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Theoretical Small-Particle Statistics:
A Summary of Techniques for Data Analysis
with Recent Developments in Data Comparison,
Notation, and Mixture Theory

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Theoretical Small-Particle Statistics:
A Summary of Techniques for Data Analysis
with Recent Developments in Data Comparison,
Notation, and Mixture Theory

by

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NOTATION AND DEFINITION

A List of Symbols and Definitions in Approximate Order of Introduction

Powder (Particulate Material):	A collection of particles of solid matter. (A very general definition including a wide range of particle "sizes.")	Weight Factor: ρC_2 = volume shape factor multiplied by particle density.
Particle:	A coherent unit of matter having a defined boundary, and whose "size" and shape depend on inter atomic or intermolecular bonding forces and its process of formation.	a : Surface area of an individual particle.
Aggregate:	A group of two or more particles held together by strong chemical bonds (ASTM Definition).	v : Volume of an individual particle.
Agglomerate:	Large groups of individual particles or aggregates, "weakly bonded."	w : Weight of an individual particle.
Population:	The main or total mass of powder particles whose properties or characteristics are in question.	"Size": A measured particle characteristic that may be a linear dimension, d ; an area, a ; a volume, v ; or a weight, w .
Population Parameters:	Constants that define the population distribution.	$d_1^* < d_{1+1}^*, a_1^* < a_{1+1}^*, v_1^* < v_{1+1}^*, w_1^* < w_{1+1}^*$: The range of sizes in the i^{th} "size" intervals; $i = 1, 2, 3, \dots, I$, where I = total number of intervals.
Sample:	A portion of the population upon which measurements are performed to obtain estimates of the characteristics of the population.	d_i, a_i, v_i, w_i : The "midpoint" values of the respective i^{th} "size" intervals.
Statistics:	The variates (numerical quantities) or functions of the variates obtained from measurements of a sample.	a_i', v_i', w_i' : The total area, volume, or weight, respectively, in the i^{th} "size" interval.
Random Sample:	A sample chosen so that it has the same probability of being selected as any other sample.	n_i : The frequency, i.e., number, of particles occurring in the i^{th} "size" interval.
Representative Sample:	A random sample whose total characteristics very closely approximate the total characteristics of the population.	N : $\sum_1^I n_i = n_1 + n_2 + n_3 \dots n_I$: Total number of particles in I "size" intervals.
d :	A linear particle dimension characteristically measurable for all particles in the population of particles.	$\frac{n_i}{N}$: Relative frequency of occurrence of particles in the i^{th} "size" interval. (Note: $\sum \frac{n_i}{N} = 1$)
k :	An integer = 0, 1, 2, 3, ... determined by a particular defined geometric property of the particle.	$A = \sum_1^I a_i' \approx \sum_1^I n_i C_2 d_i^2$: The total surface area of all particles in I "size" intervals.
C_k :	Shape Factor: a coefficient constant relating the k^{th} power of d to a geometric property of the particle (e.g. for $k = 2$, and spherical particles, $C_2 = \pi$ and $C_2 d^2$ = surface area of the particle).	$\frac{a_i'}{A}$: The relative surface area or surface area fraction of particles in the i^{th} "size" interval.
		$V = \sum_1^I v_i' \approx \sum_1^I n_i C_3 d_i^3$: The total volume of all the particles in I "size" intervals.
		$\frac{v_i'}{V}$: The relative volume or volume fraction of particles in the i^{th} size interval.
		ρ : Particle density, weight/unit volume.
		$W = \sum_1^I w_i' \approx \sum_1^I \rho n_i C_3 d_i^3$: The total weight of all the particles in I "size" intervals.

$\frac{w_i}{W}$: Relative weight or weight fraction of particles in the i th "size" interval.

$\sum_{i=1}^r \frac{C_{k1} n_i d_i^k}{\sum_{i=1}^r C_{k1} n_i d_i^k}$: The general expression for the cumulative fraction less than "size" for a fractile diagram, or cumulative frequency polygon, where r refers to the r th "size" interval through which the partial sum is computed. For example, if $k = 0$, then,

$$\sum_{i=1}^r \frac{n_i}{N}$$

is the partial sum of all values of n_i/N of a relative frequency histogram for $i = 1, 2, 3, \dots, r$, and r may take any value of $i = 1, 2, \dots, I$. The series of partial sums,

$$\frac{n_1}{N}, \frac{n_1 + n_2}{N}, \frac{n_1 + n_2 + n_3}{N}, \dots,$$

$$\sum_{i=1}^I \frac{n_i}{N} = 1,$$

gives the fraction less than "size" for the fractile diagram.

$[C_{k1} n_i d_i^k]$: Notation referring to a measured fraction for Type II data, or a measured property related to "size" for Type I data.

$m'_k = \frac{\sum_{i=1}^I n_i d_i^k}{N}$: The k th moment about the origin of the frequency histogram of d .

$m'_1 = \bar{d} = \frac{\sum_{i=1}^I n_i d_i}{N}$: The first moment about the origin of the frequency histogram of d , the arithmetic mean of d .

$\bar{d}_k = \frac{\sum_{i=1}^I n_i d_i^{(k+1)}}{\sum_{i=1}^I n_i d_i^k}$: An average dimension of sample particles based on a k th moment relationship. (When $k = 0$,

$\bar{d}_0 = \bar{d} = \frac{\sum_{i=1}^I n_i d_i}{N}$, and $\bar{d}$ is the arithmetic mean which is identically equal to m'_1 .)

$m_k = \frac{\sum_{i=1}^I n_i (d_i - \bar{d})^k}{N}$: The k th moment about the mean of the frequency histogram of d .

$m_2 = s^2 = \frac{\sum_{i=1}^I n_i (d_i - \bar{d})^2}{N}$: The second moment about the mean of the sample distribution (frequency histogram) of d , the sample variance of d . For s^2 to be an unbiased estimate of the population variance, the denominator must be $N - 1$.

$s_{dk}^2 = \frac{\sum_{i=1}^I n_i d_i^k (d_i - \bar{d}_k)^2}{\sum_{i=1}^I n_i d_i^k}$: The measure of sample dispersion for the k th moment relationship. s_{dk}^2 will be

called the sample variance of d for the k th moment relationship.

$\bar{C}_k d^k = \frac{\sum_{i=1}^I n_i C_{k1} d_i^k}{N}$: The general expression for an average characteristic property of the particles in a sample. The basic definition of $\bar{d}$, $\bar{a}$, $\bar{v}$, or $\bar{w}$.

$\bar{a} = \frac{\sum_{i=1}^I n_i a_i}{N} \approx \frac{\sum_{i=1}^I n_i C_{21} d_i^2}{N}$: Average individual surface area of particles in the sample.

$\bar{v} = \frac{\sum_{i=1}^I n_i v_i}{N} \approx \frac{\sum_{i=1}^I n_i C_{31} d_i^3}{N}$: Average individual volume of particles in the sample.

$\bar{w} = \frac{\sum_{i=1}^I n_i \rho C_{31} d_i^3}{N} \approx \rho \bar{v}$: Average individual weight of particles in the sample.

$s_{(C_k d^k)}^2 = \frac{\sum_{i=1}^I n_i (C_{k1} d_i^k - \bar{C}_k d^k)^2}{N - 1}$: The basic definition of the variance of a characteristic property of particles in a sample; i.e., the basic definition of s_a^2 , s_v^2 , and s_w^2 .

$s_a^2 = \frac{\sum_{i=1}^I n_i (a_i - \bar{a})^2}{N - 1}$: Sample variance of particle surface areas.

$s_v^2 = \frac{\sum_{i=1}^I n_i (v_i - \bar{v})^2}{N - 1}$: Sample variance of particle volumes.

$s_w^2 = \frac{\sum_{i=1}^I n_i (\rho C_{31} d_i^3 - \bar{w})^2}{N - 1} = \rho^2 s_v^2$: Sample variance of particle weights.

$s_{dk} = \frac{\sum_{i=1}^I n_i d_i^k (d_i - \bar{d}_k)^3}{\sum_{i=1}^I n_i d_i^k}$: The basic definition of sample skewness.

$p(h) = \frac{1}{\sqrt{2\pi} \sigma_h} e^{-\frac{(h - \mu_h)^2}{2\sigma_h^2}}$: The probability density of a normally distributed population of the random variable h , having mean μ_h and variance σ_h^2 .

$$P(h_0 < h < h_1) = \frac{1}{\sqrt{2\pi} \sigma_h} \int_{h_0}^{h_1} e^{-\frac{(h-\mu_h)^2}{2\sigma_h^2}} dh:$$

The probability that h is found in the interval (h_0, h_1) .

$x = \ln d$: The definition of x ; $\ln d$ is the natural logarithm of d .

μ_x : The mean value of a normal distribution of the population of x .

σ_x^2 : The variance of a normal distribution of the population of x .

$z_k = \ln C_k d^k$: The definition of z_k .

μ_{z_k} : The mean value of a normal distribution of the population of z_k .

$\sigma_{z_k}^2$: The variance of a normal distribution of the population of z_k .

$$f_k(x) = \frac{e^{\frac{kx}{\sigma_x}} e^{-\frac{(x-\mu_x)^2}{2\sigma_x^2}}}{\sqrt{2\pi} \sigma_x \exp\left(k\mu_x + \frac{k^2\sigma_x^2}{2}\right)}: \text{The } k^{\text{th}} \text{ moment relationship for the log normal function.}$$

μ_{xk} : The first moment about the origin of $f_k(x)$. This parameter is analogous to μ_x but is not a "mean" in the strict technical sense.

σ_{xk}^2 : The second moment about μ_{xk} . This parameter is identically equal to σ_x^2 ; however, it is not a variance in the strict technical sense.

$\approx$: Approximately equal to.

$\hat{\approx}$: Estimates or is estimated by.

$\hat{\sim}$: Designator of a sample statistic for samples represented by a functional model.

(Example: $\bar{d} \approx \hat{u}_d \hat{\approx} \mu_d$; read as $\bar{d}$ is approximately equal to $\hat{\mu}_d$ which estimates μ_d , the mean of the population of d .)

(j) : Subscript denoting the j^{th} component of a mixture, where $j = 1, 2, \dots, J$. For example, $n_1(j)$ denotes the number of particles in the 1th "size" interval of the j^{th} component.

$N_{(M)}$: Total number of particles in a mixture.

$\beta_{(j)}$: Frequency mixing fraction of the j^{th} mixture component.

$$\beta_{(j)} = \frac{N_{(j)}}{N_{(M)}} = \frac{N_{(j)}}{\sum_{j=1}^J \sum_{i=1}^I n_{i(j)}}$$

$W_{(M)}$: Total weight of particles in a mixture.

$\alpha_{(j)}$: Weight mixing fraction of the j^{th} mixture component,

$$\alpha_{(j)} = \frac{W_{(j)}}{W_{(M)}} = \frac{W_{(j)}}{\sum_{j=1}^J \sum_{i=1}^I w_{i(j)}}$$

(k, I) : Notation referring to k^{th} order Type I data.

(k, II) : Notation referring to k^{th} moment Type II data.

$\beta_{(j)}(\alpha_{(j)}, k, I)$: Notation referring to $\beta_{(j)}$ computed from $\alpha_{(j)}$ and k^{th} order Type I data.

$\frac{n_{i(M)}}{N_{(M)}}(\alpha_{(j)}, k, II)$: Notation referring to relative frequency of particles in the i^{th} "size" interval of a mixture computed from $\alpha_{(j)}$ and k^{th} moment Type II data.

$\beta'_{(1)}$: Binary frequency mixing fraction at maximum value of $\hat{\sigma}_{x(M)}^2$.

$\alpha'_{(1)}$: Binary weight mixing fraction at maximum value of $\hat{\sigma}_{x(M)}^2$.

$\beta_{(1)}\hat{\gamma}_0$: Binary frequency mixing fraction for $\hat{\gamma}_x = 0$.

$\alpha_{(1)}\hat{\gamma}_0$: Binary weight mixing fraction for $\hat{\gamma}_x = 0$.

THEORETICAL SMALL-PARTICLE STATISTICS: A SUMMARY OF TECHNIQUES FOR DATA ANALYSIS
WITH RECENT DEVELOPMENTS IN DATA COMPARISON, NOTATION, AND MIXTURE THEORY

by

H. D. Lewis and A. Goldman*

ABSTRACT

This report presents a rigorous development of methods for "particle size" data analysis based upon the form of the data generated by the various methods available for measurement of "particle size distributions." Data are classified into two general types, and methods for computing and comparing sample statistics are developed on the basis of Type I and II classifications for both the functional and nonfunctional representations of the sample data. An attempt is made to demonstrate the compatibility of recognized statistical notation and definition with the problem of particle "size" data analysis.

A general theory and required notation is developed for description of mixtures of particulate systems, with emphasis on the practical relationship between mixtures proportioned by component weight, frequency or numbers of component particles, and Type I and II data forms. Application of the general theory for mixtures in the study of packing behavior of particulate systems is discussed.

Formulae for computing and comparing sample statistics generated by the various particle "size" measurement methods are summarized in tables for both single-component systems and mixtures.

INTRODUCTION

The quantitative description of the characteristic properties of a particulate material is of interest in many scientific fields, such as powder metallurgy, ceramics, high-explosive research, paint pigment research, and health physics. The health physicist investigating the physiological effect of blood cell "size" distribution or the particle "size" distribution of an ingested dust or aerosol, the ceramist studying the effect of particle "size" on the process characteristics of refractory bodies, and the powder metallurgist attempting to predict process behavior of a metal powder, all seek a definitive description of particulate materials. A

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complete description of a particulate material includes consideration of particle shape and surface characteristics; mechanical, chemical, and physical properties of the individual particles; and a definition of "average particle size." This description, to be quantitative, must involve some type of statistical model. This discussion is based on consideration of metal and ceramic powders, but the statistical results are applicable to many fields, such as blood cell analysis and high-explosive research.

Some of the basic problems of small-particle technology are:

1. Definition of particle "size."
2. Proper use of statistical methods in defining the distribution of "sizes" and in computing sample statistics.

3. Making meaningful comparisons of data and sample statistics obtained using different particle "size" measuring devices.
4. Use of proper statistical techniques to describe data for which no functional description is recognized.
5. Proper use of the log normal function as a model describing sample data.
6. Proper theoretical description of mixtures of powders.

This report summarizes basic theoretical developments in small-particle technology and suggests approaches to the above problems. The main developments are:

1. Classification of all forms of particle "size" data as one of two types.
2. Definition of statistical relationships that permit comparisons of data obtained from the many existing types of "size" measuring devices.
3. A suggested standard notation for use in all fields concerned with small-particle statistics.
4. A practical statistical description of powder mixtures.
5. Theorems utilizing sample statistics to predict weight ratios to give maximum packing density for powder mixtures.

Particle "size," "size distribution," and data comparisons have been discussed by many authors. However, complete statistical descriptions of "size" and "size distribution" with respect to the "particle size" measuring instrument and proper methods of data comparison for both functional and nonfunctional models are not found in the literature. The following historical discussion indicates the inadequacies in the literature and establishes the statistical and technological basis on which this report is written.

Historical Review

Pioneer workers in fields related to small-particle technology sought convenient graphical or functional representations of particle "size" data. Hazen¹ developed the use of probability paper to display particle "size" data. Similar work was published earlier by Henry (1896).² Their work was based on the use of the Gaussian³ function to approximate the sample data. It was recognized by early investigators that, in general, small-particle sample

distributions were skewed. The mathematical consideration by Galton and MacAlister (1879)⁴ of an asymmetrical function was the basis of the so-called log normal function utilized, among others, by Kapteyn and Vanuven (1916)⁵ Wightman et al. (1921-1924),⁶ and Loveland and Trivelli (1927).⁷ Hatch and Choate (1929)⁸ and Hatch (1933)⁹ published two classic papers in which the log normal function and log probability paper were used in presentation and interpretation of particle "size" data relative to two methods of particle "size" measurement, namely, the optical count and screen analysis. These papers were the origin of the Hatch-Choate equations and gave experimental evidence of the functional relation between the sample statistics obtained from screen analysis and optical count.

Several important books were written on small-particle technology and small-particle statistics in the period 1940 to 1963.¹⁰⁻¹⁵ The authors of all the reference works cited in this report have discussed in varied detail the methods of particle "size," surface area, and porosity measurement. In these books the discussions of the statistical and functional models used for particle "size" data analysis are patterned after those of Hatch and Choate. The Hatch-Choate notation is used notably by Dalla Valle¹⁰ and Herdan,¹¹ and with some modification by Cadle,¹³ and Irani and Callis.¹⁵ The work of these authors is invaluable; however, we believe the following inadequacies exist in the literature:

1. A standard notation consistent with accepted statistical definitions and notation and practical small-particle technology has not been adopted.
2. The proper functional or nonfunctional representation of sample data obtained by various measuring devices has not been rigorously discussed.
3. Proper methods of data comparison and estimation of powder properties from sample statistics have not been completely developed.
4. A useful theory for description of powder mixtures has not been developed.

The developments discussed in this report clarify problems in the field of small-particle technology and indicate approaches to their solutions, especially where we believe inadequacies to exist.

TYPES OF PARTICLE "SIZE" DATA

It is virtually impossible to formulate a definition of particle "size" that uniquely determines which of several measurable particle characteristics should be considered as "size." A basic reason for this difficulty is the existence of a wide variety of instruments available for measuring a so-called particle "size" distribution. Table I shows the type of data obtained from four such typical devices. Notice that each device measures the amount of particles observed relative to the "size" of the particles observed and that the definitions of amount of particles and observed "size" depend upon the measuring instrument used.

A discussion of the measurement or interpretation of particle "size" data must be related to the concept of a sample. The concepts of random and representative sampling are extremely complex and have been described frequently.²²⁻²⁴ Particle "size" measurements are, in general, made on samples, and the resulting sample data estimate the properties of the material (powder) from which the sample was taken. The statistical development will utilize these concepts and the definitions of populations, population parameters, sample, statistics, random sample and a representative sample, given on page vi.

It is important to realize that a representative sample can be obtained in practice only by taking a volume sample (e.g., with a flour scoop, microscope, or by dumping the entire population through a sample splitter) from a large batch of material that has been mixed (blended) as thoroughly as possible in an attempt to produce the ideal random distribution of particles in the batch.

It will be assumed that all measurements are made using representative samples. However, it is emphasized that sample data are only estimates of the characteristics of the population.

SHAPE FACTORS

The difficulty in defining "size" has an attendant problem in the meaningful definition of shape factor. Shape factor has been defined in a variety of ways. An excellent discussion of shape factors is summarized by Herdan (Ref. 11, Chap. 11, p. 173), as follows.

1. They are the factors of proportionality between particle 'size' determination results by different methods;
2. They are the conversion factors for expressing determination results in terms of an 'equivalent' sphere;
3. They transform the second and third power of the variable, particle diameter, into the particle surface and particle volume, respectively."

TABLE I

Data Forms Obtained from Typical Measuring Devices

Instrument	Measured "Size"	Basis of Measurement	Measured Relationship	Statistical Tabulation			
Microscope (Ref. 16)	d	Linear dimension, using template, reticule, or filar eyepiece.	n_i vs d	"Size" Interval (d_i^* , d_{i+1}^*) = =	d_i	n_i	$\frac{n_i}{N}$
Sieves (Ref. 17)	d	Maximum particle dimension which will pass through a given mesh opening.	w_i' vs d where w_i' is the weight of particles in the interval (d_i^* , d_{i+1}^*).	"Size" Interval (d_i^* , d_{i+1}^*) = =	d_i	w_i'	$\frac{w_i'}{W}$
Micromerograph (Ref. 18)	d	Stokes Law (d = Stokes equivalent Diameter).	Automatic summation of particle weight vs time proportional to d.	Particle "Size" d = = =	Cumulative Weight = = =		
Coulter Counter (Refs. 19, 20)	v	Conductivity of electrolyte in "standard" orifice is proportional to particle volume.	n_i vs v where v is the "Coulter" volume of a particle.	"Size" Interval (v_i^* , v_{i+1}^*) = =	v_i	n_i	$\frac{n_i}{N}$

A generalized definition of the shape factor, C_k , is believed to embody the three points stressed by Herdan; and, as will be pointed out in the development of the statistical theory, to aid in developing a completely general treatment of particle "size" data. Consider the particle shapes schematically shown in Table II. Notice that particle "size" can be defined as a linear dimension, area, volume, or weight and, for a given shape, that the concepts of size are related by a shape factor. That is, for a characteristically measurable "size" dependent upon the k^{th} power of a linear particle dimension, d , there exists a shape factor, C_k , such that $a = C_2 d^2$ for $k = 2$, $v = C_3 d^3$ for $k = 3$, and $w = \rho C_3 d^3$. The examples that follow illustrate the generality of this definition of shape factor.

Suppose that the Stokes equivalent diameter and a Coulter volume are measured for an irregular particle as shown in column 3 of Table II. A shape factor C_3 is found by dividing the Coulter volume by the cube of the Stokes diameter. The computed C_3 would have a very special meaning; i.e., it relates the Stokes diameter of the particle to the Coulter volume. This illustrates the importance of the investigator's careful definition of what he means by d , a , v , or w when reporting particle "size" data, and places the burden of the definition exactly where it belongs -- on the investigator.¹⁹

Consider an elongated or acicular particle (column 5 of Table II). Suppose that the ratio L/d (sometimes called acicularity ratio) can be determined, where L is the maximum length of the particle and d is the measured linear dimension. The volume shape factor is then $C_3 = L/d$, since $v = (L/d) d^3$. Suppose, for example, that $L/D = 2$, then from Table II, $C_3 = 2$ and $C_2 = 10$; i.e., the area and volume shape factors can be related to an acicularity ratio. Note that L could be defined as d ; then C_3 would be L^2/d^2 , where L is defined in Table II. This again illustrates the need for a careful definition of "size" and shape factor with respect to measurement method. (See Appendices A and B for further discussion of acicularity ratio and shape factor.)

It should be realized that in any powder mass there exist not only a variety or distribution of particle "sizes," but also a distribution of particle shapes and perhaps a distribution of particle densities. The variation of shapes in a given powder obtained from a particular comminution or growth process can usually be considered small enough so that a particular characteristic shape can be ascribed to all particles in the powder. Therefore, the following assumption will be used throughout the remainder of this report.

TABLE II
Relation Between Definitions of "Size" and Shape Factor

"SIZE" DEFINITIONS	PARTICLE SHAPES
	SPHERE	IRREGULAR	REGULAR CUBIC	REGULAR PARALLELEPIPED
$d =$	diam.	max. dimension	edge	edge or length
$v = C_3 d^3 =$	$\frac{\pi}{6} d^3$	$C_3 d^3$	d^3	$\frac{L}{d} d^3$
$a = C_2 d^2 =$	πd^2	$C_2 d^2$	$6 d^2$	$(2 + \frac{4L}{d}) d^2$
$w =$	ρv	ρv	ρv	ρv

Assumption: The particles in any powder are shaped such that a particular shape, no matter how irregular or complicated, can be said to represent the individual shapes of all particles in the powder; i.e., an "average shape" can be defined.

GRAPHICAL TREATMENT OF SAMPLE DATA

Graphical methods for presenting sample particle "size" data are commonly used to give a clearer illustration of the "distribution" of particle "sizes" than that given by simple tabular data. Graphical methods of presenting the typical particle "size" data schematically shown in Table I are summarized in Table III. The following discussion of the schematic data forms presented in Table III includes several important statistical definitions related to particle "size" data analysis. (An excellent detailed discussion of the general statistical concepts may be found in Hald,²¹ Chaps. 3 and 4.) The schematic graph of microscopic count

data shown in solid outline in Table IIIa presents classified or grouped data, which represent the relative frequencies, n_i/N ; $i = 1, 2, \dots, I$, occurring in a particular set of "size" intervals, (d_i^*, d_{i+1}^*) . The fraction n_i/N is the ratio of the number of particles in the i^{th} interval to the total number of particles in a sample. The end points, d_i^* and d_{i+1}^* , of the i^{th} "size" interval are linear dimensions arbitrarily selected by the investigator. The number of size intervals is also arbitrarily selected; however, there are statistical guides to the selection of the number of "size" intervals relative to N so that the graph may best represent the distribution of "sizes" in the sample.²² A graph showing relative frequency of particles occurring in the "size" intervals is called a histogram.

A different type of graphical presentation of microscopic count data can be constructed by connecting the relative frequency values at the

TABLE III

Graphical Methods for Presenting Particle "Size" Data

TYPE of GRAPH	MEASURING INSTRUMENT			
	MICROSCOPE	SIEVES	MICROMEROGRAH	COULTER COUNTER
MEASURED DATA	(a)	(b)	(c)	(d)
TRANSFORMED DATA	(a1)	(b1)	(c1) (c2)	(d1)

midpoints, d_i , of the "size" intervals for the histogram. This presentation is called a relative frequency polygon and is shown by the broken line of Table IIIa; its advantages are discussed later in more detail. Note, however, that the graph resembles some type of continuous function.

Another type of graphical data display is the fractile diagram shown in solid outline in Table IIIa-1. A fractile is the value of the variable "size" for any given cumulative fraction. A fractile diagram is a plot of the successive partial sums, $\sum_1^r [n_i/N]$ for $r = 1, 2, \dots, I$, of the values of n_i/N of the corresponding relative frequency histogram. A cumulative frequency polygon is formed by connecting the successive partial sums, $\sum_1^r [n_i/N]$, at the midpoints of the successive r "size" intervals. This is illustrated by the broken line of Table IIIa-1.

The types of data displays obtained from a sieve analysis, Tables IIIb and IIIb-1, are similar to those for microscopic data. However, the fraction of occurrence plotted as ordinate is a weight fraction w_i'/W rather than n_i/N ; therefore, the solid line plot of Table IIIb should not be called a histogram. It will be called a weight fraction diagram or third moment relationship throughout this discussion. A weight fraction polygon is formed by connecting the values of w_i'/W at d_i , represented by the broken line of Table IIIb. The cumulative form of sieve data shown by Table IIIb-1 is analogous to the fractile diagram of Table IIIa-1. However, this is not a fractile diagram because the cumulative fraction of occurrence is defined by $\sum_1^r [w_i'/W]$. The plot $\sum_1^r [w_i'/W]$ vs d will be called the cumulative weight fraction diagram, or polygon.

Micromerograph data may also be presented as a cumulative weight fraction diagram; however, the raw data are obtained automatically as a continuous cumulative plot, shown schematically in Table IIIc. A set of I values of d , the Stokes equivalent diameter, is picked from the raw-data plot, and the cumulative weight fraction polygon is formed by connecting the set of values of $\sum_1^r \left[\frac{w_i'}{W} \right]$ corresponding to the values of d , as shown in Table IIIc-1. A weight fraction diagram, or polygon, could be constructed as shown in Table IIIc-2. The problem of selecting proper interval width and number of intervals is extremely

complex for changing cumulative data to data in the form of Table IIIc-2. Some rules for determination of interval width and number of intervals are suggested in the section on Graphical Data Comparison.

Coulter counter data as shown in Tables IIId and IIId-1 are analogous to microscopic data except for the definition of particle "size." The solid line plot in Tables IIId and IIId-1, are, respectively, a histogram and fractile diagram in which "size" is the Coulter particle volume. Note that Tables IIIa and IIId are special forms of the general case definition of "size" $C_k d^k$, where in Table IIIa $k = 1$ and in Table IIId $k = 3$.

COMPUTATION OF SAMPLE STATISTICS

Sample Statistics (Computing Formulae)

The utility of sample data is enhanced if a quantitative description of data such as those shown in Table III can be given by a few constants. The natural procedure would be for the investigator to compute the sample statistics which are used to define sample data. The sample data shown in Tables IIIa and IIId are truly sample distribution data in that they estimate the properties of a population distribution. Sample statistics are estimates of the defining population parameters. A population distribution, defined by its moment generating function,²⁵ has parameters which are functions of the moments obtained from the moment generating function. In general, the first three moments about the origin or functions of these moments adequately define a population distribution.

The sample distribution moments are estimates of the population distribution moments. Definitions of sample statistics will be developed by considering data of the form illustrated by Table IIIa. The general k^{th} moment can be defined as

$$m_k' = \frac{\sum_1^I n_i d_i^k}{\sum_1^I n_i}, \quad k = 1, 2, \dots, \quad (1)$$

where the prime indicates a moment about the origin of the sample distribution of d . Note the analogy to mechanical moment if n_i/N is considered as a weighting fraction, and d_i a distance, ($d_i - 0$), then m_k' is an estimate of μ_k' , the k^{th} moment about the origin of the population distribution, written as $\mu_k' \approx m_k'$. (The symbol $\approx$ is read, "is estimated by.")

The first moment about the origin of a sample distribution, m'_1 customarily denoted by m_1 , is called the sample mean or arithmetic mean value of the variable, d . The arithmetic mean of d is called $\bar{d}$:

$$\bar{d} = m_1 = \frac{\sum_1^I n_1 d_1}{\sum_1^I n_1} \quad (2)$$

Average values, in general, do not define a sample distribution; therefore, some measures of dispersion and asymmetry about the mean, i.e., distribution shape, are necessary. The general measure of dispersion and of asymmetry is the k^{th} moment about the mean, defined as

$$m_k = \frac{\sum_1^I n_1 (d_1 - \bar{d})^k}{\sum_1^I n_1} \quad (3)$$

The spread about the mean of d is m_2 , called the variance of d , which is given the symbol s_d^2 .

$$s_d^2 = m_2 = \frac{\sum_1^I n_1 (d_1 - \bar{d})^2}{N} \quad (4)$$

The denominator for s_d^2 should be written $N - 1$ instead of N if the sample variance s_d^2 is to be an unbiased estimator^{24,25} of the variance of the population distribution of d . However, sample size in small-particle statistics is, in general, $N > 10^3$; therefore, the above definition of s_d^2 can be considered proper. The variance can be expressed in terms of moments about the origin by expanding Eq. (4). Then,

$$s_d^2 = m_2' - (m_1')^2 \quad (5)$$

The fundamental measure of asymmetry of a sample distribution is the third moment about the mean, called the skewness,

$$g = m_3 = \frac{\sum_1^I n_1 (d_1 - \bar{d})^3}{N} \quad (6)$$

The population skewness $\mu_3 \approx m_3$. The values of $m_k = 0$ for odd values of k of a symmetrical sample distribution. When m_3 is greater than zero (positive skewness), the sample distribution is asymmetric with the value of d corresponding to the

maximum value of n_1/N to the left of $\bar{d}$, i.e., the distribution tails to higher values of d as shown by Table IIIa. The value of d corresponding to the maximum value of n_1/N is called the mode. When m_3 is less than zero (negative skewness), the distribution mode is displaced to higher values of d and the mode is greater than $\bar{d}$. The skewness can be computed as a function of the first three moments by expanding Eq. (6) to obtain

$$m_3 = m_3' - 3 m_2' m_1' + 2 (m_1')^3 \quad (7)$$

Another sample statistic sometimes considered is the median, defined as the 50th percentile; i.e., the value of d such that 50% of the observations lie above and below that particular value. For example, the median of the schematic diagram in Table III would be the value of d corresponding to

$$\sum_1^r \frac{n_1}{N} = 0.5$$

The mean, median, and mode are identical for a symmetrical distribution about the mean for a unimodal distribution.

A skewed distribution is not uniquely defined by m_1' , m_2' , and m_3' ; however, these three statistics, in general, adequately describe a sample distribution.

The other type of sample distribution is shown in Table IIId. The "size" is dependent upon what is measured by the apparatus, in this case, a measure of particle volume, i.e., Coulter volume. Sample statistics are computed in the same manner as in Eqs. (1) through (7) except that " d " is replaced by " v ," that is, the "size" is now volume. For example, the expression for k^{th} moment about the origin is

$$m_k' = \frac{\sum_1^I n_k v_1^k}{N} \quad (8)$$

and average particle volume is

$$m_1' = \bar{v} = \frac{\sum_1^I n_1 v_1}{N} \approx \frac{\sum_1^I n_1 C d_1^3}{N} \quad (9)$$

The sample variance would be obtained as

$$s_v^2 = \frac{\sum_1^I n_1 (v_1 - \bar{v})^2}{N - 1} \quad (10)$$

and the skewness as

$$g_v = \frac{\sum_1^I n_i (v_i - \bar{v})^3}{N} \quad (11)$$

Sample statistics can be computed by methods similar to Eqs. (1) through (7) for the weight fraction data depicted by Tables IIb and IIc. It is emphasized that the resulting sample statistics are not true sample distribution statistics or estimates of particle "size" distribution parameters.

Sample statistics for the weight fraction data are defined and computed as follows:

$$\text{The sample mean} = \bar{d}_3 = \frac{\sum_1^I w_i' d_i}{W} \quad (12)$$

$$\text{The sample variance} = s_{d_3}^2 = \frac{\sum_1^I w_i' (d_i - \bar{d}_3)^2}{W} - \left(\frac{\sum_1^I w_i' d_i^2}{W} - (\bar{d}_3)^2 \right) \quad (13)$$

$$\text{The sample skewness} = g_{d_3} = \frac{\sum_1^I w_i' (d_i - \bar{d}_3)^3}{W} \quad (14)$$

$$= \sum_1^I \frac{w_i'}{W} d_i^3 - 3\bar{d}_3 \sum_1^I \frac{w_i'}{W} d_i^2 + 2\bar{d}_3^3.$$

These expressions can be computed in terms of n_i and d_i alone. This gives a method of computing statistics for moment relationships from sample distribution data. This type of data conversion, illustrated below, should be used with caution for reasons discussed in the section on Data Comparison: Nonfunctional Model. The weight of material in an interval can be defined as

$$w_i' = \rho C_3 n_i d_i^3 \quad (15)$$

where d_i is the interval midpoint. The value of w_i' could be computed using many definitions of d_i . The validity of the computed w_i' depends upon how well the value picked for d_i represents the distribution of d in (d_i^*, d_{i+1}^*) . Using Eq. (15), then Eqs. (12), (13), and (14) can be written in terms of d . For example, the mean can be written as

$$\bar{d}_3 = \frac{\sum_1^I n_i d_i^3 d_i}{\sum_1^I n_i d_i^3} = \frac{m_4'}{m_3'} \quad (16)$$

illustrating the reason for denoting the mean of the third moment relationship as $\bar{d}_3$.

The statistic $\bar{d}_3$ does not estimate a distribution mean; it estimates the mean of sample data obtained with a device which measures the weight-fraction or third moment relationship illustrated by Tables IIb and IIc.

The sample variance defined in Eq. (13) could be computed as

$$s_{d_3}^2 = \frac{\sum_1^I n_i d_i^3 (d_i - \bar{d}_3)^2}{\sum_1^I n_i d_i^3} = \frac{m_5'}{m_3'} - \left(\frac{m_4'}{m_3'} \right)^2 \quad (17)$$

and skewness could be computed as

$$g_{d_3} = \frac{\sum_1^I n_i d_i^3 (d_i - \bar{d}_3)^3}{\sum_1^I n_i d_i^3} = \frac{m_6'}{m_3'} - 3 \frac{m_4' m_5'}{(m_3')^2} + \frac{2(m_4')^3}{(m_3')^3} \quad (18)$$

The computation of sample statistics, as defined in Eqs. (12) through (18), for data obtained with a device such as the Micromerograph is complicated by the fact that sample data are obtained in continuous cumulative form such as shown in Table IIc. The expressions above apply directly to data obtained in discrete form; i.e., some defined fraction of material in a given "size" interval. Micromerograph or similar continuous data can be treated by first constructing the cumulative weight fraction diagram as shown in Table IIc-1, and then, as shown in Table IIc-2, by difference technique, the weight fraction polygon is constructed. The Micromerograph manual¹⁸ describes the method used to construct the cumulative weight fraction diagram; however, the selection of interval widths for construction of the weight fraction polygon is arbitrary. Some guides to interval width selection are discussed in the section on Graphical Data Comparison.

Sample Statistics Computed from Log Normal Data

The proper use of various forms of the log normal function in describing sample data has been discussed in Ref. 26 on the basis of appropriate forms of the distribution function. The main points of this reference as related to the measuring devices and types of data shown in Table III are summarized in this section. The validity of a log normal function in representing sample data is determined if the data plotted on log probability paper can be adequately represented by a straight line (see Ref. 21, Chap. 7). Techniques for fitting the log normal functions to the sample data have been discussed in detail by Kottler.²⁷ The usefulness of the log normal function in representing small-particle data has been demonstrated by many investigators. Its practical value stems from the fact that this function is completely defined by two parameters. This implies that a sample represented by a log normal function can be completely described by these two parameters or by functions of these parameters.

Assume, for example, that typical microscopic count data schematically shown in Tables IIIa and IIIa-1 may be represented by a log normal function. A so-called log probability plot of this data is illustrated by Fig. 1. This is another way of

Fig. 1. Schematic log probability plot of sample data.

drawing the cumulative frequency polygon of Table IIIa-1. The straight line fitted to the data represents the cumulative frequency polygon, then points on the line, $P(x)$ values, are approximations for values $\sum_{i=1}^r \frac{n_i}{N}$. Thus, cumulative partial sums may be written as

$$\sum_{i=1}^r \frac{n_i}{N} \approx P(x) = \int_{-\infty}^x p(x) dx = \frac{1}{\sqrt{2\pi} \sigma_x} \int_{-\infty}^x \exp\left[-\frac{(x-\mu_x)^2}{2\sigma_x^2}\right] dx, \quad (19)$$

where $x = \ln d$, and μ_x and σ_x^2 are the defining parameters of the normal function, $p(x)$. The above expression illustrates several important concepts.

1. The values of $\sum_{i=1}^r \frac{n_i}{N}$ are estimators of the values of $P(x)$.
2. The values of $P(x)$ are never actually known or determined; however, the values of $\int_{-\infty}^x p(x) dx$ are approximated by experimental determination of estimates of μ and σ_x^2 , the parameters of $p(x)$.
3. The sample statistics $\hat{\mu}_x$ and $\hat{\sigma}_x^2$ are the experimentally determined estimators of the parameters of $p(x)$; i.e., $\hat{\mu}_x \approx \mu_x$ and $\hat{\sigma}_x^2 \approx \sigma_x^2$.
4. The sample statistics are then used to approximate the values $\sum_{i=1}^r \frac{n_i}{N}$; i.e.,

$$\sum_{i=1}^r \frac{n_i}{N} \approx \frac{1}{\sqrt{2\pi} \hat{\sigma}_x} \int_{-\infty}^{\hat{\mu}_x} \exp\left[-\frac{(x-\hat{\mu}_x)^2}{2\hat{\sigma}_x^2}\right] dx. \quad (20)$$

5. The sample statistics $\hat{\mu}_x$ and $\hat{\sigma}_x^2$ are the mean and variance of the sample distribution which can be represented by the normal distribution of x or the log normal distribution of d , since $x = \ln d$.

The mean, $\hat{\mu}_x$ = median, is defined as the fractile such that the value

$$\sum_{i=1}^r \frac{n_i}{N} \approx \int_{-\infty}^{\hat{\mu}_x} p(x) dx = 0.5. \quad (21)$$

This means that the value for $\hat{\mu}_x$ may be obtained from a straight-line fit as shown in Fig. 1 by picking the fractile value $\hat{\mu}_x = x$ at $P(x) = 0.5$. The variance $\hat{\sigma}_x^2$ is computed as the square of the standard

deviation $\hat{\sigma}_x$. The value of $\hat{\sigma}_x$ is defined as the fractile value such that

$$\sum_{i=1}^r \frac{n_i}{N} \approx \int_{-\infty}^{\hat{\mu}_x + \hat{\sigma}_x} p(x) dx = 0.8413 \quad (22)$$

or, as the difference between two fractile values such that

$$\sum_{i=1}^{r_2} \frac{n_i}{N} = \sum_{i=1}^{r_2} \frac{n_i}{N} - \sum_{i=1}^{r_1} \frac{n_i}{N} \approx \frac{1}{\sqrt{2\pi} \hat{\sigma}_x} \times \int_{\hat{\mu}_x}^{\hat{\mu}_x + \hat{\sigma}_x} \exp \left[\frac{-(x - \hat{\mu}_x)^2}{2\hat{\sigma}_x^2} \right] dx = 0.3413. \quad (23)$$

Thus, values of Eqs. (21), (22), or (23) may be checked by performing the integration of the exponential expanded as a power series about $\hat{\mu}_x$, or more simply by examining tables of the normal functions such as may be found in Ref. 28. The value of $\hat{\sigma}_x$ may be determined by using Eq. (23) and Fig. 1. The numerical value is then the difference between the values of $x = \ln d$ at the values $P(x) = 0.8413$ and the mean.

It is emphasized that the numerical values obtained from the integration of Eqs. (22) and (23) are properties of the function $p(x)$. The use of the values 0.8413 or 0.3413 to estimate experimentally the value of the variance of a function of form other than $p(x)$ is not valid. That is, integration of a function $h(x)$, not of the form $p(x)$, over the interval $(\mu_x, \mu_x + \sigma_x)$ would yield a value $\neq 0.3413$. It can be shown that the slope of the straight-line data fit is equal to $1/\hat{\sigma}_x$. It is shown that

$$\mu_x = \int_{-\infty}^{\infty} xp(x) dx, \quad (24)$$

and

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \mu_x)^2 p(x) dx, \quad (25)$$

where

$$p(x) = \frac{1}{\sqrt{2\pi} \sigma_x} \exp \left[\frac{-(x - \mu_x)^2}{2\sigma_x^2} \right]$$

in Ref. 21, pp. 120-21. The use of the integral of the log normal function to approximate the sample values of the cumulative frequency polygon is based upon the use of a functional representation as approximation for the experimental values of n_i/N

of Table IIIa. Figure 2 illustrates the functional representation. The integration of the normal distribution function $p(x)$, i.e., the log normal distribution function of d , over the interval (x_1^*, x_{1+1}^*) gives a fraction which approximates the relative frequency value experimentally measured in the same interval. This is shown by the shaded areas of Fig. 2 and may be expressed,

$$\frac{n_1}{N} \approx \int_{x_1^*}^{x_{1+1}^*} p(x) dx \approx \frac{1}{\sqrt{2\pi} \hat{\sigma}_x} \int_{x_1^*}^{x_{1+1}^*} \exp \left[\frac{-(x - \hat{\mu}_x)^2}{2\hat{\sigma}_x^2} \right] dx. \quad (26)$$

The functional approximation for the experimental fraction w_1'/W in a given size interval as illustrated in Tables IIb and IIc-2 can be written as

$$\frac{w_1'}{W} = \frac{\rho C_3 n_1 d_1^3}{W} = \frac{N \rho C_3 \frac{n_1}{N} d_1^3}{N \rho C_3 \sum_{i=1}^I \frac{n_i}{N} d_i^3}. \quad (27)$$

Then, using (26),

$$\frac{w_1'}{W} \approx \frac{N \rho C_3 \int_{x_1^*}^{x_{1+1}^*} e^{3x} p(x) dx}{N \rho C_3 \int_{-\infty}^{\infty} e^{3x} p(x) dx}. \quad (28)$$

By completing the square in the integrands and collecting constant terms,

$$\begin{aligned} \frac{w_1'}{W} &\approx \frac{\frac{N}{\sqrt{2\pi} \hat{\sigma}_x} \int_{x_1^*}^{x_{1+1}^*} e^{3x} \exp \left[\frac{-(x - \hat{\mu}_x)^2}{2\hat{\sigma}_x^2} \right] dx}{N \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right]} \\ &= \frac{1}{\sqrt{2\pi} \hat{\sigma}_x} \int_{x_1^*}^{x_{1+1}^*} \exp \left\{ \frac{- \left[x - (\hat{\mu}_x + 3 \hat{\sigma}_x^2) \right]^2}{2\hat{\sigma}_x^2} \right\} dx. \end{aligned} \quad (29)$$

(A proof for the general case appears in Appendix II of Ref. 26.) This expression illustrates the following concepts to be utilized throughout this discussion.

1. The third moment about the origin of the distribution of d is $\int_{-\infty}^{\infty} d^3 p(x) dx$; therefore, the third moment of the sample distribution may be approximated by

$$\frac{n_i}{N} \approx \int_{x_i^*}^{x_{i+1}^*} p(x) dx$$

Fig. 2. Functional approximation of n_i/N .

$$m_3' \approx \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right]. \quad (30)$$

2. Analogous to

$$\frac{n_i}{N} \approx \int_{x_i^*}^{x_{i+1}^*} p(x) dx,$$

a function can be defined such that

$$\frac{w_i}{W} \approx \int_{x_i^*}^{x_{i+1}^*} f_3(x) dx, \quad (31)$$

where

$$f_3(x) = \frac{d^3 p(x)}{\exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right]} = \frac{1}{\sqrt{2\pi} \sigma_x} \times \exp \left\{ - \frac{\left[x - (\hat{\mu}_x + 3\hat{\sigma}_x^2) \right]^2}{2\hat{\sigma}_x^2} \right\} \quad (32)$$

It should be noted that $f_3(x)$ is not a distribution function, but a third moment relationship that is used in a manner analogous to $p(x)$.

3. The defining parameters of the third moment relationship $f_3(x)$ are defined as μ_{x3} and σ_{x3}^2 , analogous to the parameters μ_x and σ_x^2 , which define $p(x)$. Equation (29) illustrates the following relationships among these parameters, and the fact that $f_3(x)$ is a normal function (log normal function of d) if $p(x)$ is normal

$$\mu_{x3} = \mu_x + 3\sigma_x^2, \quad (33)$$

$$\sigma_{x3}^2 = \sigma_x^2. \quad (34)$$

4. The total weight of particles and total number of particles in a distribution can be related as

$$W \approx NpC_3 \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right] = NpC_3 m_3' \quad (35)$$

with proper attention to units.

5. A general expression for the k^{th} moment about the origin of the distribution of d is

$$\int_{-\infty}^{\infty} d^k p(x) dx. \quad (36)$$

Then the k^{th} moment of the sample distribution of d may be approximated as

$$m_k' \approx \exp \left[k\hat{\mu}_x + \frac{k^2}{2} \hat{\sigma}_x^2 \right]. \quad (37)$$

6. A k^{th} moment relationship may be defined as

$$T_k(x) = \frac{d^k p(x) dx}{\exp \left[k\hat{\mu}_x + \frac{k^2}{2} \hat{\sigma}_x^2 \right]} = \frac{1}{\sqrt{2\pi} \sigma_x} \times \exp \left\{ -\frac{\left[x - (\hat{\mu}_x + k\hat{\sigma}_x^2) \right]^2}{2\hat{\sigma}_x^2} \right\} \quad (38)$$

having the following defining parameters related to those of $p(x)$:

$$\mu_{xk} = \hat{\mu}_x + k\hat{\sigma}_x^2, \quad (39)$$

$$\sigma_{xk}^2 = \hat{\sigma}_x^2. \quad (40)$$

7. The sample statistics $\hat{\mu}_{x3}$ and $\hat{\sigma}_{x3}^2$ may be estimated from a straight line fitted to a log-probability plot of the values $\frac{r}{S} \frac{w_1'}{W}$ by the method discussed for obtaining $\hat{\mu}_x$ and $\hat{\sigma}_x^2$. The values of the partial sums for weight fraction data may be approximated by

$$\frac{r}{S} \frac{w_1'}{W} \approx \int_{-\infty}^x f_3(x) dx = F_3(x). \quad (41)$$

It is emphasized that $\hat{\sigma}_x^2 \neq \hat{\sigma}_{x3}^2$ because these are sample statistics. However, because of the identity given in Eq. (40), the approximation $\hat{\sigma}_{x3}^2 \approx \hat{\sigma}_x^2$ will be used. Therefore, in general, for higher moment relationships, sample variance will be written $\hat{\sigma}_x^2$.

Sample statistics for log normal sample data obtained from Coulter C under measurements may be computed in the manner discussed for log normal

data obtained using the microscope. However, in this case the sample histogram would be represented by a log normal distribution of particle volumes rather than linear particle dimension. The approximation for relative frequency in a $\ln$ volume "size" interval would be written

$$\frac{n_1}{N} \approx \int_{z_{3,1}^*}^{z_{3,i+1}^*} p(z_3) dz_3 \approx \frac{1}{\sqrt{2\pi} \hat{\sigma}_{z_3}} \times \int_{z_{3,1}^*}^{z_{3,i+1}^*} \exp \left[-\frac{(z_3 - \hat{\mu}_{z_3})^2}{2\hat{\sigma}_{z_3}^2} \right] dz_3, \quad (42)$$

where $z_3 = \ln v$. Since v is the particle volume, there exists a C_3 such that $v = C_3 d^3$ no matter how v and d are measured. Therefore, $z_3 = \ln C_3 + 3 \ln d = \ln C_3 + 3x$, and it can be easily shown (Appendix I of Ref. 26) that

$$\frac{n_1}{N} \approx \frac{1}{\sqrt{2\pi} \hat{\sigma}_{z_3}} \int_{z_{3,1}^*}^{z_{3,i+1}^*} \exp \left\{ -\frac{\left[z_3 - (\ln C_3 + 3\hat{\mu}_x) \right]^2}{2(9\hat{\sigma}_x^2)} \right\} dz_3. \quad (43)$$

Expressions (41), (42), and (43) illustrate several concepts.

1. The sample values of n_1/N are approximated by

$$\frac{n_1}{N} \approx \int_{z_{3,1}^*}^{z_{3,i+1}^*} p(z_3) dz_3,$$

where $p(z_3)$ is a log normal function of v , a normal function of $\ln(C_3 d^3) = z_3$, and

$$p(z_3) = \frac{1}{\sqrt{2\pi} \sigma_{z_3}} \exp \left[-\frac{(z_3 - \mu_{z_3})^2}{2\sigma_{z_3}^2} \right]. \quad (44)$$

2. The defining parameters of $p(z_3)$ are the mean μ_{z_3} and the variance $\sigma_{z_3}^2$, which are related to μ_x and σ_x^2 as follows.

$$\mu_{z_3} = \ln C_3 + 3\mu_x, \quad (45)$$

$$\sigma_{z_3}^2 = 9\sigma_x^2. \quad (46)$$

3. $p(z_3)$ is normal in $\ln v$ and log normal in v if $p(x)$ is normal, i.e. log normal in d .

4. A general expression can be written for a normal distribution $\ln(C_k d^k)$ as

$$p(z_k) = \frac{1}{\sqrt{2\pi} \sigma_{z_k}} \exp \left[-\frac{(z_k - \mu_{z_k})^2}{2\sigma_{z_k}^2} \right] \quad (47)$$

$$= \frac{1}{\sqrt{2\pi} k \sigma_x} \exp \left[-\frac{[z_k - (\ln C_k + k \mu_x)]^2}{2k^2 \sigma_x^2} \right]$$

This illustrates the following general relationships among parameters defining the distribution functions $p(x)$ and $p(z_k)$:

$$\mu_{z_k} = \ln C_k + k \mu_x, \quad (48)$$

and

$$\sigma_{z_k}^2 = k^2 \sigma_x^2. \quad (49)$$

The statistics and distribution parameters previously discussed completely define the distribution of "sizes" in a sample. However, it is often of interest to compute the sample statistics for the untransformed "size" variable; i.e., d instead of x , or v instead of z_3 . Recall that $p(x)$, $f_k(x)$, and $p(z_k)$ are used in the functional model to represent the fraction of material in a given related particle "size" interval. Using the basic definitions of moments, Eqs. (1) through (18) may be developed as follows:

A. For the sample distribution of d

$$m'_k \approx \int_{-\infty}^{\infty} d^k p(x) dx \approx \exp \left[k \hat{\mu}_x + \frac{k^2}{2} \hat{\sigma}_x^2 \right], \quad (50)$$

$$\bar{d} \approx \mu_d = \int_{-\infty}^{\infty} d p(x) dx \approx \exp \left[\hat{\mu}_x + 0.5 \hat{\sigma}_x^2 \right], \quad (51)$$

$$m_k \approx \int_{-\infty}^{\infty} (d - \mu_d)^k p(x) dx, \quad (52)$$

$$s_d^2 = m_2 \approx \int_{-\infty}^{\infty} (d - \mu_d)^2 p(x) dx \approx \exp \left[2\hat{\mu}_x + 2\hat{\sigma}_x^2 \right] - (\bar{d})^2 \quad (53)$$

$$g_d = m_3 \approx \int_{-\infty}^{\infty} (d - \mu_d)^3 p(x) dx \approx \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right] - 3 \exp \left[3\hat{\mu}_x + 2.5 \hat{\sigma}_x^2 \right] + 2(\bar{d})^3. \quad (54)$$

Note that the estimate of d is not $e^{\hat{\mu}_x}$ and the estimate of s_d^2 is not $e^{\hat{\sigma}_x^2}$. The value of $e^{\hat{\mu}_x}$ is an estimate of the median of the sample distribution of d and the geometric mean $\left[\prod_{i=1}^N d_i \right]^{1/N}$. The consideration of definitions $x = \ln d$, s_d^2 , and σ_x^2 , and the discussion of Eqs. (22) and (23) should indicate the lack of meaning of the term "geometric standard deviation" so frequently found in the literature. Geometric standard deviation has been defined by many authors as the antilog of σ_x^2 . This does not define any parameter of the distribution of d or x .

B. For the sample distribution of v :

$$\bar{v} \approx \mu_v = \int_{-\infty}^{\infty} v p(z_3) dz_3 = C_3 \int_{-\infty}^{\infty} d^3 p(x) dx \quad (55)$$

$$\approx \exp \left[\hat{\mu}_{z_3} + 0.5 \hat{\sigma}_{z_3}^2 \right] \approx C_3 \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right],$$

$$s_v^2 \approx \mu_{2v} = \int_{-\infty}^{\infty} (v - \mu_v)^2 p(z_3) dz_3 \quad (56)$$

$$\approx \exp \left[2\hat{\mu}_{z_3} + 2\hat{\sigma}_{z_3}^2 \right] - (\bar{v})^2,$$

$$g_v \approx \mu_{3v} = \int_{-\infty}^{\infty} (v - \mu_v)^3 p(z_3) dz_3 \approx \exp \left[3\hat{\mu}_{z_3} + 4.5 \hat{\sigma}_{z_3}^2 \right] - 3 \exp \left[3\hat{\mu}_{z_3} + 2.5 \hat{\sigma}_{z_3}^2 \right] + 2\bar{v}^3. \quad (57)$$

C. For the sample weight fraction relationship, w'/W vs d ,

$$\bar{d}_3 = \frac{m'_4}{m'_3} \approx \mu_{d_3} = \int_{-\infty}^{\infty} d f_3(x) dx \approx \exp \left[\hat{\mu}_x + 3.5 \hat{\sigma}_x^2 \right] \quad (58)$$

$$\approx \exp \left[\hat{\mu}_{x_3} + 0.5 \hat{\sigma}_x^2 \right]$$

$$s_{d_3}^2 \approx \mu_{2d_3} = \int_{-\infty}^{\infty} d^2 f_3(x) dx - (\mu_{d_3})^2$$

$$\approx \exp \left[2\hat{\mu}_{x_3} + 2\hat{\sigma}_x^2 \right] - (\bar{d}_3)^2 \quad (59)$$

$$\approx \exp \left[2\hat{\mu}_x + 8\hat{\sigma}_x^2 \right] - \exp \left[2\hat{\mu}_x + 7\hat{\sigma}_x^2 \right].$$

Equation (59) can be obtained by substituting proper forms in the moment expression of Eq. (17).

$$\begin{aligned}
g_{d_3} &\approx \mu_{3d_3} = \int_{-\infty}^{\infty} (d - \mu_{d_3})^3 f_3(x) dx \\
&\approx \exp \left[3\hat{\mu}_{x3} + 4.5 \hat{\sigma}_x^2 \right] - 3 \exp \left[3\hat{\mu}_{x3} + 2.5 \hat{\sigma}_x^2 \right] \\
&+ 2 \exp \left[3\hat{\mu}_{x3} + 1.5 \hat{\sigma}_x^2 \right] - \exp \left[3\hat{\mu}_{x3} + 0.5 \hat{\sigma}_x^2 \right] \\
&- 3 \exp \left[3\hat{\mu}_x + 11.5 \hat{\sigma}_x^2 \right] + 2 \exp \left[3\hat{\mu}_x + 10.5 \hat{\sigma}_x^2 \right].
\end{aligned} \quad (60)$$

Equation (60) can be obtained by substituting proper exponential forms in the moment expressions of Eq. (18).

Summary: Definition of Type I and Type II Data

This section has demonstrated the methods of computing the statistics which describe the sample data obtained from typical particle "size" measuring devices. The above discussion can be summarized by classifying all particle "size" data, no matter how measured, into the two general types illustrated by Figs. 3 and 4. The type schematically shown in Fig. 3 is the frequency distribution of some property of the particle expressed as some power of d . The consideration of two general particle "size" data types will simplify a following discussion on data comparison. The type schematically shown in Fig. 4 is simply the moment relationship which includes weight fraction, w_i'/W , volume fraction, v_i'/V , and area fraction, a_i'/A , versus a linear particle

$$\frac{1}{N} \sum \frac{n_i}{N} \approx P(z_k)$$

LOG NORMAL MODEL (PROBABILITY PLOT)

Fig. 3. Graphical representation of sample distributions: Type I data.

dimension, d . The general case expressions for sample mean, sample variance, and sample skewness are:

Case I. General Distribution of the k^{th} Power of d where $D_k = C_k d^k$: Type I Data.

A. Nonfunctional Model

$$\bar{D}_k = \frac{\sum_{i=1}^I n_i C_k d_i^k}{N}, \quad (61)$$

$$s_{D_k}^2 = \frac{\sum_{i=1}^I n_i (C_k d_i^k - \bar{D}_k)^2}{N}, \quad (62)$$

$$g_{D_k} = \frac{\sum_{i=1}^I n_i (C_k d_i^k - \bar{D}_k)^3}{N - 1}. \quad (63)$$

Note:

$$\text{for } k = 1 \quad \bar{D}_k = \bar{d}, \quad s_{D_k}^2 = s_d^2, \quad \text{and } g_{D_k} = g_d.$$

$$\text{for } k = 3 \quad \bar{D}_k = \bar{v}, \quad s_{D_k}^2 = s_v^2, \quad \text{and } g_{D_k} = g_v.$$

B. Log Normal Model

$$\bar{D}_k \approx \mu_{D_k} = \int_{-\infty}^{\infty} C_k d^k p(z_k) dz_k \quad (64)$$

$$\approx \exp \left[\hat{\mu}_{z_k} + 0.5 \hat{\sigma}_{z_k}^2 \right] \approx C_k \exp \left[k \hat{\mu}_x + \frac{k^2}{2} \hat{\sigma}_x^2 \right].$$

NO FUNCTIONAL MODEL

$$\sum_1 \frac{C_k n_i d_i^k}{\sum_1 C_k n_i d_i} \approx F_k(x)$$

LOG NORMAL MODEL (PROBABILITY PLOT)

Fig. 4. Data described by moment relationships: Type II data.

$$s_{D_k}^2 \approx \sigma_{D_k}^2 = \int_{-\infty}^{\infty} (C_k d^k - \mu_{D_k})^2 p(z_k) dz_k = \int_{-\infty}^{\infty} \exp \left[2\hat{\mu}_{z_k} + 2\hat{\sigma}_{z_k}^2 \right] - \exp \left[2\hat{\mu}_{z_k} + \hat{\sigma}_{z_k}^2 \right] \quad (65)$$

$$\approx C_k^2 \left[\exp \left(2k\hat{\mu}_x + 2k^2\hat{\sigma}_x^2 \right) - \exp \left(2k\hat{\mu}_x + k^2\hat{\sigma}_x^2 \right) \right]$$

$$g_{D_k} = m_{D_k} \approx \mu_{D_k} = \int_{-\infty}^{\infty} (C_k d^k - \mu_{D_k})^3 p(z_k) dz_k \approx \exp \left[3\hat{\mu}_{z_k} + 4.5\hat{\sigma}_{z_k}^2 \right] - 3 \exp \left[3\hat{\mu}_{z_k} + 2.5\hat{\sigma}_{z_k}^2 \right] + 2 \exp \left[3\hat{\mu}_{z_k} + 1.5\hat{\sigma}_{z_k}^2 \right] \quad (66)$$

$$\approx C_k^3 \left[\exp \left(3k\hat{\mu}_x + 4.5k^2\hat{\sigma}_x^2 \right) - 3 \exp \left(3k\hat{\mu}_x + 2.5k^2\hat{\sigma}_x^2 \right) + 2 \exp \left(3k\hat{\mu}_x + 1.5k^2\hat{\sigma}_x^2 \right) \right]$$

Case II. Moment Relationships: Type II Data

A. Nonfunctional Model

$$\bar{d}_k = \frac{\sum_1 \left[C_k n_i d_i^k \right] d_i}{\sum_1 \left[C_k n_i d_i^k \right]} \approx \frac{m'_{k+1}}{m'_k} \quad (67)$$

$$s_{d_k}^2 = \frac{\sum_1 \left[C_k n_i d_i^k \right] (d_i - \bar{d}_k)^2}{\sum_1 \left[C_k n_i d_i^k \right]} \approx \frac{m'_{k+2}}{m'_k} - \left(\frac{m'_{k+1}}{m'_k} \right)^2 \quad (68)$$

$$g_{d_k} = \frac{\sum_1 \left[C_k n_i d_i^k \right] (d_i - \bar{d}_k)^3}{\sum_1 \left[C_k n_i d_i^k \right]} \approx \frac{m'_{k+3}}{m'_k} - \frac{3(m'_{k+2})(m'_{k+1})}{(m'_k)^2} + \frac{2(m'_{k+1})^3}{(m'_k)^3} \quad (69)$$

where $m'_0 = 1$ and, $\left[C_k n_i d_i^k \right]$ is a measured property, e.g., for $k = 2$, $\left[C_2 n_i d_i^2 \right] \equiv a'_1$. The approximation signs are necessary, because $C_k n_i d_i^k$ is an approximation for the measured quantity $\left[C_k n_i d_i^k \right]$. For example, an approximation for a'_1 can be obtained from an observed sample distribution of d as $C_2 n_i d_i^2 \approx a'_1 \equiv \left[C_2 n_i d_i^2 \right]$. The validity of the approximation depends upon the selection of d_1 , N and I . This point will be discussed in the next section.

B. Log Normal Model

$$\bar{d}_k \approx \mu_{d_k} \int_{-\infty}^{\infty} d f_k(x) dx \approx \exp \left[\hat{\mu}_{xk} + 0.5 \hat{\sigma}_x^2 \right] \approx \exp \left[\hat{\mu}_x + \frac{2k+1}{2} \hat{\sigma}_x^2 \right] \quad (70)$$

$$s_{d_k}^2 \approx \sigma_{d_k}^2 = \int_{-\infty}^{\infty} d^2 f_k(x) dx - (\mu_{d_k})^2 \approx \exp \left[2\hat{\mu}_{xk} + 2\hat{\sigma}_x^2 \right] - \exp \left[2\hat{\mu}_{xk} + \hat{\sigma}_x^2 \right] \approx \exp \left[2\hat{\mu}_x + 2(k+1) \hat{\sigma}_x^2 \right] - \exp \left[2\hat{\mu}_x + (2k+1) \hat{\sigma}_x^2 \right]. \quad (71)$$

$$g_{d_k} = m_{d_k} \approx \mu_{d_k} = \int_{-\infty}^{\infty} (d - \mu_{d_k})^3 f_k(x) dx \approx \exp \left[3\hat{\mu}_{xk} + 4.5 \hat{\sigma}_x^2 \right] - 3 \exp \left[3\hat{\mu}_{xk} + 2.5 \hat{\sigma}_x^2 \right] + 2 \exp \left[3\hat{\mu}_{xk} + 1.5 \hat{\sigma}_x^2 \right] \approx \exp \left[3\hat{\mu}_x + (3k+4.5) \hat{\sigma}_x^2 \right] - 3 \exp \left[3\hat{\mu}_x + (3k+2.5) \hat{\sigma}_x^2 \right] + 2 \exp \left[3\hat{\mu}_x + (3k+1.5) \hat{\sigma}_x^2 \right]. \quad (72)$$

Note: for $k = 0$, $\bar{d}_k = \bar{d}$, $s_{d_k}^2 = s_d^2$, and $g_{d_k} = g_d$.

COMPARISON OF SAMPLE DATA AND SAMPLE STATISTICS

A quantitative comparison of properties or process behavior of powders necessitates a quantitative comparison of the sample statistics or of the graphical data representations discussed in the previous section. Two other typical situations involving comparison of sample data are:

1. Calibration of two or more measuring devices using a standard powder sample. For example, calibration of a Coulter Counter, and a Micromerograph, using a sample whose distribution had been checked previously by a microscopic count.
2. Comparison of sample data obtained by two or more investigators using two or more measuring devices.

In any situation requiring data comparison, the selection of a comparison technique depends upon the type of measuring device used to obtain the data, and whether a usable functional model for the data can be assumed or no functional model can be recognized.

Data Comparison: Nonfunctional Model

This discussion concerns comparison of data, for which no functional model is recognized, as obtained from the typical "size" measuring devices. Two related methods of approach in this first case are

comparison of graphical data, and comparison of computed statistics.

Graphical Data Comparison

Comparison of graphical data involves the following concepts:

1. A comparison of data obtained from two measuring devices demands the transformation of the data from one device into the form of those obtained from the other.
2. The method of the transformation between moment relationship data and relative frequency data is determined by the total number of particles in the relative frequency sample.
3. The validity of the data comparison depends upon proper selection of interval width, number of "size" intervals, and midpoint value of the transformed data.

These points can be illustrated by use of the moment relationship diagrams and schematic histograms of Figs. 5 and 6. A comparison of Type II data shown in Fig. 5 would involve a transformation of the fraction of material w'_1/W in the interval (d_1^*, d_{1+1}^*) to the fraction n_1/N in the same interval, or a transformation of n_1/N to w'_1/W . Results of Monte Carlo experiments (Appendix C) have indicated that the proper direction of the transform is from w'_1/W to n_1/N for N less than about 20,000 particles for a typical particle "size" distribution. To compare weight fraction data with relative frequency data, careful selection of an appropriate "midpoint" value should be made for converting w'_1 to n_1 . Mellor's midpoint value d_{Mi} (29) is recommended, and is computed,

$$d_{Mi} = \left\{ \left[(d_1^*)^2 + (d_{1+1}^*)^2 \right] (d_1^* + d_{1+1}^*) / 4 \right\}^{1/3}. \quad (73)$$

The number of particles in the i^{th} size interval is

$$n_i = \frac{w'_1}{\rho C_3 d_{Mi}^3}. \quad (74)$$

The relationship n_1/N vs d_1 or the plot of n_1/N versus the intervals (d_1^*, d_{1+1}^*) is then constructed and compared with the original relative frequency data.

Data obtained from the Micromerograph and the Sedibal* pose special problems in that they are

*The Sedibal is an automatic recording balance which measures the cumulative weight of particles settling through a liquid as a function of time.

Fig. 5. Graphical comparison of sample distribution and weight fraction data.

Fig. 6. Graphical comparison sample distribution of d and volume data.

obtained as continuous cumulative weight curves. To graphically compare these data with data in the usual form (moment relationship diagrams in general), the cumulative curve should be transformed into the weight fraction diagram. This involves selection of the proper "size" interval width and the proper number of intervals. The following rules of thumb are suggested for interval width selection:

1. The transformed Micromerograph data should match in width and number the "size"

intervals of the data with which they are being compared.

2. The first rule assumes that the untransformed data have been graphed using the proper number and size interval selection.
3. The proper number of intervals can be taken as approximately 30 for the general powder sample, assuming that 1000 counts could be made in a microscopic count. Table IV⁽²²⁾ indicates the dependence of interval width selection (number of intervals, I) on sample size, N . This table

is just an approximate guide.

TABLE IV

The Number of "Size" Intervals for Sample Size, N

N	200	400	600	800	1000	1500	2000
I	12	20	24	27	30	35	39

Coulter Counter data and Type I data in general necessitate a somewhat more complicated method of graphical comparison. The basic reason for this is that the abscissa value, or "size," is transformed rather than the general fraction representing the amount of material in a given "size" interval. Consider the comparison of the graphed sample distribution, i.e., histogram, of the dimension d with the histogram of particle volume v as shown schematically in Fig. 6, where the histograms n_1/N vs d and n_1/N vs v both belong to the general family n_1/N vs $C_k d^k$. The proper comparison involves making a one-to-one correspondence between the intervals (d_1^*, d_{1+1}^*) and (v_1^*, v_{1+1}^*) by the expression

$$v_1^* = C_3 (d_1^*)^3, \quad (75)$$

where C_3 is the Coulter volume shape factor. Note that the volume size intervals will not be equal over the "size" range; however, the relative frequency is the same in corresponding d and v "size" intervals. In graphically comparing Coulter data with weight fraction, or general moment relationship data, the weight fraction data should be converted to relative frequency data. The comparison is then made by changing the Coulter data to n_1/N vs d as shown in Fig. 6, observing the rules of thumb and information in Table IV for interval width selection. An important fact overlooked in the Coulter counter manual²⁰ is that the discriminator or "window" setting can be made to give the proper intervals (d_1^*, d_{1+1}^*) for direct comparison with n_1/N vs d data through Eq. (75).

Although the transformation from Coulter counter to weight fraction data would not be proper for N less than approximately 20,000, as indicated by Monte Carlo experiments previously discussed, the proper conversion techniques are found in Ref. (19). The main points are summarized below.

1. The end points of the volume "size" interval are converted to the d "size" interval by

$$d_1^* = \sqrt[3]{v_1^*/C_3}. \quad (76)$$

2. Mellor's Eq. (73) is used to compute d_{M1} , and the weight in the interval (d_1^*, d_{1+1}^*) is computed as

$$w_1' = \rho n_1 C_3 d_{M1}^3. \quad (77)$$

3. The relationship w_1'/W vs d_1 , or vs the intervals (d_1^*, d_{1+1}^*) , is then plotted.

In general, intercomparisons of data based on any moment relationship,

$$\frac{C_k n_1 d_1^k}{\sum_{k=1}^I C_k n_1 d_1^k}$$

vs d_1 , or any distribution of the k^{th} power of d , n_1/N vs $C_k d^k$, can be treated as discussed above.

Comparison of Sample Statistics: Nonfunctional Model

The definitions and methods for computing sample statistics were summarized in (61) through (72). The following statements of nonequivalence among sample statistics should be obvious.

$$\bar{d} \neq \bar{d}_3 \neq \bar{v}, \sqrt[3]{\frac{\bar{v}}{C_3}} \approx \exp \left[\hat{\mu}_x + 1.5 \hat{\sigma}_x^2 \right] \neq \bar{d},$$

$$s_d^2 \neq s_{d_3}^2 \neq s_v^2,$$

and

$$g_d \neq g_{d_3} \neq g_v.$$

Therefore, analytical relationships among the sample statistics are necessary for valid comparisons. Because no functional model is recognized for the data, the analytical relationships are really derived from the graphical conversions discussed above. The sample statistics of interest are computed from the graphical (or tabular) data conversions; therefore, the same caution in interval-width selection and direction of conversion should be observed as discussed for graphical comparison. The relationship between statistics from Type I and Type II data is developed as follows. In the case of microscopic count data Type (0,I), the mean, variance, and skew-

ness are given by Eqs. (2), (4), and (6), respectively. The first term in the parentheses refers to the power of d concerned with either Type I or Type II data which is identified by the second term. Assume that we wish to compare these statistics with the sample statistics given by Eqs. (12), (13), and (14); that is, two powders are being compared through particle "size" measurements from two different devices. If N in the microscopic count is very large, the expressions for $\bar{d}_3$, $s_{d_3}^2$, and g_{d_3} can be written in terms of moments about the origin of the sample distribution of d , as shown in Eqs. (16), (17), and (18). The values are then compared directly with the $\bar{d}_3$, $s_{d_3}^2$, and g_{d_3} values obtained directly from weight fraction data computed by Eqs. (12), (13), and (14). Analogous methods are used for comparisons involving any order moment relationship.

N is nearly always less than 20,000 in a microscopic count. In this case the statistics from weight fraction data should be converted into $\bar{d}$, s_d^2 , and g_d using the definition $w'_1 = \rho C_3 n_1 d_1^3 / M_1$ and Eqs. (2), (4), (6), (12), (13), and (14). The moment relationship statistics may be converted for comparisons as shown in Table V. An examination of Table V indicates that it would be very time-consuming to compare statistics describing sample data for which no functional model is recognized unless proper computer programs were available. Consider the case that Type (k,II) -- k^{th} moment -- data were to be compared with Type (k,I) -- relative frequency data. For example, consider comparisons of a_1'/A vs d for $k=2$ with n_1/N vs d , where surface area $A \approx \sum u_1 C_2 d_1^2$. The conversions would be developed as indicated in Table V.

One final note concerning this type of comparison: we consider the use of Mellor's d proper in the definition

$$w'_1 = \rho C_3 n_1 d_{M1}^3 \quad (78)$$

and the usual definition of $\bar{d}_3$. The expressions for $\bar{d}$, s_d^2 , and g_d derived from weight fraction data would then be in the form shown in Table V with d_1 replaced by d_{M1} in the denominators and d_1 , the midpoint value remaining in the numerators. For example, the computation of $\bar{d}$ would be

$$\bar{d} \approx \frac{\sum_1^I \left[\frac{w'_1}{W} \right] \left(\frac{d_1}{d_{M1}} \right)}{\sum_1^I \left[\frac{w'_1}{W} \right] \left(\frac{1}{d_{M1}} \right)} \quad (79)$$

with no further simplification. We base this consideration on the premise that use of Mellor's d_{M1} in Eq. (78) gives a better estimate of n_1 from weight fraction data. If, for some reason, d_{M1} is not used, obvious simplifications can be made in Table V. For example,

$$\bar{d} \approx \frac{\sum_1^I \left[\frac{w'_1}{W} \right] \left(\frac{1}{d_1^2} \right)}{\sum_1^I \left[\frac{w'_1}{W} \right] \left(\frac{1}{d_1} \right)} \quad (80)$$

The approximation of the statistics $\bar{d}$, s_d^2 , g_d , $\bar{d}_3$, $s_{d_3}^2$, g_{d_3} from Coulter Counter data requires computation of the (d_{i-1}^*, d_{i+1}^*) interval end points using Eq. (76). Then $\bar{d}$, s_d^2 , and g_d can be approximated from the converted n_1/N vs (d_{i-1}^*, d_{i+1}^*) data using the midpoint value d_i , and Eqs. (2), (4), and (6). The comparison would be facilitated by proper selection of the (v_{i-1}^*, v_{i+1}^*) intervals to match the (d_{i-1}^*, d_{i+1}^*) intervals of the original relative frequency data as previously discussed. The statistics $\bar{d}_3$, $s_{d_3}^2$, and g_{d_3} can be approximated by using Eqs. (76) and (77) to convert (v_{i-1}^*, v_{i+1}^*) to (d_{i-1}^*, d_{i+1}^*) , and n_1/N to w'/W , and then the Eqs. (12), (13), and (14), using the midpoint value d_i . Methods are given in Table VI for converting data of the general type which includes Coulter Counter data to sample distribution statistics.

Data Comparison: Log Normal Model

The previous discussion on computation of statistics for data represented by a log normal function clearly demonstrated that:

1. Sample mean and variance completely define the sample distribution.
2. No matter what device is used to measure the so-called "size" distribution, the sample statistics may be functionally related for purposes of data comparison.

It is emphasized that for log normal data, the sample is completely defined by the mean and variance. To compare samples that can be represented by log normal data, obtained from different measuring devices, the values of $\hat{\mu}_x$ and $\hat{\sigma}_x^2$ should be com-

TABLE V

Nonfunctional Conversion of Moment Data to Sample Distribution Statistics

Sample Statistic	Third Moment or Weight Fraction Type (3,II)	k th Moment Type (k,II)
$\bar{d} \approx$	$\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)}$	$\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)}$
$s_d^2 \approx$	$\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i^2}{d_1^2} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)} - \left[\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)} \right]^2$	$\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i^2}{d_1^2} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)} - \left[\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)} \right]^2$
$s_d \approx$	$\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i^3}{d_1^3} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)} - 3 \left[\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)} \right] \left[\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i^2}{d_1^2} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)} \right] + 2 \left[\frac{\sum \left[\frac{v_i}{w} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{v_i}{w} \right] \left(\frac{1}{d_1} \right)} \right]^3$	$\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i^3}{d_1^3} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)} - 3 \left[\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)} \right] \times \left[\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i^2}{d_1^2} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)} \right] + 2 \left[\frac{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{d_i}{d_1} \right)}{\sum \left[\frac{n_i C_k d_i^k}{\sum n_i C_k d_i^k} \right] \left(\frac{1}{d_1} \right)} \right]^3$

Note: All summations are over $i = 1, \dots, I$

TABLE VI

Nonfunctional Transformation of Type (3,I) and Type (k,I) Data

Sample Statistic	Coulter Counter Type (3,I), $\frac{n_i}{N} \text{ vs } C_3 d^3 = v$	General Form Type (k,I), $\frac{n_i}{N} \text{ vs } C_k d^k = D_k$
$\bar{d} \approx$	$\sum_1^I \frac{n_i \left[\left(\frac{v_i^*}{C_3} \right)^{\frac{1}{3}} + \left(\frac{v_{i+1}^*}{C_3} \right)^{\frac{1}{3}} \right]}{2N}$	$\sum_1^I \frac{n_i \left[\left(\frac{D_{k,i}^*}{C_k} \right)^{\frac{1}{k}} + \left(\frac{D_{k,i+1}^*}{C_k} \right)^{\frac{1}{k}} \right]}{2N}$
$s_d^2 \approx$	$\sum_1^I \frac{n_i \left[\left(\frac{v_i^*}{C_3} \right)^{\frac{1}{3}} + \left(\frac{v_{i+1}^*}{C_3} \right)^{\frac{1}{3}} - 2\bar{d} \right]^2}{4N}$	$\sum_1^I \frac{n_i \left[\left(\frac{D_{k,i}^*}{C_k} \right)^{\frac{1}{k}} + \left(\frac{D_{k,i+1}^*}{C_k} \right)^{\frac{1}{k}} - 2\bar{d} \right]^2}{4N}$
$s_d \approx$	$\sum_1^I \frac{n_i \left[\left(\frac{v_i^*}{C_3} \right)^{\frac{1}{3}} + \left(\frac{v_{i+1}^*}{C_3} \right)^{\frac{1}{3}} - 2\bar{d} \right]^3}{8N}$	$\sum_1^I \frac{n_i \left[\left(\frac{D_{k,i}^*}{C_k} \right)^{\frac{1}{k}} + \left(\frac{D_{k,i+1}^*}{C_k} \right)^{\frac{1}{k}} - 2\bar{d} \right]^3}{8N}$

Note: The $\bar{d}$ in expressions for s_d^2 and s_d are calculated from the transformed interval end points as shown.

puted, no matter what measuring device was used to obtain the original data. The expressions relating log normal functional parameters were developed in the section on Computation of Sample Statistics. These relationships are summarized in Tables VII and VIII for convenience in data comparison. It is emphasized that these two tables are in terms of functional parameters. Their use in comparing sample statistics would involve consideration of sample data, for example $\hat{\mu}_{x3} \approx \hat{\mu}_x + 3\hat{\sigma}_x^2$. It is

emphasized that in comparing sample statistics for a set of sample distributions measured with the same device, data transformation is not necessary.

Although the sample means and variances should be used as comparison criteria for sample data represented by a log normal function, there may be cases in which an investigator needs to compare log normal data, i.e., sample data, with statistics such as $\bar{d}_3$, $\bar{d}$, s_{d3}^2 which may or may not have been derived from log normal data. Statistics for the sample distribution of d or powers of d and moment relationships can be computed conveniently for data approximated by a log normal function. The distribution function of d , $h(d)$, has mean μ_d and variance σ_d^2 . In the case of a log normal distribution of d , $h(\ln d)$ is normal by definition. Then, $h(\ln d) = h(x) = p(x)$.

The parameters μ_d and σ_d^2 are estimated by the statistics $\bar{d}$ and s_d^2 , respectively.

General notation for the function describing the k^{th} moment relationship normal in $x = \ln d$ is $h_k(d)$ with mean μ_{dk} , variance σ_{dk}^2 , and skewness μ_{3dk} where $\bar{d}_k \approx \hat{\mu}_{dk} \approx \mu_{dk}$; $s_{dk}^2 \approx \hat{\sigma}_{dk}^2 \approx \sigma_{dk}^2$; and $g_{dk} \approx \hat{\mu}_{3dk} \approx \mu_{3dk}$.

Similarly, the function describing the distribution of the k^{th} power of d normal in $z_k = \ln(C_k d^k) = \ln D_k$ is $h_k(D_k)$ with mean μ_{Dk} , variance σ_{Dk}^2 , and skewness μ_{3Dk} . The relationships permitting data comparison of the type discussed above are summarized in Tables IX and X. The relationships are written in terms of functional parameters rather than sample statistics.

Summary

The utility of the previous section can be summarized by considering some hypothetical but typical practical problems. A sample of atmospheric dust was divided and sent to three different investigators for extended analysis of its properties. As an initial phase of the analysis, each investigator determined the particle "size" distribution of his sample, but each used a different measurement technique. Investigator A made an optical

TABLE VII

Functional Transforms of Type I Data

Linear Transforms [ordinate = $p(z_k)$]				
Abcissa Value				
	$x = \ln d$	$z_2 = \ln a = \ln C_2 d^2$	$z_3 = \ln v = \ln C_3 d^3$	$z_k = \ln C_k d^k$
Parameters	μ_x	$\mu_{z_2} = \ln C_2 + 2\mu_x$	$\mu_{z_3} = \ln C_3 + 3\mu_x$	$\mu_{z_k} = \ln C_k + k\mu_x$
	σ_x^2	$\sigma_{z_2}^2 = 4\sigma_x^2$	$\sigma_{z_3}^2 = 9\sigma_x^2$	$\sigma_{z_k}^2 = k^2\sigma_x^2$

TABLE VIII

Functional Conversions of Type II Data

Moment Conversions (abscissa = x)

Ordinate Value				
	$p(x)$	$f_2(x)$	$f_3(x)$	$f_k(x)$
Parameters	μ_x	$\mu_x + 2\sigma_x^2 = \mu_{x2}$	$\mu_x + 3\sigma_x^2 = \mu_{x3}$	$\mu_x + k\sigma_x^2 = \mu_{xk}$
	σ_x^2	σ_x^2	σ_x^2	σ_x^2

particle count and reported the sample statistics $\bar{d}$, s_d^2 , and g_d using the general definitions given by Eqs. (2), (4), and (6), making no inference as to whether or not his data were log normal. Investigator B, using a Micromerograph, found that his data were log normal, and reported the values $\hat{\mu}_x$ and $\hat{\sigma}_x^2$. Investigator C, using a Coulter Counter, also noted that his data gave a good log normal fit and reported the values $\hat{\mu}_x$ and $\hat{\sigma}_x^2$. As the investigation of the properties of the dust progressed, some discrepancies were noted among the three sets of measurements, raising doubt as to the homogeneity of the initial sample; that is, whether each subsample represented the original dust. As a quick check, the investigators decided to compare particle "size" data. The statistics computed for as-measured data and the transformed statistics obtained by each investigator using Tables IX and X are summarized in Table XI. Note several important facts:

1. Since the data of B and C were recognized to be log normal, it would have been more convenient to fit A's data to a log normal $p(x)$ and compute $\hat{\mu}_x$ and $\hat{\sigma}_x^2$ in each case for comparison, using the conversions in Tables VII and VIII.

2. The expressions in Table XI can be used only if the data were log normal.

3. Tables IX, X, and XI illustrate the following inequalities:

a. $\mu_d \neq \mu_{d_3} \neq \mu_v$

b. $\sigma_d^2 \neq \sigma_{d_3}^2 \neq \sigma_v^2$

c. $C_3 \bar{d}^3 \neq \bar{v}$

4. The statistics $\hat{\mu}_x$, $\hat{\sigma}_x^2$, or $\bar{d}$, s_d^2 , g_d , obtained through conversion of statistics from different methods of measurement as illustrated by Table XI will never be in exact agreement because of uncertainty in definition of C_k , d , inherent measurement errors, and inexactness of the log normal fit.

The relationships of Tables IX, X, and XI are primarily of academic interest because $\hat{\mu}_x$ and $\hat{\sigma}_x^2$ completely define a log normal sample distribution. The relationships only provide a method which independent investigators can use to compare data.

TABLE IX

Parametric Equations Based on Moment Relationships (Type II)

(Functions normal in $x = \ln d$)

	$h(d)$	Ordinate Value	$h_3(d)$	$h_k(d)$
Parametric Relationships	$\mu_d = \exp \left[\mu_x + .5 \sigma_x^2 \right]$		$\mu_{d_3} = e^{3\sigma_x^2} \mu_d$	$\mu_{d_k} = e^{k\sigma_x^2} \mu_d$
	$\sigma_d^2 = \exp \left[2\mu_x + 2\sigma_x^2 \right] - \exp \left[2\mu_x + \sigma_x^2 \right]$		$\sigma_{d_3}^2 = e^{6\sigma_x^2} \sigma_d^2$	$\sigma_{d_k}^2 = e^{2k\sigma_x^2} \sigma_d^2$
	$\mu_{3d} = \left\{ \exp \left[3\mu_x + 1.5 \sigma_x^2 \right] \right\} \left[e^{3\sigma_x^2} - 3e^{\sigma_x^2} + 2 \right]$		$\mu_{3d_3} = e^{9\sigma_x^2} \mu_{3d}$	$\mu_{3d_k} = e^{3k\sigma_x^2} \mu_{3d}$

TABLE X

Parametric Equations for Type I Distributions

Parametric Relationships	Ordinate Value		
	$q(d) = h(d)$	$q(D_3) = q(v)$	$q(D_k)$
	$\mu_d = (C_k)^{-\frac{1}{k}} \exp \left[\frac{2k\mu_{z_k} + \sigma_{z_k}^2}{2k^2} \right]$	$\mu_v = \exp \left[\mu_{z_3} + .5 \sigma_{z_3}^2 \right]$	$\mu_{D_k} = C_k \left[k\mu_x + \frac{k^2 \sigma_x^2}{2} \right]$
	$\sigma_d^2 = \left\{ (C_k)^{-\frac{2}{k}} \exp \left[\frac{2k\mu_{z_k} + \sigma_{z_k}^2}{k^2} \right] \right\} \times \left[e^{k^{-2} \sigma_{z_k}^2} - 1 \right]$	$\sigma_v^2 = \left\{ \exp \left[2\mu_{z_3} + \sigma_{z_3}^2 \right] \right\} \left[e^{\sigma_{z_3}^2} - 1 \right]$	$\sigma_{D_k}^2 = \left\{ C_k^2 \exp \left[2k\mu_x + k^2 \sigma_x^2 \right] \right\} \times \left[e^{k^2 \sigma_x^2} - 1 \right]$
	$\mu_{3d} = \left\{ (C_k)^{-\frac{3}{k}} \exp \left[\frac{3k\mu_{z_k} + .5 \sigma_{z_k}^2}{k^2} \right] \right\} \times \left[e^{3k^{-2} \sigma_{z_k}^2} - 3e^{k^{-2} \sigma_{z_k}^2} + 2 \right]$	$\mu_{3v} = \left\{ \exp \left[3\mu_{z_3} + 1.5 \sigma_{z_3}^2 \right] \right\} \times \left[e^{3\sigma_{z_3}^2} - 3e^{\sigma_{z_3}^2} + 2 \right]$	$\mu_{3D_k} = \left\{ C_k^3 \exp \left[3k\mu_x + 1.5 k^2 \sigma_x^2 \right] \right\} \times \left[e^{3k^2 \sigma_x^2} - 3e^{k^2 \sigma_x^2} + 2 \right]$

TABLE XI

Statistics from Log Normal Data Transformed for Comparison

A (Microscope) $\bar{d}, s_d^2, g_d$	B (Micromerograph) $\hat{\mu}_{x3}, \hat{\sigma}_x^2$	C (Coulter Counter) $\hat{\mu}_{z3}, \hat{\sigma}_{z3}^2$
Transformed Statistics	$\bar{d} \approx \exp \left[\hat{\mu}_{x3} - 2.5 \hat{\sigma}_x^2 \right]$	$\bar{d} \approx C_3^{-\frac{1}{3}} \exp \left[\frac{6\hat{\mu}_{z3} + \hat{\sigma}_{z3}^2}{18} \right]$
	$s_d^2 \approx \left\{ \exp \left[2\hat{\mu}_{x3} - 5 \hat{\sigma}_x^2 \right] \right\} \left[e^{\hat{\sigma}_x^2} - 1 \right]$	$s_d^2 \approx \left\{ (C_3)^{-\frac{2}{3}} \exp \left[\frac{6\hat{\mu}_{z3} + \hat{\sigma}_{z3}^2}{9} \right] \right\} \left[e^{\frac{1}{9} \hat{\sigma}_{z3}^2} - 1 \right]$
	$g_d \approx \left\{ \exp \left[3\hat{\mu}_{x3} - 7.5 \hat{\sigma}_x^2 \right] \right\} \left[e^{3\hat{\sigma}_x^2} - 3e^{\hat{\sigma}_x^2} + 2 \right]$	$g_d \approx \left\{ \frac{\exp \left[\hat{\mu}_{z3} + \frac{1}{6} \hat{\sigma}_{z3}^2 \right]}{C_3} \right\} \left[e^{\frac{1}{3} \hat{\sigma}_{z3}^2} - 3e^{\frac{1}{9} \hat{\sigma}_{z3}^2} + 2 \right]$

COMPUTATION OF GEOMETRIC PROPERTIES AS SAMPLE STATISTICS

Specific surface is one of the properties often considered in attempts to characterize a powder or predict process behavior. This property is defined as the ratio of total powder surface area to weight,

$S_w = A/W$, or total surface area to volume, $S_v = A/V$, of the particles in a sample. The literature seems to lack a complete discussion of methods of computing estimates of specific surface directly from sample statistics; therefore, the following discussion is presented. Specific surface is dependent upon surface characteristics of the particles, distributional properties such as means and variances, and the particle shape factors. Estimates of specific surface may be obtained by gas absorption or chromatography, or by computations based on a statistical model representing the distribution of "size" of particles in the material.

Specific surface can be estimated using the type of data schematically illustrated in Table IIIa. An estimate may be obtained by computing the surface area and weight in each "size" interval, using d_i to estimate the average particle dimension in the i^{th} interval and C_2 and C_3 as the appropriate shape factors. Specific surface would be expressed as

$$S_w \approx \frac{C_2 \sum_1^I n_i d_i^2}{\rho C_3 \sum_1^I n_i d_i^3} = \frac{C_2 m'_2}{\rho C_3 m'_3} \quad (81)$$

Specific surface can be approximated directly from weight fraction data using the expression

$$S_w \approx \frac{\sum_1^I a'_i}{W} \approx \frac{C_2}{\rho C_3} \sum_1^I \frac{w'_i}{W} \left(\frac{1}{d_i} \right) \quad (82)$$

We believe that a better estimate of S_w can be obtained using Mellor's d (Ref. 11, p. 33) as follows:

$$S_w \approx \frac{C_2}{\rho C_3} \sum_1^I \frac{w'_i}{W} \left(\frac{d_i^2}{d_{Mi}} \right) \quad (83)$$

Specific surface may be estimated from Coulter Counter sample data using the expression

$$S_w \approx \frac{C_2}{\rho C_3} \frac{\sum_1^I n_i^{\frac{1}{3}} v_i^{\frac{2}{3}}}{\sum_1^I n_i v_i} \quad (84)$$

This expression for S_w makes direct use of sample data, and the validity of S_w depends upon the meaningful selection of C_2 and C_3 with respect to the definition of d_i . The above expression for S_w is not dependent upon the interpretation of the sample data in terms of the distribution of d .

We believe that a better estimate of S_w can be obtained using a value d_{Li} which corresponds to the average particle area in the size interval (v_i^*, v_{i+1}^*) to estimate the numerator A , in (82), (83), and (84). The following definition for d_{Li} was derived in a manner similar to that used by Mellor to obtain d_{Mi} .

$$d_{Li} = \left[\frac{(d_{i+1}^*)^2 + (d_{i+1}^*) (d_i^*) + (d_i^*)^2}{3} \right]^{\frac{1}{2}} \quad (85)$$

For example, (84) is modified as follows:

$$d_i^* = \left(\frac{v_i^*}{C_3} \right)^{\frac{1}{3}}$$

Then

$$a'_i = n_i C_2 d_{Li}^2 \quad (86)$$

and

$$S_w \approx \frac{C_2 \sum_1^I n_i d_{Li}^2}{\rho \sum_1^I n_i v_i} \quad (87)$$

When functional approximations are used to describe "size" distributions, specific surface can be estimated without special definitions of mid-point values of "size" interval widths. The use of log normal functions to approximate sample data makes possible the convenient estimation of particle surface area and weight. Approximations for a'_i , A , w'_i , and W can be obtained directly from (37) because of the properties of the log normal function which make possible the definitions of area and weight in terms of moments of the appropriate functions.

For example, the functional approximations for a'_i or A can be derived in a manner similar to the derivation of (35). The total particle surface area in an interval may be approximated as

$$a'_i \approx \frac{n_i}{N} N C_2 d_i^2 \quad (88)$$

Since $\frac{n_i}{N} \approx \int_{x_i^*}^{x_{i+1}^*} p(x) dx$, the approximation

$$a_1^* \approx N C^2 \int_{x_1}^{x_{1+1}^*} d^2 p(x) dx \quad (89)$$

may be written. Thus, specific surface can be expressed in terms of the defining statistics for any form of log normal sample data by utilizing the functional approximation for area, volume, and weight. Expressions for estimating these properties are summarized in Table XII. Note that the accuracy of these estimates depends upon the accuracy of the measuring instrument, the meaningfulness of the relationship between shape factor and d , and how well the sample data are represented by the approximating log normal function.

The validity of the type of estimation shown in Table XII has been demonstrated using Monte Carlo techniques applied to random sampling of log normal functions (see Appendix C).

It is sometimes desirable to estimate the surface area or volume or specific surface of material in a particular "size" range for a given sample. The methods used in the case of nonfunctional models are evident on examination of (81), (83), and (84). The methods used for a sample represented by a log normal function are illustrated as follows for estimating S_w in the "size" range d_1 to d_2 , where d is in microns. Expression (37) is used to define S_w as

$$S_w \approx \frac{N C_2 \int_{x_1}^{x_2} d^2 p(x) dx}{\rho N C_3 \int_{x_1}^{x_2} d^3 p(x) dx}$$

Simplification of the integral gives

$$S_w \approx \frac{10^{-8} C_2 \exp \left[2\hat{\mu}_x + 2\hat{\sigma}_x^2 \right] \frac{1}{\sqrt{2\pi}\hat{\sigma}_x} \int_{x_1}^{x_2} \exp \left[\frac{-(x-\hat{\mu}_x)^2}{2\hat{\sigma}_x^2} \right] dx}{10^{-12} \rho C_3 \exp \left[3\hat{\mu}_x + 4.5\hat{\sigma}_x^2 \right] \frac{1}{\sqrt{2\pi}\hat{\sigma}_x} \int_{x_1}^{x_2} \exp \left[\frac{-(x-\hat{\mu}_x)^2}{2\hat{\sigma}_x^2} \right] dx} \quad (90)$$

The values of $\hat{\mu}_x$, $\hat{\mu}_{x2}$, $\hat{\mu}_{x3}$, and $\hat{\sigma}_x^2$ are obtained from the fitted function representing the sample data and appropriate transformations (Tables VII, VIII). The values of the integrals can be obtained from error function tables²⁸ or estimated graphically from the

log probability plots of the straight lines defined by $\hat{\mu}_{x2}, \hat{\sigma}_x^2$ and $\hat{\mu}_{x3}, \hat{\sigma}_x^2$.

The computational constants in Table XII are based on expressing d in microns, surface area in square centimeters, weight in grams, and ρ in grams per cubic centimeter.

Note that properties should be estimated in terms of the appropriate sample means and variances. The quantities estimated from Micromerograph and Coulter Counter data are not obtained by redefining the sample data in terms of a distribution of d . We emphasize that the estimates obtained for specific surface using Table XII and measured distribution data, even if the data are well represented by log normal function, may not agree with BET³⁰ or similar measurements. This is because BET measurements take into account surface connected porosity and microcrevices in the particle surface, which are not detected by the standard methods of particle "size" distribution analysis. Except for clean "smooth-surface" particles of near theoretical crystal density, BET measurements may be expected to give, in general, higher specific surface estimates than the methods of Table XII. The utility of either type of estimation depends upon what characteristics of the powder the investigator is trying to define.

MIXTURE THEORY

Introduction

The development of a general theory for mixtures is important for the following reasons:

1. It has been observed that the process behavior of a powder can in some cases be "improved" by mixing the powder with another having different distribution characteristics. For example, the ceramics technician empirically varies milling time or mixes two slips to achieve the optimum particle "size" distribution in an attempt to minimize as-fired shrinkage of a slip cast body. The metallurgist observes changes in as-pressed density and powder rolling characteristics of a powder mixture as the mixing proportion of component powders is changed. To explain the behavior of mixtures of powders, a description of the "size" distribution properties of the mix if necessary.

TABLE XII
Functional Estimates of Particle Surface Area, Volume, and Weight

Property Estimated	Measuring Devices		
	Microscope (relative frequency of d)	Micromerograph, Sedibal, etc. (weight fraction of d)	Coulter Counter (relative frequency of v)
N	Measured	$\frac{W}{\rho C_3} \exp \left[-(\hat{\mu}_{x3} - 4.5 \hat{\sigma}_x^2) \right] 10^{-12}$	Measured
A(cm ²)	$NC_2 \exp \left[2\hat{\mu}_x + .2\hat{\sigma}_x^2 \right] 10^{-8}$	$\frac{WC_2}{\rho C_3} \exp \left[-(\hat{\mu}_{x3} - .5 \hat{\sigma}_x^2) \right] 10^4$	$\frac{NC_2}{C_3^{2/3}} \exp \left[\frac{2}{9} (3\hat{\mu}_{z3} + \hat{\sigma}_{z3}^2) \right] 10^{-8}$
V(cm ³)	$NC_3 \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right] 10^{-12}$	$\frac{W}{\rho}$	$N \exp \left[\hat{\mu}_{z3} + .5 \hat{\sigma}_{z3}^2 \right] 10^{-12}$
W (g)	$\rho NC_3 \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right] 10^{-12}$	Measured	$\rho N \exp \left[\hat{\mu}_{z3} + .5 \hat{\sigma}_{z3}^2 \right] 10^{-12}$
S _v (cm ⁻¹)	$\frac{C_2}{C_3} \exp \left[-(\hat{\mu}_x + 2.5 \hat{\sigma}_x^2) \right] 10^4$	$\frac{C_2}{C_3} \exp \left[-(\hat{\mu}_{x3} - .5 \hat{\sigma}_x^2) \right] 10^4$	$\frac{C_2}{C_3^{2/3}} \exp \left[-\frac{1}{18} (6\hat{\mu}_{z3} + 5\hat{\sigma}_{z3}^2) \right] 10^4$
S _v (cm ² /g)	$\frac{C_2}{\rho C_3} \exp \left[-(\hat{\mu}_x + 2.5 \hat{\sigma}_x^2) \right] 10^4$	$\frac{C_2}{\rho C_3} \exp \left[-(\hat{\mu}_{x3} - .5 \hat{\sigma}_x^2) \right] 10^4$	$\frac{C_2}{\rho C_3^{2/3}} \exp \left[-\frac{1}{18} (6\hat{\mu}_{z3} + 5\hat{\sigma}_{z3}^2) \right] 10^4$

Units: d in microns, ρ in g/cm³.

2. A measurement of the "size" distribution of mixtures of powders is difficult if the mix components have different particle densities; therefore, a development of a mixing theory is necessary to estimate the distributional properties of the mixture from the properties of the mixture components.

The development of the general mixture theory is based on two interrelated concepts of methods of mixing. The first is the manner in which mixing is practically accomplished on a weight basis. The second is mixing on a frequency basis or the relative number of component particles. This second concept is required as the basis for computation of statistics for the mixture.

The development of the mixture theory is also based on the consideration of the type of measuring device used to obtain the particle "size" data, and whether the data can be represented by a functional model.

The subsequent discussion is based on the concept that a mixture is the combination of two or more component powders whose particle "size" distributions have been measured. Each component of the mixture in the above sense could, indeed, be a combination of powders.

Definition of Mixture and Mixing Fraction

The development of the mixture theory is based on the assumption that the practical mixing of powders by weight does not alter the "size" distribution of the components. That is, the components of the mix are obtained as representative samples.

The construction of a histogram for a two-component mixture is schematically illustrated by Fig. 7. The number of particles in the *i*th "size" interval for the mix is

$$n_{i(M)} = n_{i(1)} + n_{i(2)}, \quad (91)$$

and the total number of particles in the mix is

Fig. 7. Schematic development of histogram for a mixture.

$$N_{(M)} = \sum_1^I n_{i(1)} + \sum_1^I n_{i(2)} = N_{(1)} + N_{(2)} \quad (92)$$

In general, the number of component powders in a mix is J . The number of particles in the i^{th} "size" interval of the j^{th} component is $n_{i(j)}$, where $i = 1, 2, 3, \dots, I$, and $j = 1, 2, 3, \dots, J$.

The parenthetic subscript notation, (j) , is reserved for mixture component identification. The number of particles in the i^{th} "size" interval of the mix is

$$n_{i(M)} = \sum_{j=1}^J n_{i(j)} \quad (93)$$

and the total number of particles in the mix is

$$N_{(M)} = \sum_1^J \sum_1^I n_{i(j)} = \sum_1^J N_{(j)} \quad (94)$$

The relative frequency for the i^{th} "size" interval of the mix is

$$\frac{n_{i(M)}}{N_{(M)}} = \frac{n_{i(M)}}{\sum_1^J N_{(j)}} \quad (95)$$

Equation (95) can be written in a convenient form as

$$\frac{n_{i(M)}}{N_{(M)}} = \frac{\sum_1^J \frac{N_{(j)}}{N_{(M)}} n_{i(j)}}{\sum_1^J \frac{N_{(j)}}{N_{(M)}}} = \sum_1^J \beta_{(j)} \frac{n_{i(j)}}{N_{(j)}} \quad (96)$$

where

$$\beta_{(j)} = \frac{N_{(j)}}{N_{(M)}} \quad (97)$$

is the definition of the frequency mixing fraction of the j^{th} component, or the fraction of the total

number of particles in the mix contributed by the j^{th} component. The relative frequency in the i^{th} interval of the j^{th} component is $n_{i(j)}/N_{(j)}$.

Consider the development of weight fractions for a mixture. The weight of particles in the i^{th} interval of the mix is

$$w'_{i(M)} \approx \sum_1^J \rho_{(j)} C_{3(j)} n_{i(j)} d_i^3 \quad (98)$$

the total weight of the mix is

$$W_{(M)} \approx \sum_1^J \sum_1^I \rho_{(j)} C_{3(j)} n_{i(j)} d_i^3 \approx \sum_1^J \sum_1^I w'_{i(j)} = \sum_1^J W_{(j)} \quad (99)$$

and the weight fraction in the i^{th} "size" interval of the mix is then

$$\frac{w'_{i(M)}}{W_{(M)}} = \frac{w'_{i(M)}}{\sum_1^J W_{(j)}} \quad (100)$$

Note that although $\rho_{(j)}$ and $C_{3(j)}$ are assumed to be constants in each of I "size" intervals for a given component, each of the J components may have different values of density and shape factor. It is emphasized that the definitions of d_i and the intervals (d_i^*, d_{i+1}^*) must be the same for all components. This consistency in interval endpoint definition for all of the J components must be observed, no matter what form of data is being considered.

Equation (100) can be written as

$$\frac{w'_{i(M)}}{W_{(M)}} = \frac{\sum_1^J \frac{W_{(j)}}{W_{(M)}} w'_{i(j)}}{\sum_1^J \frac{W_{(j)}}{W_{(M)}}} = \sum_1^J \alpha_{(j)} \frac{w'_{i(j)}}{W_{(j)}} \quad (101)$$

where

$$\alpha_{(j)} = \frac{W_{(j)}}{W_{(M)}} \quad (102)$$

is the definition of the weight mixing fraction of the j^{th} component, or fraction of the total weight of particles in the mix contributed by the j^{th} component. These definitions of $\alpha_{(j)}$ and $\beta_{(j)}$ will be used as a basis for the development of mixing theory. Conversions between $\alpha_{(j)}$ and $\beta_{(j)}$ will be developed in a following section on comparison of statistics for mixtures.

The weight fraction in the i^{th} interval for a mix can be expressed in terms of the frequency mixing fraction $\beta_{(j)}$. Using (98) and (99) to define $w'_{i(M)}/W_{(M)}$ and multiplying numerator and

denominator of Eq. (100) by $N_{(j)}/N_{(j)}^{N(M)}$, yields

$$\frac{w'_{i(M)}}{w_{(M)}} \approx \frac{\sum_1^J \beta_{(j)} \left(\frac{n_{i(j)}}{N_{(j)}} \right) \rho_{(j)} c_{3(j)} d_i^3}{\sum_1^J \beta_{(j)} \left[\sum_1^I \left(\frac{n_{i(j)}}{N_{(j)}} \right) \rho_{(j)} c_{3(j)} d_i^3 \right]} \quad (103)$$

Similarly, the relative frequency in the i^{th} interval for a mix can be expressed in terms of the weight mixing fraction $\alpha_{(j)}$. Using (93), (94), and (98) to define $n_{i(M)}/N_{(M)}$ in terms of $w'_{i(M)}$, and multiplying numerator and denominator of Eq. (95) by $w_{(j)}/w_{(j)}^{w(M)}$, yields

$$\frac{n_{i(M)}}{N_{(M)}} \approx \frac{\sum_1^J \alpha_{(j)} \left(\frac{w'_{i(j)}}{w_{(j)}} \right) \left(\frac{1}{\rho_{(j)} c_{3(j)} d_i^3} \right)}{\sum_1^J \alpha_{(j)} \left[\sum_1^I \left(\frac{w'_{i(j)}}{w_{(j)}} \right) \left(\frac{1}{\rho_{(j)} c_{3(j)} d_i^3} \right) \right]} \quad (104)$$

Note that (98), (103), and (104) are concerned with conversions between weight and number, therefore d_{M1} , Mellor's d defined in Eq. (73), may be more appropriately used than the midpoint value, d_i . Expressions (103) and (104) will be of use in computation and conversion of statistics for mixtures.

Computation of Statistics for Mixtures

Computation of defining statistics for mixtures of powders is performed in essentially the same manner as for unmixed powders. It will be seen that the difference in methods of computation of statistics for mixtures as compared to methods for unmixed powders is in the more complex definition of the fraction of mixed material in the I "size" intervals as shown by Eqs. (96) and (100).

Because of the similarity in computation and comparison of statistics, the development for mixtures will not be so detailed as that for unmixed powders. The development of computational methods will be restricted to the three representative types of data: microscopic, Micromerograph, and Coulter counter. These developments can be made for the general cases using the same techniques. It is emphasized that the computations which follow presume the definition of "size" and "size" interval are the same for each component.

For simplicity it will be assumed that sample data were obtained for each mix component using the same measuring instrument. However, use of the interconversions previously discussed for statistics for single component powders would permit subsequent calculations using component sample data obtained from different measuring devices.

Nonfunctional Model

Computation of statistics for mixtures whose component particle "size" data cannot be functionally represented is developed in this section.

The statistics -- mean, variance, and skewness -- for a mixture whose component sample data are of the type obtained by microscopic count are developed as follows:

$$\text{Mean: } \bar{d}_{(M)} = \sum_1^I \frac{n_{i(M)}}{N_{(M)}} d_i \quad (105)$$

Using Eq. (96),

$$\bar{d}_{(M)} = \sum_1^J \beta_{(j)} \left\{ \sum_1^I \left[\frac{n_{i(j)}}{N_{(j)}} \right] d_i \right\} = \sum_1^J \beta_{(j)} \bar{d}_{(j)} \quad (106)$$

$$\text{Variance: } s_{d(M)}^2 = \sum_1^I \frac{n_{i(M)}}{N_{(M)}} (d_i - \bar{d}_{(M)})^2 = \sum_1^I \frac{n_{i(M)}}{N_{(M)}} d_i^2 - \bar{d}_{(M)}^2 \quad (107)$$

Using Eqs. (5) and (96),

$$s_{d(M)}^2 = \sum_1^J \beta_{(j)} \left[s_{d(j)}^2 + \bar{d}_{(j)}^2 \right] - \bar{d}_{(M)}^2 \quad (108)$$

$$\text{Skewness: } g_{d(M)} = \sum_1^I \frac{n_{i(M)}}{N_{(M)}} (d_i - \bar{d}_{(M)})^3 \quad (109)$$

Using Eqs. (7) and (96),

$$g_{d(M)} = \sum_1^J \beta_{(j)} m'_{3(j)} - 3 \left[\sum_1^J \beta_{(j)} m'_{2(j)} \right] \left[\sum_1^J \beta_{(j)} \bar{d}_{(j)} \right] + 2 \bar{d}_{(M)}^3 \quad (110)$$

where, in general,

$$m'_{k(j)} = \sum_1^I \left[\frac{n_{i(j)}}{N_{(j)}} \right] d_i^k$$

The third moment sample statistics for a mixture whose component sample data are in weight fraction form can be developed in a similar manner.

$$\text{Mean: } \bar{d}_{3(M)} = \sum_1^I \frac{w'_{i(M)}}{w_{(M)}} d_i \quad (111)$$

Using Eq. (101),

$$\bar{d}_{3(M)} = \sum_1^J \alpha_{(j)} \left\{ \sum_1^I \left[\frac{w'_1(j)}{w_{(j)}} \right] d_1 \right\} = \sum_1^J \alpha_{(j)} \bar{d}_{3(j)} \quad (112)$$

$$\begin{aligned} \text{Variance: } s_{d_3(M)}^2 &= \sum_1^I \frac{w'_1(M)}{w_{(M)}} (d_1 - \bar{d}_{3(M)})^2 \\ &= \sum_1^I \frac{w'_1(M)}{w_{(M)}} d_1^2 - \bar{d}_{3(M)}^2, \end{aligned} \quad (113)$$

or, using Eqs. (13) and (101),

$$s_{d_3(M)}^2 = \sum_1^J \alpha_{(j)} \left[s_{d_3(j)}^2 + \bar{d}_{3(j)}^2 \right] - \bar{d}_{3(M)}^2 \quad (114)$$

$$\text{Skewness: } g_{d_3(M)} = \sum_1^I \frac{w'_1(M)}{w_{(M)}} (d_1 - \bar{d}_{3(M)})^3,$$

or, using Eqs. (14) and (101),

$$\begin{aligned} g_{d_3(M)} &= \sum_1^J \alpha_{(j)} \left\{ \sum_1^I \left[\frac{w'_1(j)}{w_{(j)}} \right] d_1^3 \right\} \\ &\quad - 3 \bar{d}_{3(M)} \sum_1^J \alpha_{(j)} \left[\sum_1^I \frac{w'_1(j)}{w_{(j)}} d_1^2 \right] + 2 \left[\bar{d}_{3(M)} \right]^3. \end{aligned} \quad (115)$$

The statistics for a mixture whose component sample data are obtained using a Coulter Counter, i.e., in the form n_1/N vs v , are developed in the same manner as Eqs. (105) to (110). The differences are in the definition of "size" and "size" interval.

$$\text{Mean: } \bar{v}_{(M)} = \sum_1^J \beta_{(j)} \bar{v}_{(j)} \quad (116)$$

$$\text{Variance: } s_{v(M)}^2 = \sum_1^J \beta_{(j)} \left[s_{v(j)}^2 + \bar{v}_{(j)}^2 \right] - \bar{v}_{(M)}^2 \quad (117)$$

$$\begin{aligned} \text{Skewness: } g_{v(M)} &= \sum_1^J \beta_{(j)} \left\{ \sum_1^I \left[\frac{n_1(j)}{N_{(j)}} \right] v_1^3 \right\} \\ &\quad - 3 \bar{v}_{(M)} \sum_1^J \beta_{(j)} \left\{ \sum_1^I \left[\frac{n_1(j)}{N_{(j)}} \right] v_1^2 \right\} + 2 \bar{v}_{(M)}^3. \end{aligned} \quad (118)$$

Notice that the expressions for mixture statistics containing $\beta_{(j)}$ are of no practical use in their stated form. It is emphasized that practical mixing is performed on a weight basis; therefore, conversions between $\beta_{(j)}$ and $\alpha_{(j)}$ and expressions (103) and (104) are required so that the expressions for mixture statistics have practical meaning. The conversions will be developed and their use discussed in detail in a following section on Comparison of Sample Statistics for Mixtures.

Log Normal Model

If the sample particle "size" data for the components of a mixture can be represented by some form of a log normal function, statistics for the mixture can be computed using the concepts of the section on the log normal model. The definitions of, or approximations for relative frequency and weight fraction of material in the i^{th} mixture "size" interval are developed using the log normal model as follows:

Relative frequency:

$$\frac{n_1(j)}{N_{(j)}} \approx \int_{x_1^*}^{x_{i+1}^*} p(x)_{(j)} dx,$$

$$\frac{n_1(M)}{N_{(M)}} = \sum_1^J \beta_{(j)} \frac{n_1(j)}{N_{(j)}} \approx \sum_1^J \beta_{(j)} \int_{x_1^*}^{x_{i+1}^*} p(x)_{(j)} dx. \quad (119)$$

Weight fraction:

$$\frac{w'_1(j)}{w_{(j)}} \approx \int_{x_1^*}^{x_{i+1}^*} f_3(x)_{(j)} dx,$$

$$\frac{w'_1(M)}{w_{(M)}} = \sum_1^J \alpha_{(j)} \frac{w'_1(j)}{w_{(j)}} \approx \sum_1^J \alpha_{(j)} \int_{x_1^*}^{x_{i+1}^*} f_3(x)_{(j)} dx. \quad (120)$$

The statistics for a mixture whose component data are log normal in the form $n_1(j)/N_{(j)}$ vs d (microscope data) are developed using expressions (24), (25), (51), (53), (54), and (119), and a development of skewness for the mixture in terms of the mixed "sample" distribution of $x = \ln d$. The development is analogous to that for the nonfunctional model. The implication of the existence of a nonzero value for skewness of the mixed distribution of $x = \ln d$ will be discussed later.

Mean of x :

$$\begin{aligned} \bar{x}_{(M)} &\approx \hat{\mu}_{x(M)} \approx \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} x p(x)_{(j)} dx \right] \\ &\approx \sum_1^J \beta_{(j)} \hat{\mu}_{x(j)}. \end{aligned} \quad (121)$$

Variance of x :

$$s_{x(M)}^2 \approx \hat{\sigma}_{x(M)}^2 \approx \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (x - \mu_{x(M)})^2 p(x)_{(j)} dx \right]$$

$$\hat{\sigma}_{x(M)}^2 \approx \sum_1^J \beta_{(j)} \left[\hat{\sigma}_{x(j)}^2 + \hat{\mu}_{x(j)}^2 \right] - \left[\hat{\mu}_{x(M)} \right]^2. \quad (122)$$

Skewness of x:

$$\varepsilon_{x(M)} \approx \hat{\gamma}_{x(M)} \approx \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (x - \mu_{x(M)})^3 p(x)_{(j)} dx \right]$$

$$\hat{\gamma}_{x(M)} \approx \sum_1^J \beta_{(j)} \left[3 \left(\hat{\sigma}_{x(j)}^2 + \hat{\mu}_{x(j)}^2 \right) \left(\hat{\mu}_{x(j)} - \hat{\mu}_{x(M)} \right) - 2 \left(\hat{\mu}_{x(j)}^3 - \hat{\mu}_{x(M)}^3 \right) \right]. \quad (123)$$

$\hat{\gamma}_{x(M)}$ was developed as follows.

The skewness of the j^{th} component distribution is

$$\mu_{3x(j)} = \int_{-\infty}^{\infty} (x - \mu_{x(j)})^3 p(x)_{(j)} dx = 0, \quad (124)$$

since the distribution is normal in x; i.e., symmetric about $\mu_{x(j)}$. (Note that the third moment about the mean of x, $\mu_{3x} \neq \mu_{x3}$ the mean of the third moment vs x relationship.)

The expression for skewness of the mix

$$\gamma_{x(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (x - \mu_{x(M)})^3 p(x)_{(j)} dx \right]$$

when expanded gives

$$\gamma_{x(M)} = \sum_1^J \left[\beta_{(j)} \left\{ \int_{-\infty}^{\infty} x^3 p(x)_{(j)} dx - 3\mu_{x(M)} \int_{-\infty}^{\infty} x^2 p(x)_{(j)} dx + 2\mu_{x(M)}^3 \right\} \right].$$

Since the distribution of x is symmetric about μ_x ,

$$\mu_{3x(j)} = \int_{-\infty}^{\infty} x^3 p(x)_{(j)} dx - 3\mu_{x(j)} \int_{-\infty}^{\infty} x^2 p(x)_{(j)} dx + 2\mu_{x(j)}^3 = 0,$$

thus

$$\int_{-\infty}^{\infty} x^3 p(x)_{(j)} dx = 3\mu_{x(j)} \int_{-\infty}^{\infty} x^2 p(x)_{(j)} dx - 2\mu_{x(j)}^3,$$

where

$$\int_{-\infty}^{\infty} x^2 p(x)_{(j)} dx = \sigma_{x(j)}^2 + \mu_{x(j)}^2.$$

Then

$$\gamma_{x(M)} = \sum_1^J \beta_{(j)} \left[3\mu_{x(j)} \left(\sigma_{x(j)}^2 + \mu_{x(j)}^2 \right) - 2\mu_{x(j)}^3 - 3\mu_{x(M)} \left(\sigma_{x(j)}^2 + \mu_{x(j)}^2 \right) + 2\mu_{x(M)}^3 \right], \quad (125)$$

giving expression (123). Skewness of the mixed distribution of x can be obtained in this form because of the distribution symmetry about the respective values $\mu_{x(j)}$ of the component distributions.

Mean of d:

$$\bar{d}_{(M)} \approx \mu_{d(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} d p(x)_{(j)} dx \right] \approx \sum_1^J \beta_{(j)} \exp \left[\hat{\mu}_{x(j)} + 0.5 \hat{\sigma}_{x(j)}^2 \right]. \quad (126)$$

Variance of d:

$$\varepsilon_{d(M)}^2 \approx \mu_{2d(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (d - \mu_{d(M)})^2 p(x)_{(j)} dx \right] \approx \sum_1^J \beta_{(j)} \exp \left[2\hat{\mu}_{x(j)} + 2\hat{\sigma}_{x(j)}^2 \right] - \bar{d}_{(M)}^2. \quad (127)$$

Skewness of d:

$$\varepsilon_{d(M)} \approx \mu_{3d(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (d - \mu_{d(M)})^3 p(x)_{(j)} dx \right] \approx \sum_1^J \beta_{(j)} \exp \left[3\hat{\mu}_{x(j)} + 4.5 \hat{\sigma}_{x(j)}^2 \right] - 3\bar{d}_{(M)} \sum_1^J \beta_{(j)} \exp \left[2\hat{\mu}_{x(j)} + 2\hat{\sigma}_{x(j)}^2 \right] + 2\bar{d}_{(M)}^3. \quad (128)$$

The statistics for a mixture whose component sample data are log normal in the form w_1/W vs d (sieve or Micromerograph data) are developed in an analogous manner using expressions (29), (58), (79), (60), and (120).

Mean of x:

$$\hat{\mu}_{x3(M)} \approx \sum_1^J \left[\alpha_{(j)} \int_{-\infty}^{\infty} x f_3(x)_{(j)} dx \right] \approx \sum_1^J \alpha_{(j)} \hat{\mu}_{x3(j)}. \quad (129)$$

Variance of x:

$$\hat{\sigma}_{x3(M)}^2 \approx \sum_1^J \left[\alpha_{(j)} \int_{-\infty}^{\infty} (x - \mu_{x3(M)})^2 f_3(x)_{(j)} dx \right] \approx \sum_1^J \alpha_{(j)} \left[\hat{\sigma}_{x(j)}^2 + \hat{\mu}_{x3(j)}^2 \right] - \hat{\mu}_{x3(M)}^2. \quad (130)$$

Skewness of x:

$$\begin{aligned}\hat{\gamma}_{x3(M)} &\approx \sum_1^J \left[\alpha_{(j)} \int_{-\infty}^{\infty} (x - \mu_{x3(M)})^3 f_3(x)_{(j)} dx \right] \\ \hat{\gamma}_{x3(M)} &\approx \sum_1^J \alpha_{(j)} \left[3 \left(\hat{\sigma}_{x(j)}^2 + \hat{\mu}_{x3(j)}^2 \right) \left(\hat{\mu}_{x3(j)} - \hat{\mu}_{x3(M)} \right) \right. \\ &\quad \left. - 2 \left(\hat{\mu}_{x3(j)}^3 - \hat{\mu}_{x3(M)}^3 \right) \right].\end{aligned}\quad (131)$$

Mean of d:

$$\begin{aligned}\bar{d}_{3(M)} &\approx \mu_{d3(M)} = \sum_1^J \left[\alpha_{(j)} \int_{-\infty}^{\infty} d f_3(x)_{(j)} dx \right] \\ &\approx \sum_1^J \alpha_{(j)} \exp \left[\hat{\mu}_{x3(j)} + 0.5 \hat{\sigma}_{x(j)}^2 \right]\end{aligned}\quad (132)$$

Variance of d:

$$\begin{aligned}s_{d3(M)}^2 &\approx \mu_{2d3(M)} = \sum_1^J \left[\alpha_{(j)} \int_{-\infty}^{\infty} (d - \mu_{d3(M)})^2 f_3(x)_{(j)} dx \right] \\ s_{d3(M)}^2 &\approx \sum_1^J \alpha_{(j)} \exp \left[2\hat{\mu}_{x3(j)} + 2 \hat{\sigma}_{x(j)}^2 \right] - \bar{d}_{3(M)}^2.\end{aligned}\quad (133)$$

Skewness of d:

$$\begin{aligned}s_{d3(M)} &\approx \mu_{3d3(M)} = \sum_1^J \left[\alpha_{(j)} \int_{-\infty}^{\infty} (d - \mu_{d3(M)})^3 f_3(x)_{(j)} dx \right] \\ s_{d3(M)} &\approx \sum_1^J \alpha_{(j)} \exp \left[3\hat{\mu}_{x3(j)} + 4.5 \hat{\sigma}_{x(j)}^2 \right] \\ &\quad - 3\bar{d}_{3(M)} \sum_1^J \alpha_{(j)} \\ &\quad \exp \left[2\hat{\mu}_{x3(j)} + 2 \hat{\sigma}_{x(j)}^2 \right] + 2\bar{d}_{3(M)}^3.\end{aligned}\quad (134)$$

The statistics for a mixture whose component sample data are log normal sample distributions of v (Coulter Counter data, $n_{i(j)}/N_{(j)}$ vs v) are developed using expressions (42), (55), (56), and (57) in a manner similar to the development of expressions (121) through (128).

Mean of z_3 :

$$\begin{aligned}\bar{z}_{3(M)} &\approx \hat{\mu}_{z3(M)} \approx \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} z_3 p(z_3)_{(j)} dz_3 \right] \\ \hat{\mu}_{z3(M)} &\approx \sum_1^J \beta_{(j)} \hat{\mu}_{z3(j)}.\end{aligned}\quad (135)$$

Variance of z_3 :

$$\begin{aligned}s_{z3(M)}^2 &\approx \hat{\sigma}_{z3(M)}^2 \approx \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (z_3 - \mu_{z3(M)})^2 p(z_3)_{(j)} dz_3 \right] \\ \hat{\sigma}_{z3(M)}^2 &\approx \sum_1^J \beta_{(j)} \left[\hat{\sigma}_{z3(j)}^2 + \hat{\mu}_{z3(j)}^2 \right] - \hat{\mu}_{z3(M)}^2.\end{aligned}\quad (136)$$

Skewness of z_3 :

$$\begin{aligned}s_{z3(M)} &\approx \hat{\gamma}_{z3(M)} \approx \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (z_3 - \mu_{z3(M)})^3 p(z_3)_{(j)} dz_3 \right] \\ \hat{\gamma}_{z3(M)} &\approx \sum_1^J \beta_{(j)} \left[3 \left(\hat{\sigma}_{z3(j)}^2 + \hat{\mu}_{z3(j)}^2 \right) \left(\hat{\mu}_{z3(j)} - \hat{\mu}_{z3(M)} \right) \right. \\ &\quad \left. - 2 \left(\hat{\mu}_{z3(j)}^3 - \hat{\mu}_{z3(M)}^3 \right) \right].\end{aligned}\quad (137)$$

Mean of v:

$$\begin{aligned}\bar{v}_{(M)} &\approx \mu_{v(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} v p(z_3)_{(j)} dz_3 \right] \\ &\approx \sum_1^J \beta_{(j)} \exp \left[\hat{\mu}_{z3(j)} + 0.5 \hat{\sigma}_{z3(j)}^2 \right].\end{aligned}\quad (138)$$

Variance of v:

$$\begin{aligned}s_{v(M)}^2 &\approx \mu_{2v(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (v - \mu_{v(M)})^2 p(z_3)_{(j)} dz_3 \right] \\ s_{v(M)}^2 &\approx \sum_1^J \beta_{(j)} \exp \left[2\hat{\mu}_{z3(j)} + 2\hat{\sigma}_{z3(j)}^2 \right] - \bar{v}_{(M)}^2.\end{aligned}\quad (139)$$

Skewness of v:

$$\begin{aligned}s_{v(M)} &\approx \mu_{3v(M)} = \sum_1^J \left[\beta_{(j)} \int_{-\infty}^{\infty} (v - \mu_{v(M)})^3 p(z_3)_{(j)} dz_3 \right] \\ s_{v(M)} &\approx \sum_1^J \beta_{(j)} \exp \left[3\hat{\mu}_{z3(j)} + 4.5 \hat{\sigma}_{z3(j)}^2 \right] \\ &\quad - 3\bar{v}_{(M)} \sum_1^J \beta_{(j)} \exp \left[2\hat{\mu}_{z3(j)} + 2\hat{\sigma}_{z3(j)}^2 \right] + 2\bar{v}_{(M)}^3.\end{aligned}\quad (140)$$

The computational methods for mixtures whose component sample data can be represented by a log normal function illustrate the following concepts:

1. The statistics computed for the mixture are independent of a functional description of the mixture. The computational methods are dependent only on the log normality of the component sample data.
2. Since $\sigma_{x(j)}^2 \equiv \sigma_{x3(j)}^2$ for a log normal function, the approximation $\hat{\sigma}_{x3(j)}^2 \approx \hat{\sigma}_{x(j)}^2$ can be used in the computations.

3. The existence of nonzero values for $\hat{\gamma}_{x(M)}$, $\hat{\gamma}_{x3(M)}$ and $\hat{\gamma}_{x2(M)}$ has been indicated. This shows that a mixture of components whose sample data are log normal does not in general result in a log normal "size" distribution for the mixture.
4. In general, $\hat{\sigma}_{x(M)}^2 \neq \hat{\sigma}_{x3(M)}^2$, because $\sigma_{x(M)}^2 \neq \sigma_{xk(M)}^2$.

The statistics computed for the mixture by methods of this section are valid, definitive statistics for the mix and can be readily used for data comparison as will be shown in the next section. There are other statistics, such as particle surface area and particle volume, which can be computed for the mixture on the basis of log normality of the components independent of a functional description of the mixture distribution. However, the convenience of ascribing log normal properties to the mixture is often tempting to an experimenter, and, in some cases surprisingly valid. The following tests can be used to indicate the "nonlog normality" of a mixture.

1. Test for Bimodal Distribution

A study of the conditions for which the mixture of two normal distributions results in a bimodal distribution has been accomplished by Isidore Eisenberger.³¹ He developed tests for sufficient condition for unimodality, sufficient condition for bimodality, and methods for estimating the mixing fraction range resulting in bimodality for binary mixtures. Two important results of Eisenberger's work can be used easily to check for nonlog normality of mixtures.

Sufficient condition that the mixture of two log normal sample distributions be unimodal for all values of β , $0 < \beta < 1.0$ is

$$(\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)})^2 < \frac{27\hat{\sigma}_{x(1)}^2 \hat{\sigma}_{x(2)}^2}{4(\hat{\sigma}_{x(1)}^2 + \hat{\sigma}_{x(2)}^2)} \quad (141)$$

Sufficient condition that values of β exist, $0 < \beta < 1$, such that the mixture is bimodal:

$$(\hat{\mu}_{x(2)} - \hat{\mu}_{x(1)}) > \frac{8\hat{\sigma}_{x(1)}^2 \hat{\sigma}_{x(2)}^2}{\hat{\sigma}_{x(1)}^2 + \hat{\sigma}_{x(2)}^2} \quad (142)$$

2 Test for Skewness

A very powerful test for nonlog normality of a particular mixture of two log normal sample

distributions is the use of expression (123). A nonzero value for $\hat{\gamma}_{x(M)}$ indicates that the log normal function would not adequately describe the mixture. The signed value of $\hat{\gamma}_{x(M)}$ indicates the direction and magnitude of the skewness. The experimenter must decide how large a value of $\hat{\gamma}_{x(M)}$ can be tolerated and still utilize the log normal model. This test can be used for mixtures containing any number, J , components.

Comparison of Sample Statistics for Powder Mixtures

The concepts involved in comparing statistics for mixtures are the same as the concepts previously discussed for comparing unmixed powders. The methods used for converting mixture statistics obtained in one form to another for sample comparison are discussed from the standpoint of whether or not a functional model has been used to describe the components. To clarify the problem, consider the hypothetical example in which an investigator wants to compare statistics for a set of mixtures of powders A and B, computed from mix component sample data obtained from Coulter Counter (Type I) measurements, with statistics for powder C whose particle "size" data were obtained as third moment or weight fraction vs d (Type II). The investigator is faced with two problems. First, the weight mixing fraction $\alpha_{(j)}$ must be converted to $\beta_{(j)}$ so that statistics can be computed for the mixed Coulter Counter (n_1/N vs v) data. Second, the interval end points, and fractions of occurrence in the interval, w_1'/w or n_1/N , must be converted to the same type. In general, the best procedure would be to convert all sets of data to Type I, i.e., n_1/N vs "size," and compute statistics for comparison on this basis.

Nonfunctional Model

The conversions between $\alpha_{(j)}$ and $\beta_{(j)}$ can be derived using the definitions $w_1'(j) \approx \rho_{(j)} C_3(j) \left(\frac{n_1(j)}{N(j)}\right) d_{M1}^3$. Mellor's d is used rather than d_1 because it more precisely estimates the particle d corresponding to the average particle weight in the interval. The conversions are written as follows:

$$\alpha_{(j)} \sim \frac{\beta_{(j)} \sum_1^I \rho_{(j)} C_3(j) \left(\frac{n_1(j)}{N(j)}\right) d_{M1}^3}{\sum_1^J \left[\beta_{(j)} \sum_1^I \rho_{(j)} C_3(j) \left(\frac{n_1(j)}{N(j)}\right) d_{M1}^3 \right]} \quad (143)$$

$$\beta_{(j)} \approx \frac{\alpha_{(j)} \sum_1^I \left(\frac{w_1^i(j)}{w_{(j)}} \right) \frac{1}{\rho_{(j)} C_3(j) d_{M1}^3}}{\sum_1^J \left[\alpha_{(j)} \sum_1^I \left(\frac{w_1^i(j)}{w_{(j)}} \right) \frac{1}{\rho_{(j)} C_3(j) d_{M1}^3} \right]} \quad (144)$$

The main use of the $\beta_{(j)} \leftrightarrow \alpha_{(j)}$ conversion is in computing statistics for mixtures using expressions (105) through (118). For example, $\bar{d}_{(M)}$ is computed for a mixture of powders in terms of $\alpha_{(j)}$ using Eq. (106) with $\beta_{(j)}$ defined as in expression (144). The sample data for each component have been obtained in the form n_1/N vs d , therefore $w_1^i(j)$ and $w_{(j)}$ are estimated using the expression $w_1^i(j) \approx n_1(j) \rho_{(j)} C_3(j) d_{M1}^3$. The expression for $\bar{d}_{(M)}$ can then be written

$$\bar{d}_{(M)} \approx \sum_1^J \left[\frac{\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j) \rho_{(j)} C_3(j) d_{M1}^3)} \right]}{\sum_1^J \left[\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j) \rho_{(j)} C_3(j) d_{M1}^3)} \right] \right]} \right] \bar{d}_{(j)}. \quad (145)$$

Expressions (108) and (110) can be written in terms of the weight mixing fraction $\alpha_{(j)}$ by substituting the coefficient of $\bar{d}_{(j)}$ in expression (145) for $\beta_{(j)}$.

Because of the complexity of the coefficient $\bar{d}_{(j)}$ in expression (145) and the complexity of subsequent expressions involving transformation of data forms, a convenient notation will be adopted. Expression (145) will be written as,

$$\bar{d}_{(M)} \approx \sum_1^J \beta_{(j)} (\alpha_{(j)}, 0, II) \bar{d}_{(j)}, \quad (146)$$

where $\beta_{(j)} (\alpha_{(j)}, 0, II)$ indicates that $\beta_{(j)}$ is computed from expression (144) as a function of $\alpha_{(j)}$ for zero-order Type II, i.e., microscopic count data.

In the development of the expression for $\beta_{(j)}$ for use in Eqs. (116), (117), and (118), i.e., statistics from Coulter Counter data, care must be used in determining d_{M1}^3 for use in estimating $w_{(j)}$. Recall that

$$d_1^* = \left(\frac{v_1^*}{C_3} \right)^{\frac{1}{3}}$$

Then, from Eq. (73),

$$d_{M1}^3 \approx \frac{(v_{1+1}^{*2} + v_{1-1}^{*2}) (v_{1+1}^{*1} + v_{1-1}^{*1})}{4C_3}. \quad (147)$$

The volume of a particle having diameter d_{M1} is then defined as

$$v_{M1(j)} = C_3(j) d_{M1}^3, \quad (148)$$

and $w_{(j)}$ can be estimated as

$$w_{(j)} \approx \sum_1^I n_1(j) \rho_{(j)} v_{M1(j)}. \quad (149)$$

Note that although d_{M1} is the same for all j components, v_{M1} may differ, because the shape factor C_3 need not be the same for all components; therefore $v_{M1(j)}$ is introduced for the approximation (143). Substituting (149) in (145), Eqs. (116), (117), and (118) may be written using $\beta_{(j)}$ in the form

$$\beta_{(j)} = \beta_{(j)} (\alpha_{(j)}, 3, I)$$

$$\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j) \rho_{(j)} v_{M1(j)})} \right] \approx \sum_1^J \left[\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j) \rho_{(j)} v_{M1(j)})} \right] \right] \beta_{(j)} (\alpha_{(j)}, 3, I), \quad (150)$$

where $\beta_{(j)} (\alpha_{(j)}, 3, I)$ indicates that $\beta_{(j)}$ is computed from expression (144) as a function of $\alpha_{(j)}$ for third power Type I (i.e., Coulter Counter) data. For example, Eq. (116) is written

$$\bar{v}_{(M)} \approx \sum_1^J \beta_{(j)} (\alpha_{(j)}, 3, I) \bar{v}_{(j)}.$$

The problem of comparison of sample statistics computed for mixtures whose components have been measured by different types of devices can be approached in several ways depending on the methods by which the mixture statistics are computed. Table XIII shows one approach to transforming data and computation of statistics for comparison. We prefer this approach because the sample data are directly used to compute transformed statistics in the form of zero-order Type II which is equivalent to first-power Type I data (i.e., microscopic count data).

This approach is consistent with the previous discussion on comparison of sample statistics.

The conversion functions for $\beta_{(j)}$ and $n_{1(M)}/N_{(M)}$ given in Table XIII are based on the following relationships. The approximation

$$W_{(j)} \approx N_{(j)} \sum_1^I p_{(j)} C_{3(j)} d_{M1}^3 \frac{n_{1(j)}}{N_{(j)}}$$

TABLE XIII

Expressions for Computing Statistics for Comparison of Mixtures -- Nonfunctional

Compared Statistic	Type of Data		
	(1,I) or (0,II) (n_1/N vs d)	(3,II) (w_1^1/W vs d)	(3,I) (n_1/N vs $C_3 d = v$)
$\bar{d}_{(M)} \approx$	$\sum_1^J \beta_{(j)}(\alpha_{(j)}, 0, II) \bar{d}_{(j)}$	$\sum_1^I \left[\frac{n_{1(M)}}{N_{(M)}} (\alpha_{(j)}, 3, II) \bar{d}_1 \right]$	$\sum_1^I \left[\frac{n_{1(M)}}{N_{(M)}} (\alpha_{(j)}, 3, I) \right] \times \frac{[(v_1^*)^{\frac{1}{3}} + (v_{i+1}^*)^{\frac{1}{3}}]}{2}$
$s_{d(M)}^2 \approx$	$\sum_1^J \beta_{(j)}(\alpha_{(j)}, 0, II) [s_{d(j)}^2 + \bar{d}_{(j)}^2] - (\bar{d}_{(M)})^2$	$\sum_1^I \left[\frac{n_{1(M)}}{N_{(M)}} (\alpha_{(j)}, 3, II) \right] d_1^2 - \bar{d}_{(M)}^2$	$\sum_1^I \left[\frac{n_{1(M)}}{N_{(M)}} (\alpha_{(j)}, 3, I) \right] \times \frac{[(v_1^*)^{\frac{1}{3}} + (v_{i+1}^*)^{\frac{1}{3}} - 2\bar{d}_{(M)}]^2}{4}$
$u_{d(M)} \approx$	$\sum_1^J \beta_{(j)}(\alpha_{(j)}, 0, II) m_{3(j)}^1 - \left[\sum_1^J \beta_{(j)}(\alpha_{(j)}, 0, II) m_{2(j)}^1 \right] \bar{d}_{(M)} + 2 [\bar{d}_{(M)}]^3$	$\sum_1^I \left[\frac{n_{1(M)}}{N_{(M)}} (\alpha_{(j)}, 3, II) \right] (d_1 - \bar{d}_{(M)})^3$	$\sum_1^I \left[\frac{n_{1(M)}}{N_{(M)}} (\alpha_{(j)}, 3, I) \right] \times \frac{[(v_1^*)^{\frac{1}{3}} + (v_{i+1}^*)^{\frac{1}{3}} - 2\bar{d}_{(M)}]^3}{8}$

TABLE XIII (Continued)

Note:

$$\beta_{(j)}(\alpha_{(j)}, 0, II) \approx \frac{\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j)^{\rho(j)} c_3(j) d_{M1}^3)} \right]}{\sum_1^I \left[\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j)^{\rho(j)} c_3(j) d_{M1}^3)} \right] \right]}$$

$$\frac{n_1(M)}{N(M)} (\alpha_{(j)}, 3, II) \approx \frac{\sum_1^J \alpha_{(j)} \left(\frac{w'_1(j)}{W(j)} \right) \left[\frac{1}{\rho(j) c_3(j) d_{M1}^3} \right]}{\sum_1^J \alpha_{(j)} \left[\sum_1^I \left(\frac{w'_1(j)}{W(j)} \right) \left(\frac{1}{\rho(j) c_3(j) d_{M1}^3} \right) \right]}$$

and

$$\frac{n_1(M)}{N(M)} (\alpha_{(j)}, 3, I) \approx \frac{\sum_1^J \left[\frac{\alpha_{(j)} n_1(j)}{\sum_1^I n_1(j)^{\rho(j)} v_{M1}(j)} \right]}{\sum_1^J \left[\frac{\alpha_{(j)} N(j)}{\sum_1^I n_1(j)^{\rho(j)} v_{M1}(j)} \right]}$$

holds for all values of $W(j)$ provided that the sample of weight $W(j)$ is representative, that is, $n_1(j)/N(j)$ is constant for any value of $W(j)$. Then the following relationships can be written:

$$\frac{W(j) \text{ obs.}}{W(j) \text{ act.}} \approx \frac{N(j) \text{ obs.}}{N(j) \text{ act.}} \quad (150a)$$

$$\frac{n_1(j) \text{ obs.}}{N(j) \text{ obs.}} = \left(\frac{n_1}{N_1} \right)_{(j) \text{ obs.}} \approx \frac{n_1(j) \text{ act.}}{N(j) \text{ act.}} \quad (150b)$$

$$\frac{w'_1(j) \text{ obs.}}{W(j) \text{ obs.}} = \left(\frac{w'_1}{W} \right)_{(j) \text{ obs.}} \approx \frac{w'_1(j) \text{ act.}}{W(j) \text{ act.}} \quad (150c)$$

and from (150a) and (150b)

$$\left(\frac{n_1}{W} \right)_{(j) \text{ obs.}} \approx \frac{n_1(j) \text{ act.}}{W(j) \text{ act.}}, \quad (150d)$$

where obs. pertains to the observations on the sample from the j^{th} component and act. pertains to the

values of n_1 , w'_1 , etc., actually existing in weight $W(j)$. For example, the definition of $\beta_{(j)}(\alpha_{(j)}, 0, II)$ can be verified using (150d). Since

$$\frac{n_1(j)}{\sum_1^I \rho(j) c_3(j) n_1(j) d_{M1}^3} \approx \left(\frac{n_1}{W} \right)_{(j) \text{ obs.}} \approx \frac{n_1(j) \text{ act.}}{W(j) \text{ act.}}$$

and

$$\alpha_{(j) \text{ act.}} = \frac{W(j) \text{ act.}}{W(M) \text{ act.}}$$

$$\beta_{(j)}(\alpha_{(j)}, 0, II) = \frac{\frac{W(j) \text{ act.} \times N(j) \text{ act.}}{W(M) \text{ act.} \times W(j) \text{ act.}}}{\sum_1^I \left[\frac{W(j) \text{ act.} \times N(j) \text{ act.}}{W(M) \text{ act.} \times W(j) \text{ act.}} \right]} \approx \frac{N(j)}{N(M)}$$

Log Normal Model

Conversions between $\alpha_{(j)}$ and $\beta_{(j)}$ are derived using the following definitions with proper attention to units,

$$W(j) \approx N(j) \rho(j) c_3(j) \int_{-\infty}^{\infty} d^3 p(x)_{(j)} dx$$

$$\approx N(j) \rho(j) c_3(j) \exp \left[3 \hat{\mu}_{x3(j)} + 4.5 \hat{\sigma}_{x3(j)}^2 \right], \quad (151)$$

$$N(j) \approx \frac{W(j)}{\rho(j) c_3(j)} \int_{-\infty}^{\infty} \frac{f_3(x)_{(j)} dx}{d^3}$$

$$\approx \frac{W(j)}{\rho(j) c_3(j)} \exp \left[-(3 \hat{\mu}_{x3(j)} - 4.5 \hat{\sigma}_{x3(j)}^2) \right]. \quad (152)$$

Thus, by dividing the numerator and denominator of the expression for $\beta(j)$ by $W(M)$ and substituting (152) for $N(j)$, $\beta(j)$ can be written as a function of $\alpha(j)$ and the sample statistics for third moment data as

$$\rho(j) = \frac{\frac{N(j)}{W(M)}}{\sum_1 \frac{N(j)}{W(M)}} = \frac{\frac{\alpha(j)}{\rho(j) c_3(j)} \exp \left[-(3 \hat{\mu}_{x3(j)} - 4.5 \hat{\sigma}_{x3(j)}^2) \right]}{\sum_1 \frac{\alpha(j)}{\rho(j) c_3(j)} \exp \left[-(3 \hat{\mu}_{x3(j)} - 4.5 \hat{\sigma}_{x3(j)}^2) \right]} \quad (153)$$

The weight mixing fraction, $\alpha(j)$, can be written as a function of $\beta(j)$ and statistics computed for Type (0,II) or (1,I) data by using expression (151) in the definition of $\alpha(j)$ as

$$\alpha(j) = \frac{\frac{W(j)}{N(M)}}{\sum_1 \frac{W(j)}{N(M)}} = \frac{\rho(j) c_3(j) \beta(j) \exp \left[3 \hat{\mu}_{x3(j)} + 4.5 \hat{\sigma}_{x3(j)}^2 \right]}{\sum_1 \rho(j) c_3(j) \beta(j) \exp \left[3 \hat{\mu}_{x3(j)} + 4.5 \hat{\sigma}_{x3(j)}^2 \right]} \quad (154)$$

Notice the similarity of expressions (153) and (154) to expressions (143) and (144). The expressions under the summation $\sum$ in (143) and (144) have been replaced with appropriate moment forms

$$\int_{-\infty}^{\infty} e^{3x} p(x) dx$$

and

$$\int_{-\infty}^{\infty} e^{-3x} f_3(x) dx$$

in (153) and (154). Also, expressions (153) and (154) are not dependent upon a functional model for the mix.

Table XIV summarizes the expressions for use in comparison of statistics for mixtures whose component sample data are log normal. Notice that in all

cases, the statistics computed from the various forms of data are transformed to (1,I) for purposes of comparison. This is not a necessary statistical requirement, because the component sample data are log normal, and any consistent sets of computed statistics can be used for comparison. However, for simplicity and consistency with previously described techniques for comparison, transformations to Type (1,I) statistics are used.

The expressions given in Table XIV are dependent only upon the assumption that the sample data of the components can be represented by a log normal function. The expressions do not imply the existence of a log normal model or any functional model describing the mix other than expressions (119) and (120).

The importance of using proper methods for computing statistics for a mixture is illustrated by Figs. 8 and 9. Although $F_3(x)_{(M)}$, the theoretical mix of the two log normal functions, is not log normal, a log normal function approximated by $\hat{\mu}_{x3(M)}$ and $\hat{\sigma}_{x3(M)}^2$ is often a good representation of the theoretical mix as shown in Fig. 8. The sample data obtained by centrifuge analysis and the appropriate $F_3(x)$ log normal representations are shown in Fig. 9 for two graphite powder samples. Figure 9 illustrates the agreement between the theoretical mix, $F_3(x)_{(M)}$, the computed log normal approximation, centrifuge data from measurements made on the mix, and results of proper and improper methods of estimating the Type (0,II) conversion of the sample data. A quantitative measure of the inadequacy of a log normal approximation using $\hat{\mu}_{x3(M)}$ and $\hat{\sigma}_{x3(M)}^2$ to represent $F_3(x)_{(M)}$ can be obtained by computing $\hat{\gamma}_{x3(M)}$ from expression (131), realizing that $\gamma_{x3} = 0$ for a log normal function.

The log normal representation for the mixture $F_3(x)_{(M)}$ must not be used in computations of estimates of transformed statistics. There are two basic reasons why the general Type (k,I) and (k,II) statistics for a mixture cannot be obtained using the log normal relationships among $\hat{\mu}_{xk}$, $\hat{\mu}_{zk}$, $\hat{\sigma}_{xk}^2$, and $\hat{\sigma}_{zk}^2$, e.g., $\hat{\mu}_{x(M)}$ is not approximated by $\hat{\mu}_{x3(M)}$ - $3\hat{\sigma}_{x3(M)}^2$. The first reason is that the mixture of two log normal functions cannot be log normal. The second is that mixture statistics obtained for $\sum_1 \alpha(j) F_k(x)_{(j)}$ or $\sum_1 \alpha(j) P(z_k)_{(j)}$, i.e., weight mixing, can be related to statistics for $\sum_1 \beta(j) F_k(x)_{(j)}$

TABLE XIV

Expressions for Comparing Statistics for Mixtures -- Functional Model

(1,I) Statistics	Component Data Type			
	(k,I)	(3,I)	(k,II)	(3,II)
$\hat{\mu}_{x(M)} \sim$	$\frac{1}{k} \sum_j \beta_{(j)}(\alpha_{(j)}, k, I) [\hat{\mu}_{z_k(j)} - \ln c_{k(j)}]$	For Coulter Counter data $k = 3$, use (k,I) forms	$\sum_j \beta_{(j)}(\alpha_{(j)}, k, II) [\hat{\mu}_{xk(j)} - k \hat{\sigma}_{x(j)}^2]$	For Micromerograph (Sieve, Sedibal) data $k = 3$, use (k,II) forms
$\hat{\sigma}_{x(M)}^2 \sim$	$\frac{1}{k^2} \left[\sum_j \beta_{(j)}(\alpha_{(j)}, k, I) \left[(\hat{\mu}_{z_k(j)} - \ln c_{k(j)})^2 - \hat{\sigma}_{z_k(j)}^2 \right] \right] - [\hat{\mu}_{x(M)}]^2$		$\sum_j \beta_{(j)}(\alpha_{(j)}, k, II) \left[(\hat{\mu}_{xk(j)} - k \hat{\sigma}_{x(j)}^2)^2 + \hat{\sigma}_{x(j)}^2 \right] - [\hat{\mu}_{x(M)}]^2$	
$\hat{\gamma}_{x(M)} \sim$	$\sum_j \beta_{(j)}(\alpha_{(j)}, k, I) \left\{ 3 \left[\frac{\hat{\sigma}_{z_k(j)}^2 + (\hat{\mu}_{z_k(j)} - \ln c_{k(j)})^2}{k^2} \right] \right.$ $\times \left[\frac{(\hat{\mu}_{z_k(j)} - \ln c_{k(j)})}{k} - \hat{\mu}_{x(M)} \right] - \left[\frac{(\hat{\mu}_{z_k(j)} - \ln c_{k(j)})^3}{k^3} \right.$ $\left. \left. - (\hat{\mu}_{x(M)})^3 \right] \right\}$		$\sum_j \beta_{(j)}(\alpha_{(j)}, k, II) \left\{ 3 \left[(\hat{\mu}_{xk(j)} - k \hat{\sigma}_{x(j)}^2)^2 + \hat{\sigma}_{x(j)}^2 \right] \right.$ $\times \left[\hat{\mu}_{xk(j)} - (\hat{\mu}_{x(M)} + k \hat{\sigma}_{x(j)}^2) \right] - 2 \left[(\hat{\mu}_{xk(j)} - k \hat{\sigma}_{x(j)}^2)^3 \right.$ $\left. \left. - (\hat{\mu}_{x(M)})^3 \right] \right\}$	
$\bar{a}_{(M)} \sim$	$\sum_j \beta_{(j)}(\alpha_{(j)}, k, I) \exp \left[\frac{\hat{\mu}_{z_k(j)} - \ln c_{k(j)}}{k} + \frac{.5 \hat{\sigma}_{z_k(j)}^2}{k^2} \right]$		$\sum_j \beta_{(j)}(\alpha_{(j)}, k, II) \exp \left[\hat{\mu}_{xk(j)} + (.5 - k) \hat{\sigma}_{x(j)}^2 \right]$	
$\bar{a}_{(M)}^2 \sim$	$\sum_j \beta_{(j)}(\alpha_{(j)}, k, I) \exp \left[2 \left(\frac{\hat{\mu}_{z_k(j)} - \ln c_{k(j)}}{k} + \frac{\hat{\sigma}_{z_k(j)}^2}{k^2} \right) \right] - [\bar{a}_{(M)}]^2$		$\sum_j \beta_{(j)}(\alpha_{(j)}, k, II) \exp \left[2 (\hat{\mu}_{xk(j)} + (1 - k) \hat{\sigma}_{x(j)}^2) \right] - \bar{a}_{(M)}^2$	
$\bar{a}_{(M)}^3 \sim$	$\sum_j \beta_{(j)}(\alpha_{(j)}, k, I) \exp \left[\frac{3(\hat{\mu}_{z_k(j)} - \ln c_{k(j)})}{k} + \frac{4.5 \hat{\sigma}_{z_k(j)}^2}{k^2} \right]$ $- 3 \bar{a}_{(M)} \bar{a}_{(M)}^2 - \bar{a}_{(M)}^3$		$\sum_j \beta_{(j)}(\alpha_{(j)}, k, II) \exp \left[3 \hat{\mu}_{xk(j)} + (4.5 - 3k) \hat{\sigma}_{x(j)}^2 \right]$ $- 3 \bar{a}_{(M)} \bar{a}_{(M)}^2 - \bar{a}_{(M)}^3$	

Note: For the functional model, $\beta_{(j)}(\alpha_{(j)}, k, I) = \frac{\alpha_{(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\frac{\hat{\mu}_{z_k(j)} - 3 \ln c_{k(j)}}{k} + \frac{4.5 \hat{\sigma}_{z_k(j)}^2}{k^2} \right) \right]$

$$\sum_j \frac{\alpha_{(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\frac{\hat{\mu}_{z_k(j)} - 3 \ln c_{k(j)}}{k} + \frac{4.5 \hat{\sigma}_{z_k(j)}^2}{k^2} \right) \right]$$

and,

$$\beta_{(j)}(\alpha_{(j)}, k, II) = \frac{\alpha_{(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- (\hat{\mu}_{xk(j)} + (4.5 - 3k) \hat{\sigma}_{x(j)}^2) \right]$$

$$\sum_j \frac{\alpha_{(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- (\hat{\mu}_{xk(j)} + (4.5 - 3k) \hat{\sigma}_{x(j)}^2) \right]$$

or $\sum_j \beta_{(j)} P(z_k)_{(j)}$, i.e., frequency mixing, only through use of the relationships $\alpha_{(j)}(\beta_{(j)}, k, I)$ and $\beta_{(j)}(\alpha_{(j)}, k, II)$. For example, the result of using the improper method of estimating $\hat{\mu}_{x(M)}$ and $\hat{\sigma}_{x(M)}^2$ from $F_3(x)_{(M)}$ obtained from log normal data in the form $\sum_j \alpha_{(j)} F_3(x)_{(j)}$ is also shown in Fig. 9. The proper method of obtaining the function $P(x)_{(M)}$ describing the mixture is by point by point integration, i.e.,

$$P(x)_{(M)} = \sum_j \beta_{(j)}(\alpha_{(j)}, 3, II) \int_{-\infty}^x p(x)_{(j)} dx,$$

where $p(x)_{(j)}$ is related to $f_3(x)_{(j)}$ through the relationships $\hat{\mu}_x \approx \hat{\mu}_{x3} - 3 \hat{\sigma}_{x3}^2$ and $\hat{\sigma}_x^2 \approx \hat{\sigma}_{x3}^2$.

This function is defined by the points enclosed in triangles in Fig. 9, and the statistics are computed by the methods of Table XIV. A log normal function approximated by $\hat{\mu}_{x(M)}$ and $\hat{\sigma}_{x(M)}^2$ is often a good representation of $P(x)_{(M)}$. However, as in the case of approximating $F_3(x)_{(M)}$, the skewness $\hat{\gamma}_{x(M)}$ should be considered as a measure of the inadequacy of the log normal approximation.

The computations for comparison of sample statistics (Tables XIII and XIV) are simplified somewhat if the assumption can be made that the densities and/or shape factors are respectively equal for all components of a particular mixture. For example, the computational form for $\beta_{(j)}(\alpha_{(j)}, 0, II)$ in Table XIII becomes,

Fig. 8. Log normal approximation for a mixture.

Fig. 9. Transformed data for a mixture.

$$\beta_{(j)}(\alpha_{(j)}, 0, II) \approx \frac{\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j) a_{M1}^3)} \right]}{\sum_j^J \left[\alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I (n_1(j) a_{M1}^3)} \right] \right]} \quad (155)$$

No attempt is made here to show the general development of techniques for estimating statistics for component powders from measurements made on a mixture. We plan to develop this theory in the future. A treatment for the special case of mixtures of normal distributions is given by Hald.²¹

Estimation of Geometric Properties of Powder Mixtures:
(Surface Area and Volume in the Interval (r_1, r_2))

The expressions for estimating particle surface area, volume, etc., for powder mixtures are given in Tables XV, XVI, and XVII for nonfunctional and functional data descriptions. The assumption is made that the particles are smooth shell, nonporous bodies as in the previous section for single-component powders. The derivations of the expression in Table XV and XVI require use of the relationships given in (150a), (150b), (150c), and (150d) and the definitions of d_{L1} and d_{M1} , respectively, given in (85) and (147).

The advantages of estimating these characteristics of mixtures through computation based on component statistics are the same as the advantages in computing the defining sample distribution statistics for a mixture. That is, (1) the necessity of performing actual measurements on a mixture is eliminated, (2) the computed estimates may be more accurate than measurements made on the mix, e.g., when component sample data are log normal, and (3) the component sample distribution means and variances and component particle densities may differ such that the resultant mixture is not amenable to measurement.

TABLE XV

Nonfunctional Estimates of Particle Surface Area, Weight, and Volume

	Type of Data		
	(1,I) or (0,II) n_1/N vs d	(3,II) v_1/w vs d	(3,I) n_1/N vs v
$N_{(M)} \approx$	$w_{(M)} \sum_1^J \alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I n_1(j) \rho_{(j)} c_{3(j)} d_{M1}^3} \right] \times 10^{12}$	$w_{(M)} \sum_1^J \alpha_{(j)} \left[\sum_1^I \left(\frac{v_1}{w} \right)_{(j)} \frac{1}{\rho_{(j)} c_{3(j)} d_{M1}^3} \right] \times 10^{12}$	$w_{(M)} \sum_1^J \alpha_{(j)} \sum_1^I \left[\frac{n_1(j)}{\sum_1^I n_1(j) \rho_{(j)} v_{M1}(j)} \right] \times 10^{12}$
$A_{(M)}(\text{cm}^2) \approx$	$w_{(M)} \sum_1^J \alpha_{(j)} \left[\frac{\sum_1^I n_1(j) c_{2(j)} d_{L1}^2}{\sum_1^I n_1(j) \rho_{(j)} c_{3(j)} d_{M1}^3} \right] \times 10^4$	$w_{(M)} \sum_1^J \alpha_{(j)} \left[\sum_1^I \left(\frac{v_1}{w} \right)_{(j)} \frac{c_{2(j)} d_{L1}^2}{\rho_{(j)} c_{3(j)} d_{M1}^3} \right] \times 10^4$	$w_{(M)} \sum_1^J \alpha_{(j)} \left[\frac{\sum_1^I n_1(j) v_{L1}(j)}{\sum_1^I n_1(j) \rho_{(j)} v_{M1}(j)} \right] \times 10^4$
$V_{(M)}(\text{cm}^3) \approx$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$
$w_{(M)}(\text{gm}) \approx$	$\sum_1^J w_{(j)}$	$\sum_1^J w_{(j)}$	$\sum_1^J w_{(j)}$

a. $v_{M1}(j) = c_{3(j)} d_{M1}^3$ (The midpoint value v_1 could be used in place of $v_{M1}(j)$, however, the authors believe $v_{M1}(j)$ gives a more accurate estimate.)

b. $v_{L1}(j) = c_{2(j)} d_{L1}^2$.

TABLE XVI

Nonfunctional Estimates of Particle Volume and Weight in the Interval (r_1, r_2)

	Type of Data		
	(1,I) or (0,II)	(3,II)	(3,I)
$V_{(M)}(r_1, r_2) \text{ cm}^3 \approx$	$w_{(M)} \sum_1^J \alpha_{(j)} \sum_{r_1}^{r_2} \left[\frac{n_1(j) c_{3(j)} d_{M1}^3}{\sum_1^I n_1(j) \rho_{(j)} c_{3(j)} d_{M1}^3} \right]$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}(r_1, r_2)}{\rho_{(j)}}$	$w_{(M)} \sum_1^J \alpha_{(j)} \sum_{r_1}^{r_2} \left[\frac{n_1(j) v_{M1}(j)}{\sum_1^I n_1(j) \rho_{(j)} v_{M1}(j)} \right]$
$w_{(M)}(r_1, r_2) \text{ gm} \approx$	$w_{(M)} \sum_1^J \alpha_{(j)} \sum_{r_1}^{r_2} \left[\frac{n_1(j) \rho_{(j)} c_{3(j)} d_{M1}^3}{\sum_1^I n_1(j) \rho_{(j)} c_{3(j)} d_{M1}^3} \right]$	$w_{(M)} \sum_1^J \alpha_{(j)}(r_1, r_2)$	$w_{(M)} \sum_1^J \alpha_{(j)} \sum_{r_1}^{r_2} \left[\frac{n_1(j) \rho_{(j)} v_{M1}(j)}{\sum_1^I n_1(j) \rho_{(j)} v_{M1}(j)} \right]$

TABLE XVII

General Form Functional Estimates of Particle Surface Area, Volume,
and Weight for Mixtures

Property Estimated	General Data Form	
	(k,I)	(k,II)
$N_{(M)} \approx$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)} c_{k(j)}^{3/k}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\frac{\hat{\mu}_{zk}(j)}{k} + \frac{4.5}{k^2} \hat{\sigma}_{zk}^2(j) \right) \right] 10^{12}$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\hat{\mu}_{zk}(j) + (4.5 - k) \hat{\sigma}_{zk}^2(j) \right) \right] 10^{12}$
$A_{(M)}(\text{cm}^2) \approx$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)} c_{2(j)} c_{k(j)}^{1/k}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\frac{\hat{\mu}_{zk}(j)}{k} + \frac{2.5}{k^2} \hat{\sigma}_{zk}^2(j) \right) \right] 10^4$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)} c_{2(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\hat{\mu}_{zk}(j) + (2.5 - k) \hat{\sigma}_{zk}^2(j) \right) \right] 10^4$
$V_{(M)}(\text{cm}^3) \approx$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$	$w_{(M)} \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$
$W_{(M)}(\text{g}) \approx$	$\sum_1^J w_{(j)} \quad (\text{Measured})$	$\sum_1^J w_{(j)} \quad (\text{Measured})$
$S_{V(M)} \approx$ (cm^{-1})	$\sum_1^J \frac{\alpha_{(j)} c_{2(j)} c_{k(j)}^{1/k}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\frac{\hat{\mu}_{zk}(j)}{k} + \frac{2.5}{k^2} \hat{\sigma}_{zk}^2(j) \right) \right] \times 10^4 / \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$	$\sum_1^J \frac{\alpha_{(j)} c_{2(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\hat{\mu}_{zk}(j) + (2.5 - k) \hat{\sigma}_{zk}^2(j) \right) \right] 10^4 / \sum_1^J \frac{\alpha_{(j)}}{\rho_{(j)}}$
$S_{W(M)} \approx$ (cm^2/g)	$\sum_1^J \frac{\alpha_{(j)} c_{2(j)} c_{k(j)}^{1/k}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\frac{\hat{\mu}_{zk}(j)}{k} + \frac{2.5}{k^2} \hat{\sigma}_{zk}^2(j) \right) \right] \times 10^4$	$\sum_1^J \frac{\alpha_{(j)} c_{2(j)}}{\rho_{(j)} c_{3(j)}} \exp \left[- \left(\hat{\mu}_{zk}(j) + (2.5 - k) \hat{\sigma}_{zk}^2(j) \right) \right] \times 10^4$

Units: d in microns
ρ in g/cm³

Nonfunctional Estimates

The expressions in Table XV can be used to estimate the properties in any set of "size" intervals (r_1, r_2) where $i = 1, 2, \dots, r_1, \dots, r_2, \dots, I$, if $\alpha_{(j)}(r_1, r_2)$ is computed as

$$\alpha_{(j)}(r_1, r_2) = \frac{\sum_{r_1}^{r_2} w_i(j) \text{ act.}}{w_{(M)} \text{ act.}} \approx \frac{\sum_{r_1}^{r_2} w_i(j) \text{ obs.}}{\sum_1^J \sum_1^I w_i(j) \text{ obs.}}, \quad (156)$$

and $\beta_{(j)}$ is defined as

$$\rho_{(j)}(r_1, r_2) = \frac{\sum_{r_1}^{r_2} n_i(j) \text{ act.}}{N_{(M)} \text{ act.}} \approx \frac{\sum_{r_1}^{r_2} n_i(j) \text{ obs.}}{\sum_1^J \sum_1^I n_i(j) \text{ obs.}} \quad (157)$$

The relationship (150d) is valid if summed over the intervals (r_1, r_2); therefore, the following expressions can be written.

$$\sum_{r_1}^{r_2} \left(\frac{n_i}{w} \right)_{(j) \text{ obs.}} \approx \sum_{r_1}^{r_2} \frac{n_i(j) \text{ act.}}{w_{(j)} \text{ act.}} \quad (158)$$

$$\sum_{r_1}^{r_2} \left(\frac{n_i d_{Li}^2}{w} \right)_{(j) \text{ obs.}} \approx \sum_{r_1}^{r_2} \frac{d_{Li}^2 n_i(j) \text{ act.}}{w_{(j)} \text{ act.}} \quad (159)$$

For example, consider estimating the surface area in square centimeters of particles in the interval (r_1, r_2) using the expression for Type (1,I) data in Table XV.

$$A_{(M)}(r_1, r_2) \approx w_{(M)} \sum_1^J \alpha_{(j)} \left[\frac{\sum_{r_1}^{r_2} n_i(j) c_{2(j)} d_{Li}^2}{\sum_1^I n_i(j) \rho_{(j)} c_{3(j)} d_{M1}^3} \right] \times 10^4 \quad (160)$$

The estimate of $A_{(M)}(r_1, r_2)$ from Type (3,II) data is written

$$A_{(M)}(r_1, r_2) \approx w_{(M)} \sum_1^J \alpha_{(j)} \left[\sum_{r_1}^{r_2} \left(\frac{w_i}{w_{(j)}} \right) \frac{c_{2(j)} d_{Li}^2}{\rho_{(j)} c_{3(j)} d_{M1}^3} \right] \times 10^4 \quad (161)$$

The expressions for estimating $V_{(M)}(r_1, r_2)$ and $W_{(M)}(r_1, r_2)$ are given in Table XVI.

Specific surface for a mixture can be estimated from any data form, for any "size" interval using the appropriate expressions in the form

$$\frac{A_{(M)}(r_1, r_2)}{W_{(M)}(r_1, r_2)} \approx S_{W(M)}(r_1, r_2) \quad (162)$$

Log Normal Model (Functional Estimates)

The general expressions in Table XVII give the estimates listed, for the entire "size" range for each component, for any component data form. The reader is advised to review Table XII for insight into derivation of Table XVII. For example, the properties are estimated from Type (3,I) data using $k = 3$, C_3 , $\hat{\mu}_{z_3}$, and $\hat{\sigma}_{z_3}^2$ in column (k,I) of Table XVII. The properties may be estimated for the general interval (r_1, r_2) from expressions in Table XVII by performing the integration of the appropriate log normal function over the proper interval. For type (3,I) data the number of particles in the interval (z_{3,r_1}, z_{3,r_2}) would be estimated as

$$N_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j)}{\rho(j)} \exp \left[- \left(\hat{\mu}_{z_3(j)} + 5 \hat{\sigma}_{z_3(j)}^2 \right) \right] \times \int_{z_{3,r_1}}^{z_{3,r_2}} p(z_3(j)) dz_3 \times 10^{12}. \quad (163)$$

The general form of expression (163) is obtained by multiplying the expression given in Table XVII by

$$\int_{z_{k,r_1}}^{z_{k,r_2}} p(z_k(j)) dz_k.$$

The estimate of particle surface area in the interval (z_{3,r_1}, z_{3,r_2}) is obtained from Type (3,I) data by multiplying the expression for the estimate of $A_{(M)}$, Table XVII, Type (3,I), by

$$\frac{1}{\sqrt{2\pi} \hat{\sigma}_x(j)} \int_{x_{r_1}(j)}^{x_{r_2}(j)} \exp \left[- \frac{(x - \hat{\mu}_{x2(j)})^2}{2 \hat{\sigma}_x(j)^2} \right] dx, \quad (164)$$

where the integral limits must be defined in the form

$$x_{r_1}(j) = \frac{z_{3,r_1} - \ln C_3(j)}{3}.$$

Notice that the limits must be subscripted unless the shape factor C_3 is the same for all components.

The integral (164) can be written in terms of the defining statistics for Type (3,I) data as

$$\frac{1}{\sqrt{2\pi} \hat{\sigma}_{z_3(j)}} \int_{z_{3,r_1}}^{z_{3,r_2}} \exp \left[- \frac{(z_3 - (\hat{\mu}_{z_3(j)} + \frac{2}{3} \hat{\sigma}_{z_3(j)}^2))^2}{2 \hat{\sigma}_{z_3(j)}^2} \right] dz_3 \quad (165)$$

by transforming the variable x to z_3 . The general expression for $A_{(M)}(r_1, r_2)$ square centimeters can then be written as

$$A_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j) C_3(j) C_k(j)^{1/k}}{\rho(j) C_3(j)} \times \exp \left[- \left(\frac{\hat{\mu}_{z_k(j)}}{k} + \frac{2.5}{k^2} \hat{\sigma}_{z_k(j)}^2 \right) \right] \times \frac{1}{\sqrt{2\pi} \hat{\sigma}_{z_k(j)}} \quad (166)$$

$$\times \int_{z_{k,r_1}}^{z_{k,r_2}} \exp \left[- \frac{\left[z_k - \left(\hat{\mu}_{z_k(j)} + \frac{2}{k} \hat{\sigma}_{z_k(j)}^2 \right) \right]^2}{2 \hat{\sigma}_{z_k(j)}^2} \right] dz_k \times 10^4$$

by transforming the variable x to z_3 . Notice that the integral limits in (166) are values of the variable z_k ; therefore, for Type (k,I) data, the integral in (166) would be more convenient to evaluate than (164) using the normal distribution tables.

The volume of the particles in the interval (z_{3,r_1}, z_{3,r_2}) is written

$$V_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j)}{\rho(j)} \int_{x_{r_1}}^{x_{r_2}} f_3(x(j)) dx, \quad (167)$$

where the limits are in the form,

$$x_{r_1}(j) = \frac{z_{3,r_1} - \ln C_3(j)}{3}.$$

Note that integral limits must differ for each component if the values $C_3(j)$ differ. Upon changing the variable in the integral

$$\frac{1}{\sqrt{2\pi} \hat{\sigma}_x(j)} \int_{x_{r_1}(j)}^{x_{r_2}(j)} \exp \left[- \frac{(x - \hat{\mu}_{x3(j)})^2}{2 \hat{\sigma}_x(j)^2} \right] dx$$

to z_3 , (167) may be written in terms of Type (3,I) data as

$$V_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j)}{\rho(j) \sqrt{2\pi} \hat{\sigma}_{z_3(j)}} \quad (168)$$

$$\times \int_{z_{3,r_1}}^{z_{3,r_2}} \exp \left[\frac{- \left[z_3 - \left(\hat{\mu}_{z_3(j)} + \hat{\sigma}_{z_3(j)}^2 \right) \right]^2}{2 \hat{\sigma}_{z_3(j)}^2} \right] dz_3,$$

where the limits of integration are the same for all components.

A general expression for $V_{(M)}(r_1, r_2)$ from Type (k,I) data can be written as

$$V_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j)}{\rho(j) \sqrt{2\pi} \hat{\sigma}_{z_k(j)}} \quad (169)$$

$$\times \int_{z_{k,r_1}}^{z_{k,r_2}} \exp \left[\frac{- \left[z_k - \left(\hat{\mu}_{z_k(j)} + \frac{3}{k} \hat{\sigma}_{z_k(j)}^2 \right) \right]^2}{2 \hat{\sigma}_{z_k(j)}^2} \right] dz_k.$$

The expression for $W_{(M)}(r_1, r_2)$ is obtained by multiplying by $\rho(j)$ the terms under the summation in (168) and (169).

The estimate of $N_{(M)}(r_1, r_2)$ for Type (k,II) data is written as

$$N_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j)}{\rho(j) C_3(j)} \quad (170)$$

$$\times \exp \left[- \left(3 \hat{\mu}_{xk(j)} + (4.5 - 3k) \hat{\sigma}_{xk(j)}^2 \right) \right]$$

$$\times \frac{1}{\sqrt{2\pi} \hat{\sigma}_{x(j)}} \int_{x_{r_1}}^{x_{r_2}} \exp \left[\frac{- \left[x - \left(\hat{\mu}_{xk(j)} - k \hat{\sigma}_{xk(j)}^2 \right) \right]^2}{2 \hat{\sigma}_{xk(j)}^2} \right] dx \times 10^{12}.$$

The estimate of $N_{(M)}(r_1, r_2)$ for the special case of weight fraction or Type (3,II) data is obtained from (170) for $k = 3$.

The expression for $A_{(M)}(r_1, r_2)$ for Type (k,II) data is written as

$$A_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j) C_2(j)}{\rho(j) C_3(j)} \quad (171)$$

$$\times \exp \left[- \left(\hat{\mu}_{xk(j)} + (2.5 - k) \hat{\sigma}_{xk(j)}^2 \right) \right] \frac{1}{\sqrt{2\pi} \hat{\sigma}_{xk(j)}} \quad (\text{Equation Continued})$$

$$\times \int_{x_{r_1}}^{x_{r_2}} \exp \left[\frac{- \left[x - \left(\hat{\mu}_{xk(j)} - (k-2) \hat{\sigma}_{xk(j)}^2 \right) \right]^2}{2 \hat{\sigma}_{xk(j)}^2} \right] dx \times 10^4.$$

The integrals in the expressions (163) through (171) are readily evaluated using the standard normal distribution tables. For example, in expression (171) for Type (3,II) data, the value of the integral for the j^{th} component would be equal to the tabulated area under the standard normal curve between

$$\frac{x_{r_1} - (\hat{\mu}_{x3} - \hat{\sigma}_x^2)}{\hat{\sigma}_x} \quad \text{and} \quad \frac{x_{r_2} - (\hat{\mu}_{x3} - \hat{\sigma}_x^2)}{\hat{\sigma}_x}.$$

The estimate of $V_{(M)}(r_1, r_2)$ is obtained directly from (167) and can be written for the general case as

$$V_{(M)}(r_1, r_2) \approx W_{(M)} \sum_{j=1}^J \frac{\alpha(j)}{\rho(j) \sqrt{2\pi} \hat{\sigma}_{xk(j)}} \quad (172)$$

$$\times \int_{x_{r_1}}^{x_{r_2}} \exp \left[\frac{- \left[x - \left(\hat{\mu}_{xk(j)} - (k-3) \hat{\sigma}_{xk(j)}^2 \right) \right]^2}{2 \hat{\sigma}_{xk(j)}^2} \right] dx.$$

The estimate of $W_{(M)}(r_1, r_2)$ is obtained by multiplying by $\rho(j)$ the terms under the summation in (172). The expressions for $S_{V(M)}(r_1, r_2)$ and $S_{W(M)}(r_1, r_2)$ are obtained by forming the appropriate ratios. For example,

$$S_{V(M)}(r_1, r_2) \approx \frac{A_{(M)}(r_1, r_2)}{V_{(M)}(r_1, r_2)}. \quad (173)$$

The integrals in expressions (163) through (172) can be evaluated using different integral limits for any of the J components.

Application and Extension of Theory of Mixtures

The following three problems are basic in any study of particulate systems (powders).

1. Characterization of a representative sample taken from a population, thereby inferring some knowledge of the defining properties of the population.

2. Use of the characterizing sample statistics for sample, hence population, comparison.

3. Use of the sample statistics to make useful inferences or predictions of the behavior of the population in a physical process.

The previous development is a rigorous and consistent description of methods for obtaining and correlating pertinent sample statistics from any form of sample data and then serves as an approach to the solution of the first two problems. The third problem, although perhaps most interesting and important of the three, is often avoided by the investigator because of the complexity involved in relating the proper pertinent sample statistics to the appropriate process parameters.

An attempt to utilize statistics from particle "size" analysis in the formulation of a practical theoretical approach to the solution of an important problem common in ceramics and powder metallurgy is discussed in the following section.

Proposed Theorems for Prediction of Packing Behavior of Binary System

The two mixing theorems discussed are results from a part of the general investigation into the use of small-particle statistics in attempts to predict or explain the process behavior of powders. The theorems attempt to predict 1) whether the mixing of two or more powders, whose particle size distributions are known, will increase the packing density of the mixture as compared to the unmixed components, 2) the weight ratio in which the components should be mixed, and 3) the best of several possible component combinations to provide maximum packing density.

There are processes in which the increase of packing density, i.e., reduction of void fraction, in an unsintered powder mass is desirable. For example, 1) the ceramist attempts to produce a high-density slip, by adjusting milling time or mixing slips, to minimize as-fired shrinkage of the ceramic body; 2) the production of a high-density vibratory compact depends in final analysis on selecting a powder which will possess the smallest possible void volume with the powder particles arranged in closest packing geometry; and 3) the production of high-density extruded or molded graphites depends in part on minimizing void volume, hence binder addition. These general examples indicate that the particulate material selected for processing should contain some proportion of fine particles of varied "size" to fill

in the interstices formed by contact of the larger particles.

A frequent situation is one in which several batches of material are available for a process and a higher density process product is desirable than could be obtained by using any one batch. An estimate of the desirability of mixing two batches to achieve a higher packing density for the system, and also perhaps for the process product, is predicted by the theorems.

Other investigators, notably Furnas³² and Wise,^{33,34} proposed theorems related to maximizing particulate system packing. Furnas proposed a maximum packing density theorem based on mixing volume batches of monosized spheres, graded so that each addition of smaller particles did not appreciably increase the total particle bed volume.

Wise proposed a theorem for calculating the mean packing density, mean number of interstices, and the number of spheres touching a sphere of given radius assuming tetrahedral packing and a log normal distribution of sphere radii. Wise did not consider mixing two or more powders of known particle "size" distribution to maximize packing density.

Lewis and Goldman have proposed the following theorems,³⁵ based in part on intuitive reasoning.

Theorem I

The weight ratio for mixing two or more powders to increase theoretical packing density can be computed as a function of the defining statistics of the sample distribution of $x = \ln d$.

The ratio, β'_1 , which maximizes the variance in x for the mix, $\hat{\sigma}_{x(M)}^2$ defines the binary mixture which gives highest packing density.

Theorem II

The coefficient of variation of the sample distribution of d , calculated for a powder or mixture of powders, can be used as a criterion for selecting the powder or mixture of several possible combinations to produce the highest packing density.

The theorems are based on the following conditions:

1. The powders in question are "hard" with respect to the compaction or packing process used (e.g., isostatic or unidirectional pressing, vibratory compaction, or slip casting) so that the particles are not plastically deformed to fill voids formed by particle contact.

2. The "size" distributions of d which characterize the mixture components can be represented by continuous relative frequency polygons having finite variance and positive skewness.
3. The variance of the sample distribution of $x = \ln d$ for the mixture can be computed and has a value greater than the variance of x for the respective components if the packing density can be increased.
4. The method used for the mechanical mixing (admixing) of the components results in a random mixture.

We offer the following conjectures as intuitive limitations on the "size" distributions of the components and resultant mixture to which the theorems may be most applicable.

1. The component "size" distributions are approximately log normal.
2. The "size" distribution of d for the mix is positively skewed, and the skewness of the distribution of $x = \ln d$ for the mix approaches zero, i.e., $\gamma_{d(M)} > 0$ and $\gamma_{x(M)} \rightarrow 0$.
3. The absolute value $|\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)}| < 2.5 \hat{\sigma}_{x(2)}^2$ where $\hat{\sigma}_{x(2)}^2$ is the value of the smaller variance, or the mix does not tend to definite bimodality using some test such as the Eisenberger test [see Eqs. (141) and (142)].

Considerations other than geometric packing arrangement affect the absolute as-compacted density of a powder; e.g., die wall friction, interparticle friction, gaseous environment, and pressing pressure and temperature. The theorems do not offer a method for computing the absolute density resulting from a particular compaction process, but provide only an approach to the computation of the mixing ratio and component combination that would ideally produce the highest relative packing density. The theorems are not dependent on particle shape, and they take into account the entire "size" spectrum of the components.

The theorems do not pertain to the problem of mechanical mixing, admixing, or blending of powders. The fourth condition above requires the assumption that randomness of the mix can be obtained. The authors define ideal randomness of the mixture as being equivalent to

$$\hat{p}(x)_{(M)} \approx p(x)_{(M)} = \sum_j \beta_{(j)} p(x)_{(j)}, \quad (174)$$

where $\hat{p}(x)_{(M)}$ is the distribution function describing

a sample taken from the mixture. Expression (174) then signifies that any sample taken from the random mixture does not differ significantly from the theoretical distribution of the mixture. The investigation of methods to obtain ideal randomness of mixtures is an entirely separate, although related, study,^{36,37} and will not be discussed here.

The intuitive basis for the theorems is illustrated by the schematic sample distributions and their representative distribution functions shown in Figs. 10 and 11. Consider a positively skewed sample distribution of d such that

$$\frac{n_1}{N} \approx \int_{d_1^*}^{d_{1+1}^*} h(d) d d. \quad (175)$$

Consider a powder, A, represented by distribution curve A, Fig. 10. Assume that the variance of A could be increased by some process that increases the total number of powder particles, e.g., by ball-milling or by the addition of another powder, i.e., powder B and its representative distribution are formed. Then the probability of finding more small particles in the powder will increase compared to that of finding more large particles, as schematically indicated by the shaded areas between curves A and B. This indicates the availability of many more small particles to fill interstices formed by contact of larger particles. Therefore, it is assumed that mixing to give maximum density should be performed so that the variance of the mixed sample distribution is maximized. The computation of the mixture fraction, however, is based on the maximum variance of the sample distribution of $x = \ln d$ rather than d . The explanation for this is as follows.

Assume that the positively skewed sample distribution of d representing powder A, Fig. 1, can be transformed so that n_1/N is approximated as before by

$$\int_{x_1^*}^{x_{1+1}^*} p(x) dx.$$

This transformation tends to make the representative distribution curve symmetrical as illustrated by curve A', Fig. 11, and, for log normal sample data, the distribution of x is, of course, normal. For the purpose of this explanation, the transformation makes it possible to relate the maximization of the variance of powder B represented by curve B', Fig. 11,

Fig. 10. Effect of increasing σ_x^2 on distribution of d .

Fig. 11. Effect of increasing σ_x^2 on distribution of x .

to the increase in probability, i.e., increase in fraction of occurrence, of particles in equal $x = \ln d$ size intervals, equidistant from the mean. These intervals are denoted in Fig. 11 as $(\mu_x + a, \mu_x + b)$ and $(\mu_x - b, \mu_x - a)$ where μ_x is the mean of the distribution function representing the particular powder, and a and b are constants so that $b - a$ is the interval width. If the curves A' and B' tend to be symmetrical about their respective means, the change in n_i/N is about equal in each pair of related $x = \ln d$ "size" intervals as illustrated by the shaded areas between the curves A' and B'. In considering the change in n_i/N in the corresponding d "size" intervals, however, the effect would be as illustrated by Fig. 10.

Theorem II concerning the use of the coefficient of variation, CV_d , is based on the distribution of d rather than that of x for the following intuitive reason: The coefficient of variation of the distribution of d gives a better indication of the contribution of the spread of particle "sizes," i.e., variance, to the packing density because the variance, s_d^2 , is related to a mean linear particle dimension, $\bar{d}$, by the definition $CV_d = s_d/\bar{d}$. This is schematically illustrated by Fig. 12, which demonstrates that CV for curve C is greater than CV for curve D, i.e., a powder D represented by curve D is more nearly monosized with respect to particle packing than a powder C represented by curve C, although the curves have the same variance.

The sample statistics required for calculations based on the two mixing theorems are $\bar{x} \approx \hat{\mu}_x$, $s_x^2 \approx \hat{\sigma}_x^2$, $\bar{d}$, and s_d^2 . Methods of computing $\bar{d}$ and s_d^2 from any form of sample data have been discussed in detail (Tables V, VI, VII, VIII, IX, and X). Methods of obtaining $\bar{x}$ and s_x^2 are analogous to those for obtaining $\bar{d}$ and s_d^2 for nonlog normal data.

Fig. 12. "Relative monosizedness."

Recall that log normal sample statistics for nonfunctional and log normal data forms are related as, $\bar{d} \approx \hat{\mu}_d$, $s_d^2 \approx \hat{\sigma}_d^2$, $\bar{x} \approx \hat{\mu}_x$, and $s_x^2 \approx \hat{\sigma}_x^2$. For example, for nonfunctional data from the Coulter Counter, Type (3,I):

$$\hat{\mu}_x \approx \bar{x} \approx \sum_{i=1}^I \frac{n_i \left[\ln \left(\frac{v_i^*}{C_3} \right)^{\frac{1}{3}} + \ln \left(\frac{v_{i+1}^*}{C_3} \right)^{\frac{1}{3}} \right]}{2N} \quad (176)$$

$$\text{and} \quad \hat{\sigma}_x^2 \approx s_x^2 \approx \sum_{i=1}^I \frac{n_i \left[\ln \left(\frac{v_i^*}{C_3} \right)^{\frac{1}{3}} + \ln \left(\frac{v_{i+1}^*}{C_3} \right)^{\frac{1}{3}} - 2\bar{x} \right]^2}{4N} \quad (177)$$

Computations: Theorem I

The mean and variance for a mixture are computed

$$\bar{x}_{(M)} = \sum_{j=1}^J \beta_j \bar{x}_{(j)} \quad (178)$$

and

$$s_{x(M)}^2 = \left[\sum_{j=1}^J \beta_j \left(\bar{x}_{(j)}^2 + s_{x(j)}^2 \right) \right] - \bar{x}_{(M)}^2 \quad (179)$$

Only binary mixtures of powders, having similar shape factors, will be considered in deriving the expressions for β'_j and α'_j . β'_j and α'_j are, respectively, the frequency and weight mixing ratios of the j^{th} component at the maximum value of $s_{x(M)}^2 \approx \hat{\sigma}_{x(M)}^2$.

The expression for $\hat{\sigma}_{x(M)}^2 \approx s_{x(M)}^2$ obtained from expression (179) for a binary mixture, when expanded, yields the parabolic function

$$\hat{\sigma}_{x(M)}^2 \approx a\beta_{(1)}^2 + b\beta_{(1)} + c, \quad (180)$$

where

$$a = -(\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)})^2.$$

$$b = (\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)})^2 + \hat{\sigma}_{x(1)}^2 - \hat{\sigma}_{x(2)}^2.$$

$$c = \hat{\sigma}_{x(2)}^2.$$

The components are identified so that $\hat{\sigma}_{x(1)}^2$ is greater than or equal to $\hat{\sigma}_{x(2)}^2$. Examination of the first and second derivatives of expression (180) with respect to $\beta_{(1)}$ indicates a maximum value of $\hat{\sigma}_{x(M)}^2$ at the value

$$\beta'_{(1)} \approx \frac{1}{2} + \frac{\hat{\sigma}_{x(1)}^2 - \hat{\sigma}_{x(2)}^2}{2[\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)}]^2} \quad (181)$$

Ranges for the computed values of $\beta_{(1)}$ are illustrated in Fig. 13. Cases I and II illustrate $\hat{\sigma}_{x(M)}^2$ is maximum for $\beta'_{(1)}$ between 0.5 and 1.0. Case III illustrates that, since mixing ratios > 1.0 are not defined, mixing would not result in a value of $\hat{\sigma}_{x(M)}^2 > \hat{\sigma}_{x(1)}^2$.

The useful form of the mixing ratio is α ; therefore, $\beta'_{(1)}$ must be converted to $\alpha'_{(1)}$. Recall that the expression is

$$\alpha'_{(1)} \approx \frac{\beta'_{(1)} \exp \left[3\hat{\mu}_{x(1)} + 4.5 \hat{\sigma}_{x(1)}^2 \right]}{\sum_j \beta'_{(j)} \exp \left[3\hat{\mu}_{x(j)} + 4.5 \hat{\sigma}_{x(j)}^2 \right]} \quad (182)$$

$$\text{Case I } \left[\hat{\sigma}_{x(1)}^2 - \hat{\sigma}_{x(2)}^2 \right] \rightarrow 0, \left[\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)} \right] > 0 \\ \beta'_{(1)} \rightarrow \frac{1}{2}$$

$$\text{Case II } \left\{ \left[\hat{\sigma}_{x(1)}^2 - \hat{\sigma}_{x(2)}^2 \right] / \left[\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)} \right]^2 \right\} \rightarrow 1.0 \\ \beta'_{(1)} \rightarrow 1.0$$

$$\text{Case III } \left[\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)} \right] \rightarrow 0, \hat{\sigma}_{x(1)}^2 \neq \hat{\sigma}_{x(2)}^2 \\ \beta'_{(1)} \rightarrow \infty$$

Fig. 13. Theoretical ranges of values of $\beta'_{(1)}$.

for log normal component data forms. It is possible that $\alpha'_{(1)} = \beta'_{(1)}$ for a binary mixture. This occurs when

$$3\hat{\mu}_{x(1)} + 4.5 \hat{\sigma}_{x(1)}^2 = 3\hat{\mu}_{x(2)} + 4.5 \hat{\sigma}_{x(2)}^2 \quad (183)$$

It has been shown in the section on Comparison of Sample Statistics for Mixtures that for the case of a nonfunctional model.

$$\alpha'_{(1)} \approx \frac{\beta'_{(1)} \sum_1^I \rho C_3 \frac{n_1(1)}{N(1)} d_{M1}^3}{\sum_{j=1}^I \beta'_{(j)} \sum_1^I \rho C_3 \frac{n_1(j)}{N(j)} d_{M1}^3} \quad (184)$$

Computations: Theorem II

The application of Theorem II requires the computation of the coefficient of variation of the sample distribution of d ,

$$CV_d = \frac{s_d}{\bar{d}} \quad (185)$$

for binary combinations at the respective values of $\beta'_{(1)}$ for each combination. According to Theorem II, the combination having the greatest value of $CV_{d(M)}$, i.e., the system which has the lesser tendency to be monosized, will give the highest packing density. $CV_{d(M)}$ is calculated as

$$CV_{d(M)} = \frac{\sqrt{s_{d(M)}^2}}{\bar{d}_{(M)}} \quad (186)$$

at $\beta'_{(1)}$.

Experimental Example

The applicability of Theorem I is illustrated by the experimental data shown in Fig. 14. Two tungsten powders, WC and RR, were mixed in various ratios, and samples of these mixtures were both unidirectionally and isostatically pressed at 30 tsi. Each isostatic "sock" was uniformly loaded so that each powder sample was the same diameter before compaction. The effect of the critical mixing ratio α' and the agreement between the calculated α' and the experimentally observed value is shown by the minimum value of the isostatic sample diameters and the maximum value in the as-compacted densities.

Fig. 14. Agreement of experimental data with theoretical $\alpha'_{(j)}$.

The calculated value $\alpha' = 0.0199$ was obtained from the sample statistics,

$$\hat{\mu}_{x(1)} = -0.2670, \hat{\sigma}_{x(1)}^2 = 0.6546 \text{ for RR}$$

and

$$\hat{\mu}_{x(2)} = 1.5299, \hat{\sigma}_{x(2)}^2 = 0.3625 \text{ for WC}$$

and the use of expressions (181) and (182).

The applicability of Theorem II is illustrated by Fig. 15, which indicates an increase in the as-pressed density with increasing coefficient of variation for both mixed and unmixed powders.

Fig. 15. Relation between measured density and CV_d .

Application of Maximum Packing Density Theorem to Ternary Systems

Equation (179) for $s_{x(M)}^2$ can be written as

$$s_{x(M)}^2 = \sum_{j=1}^{J-1} \beta_{(j)} \left(\bar{x}_{(j)}^2 + s_{x(j)}^2 \right) + \left(1 - \sum_{j=1}^{J-1} \beta_{(j)} \right) \left(\bar{x}_{(J)}^2 + s_{x(J)}^2 \right) - \left[\sum_{j=1}^{J-1} \beta_{(j)} \bar{x}_{(j)} + \left(1 - \sum_{j=1}^{J-1} \beta_{(j)} \right) \bar{x}_{(J)} \right]^2, \quad (187)$$

because $\beta_{(J)} = 1 - \sum_{j=1}^{J-1} \beta_{(j)}$. The derivative of $s_{x(M)}^2$ with respect to $\beta_{(j)}$ yields the set of $J-1$ equations, for which the j^{th} equation is,

$$\frac{\partial s_{x(M)}^2}{\partial \beta_{(j)}} = \left(\bar{x}_{(j)}^2 + s_{x(j)}^2 \right) - \left(\bar{x}_{(J)}^2 + s_{x(J)}^2 \right) - 2 \left[\sum_{j=1}^{J-1} \beta_{(j)} \bar{x}_{(j)} + \left(1 - \sum_{j=1}^{J-1} \beta_{(j)} \right) \bar{x}_{(J)} \right] \left[\bar{x}_{(j)} - \bar{x}_{(J)} \right]. \quad (188)$$

On setting the $J-1$ equations equal to zero and attempting to solve for $\beta_{(j)}$, it is seen that the system is inconsistent; i.e., there exists no unique set of solutions for $\beta'_{(j)}$ for $J > 2$. This becomes clear if $\partial s_{x(M)}^2 / \partial \beta_{(j)} = 0$ and Eq. (188) is written in the form

$$\sum_{j=1}^{J-1} \beta'_{(j)} \left(\bar{x}_{(j)} - \bar{x}_{(J)} \right) = \frac{(\bar{x}_{(j)} - \bar{x}_{(J)})^2 + s_{x(j)}^2 - s_{x(J)}^2}{2(\bar{x}_{(j)} - \bar{x}_{(J)})}. \quad (189)$$

Equation (189) reduces to (181) for a binary mixture, i.e., $J = 2$. It is possible that a set of solutions for Eq. (189) having practical meaning could be found, if a meaningful set of constraints could be imposed on the values $\beta_{(j)}$. A possible set of constraints will be discussed in the following section as conjecture for both binary and ternary systems.

The need for consideration of maximizing packing density of ternary systems is not uncommon in practice. Although a unique set of $\rho'_{(j)}$ to maximize $\hat{\sigma}_{x(M)}^2$ for $J = 3$ cannot be determined, a procedure to obtain a set of $\beta'_{(j)}$ which may tend to maximize packing density is outlined as follows:

1. Compute $\beta'_{(1)}$ for the three possible binary combinations.
2. Compute $CV_{d(M)}$ at $\beta'_{(1)}$ for each binary combination.
3. Select the binary combination giving the highest value of CV_d , and compute $\bar{x}_{(M)} \approx \hat{\mu}_{x(M)}$ and $s_{x(M)}^2 \approx \hat{\sigma}_{x(M)}^2$ at $\beta'_{(1)}$.
4. Treat the binary combination as a component having $\bar{x} = \bar{x}_{(M)}$ and $s_x^2 = s_{x(M)}^2$, and compute the $\beta'_{(1)}$ for the binary combination mixed with the remaining component.
5. Compute the new $CV_{d(M)}$ at $\beta'_{(1)}$ for the ternary system and compare with $CV_{d(M)}$ for the binary.
6. Compute $\alpha'_{(1)}$, hence $\alpha'_{(2)}$ and $\alpha'_{(3)}$ for the system having the greatest value of $CV_{d(M)}$.

Few packing density experiments have been performed with ternary systems. No general conclusions could be drawn from the results, therefore, the experiments are not described here. An interesting observation was made in these experiments with iso-statically pressed tungsten powders; namely two density peaks were observed in plotting density of

pressed compacts vs α , the weight mixing fraction.

Conjectures Concerning Mixing Theorems

In the discussion of the development of the mixing theorems, a set of intuitive limitations was given for the "size" distribution of the component powders and resultant mixtures. One of these was $\hat{\gamma}_{d(M)} > 0$ and $\hat{\gamma}_{x(M)} \rightarrow 0$. This leads to the question of the existence of a set of $\beta_{(j)}$, for a binary system whose components are log normal, such that $\hat{\gamma}_{x(M)} = 0$. The implication of the set of limitations is that the mixing theorems for maximum packing density are most applicable if the "size" distribution of the mixture tends to be log normal, although the distribution of the mixture cannot be truly log normal. Values of $\beta_{(j)}$, $0 < \beta_{(j)} < 1$, do exist for $J = 2$, i.e., a binary mixture, such that $\hat{\gamma}_{x(M)} = 0$ if the components are log normal. This can be shown as follows. From expression (123) and the identities

$$\mu_{(1)} - \mu_{(M)} = (1 - \beta_{(1)}) (\mu_{(1)} - \mu_{(2)}) \quad (190)$$

and

$$\mu_{(2)} - \mu_{(M)} = -\beta_{(1)} (\mu_{(1)} - \mu_{(2)}), \quad (191)$$

The expression for $\gamma_{x(M)} = 0$ can be written as

$$\begin{aligned} \gamma_{x(M)} = 0 = & 3\beta_{(1)} (1 - \beta_{(1)}) \left[(\mu_{x(1)} - \mu_{x(2)}) \right. \\ & \times \left[(\sigma_{x(1)}^2 + \mu_{x(1)}^2) - (\sigma_{x(2)}^2 + \mu_{x(2)}^2) \right] \\ & - 2\beta_{(1)} (\mu_{x(1)}^3 - \mu_{x(2)}^3) - 2\mu_{x(2)}^3 + 2\mu_{x(M)}^3 \end{aligned} \quad (192)$$

Substituting in Eq. (192),

$$\mu_{x(M)} = \beta_{(1)} (\mu_{x(1)} - \mu_{x(2)}) + \mu_{x(2)}, \quad (193)$$

with algebraic manipulation, $\gamma_{x(M)} = 0$ can be written in the form

$$\begin{aligned} 0 = & 2\beta_{(1)}^2 (\mu_{x(1)} - \mu_{x(2)})^2 - 3\beta_{(1)} \left[(\mu_{x(1)} - \mu_{x(2)})^2 \right. \\ & + (\sigma_{x(1)}^2 - \sigma_{x(2)}^2) \left. \right] + \left[3(\sigma_{x(1)}^2 - \sigma_{x(2)}^2) \right. \\ & \left. + (\mu_{x(1)} - \mu_{x(2)})^2 \right] \end{aligned} \quad (194)$$

Then,

$$\begin{aligned} 0 = & \beta_{(1)}^2 - \beta_{(1)} \left[\frac{3}{2} + \frac{3(\sigma_{x(1)}^2 - \sigma_{x(2)}^2)}{2(\mu_{x(1)} - \mu_{x(2)})^2} \right] \\ & + \left[\frac{3(\sigma_{x(1)}^2 - \sigma_{x(2)}^2)}{2(\mu_{x(1)} - \mu_{x(2)})^2} + \frac{1}{2} \right] \end{aligned} \quad (195)$$

and

$$0 = \left\{ \beta_{(1)} - \left[\frac{1}{2} + \frac{3(\sigma_{x(1)}^2 - \sigma_{x(2)}^2)}{2(\mu_{x(1)} - \mu_{x(2)})^2} \right] \right\} [\beta_{(1)} - 1] \quad (196)$$

There are then two solutions satisfying Eq. (196).

If $\beta_{(1)\gamma_0}$ is defined as the mixing fraction, such that $\hat{\gamma}_{x(M)} = 0$, of the binary component having the greater variance, the solutions to $\hat{\gamma}_{x(M)} = 0$ can be written,

$$\beta_{(1)\gamma_0} \approx 1, \quad \beta_{(2)\gamma_0} \approx 0 \quad (197)$$

and

$$\begin{aligned} \beta_{(1)\gamma_0} & \approx \frac{1}{2} + \frac{3(\hat{\sigma}_{x(1)}^2 - \hat{\sigma}_{x(2)}^2)}{2(\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)})^2}, \\ \beta_{(2)\gamma_0} & \approx \frac{1}{2} - \frac{3(\hat{\sigma}_{x(1)}^2 - \hat{\sigma}_{x(2)}^2)}{2(\hat{\mu}_{x(1)} - \hat{\mu}_{x(2)})^2} \end{aligned} \quad (198)$$

The solutions given by (197) are obvious, since it was assumed in the derivation that the components were log normal. The form of the solutions (198) is remarkably similar to $\beta'_{(1)}$, which was derived for the independent condition of maximum $\hat{\sigma}_{x(M)}^2$. For any particular binary system, the relation between $\beta'_{(1)}$ and $\beta_{(1)\gamma_0}$ can be written as

$$\beta_{(1)\gamma_0} = 3\beta'_{(1)} - 1. \quad (199)$$

It is interesting to speculate on the applicability of the maximum variance theorem for maximum packing density of binary systems if Eq. (199) were used to establish boundary values for $\beta_{(1)}$ as illustrated in Fig. 16. For example, if for a given binary system, $\beta'_{(1)}$ is calculated as 0.6, the $\beta_{(1)\gamma_0} = 0.8$ and a range of values from $0.6 < \beta_{(1)} < 0.8$ would be contained between the number mixing fraction giving maximum variance and a symmetric distribution. The value of $\beta_{(1)}$ which maximizes the packing density of the system then may not be $\beta'_{(1)}$ but some value between $\beta'_{(1)}$ and $\beta_{(1)\gamma_0}$. Note that for a binary mixture in which $\hat{\sigma}_{x(1)}^2 \rightarrow \hat{\sigma}_{x(2)}^2$, $\beta_{(1)\gamma_0} \rightarrow \beta'_{(1)} \rightarrow \frac{1}{2}$.

Fig. 16. $\beta'_{(1)}$ and related $\beta_{(1)}\hat{\gamma}_0$ values as boundary values for mixing.

SUMMARY

The authors have attempted a consistent, rigorous development of methods for obtaining the statistics describing particulate systems, utilizing data obtained from any type of measuring device. Throughout, logical statistical notation was developed and used to distinguish between sample statistics and distribution parameters, functional (i.e., log normal) and nonfunctional data descriptions, type of data relative to the type of measuring device used, and to develop a descriptive theory for mixtures. The development of the theorems for predicting maximum packing density illustrates the importance of using particle size statistics in attempts to explain process behavior of particulates. The development of the general theory for mixtures is by no means complete.

The discussion of mixtures indicates the enormous amount of experimental work which should be done in this field. It is hoped that our work will stimulate the interest of others both in the general technology of particulates and particulate mixtures, and in the applicable statistical theory.

REFERENCES

1. A. Hazen, "Storage to be Provided in Impounding Reservoirs for Municipal Water Supply," *Trans. ASCE*, vol. 77, pp. 1549-50 (1914).

2. M. P. Henry, *Probabilite du Tir*, Cours de Fontainebleau, fasc. I, 1896.
3. A. T. Trotter, *Gauss' Work (1802-1826) on Theory of Least Squares*, an English translation, AEC-TR-3049 (1957).
4. F. Galton and D. MacAlister, "The Law of the Geometric Mean," *Proc. Roy. Soc. (London)* vol. 29, pp. 365-67 (1879).
5. J. C. Kapteyn and M. J. Van Uven, *Skew Frequency Curves in Biology and Statistics*, Groningen (1916).
6. Wightman et. al., "The Size Frequency Distribution of Particles of Silver Halide in Photographic Emulsions and Its Relation to Sensitometric Characteristics," *J. Phys. Chem.*, vol. 25, p. 181 (1921); Second Paper of Series *J. Phys. Chem.*, vol. 25, p. 561 (1921); Papers III, IV, and V, *J. Phys. Chem.*, vol. 27, pp. 1, 141, 466 (1923); Paper VI, vol. 28, p. 529 (1924).
7. R. Loveland and A. Trivelli, "Mathematical Methods of Frequency Analysis of Size of Particles," *J. Franklin Inst.*, pp. 193-217, 377-89 (August-September 1927).
8. T. Hatch and S. Choate, "Statistical Description of the Size Properties of Non-Uniform Particulate Substances," *J. Franklin Inst.*, pp. 369-87 (March 1929).
9. T. Hatch, "Determination of 'Average Particle Size' From Screen Analysis of Non-Uniform Particulate Substances," *J. Franklin Inst.*, pp. 27-37 (January 1933).
10. DallaValle, *Micromeritics*, Pitman Publishing Corp., New York, First Ed. (1943); Second Ed. (1948).
11. G. Herden, *Small Particle Statistics*, First Ed., Elsevier Publishing Co., New York (1953); Second Ed., Academic Press, Inc., New York (1960).
12. "Symposium on Particle Size Analysis," *Supp. to Trans. Inst. Chem. Engs.*, vol. 25 (1947).
13. R. D. Cadle, *Particle Size Determination*, Interscience Publishers, Inc., New York (1955).
14. C. Orr and J. M. DallaValle, *Fine Particle Measurement*, The Macmillan Company, New York (1959).
15. R. R. Irani and C. F. Callis, *Particle Size Measurement, Interpretation, and Application*, John Wiley and Sons, Inc., New York (1963).
16. C. Orr and J. M. DallaValle, *Fine Particle Measurement*, Chap. 2.
17. *Ibid.*
18. *Operation and Maintenance Manual for the Sharples Micromerograph*, Sharples Corporation, 2300 Westmoreland, Philadelphia, Pennsylvania.

19. H. D. Lewis and A. Goldman, "Proper Analysis of Coulter Counter Data," Rev. Sci. Instr., pp. 868-69 (June 1965).
20. Coulter Counter Instruction Manual, Coulter Electronics, Chicago, Illinois.
21. A. Hald, Statistical Theory with Engineering Applications, John Wiley and Sons, Inc., New York (1952).
22. W. G. Cochran, "The χ^2 Test of Goodness of Fit," Annals of Math. Stat., vol. 23, No. 3, pp. 315-45 (September 1952).
23. P. G. Hoel, Introduction to Mathematical Statistics, John Wiley and Sons, Inc., 2nd Ed. (1954).
24. Ibid., p. 52, Sec. (10.2); pp. 196-200.
25. A. Hald, Statistical Theory with Engineering Applications, pp. 72-76.
26. A. Goldman, H. D. Lewis, and R. Moore, "On the Proper Use of Transformations of Log Normal Functions in Small-Particle Statistics," Los Alamos Scientific Laboratory Report LA-3262 (December 1964).
27. F. Kottler, "The Goodness of Fit and the Distribution of Particle Sizes, Part I," Franklin Inst., pp. 499-514 (May 1951); Part II, pp. 627-641 (June 1951).
28. A. Hald, Statistical Tables and Formulas, John Wiley and Sons, Inc., New York (1952).
29. J. W. Mellor, Trans. Ceram. Soc., (9), p. 94 (1910).
30. S. J. Greggand and K. S. W. Sing, Adsorption, Surface Area, and Porosity, Academic Press, New York (1967).
31. Isidore Eisenberger, "Genesis of Bimodal Distributions," Technometrics, vol. 6, No. 4, pp. 357-63 (1964).
32. C. C. Furnas, "Grading Aggregates: I," Ind. Eng. Chem. vol. 23, No. 9, pp. 1052-58 (1931).
33. M. E. Wise, "Dense Random Packing of Unequal Spheres," Philips Res. Rep., vol. 7, pp. 321-43 (October 1952).
34. M. E. Wise, "Converting a Number Distribution of Particle Size into One for Volume or Surface Area," Philips Res. Rep., vol. 9, pp. 231-37 (June 1954).
35. H. D. Lewis and A. Goldman, J. Am. Ceram. Soc. 49, p. 323 (1966).
36. H. E. Rose and D. J. Robinson, "The Application of the Digital Computer to the Study of Some Problems in Mixing Powders," AICHE E-I. Chem. E. Symposium Series No. 10 (London: Inst. Chem. Engrs.), pp. 10:61 - 10:70 (1965).
37. D. W. Fuerstenau, et al., "A Fundamental Study of the Mixing of Particulate Materials in

Ceramic Processing," ASD-TDR-62-732 Pt. III (1964).

38. DallaValle, Micromeritics, Pitman Publishing Corp., pp. 64-66 (1943).

APPENDIX A

PROPOSED TECHNIQUE FOR EXPERIMENTAL DETERMINATION OF C_3 .

The proposed techniques for determination of C_3 involves the comparison of Coulter Counter and sedimentation or microscopic data.³⁸ From Tables VII and VIII, it is seen that a value for C_3 for a given powder can be computed from the expression

$$\ln C_3 \approx \hat{\mu}_{z_3} - 3\hat{\mu}_x,$$

assuming the Coulter Counter has been carefully calibrated using a standard sample of known shape such that the Coulter Counter and microscopic or sedimentation data are in agreement for the standard sample. A value of $C_{3(M)}$ for a mixture can then be estimated using the expression,

$$\ln C_{3(M)} \approx \sum_1^J \beta_{(j)} \ln C_{3(j)}.$$

APPENDIX B

ACICULARITY RATIO

The section on Shape Factors indicated the complexity of the general concept of shape factor and the related concept of acicularity ratio. The quantitative definition of "average acicularity ratio" for a powder could be a valuable comparative statistic. One method of obtaining the average acicularity ratio based on an optical (microscopic) particle count is outlined below. The obvious disadvantage of this method is the consideration of the particle as a two-dimensional rather than a three-dimensional object; however, logical selection of sample preparation procedures to provide selective particle orientation in the optical sample would tend to negate the disadvantage of the method with respect to information obtained.

Figure B-1 (a-e) schematically illustrates powder particle shapes commonly observed under the microscope. In optical counting the particle "size" can be determined as the diameter of a circle visually judged to be equal to the silhouette or projected area of the particle observed under the

Fig. B-1. Acicularity ratio measurement.

microscope, as illustrated in Fig. B-1, f. This technique has been found to give good accuracy and precision, even for acicular particles, especially if the technique is modified so that the particle area is compared to concentric circles giving a maximum-minimum range for area comparison. The equivalent particle area determined by this technique is then $A_e = \pi d^2/4$, where d is the diameter of the "equivalent circle" as illustrated by Fig. B-1, f.

The acicularity ratio is sometimes defined as the ratio of particle length to particle width. The difficulty in defining a width for some particle shape is illustrated by Fig. B-1, d. If, however, an equivalent particle width is defined as

$$W_e = \frac{A_e}{L},$$

where L is the maximum linear particle dimension, the acicularity ratio is readily defined and measured as

$$R_{Ac} = \frac{L}{W_e} = \frac{L^2}{A_e}.$$

Acicularity ratios for some simple geometric shapes are shown in Fig. B-1, g, h, and i. Note that the W_e for a circle is $\pi d/4$ and $R_{Ac} = 4/\pi$, which is the reciprocal of $C_2 = \pi/4$, the area shape factor for a circle.

The average acicularity ratio can be computed from optical "size" data and the readily measured L values as

$$\bar{R}_{Ac} = \frac{\sum_{n=1}^N \frac{L_n^2}{A_{ei}}}{N},$$

where N = number of particles counted and A_{ei} is the midpoint of the interval $(\frac{\pi}{4} d_i^2, \frac{\pi}{4} d_{i+1}^2)$ containing the n^{th} particle of length L . The variance of the sample distribution of acicularity ratios is computed as

$$s_R^2 = \frac{\sum_{n=1}^N \left(\frac{L_n^2}{A_{ei}} - \bar{R}_{Ac} \right)^2}{N-1}.$$

APPENDIX C

MONTÉ CARLO EXPERIMENT

A Monte Carlo study was made to check some of the important relationships and formulas found in the text. "Monte Carlo" in this case is defined as a technique for simulating an actual physical experiment on a high-speed digital computer. This process is repeated many times so that an accurate prediction can be made about the experimental results. The study was made with the following hypothetical experiment in mind.

An optical (microscopic) count is used to determine the "size" distribution of a particular powder sample. Two questions are posed:

1. How large should the sample have been if it is desired to construct an accurate representation of the weight fraction relationship from the optical count data without implying a functional relationship between the sample distribution of the optical count and the weight fraction relationship?
2. Assuming that the optical count data are log normal, does the functional relationship $W \approx \rho C_3 N \exp \left[\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right] \times 10^{-12}$ provide an accurate estimate W from samples of reasonable N , or an accurate estimate of N from samples of reasonable W ?

The Monte Carlo program method is briefly described as follows:

1. The hypothetical powder was assumed to be made up of spherical tungsten particles

having density $\rho = 19.3 \text{ g/cm}^3$.

- The hypothetical population distribution was assumed to be log normal in d (the spherical particle diameter), i.e., normal in $x = \ln d$, with μ_x and σ_x chosen as 0.26704 and 0.80907, respectively.

- Random samples of size N were taken from the population by selecting particles until the sample weight

$$W = \sum_{n=1}^N w_n \approx 1 \times 10^{-6} \text{ g,}$$

where each n^{th} particle was weighted as

$$w_n = (\pi/6) \rho d_n^3.$$

- The sampling experiment was repeated ten times.

A check was made to determine the validity of the sampling procedure. The following summary of the results of the ten sampling experiments seems to indicate valid sampling of the population having mean $\mu_x = 0.26704$ and standard deviation $\sigma_x = 0.80907$.

TABLE C-1

Experiment No.	$\hat{\mu}_x$	$\hat{\sigma}_x^2$	N	$W \times 10^{-6}$
1	0.24431	0.6695	2341	1.002
2	0.28464	0.6573	2559	1.015
3	0.27825	0.6565	2315	1.001
4	0.23598	0.6560	2991	1.001
5	0.25013	0.6526	2780	1.015
6	0.29021	0.6420	2717	1.009
7	0.29593	0.6442	2803	1.036
8	0.28104	0.6620	2818	1.000
9	0.26664	0.6667	2093	1.005
10	0.26832	0.6550	1585	1.000
Average	0.26953	0.6557	Total 25002	10.084

The average statistics for the $J = 10$ samples were computed as

$$\text{Average } \hat{\mu}_x = \frac{\sum_{j=1}^{10} N(j) \hat{\mu}_{x(j)}}{\sum_{j=1}^{10} N(j)}.$$

$$\text{Average } \hat{\sigma}_{x(j)}^2 = \frac{\sum_{j=1}^{10} (N(j) - 1) \hat{\sigma}_{x(j)}^2}{\sum_{j=1}^{10} (N(j) - 1)}.$$

The weight fraction diagram was constructed

from the relative frequency (optical count) data from the total 25,002 particle count. The relative frequency histogram and the weight fraction diagram are shown in Fig. C-1. Note that the relative frequency polygon is symmetrical about the mode, whereas the weight fraction polygon constructed from a sample of 25,000 particles is not symmetrical. Because the original population sampled was normal in $x = \ln d$, the third moment relationship should also be normal. Therefore, the experiment indicates that values as large as $N = 25,000$ may not provide a large enough sample to permit accurate conversion of relative frequency data to third moment data without implying a functional relationship between the two forms of data. Samples as large or larger than 25,000 for optical counting are certainly of questionable practicality.

The value of $\hat{\sigma}_{x3}^2$ calculated from Fig. C-1 is $\hat{\sigma}_{x3}^2 = 0.54$, and the calculated value of $\hat{\sigma}_x^2 = 0.65$. Recall that $\sigma_x^2 = \sigma_{x3}^2$ for a population normal in x .

The experiment illustrates the importance of recognizing and using the log normal model if applicable to a given set of data.

The validity of the expression for computing N or W from log normal sample statistics was checked as follows:

$$W \approx \rho C_3 N \exp \left[3\hat{\mu}_x + 4.5 \hat{\sigma}_x^2 \right] \times 10^{12}.$$

$$N = 25002.$$

$$\hat{\mu}_x = 0.26953.$$

$$\hat{\sigma}_x^2 = 0.6557.$$

$$W \approx 19.3 \times \frac{\pi}{6} \times 25002 \exp [3.7592] \times 10^{12}.$$

$$W \approx 10.84 \times 10^{-6} \text{ g.}$$

This value of W is in good agreement with the value of 10.08 computed directly from sample observations on 25,002 particles.

Fig. C-1. Conversion of relative frequency distribution to weight fraction for N = 25,002.

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