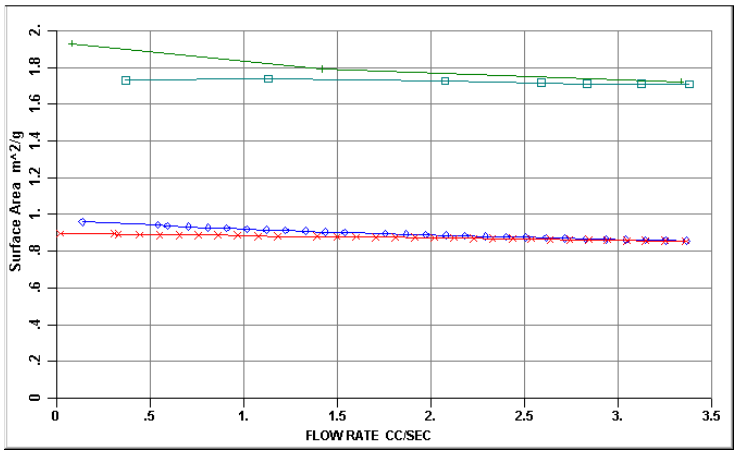


Figure 2. Typical Results of ESA.

Alumina powders having a wide range of particle sizes (28 to 800 grit) were examine by BET and ESA. The results are presented in Table 3. The values hardly differ for course powders, but with decreasing particle size the BET surface area is higher. This is attributed to the creation of greater internal porosity in the finer powders. Thus, the results are in excellent agreement.

The average particle size is related to the envelope surface area rather than the total surface area. Therefore, the envelope surface area measured in ESA is more appropriate for estimating the average particle size of the powders (Table 3).

Table 3.BET and ESA Results on Alumina Powders.

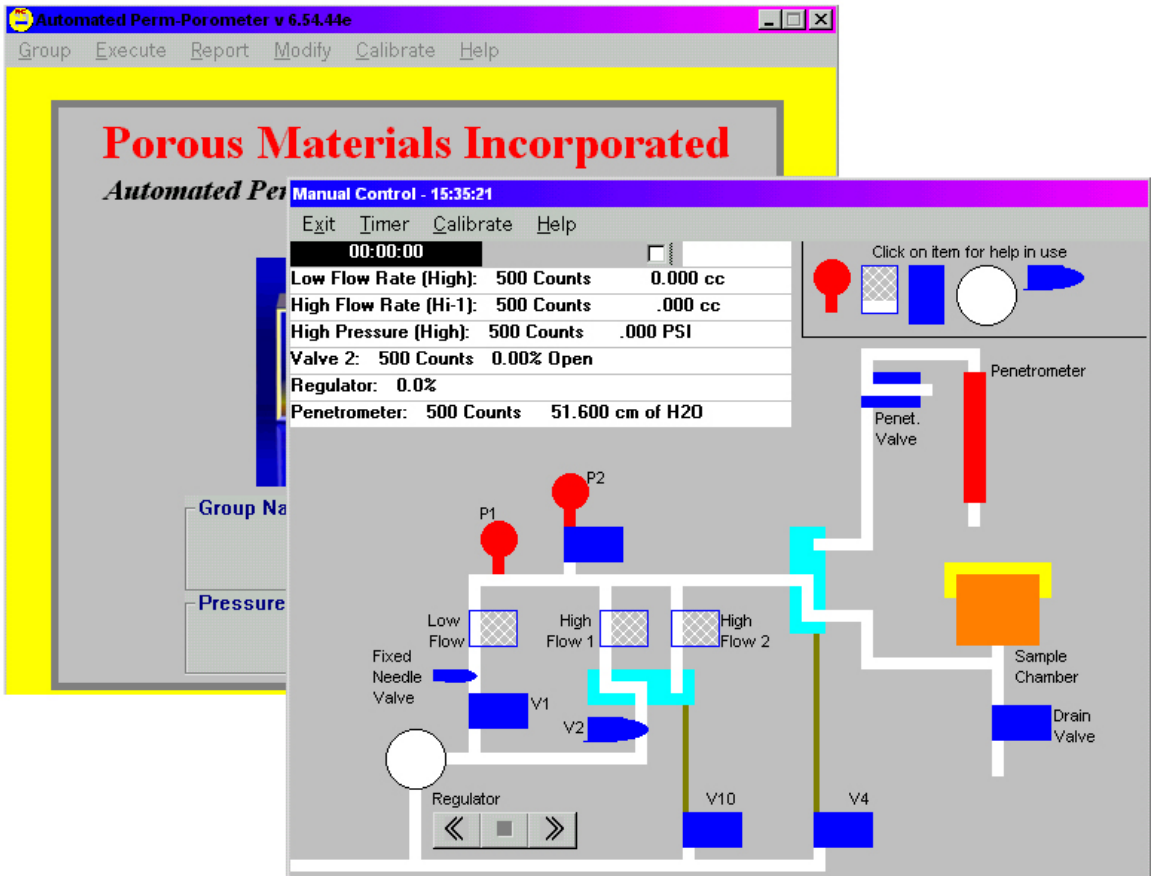
Alumina powder	Krypton adsorption Surface area, m^2/g	Flow porometry Surface area , m^2/g	Average particle size, microns
24 #	0.018	0.017	90.50
54 #	0.028	0.019	80.97
180 #	0.079.	0.047	32.73
320 #	0.258	0.144	10.68
500 #	0.415	0.304	5.06
800 #	0.827	0.578	2.66

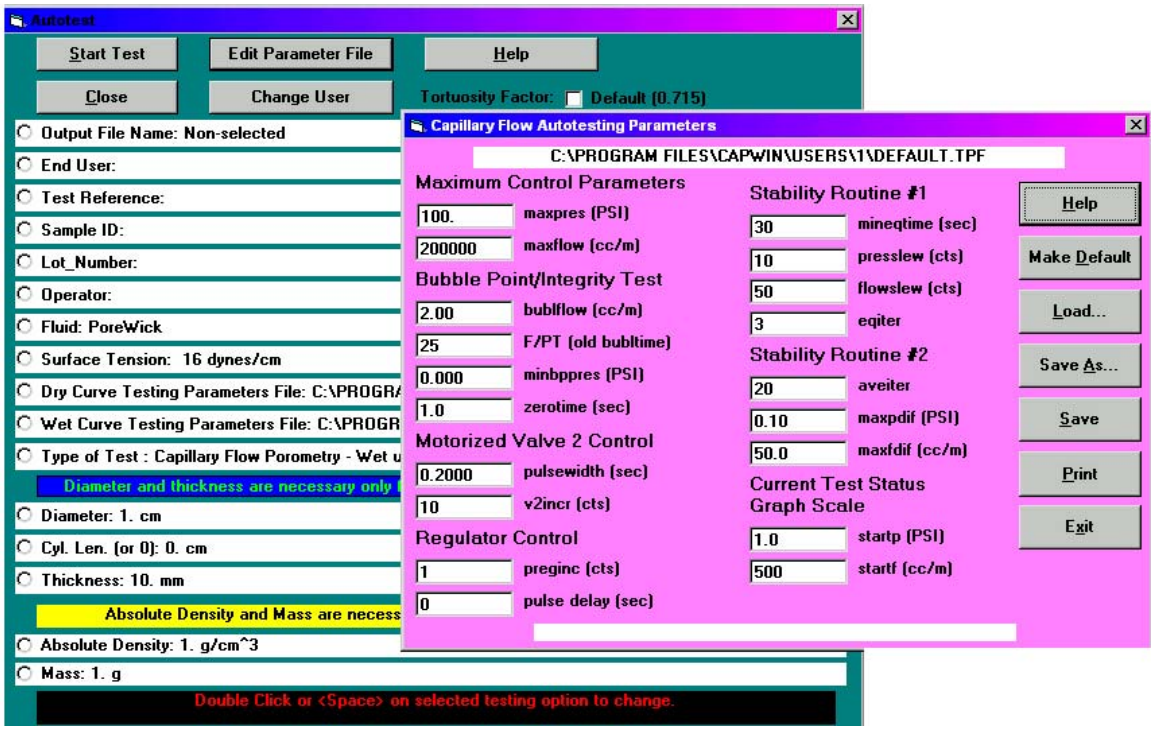
The good comparison to the BET results shows that the ESA method can be used to find the external surface area of samples over a range of specific surface areas. The data also shows the reproducibility of the results. Because the ESA method does not use

cryogenic temperatures, it is much less expensive than BET methods. Also, as the ESA method does not use the mechanics of adsorption, it is much faster than BET methods. These advantages of the ESA mean that it can be used for analyzing samples in a quality control or product development environment at a reduced cost and increased speed over the standard BET method.

References

1.) Carman, P. C. *Flow of Gases Through Porous Media*, Academic Press Inc., 1956
2.) Kraus, Gerard, Ross, John W., and Girifalco, L. A., J. Phys. Chem., **57**, 330 (1953)
3.) Emmett, P. H., Catalysis, Vol. 1, 58, (1957)
4.) Lowell, S. and Shields, E., *Powder Surface Area and Porosity*, Chapman Hall, 1984.

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