

# Effect of Particle Size Distribution in Determining a Powder's Fractal Dimension by Single Gas BET: A Mathematical Model

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Received March 8, 1991; accepted July 30, 1991

It is shown that particle size distribution plays an important role in determining the fractal dimension of a material when using gas adsorption techniques. The model currently being used to determine a material's fractal dimension is examined. In many cases this model works well. However, it is shown that errors may result if this model is applied to samples with specific particle size distributions. A new mathematical model which incorporates the particle size distribution is proposed. The new model is shown to produce the correct value for the fractal dimension under a number of conditions for which the current method fails. Conditions under which the currently used model can be expected to perform well are also given. © 1992 Academic Press, Inc.

## INTRODUCTION

The use of fractal concepts to characterize the surfaces of powders and other solids has recently experienced tremendous growth with applications in pharmaceuticals (1, 2), biology (3), and general chemistry (4–7) appearing frequently in the literature. Fractal measures, primarily the fractal dimension  $D$ , provide information on surface roughness or total surface area and hence on the potential reactivity of the material with whatever environment in which it is placed. In pharmaceuticals, surface properties may relate to how the drug is adsorbed into the blood stream or transported to the site where its action is required. Physical properties, such as the ability to compact and dissolve, may also depend on fractal measures. Biological applications may include the interaction of the blood with viruses, bacteria, and other agents or its ability to flow freely through natural or artificial arteries. In chemistry, surface properties as characterized by fractal measures might determine reaction rates, heats of adsorption/desorption, and general reactivity.

Avnir and co-workers (8–10) have used the fractal dimension to characterize the surfaces of quartz particles, silica gels, and other powders. The present authors (11) recently applied fractal measures to determine the surface characteristics of natural polymers (chitosan) and their relationships to the adsorption of and reactivity with various compounds.

The standard procedures applied to powders often require a measurement of particle size, usually a diameter, as one of the parameters involved in determining the fractal dimension. The second parameter might be the specific surface area from gas adsorption. These measurements are made on several groups of particles; the groups differ in mean particle size and are usually obtained by sieving. No matter what method is used to obtain the data, it is usually assumed that the particles are monodisperse, and the average particle diameter is taken as the midpoint between the sieves which created the size group. This scaling parameter, combined with the surface area or other measure, then provides the fractal dimension,  $D$ .

This paper shows that particle size distribution plays an important role in determining the fractal dimension of a material when this

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dimension is based on gas adsorption techniques. The fractal dimension of perfectly smooth spheres may be artificially increased by as much as 30% of its allowed range by judicious choice of particle size distributions. Other distributions may produce curvature of the standard plots for obtaining  $D$  and could incorrectly signal the existence of regions of different fractal dimension.

ANALYSIS

For a group of  $n$  smooth spherical particles of size  $d_i$  where  $i = 1$  to  $n$ , the surface area of each particle can be written as

$$S_i = k_1 d_i^2, \quad [1]$$

where  $k_1 = \pi$ . The mass of a particle can be written as

$$m_i = \rho V_i = k_2 d_i^3, \quad [2]$$

where  $k_2 = \rho \pi / 6$  for spherical particles. If the particles are fractal, then the surface area  $S_i$  will not scale as  $d_i$  raised to the power 2, but will scale as  $d_i$  raised to some power  $D$ , where  $2 \leq D \leq 3$ , i.e.,

$$S_i = k_1 d_i^D. \quad [3]$$

Taking the sum of all particles gives the total surface area  $S_T$  and mass  $m$  as

$$S_T = k_1 \sum_{i=1}^n d_i^D \quad [4]$$

$$m = k_2 \sum_{i=1}^n d_i^3; \quad [5]$$

whence the specific surface area  $s$  becomes

$$s = \frac{S_T}{m} = k \frac{\sum_{i=1}^n d_i^D}{\sum_{i=1}^n d_i^3}. \quad [6]$$

Expressing the  $d_i$ 's in terms of the mean value  $\bar{d}$ ,

$$d_i = \bar{d} + v_i, \quad [7]$$

where  $v_i$  is the deviation of  $d_i$  from the median  $\bar{d}$  for each particle, Eq. [6] becomes

$$s = k \frac{\sum_{i=1}^n (\bar{d} + v_i)^D}{\sum_{i=1}^n (\bar{d} + v_i)^3}. \quad [8]$$

Applying the assumption that the particles are monodisperse, i.e.,  $v_i = 0$ , Eq. [8] becomes

$$s = k \frac{\bar{d}^D}{\bar{d}^3} = k \bar{d}^{(D-3)}. \quad [9]$$

Taking logs gives

$$\ln(s) = \ln(k) + (D - 3)\ln(\bar{d}), \quad [10]$$

the equation most often used in determining the fractal dimension of powders. Equation [8] is the general expression for the specific surface area of a group of fractal particles of varying particle size and is the starting point for deriving the correction term for particle distribution.

We write  $d_i = \bar{d} + \sigma z_i$ , where  $z$  is the standard normal random variable,  $\bar{d}$  the sample mean, and  $\sigma$  the sample standard deviation. We have assumed that the distribution is normal (this assumption is verified experimentally for the chitosan samples (11)). Under these conditions it is well known that for a large number of normally distributed values  $d_i$ ,

$$\sum_{d_i} d_i^3 = \sum_{z_i} (\bar{d} + \sigma z_i)^3 = \bar{d}^3 + 3\sigma^2 \bar{d} \quad [11]$$

and

$$\sum_{d_i} d_i^2 = \sum_{z_i} (\bar{d} + \sigma z_i)^2 = \bar{d}^2 + \sigma^2. \quad [12]$$

As is seen from Eq. [6], the quantity we wish to approximate is

$$\sum_{d_i} d_i^D = \sum_{z_i} (\bar{d} + \sigma z_i)^D, \quad [13]$$

where  $2 \leq D \leq 3$ .

The approach taken here is to find a transformation  $F(\bar{d}, \sigma, D)$  such that

$$F(\bar{d}, \sigma, 3) = \bar{d}^3 + 3\sigma^2 \bar{d} \quad [14a]$$

$$F(\bar{d}, \sigma, 2) = \bar{d}^2 + \sigma^2 \quad [14b]$$

and  $F(\bar{d}, \sigma, D)$  varies smoothly with  $D$ .

A suitable  $F(\bar{d}, \sigma, D)$  is simply

$$F(\bar{d}, \sigma, D) = \bar{d}^D + \bar{d}^{(D-2)} 3^{(D-2)} \sigma^2, \quad [15]$$

which yields Eqs. [14a] and [14b] and is smooth in  $D$ . Thus Eq. [6] becomes

$$s = k \frac{\bar{d}^D + \bar{d}^{(D-2)} 3^{(D-2)} \sigma^2}{\bar{d}^3 + 3\sigma^2 \bar{d}}. \quad [16]$$

We see that Eq. [16] is still somewhat intractable and hence make one more transformation. Since  $F(\bar{d}, \sigma, D)$  is smooth in  $D$ , all derivatives with respect to  $D$  exist. We expand  $F(\bar{d}, \sigma, D)$  in a Taylor series around  $D = 3$ , substitute the series (truncated after the linear  $(D - 3)$  term) into Eq. [16], take the log of both sides and expand again to obtain

$$\ln(s) = \ln(C_1) + (D - 3) \times \left[ \ln(\bar{d}) + \frac{3\sigma^2 \ln(3)}{\bar{d}^2 + 3\sigma^2} \right] \quad [17a]$$

or

$$\ln(s) = \ln(C_1) + (D - 3)[\ln(\bar{d}) + \beta], \quad [17b]$$

where  $C_1$  is a constant involving  $k$  and

$$\beta = \frac{3\sigma^2 \ln(3)}{\bar{d}^2 + 3\sigma^2}. \quad [18]$$

Note that the correction term goes to zero as  $\sigma$  approaches 0, since the samples are then monodispersed. Also in the case of  $D = 3$ , the correction term  $\beta$  has no effect since it merely shifts the horizontal  $\ln(s)$  vs  $\ln(d)$  line.

While the correction for sample particle size distribution has been demonstrated for normal distributions, a similar calculation could be performed for other distributions such as log normal. The normal distribution was chosen because of our experience with chitosan (11).

Following the above approach, determination of the fractal dimension requires some measurement of particle size ( $d$ ). In previous work on chitosan powders (11) it was decided to use the maximum diameter, measured perpendicular to the longest axis of the irregular shaped particle, for this parameter. The Optimax image analyzer system that was available could not provide this measurement directly and the actual measurements of  $d$  were made

manually using a handheld scale. The analyzer provided the enlargement, necessary contrast, and mobility to select sufficient numbers of particles for the measurement. The particles were thinly spread on a microscope slide and the diameters of all separate particles were measured (only dense aggregates were avoided). Particle size distributions for several groups of sieved chitosan particles were measured using this procedure. Particle size distributions having preselected mean and standard deviation were also computer generated using a statistical application package for a Hewlett-Packard 9836C computer. The program (RNORM) provided normally distributed random numbers.

Figure 1 compares the actual distribution of particle diameters measured as described above with a computer-generated set of numbers having a normal distribution with the same mean and standard deviation as the measured diameters. Statistical analysis of the measured distribution cannot rule out the possibility that the distribution is normal at the 95% confidence level. Although some differences exist between the two distributions of Fig. 1, it is clear that the measured distribution is no more varied or of broader range than the computer-generated normal distribution. Data from other size groups gives similar results. Thus it is reasonable to conclude that the particle sizes, in any group of sieved particles, are normally distributed and that computer-generated normal distributions are valid substitutes for experimental data. Therefore, the calculations and analyses presented in this paper are based on computer-generated particles; particle sizes for each group are normally distributed and all particles are spherical.

With a given distribution of smooth spherical particles, it is a straightforward calculation to obtain the volume (or mass if the density,  $\rho$ , is known) and surface area of the particles. Figure 2 is a plot of  $\ln(s)$  vs  $\ln(\bar{d})$  as suggested by Eq. [10], where  $s$  is the specific surface area calculated for a group of smooth spheres (computer generated) using Eq. [6] and  $\bar{d}$  is the average particle diameter. Curve A results

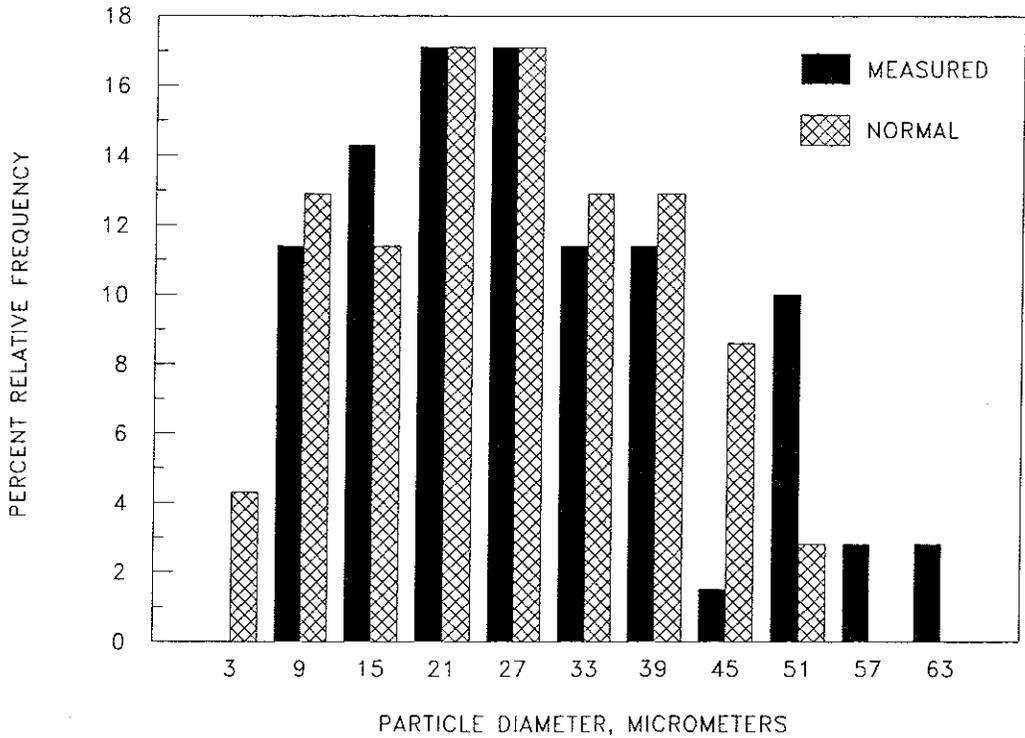


FIG. 1. Bar graph comparing particle size distributions for 70 measured chitosan particles and 70 computer-generated particles having a normal distribution with the same mean and standard deviation as the measured particles.

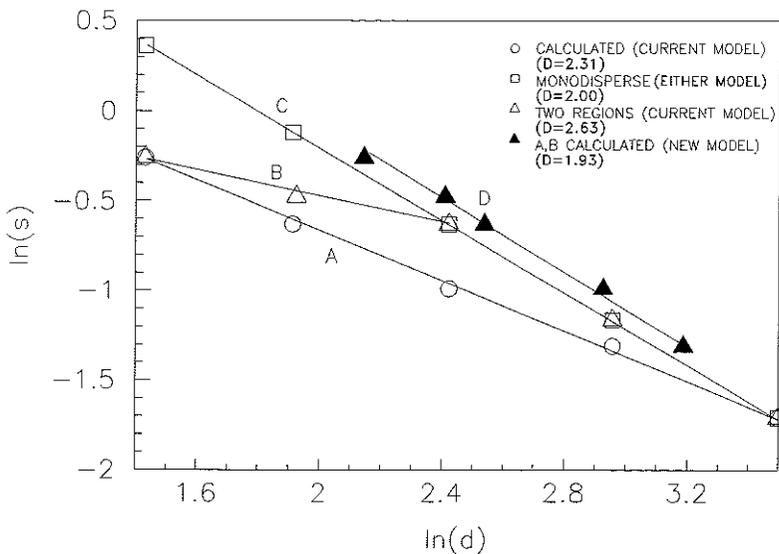


FIG. 2. Plot of  $\ln(s)$  vs  $\ln(d)$  for groups of computer-generated smooth particles with particle size distributions chosen to give fractal dimensions greater than 2. The corrected curve is also shown.  $S$  is calculated by applying Eq. [6] to spherical particles.

from five groups of normally distributed particles having diameters of  $33.1 \pm 0$  (monodisperse),  $19.2 \pm 5.7$ ,  $11.3 \pm 6.0$ ,  $6.77 \pm 4.49$ , and  $4.18 \pm 3.29$ . The three points of curve B are obtained from particle groups having diameters of  $11.3 \pm 0$ ,  $6.86 \pm 3.52$ , and  $4.18 \pm 3.29$ . Curve C represents monodisperse particle groups of diameters 33.1, 19.2, 11.3, 6.77, and 4.18. Three different situations are represented by the curves A, B, and C in this figure. The slope of the linear curve A gives a fractal dimension of  $D = 2.31$  for the smooth spheres. Curve B shows what could happen if the changes in the particle size distributions were not a uniform function of the mean value. The three groups having the largest particles are monodisperse while the two groups of smaller particles are not. This curve could be viewed as having concave downward curvature with questionable fractal dimension, or as a curve representing two zones of different fractal dimension. For this case, the finer powders would show a fractal dimension of about  $D = 2.63$  while the larger particles

(monodisperse) give a fractal dimension of  $D = 2.00$ . Curve C is the result obtained for monodisperse particles; the fractal dimension from this curve is  $D = 2.00$ . Curve D shows the data corrected according to the model just described. This curve has a fractal dimension of 1.93, very close to the correct value (for smooth particles) of 2.0. Also,  $D$  values outside the range allowed ( $D < 2$ ,  $D > 3$ ) are possible with still further changes in the particle size distribution.

Errors will also occur for particles which have a fractal dimension if the size distribution of the particles is not taken into account. Figure 3 is a plot similar to Fig. 2 where the monodisperse particles have a fractal dimension of  $D = 2.50$  (curve A). When the computer-generated particle diameters (six groups having  $d = 2.71 \pm 2.25$ ,  $4.50 \pm 2.81$ ,  $7.42 \pm 3.52$ ,  $12.18 \pm 4.25$ ,  $20.07 \pm 4.60$ , and  $33.12 \pm 0$ ) are used to calculate the total surface area  $S$ , total volume  $V$  (or mass  $m$ ), and the specific surface area  $s = S/m$ , curve B is obtained. This curve, although not exactly linear,

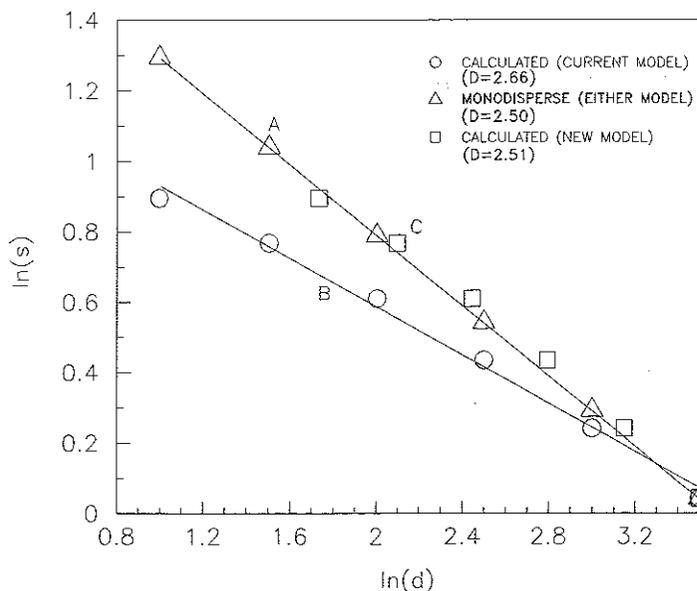


FIG. 3. Plot of  $\ln(s)$  vs  $\ln(d)$  for groups of computer-generated rough particles of fractal dimension  $D = 2.50$  with particle size distributions chosen to give a higher value. The corrected curve is also shown.  $S$  is calculated by applying Eq. [6] to spherical particles.

has a fractal dimension of about 2.66. Applying the correction of Eq. [18] gives curve C, which has a fractal dimension of 2.51, very close to the correct value given by the monodisperse particles.

DISCUSSION

It has been shown that significant errors (up to 30% of maximum range) may occur if the size distribution of the particles in the powder being analyzed is not considered. The fundamental principle responsible for this error is the nonequivalence of  $\sum_{i=1}^n d_i^D$  and  $nd_i^D$  when the  $d_i$ 's are not equal. Under these conditions it is clear that Eq. [6],

$$s = k \frac{\sum_{i=1}^n d_i^D}{\sum_{i=1}^n d_i^3}, \tag{6}$$

is not the same as

$$s = \frac{kn\bar{d}^D}{n\bar{d}^3} = k\bar{d}^{(D-3)}, \tag{9}$$

which is the form normally used. It is easily demonstrated that the simplification made possible by assuming monodisperse particles can result in significant errors.

The model derived in the previous section can be readily used to identify conditions when corrections may be necessary. The correction term given by Eq. [18] approaches zero (no correction necessary) as  $\sigma$  (the standard deviation) approaches zero. Thus, if very narrow sieve ranges are used (approximating monodisperse particles), corrections may not be required. Also, as the mean diameter  $\bar{d}$  increases the correction term decreases. Hence the correction term is most significant at small particle diameters where the separation between adjacent sieves may be large. Thus, as particles get larger and/or more uniform in size, the correction term becomes less significant and may not be needed.

If the numerator and denominator of Eq. [18] are divided by  $\bar{d}^2$ ,  $\beta$  is obtained in terms

of the coefficient of variation (C.V. =  $\sigma/\bar{d}$  or % deviation). Then

$$\beta = \frac{3(\text{C.V.})^2 \ln(3)}{1 + 3(\text{C.V.})^2}. \tag{19}$$

This equation shows the correction factor to be constant for constant coefficient of variation. Under these conditions, the correction factor has no effect on the fractal dimension  $D$ . However, if the range or spread of particle size remains nearly constant as the mean value increases,  $\beta$  will decrease and the fractal dimension determined assuming monodisperse particles will be smaller than the true value.

As discussed above, the particle separation required to obtain the data of Fig. 2 was obtained by sieving. The mean diameter was taken as the midpoint between two adjacent sieve sizes. Several groups of particles were examined with the image analyzer and for every group examined, particles that were larger than the mesh size were found. Many particles smaller than the smaller sieve size were also found. Electron micrographs showed many particles that appeared plate-like mixed in with other more three-dimensional particles. It was theorized that these plate-like particles passed through the sieve along the diagonal. When the mesh size was multiplied by  $\sqrt{2}$ , nearly all of the large particles in a group could be explained. Also, a photograph of a sieve immediately after sieving showed many particles wedged across the diagonals, a strong indication that the theorized behavior was in fact occurring. The appearance of smaller particles than expected is thought to be due to electrostatic forces existing at the time of sieving holding the small particles firmly to the larger pieces. With time, the charge decays, releasing the small particles. No verification of this action was attempted. Both of these actions increase the range and standard deviation significantly and may cause the coefficient of variation to change with mean particle size. Under these conditions, corrections to the raw data may be required.

If the coefficient of variation changes with mean particle size, then the resulting plot of  $\ln(s)$  vs  $\ln(\bar{d})$  may take on one of several shapes, as shown in Fig. 2. The curve may be linear but of the wrong slope to give the correct value of  $D$ . The curve may be nonlinear, curving either toward or away from the  $x$ -axis depending on the way the C.V. changes with mean particle diameter. The data may also appear to show regions of different fractal dimension for the powder, showing either a higher or lower fractal dimension toward the finer particle sizes depending on the specific nonlinear behavior of the C.V. vs  $\bar{d}$  relationship.

With these various possibilities for the slope of the standard  $\ln(s)$  vs  $\ln(\bar{d})$  plots, the potential for reaching the wrong conclusion about the fractal nature of the material is high. Fractal behavior (i.e.,  $D > 2$ ) could be incorrectly found for a collection of smooth particles (Fig. 2). Fractal materials might be found to be nonfractal. Nonlinear behavior might be concluded where corrected data would show linearity (Fig. 2). In all cases, incorrect values of the fractal dimension would be expected.

The new equation [17] derived in the previous section can be directly applied to surface area measurements obtained on sieved particles. This equation requires the measurement of the mean and standard deviation of the parameter used as a measure of the particle size for the particles within each group. With this information Eq. [18] allows the calculation of the correction factor  $\beta$  and the determination of the appropriate independent variable. The plot of  $\ln(s)$  versus this new independent variable produces a linear curve whose slope is  $D - 3$  as before.

#### CONCLUSIONS

The assumption of monodisperse particles may lead to serious errors (up to 30% of the

total range) in the determination of the fractal dimension. The magnitude and appearance of this effect depend on the relationship between the mean and standard deviation of the particle size as the mean value is changed.

Curvature in plots of  $\ln(s)$  vs  $\ln(\bar{d})$  may be due to the dependence of C.V. on  $\bar{d}$  in the particle size distributions. Also, regions of different fractal dimension may in some cases result from nonlinearities in the relationship between the mean and standard deviation.

A simple correction can be applied to account for particle size distributions if the mean and standard deviation of the distributions are known.

The correction may be unnecessary if

- (a) the coefficient of variance is constant for all groups
- (b) the fractal dimension is high (very rough surface)
- (c) particle size range (sigma) is small for every group (nearly monodisperse).

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