A New Technique Provides Faster Particle Size Analysis at a Lower Cost Compared to Conventional Methods

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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, which is used to calculate the average particle size..

Introduction

Recently, PMI finished development of an automated method for determining the envelope surface area of powders from their gas permeability. The method 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 method for determining the exterior surface area and therefore average particle size of a sample. The average particle size is the diameter of a sphere of equivalent exterior surface area. For spherical sample particles, the ESA results compare well with the real particle diameter. The results can be used to determine specific surface area as does BET adsorption methods. For sample particles of no internal void volume, the ESA results compare well with the BET results. Before the results are discussed, a review of the theoretical background and the method of operation of the equipment will be discussed.

Theoretical Background

Carman first suggested in 1937[1] using liquid permeability and the Kozeny equation, equation (1), to measure 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 particle size in comparison to nitrogen adsorption methods. In the 50's, gas permeability was developed as an alternative to using liquid permeability. Because it left the sample physically unaltered as a result of the test, it became the preferred method. 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 atmospheric pressures. 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 $48\pi/13$
ρ = density of the gas at the average pressure
P = mean pressure of gas in sample

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

S_o = specific surface area = surface area of sample/ mass of sample
ρ = true density of material

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Method of Operation

The ESA is based on already existing gas permeability technology developed by PMI. Figure 1 shows the manual control screen provided in the software, which shows the layout of the system as developed by PMI. The trest monitors the gas flow through the sample as a function of the differential pressure across the sample. To insure a sufficient average, the test is designed to take data at several differential pressures. A pneumatic controlled pressure regulator and a motorized flow constriction valve are used to control

the differential pressure across the sample. Together, they provide fine pressure control 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. The valves, the regulator, the pressure sensors and flow sensors are connected to a computer using a PMI software interface. Thus, 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 then analyzed using PMI analysis software. The results are provided automatically at the end of each test and can be reviewed at any future point.

Figure 1: Envelope Surface Area Analysis Test Setup
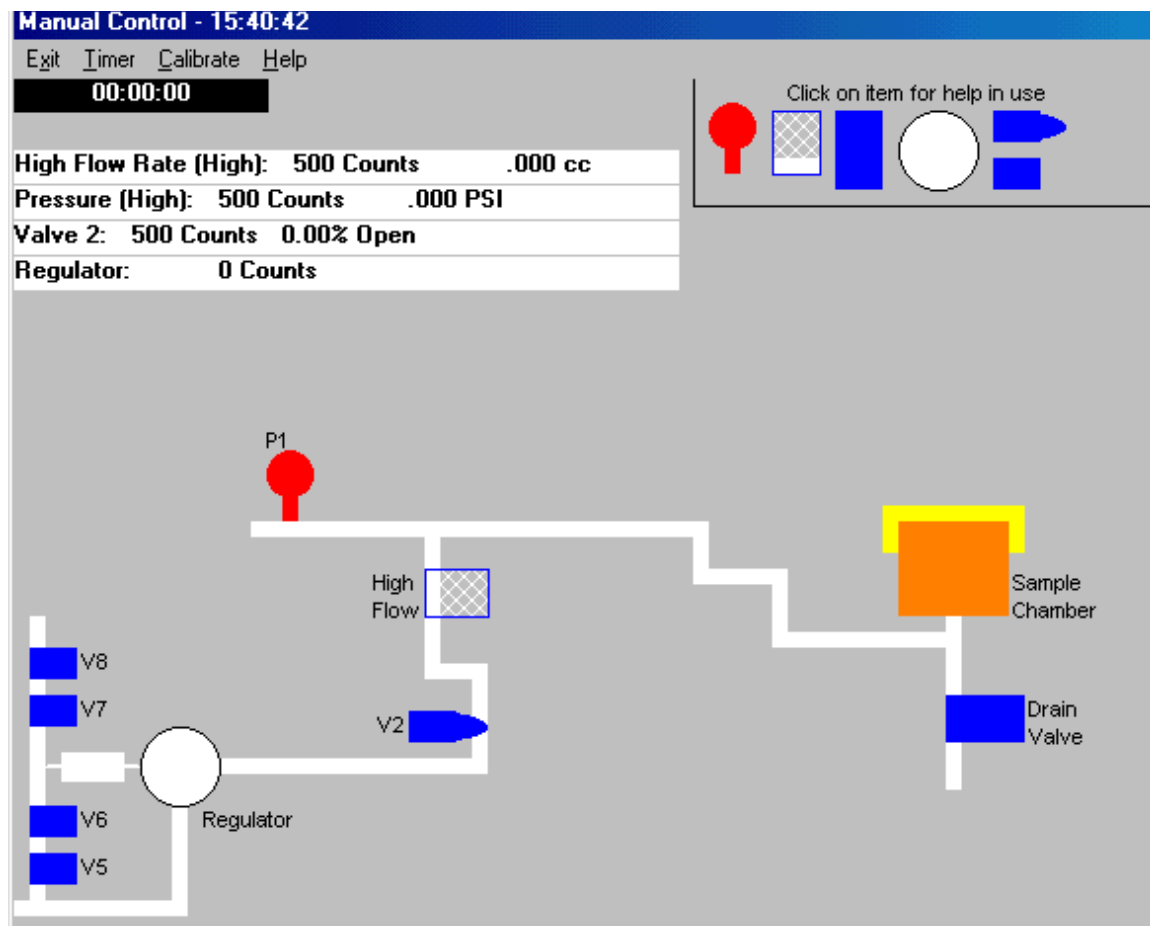
The basic system uses a 2000 Torr absolute pressure transducer and a 500 ccpm flow meter. This allows for a wide range of sample surface areas to be tested, from 0.1 to 10 m^2/g. These ranges can be extended by using an additional low differential pressure transducer attached near the sample chamber, and by using a high volume flow meter instead of the 500 ccpm flow meter. The cascade valves (V5 through V8 on Figure 1) control the pneumatic pressure regulator. The motorized valve (V2 in Figure 1) constricts

the flow, which controls the pressure at the sample chamber. The drain valve relieves the pressure at the end of a test. Initially, there is zero differential pressure across the sample. The pressure is increased throughout the test until a preset flow or pressure criterion is reached. Once the test is completed, the system is vented and reset for the next test.

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 were alumina powders. The three types of samples were also tested using BET for comparison of BET data with those of ESA. This paper will not go into an explanation of the BET method, which already has sufficient reference material covering it[4]. The BET results for the magnesium stearate samples were using nitrogen adsorption while the glass bubbles used krypton. Figure 1 shows the comparison of the two methods. This figure shows that there is a very good comparison between the BET and ESA results. Figure 2 shows the reproducibility of the ESA method. Here again the results mainly were reproducible to within a couple of percent. Figure 3 shows typical results for samples C and D.


Figure 1: Comparisons 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

Figure 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 3: Typical Results of the ESA Method
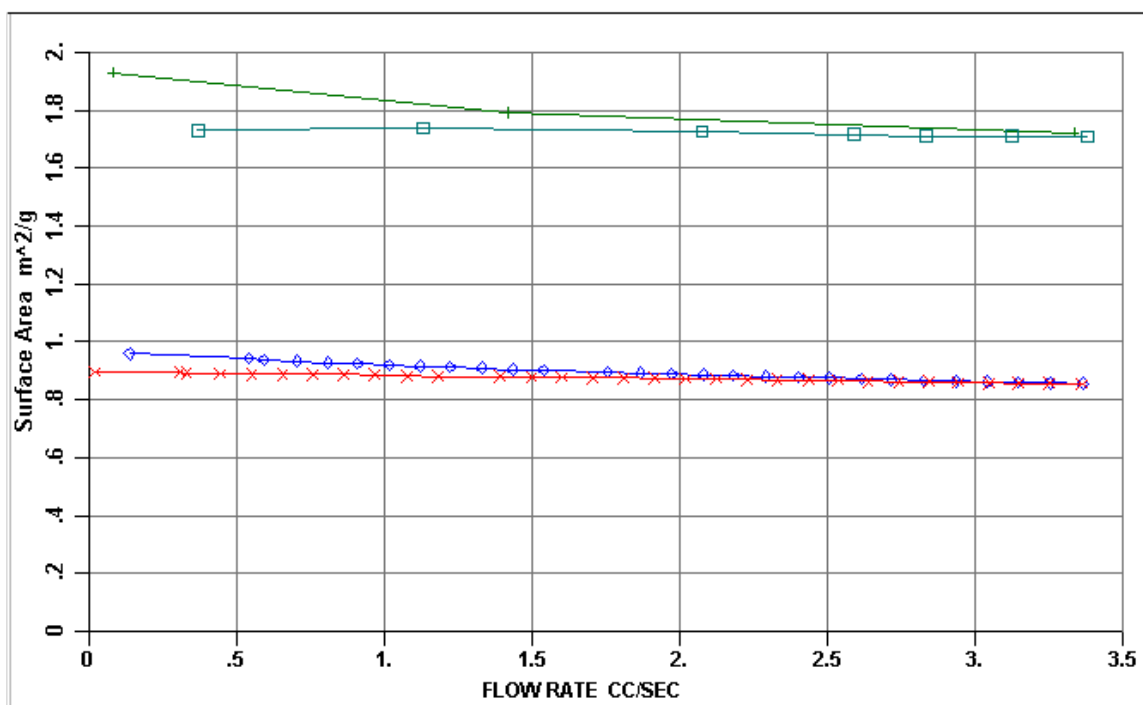
The good comparison to the BET results show that the ESA method can be used to find the external surface area of samples over a range of specific surface areas. The data also showed the reproducibility of the results. Because the ESA method does not use cryogenic temperatures, it is much less expensive 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 testing method 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 methods.

References

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3) Carman, P. C. *Flow of Gases Through Porous Media*, Academic Press Inc., 1956
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