

STUDIES ON MULTICOMPONENT SOLIDS MIXING AND MIXTURES

by

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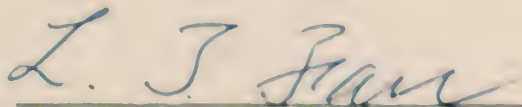

Major Professor

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CHAPTER I

INTRODUCTION

Solids mixing or powder blending is an operation by which two or more solid materials in particulate form are scattered randomly or uniformly among each other by the movement of the particles in a mixer. This operation may be broadly defined as any process that tends to eliminate existing inhomogeneities, or to reduce existing gradients. On the other hand, mixing may be performed to achieve an acceptable product quality or to control rates of heat transfer, mass transfer or chemical reaction. Although it is one of the oldest unit operations, it is still one of the most widely employed in industries. For example, it is essential in plastic processing, ore smelting, fertilizer production, pharmaceutical preparation, food manufacture and catalytical synthesis of chemicals. However, in spite of the practical importance of the mixing or blending operation, the fundamental theories underlying this operation and the procedure for appraising the performance of mixers have not been firmly established.

Solids mixing processes in many industries are multicomponent in nature in that more than two ingredients are blended, and thus, the study of solids mixing for multicomponent mixtures is of utmost practical significance.

Chapter II review the literature on mixing and mixtures of multicomponent solid particle systems. The recent publications on the characterization of binary mixtures and the mixing of such mixtures are also included.

The concept of the contact number is extended to a multicomponent solids mixture in the completely mixed state in chapter III. Such an approach has been applied only to the analysis of a binary mixture [1]. Chapter III also presents an estimation of the mean contact number by spot sampling and the results of computer simulation of mixtures at various concentrations of the key component. The number of spot samples necessary for a specified value of the relative standard error is derived in this chapter.

In Chapter IV, a Dirichlet-multinomial model is proposed to describe a multicomponent mixture in an incompletely mixed state. Estimates of the parameters of the Dirichlet distribution are derived and the precision of the estimated population mean contact number is assessed. This model extends the beta-binomial model for a binary mixture in an incompletely mixed state [2] to the multicomponent case. Computer simulations are included to demonstrate the effectiveness of the derived model.

To characterize the homogeneity of a solids mixture, a mixing index is usually employed as a measure of the degree of mixedness. Over thirty different criteria for the degree of mixedness have been reviewed and summarized by Fan et al. [3]. Unfortunately, the general criterion for characterizing a multicomponent mixture is still lacking. Chapter V presents some approaches to define the mixing indices for multicomponent mixtures.

Chapter VI summarizes significant conclusions and proposes several promising areas of future research.

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1. INTRODUCTION

This review is focused on the literature related to the characterization of multicomponent solids mixtures and to mixing of multicomponent particle systems.

Solids mixing is an important unit operation in many industries. For example, it is essential in plastic processing, ore smelting, pharmaceutical preparation, fertilizer production, food manufacture, and catalytic synthesis of chemicals. This operation may be performed to achieve an acceptable product quality or to control rates of heat transfer, mass transfer or chemical reaction.

A convenient scheme for classifying particle systems should be established to facilitate the investigation of solids mixing. Particle systems may be classified mainly into two classes, binary and multicomponent systems. A binary particle system contains two different types of particles while a multicomponent particle system contains more than two different types. Strictly speaking, however, the binary particle system belongs to a special class of multicomponent particle systems.

Most of the early investigations on the mixture characterization and mixing was carried out with binary solids particle systems, which were identical in all aspects except for a small number of physical properties, e.g., color, which did not affect the mixing process. However, solid particles to be mixed often consist not only of particles of varying size and density but also of widely differing chemical and physical properties. Thus, the study of mixing and sampling of multicomponent heterogeneous solid particles is of practical significance.

Numerous publications on binary solids mixtures and mixing of binary systems are contained in a number of surveys and review articles, including those published by Weidenbaum [1], Bourne [2], Fan et al. [3-6], Valentin [7-9], Yano [10], William [11,12], Cooke et al. [13]. Since the study on mixing of binary particle systems and their characterization is essential to the understanding of multicomponent systems, the recent publications on binary mixtures and mixing, which are not included in the previous survey and review articles, are also reviewed in this article.

There are two broad and equally important aspects in the study of solids mixing. One is concerned with the characterization of a mixture and the other with the mechanism and rate by which the state of a mixture changes. Both aspects are included in this review.

2. RECENT PUBLICATIONS ON BINARY SOLIDS MIXTURES AND MIXING

This section contains a brief review of the recent literature on mixtures and mixing of binary solids particle systems.

2.1. Mixtures

According to Schofield [14], three criteria are required to rigorously define mixture quality. These are between-sample variance (intensity of segregation), scale of segregation (small scale structure), and long range structure. Yip and Hersey [15] utilized Buslik's concept of homogeneity to define the homogeneity of a perfect mixture, which has zero standard deviation for the concentration of a minor ingredient between samples.

Eisenhart-Rothe and Peschl [16] introduced concepts of testing equipment for bulk materials handling and also described tests for characterizing the flow properties of powders. Wicks [17] blended solid particles with known particle size distributions to achieve a target particle size distribution.

Akdel-Aziz [18] developed a new technique for determining particle size of dispersing powders.

There are two approaches to the determination of the mixing index based on the contact number. One is based on the coordination number sampling, and the other on the spot sampling. By these two approaches, Shindo et al. [19,20] proposed theoretical models of the distribution of the contact number for a binary mixture in an incompletely mixed state.

2.2. Mixing

Rátkai [21] studied solids mixing in vertically vibrated beds. The effect of vertical vibration on the hydrodynamics of granular materials flow and the conditions necessary for the emergence of a regular particle stream were discussed. He also showed that the flow pattern in the bed and the change of velocities are functions of the vibration parameters.

Williams [11] reviewed three mechanisms of segregation: trajectory segregation, percolation of fine particles, and the rise of coarse particles on vibration. Koseki et al. [22] studied segregating phenomena in a horizontal rotating drum mixer. Steedman et al. [23] investigated solids segregation in a coal gasification burner. Sugimoto [24] studied solids mixing from some segregation characteristics of mixtures.

Segregation of powder particles by tapping or vibration, which is a phenomenon caused by a shifting of fines toward the bottom of the container, has been reported for the systems with particle diameters in the range of 0.2 to 12 mm [25]. Parson [26] extended this effort to micrometer-sized particle systems with and without the presence of agglomerates.

Row and Nienow [27] reviewed critically some of their earlier works on particle mixing and segregation in gas fluidized beds. They also reported briefly on recent works and drew attention to present unsolved problems.

Burgess et al. [28] used gas fluidized beds to study solids mixing and segregation. They found that mixing commences at gas velocities just above the minimum fluidization velocity of the non-segregating component for particle systems of equal density, but mixing does not commence until the gas velocity exceeds the minimum fluidization velocity of the segregating component for systems of different density. They also developed a model for segregation and mixing, which is capable of predicting the complex behavior found experimentally.

Fitzgerald et al. [29] used a fluidized bed to study solids mixing and calculated solids flow patterns by use of a general compartmental model. Rengarajan et al. [30] employed the single phase backflow cell model to simulate the solids mixing in a fluidized bed coal combustor.

Highley and Merrick [31] developed a mathematical model to calculate the lateral concentration gradients of reactant solids in a large bed and used it to predict the effect of coal feed spacing on the combustion of coal in a fluidized bed boiler. Lateral-solids mixing diffusivities were measured in a 5 ft. diameter bed.

The economic advantages of using a continuous process are now widely accepted. However, processes involving the handling and processing of particulate solids are often designed as batch processes. Such systems should be examined to determine if it would be advantageous to employ continuous mixing. Williams [12] reviewed the continuous mixing of solids, in which the advantages of continuous mixing and the equipment for continuous mixing are also reported. Miyanami et al. [32] developed a continuous mixing process for fine and cohesive powders. The vertical cylinder mixer provided with an impeller of multistage comblike blades has been proven effective.

Carstensen [33] showed that the mixing of a binary mixture of non-spherical particles with rough surfaces obeys to diffusional equations as long as the mean diameters of the two fractions are identical. Hogg and Hwang [34] carried out experiments on the mixing of a thin layer of tracer fed onto the surface of a flowing bed of sand. The results of their experiments were analyzed in terms of a diffusion model in which it is assumed that the diffusion coefficient is a function of the velocity gradient at any level in a flowing stream.

Wang and Fan [35] presented discrete deterministic and random walk models to describe the axial mixing of grains in a motionless Sulzer (Koch) mixer. They [36] also proposed a discrete steady-state Markov chain model for the axial segregation of solid particles in a motionless mixer. This model can predict the concentration profiles, the degree of mixedness, and the equilibrium states of these particle mixtures blended by passing the particles through a motionless mixer.

Thyn and Duffek [37] investigated the mixing process in a horizontal batch mixer with a twin spiral rotor. Krambrock [38] used a pneumatic mixer unit to study the mixing and homogenizing of granular bulk materials. Bridgwater [39] reviewed fundamental powder mixing mechanisms. Yamaguchi [40] developed some rate equations for solids mixing.

3. MULTICOMPONENT MIXTURES AND MIXING

The publications on multicomponent mixtures and mixing are reviewed extensively in this section.

3.1 Mixtures

Gayle et al. [41] used chi-square as a criterion to characterize the homogeneity of a multicomponent solids mixture instead of a conventional mixing index based on the sample variance (or standard deviation).

According to them,

$$\chi_n^2 = \sum_{i=1}^n \frac{(O_i - E_i)^2}{E_i} \quad (1)$$

where

n = number of samples,

χ_n^2 = chi-square with n degrees of freedom,

O_i = observed number of particles of any given color in the i -th sample,

E_i = corresponding expected number in the i -th sample, based on the average distribution of components in the mixture.

They also proposed a segregation index as

$$I_s = \frac{\chi_o^2 - \chi_r^2}{\chi_s^2 - \chi_r^2} \quad (2)$$

where

I_s = numerical index which indicates degree of segregation of the mixture,

χ_o^2 = observed chi-square for any mixture,

χ_r^2 = expected chi-square for the random mixture,

χ_s^2 = expected chi-square for the segregated mixture.

Buslik [42] developed a formula for the variance of a single size fraction of the given particle size v_i in random samples from a granular material with a known size distribution as

$$\sigma_i^2 = \frac{q_i(1 - q_i)\bar{v}_i^2 + q_i^2(\bar{v} - \bar{v}_i)^2}{V} \quad (3)$$

where

V = volume of solid material in each sample,

\bar{v}_i = average volume per piece of size v_i being investigated,

q_i = volume fraction of an aggregate which has size v_i ,

c_i = standard deviation of volume fraction of size v_i in random samples of constant volume V and

\bar{v} = average volume of a particle in the mixture

\bar{v} is defined as

$$\bar{v} = q_1 v_1 + q_2 v_2 + \dots + q_k v_k$$

where q_1, q_2, \dots, q_k are the volume fractions of the particle sizes v_1, v_2, \dots, v_k in the aggregate.

Stange [43] characterized the quality of a mixture consisting of granular particles of different sizes, denoted by 1,2,3,... He developed the following formula for the variance of one of the components by lumping the remaining components as a fictitious component.

$$\sigma_a^2 = \frac{p_1}{\bar{w}} \left[\left(\frac{1 - p_1}{p_1} \right) p_1 (\sum_j w_j)_1 + p_2 (\sum_j w_j)_2 + p_3 (\sum_j w_j)_3 + \text{etc.} \right] \quad (4)$$

where

- p_1, p_2 etc. = weight proportions of component 1, 2, etc.,
- $(\sum_j w_j)_i$ = effective mean particle weight of component i.

This expression can be confirmed by extending Buslik's eqn. (3) to cover multicomponent system [44].

Knott [45] analyzed a mixture of particles of different sizes by employing a technique used in the study of a joint number of occurrences of various types in a renewal process up to a fixed time. He derived expressions for the asymptotic means, variances, and covariances of the volumes of different types of particles as the total volume sampled becomes large. The obtained asymptotic variance of type i, c_i^2 , is

$$c_i^2 = \frac{V n_i \nu^2(i)}{\mu^3} \left\{ \left[\nu - h_i \mu(i) \right]^2 - h_i \left[m - h_i \nu^2(i) \right] \right\} + \frac{V h_i \left[m(i) - \nu^2(i) \right]}{\nu^2} \left[\nu - 2h_i \nu(i) \right] \quad (5)$$

where

- h_i = number fraction of particles of type i in the mixture,
- V = volume of particles in each sample,
- $\nu(i)$ = mean of the size (or volume) distribution of particles of type i,
- $m(i)$ = second moment about the origin of the volume distribution of particles of type i.

$$\mu = \sum_{i=1}^k h_i u(i),$$

$$\sigma = \sum_{i=1}^k h_i m(i),$$

k = number of types of different particles.

Scheaffer [46] applied the renewal theory to find the asymptotic distribution of the sample amounts of the different types of items, to estimate the population amount proportions, and to estimate the average item amount. His results of asymptotic variance and covariance are essentially the same as Knott's [45]. Scheaffer [47] proposed a homogeneity index for a multicomponent mixture. He assumed that the population mean and covariance are known. A test statistic, T , was proposed as

$$T = \lambda \sum_{i=1}^n (\hat{\underline{B}}^{(i)} - \underline{B})' \Sigma^{-1} (\hat{\underline{B}}^{(i)} - \underline{B}) \quad (6)$$

where λ is the fixed total amount of a sample, n is the number of samples, $\hat{\underline{B}}^{(i)}$ is asymptotically distributed as a multivariate normal random vector with the mean vector, \underline{B} , and a covariance matrix, $\lambda^{-1}\Sigma$. From the asymptotic normality of $\hat{\underline{B}}^{(i)}$, T has a $\chi^2_{n(k-1)}$ distribution as $\lambda \rightarrow \infty$ asymptotically under the hypothesis of a thoroughly mixed aggregate. T should be close to the mean value of this χ^2 distribution for a thoroughly mixed aggregate, and is much larger for a poorly mixed one. But this test statistic does not give a good approximation of the exact distribution except in the case of a very large sample.

Buslik [48] introduced a concept of homogeneity of binary mixtures based on the weight of sample, W_1 , necessary to give a specified variation (e.g., a standard deviation of 1%) between samples. The so-called universal homogeneity

is defined as the negative logarithm of the sample weight. Hersey et al. [49,50] extended this concept to a multicomponent mixture by using the standard deviation of an ingredient 1 in a completely random mixture, eqn. (4). They assumed that the components must be reduced to the same particle-size level prior to mixing, i.e., particles of each component have the same particle weight.

$$\Sigma (f_j w_j)_1 = \Sigma (f_j w_j)_2 = \dots = w \quad (7)$$

where w is the effective mean weight of all particles in the mixture. Thus, eqn. (4) reduces to

$$\sigma_1^2 = \frac{w}{W} p_1 (1 - p_1) \quad (8)$$

When $C_1^2 = 0.01$ and $W = W_1$ gives a different equation for the homogeneity of an individual ingredient in the multicomponent mixture as

$$\Sigma 1(j) = -\log [p_j (100 - p_j) w] , \quad j = 1, 2, \dots \quad (9)$$

The equations can be used to follow the course of mixing of a single component in a mixing operation or to compare the various requirements of powders necessary for mixing them to a desired degree of homogeneity in a multicomponent mixing operation.

Cook and Hersey [51,52] evaluated a Nauta DX 600 mixer for the mixing of a multicomponent tablet preblend. Four ingredients (phenobarbitone, butobarbitone, quinalbabitone and lactose) were mixed. During the mixing operation samples were removed from the mixer and assayed for each ingredient

by using gas liquid chromatography. The degree of mixing for each of the four components was calculated according to eqn. (9). Each component behaved in a unique manner during mixing. The control of mixing time is very important for multicomponent mixtures, since at any one time one ingredient may have segregated to the extent that it does not meet the necessary specification for homogeneity.

Lai and Fan [53] proposed a discrete steady-state Markov chain model for the mixing process of a multicomponent homogeneous particle system in a motionless mixer. The concentration variance, c_N^2 , of the mixture at time Nt is given by

$$c_N^2 = \frac{1}{k} \sum_{j=1}^k \sum_{i=1}^a \bar{n}_i [C_{ij}(N) - (C_j)_\infty]^2 \quad (10)$$

where

$C_{ij}(N)$ = number concentration of component j in cell i at time Nt ,

$(C_j)_\infty$ = equilibrium concentration of component j ,

\bar{n}_i = number fraction of particles in cell i ,

a = total number of cells in a mixer,

k = total number of components in a mixer.

The variance of sample compositions in the completely segregated state, c_0^2 , was derived from the model as

$$c_0^2 = \frac{1}{k} \sum_{j=1}^k \sum_{i=1}^a \bar{n}_i [C_{ij}(0) - (C_j)_\infty]^2$$

$$= \frac{1}{k} \sum_{j=1}^k \sum_{i=1}^a [(C_j)_\infty]^2 \bar{n}_i \left[\frac{1}{\bar{n}_i} \sum_{i=1}^a P_{ii}(N) C_{ii}(0) - 1 \right]^2 \quad (11)$$

where

P_{ij} = transition probability of the particles from cell i to cell j ,

$$Q_{ij}(0) = \pi_i \frac{C_{ij}(0)}{(C_j)_\infty}$$

The variance reduction ratio, ψ , can be written as

$$\psi = \frac{\sigma_K^2}{\sigma_0^2} \quad (12)$$

The degree of mixedness may be defined as

$$M = 1 - \psi \quad (13)$$

Lai and Fan [53] proposed the idea of using the entropy of a solid mixture as a criterion for characterizing the mixture. The entropy of the solid mixture at cell i can be defined as

$$S_i(N) = - \sum_{j=1}^k C_{ij}(N) \ln C_{ij}(N) \quad (14)$$

and the total entropy of the system is then

$$S(N) = \sum_{i=1}^a \pi_i S_i(N) \quad (15)$$

If the system is in the segregated state at the beginning of the mixing process,

$$S_i(0) = 0 \quad (16)$$

and therefore,

$$S(0) = \sum_{i=1}^a S_i = 0 \quad (17)$$

The entropy of a mixture will change from zero in the completely segregated state to a constant value in the completely random state. Hence, the entropy of a mixture can be similarly defined as a measure of the degree of mixedness of a mixture.

Wang et al. [54] applied multivariate statistical methods to test a variety of hypotheses which consist of the equality of mean vectors and that of covariance matrices. The applicability of the multivariate statistics to analyses of mixing processes and mixtures of multicomponent particles has been successfully demonstrated. They have defined the degree of mixedness, M , for a multicomponent solids mixture as

$$M = \frac{|\bar{c}_s| - |S|}{|\bar{c}_s| - |\bar{c}_r|} \quad (18)$$

where

$|S|$ = determinant of the sample covariance matrix,

$|\bar{c}_s|$ = determinant of the covariance matrix in the completely segregated state,

$|\bar{c}_r|$ = determinant of the covariance matrix in the completely random state

M assumes the values of 0 and 1 in the completely segregated state and the completely random state, respectively.

In mixing several monosized particle fractions, Sommer [55] assumed that the volume of a particle of a given size, v_i , is always an integral multiple of that of the next smaller size particle, v_{i-1} , i.e.,

$$v_1 = u_2 v_2 = u_2 u_3 v_3 = \dots, \quad u_i = 1, 2, \dots \quad (19)$$

where v_1 is the volume of the particle with the greatest size and v_n the smallest size. Under this assumption, the formula can be used to calculate the variance of the stochastic homogeneity as

$$\sigma_r^2(X_j) = q_j(1 - q_j) \frac{v_j}{v_p} + q_j c_r^2 \sum_{i=1}^{j-1} X_j \quad (20)$$

and

$$\sigma_r^2 \left(\sum_{i=1}^j X_i \right) = q_j (1 - q_j') \frac{v_i}{V_p} + (1 - q_j') c_r^2 \left(\sum_{i=1}^{j-1} X_i \right) \quad (21)$$

where

$$q_j' = \frac{q_j}{1 - \sum_{i=1}^{j-1} q_i} ,$$

X_i = volume concentration in a sample,

q_i = theoretic volume concentration of component i.

3.2. Mixing

Gayle et al. [41] carried out mixing experiments by using a mixing wheel, which was designed for mixing samples of coal and coke. Granules which were similar in surface characteristics, shape and density but different in color, were used. During mixing, the value of chi-square, as defined in eqn. (2), decreases with an increase in the number of revolutions of the mixing wheel and approaches a mean lower limit asymptotically. The initial value, χ_s^2 , for chi-square (before mixing) is equal to the number of degrees of freedom multiplied by the number of particles counted for each sample. The number of degrees of freedom is defined as the number of items of data. The segregation index of eqn. (3), which varies from unity to zero as mixing proceeds from complete segregation to complete randomization, was used to establish a conventional rate equation as

$$- \frac{dI_s}{dr} = \eta I_s^\theta \quad (22)$$

where

I_s = degree of segregation

r = number of revolutions of the mixer,

η = rate constant,

θ = constant

Lai and Fan [53] developed a stochastic model for the mixing of multi-component homogeneous particles by passing them through a motionless mixer from the experimentally determined transition probabilities of a binary homogeneous particle system. The model permits prediction of the concentration distribution and the degree of mixedness of a multicomponent homogeneous particle mixture.

Wang et al. [54] employed a drum mixer to study multicomponent solids mixing. Three types of particles having identical properties except color were used. They indicated that the determinant of a sample covariance matrix, $|S|$, monotonically decreases as the mixing time increases. They also showed the mixing index M , as defined in eqn. (18), increases and approaches 1 as the mixing time increases. For mixing a multicomponent heterogeneous mixture, it is expected that M increases up to a certain maximum and decreases asymptotically to the equilibrium state because of the segregating tendency of such a mixture.

4. CONCLUDING REMARKS

This review of the literature on binary mixtures and mixing indicates that mixing of binary components systems in fluidized beds fairly extensively studied in the last several years. This is a natural consequence of the fact that the use of fluidized beds in many areas of material processing is increasing rapidly. This review also indicates that segregation or demixing, which is the counterpart of mixing, rather than mixing itself has become the emphasis of the recent investigations.

Mixing and sampling of multicomponent heterogeneous solids mixtures and their interrelations have been of intense interest. Yet, the literature on this subject is still very limited. For instance, the criteria for testing

the homogeneity of a heterogeneous multicomponent mixture is still lacking. Since any knowledge of multicomponent solids mixing and mixtures should reduce to that of binary mixing, to establish a broad, systematic and analytic approach to this subject is of importance and significance.

Notations

$\underline{B}^{(i)}$	sample amount proportion vector of the i-th sample.
\underline{B}	mean vector of $\underline{B}^{(i)}$
$C_{ij}(N)$	number of concentration of component j in cell i at time Nt
$(C_j)_\infty$	equilibrium concentration of component j
E_i	corresponding expected number in the i-th sample, based on the average distribution of components in the mixture
$(\text{Efw})_i$	effective mean particle weight of component i
W_i	negative logarithm of $W_i = -\log W_i$
h_i	number fraction of particles of component i in the mixture
I_s	numerical index indicating degree of segregation of the mixture
k	total number of components in the mixture
$m(i)$	second moment about the origin of the volume distribution of particles of type i
m	$= \sum_{i=1}^k h_i m(i)$
N	number of passes
n	number of samples
C_i	observed number of particles of any given color in the i-th sample
P_{ij}	transition probability of the particles from cell i
P_i	weight proportion of component i
q_i	theoretical volume concentration of component i
q_j'	as defined in eqn. (21) = $\frac{q_j}{j-1} \frac{1 - \sum_{i=1}^k q_i}{1 - \sum_{i=1}^k q_i}$
Q_{ij}	as defined in eqn. (11) = $n_i \frac{C_{ij}(0)}{(C_j)_\infty}$
r	number of revolutions of the mixer
$\underline{\Sigma}$	sample variance-covariance matrix

\bar{T}	testing statistic as defined in eqn. (6)
t	required time for one pass
V	volume of particles in each sample
v_i	volume of a particle of component i
\bar{v}	average volume of a particle in the mixture
W	weight of a sample
W_1	weight of sample necessary to give a standard deviation of 1%.
w	effective mean weight of all particles in the mixture
X_i	volume concentration in a sample
Greek	
α	total number of cells in a mixer
η	rate constant
λ	fixed total amount of a sample
$\mu(i)$	mean of the size (or volume) distribution of particles of type i
ν	as defined in eqn. (5) = $\sum_{i=1}^k h_i \mu(i)$
\bar{n}_i	number fraction of particles in cell i
Σ_r	variance-covariance matrix of a mixture in the completely mixed state
Σ_s	variance-covariance matrix of a mixture in the completely segregated state
σ_i	standard deviation of volume fraction of size v_i in random samples of constant volume V
χ_n^2	chi-square value with n degrees of freedom
χ_0^2	observed chi-square value for a mixture
χ_r^2	expected chi-square value for a random mixture.
χ_s^2	expected chi-square value for a segregated mixture

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ESTIMATION OF A MIXING INDEX FROM CONTACT NUMBER FOR A HOMOGENEOUS MULTICOMPONENT MIXTURE IN THE COMPLETELY MIXED STATE

1. INTRODUCTION

Statistical analysis has been a major tool for studying solids mixing because of the random nature of mixing processes. Most available definitions of the mixing index or the degree of mixedness, which specifies the homogeneity in a solids mixture, are based on the variance of the concentration of a certain component among spot samples (see, e.g., Fan et al. [1]). However, in the study of the compactness of a solid mixture or the rate of reaction between solids, a definition of the degree of mixedness based on the variance of the concentration of a certain component often fails to provide physical significance of the definition.

Akao et al. [2] have proposed a new definition of the degree of mixedness based on the mean contact number from a microscopic and geometric viewpoint for a homogeneous binary solids mixture. The contact number is the number of points of contact between types of particles with one key particle, a particle species which is selected as a reference. Smith et al. [3] determined the relationship between the porosity and the average number of contact points among particles. Selection of a key component simplifies the sampling procedure and broadens its applications in studies of solids mixing, heterogeneous chemical reaction, and other operations involving contact between different solid phases.

In this study, the concept of the contact number is extended to a multicomponent solids mixture in the completely mixed state. Such an approach has been applied only to the analyses of a binary particles mixture. Specifically, this paper presents an estimation of the mean contact number by measuring the concentration of particles by spot sampling instead of the

direct counting of the contact number. The mean contact number and its precision from the computer simulation of the two-dimensional cubic and hexagonal packing arrangements at different concentrations of the key component are reported. Although the mixtures studied in this work are observed on two-dimension cross-sections, the data obtained can be transformed into a three-dimensional sample space by resorting to stereological approaches [8].

2. ESTIMATION OF THE DISTRIBUTION OF MEAN CONTACT NUMBER IN THE COMPLETELY RANDOM STATE

A. Concept of the Contact Number

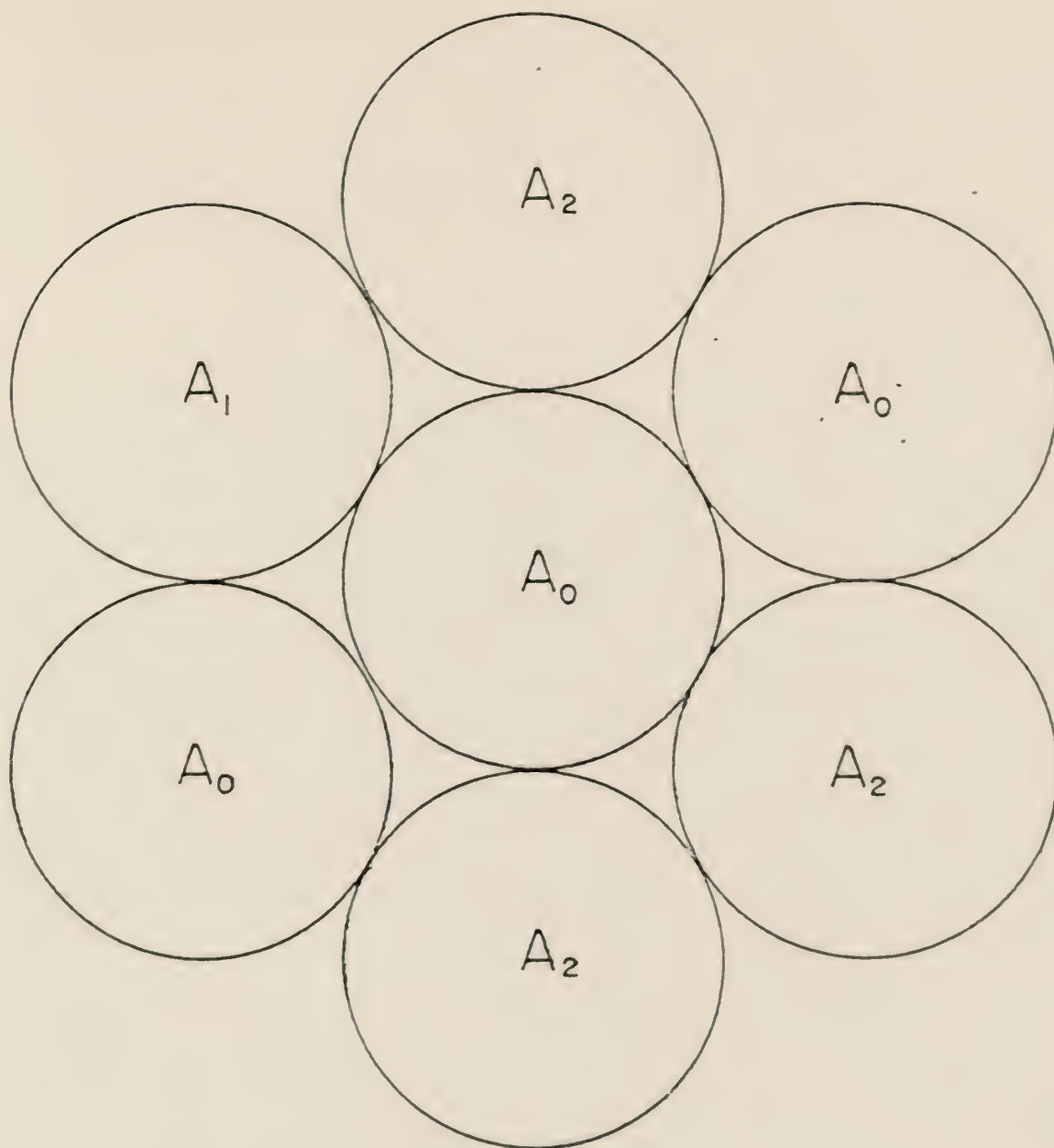
When a particle is taken randomly from a mixture, the number of all particles which are in contact with this particular particle is called the total coordination number denoted by n^* , and the particle is called the sample particle. Such a sampling is called the coordination number sampling of size n^* . For example, the total coordination number of the two-dimensional cubic packing arrangement is 4 and that of the hexagonal packing arrangement is 6.

Let A_0 particles be key particles in a multicomponent mixture containing p kinds of particles of the same size, A_0, A_1, \dots, A_{p-1} . The number of particles of component A_j in contact with a key particle is defined as the contact number contributed by component A_j , and is denoted by $C_j(0)$. For example, we see in Fig. 1 that $C_1(0) = 1$, $C_2(0) = 3$.

B. Distribution of the Contact Number

In the completely mixed state, particles of each component are expected to be randomly distributed in a sample from the coordination number sampling of size n^* . Therefore, the distribution of the contact numbers, $C_1(0), C_2(0), \dots, C_{p-1}(0)$, follows the multinomial distribution, i.e. [7],

$$\Pr\{Y_0 = C_0(0), Y_1 = C_1(0), \dots, Y_{p-1} = C_{p-1}(0)\}$$



$$\bar{n} = 6, \quad C_{1(0)} = 1, \quad C_{2(0)} = 3$$

Fig. 1. Illustration of a coordination number sampling of size $n^* = 6$.

$$\begin{aligned}
&= \frac{n^*!}{C_0(0)! C_1(0)! \dots C_{(p-1)}(0)!} \bar{x}_0^{C_0(0)} \bar{x}_1^{C_1(0)} \dots \bar{x}_{(p-1)}^{C_{(p-1)}(0)} \\
&= \frac{n^*!}{\prod_{j=0}^{p-1} C_j(0)!} \prod_{j=0}^{p-1} \bar{x}_j^{C_j(0)} \quad (1)
\end{aligned}$$

where X_j is the population concentration of particles of component A_j and Y_j is the random variable of the contact number, $C_j(0)$. Thus, the expected value and the variance of the contact number, Y_j , in the completely mixed state are, respectively:

$$E_{\bar{r}}[Y_j] = n^* \bar{X}_j, \quad j = 1, 2, \dots, (p-1) \quad (2)$$

$$V_{\bar{r}}[Y_j] = n^* \bar{X}_j (1 - \bar{X}_j), \quad j = 1, 2, \dots, (p-1) \quad (3)$$

On the other hand, we have a one-point distribution in the completely segregated state, if the points of contact between different particles at the boundaries are neglected, i.e.,

$$\text{Pr}\{Y_j = 0 \mid \text{the sample particle is of component } A_0\} = 1. \quad (4)$$

$$j = 1, 2, \dots, (p-1)$$

$$\text{Pr}\{Y_j > 0 \mid \text{the sample particle is of component } A_0\} = 0. \quad (5)$$

$$j = 1, 2, \dots, (p-1)$$

This means that the expected value and the variance of the contact number in the completely segregated state are both zero, i.e.,

$$E_s [Y_j] = 0, \quad j = 1, 2, \dots, (p-1) \quad (6)$$

$$V_s [Y_j] = 0, \quad j = 1, 2, \dots, (p-1) \quad (7)$$

From eqns. (2) and (6), we find that the mean contact number based on component A_j changes from zero in the completely segregated state to $n \cdot \bar{X}_j$ in the completely mixed state. Akao et al. [2] have used this idea to define the degree of mixedness, M , for a homogeneous binary system as follows:

$$M = \frac{\hat{C}_{1(0)} - E_s [C_{1(0)}]}{E_r [C_{1(0)}] - E_s [C_{1(0)}]} \quad (8)$$

where $\hat{C}_{1(0)}$ is the mean contact number of component A_1 estimated from samples of the mixture.

C. Estimation of the Mean Contact Number by Spot Sampling

When a spot sample of size n is drawn from the completely random mixture, the concentration of particles of component A_j is

$$x_j = \frac{a_j}{n}, \quad j = 0, 1, 2, \dots, (p-1) \quad (9)$$

where a_j denotes the number of particles of component A_j in the spot sample. The mean contact number is, therefore,

$$C_j(0) = n \cdot x_j, \quad j = 1, 2, \dots, (p-1) \quad (10)$$

Suppose that k spot samples of an identical size n are obtained from the completely random mixture. The contact number contributed by the particles of component A_j per key particle is

$$[C_j(0)]_i = [n \cdot x_j]_i, \quad i = 1, 2, \dots, k \quad (11)$$

where subscript i denotes the i -th spot sample. The number of key particles in each spot sample is

$$n \left(1 - \prod_{j=1}^{p-1} (x_j)_i \right) \text{ or } n(x_0)_i$$

Hence, the contact number contributed by component A_j in the i -th spot sample becomes $(n \cdot x_j)_i \cdot n(x_0)_i$. Note that the total number of particles in the k spot samples is kn .

The estimation of the population mean contact number contributed by component A_j per key particle in k spot samples is, therefore,

$$\begin{aligned} \hat{C}_j(0) &= \frac{\text{total contact no. contributed by component } A_j \text{ in } k \text{ sample}}{\text{total no. of key particles in } k \text{ spot samples}} \\ &= \frac{\sum_{i=1}^k (n \cdot x_j)_i \cdot n \cdot (x_0)_i}{\sum_{i=1}^k n \cdot (x_0)_i} \\ &= \frac{\sum_{i=1}^k (n \cdot x_j)_i (x_0)_i}{k \bar{x}_0} \end{aligned} \quad (12)$$

where

$$\bar{x}_0 = \frac{\sum_{i=1}^k (x_0)_i}{k}$$

If the population concentration of particles of component A_0 (key component) is known, its sample mean, \bar{x}_0 , can be replaced by its population mean, \bar{X}_0 , i.e.,

$$\hat{C}_j(0) = \frac{\sum_{i=1}^k (n \cdot x_j)_i (x_0)_i}{k \bar{X}_0} \quad (13)$$

Equation (13) enables us to determine the precision of the population mean contact number estimator.

D. Statistical Characteristics of the Estimator, $\hat{C}_j(0)$

The expected value of the estimator, $\hat{C}_j(0)$, is (see Appendix A)

$$E_{\tau}[\hat{C}_j(0)] = \frac{n^*}{k\bar{X}_0} E_{\tau} \left[\sum_{i=1}^k (x_0 x_j)_i \right], \quad j = 1, 2, \dots, (p-1) \quad (14)$$

or

$$E_{\tau}[\hat{C}_j(0)] = \frac{n-1}{n} n^* \bar{X}_j, \quad j = 1, 2, \dots, (p-1) \quad (15)$$

Equations (2) and (15) imply that the estimator, $\hat{C}_j(0)$, is biased, but it is consistent, since

$$E_{\tau}[\hat{C}_j(0)] = E_{\tau}[C_j(0)] \text{ as } n \rightarrow \infty$$

From eqn. (15), we can define the unbiased consistent estimator, $\hat{C}'_j(0)$, as

$$\begin{aligned} \hat{C}'_j(0) &= \frac{n}{n-1} \hat{C}_j(0) \\ &= \frac{n}{n-1} \frac{\sum_{i=1}^k [n^* x_j]_i [x_0]_i}{k\bar{X}_0}, \quad j = 1, 2, \dots, (p-1) \end{aligned} \quad (16)$$

From eqns. (15) and (16), it can be shown that the expected value of $\hat{C}'_j(0)$ is

$$E_{\tau}[\hat{C}'_j(0)] = n^* \bar{X}_j, \quad j = 1, 2, \dots, (p-1) \quad (17)$$

We shall use the unbiased consistent estimator, $\hat{C}'_j(0)$, to calculate the population mean contact number.

E. Precision of the Population Mean Contact Number Estimator, $\hat{C}'_j(0)$

The precision of the estimator, $\hat{C}'_j(0)$, in estimating the population mean contact number is determined through evaluation of the variance of its distribution, which is given by (see Appendix B)

$$V_{\tau}[\hat{C}'_j(0)] = \frac{n^* \bar{X}_j}{k \cdot n (n-1) \bar{X}_0} (1 + (n-2) (\bar{X}_0 - \bar{X}_j))$$

$$-2(2n-3) \bar{X}_0 \bar{X}_j, \quad j = 1, 2, \dots, (p-1) \quad (18)$$

Note that for a two-component mixture, $j=1$, this equation reduces to a known expression [4]

$$V_r[\hat{C}'_1(0)] = \frac{n^2 \bar{X}_1}{k \cdot n \cdot (n-1) \bar{X}_0} [(n-1) - 2(2n-3) \bar{X}_0 \bar{X}_1] \quad (18-a)$$

A criterion often used for describing the extent of the variation in a population is the coefficient of variation or the relative standard error:

$$R.S.E. [C'_j(0)] = \frac{D[\hat{C}'_j(0)]}{E[C'_j(0)]} \quad (19)$$

where $D[\hat{C}'_j(0)]$ is the standard deviation of the unbiased consistent estimator $\hat{C}'_j(0)$, i.e.,

$$D[\hat{C}'_j(0)] = \sqrt{V_r[C'_j(0)]} \quad (20)$$

Hence,

$$R.S.E. [\hat{C}'_j(0)] = \left\{ \frac{1 + (n-2) (\bar{X}_0 + \bar{X}_j) - 2(2n-3) \bar{X}_0 \bar{X}_j}{k \cdot n \cdot (n-1) \bar{X}_0 \bar{X}_j} \right\}^{\frac{1}{2}} \quad (21)$$

By setting $j=1$, this reduces to a known expression for a binary mixture, i.e. [4],

$$R.S.E. [\hat{C}'_1(0)] = \left\{ \frac{1}{kn \bar{X}_1 (1-\bar{X}_1)} \left[1 - \frac{2(2n-3)}{n-1} \bar{X}_1 (1-\bar{X}_1) \right] \right\}^{\frac{1}{2}} \quad (21-a)$$

Equation (21) yields the number of samples, k , necessary for a specified value of the relative standard error, i.e.,

$$k = \frac{1 + (n-2) (\bar{X}_0 + \bar{X}_j) - 2(2n-3) \bar{X}_0 \bar{X}_j}{n(n-1) \bar{X}_0 \bar{X}_j (R.S.E. [\hat{C}'_j(0)])^2} \quad (22)$$

3. DEGREE OF MIXEDNESS BASED ON THE SAMPLE VARIANCE AND ESTIMATION OF PRECISION OF THE DEGREE OF MIXEDNESS

Over 30 different criteria for the degree of mixedness have been reviewed and summarized by Fan et al. [1]. Here we are concerned only with the estimator of the population variance of an individual component from spot samples, $\hat{\sigma}_j^2$, which has been frequently employed in defining the degree of mixedness. Suppose that a_j denotes the number of particles of component A_j in a spot sample of size n . Since a spot sample is assumed to be completely mixed, this random variable a_j obeys the 'pseudo' binomial distribution in the completely mixed state if we choose A_j as one component and lump all the remaining components as the other (pseudo) component. Thus, we have

$$E_r[a_j] = n\bar{X}_j, \quad j = 1, 2, \dots, (p-1) \quad (23)$$

and

$$V_r[a_j] = n\bar{X}_j (1 - \bar{X}_j), \quad j = 1, 2, \dots, (p-1) \quad (24)$$

The binomial distribution can be approximated as the normal distribution when $n\bar{X}_j \geq 4$ [7]. Therefore, the following approximate equations can be obtained from the property of the distribution of the variance of the normal distribution (see Appendix C).

$$E_r[\hat{\sigma}_j^2] = [n\bar{X}_j (1 - \bar{X}_j)], \quad j = 1, 2, \dots, (p-1) \quad (25)$$

and

$$V_r[\hat{\sigma}_j^2] = \frac{2}{(k-1)} [n\bar{X}_j (1 - \bar{X}_j)]^2, \quad j = 1, 2, \dots, (p-1) \quad (26)$$

Thus the relative standard error of $\hat{\sigma}_j^2$, R.S.E. $[\hat{\sigma}_j^2]$, is

$$\text{R.S.E.}[\hat{\sigma}_j^2] = \frac{D(\hat{\sigma}_j^2)}{E(\hat{\sigma}_j^2)}$$

$$= \frac{\sqrt{V_j(\hat{\sigma}_j^2)}}{E(\hat{\sigma}_j^2)}$$

$$= \sqrt{\frac{2}{k-1}}$$

$$j = 1, 2, \dots, (p-1)$$

(27)

4. COMPUTER SIMULATION

A. Procedure

Random numbers (between 0 and 1) with a uniform distribution are generated by SUBROUTINE RANDU [5] to simulate a multicomponent mixture in the completely mixed state. For example, in a ternary particles mixture, any random number, which is less than 0.2, represents a particle of component A_1 if the concentration of component A_1 is 20%, i.e., if $\bar{X}_1 = 0.2$. Similarly, we may use a random number, which is between 0.2 and 0.5, to represent a particle of component A_2 if the concentration of component A_2 is 30%, i.e., if $\bar{X}_2 = 0.3$. Uniformly distributed n random number are generated to represent a spot sample of size n , and x_j ($j = 1,2$) is determined from eqn. (9). The mean contact numbers, $\hat{C}_{1(0)}$ and $\hat{C}_{2(0)}$, are then calculated by means of eqn. (13). For precision, the experiment is replicated N times.

Specifically, the following simulation algorithm has been employed in the present work.

- (a) Specify the spot sample size, n , the total coordination number, n^* , the number of replications, N , and the population concentration of each component, \bar{X}_j ($j = 1,2$).
- (b) Pre-select the number of samples, k , to be taken.
- (c) Determine the estimators, $\{\hat{C}'_{j(0)}\}_m$ ($j = 1,2$) of the population contact number, $\hat{C}'_{j(0)}$, N times by eqn. (16).
- (d) Compute the mean, $\bar{C}'_{j(0)}$, and the sample variance, $V_r\{\hat{C}'_{j(0)}\}$, from the N estimators, respectively, as

$$\bar{C}'_{j(0)} = \frac{1}{N} \sum_{m=1}^N \{\hat{C}'_{j(0)}\}_m, \quad j = 1,2 \quad (28)$$

$$V_r\{\hat{C}'_{j(0)}\} = \frac{1}{N-1} \sum_{m=1}^N \{ \{\hat{C}'_{j(0)}\}_m - \bar{C}'_{j(0)} \}^2, \quad j = 1,2 \quad (29)$$

- (e) Estimate the relative standard error, R.S.E. $\{\hat{C}'_{j(0)}\}$ equals

$$\frac{\sqrt{V_r \{c_j^2(0)\}}}{c_j^2(0)}$$

- (f) Calculate the average number of particles of component A_j , \bar{a}_j , and the sample variance, \hat{c}_j^2 , among k spot samples, respectively, as

$$\bar{a}_j = \frac{1}{k} \sum_{i=1}^k (a_j)_i \quad (30)$$

$$\hat{c}_j^2 = \frac{1}{k-1} \sum_{i=1}^k [(a_j)_i - \bar{a}_j]^2 \quad (31)$$

- (g) Compute the mean, $\bar{\hat{c}}_j^2$, and the variance, $V_r \{\hat{c}_j^2\}$, from the N replications, respectively, as

$$\bar{\hat{c}}_j^2 = \frac{1}{N} \sum_{m=1}^N (\hat{c}_j^2)_m \quad (32)$$

$$V_r \{\hat{c}_j^2\} = \frac{1}{N-1} \sum_{m=1}^N [(\hat{c}_j^2)_m - \bar{\hat{c}}_j^2]^2 \quad (33)$$

- (h) Estimate the relative standard error based on the sample variance.

R.S.E. $\{(\hat{c}_j^2)\}$, as

$$\frac{\sqrt{V_r \{\hat{c}_j^2\}}}{\bar{\hat{c}}_j^2}$$

3. Results and Discussion

The results of the numerical experiments or simulations for ternary particle mixtures are shown in Figs. 2 through 7. Figures 2 and 3 show the mean contact number for the cases $n^* = 4$ and $n^* = 6$, respectively. The abscissa of Fig. 4 or 5 plots the number of spot samples, k , and the ordinates

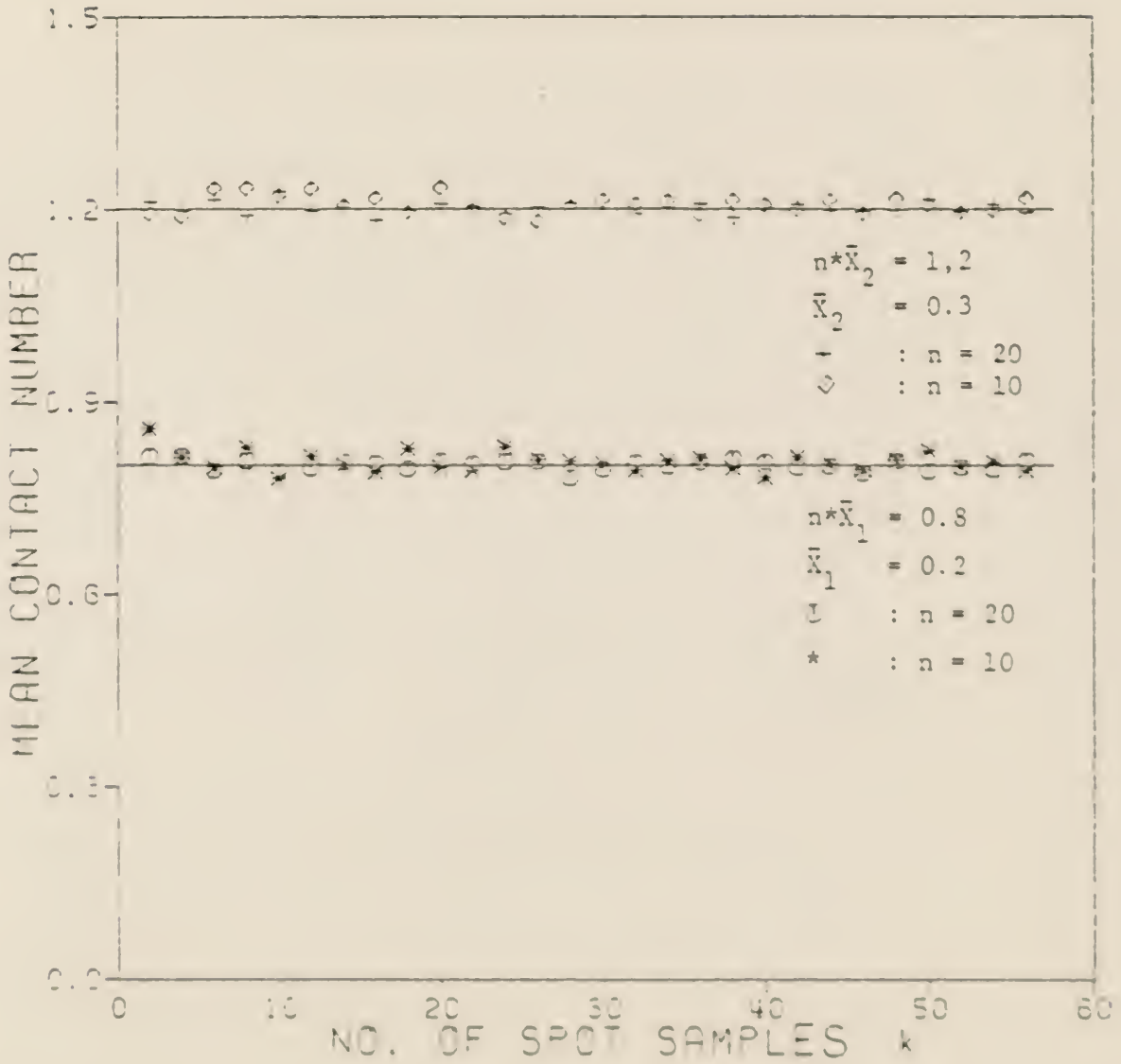


Fig. 2. Results of computer simulation for $n=4$, $\bar{X}_1=0.2$ and $\bar{X}_2=0.3$.

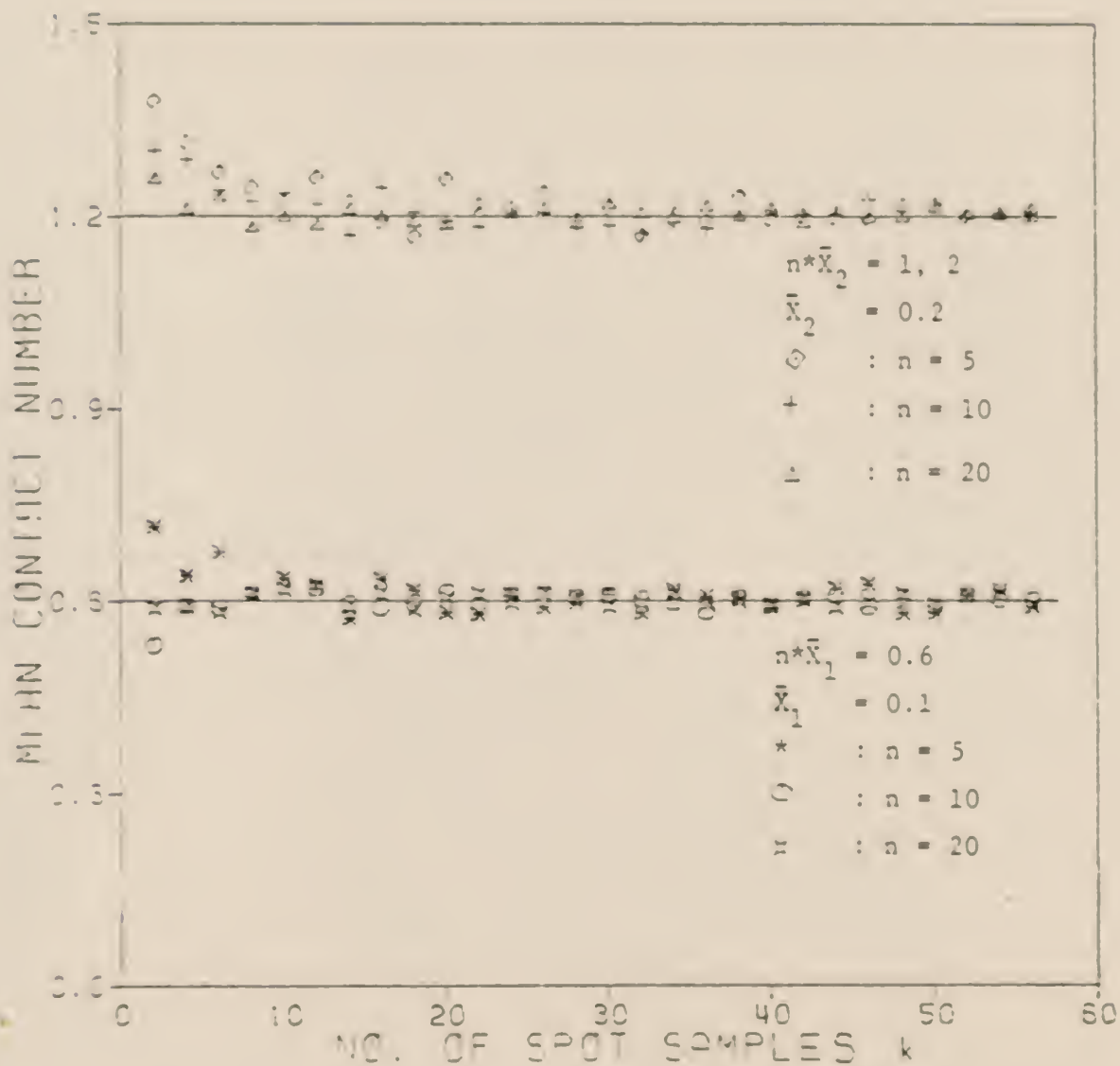


Fig. 3. Results of computer simulation for $n \cdot \bar{X}_1 = 0.6$, $\bar{X}_1 = 0.1$ and $\bar{X}_2 = 0.2$.

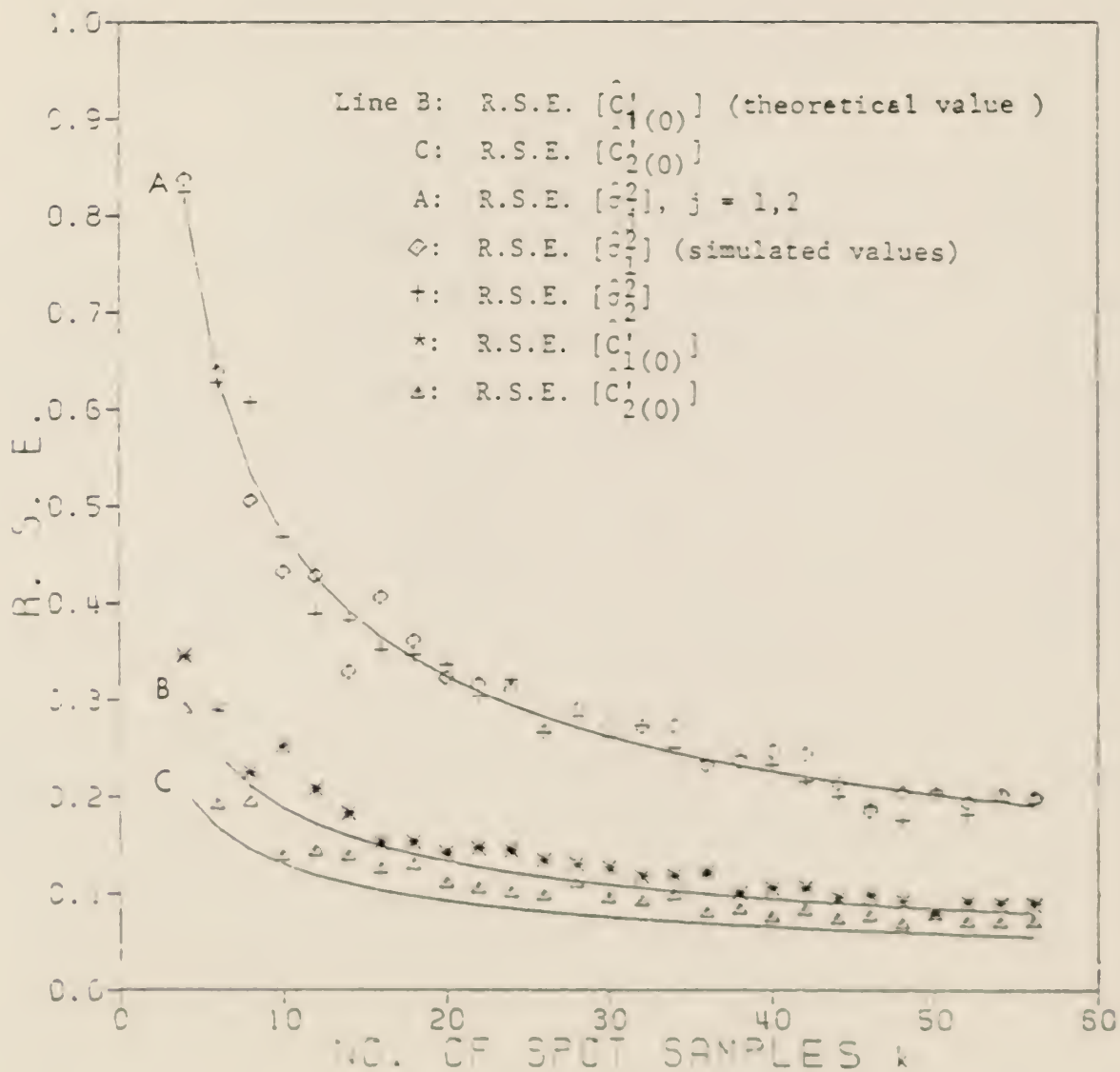


Fig. 4. Comparison of theoretical relative standard errors with those of numerical experiments: $n^*=5$, $n=10$, $\bar{X}_1=0.2$ and $\bar{X}_2=0.3$.

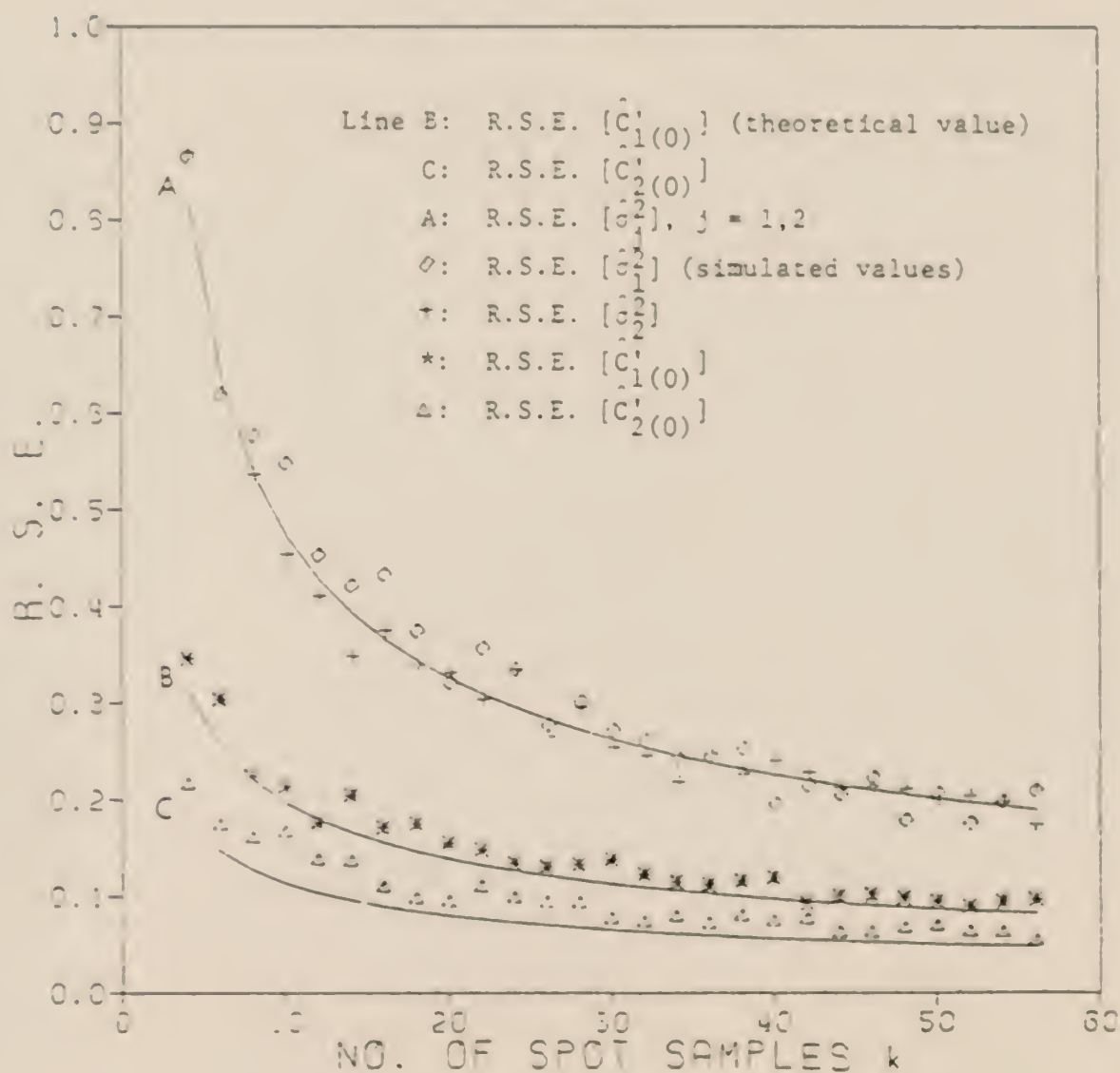


Fig. 5. Comparison of theoretical relative standard errors with those of numerical experiments: $n^*=5$, $n=20$, $\bar{X}_1=0.1$ and $\bar{X}_2=0.2$.

in the same figure plots the relative standard error of $\hat{C}'_j(0)$ or $\hat{\sigma}_j^2$ ($j = 1, 2$). Figure 4 is for $n^*=4$, and Fig. 5 is for $n^*=6$. Agreement between the results of the simulation represented by discrete symbols and the theoretical values represented by solid lines appears to be satisfactory in each case. The higher the population concentration, the smaller the relative standard error of $\hat{C}'_j(0)$. It can also be observed that R.S.E. $[\hat{C}'_j(0)]$ ($j=1, 2$) are always less than R.S.E. $[\hat{\sigma}_j^2]$ at the same k and n . Therefore, we can state that the precision of the estimator of the mean, $\hat{C}'_j(0)$, is superior to that of the estimator of the variance, $\hat{\sigma}_j^2$. Equation (21) indicates R.S.E. $[\hat{C}'_j(0)]$ depends on the population concentration as shown in Figs. 4 and 5. On the other hand, eqn. (27) indicates that R.S.E. $[\hat{\sigma}_j^2]$ is independent of the population concentration and the sample size.

The effect of the sample size, n , on the relative standard error, R.S.E. $[\hat{C}'_j(0)]$, can be observed in the results of the simulation in Figs. 6 and 7 for $n^*=4$ and 6, respectively. We observe that the larger the sample size, n , the smaller the relative standard error of $\hat{C}'_j(0)$ as predicted by eqn. (21). These figures are useful for sampling designs, in that the number of spot samples to be taken for a specified precision, can be determined from these figures. Suppose that the population concentration \bar{X}_1 and \bar{X}_2 are 0.2 and 0.3, respectively; the spot sample size, n , is 10, and the total coordination number, n^* , is 4, in estimating the population contact number within a relative standard error at 15%. Figures 7a and 7b indicate that about 16 spot samples are necessary.

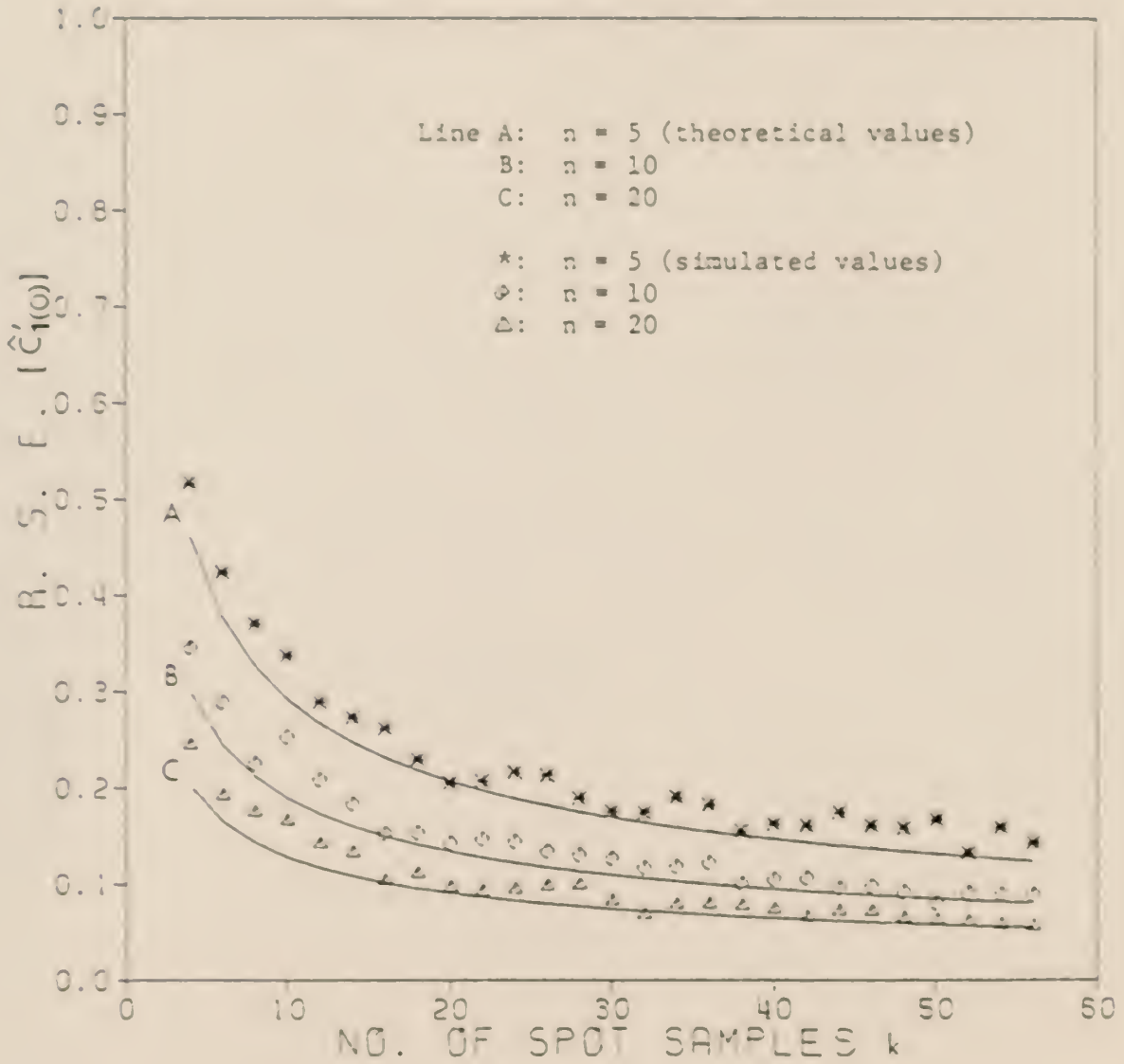


Fig. 6a. Comparison of theoretical relative standard error, R.S.E. $[C_1(0)]$, with those of numerical experiments: $\bar{X}_1 = 0.2$, $\bar{X}_2 = 0.3$ and $n^* = 4$.

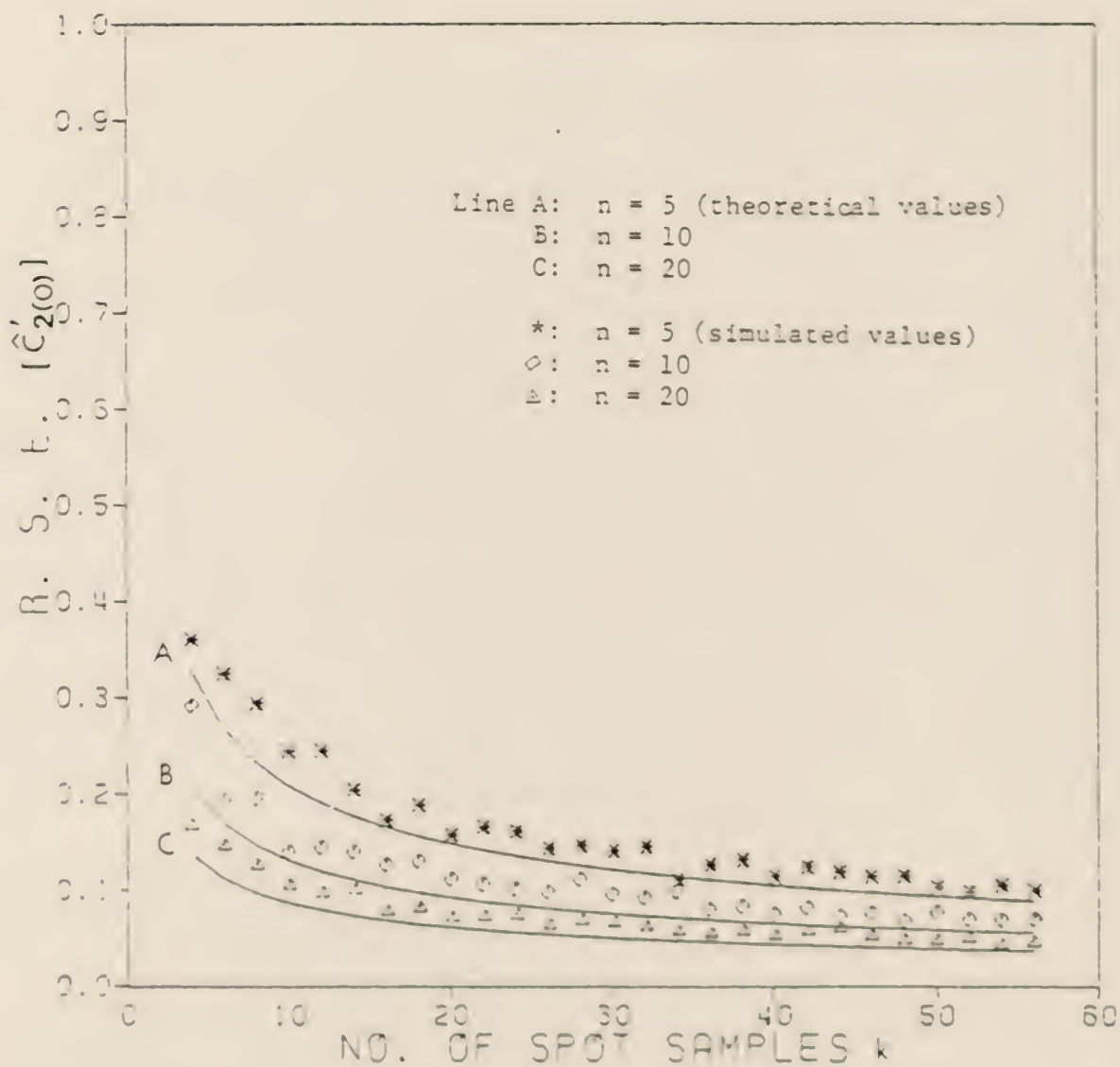


Fig. 6b. Comparison of theoretical relative standard error, R.S.E. $[\hat{C}_2(0)]$, with those of numerical experiments: $\bar{X}_1=0.2$, $\bar{X}_2=0.3$ and $n^*=4$.

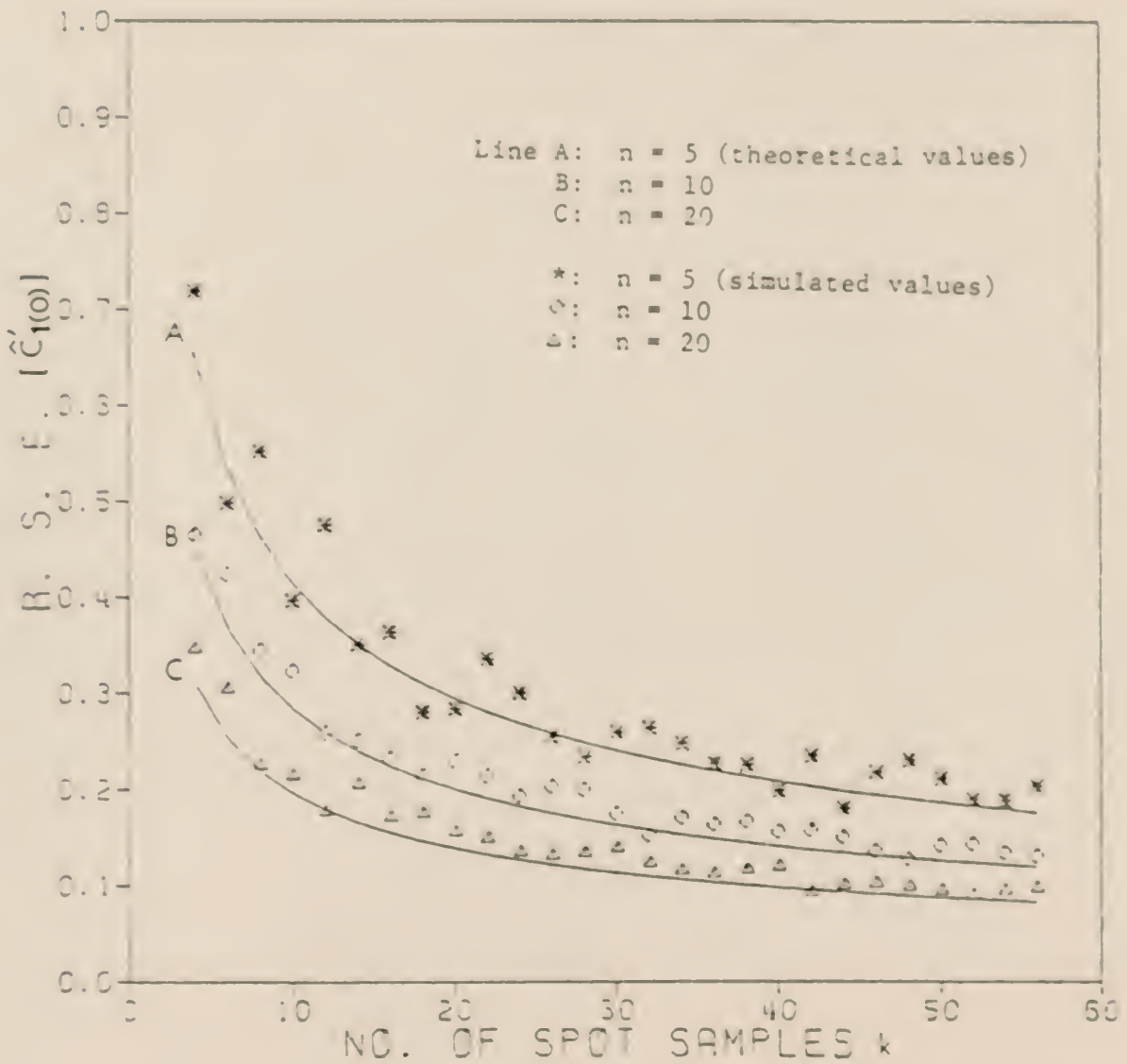


Fig. 7a. Comparison of theoretical relative standard errors, R.S.E. $[C'_1(0)]$, with those of numerical experiments: $\bar{x}_1=0.1$, $\bar{x}_2=0.2$ and $n^*=6$.

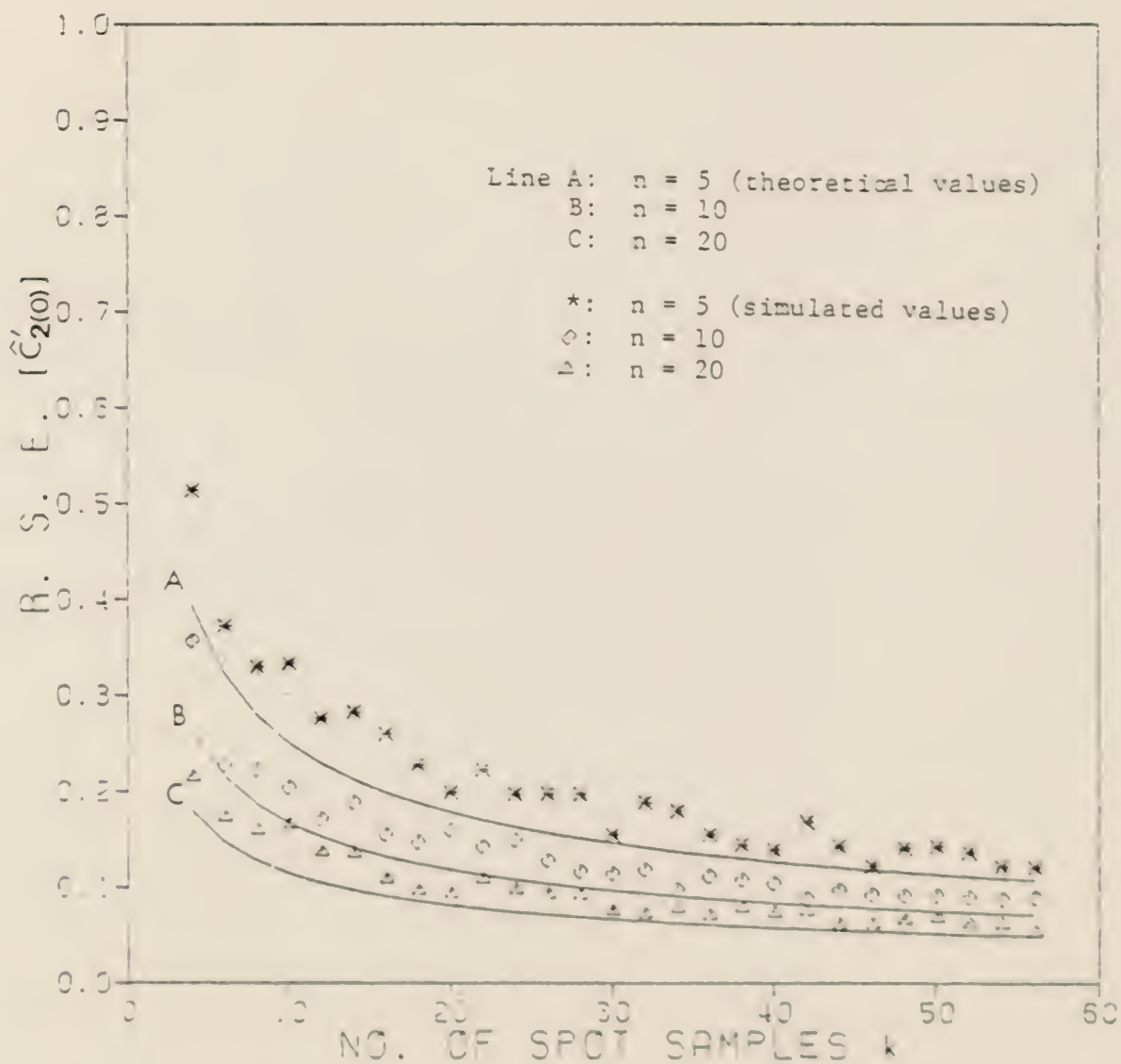


Fig. 7b. Comparison of theoretical relative standard errors, R.S.E. $[C_2'(0)]$, with those of numerical experiments: $\bar{X}_1=0.1$, $\bar{X}_2=0.2$ and $n^*=b$.

5. CONCLUSIONS

The conventional definitions of the degree of mixedness, which are mainly macroscopic and statistical in nature, do not take into account the structural and microscopic characteristics of a mixture. The mixing index proposed by Akao et al. [2] possesses some superior characteristics in comparison with conventional ones based on the variance. This study is concerned with an application of the contact number concept to estimation of the mixing index for homogeneous multicomponent mixtures. In the past such an application has been employed only to the mixing of two-component mixtures.

All equations derived in this paper can be reduced to simpler ones, which are for two-component mixtures, as described previously. Numerical experiments have also been performed to verify the theoretical expressions of the distribution of the contact number. The relative standard error of the mean contact number estimator has been shown to be smaller than that of the variance estimator of spot samples. Therefore, the precision of the mean contact number estimator is superior to that of the variance estimator. In our future work, we shall extend the estimator of contact number, $\hat{C}_j(0)$, to an incompletely mixed state.

NOTATIONS

a_j	number of particles of component A_j in a spot sample of size n
$C_j(0)$	contact number of particles of component A_j when the key particles is of component A_0 .
$\hat{C}_j(0)$	estimation of the population mean contact number of component A_j
$\hat{C}'_j(0)$	unbiased estimator of the population mean contact number of component A_j
$[C_j(0)]_i$	$C_j(0)$ in the i -th spot sample, $i=1,2,\dots,k$
$\bar{C}'_j(0)$	mean of $\hat{C}'_j(0)$ of N replications
$D\{y\}$	standard deviation of variable y
$E\{y\}$	expected value of variable y
k	number of spot samples
N	number of replications in spot sampling
n	sample size of a spot sample
n^*	coordination number, the total number of particles surrounding and in contact with a sample particle
$R.S.E.\{y\}$	relative standard error of variable y
$V\{y\}$	variance of variable y
\bar{X}_j	population mean concentration of particles of component A_j
\bar{x}_j	sample mean concentration of particles of component A_j
x_j	concentration of particles of component A_j in a spot sample
Y_j	random variable of the contact number
\hat{s}_j^2	estimator of sample variance of component A_j
\bar{s}_j^2	mean of \hat{s}_j^2 for all N replications
Subscripts	
r	completely random state
s	completely segregated state

Marka above symbol

- estimator
- mean
- unbiased estimator

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APPENDIX A. THE DERIVATION OF EQN. (14)

Equation (13), repeated below, expresses the population mean contact number of component A_j , $\bar{C}_j(0)$.

$$\bar{C}_j(0) = \frac{\sum_{i=1}^k \frac{(n^* x_i)_j (x_0)_i}{i!}}{k \bar{X}_0} \quad (13)$$

Thus, the expected value of $\bar{C}_j(0)$ in the completely random state is

$$\begin{aligned} E_r[\bar{C}_j(0)] &= E_r\left[\frac{\sum_{i=1}^k \frac{(n^* x_i)_j (x_0)_i}{i!}}{k \bar{X}_0}\right] \\ &= \frac{n^*}{k \bar{X}_0} \sum_{i=1}^k (E_r[x_0 x_j])_i \\ &= \frac{n^*}{\bar{X}_0} E_r[x_0 x_j] \end{aligned} \quad (A-1)$$

Since [6]

$$E_r[x_0 x_j] = \frac{n-1}{n} \bar{X}_0 \bar{X}_j \quad (A-2)$$

substitution of eqn. (A-2) into eqn. (A-1) yields

$$\begin{aligned} E_r[\bar{C}_j] &= \frac{n^*}{\bar{X}_0} \frac{n-1}{n} \bar{X}_0 \bar{X}_j \\ &= \frac{n-1}{n} n^* \bar{X}_j, \quad j = 1, 2, \dots, (p-1) \end{aligned} \quad (14)$$

APPENDIX B THE DERIVATION OF EQN. (18)

Equation (16), repeated below, expresses the unbiased consistent estimator of component A_j , $\hat{C}'_j(0)$,

$$\hat{C}'_j(0) = \frac{n}{n-1} \frac{\sum_{i=1}^k [n^* x_j]_i [x_0]_i}{k \bar{x}_0} \quad (16)$$

Thus, the variance of $\hat{C}'_j(0)$ in the completely random state is

$$\begin{aligned} V_r[\hat{C}'_j(0)] &= \frac{n^2}{k^2 (n-1)^2 \bar{x}_0^2} V_r \left[\sum_{i=1}^k (n^* x_0 x_j)_i \right] \\ &= \frac{n^2}{k^2 (n-1)^2 \bar{x}_0^2} \sum_{i=1}^k V_r [n^* x_0 x_j]_i \\ &= \frac{n^2 k n^{*2}}{k^2 (n-1)^2 \bar{x}_0^2} V_r [x_0 x_j] \\ &= \frac{n^2 n^{*2}}{k (n-1)^2 \bar{x}_0^2} V_r [x_0 x_j] \end{aligned} \quad (B-1)$$

Since [6]

$$\begin{aligned} E_r [x_0^2 x_j^2] &= \frac{(n-1)(n-2)(n-3)}{n^3} \bar{x}_0^2 \bar{x}_j^2 \\ &\quad + \frac{(n-1)(n-2)}{n^3} \bar{x}_0^2 \bar{x}_j \end{aligned}$$

$$\begin{aligned}
& + \frac{(n-1)(n-2)}{n^3} \bar{x}_0 \bar{x}_j^2 \\
& + \frac{(n-1)}{n^3} \bar{x}_0 \bar{x}_j
\end{aligned} \tag{B-2}$$

and

$$E_r[x_0 x_j] = \frac{n-1}{n} \bar{x}_0 \bar{x}_j \tag{B-3}$$

we have

$$\begin{aligned}
V_r[x_0 x_j] &= E_r[x_0^2 x_j^2] - [E_r[x_0 x_j]]^2 \\
&= - \frac{(n-1)(4n-6)}{n^3} \bar{x}_0^2 \bar{x}_j^2 \\
&\quad + \frac{(n-1)(n-2)}{n^3} \bar{x}_0^2 \bar{x}_j \\
&\quad + \frac{(n-1)(n-2)}{n^3} \bar{x}_0 \bar{x}_j^2 \\
&\quad + \frac{(n-1)}{n^3} \bar{x}_0 \bar{x}_j
\end{aligned} \tag{B-4}$$

Substitution of eqn. (B-4) into eqn. (B-1) gives

$$\begin{aligned}
& V_r[\dot{C}_j(0)] \\
&= \frac{n^2 n^2}{k(n-1)^2 \bar{x}_0^2} \left(- \frac{(n-1)(4n-6)}{n^3} \bar{x}_0^2 \bar{x}_j^2 \right.
\end{aligned}$$

$$+ \frac{(n-1)(n-2)}{n^3} \bar{X}_0^2 \bar{X}_j + \frac{(n-1)(n-2)}{n^3} \bar{X}_0 \bar{X}_j^2$$

$$+ \frac{(n-1)}{n^3} \bar{X}_0 \bar{X}_j]$$

$$= \frac{n \bar{X}_j^2}{k \cdot n \cdot \bar{X}_0} \left[\frac{1}{(n-1)} + \frac{(n-2)}{(n-1)} (\bar{X}_0 + \bar{X}_j) - \frac{2(2n-3)}{(n-1)} \bar{X}_0 \bar{X}_j \right]$$

$$= \frac{n \bar{X}_j^2}{kn(n-1) \bar{X}_0} [1 + (n-2)(\bar{X}_0 + \bar{X}_j) - 2(2n-3) \bar{X}_0 \bar{X}_j] \quad (16)$$

APPENDIX C. THE DERIVATION OF EQNS. (25) and (26).

The average number of particles of component A_j , \bar{a}_j , and the sample variance, $\hat{\sigma}_j^2$, among k spot samples are, respectively,

$$\bar{a}_j = \frac{1}{k} \sum_{i=1}^k (a_j)_i \quad (C-1)$$

$$\hat{\sigma}_j^2 = \frac{1}{k-1} \sum_{i=1}^k [(a_j)_i - \bar{a}_j]^2 \quad (C-2)$$

Let

$$s_j^2 = \frac{1}{k} \sum_{i=1}^k [(a_j)_i - \bar{a}_j]^2$$

Denoting its density function by $f(u_j)$, we have [6]

$$f(u_j) = \begin{cases} \frac{k-1}{k^2} \frac{k-3}{u_j^2} \exp(-ku_j/2\sigma_j^2) & \text{for } u_j > 0 \\ 2(k-1)/2 \tau [1/2(k-1)] \sigma_j^{k-1} & \\ 0 & \text{for } u_j \leq 0 \end{cases}$$

where u_j is the value of s_j^2 . This density function gives the expected value and the variance, respectively, as

$$\begin{aligned} E[s_j^2] &= \frac{k-1}{k} \sigma_j^2 \\ &= \frac{k-1}{k} [n\bar{x}_j (1 - \bar{x}_j)] \end{aligned} \quad (C-3)$$

$$\begin{aligned}
 V\{s_j^2\} &= \frac{2(k-1)}{k^2} \sigma_j^4 \\
 &= \frac{2(k-1)}{k^2} [n\bar{X}_j (1 - \bar{X}_j)]^2
 \end{aligned}
 \tag{C-4}$$

Since

$$\hat{\sigma}_j^2 = \frac{k}{k-1} s_j^2,
 \tag{C-5}$$

we have

$$\begin{aligned}
 E\{\hat{\sigma}_j^2\} &= E\left[\frac{k}{k-1} s_j^2\right] \\
 &= \frac{k}{k-1} E\{s_j^2\} \\
 &= n\bar{X}_j (1 - \bar{X}_j)
 \end{aligned}
 \tag{25}$$

$$\begin{aligned}
 V\{\hat{\sigma}_j^2\} &= V\left[\frac{k}{k-1} s_j^2\right] \\
 &= \frac{k^2}{(k-1)^2} V\{s_j^2\} \\
 &= \frac{2}{(k-1)} [n\bar{X}_j (1 - \bar{X}_j)]^2
 \end{aligned}
 \tag{26}$$

ESTIMATION OF MIXING INDEX AND CONTACT NUMBER BY SPOT SAMPLING
OF A MULTICOMPONENT MIXTURE IN AN INCOMPLETELY MIXED STATE

1. INTRODUCTION

Two sampling schemes based on the contact number, namely, spot sampling and coordination number sampling, are used to determine the mixing index (the degree of mixedness). The former is effected by randomly selecting a fixed number of particles. It is the procedure conventionally employed in solids mixing. The latter, as proposed by Akao et al. [1], gives rise to an understanding of the microscopic and geometric characteristics of solid mixtures. A "sample particle" is selected at random from a mixture, and the n_c particles which are in contact with it are examined. We refer to n_c as the "total coordination number". In spite of the difficulty in applying coordination number sampling, the statistical characteristics of the contact number and the mixing index are of theoretical importance.

Fun et al. [2] proposed an approach for estimating the population contact number of each component of a multicomponent mixture by spot sampling. Under the assumption that the completely mixed state exists in each of the spot samples, it is unnecessary to count the contact number directly in a spot sample. The population contact number of each component is estimated from its concentrations in spot samples. Compared to coordination number sampling, spot sampling can be employed with relative ease, because the structural details within a sample are neglected in its analysis.

Recently, Shindo et al. [3] proposed a beta-binomial model to describe a binary mixture in an incompletely mixed state. In the present study, a Dirichlet-multinomial model is proposed to describe the multicomponent mixture in an incompletely mixed state. Estimates of the parameters are derived and the precision of the estimated population mean contact number are assessed. Computer simulation is included to support the effectiveness of the derived model.

2. CONTACT NUMBER AND MIXING INDEX

When a particle is taken randomly from a mixture, the number of particles which are in contact with this particular particle is called the total coordination number, n^* , and this particular particle is called the sample particle [1]. Let A_0 particles be key particles in a multi-component mixture containing $(p+1)$ types of particles of the same size, denoted by A_0, A_1, \dots, A_p . The number of particles of component A_j in contact with a key particle is defined as the contact number contributed by component A_j , and is denoted by $C_j(0)$.

In the completely mixed state, particles of each component are expected to be randomly distributed in a sample from coordination number sampling of size n^* . Thus, the values of the contact number, or simply, the contact numbers, $C_0(0), C_1(0), \dots, C_p(0)$, have the following multinomial distribution [6].

$$\begin{aligned}
 &Pr\{C_0(0) = c_0(0), C_1(0) = c_1(0), \dots, C_p(0) = c_p(0)\} \\
 &= \frac{n^*!}{c_0(0)! c_1(0)! \dots c_p(0)!} \bar{x}_0^{c_0(0)} \bar{x}_1^{c_1(0)} \dots \bar{x}_p^{c_p(0)} \\
 &= \frac{n^*!}{\prod_{j=0}^p c_j(0)!} \prod_{j=0}^p \bar{x}_j^{c_j(0)}, \quad \sum_{j=0}^p c_j(0) = n^* \quad (1)
 \end{aligned}$$

where \bar{x}_j is the population concentration of particles of component A_j , and $c_j(0)$ is the value of the contact number $C_j(0)$ for the j -th component. Thus, the expected value and the variance of $C_j(0)$ in the completely mixed state are, respectively,

$$E_r[C_{j(0)}] = n \bar{X}_j, \quad j = 0, 1, 2, \dots, p \quad (2)$$

and

$$V_r[C_{j(0)}] = n \bar{X}_j (1 - \bar{X}_j), \quad j = 0, 1, 2, \dots, p \quad (3)$$

The expected value and the variance of $C_{j(0)}$ in the completely segregated state are both zero, provided that the boundaries between different types of particles are neglected, i.e.,

$$E_s[C_{j(0)}] = 0, \quad j = 1, 2, \dots, p \quad (4)$$

and

$$V_s[C_{j(0)}] = 0, \quad j = 1, 2, \dots, p \quad (5)$$

Akao et al. [1] proposed a mixing index based on the contact number, $C_{j(0)}$, for a binary mixture. Here, we extend their work to define a mixing index for the multicomponent mixture.

$$M = \frac{p}{r} \frac{E[C_{1(0)}] - E_s[C_{1(0)}]}{E_r[C_{j(0)}] - E_s[C_{j(0)}]} \frac{\bar{X}_j}{1 - \bar{X}_0}$$

$$= \frac{p}{r} \frac{E[C_{1(0)}]}{E_r[C_{j(0)}]} \frac{\bar{X}_j}{1 - \bar{X}_0} \quad (6)$$

Under the assumption that the completely mixed state exists in each spot sample, an unbiased estimator of the contact number, $\hat{C}'_{j(0)}$, is given as [2]

$$\hat{C}'_{j(0)} = \frac{n}{n-1} \frac{\sum_{i=1}^k n^* [x_j]_i [x_0]_i}{k \bar{x}_0}, \quad j = 1, 2, \dots, p \quad (7)$$

where $[x_j]_i$ denotes the concentration of A_j particles in the i -th spot sample of size n , \bar{x}_0 the sample mean concentration of the key component, and k the number of spot samples. In [2], $\hat{C}'_{j(0)}$ is referred to as the mean contact number contributed by component A_j in k spot samples. Since \bar{x}_0 is often specified in solids mixing, we may replace \bar{x}_0 with \bar{X}_0 , i.e.,

$$\hat{C}'_{j(0)} = \frac{n}{n-1} \frac{\sum_{i=1}^k n^* [x_j]_i [x_0]_i}{k \bar{X}_0} \quad (8)$$

In the completely mixed state, the expected value, $E_r[\hat{C}'_{j(0)}]$, the variance, $V_r[\hat{C}'_{j(0)}]$, and the relative standard error, R.S.E. $[\hat{C}'_{j(0)}]$, are, respectively [2],

$$E_r[\hat{C}'_{j(0)}] = n^* \bar{X}_j, \quad j = 1, 2, \dots, p \quad (9)$$

$$V_r[\hat{C}'_{j(0)}] = \frac{n^* \bar{X}_j^2}{k n(n-1) \bar{X}_0} \{ 1 + (n-2)(\bar{X}_0 + \bar{X}_j) - 2(2n-3)\bar{X}_0 \bar{X}_j \} \quad (10)$$

and

$$\text{R.S.E.}[C_j^i(0)] = \left\{ \frac{1 + (n-2)(\bar{X}_0 + \bar{X}_j) - 2(2n-3)\bar{X}_0\bar{X}_j}{kn(n-1)\bar{X}_0\bar{X}_j} \right\}^{1/2}$$

3. DESCRIPTION OF AN INCOMPLETELY MIXED STATE

3.1 Dirichlet-Multinomial Model

In the completely mixed state, the local or regional concentration of A_j particles is constant everywhere in a mixture, and its expected value is equal to the population concentration, \bar{X}_j . For a mixture in the incompletely mixed state, the population concentration is quite variable. To deal with this distribution of the concentrations or inhomogeneity among the spot samples, a compound binomial distribution has been introduced as a model of an incompletely mixed or semi-random binary mixture [3]. Here, we extend this approach to a multicomponent system.

Let z_j denote the local concentration of A_j particles in a multicomponent mixture. Under the assumption that the local concentrations are distributed according to the Dirichlet distribution which is a multivariate generalization of the beta distribution (see, e.g., [4]), the joint probability density function of $\{Y_1, Y_2, \dots, Y_p\}$ is given by (see Appendix A):

$$\begin{aligned} & \text{Pr}\{Y_1 = y_1, Y_2 = y_2, \dots, Y_p = y_p\} \\ &= \int_0^1 \int_0^{1-z_1} \dots \int_0^{1-z_1-z_2-\dots-z_{p-1}} \left\{ \frac{n!}{\prod_{j=0}^p y_j!} z_j^{y_j} \frac{\prod_{j=0}^p \Gamma(\theta_j)}{\Gamma(\sum_{j=0}^p \theta_j)} \prod_{j=1}^p z_j^{\theta_j-1} \right. \\ & \quad \left. \left(1 - \sum_{j=1}^p z_j\right)^{\theta_0-1} \right\} dz_p \dots dz_2 dz_1 \end{aligned}$$

$$= \frac{n!}{\prod_{j=0}^p y_j!} \frac{\prod_{j=0}^p \Gamma(\sum_{j=0}^p \theta_j)}{\prod_{j=0}^p \Gamma(\theta_j)} \frac{\prod_{j=0}^p \Gamma(y_j + \theta_j)}{\Gamma[\sum_{j=0}^p (y_j + \theta_j)]}, \quad (12)$$

$$0 \leq y_0, y_1, \dots, y_p \leq n \text{ and } \sum_{j=0}^p y_j = n$$

where Y_j is a random variable denoting the number of A_j particles which are contained in a spot sample, y_j the observed value of the random variable, Z_j , z_j the value of the random variable, Z_j , θ_j (> 0) parameters of the Dirichlet distribution, and $\Gamma(\cdot)$ the gamma function.

3.2 Statistical Characteristics of Random Variables, Y_1, Y_2, \dots, Y_p

The generalized factorial moment is defined as [4]

$$\mu_{(\lambda_1, \lambda_2, \dots, \lambda_p)} = E[Y_1^{(\lambda_1)} Y_2^{(\lambda_2)} \dots Y_p^{(\lambda_p)}] \quad (13)$$

where

$$Y_j^{(\lambda_j)} = \frac{Y_j!}{(Y_j - \lambda_j)!} = Y_j(Y_j - 1) \dots (Y_j - \lambda_j + 1), \quad j = 1, 2, \dots, p \quad (14)$$

Thus, the generalized factorial moment of the Dirichlet-multinomial model, defined in eqn. (12), can be derived as [see Appendix B]

$$P(x_1, x_2, \dots, x_p) = \frac{n!}{x_1! x_2! \dots x_p!} \frac{\tau^p (\tau - x_1 - 1)(\tau - x_2 - 2) \dots (\tau - x_p)}{(\tau x_1 + x_1 - 1)(\tau x_2 + x_2 - 2) \dots (\tau x_p)} \quad (15)$$

The expected value, $E[Y_j]$, and the variance, $V[Y_j]$, are obtained from eqn. (15), respectively, as

$$\begin{aligned} E[Y_j] &= \sum_{i=0}^{\tau} i \binom{\tau}{i} e_j^i (0, 0, \dots, 1, 0, \dots, 0) \\ &= n \frac{\tau e_j}{\tau - e_j} \\ &= \frac{n \tau e_j}{\tau} \end{aligned} \quad (16)$$

and

$$\begin{aligned} V[Y_j] &= E[Y_j^2] - E[Y_j]^2 \\ &= \sum_{i=0}^{\tau} i(i-1) \binom{\tau}{i} e_j^i (0, 0, \dots, 2, 0, \dots, 0) + \sum_{i=0}^{\tau} i \binom{\tau}{i} e_j^i (0, 0, \dots, 1, 0, \dots, 0) \\ &\quad - \left(\sum_{i=0}^{\tau} i \binom{\tau}{i} e_j^i (0, \dots, 1, 0, \dots, 0) \right)^2 \\ &= \frac{n(n-1) \tau e_j (1+e_j)}{(1+\tau e_j)^2 (\tau - e_j)} + \frac{n \tau e_j}{\tau - e_j} - \left(\frac{n \tau e_j}{\tau - e_j} \right)^2 \\ &= \frac{n \tau e_j (\tau - e_j) (n + \tau)}{(1 + \tau e_j)^2} \end{aligned} \quad (17)$$

where

$$\tau = \sum_{j=0}^p \theta_j \quad (18)$$

The covariance between random variables Y_j and Y_k , $\text{Cov}[Y_j, Y_k]$, is

$$\begin{aligned} & \text{Cov}[Y_j, Y_k] \\ &= E[Y_j Y_k] - E[Y_j] E[Y_k] \\ &= \frac{n(n-1)\theta_j \theta_k}{\sum_{i=0}^p \theta_i} - \frac{n\theta_j}{\sum_{i=0}^p \theta_i} \frac{n\theta_k}{\sum_{i=0}^p \theta_i} \\ &= - \frac{n(n+\sum_{i=0}^p \theta_i)\theta_j \theta_k}{(\sum_{i=0}^p \theta_i) (1+\sum_{i=0}^p \theta_i)} \\ &= - \frac{n(n+\tau)\theta_j \theta_k}{\tau(1+\tau)} \quad (19) \end{aligned}$$

3.3 Estimation of parameters, $\theta_0, \theta_1, \dots, \theta_p$

Estimates of the parameters of the Dirichlet-multinomial distribution can be obtained via the method of moments as follows [9]:

The following relationships are obtained by equating each sample mean, \bar{y}_j , to its expectation, eqn. (1b):

$$\bar{y}_j = \frac{\sum_{i=0}^p y_{ji}}{p+1}$$

$$\hat{\tau} = \frac{n\hat{\tau}_j}{\hat{\tau}}, \quad j = 1, 2, \dots, p \quad (20)$$

where

$$\hat{\tau} = \sum_{i=0}^p \hat{\tau}_i \quad (21)$$

From the variance of Y_j , eqn. (17), we have

$$S_j^2 = \frac{n\hat{\tau}_j(\hat{\tau} - \hat{\tau}_j)(n + \hat{\tau})}{(1 + \hat{\tau})\hat{\tau}^2} \quad (22)$$

Solving for $\hat{\tau}$ from eqns. (20) and (22), we obtain

$$\hat{\tau} = \frac{n\{\bar{y}_j(n - \bar{y}_j) - S_j^2\}}{nS_j^2 - \bar{y}_j(n - \bar{y}_j)} \quad (23)$$

where the sample variance of component A_j , S_j^2 , is

$$S_j^2 = \frac{\sum_{i=1}^k (y_{ji} - \bar{y}_j)^2}{(k-1)}$$

Here k is the number of spot samples of size n . From eqn. (20), we have

$$\hat{\theta}_j = \frac{\sum_{i=1}^n \bar{y}_i}{n}, \quad j = 1, 2, \dots, p \quad (24)$$

The parameter, θ_0 , can be obtained from eqns. (21) and (24) as

$$\hat{\theta}_0 = \frac{\sum_{i=1}^p [n - \sum_{i=1}^p \bar{y}_i]}{n} \quad (25)$$

4. PRECISION OF THE ESTIMATION OF MEAN CONTACT NUMBER

We now consider the precision of the estimator, $\hat{C}'_{j(0)}$, eqn. (6), of a mixture in an incompletely mixed state. This precision can be derived from the compound distribution given by eqn. (12).

The concentration of A_j particles, x_j , in a spot sample can be expressed as the ratio of the number of A_j particles, Y_j , to the spot sample size, n , i.e.,

$$x_j = \frac{Y_j}{n}, \quad j = 1, 2, \dots, p \quad (26)$$

Therefore, eqns. (16) and (17) yield, respectively,

$$\begin{aligned} E[x_j] &= \frac{1}{n} E[Y_j] \\ &= \frac{\theta_j}{\sum_{i=0}^p \theta_i} \\ &= \frac{\theta_j}{\tau} \end{aligned} \quad (27)$$

and

$$\begin{aligned}
 V(x_j) &= \frac{1}{n^2} V(y_j) \\
 &= \frac{(n+\tau)(\tau-\theta_j)\theta_j}{n(1+\tau)\tau^2}
 \end{aligned} \tag{28}$$

From eqns. (8), (27) and (28) the expected value, $E[\hat{C}'_j(0)]$, and the variance, $V[\hat{C}'_j(0)]$, can be derived as (see Appendix C)

$$E[\hat{C}'_j(0)] = \frac{n^* \tau_j \bar{r}_0}{\bar{r}_0 (1+\tau) \tau} \tag{29}$$

and

$$\begin{aligned}
 V[\hat{C}'_j(0)] &= \frac{n^{*2} (n+\tau) \theta_0 \theta_j}{n(n-1) k \bar{r}_0 \tau^2 (1+\tau)^2 (\tau+2)(\tau+3)} \\
 &\quad [2(3\tau-3n-2n\tau+3)\theta_0 \theta_j + (n-2)\tau(1+\tau)(\theta_j + \theta_0)] \\
 &\quad + (n+\tau+1)\tau(1+\tau)
 \end{aligned} \tag{30}$$

From eqns. (29) and (30), we obtain the relative standard error, R.S.E.

$[\hat{C}'_j(0)]$, in an incompletely mixed state as

$$\text{R.S.E. } [\hat{C}'_j(0)]$$

$$\begin{aligned}
 &= \frac{\sqrt{V[\hat{C}'_j(0)]}}{\Sigma[\hat{C}'_j(0)]} \\
 &= \left\{ \frac{(n+\tau)\bar{X}_0}{n(n-1)k(\tau+2)(\tau+3)\bar{\sigma}_0\bar{\sigma}_j} [2(3\tau-3n-2n\tau+3)\bar{\sigma}_0\bar{\sigma}_j \right. \\
 &\quad \left. + (n-2)\tau^2(1+\tau)(\bar{\sigma}_j+\bar{\sigma}_0) - (n+\tau+1)\tau(1+\tau)] \right\}^{\frac{1}{2}} \quad (31)
 \end{aligned}$$

By setting $p=1$, this reduces to a known expression for a binary mixture, i.e., [3]

$$\begin{aligned}
 \text{R.S.E.}(\hat{C}'_1(0)) &= \left\{ \frac{(n+\tau)\bar{X}_0}{n(n-1)k(\tau+2)(\tau+3)\bar{\sigma}_0\bar{\sigma}_1} [2(3\tau-3n- \right. \\
 &\quad \left. 2n\tau+3)\bar{\sigma}_0\bar{\sigma}_1 + \tau(1+\tau)(n\tau-\tau+n+1)] \right\}^{\frac{1}{2}} \quad (32)
 \end{aligned}$$

Equation (31) yields the number of samples, k , necessary for the relative standard error to be within a specified value, i.e.,

$$\begin{aligned}
 k &= \left\{ \frac{(n+\tau)\bar{X}_0}{n(n-1)(\tau+2)(\tau+3)\bar{\sigma}_0\bar{\sigma}_j (\text{R.S.E.}(\hat{C}'_j(r)))^2} [2(3\tau-3n- \right. \\
 &\quad \left. 2n\tau+3)\bar{\sigma}_0\bar{\sigma}_j + (n-2)\tau^2(1+\tau)(\bar{\sigma}_j+\bar{\sigma}_0) - (n+\tau+1)\tau(1+\tau)] \right\}^{\frac{1}{2}} \quad (33)
 \end{aligned}$$

As $\tau \rightarrow \infty$ (corresponding to the completely mixed state), eqns. (30) and (31) reduce to eqns. (10) and (11), respectively. Therefore [2], eqn. (33) becomes

$$k = \frac{1 + (n-2)(\bar{X}_0 + \bar{X}_j) - 2(2n-3)\bar{X}_0\bar{X}_j}{n(n-1)\bar{X}_0\bar{X}_j \text{ R.S.E.}(\hat{C}'_j(0))^2} \quad (34)$$

According to eqn. (29), the mixing index, eqn. (6), is expressed as

$$\begin{aligned}
 M &= \frac{p}{\Sigma_{j=1}^n n^* \bar{X}_j} \cdot \frac{1}{\tau+1} \cdot \frac{\bar{X}_j}{1-\bar{X}_0} \\
 &= \frac{\tau}{\tau+1} \quad (35)
 \end{aligned}$$

5. ESTIMATION OF SAMPLE VARIANCE AND ITS PRECISION

Various definitions of the degree of mixedness based on the sample variance have been reviewed and summarized by Fan et al. [5]. Here we are concerned with the estimator of the population variance of an individual component, $\hat{\sigma}_j^2$, which has been frequently employed in defining the degree of mixedness. Suppose that k spot samples of size n are taken at random from a mixture. In the incompletely mixed state, we assume that the random variables (Y_1, Y_2, \dots, Y_n) are distributed according to the Dirichlet-multinomial distribution. Sample mean and variance for each component, eqns. (16) and (17), are repeated here for convenience.

$$E[Y_j] = n\bar{X}_j, \quad j = 1, 2, \dots, p \quad (16)$$

and

$$\begin{aligned} V[Y_j] &= \sigma_j^2 \\ &= \frac{n(n+1)}{(1+\tau)} \bar{X}_j(1-\bar{X}_j), \quad j = 1, 2, \dots, p \end{aligned} \quad (17)$$

Therefore, the expected value and variance of sample variance of component A_j are [6]

$$E[S_j^2] = \sigma_j^2 \quad (36)$$

and

$$V[S_j^2] = \frac{1}{k} \left\{ \mu_{j4} - \frac{k-3}{k-1} \sigma_j^4 \right\} \quad \text{for } k > 1 \quad (37)$$

where μ_{j4} denotes the 4th central moment of y_j about $E[Y_j]$, (see Appendix D), i.e.,

$$\mu_{j4} = E(Y_j - E[Y_j])^4 \quad (38)$$

Thus, the relative standard error of σ_j^2 , R.S.E. $[\sigma_j^2]$, is

$$\begin{aligned} \text{R.S.E.}[S_j^2] &= \frac{\sqrt{V[S_j^2]}}{E[S_j^2]} \\ &= \left\{ \frac{1}{k} \left(\frac{\mu_{j4}}{\sigma_j^4} - \frac{k-3}{k-1} \right) \right\}^{\frac{1}{2}} \end{aligned} \quad (39)$$

6. COMPUTER SIMULATION

6.1 Simulation of a Ternary Mixture

For simplicity, we describe the simulation of a ternary mixture in the incompletely mixed state using the Dirichlet-multinomial distribution. As before, let Y_1 and Y_2 denote the numbers of particles from component A_1 and A_2 , respectively, in a spot sample of size n ($Y_0 = n - Y_1 - Y_2$), where Y_1 and Y_2 have the Dirichlet-multinomial distribution with parameter

$\hat{\theta}_1 = t\bar{X}_1$ and $\hat{\theta}_2 = t\bar{X}_2$. In each case, N independent samples of (Y_1, Y_2) are drawn from the underlying distribution and the estimators, $\hat{C}'_{1(0)}$ and $\hat{C}'_{2(0)}$, are computed. Relative standard errors of $\hat{C}'_{1(0)}$ and $\hat{C}'_{2(0)}$ are also calculated and compared with the theoretical value based on this model. For precision, the simulation is repeated N times.

Simulation Algorithm

(1) The following parameters are specified:

- (a) the size of the spot sample, n
- (b) the total coordination number, n^*
- (c) the parameter, t
- (d) the population concentration of each component, \bar{X}_j ($\bar{X}_j \geq 0$, $j=0, 1, 2$, and $\bar{X}_0 + \bar{X}_1 + \bar{X}_2 = 1$)
- (e) the number of spot sample, k
- (f) the number of replications, N .

(2) The random variables (Z_1, Z_2) are generated as realization of Dirichlet random variables with parameters $\hat{\theta}_1 = t\bar{X}_1$ and $\hat{\theta}_2 = t\bar{X}_2$, respectively. The simulation of the Dirichlet random variables are completed by generating independent gamma random variables (W_0, W_1, W_2) with the scale parameters, $t\bar{X}_0$, $t\bar{X}_1$, $t\bar{X}_2$, and an identical shape parameter of unity [7,10,11,13], where we define the appropriate Dirichlet random variables as

$$Z_1 = \frac{W_1}{W_0 + W_1 + W_2} \quad ,$$

$$Z_2 = \frac{W_2}{W_0 + W_1 + W_2} \quad ,$$

$$Z_0 = 1 - Z_1 - Z_2$$

- (3) A set of multinomial random variables, each with parameters n, Z_0, Z_1, Z_2 , is then generated [12,13].
- (4) Steps (2) and (3) are repeated until k realizations of the random variables (Y_1, Y_2) have been selected.
- (5) The concentration of each component is calculated according to eqn. (26), for each spot sample. The mean contact numbers, $\hat{C}'_{1(0)}$ and $\hat{C}'_{2(0)}$, are then estimated by means of eqn. (8).
- (6) Steps (2) to (5) are repeated N times, and the mean, $\bar{\hat{C}}'_j(0)$, and the variance, $V[\hat{C}'_j(0)]$, are computed from the N estimators, respectively, as

$$\bar{\hat{C}}'_j(0) = \frac{1}{N} \sum_{m=1}^N \{\hat{C}'_j(0)\}_m, \quad j = 1, 2 \quad (40)$$

$$V[\hat{C}'_j(0)] = \frac{1}{N-1} \sum_{m=1}^N \left\{ \{\hat{C}'_j(0)\}_m - \bar{\hat{C}}'_j(0) \right\}^2, \quad j = 1, 2 \quad (41)$$

- (7) The relative standard error, R.S.E. $[\hat{C}'_j(0)]$, is estimated as

$$\frac{\sqrt{V[\hat{C}'_j(0)]}}{\bar{\hat{C}}'_j(0)}, \quad j = 1, 2 \quad (42)$$

- (8) The average number of particles of component A_j , \bar{y}_j , and the variance, \hat{c}_j^2 , among k spot samples, are calculated, respectively,

as

$$\bar{y}_j = \frac{1}{k} \sum_{i=1}^k (y_j)_i, \quad j = 1, 2 \quad (43)$$

$$\hat{\sigma}_j^2 = \frac{1}{k-1} \sum_{i=1}^k (y_j)_i - \bar{y}_j)^2, \quad j = 1, 2 \quad (44)$$

(9) The mean of $\hat{\sigma}_j^2$, $\bar{\sigma}_j^2$, and the variance of $\hat{\sigma}_j^2$, $V[\hat{\sigma}_j^2]$, are evaluated from the N replications, respectively, as

$$\bar{\sigma}_j^2 = \frac{1}{N} \sum_{m=1}^N (\hat{\sigma}_j^2)_m, \quad j = 1, 2 \quad (45)$$

$$V[\hat{\sigma}_j^2] = \frac{1}{N-1} \sum_{m=1}^N \{[(\hat{\sigma}_j^2)_m - \bar{\sigma}_j^2]^2\}, \quad j = 1, 2 \quad (46)$$

(10) The relative standard error based on the sample variance, R.S.E. $[\hat{\sigma}_j^2]$, is estimated as

$$\frac{\sqrt{V[\hat{\sigma}_j^2]}}{\bar{\sigma}_j^2}, \quad j = 1, 2 \quad (47)$$

Results of Computer Simulation and Discussion

The results of computer simulation for ternary particle mixtures are shown in Figs. 1 through 5. Figure 1 illustrates the simulated mean contact number for the case of $r = 6$, $n^* = 4$, $\bar{X}_1 = 0.2$ and $\bar{X}_2 = 0.4$. It can be seen that each sample mean contact number is in good agreement with its expected value, eqn. (29). In Figs. 2 and 3, the abscissa is the

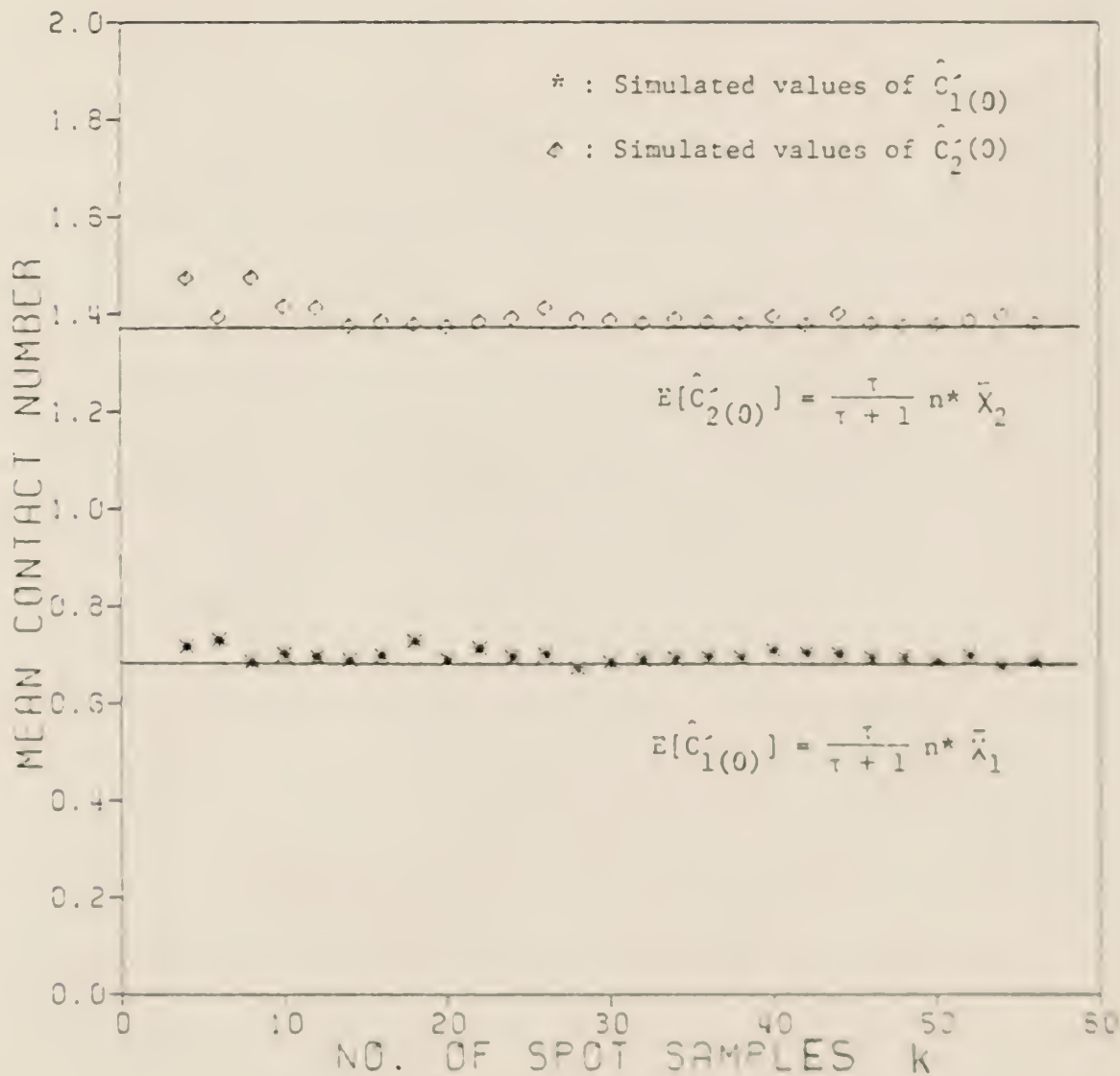


Fig. 1. Results of computer simulation for $n^* = 4$, $n = 20$, $\tau = 6$, $\bar{X}_1 = 2$ and $\bar{X}_2 = 0.4$

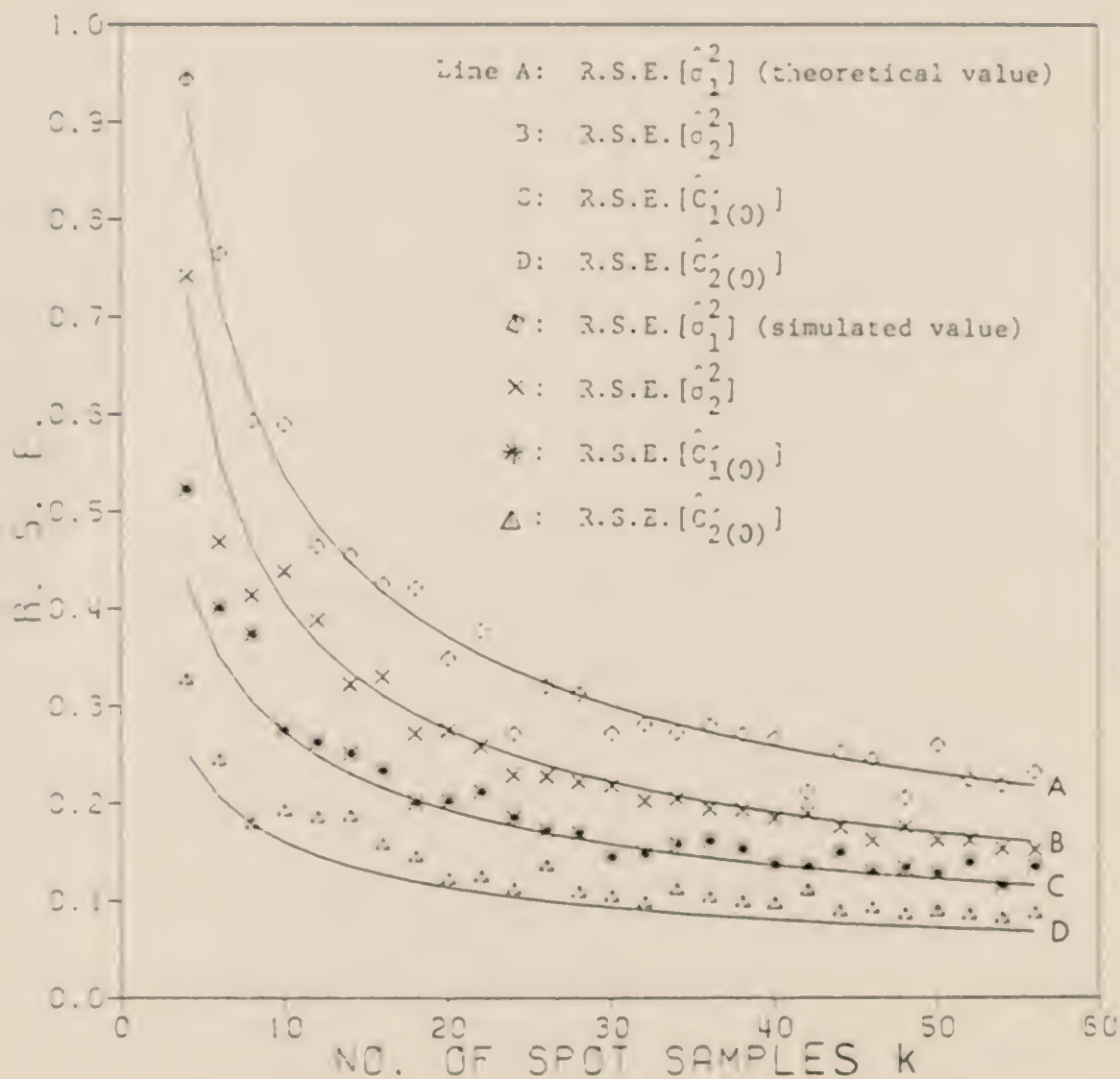


FIG. 2. Comparison of theoretical relative standard errors with those of numerical experiments: $n^* = 4, n = 20$
 $\tau = 6, \bar{X}_1 = 0.2$ and $\bar{X}_2 = 0.4$

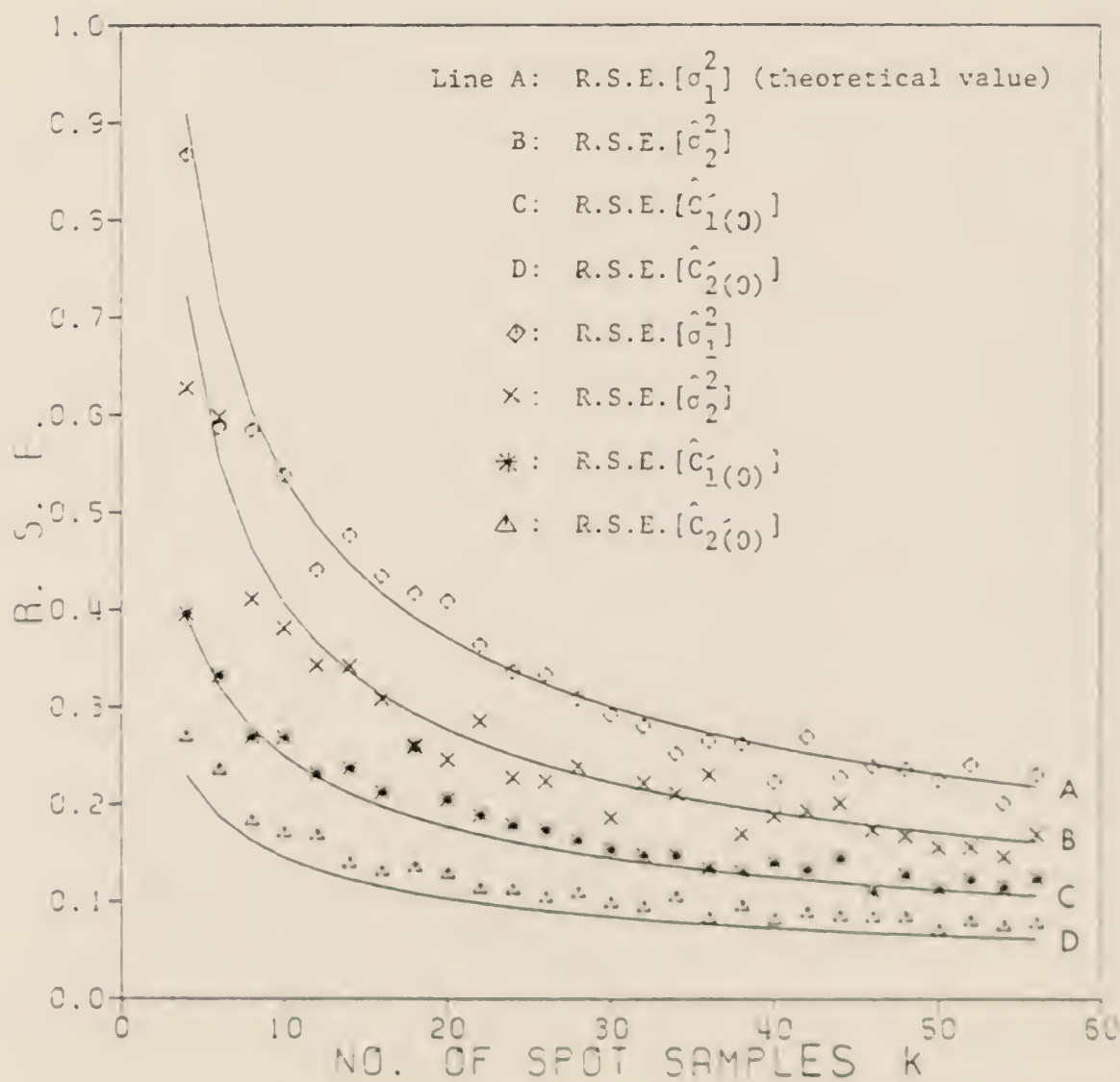


Fig. 3. Comparison of theoretical relative standard errors with those of numerical experiments
 $n^w = 4$, $n = 40$, $\tau = 6$,
 $\bar{\lambda}_1 = 0.2$ and $\bar{\lambda}_2 = 0.4$

number of spot samples, k , and the ordinate is the relative standard error of $\hat{C}'_j(0)$ or $\hat{\sigma}_j^2$ ($j=1,2$). The theoretical values derived in this work, eqns. (31) and (39), are shown in continuous lines in these figures. The simulated values of R.S.E. $\{\hat{C}'_j(0)\}$ and R.S.E. $\{\hat{\sigma}_j^2\}$ are shown in discrete symbols. It can be seen that R.S.E. $\{\hat{C}'_j(0)\}$ are always less than R.S.E. $\{\hat{\sigma}_j^2\}$ at a given set of k and n . Therefore, we can state that the precision of estimator of the mean, $\hat{C}'_j(0)$, is superior to that of the estimator of the variance, $\hat{\sigma}_j^2$. We also observe that the higher the population concentration the smaller the relative standard error.

Figures 4a and 4b show the R.S.E. $\{\hat{\sigma}_j^2\}$ vs the number of spot samples, k , for components A_1 and A_2 , respectively, at $n = 10, 20$ and 40 . We can see that R.S.E. $\{\hat{\sigma}_j^2\}$ does not appreciably change for different n . The effect of the sample size, n , on the relative standard error, R.S.E. $\{\hat{C}'_j(0)\}$, can be observed in Figs. 5a and 5b for components A_1 and A_2 , respectively. The larger the sample size, n , the smaller the relative standard error of $\hat{C}'_j(0)$ as predicted by eqn. (31). These figures are also useful for sampling designs, in that the number of spot samples to be taken for a specified precision can be determined from these figures. Suppose that the population concentrations, \bar{X}_1 and \bar{X}_2 , are 0.2 and 0.4, respectively, the spot sample size, n , is 20, and the total coordination numbers, n^* , is 4, in estimating the mixing index to be accurate within a relative standard error of 15%. Figures 5a and 5b indicate that about 31 spot samples are necessary. Equation (33) can be generally employed in estimating the value of k within a specified precision.

4.2. Mixing of Solid Particles and Estimation of Mixing Index

The following procedure was used to simulate the mixing of solid particles of a three component mixture. A (30 x 30) array of 900 locations

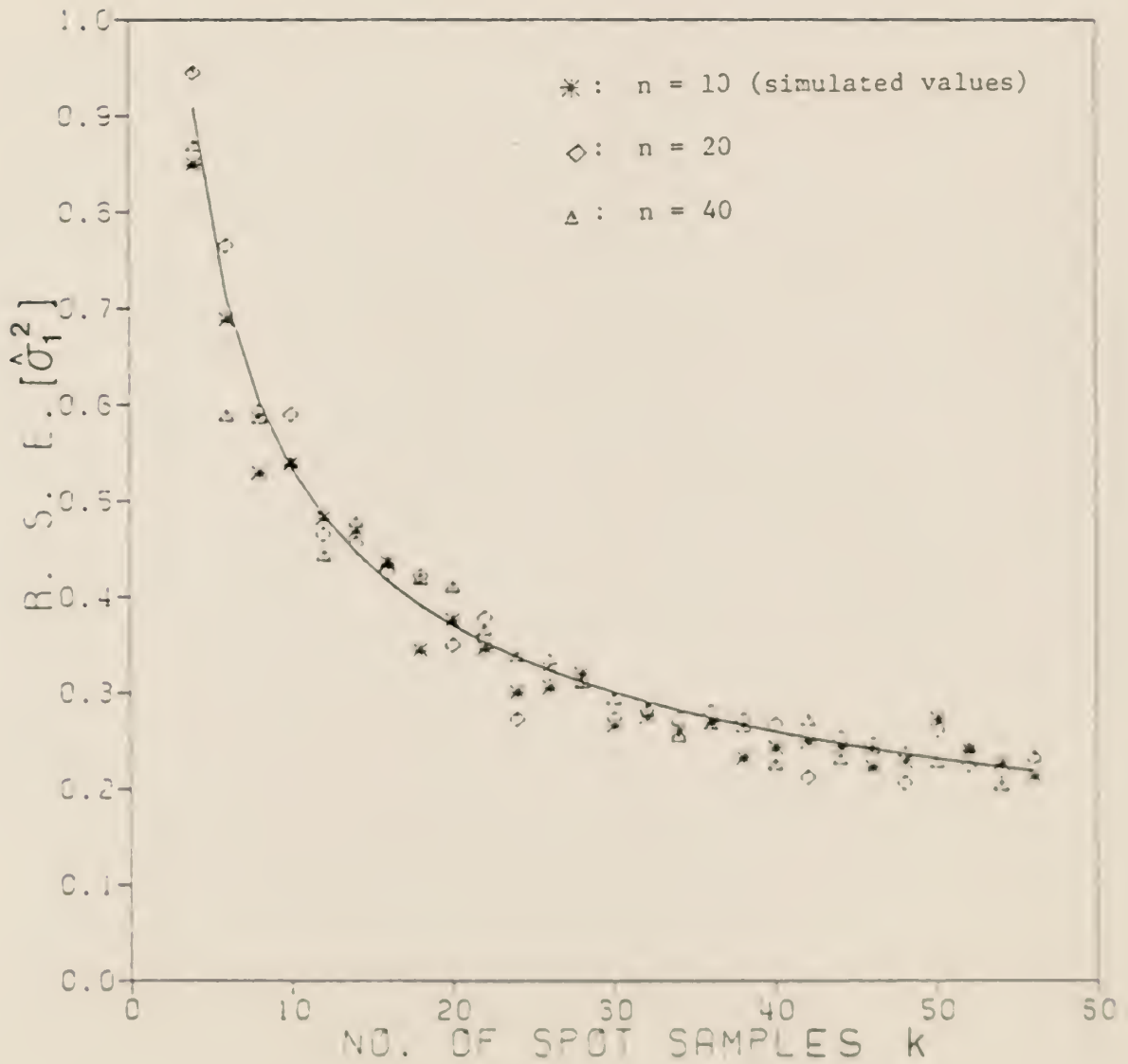


Fig. 4a. Comparison of theoretical relative standard error, R.S.E. $[\hat{\sigma}_1^2]$, with those of numerical experiments: $\gamma = 0$, $n^* = 4$, $\bar{X}_1 = 0.2$ and $\bar{X}_2 = 0.4$.

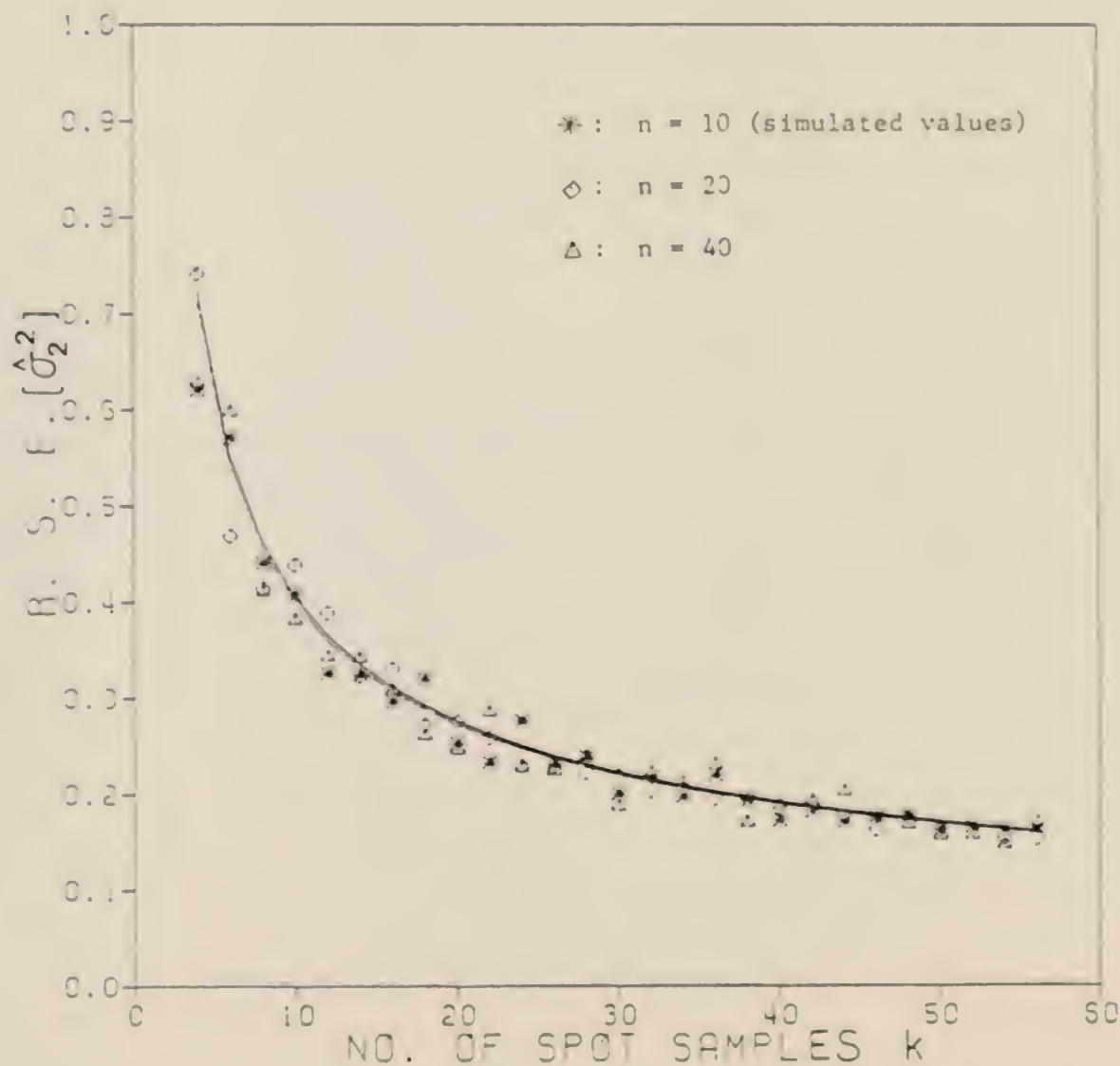


Fig. 4b. Comparison of theoretical relative standard error, R.S.E. $[\hat{\sigma}_2^2]$, with those of numerical experiments: $\tau = 6$, $n^* = 4$, $\bar{X}_1 = 0.2$ and $\bar{X}_2 = 0.4$

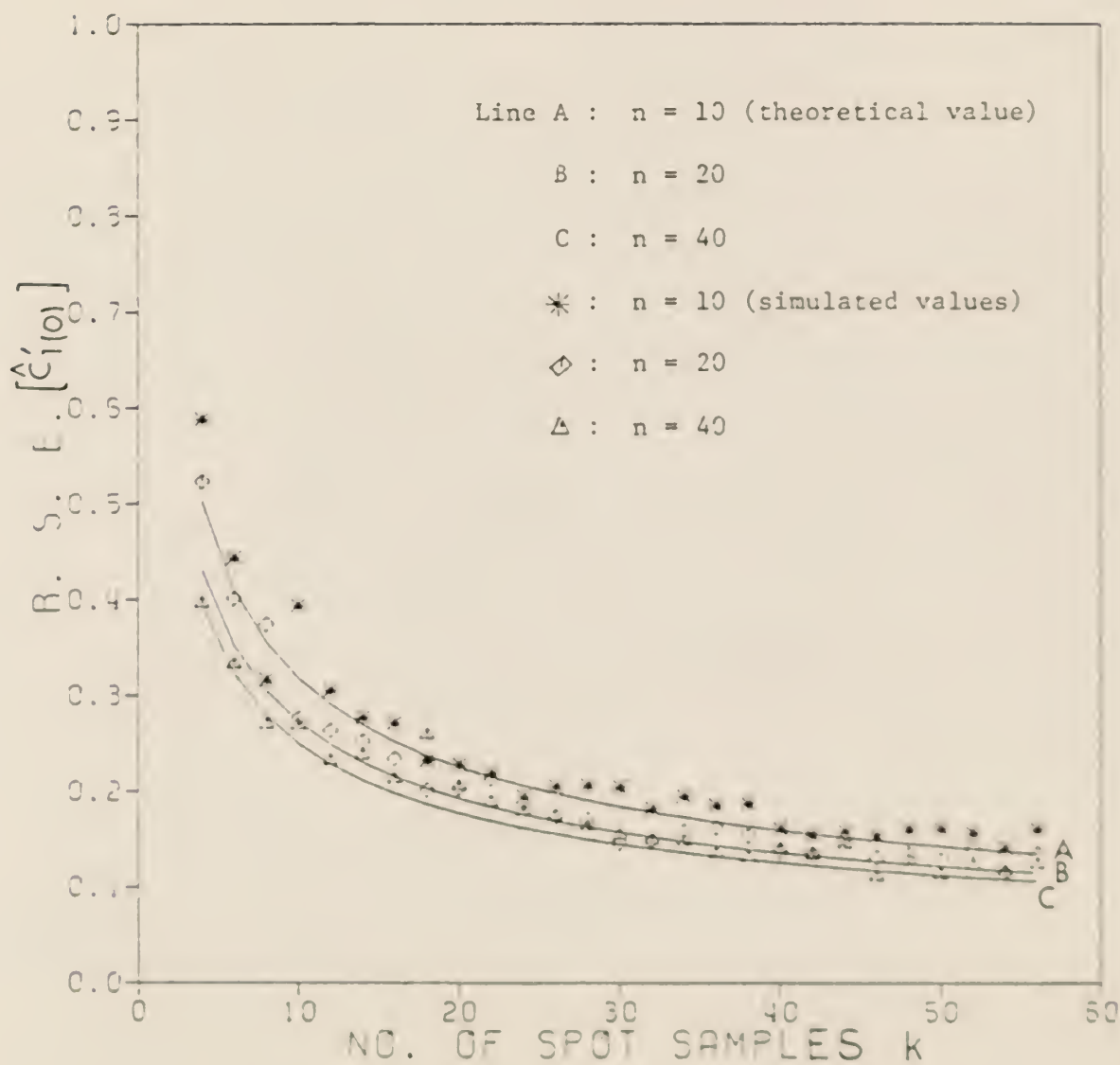


Fig. 5a. Comparison of theoretical relative standard error, $R.S.E. [C_{1(10)}]$, with those of numerical experiments: $r = 6$, $n^* = 4$, $\bar{X}_1 = 0.2$ and $\bar{X}_2 = 0.4$

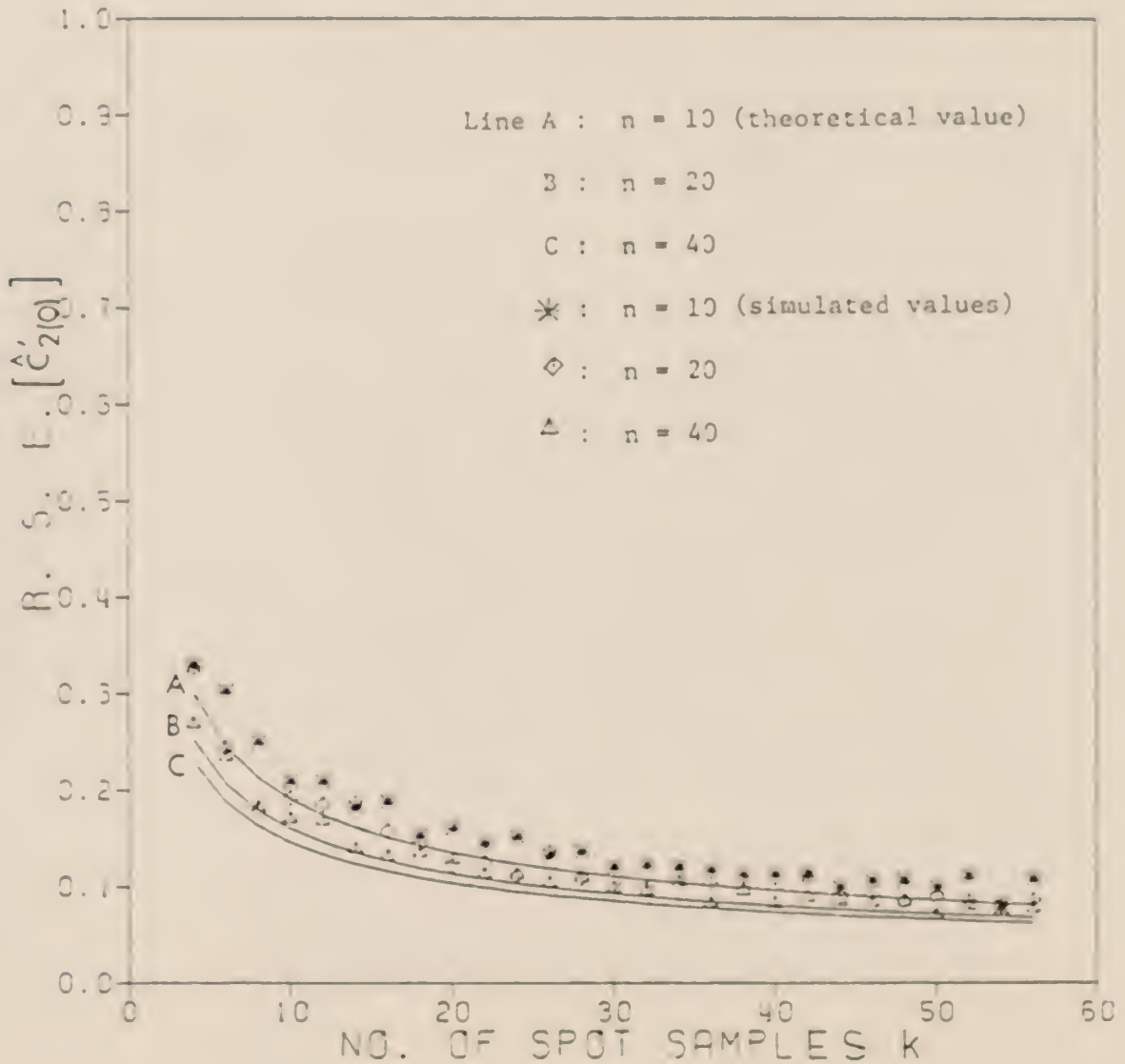


Fig. 5b. Comparison of theoretical relative standard error, $R.S.E. [\hat{C}_2(0)]$, with those of numerical experiments: $\tau = 6$, $n^* = 4$, $\bar{X}_1 = 0.2$ and $\bar{X}_2 = 0.4$.

was used to represent the spatial distribution of a ternary mixture. We assigned a value, '0', '1' or '2' in each location to represent component A_0 , A_1 or A_2 , respectively. Initially the locations in the array were arranged as shown in Fig. 6. This figure is a graphical representation of a ternary mixture in the completely segregated state.

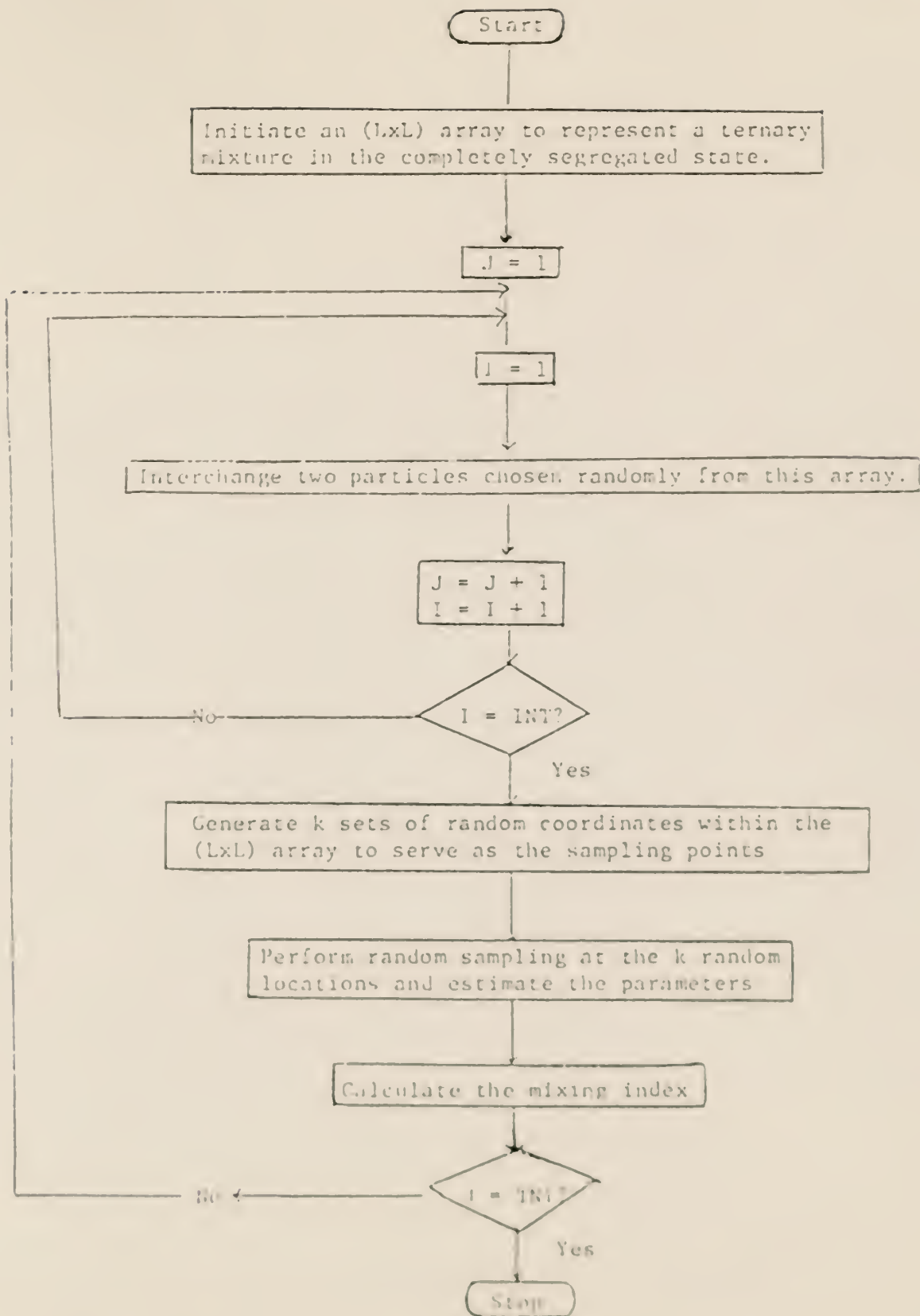
Mixing processes which gave rise to various mixture patterns were simulated by randomly interchanging particles at different locations. After a fixed number of interchanges, spot sampling was carried out and the parameter, τ , was estimated from eqn. (23). The mixing indices were calculated according to eqn. (6). The results are tabulated in Table 1.

Figure 7 shows the flow chart for the computer simulation of the three component mixing model and assessment of the homogeneity of the resulting mixture. Figure 8 gives the flow chart for generating the random sampling points and for sampling operations. The mixture pattern after 600 interchanges is shown in Fig. 9.

7. CONCLUDING REMARKS

This study is concerned with an application of the contact number to estimation of the mixing index, eqn. (6), for a multicomponent mixture. A theoretical model, namely, the Dirichlet-multinomial model, is derived for the distribution of (Y_1, Y_2, \dots, Y_p) in a spot sample of size n of a multicomponent mixture in an incompletely mixed state, where y_j denotes the number of particles of component A_j .

This model contains the parameter, τ , that defines uniquely the mixing index based on the contact number. Estimate of this parameter, τ , is derived and the precision of the estimated population mean contact number is assessed. All equations derived in this work can be reduced to simpler ones for binary mixtures. The expression of the relative standard error can also



Legend:

INT: total number of interchanges required
 INT: interval between consecutive sampling

Fig. 7. Flow chart for the computer simulation of the mixing of ternary mixture and assessment of the homogeneity of the mixture as the mixing progresses.

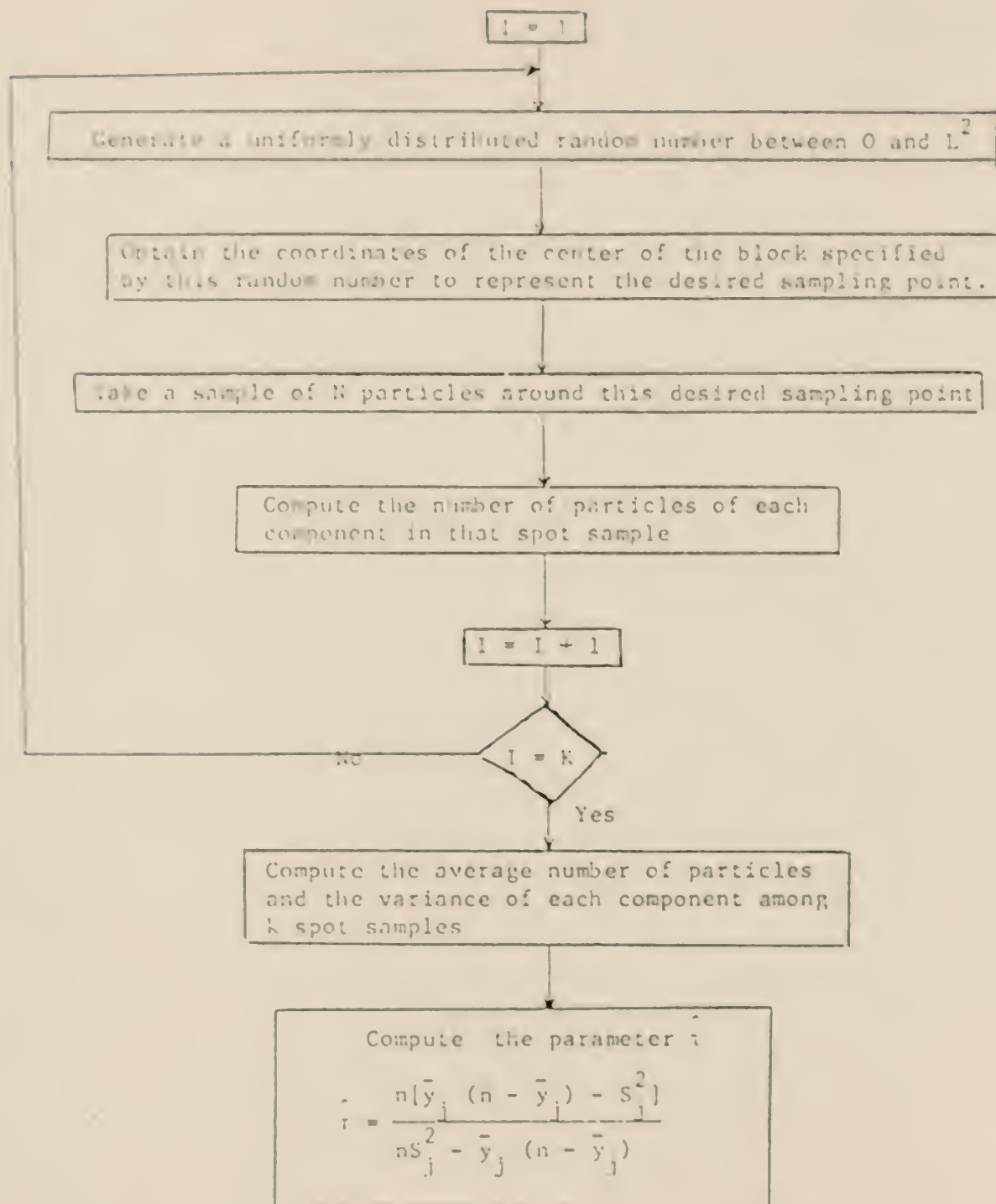


Fig. 5. Flow chart for generating random sampling points and for sampling operations.

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0 1 0 2 2 0 0 0 0 0 2 0 1 0 0 1 2 2 1 2 2 2 1 2 2 2 2 2
2 0 1 0 2 0 0 0 2 2 2 1 0 1 0 0 1 0 1 2 0 0 1 2 2 1 0 0 1
0 1 2 0 2 0 1 2 0 1 1 1 1 1 2 1 2 1 1 0 2 0 2 1 2 2 1 0 2 2
2 0 0 0 2 0 0 0 1 0 1 1 1 1 0 2 0 2 0 1 0 0 2 2 0 2 2 1 2 2 2
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2 2 2 1 2 0 0 2 1 2 1 0 2 1 1 2 1 0 2 1 2 2 2 1 2 0 0 1 2 1
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0 0 0 1 0 1 0 1 2 0 1 2 0 2 2 1 2 1 1 1 1 2 1 1 1 0 2 2 2 2
0 1 0 2 2 0 2 0 0 1 1 1 0 0 1 2 2 1 0 2 2 0 0 2 1 2 2 0 0
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2 0 0 0 1 1 1 1 0 0 1 1 2 0 0 2 2 2 1 1 1 2 2 1 2 2 1 2 1 1
1 1 0 2 2 0 2 1 1 2 1 1 1 0 1 1 0 1 1 1 1 2 2 2 2 2 1 2 0
0 2 0 2 0 0 1 0 0 1 1 2 1 1 2 2 1 2 0 1 2 0 1 2 2 1 2 1 2 2
0 2 0 2 0 0 2 0 0 1 1 2 0 2 2 1 0 1 1 0 2 1 0 1 2 2 0 2 2
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1 1 0 2 1 0 2 2 2 1 0 1 1 0 0 2 1 1 2 0 0 0 2 2 0 0 0 0
1 1 0 0 0 0 1 1 0 1 0 1 1 1 1 1 1 1 1 1 1 0 2 2 2 2 1 1 0
0 1 2 1 0 0 2 1 0 2 2 1 1 0 2 0 1 2 2 0 1 2 2 2 1 0 1 2 2 1
1 1 0 0 0 2 0 1 0 0 1 2 2 1 1 0 2 1 1 1 2 1 1 0 1 2 0 0 2 2
1 2 0 2 1 0 0 2 0 0 0 0 1 2 1 1 1 1 1 1 2 2 1 2 0 0 1 1 2
0 2 2 0 0 0 1 0 2 0 2 1 1 0 1 1 1 2 1 2 0 2 0 2 2 0 2 2 2
2 0 0 0 2 1 0 0 2 0 2 1 1 2 2 0 1 1 2 0 1 2 1 2 0 1 2 2 1
1 0 2 1 0 2 0 0 0 1 1 1 1 1 1 1 1 1 0 1 2 2 0 1 2 1 2 2 2
0 0 0 0 0 2 0 2 0 2 2 2 0 0 0 1 1 2 0 0 0 2 0 0 2 0 0 0
1 1 1 2 0 2 0 0 2 1 0 1 2 0 1 1 2 1 0 2 0 1 2 2 1 0 2 0

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Fig. 9. A ternary mixture pattern after 600 random interchanges.

be extended to that of the completely mixed state. The results of computer simulation indicate that the derived model is valid. The relative standard error of the mean contact number estimator has been shown to be smaller than that of the variance estimator of spot samples. Therefore, the precision of the mixing index based on the mean contact number estimator is superior to that conventionally based on the variance estimator.

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NOTATIONS

$c_j(0)$	contact number of particles of component A_j when the key particles is of component A
$C_j(0)$	random variable for the contact number of component A_j
$\bar{C}_j(0)$	estimation of the population mean contact number of component A_j
$\bar{C}'_j(0)$	unbiased estimator of the population mean contact number of component A_j
$\{C_j(0)\}_i$	$C_j(0)$ in the i -th spot sample, $i=1,2,\dots,k$
$\bar{C}'_j(0)$	mean of $\bar{C}'_j(0)$ of N replications
$\text{Cov}[Y_i, Y_j]$	covariance of variables Y_i and Y_j
$E\{Y\}$	expected value of variable Y
k	number of spot samples
M	mixing index
N	number of replications in spot sampling
n	sample size of a spot sample
n^*	coordination number, the total number of particles surrounding and in contact with a sample particle
R.S.E. $\{Y\}$	relative standard error of variable Y
S_j	standard deviation of component A_j
$V\{Y\}$	variance of variable Y
\bar{x}_j	population mean concentration of particles of component A_j
\bar{x}'_j	sample mean concentration of particles of component A_j
x_j	concentration of particles of component A_j in the i -th spot sample
Y_j	random variable of the number of particles of type j in a spot sample
y_j	number of particles of type j in a spot sample

Z_j	random variable for the local concentration of component A_j
z_j	local concentration of component A_j
$\Gamma(\dots)$	gamma function
θ_j	parameter of the Dirichlet distribution for component A_j
$\mu[\dots]$	generalized factorial moment
μ_i	i -th central moment
μ_i'	i -th moment about zero
$\hat{\sigma}_j^2$	estimator of sample variance of component A_j
$\bar{\sigma}_j^2$	mean of $\hat{\sigma}_j^2$ for all N replications
τ	a parameter = $\sum_{j=0}^p \theta_j$

Subscripts

r	completely mixed state
s	completely segregated state

Marks above symbol

$\hat{}$	estimator
$\bar{}$	mean
$\hat{}'$	unbiased estimator

APPENDIX A. DERIVATION OF EQUATION (12)

We assume that the local concentrations are distributed according to the Dirichlet distribution with parameters $\theta_0, \theta_1, \dots, \theta_p$ [4]

$$f_{\underline{z}}(\underline{z}) = f_{z_1, z_2, \dots, z_p}(z_1, z_2, \dots, z_p) \\ = \frac{\Gamma(\sum_{j=0}^p \theta_j)}{\prod_{j=0}^p \Gamma(\theta_j)} (1 - \sum_{j=1}^p z_j)^{\theta_0 - 1} \prod_{j=1}^p z_j^{\theta_j - 1} \quad (\text{A-1})$$

where

$$\underline{z} = [z_1, z_2, \dots, z_p]$$

$$\underline{z} = [z_1, z_2, \dots, z_p]$$

The conditional probability density function of random variables, Y_1, Y_2, \dots, Y_p , given the local concentrations, z_1, z_2, \dots, z_p , is

$$f_{\underline{Y}|\underline{z}}(\underline{Y}|\underline{z}) = \frac{n!}{\prod_{j=0}^p y_j!} \prod_{j=0}^p z_j^{y_j} \quad (\text{A-2})$$

The joint probability function of random variables vector \underline{Y} and \underline{z} is evaluated to be

$$f_{\underline{Y}, \underline{z}}(\underline{Y}, \underline{z}) = f_{\underline{Y}|\underline{z}}(\underline{Y}|\underline{z}) \cdot f_{\underline{z}}(\underline{z}) \\ = \frac{n!}{\prod_{j=0}^p y_j!} \prod_{j=0}^p z_j^{y_j} \cdot \frac{\Gamma(\sum_{j=0}^p \theta_j)}{\prod_{j=0}^p \Gamma(\theta_j)} (1 - \sum_{j=1}^p z_j)^{\theta_0 - 1} \prod_{j=1}^p z_j^{\theta_j - 1} \quad (\text{A-3})$$

Therefore, the marginal probability function of random variable vector \underline{Y} is obtained as

$$\begin{aligned}
 & \Pr[\underline{Y} = \underline{y}] \\
 &= \Pr[Y_1 = y_1, Y_2 = y_2, \dots, Y_p = y_p] \\
 &= \int_0^1 \dots \int_0^{1 - \sum_{j=1}^{p-1} z_j} \int_0^{1 - \sum_{j=1}^{p-1} z_j} \left\{ \frac{n!}{\prod_{j=0}^p y_j!} \prod_{j=0}^p z_j^{y_j} \right. \\
 & \quad \left. \frac{\Gamma(\sum_{j=0}^p \theta_j)}{\prod_{j=0}^p \Gamma(\theta_j)} \cdot (1 - \sum_{j=1}^p z_j)^{\theta_0 - 1} \cdot \prod_{j=1}^p z_j^{\theta_j - 1} \right\} dz_p dz_{p-1} \dots dz_1 \quad (A-4)
 \end{aligned}$$

Since, in general

$$\int_a^b (u-a)^{\alpha} (b-u)^{\beta} du = (b-a)^{\alpha+\beta+1} \frac{\Gamma(\alpha+1)\Gamma(\beta+1)}{\Gamma(\alpha+\beta+2)} \quad (A-5)$$

by letting

$$a = y_p + \theta_p - 1$$

$$\beta = y_0 + \theta_0 - 1$$

we can express the innermost integral in eqn. (A-4) as

$$\begin{aligned}
 & \int_0^{1 - \sum_{j=1}^{p-1} z_j} \int_0^{1 - \sum_{j=1}^{p-1} z_j} \left(z_p^{\alpha} (1 - \sum_{j=1}^{p-1} z_j - z_p)^{\beta} \right) dz_p \\
 &= (1 - \sum_{j=1}^{p-1} z_j)^{y_p + \theta_p + y_0 + \theta_0 - 1} \cdot \frac{\Gamma(y_p + \theta_p) \Gamma(y_0 + \theta_0)}{\Gamma(y_p + \theta_p + y_0 + \theta_0)} \quad (A-6)
 \end{aligned}$$

Proceeding iteratively, we finally obtain

$$\begin{aligned}
 & \int_0^1 \dots \int_0^1 \left(\prod_{j=1}^{p-2} z_j \right)^{y_1 + \theta_j - 1} \left(\prod_{j=1}^{p-1} z_j \right)^{y_2 + \theta_j - 1} \dots \left(\prod_{j=1}^p z_j \right)^{y_p + \theta_j - 1} \\
 & \cdot \left(1 - \prod_{j=1}^p z_j \right)^{y_0 + \theta_0 - 1} dz_p dz_{p-1} \dots dz_1 \\
 & = \frac{\Gamma(y_1 + \theta_1) \Gamma(y_2 + \theta_2 + \dots + y_p + \theta_p + y_0 + \theta_0)}{\Gamma(y_0 + \theta_0 + y_1 + \theta_1 + \dots + y_p + \theta_p)} \cdot \frac{\Gamma(y_2 + \theta_2) \Gamma(y_3 + \theta_3 + \dots + y_0 + \theta_0)}{\Gamma(y_2 + \theta_2 + \dots + y_p + \theta_p + y_0 + \theta_0)} \\
 & \dots \frac{\Gamma(y_{p-1} + \theta_{p-1}) \Gamma(y_p + \theta_p + y_0 + \theta_0)}{\Gamma(y_p + \theta_p + y_{p-1} + \theta_{p-1} + y_0 + \theta_0)} \cdot \frac{\Gamma(y_p + \theta_p) \Gamma(y_0 + \theta_0)}{\Gamma(y_p + \theta_p + y_0 + \theta_0)} \\
 & = \frac{\Gamma(y_0 + \theta_0) \Gamma(y_1 + \theta_1) \dots \Gamma(y_p + \theta_p)}{\Gamma(y_0 + \theta_0 + y_1 + \theta_1 + \dots + y_p + \theta_p)} \\
 & = \frac{\prod_{j=0}^p \Gamma(y_j + \theta_j)}{\Gamma\left(\sum_{j=0}^p (y_j + \theta_j)\right)} \tag{A-7}
 \end{aligned}$$

Therefore, equation (A-4) can be written as

$$\begin{aligned}
 & \Pr\{Y_1 = y_1, Y_2 = y_2, \dots, Y_p = y_p\} \\
 & = \frac{n!}{\prod_{j=0}^p y_j!} \cdot \frac{\prod_{j=0}^p \Gamma(\theta_j)}{\prod_{j=0}^p \Gamma(\theta_j)} \cdot \frac{\prod_{j=0}^p \Gamma(y_j + \theta_j)}{\Gamma\left(\sum_{j=0}^p (y_j + \theta_j)\right)} \tag{12}
 \end{aligned}$$

APPENDIX B. DERIVATION OF EQUATION (15)

The factorial moments of the Dirichlet-multinomial distribution are obtained as follows:

$$\begin{aligned}
 & \mu^{[i_1, i_2, \dots, i_p]} \\
 &= \sum_{y_1=i_1}^n \sum_{y_2=i_2}^{n-y_1} \dots \sum_{y_p=i_p}^{n-y_1-\dots-y_{p-1}} \prod_{j=1}^p \frac{1}{y_j} \frac{1-z_j}{0} \dots \prod_{j=1}^{p-1} \frac{1-z_j}{0} \\
 &= \frac{\prod_{j=0}^p \Gamma(\theta_j)}{\prod_{j=0}^p \Gamma(\theta_j)} \frac{n!}{\prod_{j=0}^p y_j!} \frac{y_1!}{(y_1-i_1)!} \frac{y_2!}{(y_2-i_2)!} \dots \frac{y_p!}{(y_p-i_p)!} \prod_{j=1}^p z_j^{\theta_j - y_j - 1} \\
 & \quad \cdot \left(1 - \sum_{j=1}^p z_j \right)^{y_0 + \theta_0 - 1} dz_p \dots dz_2 dz_1 \tag{B-1}
 \end{aligned}$$

According to the Fubini theorem [8], equation (B-1) can be written as

$$\begin{aligned}
 & \mu^{[i_1, i_2, \dots, i_p]} \\
 &= \prod_{j=0}^p \frac{1}{y_j} \frac{1-z_j}{0} \dots \prod_{j=1}^{p-1} \frac{1-z_j}{0} \frac{\prod_{i=0}^p \Gamma(\theta_i)}{\prod_{j=0}^p \Gamma(\theta_j)} \prod_{j=0}^p z_j^{\theta_j - 1} \sum_{y_1=i_1}^n \sum_{y_2=i_2}^{n-y_1} \dots \\
 & \quad \dots \sum_{y_p=i_p}^{n-y_1-\dots-y_{p-1}} \frac{y_1!}{(y_1-i_1)!} \frac{y_2!}{(y_2-i_2)!} \dots \frac{y_p!}{(y_p-i_p)!} \frac{n!}{\prod_{j=0}^p y_j!} \\
 & \quad \cdot \left. \prod_{j=0}^p z_j^{y_j} \right\} dz_p \dots dz_2 dz_1 \tag{B-3}
 \end{aligned}$$

Since the factorial moments of the multinomial distribution are [9]

$$\mu^{[i_1, i_2, \dots, i_p]} = n \prod_{j=1}^p \binom{\theta_j}{i_j} z_1^{i_1} z_2^{i_2} \dots z_p^{i_p} \tag{B-4}$$

equation (B-3) can be written as

$$\begin{aligned}
 & \psi(z_1, z_2, \dots, z_p) \\
 &= \frac{\prod_{j=0}^p \Gamma(\frac{p}{j})}{\prod_{j=0}^p \Gamma(\frac{p}{j})} \int_0^1 \int_0^{1-z_1} \dots \int_0^{1-\sum_{j=1}^{p-1} z_j} \left\{ \prod_{j=0}^p z_j^{\frac{p}{j}-1} \right. \\
 & \quad \left. \prod_{j=1}^p \frac{\Gamma(\frac{p}{j})}{z_1^{i_1} z_2^{i_2} \dots z_p^{i_p}} \right\} dz_p \dots dz_2 dz_1 \\
 &= \frac{\prod_{j=0}^p \Gamma(\frac{p}{j})}{\prod_{j=0}^p \Gamma(\frac{p}{j})} \cdot \prod_{j=1}^k \frac{\Gamma(\frac{p}{j})}{\Gamma(\frac{p}{j} + \sum_{j=1}^p i_j)} \\
 &= \prod_{j=1}^k \frac{\Gamma(\frac{p}{j})}{\prod_{j=0}^p (\frac{p}{j} + i_j - 1)(\frac{p}{j} + i_j - 2) \dots (\frac{p}{j})} \\
 & \quad \frac{\prod_{j=0}^p (\frac{p}{j} + i_j - 1)(\frac{p}{j} + i_j - 2) \dots (\frac{p}{j})}{\prod_{j=0}^p (\frac{p}{j} + i_j - 1)(\frac{p}{j} + i_j - 2) \dots (\frac{p}{j})} \tag{15}
 \end{aligned}$$

APPENDIX C. DERIVATION OF EQUATIONS (30) and (31).

The unbiased estimator of the contact number contributed by component A_j , eqn. (6), is repeated below.

$$\hat{C}'_{j(0)} = \frac{n}{n-1} \cdot \frac{\sum_{i=1}^k n^* [x_j]_i [x_0]_i}{k \bar{X}_0} \quad (8)$$

The expected value $E[\hat{C}'_{j(0)}]$ is

$$\begin{aligned} E[\hat{C}'_j] &= \frac{n}{n-1} \cdot \frac{1}{k \bar{X}_0} E \left[\sum_{i=1}^k n^* [x_j]_i [x_0]_i \right] \\ &= \frac{n}{n-1} \cdot \frac{n^*}{k \bar{X}_0} \sum_{i=1}^k E[x_j x_0]_i \\ &= \frac{n}{n-1} \cdot \frac{n^* k}{k \bar{X}_0} E[x_j x_0] \end{aligned} \quad (C-1)$$

Since

$$\begin{aligned} E[x_j x_0] &= E\left[\frac{Y_j}{n} \frac{Y_0}{n}\right] \\ &= \frac{1}{n^2} E[Y_j Y_0] \\ &= \frac{1}{n^2} \cdot \frac{n(n-1) \tau_i \tau_0}{(1+\tau) \tau} \end{aligned} \quad (C-2)$$

we have

$$\begin{aligned} E[\hat{C}'_{j(0)}] &= \frac{1}{n-1} \cdot \frac{n^*}{\bar{X}_0} \cdot \frac{(n-1) \tau_i \tau_0}{n(1+\tau) \tau} \\ &= \frac{\tau_i}{1+\tau} n^* \bar{X}_j \end{aligned} \quad (30)$$

The variance $V[\hat{C}'_{j(0)}]$ is

$$\begin{aligned} V[\hat{C}'_{j(0)}] &= \frac{n^2}{(n-1)^2} \cdot \frac{1}{k^2 \bar{X}_0^2} V \left[\sum_{i=1}^k n^* [X_j]_i [x_0]_i \right] \\ &= \frac{n^2}{(n-1)^2} \cdot \frac{1}{k^2 \bar{X}_0^2} \sum_{i=1}^k V[n^* x_j x_0]_i \end{aligned}$$

$$= \frac{n^2}{(n-1)^2} \cdot \frac{n^2}{k\bar{X}_0^2} [E(x_j^2 x_0^2) - (E(x_j x_0))^2] \quad (C-3)$$

Since

$$\begin{aligned} E\{Y_i^2 Y_j^2\} &= E\{Y_i(Y_i-1)Y_j(Y_j-1)\} + E\{Y_i Y_j^2\} \\ &\quad + E\{Y_i^2 Y_j\} - E\{Y_i Y_j\} \end{aligned} \quad (C-4)$$

$$E\{Y_i^2 Y_j\} = E\{Y_i Y_j (Y_i-1)\} + E\{Y_i Y_j\} \quad (C-5)$$

$$E\{Y_i Y_j^2\} = E\{Y_i Y_j (Y_j-1)\} + E\{Y_i Y_j\} \quad (C-6)$$

we have, from eqn. (15),

$$E\{Y_i(Y_i-1)Y_j(Y_j-1)\} = \frac{n(n-1)(n-2)(n-3)(\theta_i+1)(\theta_j+1)\theta_i\theta_j}{(\tau+3)(\tau+2)(\tau+2)\tau} \quad (C-7)$$

$$E\{Y_i Y_j (Y_i-1)\} = \frac{n(n-1)(n-2)(\theta_i+1)\theta_i\theta_j}{(\tau+2)(\tau+1)\tau} \quad (C-8)$$

$$E\{Y_i Y_j (Y_j-1)\} = \frac{n(n-1)(n-2)(\theta_j+1)\theta_i\theta_j}{(\tau+2)(\tau+1)\tau} \quad (C-9)$$

and

$$E\{Y_i Y_j\} = \frac{n(n-1)\theta_i\theta_j}{\tau(\tau+1)} \quad (C-10)$$

From eqns. (C-4) through (C-10), we obtain

$$\begin{aligned} E\{Y_i^2 Y_j^2\} &= \frac{n(n-1)\theta_i\theta_j}{\tau(\tau+1)(\tau+2)(\tau+3)} [(n-2)(n-3)\theta_i\theta_j \\ &\quad + (n-2)(n+\tau)\theta_i + (n-2)(n+\tau)\theta_j \\ &\quad + (n+\tau)(n-\tau+1)] \end{aligned} \quad (C-11)$$

Thus, we have

$$\begin{aligned} E\{x_i^2 x_j^2\} &= E\left\{\left(\frac{Y_i Y_j}{n}\right)^2\right\} \\ &= \frac{1}{n^2} E\{Y_i^2 Y_j^2\} \end{aligned}$$

$$\begin{aligned}
&= \frac{(n-1)\theta_i\theta_j}{n^3\tau(\tau+1)(\tau+2)(\tau+3)} [(n-2)(n-3)\theta_i\theta_j \\
&\quad + (n-2)(n+\tau)\theta_i + (n-2)(n+\tau)\theta_j \\
&\quad + (n+\tau)(n+\tau+1)] \tag{C-12}
\end{aligned}$$

Substitution of eqns. (C-2) and (C-12) into eqn. (C-3) gives

$$\begin{aligned}
V[\hat{C}'_{j(0)}] &= \frac{n^2}{(n-1)^2} \cdot \frac{n^{*2}}{k\bar{X}_0^2} \cdot \frac{(n-1)(n+\tau)\theta_0\theta_j}{n^3\tau^2(\tau+1)^2(\tau+2)(\tau+3)} \\
&\quad \{2(3-3n-3\tau-2n\tau)\theta_0\theta_j + (n-2)\tau(\tau+1)(\theta_0+\theta_j) \\
&\quad + \tau(\tau+1)(n+\tau+1)\} \\
&= \frac{n^{*2}(n+\tau)\theta_0\theta_j}{n(n-1)k\bar{X}_0^2\tau^2(\tau+1)^2(\tau+2)(\tau+3)} \{2(3-3n+3\tau-2n\tau)\theta_0\theta_j \\
&\quad + (n-2)\tau(\tau+1)(\theta_0+\theta_j) + \tau(\tau+1)(n+\tau+1)\} \tag{31}
\end{aligned}$$

APPENDIX D. DETAILED EXPRESSION OF THE FOURTH CENTRAL MOMENT OF THE DIRICHLET-MULTINOMIAL DISTRIBUTION

According to eqn. (15), the first four descending factorial moments of component Λ_j can be expressed as

$$E\{Y_j\} = n\bar{X}_j \quad (D-1)$$

$$E\{Y_j(Y_j-1)\} = \frac{n(n-1)(1+\tau\bar{X}_j)\bar{X}_j}{(\tau+1)} \quad (D-2)$$

$$E\{Y_j(Y_j-1)(Y_j-2)\} = \frac{n(n-1)(1+\tau\bar{X}_j)(2+\tau\bar{X}_j)\bar{X}_j}{(\tau+1)(\tau+2)} \quad (D-3)$$

and

$$\begin{aligned} & E\{Y_j(Y_j-1)(Y_j-2)(Y_j-3)\} \\ &= \frac{n(n-1)(n-2)(n-3)(1+\tau\bar{X}_j)(2+\tau\bar{X}_j)(3+\tau\bar{X}_j)\bar{X}_j}{(\tau+1)(\tau+2)(\tau+3)} \end{aligned} \quad (D-4)$$

The i -th moment about zero of random variable Y_j , denoted by μ_i' , is defined as [6]

$$\mu_i' = E\{Y_j^i\} \quad (D-5)$$

Therefore, the first four moments about zero can be expressed in terms of factorial moments.

$$\mu_1' = E\{Y_j\} \quad (D-6)$$

$$\mu_2' = E\{Y_j(Y_j-1)\} + E\{Y_j\} \quad (D-7)$$

$$\mu_3' = E\{Y_j(Y_j-1)(Y_j-2)\} + 3E\{Y_j(Y_j-1)\} + E\{Y_j\} \quad (D-8)$$

$$\begin{aligned} \mu_4' &= E\{Y_j(Y_j-1)(Y_j-2)(Y_j-3)\} + 6E\{Y_j(Y_j-1)(Y_j-2)\} \\ &\quad + 7E\{Y_j(Y_j-1)\} + E\{Y_j\} \end{aligned} \quad (D-9)$$

The fourth central moment of component Λ_j , eqn. (38), can be evaluated as

$$\begin{aligned} \mu_{42} &= E\{(Y_j - E\{Y_j\})^4\} \\ &= E\{Y_j^4\} - 4E\{Y_j\}E\{Y_j^3\} + 6E\{Y_j^2\}(E\{Y_j\})^2 \\ &\quad - 3(E\{Y_j\})^4 \end{aligned} \quad (D-10)$$

Substituting eqns. (D-6) through (D-9) into eqn. (D-10), we finally obtain the detailed expression of the fourth central moment of the Dirichlet-multinomial distribution for component A_j .

MIXING INDEXES FOR MULTICOMPONENT SOLID MIXTURES

1. INTRODUCTION

There are two broad aspects in the investigation of solids mixing. One is concerned with the characterization of mixtures and the other with the mechanism and rate by which the state of a mixture changes. The work described in this study is concerned with the former.

Solids mixing or powder blending is the operation by which two or more solid materials in particulate form are scattered randomly in a mixer by the random movement of the particles. This operation is performed to achieve an acceptable mixing quality. In other words, the ultimate object of mixing is to attain the most uniform distribution; thus, the mixing procedure and measures of homogeneity become important aspects of this subject.

The quality of a mixture is often assessed by withdrawing samples of a specified size and calculating the variance of the components. The method used for assessing the quality of a mixture should [1]:

- (a) have some physical significance with regard to the process under investigation,
- (b) be sufficiently sensitive to changes in the state of mixing,
- (c) cause no appreciable disturbance in the mixture under investigation,
- (d) be applicable to as many different systems as possible, and
- (e) be mathematically and statistically rigorous.

To characterize the homogeneity of a solids mixture, a mixing index is usually employed to represent its degree of mixedness. A useful and general index should be related as closely as possible to the specific characteristics of the mixture, should be independent of the mixing process, and should be easily determined. The choice of an index also depends on its application. It is often desirable that the index ranges between 0 and 1.

Statistical analysis has been a major tool of solids mixing investigations because of the stochastic nature of mixing processes. Over thirty different criteria for the degree of mixedness have been reviewed and summarized by Fan et al. [2]. The relationships among some of the criteria have been studied and tabulated by Fan and Wang [3]. Table 1 lists these criteria and investigators who have proposed them. Most of the criteria are based on the composition analysis of equi-sized particle samples of a binary mixture. However, solid particles to be blended often consist not only of particles of varying size and density but also of widely different chemical and physical properties. Thus, a study of mixing indices for multicomponent heterogeneous solid particles is of practical significance.

A convenient scheme for classifying particle systems should be established to facilitate the investigation of solids mixing. Usually, particle systems are classified as homogeneous or heterogeneous (or dispersed) systems. Particles of a homogeneous system have the same physical properties (e.g. density, size, shape, etc.) and are distinguishable through the characteristics of tracers, such as color and radioactivity, which do not physically alter the course of the mixing process. Here materials with physical properties which do not interact with the operation of a mixer are considered as tracers. On the other hand, particles of a heterogeneous system have different physical properties.

The extent of the variation in the characteristics of a mixture may be expressed in terms of weight, volume or number fraction of each constituent in the mixture [4,5]. The three bases yield an identical result for a homogeneous system. However, sampling by counting the number of particles is difficult and impractical for a fine particle or powder system. Measurement by volume fraction is not easy, because the bulk volume of solid

Mixing index used in approaches 1 and 2	Mixing index used in approach 3	original investigators and references	Mixing index used in approaches 1 and 2	Mixing index used in approach 3	original investigators and references
$M_1 = 1 - \frac{\sigma}{\sigma_0}$	$1 - \frac{\sqrt{ \Sigma }}{\sqrt{ \Sigma_s }}$	cited in [3]	$M_6 = \frac{\sigma}{\sigma_0}$	$\frac{\sqrt{ \Sigma }}{\sqrt{ \Sigma_s }}$	Yano, Kanise & Tanaka [25]
$M_2 = \frac{\sigma^2}{\sigma_0^2} - 1$	$\frac{ \Sigma }{ \Sigma_s } - 1$	Miles [21]	$M_7 = \frac{\sqrt{\ell n \sigma_0^2 - \ell n \sigma^2}}{\sqrt{\ell n \sigma_0^2 - \ell n \sigma_r^2}}$	$\frac{\sqrt{\ell n \Sigma_s - \ell n \Sigma }}{\sqrt{\ell n \Sigma_s - \ell n \Sigma_r }}$	Ashton & Valentine [17]
$M_3 = \frac{\sigma_0^2 - \sigma^2}{\sigma_0^2 - \sigma_r^2}$	$\frac{ \Sigma_s - \Sigma }{ \Sigma_s - \Sigma_r }$	Lacey [16]	$M_8 = \frac{\sigma_0 - \sigma}{\sigma_0 - \sigma_r}$	$\frac{\sqrt{ \Sigma_s } - \sqrt{ \Sigma }}{\sqrt{ \Sigma_s } - \sqrt{ \Sigma_r }}$	Kramer [22]
$M_4 = \frac{\sigma_r}{\sigma}$	$\frac{\sqrt{ \Sigma_r }}{\sqrt{ \Sigma }}$	Lacey [22] & Weidenbaum & Bonilla [23]	$M_9 = \frac{\sigma^2}{\sigma_0^2}$	$\frac{ \Sigma }{ \Sigma_s }$	Westcott & Linehan [26]
$M_5 = \frac{\sigma_0 - 1}{\sigma_0 - 1} \frac{\sigma_r}{\sigma_r}$	$\frac{\sqrt{\frac{ \Sigma_s }{ \Sigma } - 1}}{\sqrt{\frac{ \Sigma_r }{ \Sigma } - 1}}$	Beaudry [24]	$M_{10} = \frac{\sigma}{\sigma_r}$	$\frac{\sqrt{ \Sigma }}{\sqrt{ \Sigma_r }}$	lexis cited in [27]

Table 1. Commonly used mixing indices, which have been extended to multicomponent systems.

particles consists of the true volume of particles and the volume of voidage, i.e., the bulk volume of each constituent is not additive. Since the practical difficulties of measuring the volume in a mixer exist, the mean and variance of the weight fraction are chosen here as unit of measurement.

The literature on the assessment of mixture quality is generally very scarce. This is especially true for multicomponent mixtures. Gayle et al. [6] used chi-square as a criterion instead of conventional definitions of mixing index, which utilize the sample variance (or standard deviation). Granules used in their experiments were similar in surface characteristics, shape and density but different in color only. Buslik [7] proposed a numerical homogeneity index to express quantitatively varying degrees of homogeneity, namely, the negative logarithm of the sample weight required to obtain a standard deviation of 1%. Hersey et al. [8,9] used this concept to calculate the homogeneity of single ingredients in a multicomponent mixture. They also assumed that the components must be reduced to the same particle size level prior to mixing.

In the present study, some approaches to assess the quality of a mixture have been proposed and the approximate distribution of a heterogeneous multicomponent mixture is derived.

2. STATISTICAL ANALYSIS OF BINARY MIXTURES

The expressions of some statistical quantities associated with a binary mixture are summarized below [2]:

A sample variance is defined as

$$s^2 = \frac{1}{m} \sum_{j=1}^m (x_{1j} - \bar{x}_1)^2 \quad (1)$$

An unbiased sample variance is defined as

$$s^2 = \frac{1}{m-1} \sum_{j=1}^m (x_{1j} - \bar{x}_1)^2 \quad (2)$$

where

m = number of spot samples,

x_{1j} = fraction of component 1 in the j -th sample,

\bar{x}_1 = sample mean which is $\frac{1}{m} \sum_{j=1}^m x_{1j}$

Note that the variance calculated from component 1 is equal to that calculated from component 2 for a binary mixture. The population mean (or expectation) for component 1 is

$$E[x_1] = P_1 \quad (3)$$

It can be seen from Table 1 that the standard deviation or variance of the mixture in the completely random or mixed state and that of the mixture in the completely segregated state are often used as the boundary values of a mixing index. The variance in composition among a group of samples drawn from a mixture in the completely random state is derived by Stange [10] as

$$s_r^2 = \frac{P_1 P_2}{W} \left\{ P_1 \left[\bar{w}_2 \left(1 + \frac{\bar{s}_2^2}{\bar{w}_2^2} \right) \right] + P_2 \left[\bar{w}_1 \left(1 + \frac{\bar{s}_1^2}{\bar{w}_1^2} \right) \right] \right\} \quad (4)$$

where

P_1, P_2 = weight fractions of components 1 and 2, respectively,
($P_1 + P_2 = 1$),

\bar{w}_1, \bar{w}_2 = mean particle weights of components 1 and 2, respectively,

\bar{s}_1, \bar{s}_2 = standard deviations of particle weight of components 1 and 2, respectively,

W = weight of a sample.

If particle size is uniform, eqn. (4) is reduced to

$$c_r^2 = \frac{P_1 P_2}{W} [P_1 \bar{w}_2 + P_2 \bar{w}_1] \quad (5)$$

If each component consists of particles of the same particle weight, w , ($\bar{w}_1 = \bar{w}_2 = w$), eqn. (5) can be written as

$$\begin{aligned} c_r^2 &= \frac{w}{W} P_1 P_2 \\ &= \frac{1}{N} P_1 P_2 \end{aligned} \quad (6)$$

which is the original formula of Lacey [11] where N is the number of particles in a spot sample.

Under the assumption that the probability of sampling a particle of the given component is proportional to its volume fraction, the variance for a mixture in the completely segregated state is derived here as [see Appendix A]

$$\begin{aligned} c_0^2 &= \frac{c}{\rho_1} (1-P_1)^2 P_1 + P_1^2 (1 - \frac{c}{\rho_1} P_1) \\ &= \frac{c}{\rho_2} (1-P_2)^2 P_2 + P_2^2 (1 - \frac{c}{\rho_2} P_2) \end{aligned} \quad (7)$$

where ρ_1 and ρ_2 denote the densities of components 1 and 2, respectively, and c the mean density. If the components have the same particle density ($\rho_1 = \rho_2 = \rho$),

$$c_0^2 = P_1 P_2 \quad (8)$$

It can be seen that the variance of a mixture in the completely segregated state is independent of sample size, provided that sampling is not taken at the interface between the components and that the variance of the concentration (distribution) in a mixture in the completely mixed state is inversely proportional to sample size. The ten most frequently used indices for binary mixtures are shown in Table 1.

A mixture with a completely ordered arrangement of particles is often regarded as a perfect mixture, i.e., the mixture is ideally homogeneous. For the ideally homogeneous mixture, the concentration in each sample is identical to the theoretical concentration. Thus, the variance of the concentration becomes zero

$$c_p^2 = 0 \quad (9)$$

Although spot samples taken from the perfect mixture have an identical composition, such a mixture cannot be realized by means of a conventional mixing operation. We can define another final state so called the completely mixed state that is different from ideal homogeneity. It is characterized by the fact that the probability of sampling a particle of one of the components from any point in the mixture is identical, even though the composition may not be identical everywhere. For a homogeneous binary system, particles in a spot sample of size N are distributed according to the binomial distr., i.e., [15],

$$\Pr\{Y_1 = n_1\} = \frac{N!}{n_1!(N-n_1)!} P_1^{n_1} (1-P_1)^{n_2} \quad (10)$$

where Y_1 is the random variable that denotes the number of particles of component 1 in a spot sample. According to this probability density function, therefore, the variance of the mixture is

$$\begin{aligned} c_r^2 &= \text{Var} [x_1] \\ &= \text{Var} \left[\frac{Y_1}{N} \right] \\ &= \frac{P_1 P_2}{N} \end{aligned}$$

which is eqn. (6).

In practice a mixing process rarely yields a completely mixed mixture, either because the process is incomplete or because segregation occurs by differences in the physical properties of the components. This implies

that the probability distributions of the components during mixing are unknown. The probability of sampling a particle of a given component is proportional to the volume fraction of that component. Under the hypothesis of mixtures in the completely random state, particles in a sample can be assumed to be approximately distributed according to the binomial distribution with parameters N^* and q_1 , where N^* is the expected number of particles in a sample of constant weight, W , and q_1 is the volume fraction of component 1. The variance of the weight fraction of component 1 or 2 is derived as [see Appendix B]

$$c_r^2 = \frac{P_1 P_2}{W} \frac{c^2}{\rho_1 \rho_2} \cdot \frac{\bar{w}_1 \bar{w}_2}{(P_1 w_2 + P_2 w_1)} \quad (11)$$

Since, in practice, solid particles to be mixed are usually measured in the same dimensions, this distribution seems to be a good approximation for most mixtures. Notice that eqn. (11) reduces to eqn. (6) for a homogeneous system.

3. MIXING INDICES FOR MULTICOMPONENT MIXTURES

The purpose of this section is to develop mixing indices for a multicomponent mixture. We assume throughout this section that samples are taken from a known volume of a multicomponent mixture and the proportion (by weight) of each component is recorded. From the sample proportions, an indication of the degree of mixedness will be calculated. Methods of sampling, determination of sample size, and the number of samples drawn will depend on the degree of precision required, the cost and practicality of sampling, and possibly physical constraints on the sampling process.

3.1. "Pseudo" Binary Mixture

Suppose that a multicomponent mixture consists of components 1, 2, 3, In describing the homogeneity of the key component, say, component 1, the mixture is considered to consist of component 1 and another (pseudo-) component x, which contains the remaining (k-1) components. Component x is present in the mixture in a proportion of $(1 - P_1)$. The particle weight and density of component x are given, respectively, as

$$\bar{w}_x = \frac{(1 - P_1)}{\frac{P_2}{\bar{w}_2} + \frac{P_3}{\bar{w}_3} + \dots + \frac{P_k}{\bar{w}_k}} \quad (12)$$

$$\rho_x = \frac{(1 - P_1)}{\frac{P_2}{\rho_2} + \frac{P_3}{\rho_3} + \dots + \frac{P_k}{\rho_k}}$$

Thus, component x may be treated as component 2 of a binary mixture as described in section 2. For instance, in the pharmaceutical industry, usually only one active ingredient and several diluents (lactose, starch, glucose, etc.) are in a dosage; therefore, the homogeneity of this active ingredient (key component) is the main concern. The mixing index for the key component may be determined as described in the preceding section [4].

The present approach based on the concept of a pseudo-binary mixture can be applied to each component in a multicomponent mixture to define an index of mixedness for each component. Sometimes this method is more useful than a single-valued index, because its application may indicate that a different degree of mixing is required for each component, i.e., some components may be required to be mixed to a much greater extent than others [1].

3.2 Pooled Variance

The sample variance of the concentration in a multicomponent mixture is defined as follows:

$$c^2 = \frac{1}{m-1} \sum_{i=1}^k \left[\sum_{j=1}^m (x_{ij} - \bar{x}_i)^2 P_i \right] \quad (14)$$

where

k = number of components,

m = number of spot samples,

x_{ij} = fraction of component i in the j -th spot sample

\bar{x}_i = sample mean of component i

$$= \frac{1}{m} \sum_{j=1}^m x_{ij}$$

When $k = 2$, eqn. (14) can be reduced to eqn. (2), which expresses the variance of a binary mixture. Similarly, we may express the variances for multicomponent mixtures in the completely mixed and segregated state, respectively, as

$$c_r^2 = \sum_{i=1}^k \frac{W_i}{W} \frac{\rho}{\rho_i} P_i^2 \left(1 - \frac{\rho}{\rho_i} P_i \right) \quad (15)$$

and

$$c_0^2 = \sum_{i=1}^k \left[\frac{\rho}{\rho_i} (1 - P_i)^2 P_i^2 + P_i^3 \left(1 - \frac{\rho}{\rho_i} P_i \right) \right] \quad (16)$$

Now, we are ready to define mixing indices for multicomponent mixtures as similar to those for binary mixtures in Table 1. For the homogenous particles system, eqns. (15) and (16) can be reduced, respectively, to

$$c_r^2 = \frac{1}{N} \sum_{i=1}^k P_i^2 (1 - P_i) \quad (17)$$

$$c_0^2 = \sum_{i=1}^k P_i^2 (1 - P_i) \tag{18}$$

Thus, we have

$$c_0^2 = Nc_1^2 \tag{19}$$

Accordingly, the relationships between these mixing indices shown in Table 1 are identical to those for binary mixtures [3]. Figures 1 and 2 plot the values of the nine mixing indices against one of them, namely, M_8 , for the samples of sizes 20 and 200 (no. of particles), respectively. It can be seen that M_1 and M_6 are linearly related to M_8 . M_2 , M_4 , and M_5 appear to be more dependent upon the sample size than the others. However, only M_7 is sensitive to the variation in the extent of mixedness in the range from the completely segregated state to the completely mixed state.

3.3 Determinant of the Sample Covariance Matrix

Multivariate analysis is an effective tool for solving multicomponent solids mixing problems [13]. Instead of observing the concentration of a single component, sampling of a k -component mixture is primarily concerned with random samples of $(k-1)$ vector-valued random response variables. Notice that only $(k-1)$ of the k concentrations need to be considered. When samples are obtained from a $(k-1)$ -variate population instead of a univariate population, the data can be represented as

component sample no.	1	2	. . .	i	. . .	(k-1)
1	x_{11}	x_{21}	. . .	x_{i1}	. . .	$x_{(k-1)1}$
2	x_{12}	x_{22}	. . .	x_{i2}	. . .	$x_{(k-1)2}$
.
.
.

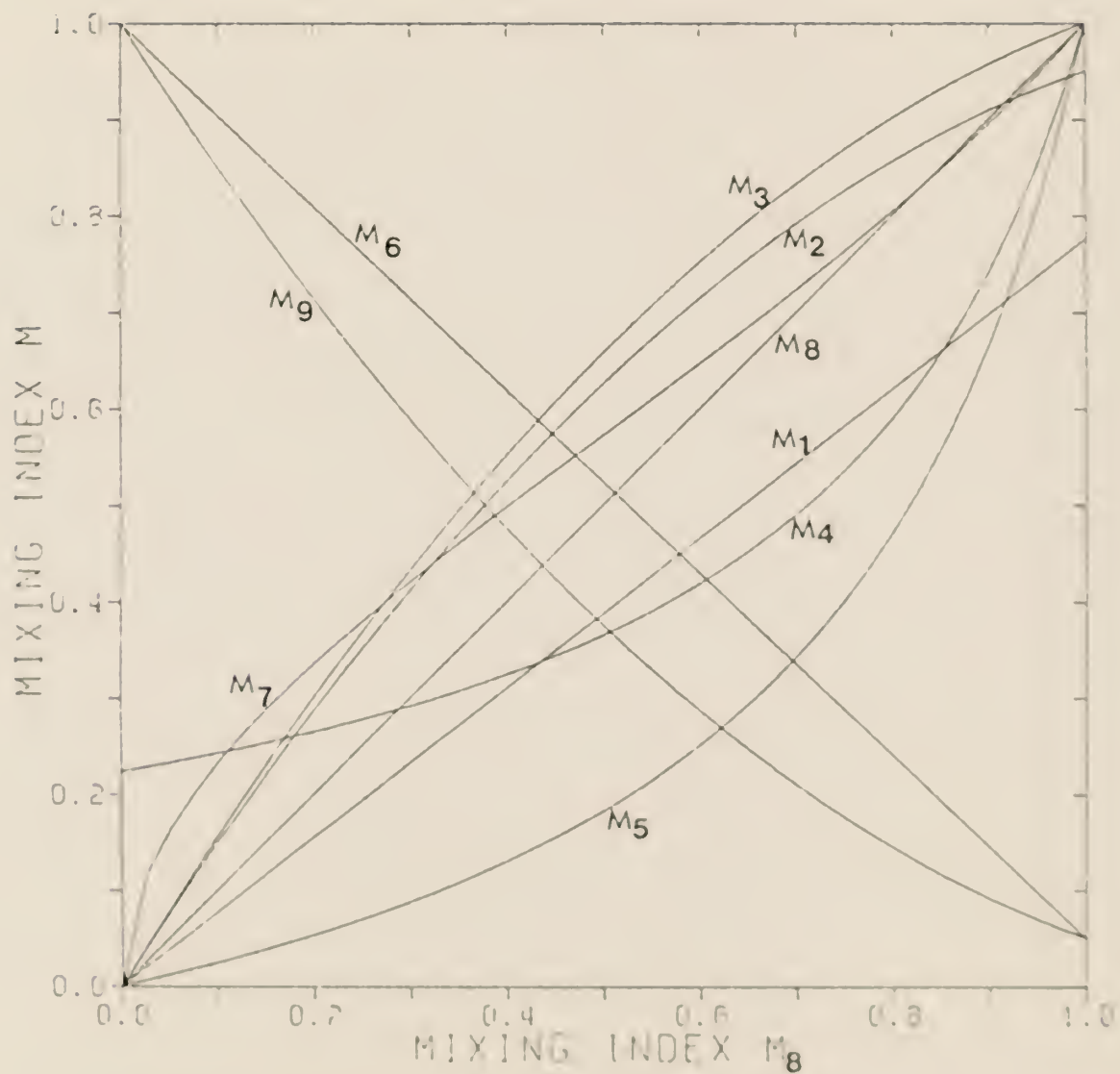


Fig. 1 Comparison of mixing indices based on the 2nd approach (pooled variance) for sample size of 20.

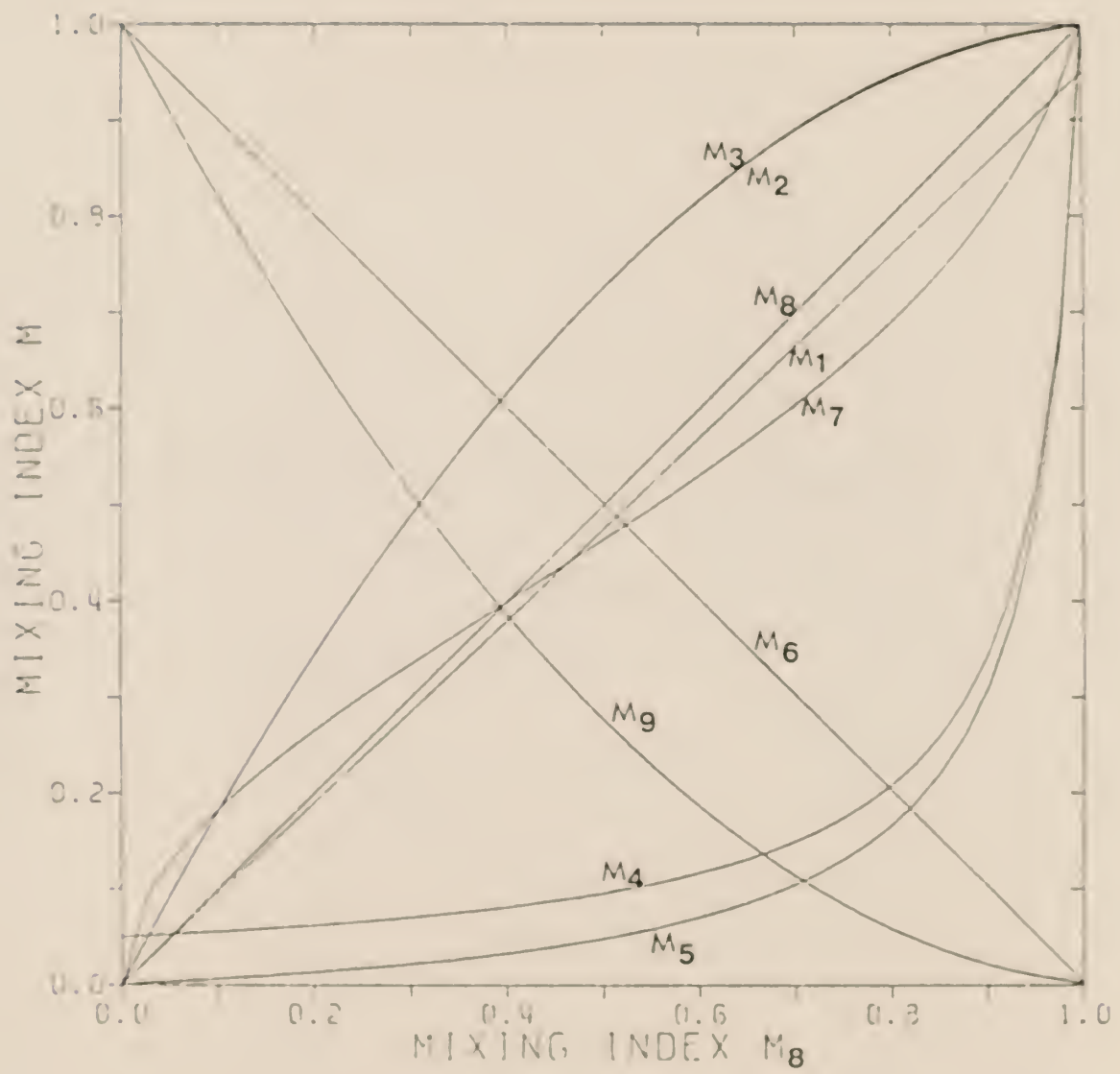


Fig. 2 Comparison of mixing indices based on the 2 nd approach (pooled variance) for sample size of 200.

component \ sample no.	1	2	. . .	i	. . .	(k-1)
j	x_{1j}	x_{2j}	. . .	x_{ij}	. . .	$x_{(k-1)j}$
.
.
.
m	x_{1m}	x_{2m}	. . .	x_{im}	. . .	$x_{(k-1)m}$

The sample mean of the i -th component is defined as

$$\bar{x}_{i.} = \frac{1}{m} \sum_{j=1}^m x_{ij}$$

The sums of squares and cross products are defined, respectively, as [13]

$$\begin{aligned} SS_{x_i} &= \sum_{j=1}^m (x_{ij} - \bar{x}_{i.})^2 \\ &= \sum_{j=1}^m x_{ij}^2 - \frac{1}{m} \left(\sum_{j=1}^m x_{ij} \right)^2 \end{aligned} \quad (20)$$

and

$$\begin{aligned} SP_{x_i x_l} &= \sum_{j=1}^m (x_{ij} - \bar{x}_{i.})(x_{lj} - \bar{x}_{l.}) \\ &= \sum_{j=1}^m x_{ij} x_{lj} - \frac{1}{m} \left(\sum_{j=1}^m x_{ij} \right) \left(\sum_{j=1}^m x_{lj} \right) \end{aligned} \quad (21)$$

The estimated variances of x_i and covariance of x_i and x_l are, respectively,

$$\begin{aligned} \widehat{\text{Var}}[x_i] &= s_{ii} \\ &= \frac{SS_{x_i}}{m-1}, \quad i = 1, 2, \dots, (k-1) \end{aligned} \quad (22)$$

and

$$\widehat{\text{Cov}}[x_i, x_l] = s_{il}$$

$$= \frac{SP_{x_i x_i}}{n-1} \quad i, i = 1, 2, \dots, (k-1) \quad i \neq i \quad (23)$$

Thus, the sample variance-covariance matrix is

$$\underline{S} = \begin{bmatrix} s_{11} & s_{12} & \cdot & \cdot & \cdot & s_{1(k-1)} \\ s_{12} & s_{22} & \cdot & \cdot & \cdot & s_{2(k-1)} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ s_{1(k-1)} & s_{2(k-2)} & \cdot & \cdot & \cdot & s_{(k-1)(k-1)} \end{bmatrix} \quad (24)$$

For a homogeneous system, particles in a completely random mixture are expected to be randomly distributed in a spot sample of size N taken from the mixture. Let us define a random vector $[Y_1, Y_2, \dots, Y_k]$ for a mixture of k components, where $Y_j = n_j$, $0 \leq n_j \leq N$. This implies that n_j particles of component j fall into the spot sample. Then the joint probability density function of random variables, Y_1, Y_2, \dots, Y_k , is

$$\begin{aligned} & \text{Pr}[Y_1 = n_1, Y_2 = n_2, \dots, Y_k = n_k] \\ &= \frac{N!}{n_1! n_2! \dots n_k!} p_1^{n_1} p_2^{n_2} \dots p_k^{n_k} \\ &= \frac{N!}{\prod_{i=1}^k n_i!} \prod_{i=1}^k p_i^{n_i} \end{aligned} \quad (25)$$

where

$$n_1 + n_2 + \dots + n_k = N$$

$$p_1 + p_2 + \dots + p_k = 1$$

p_i = weight fraction of the i -th component in the mixture

= number fraction of the i -th component in the mixture (for a homogeneous system)

Note that the multinomial distribution is a generalization of the binomial distribution. According to this probability density function, eqn. (25), the means, variances and covariances of the random variables, Y_1, Y_2, \dots, Y_k are given, respectively, by: [14,15]

$$E[Y_i] = NP_i, \quad (26)$$

$$\text{Var}[Y_i] = NP_i(1-P_i), \quad (27)$$

$$\text{Cov}[Y_i, Y_k] = -NP_i P_k \quad (28)$$

or equivalently,

$$\begin{aligned} E[x_i] &= E\left[\frac{Y_i}{N}\right] \\ &= P_i, \end{aligned} \quad (29)$$

$$\begin{aligned} \text{Var}[x_i] &= \text{Var}\left[\frac{Y_i}{N}\right] \\ &= \frac{P_i(1-P_i)}{N} \end{aligned} \quad (30)$$

$$\begin{aligned} \text{Cov}[x_i, x_k] &= \text{Cov}\left[\frac{Y_i}{N}, \frac{Y_k}{N}\right] \\ &= -\frac{P_i P_k}{N}, \end{aligned} \quad (31)$$

Therefore, the variance-covariance matrix for the mixture in the completely mixed state can be expressed as

$$\underline{\Sigma}_r = \frac{1}{N} \begin{bmatrix} P_1(1-P_1) & -P_1 P_2 & \cdot & \cdot & \cdot & -P_1 P_{(k-1)} \\ -P_1 P_2 & P_2(1-P_2) & \cdot & \cdot & \cdot & -P_2 P_{(k-1)} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ -P_1 P_{(k-1)} & -P_2 P_{(k-1)} & \cdot & \cdot & \cdot & P_{(k-1)}(1-P_{(k-1)}) \end{bmatrix} \quad (32)$$

In the completely segregated state, each different component is separated according to particle type. In this state, we have [14,15]

$$\text{Var}[x_i] = P_i(1-P_i) \quad (33)$$

and

$$\text{Cov}[x_i, x_j] = -P_i P_j \quad (34)$$

Therefore, the variance-covariance matrix for a multicomponent mixture in the completely segregated state can be expressed as

$$\underline{\underline{S}} = \begin{bmatrix} P_1(1-P_1) & -P_1P_2 & \cdot & \cdot & \cdot & -P_1P_{(k-1)} \\ -P_1P_2 & P_2(1-P_2) & \cdot & \cdot & \cdot & -P_2P_{(k-1)} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ -P_1P_{(k-1)} & -P_2P_{(k-1)} & \cdot & \cdot & \cdot & P_{(k-1)}(1-P_{(k-1)}) \end{bmatrix} \quad (35)$$

The sample variance-covariance matrix, $\underline{\underline{S}}$, characterizes the degree of the dispersion of concentration of each component. Thus, the determinant of this matrix, $|\underline{\underline{S}}|$, reflects the extent of the variation in this system (mixture) similar to the variance in the univariate analysis. Therefore, replacing c^2 , c_r^2 and c_0^2 by $|\underline{\underline{S}}|$, $|\underline{\underline{S}}_r|$, and $|\underline{\underline{S}}_0|$, respectively, we can also define the mixing index for a multicomponent mixture. Thus, we can extend the mixing index

$$M_3 = \frac{c^2 - c_r^2}{c^2 - c_0^2} \quad (36)$$

proposed by Lacey [16] for a binary mixture to a multicomponent mixture by defining

$$M_3 = \frac{|\underline{\underline{S}}| - |\underline{\underline{S}}_r|}{|\underline{\underline{S}}| - |\underline{\underline{S}}_0|} \quad (37)$$

Other examples are tabulated in Table 1. Note that the expressions for multicomponent mixtures are reduced to those for binary mixtures.

According to eqns. (32) and (35), we have

$$\underline{\Sigma}_S = N \underline{\Sigma}_r \quad (38)$$

and

$$|\underline{\Sigma}_S| = N^{k-1} |\underline{\Sigma}_r| \quad (39)$$

The relationships among the mixing indices tabulated in Table 1 are evaluated in Table 2. Figures 3 and 4 plot the values of the nine mixing indices against that of M_8 for the samples of sizes 20 and 200, respectively. A mixing index should be sensitive to changes in the mixture quality of a mixture in order to be useful in following the progress of mixing. Ashton and Valentin [17] pointed out that Lacey's index, eqn. (37), was very sensitive to changes near the completely segregated state and relatively insensitive during the process of mixing near the completely mixed state. Their more complicated index, M_7 , was thus devised to exhibit greater sensitivity.

Mixing indices defined by the determinant of the sample variance-covariance matrix for multicomponent mixtures can be generalized as in Table 1, where $\underline{\Sigma}_r$ and $\underline{\Sigma}_S$ are the variance-covariance matrices of weight proportion in the completely mixed and completely segregated state, respectively. The development of $\underline{\Sigma}_r$ and $\underline{\Sigma}_S$ presented so far was concerned only with homogeneous systems. Consider the heterogeneous case. Throughout probability of selecting a particle of a given component is proportional to volume fraction of that component and the probability of finding a particle of one component is identical everywhere in a completely random mixture. Under these assumptions, particles taken from a spot sample are distributed approximately according to the multinomial distribution with the parameters, N^* and $q_i (i=1, 2, \dots, k)$, where N^* is the expected number of particles in a

Table 2. Equivalent forms of mixing indices for multicomponent mixtures

M_1	M_2	M_3	M_4	M_5
$1 - \frac{\sqrt{ S }}{\sqrt{ \Sigma_g }}$	$2M_1 - M_1^2$	$\frac{2M_1 - M_1^2}{1 - \frac{1}{\Lambda}}$	$\frac{1}{\sqrt{\Lambda}(1 - M_1)}$	$\frac{M_1}{(1 - M_1)(\sqrt{\Lambda} - 1)}$
$1 - \sqrt{1 - M_2}$	$1 - \frac{ S }{ \Sigma_g }$	$\frac{M_2}{1 - \frac{1}{\Lambda}}$	$\frac{1}{\sqrt{\Lambda}(1 - M_2)}$	$\frac{1 - \sqrt{1 - M_2}}{\sqrt{1 - M_2}(\sqrt{\Lambda} - 1)}$
$1 - \sqrt{1 - M_3} \left(1 - \frac{1}{\Lambda}\right)$	$M_3 \left(1 - \frac{1}{\Lambda}\right)$	$\frac{ \Sigma_g - S }{ \Sigma_g - \Sigma_r }$	$\frac{1}{\sqrt{\Lambda}(1 - M_3) + M_3}$	$\frac{1 - \sqrt{1 - M_3} \left(1 - \frac{1}{\Lambda}\right)}{\sqrt{1 - M_3} \left(1 - \frac{1}{\Lambda}\right) (\sqrt{\Lambda} - 1)}$
$1 - \frac{1}{\sqrt{\Lambda} M_4}$	$1 - \frac{1}{M_4^2 \Lambda}$	$\frac{\Lambda M_4^2 - 1}{M_4^2 (\Lambda - 1)}$	$\frac{\sqrt{ \Sigma_r }}{\sqrt{ S }}$	$\frac{M_4 \sqrt{\Lambda} - 1}{\sqrt{\Lambda} - 1}$
$\frac{M_5 (\sqrt{\Lambda} - 1)}{M_5 (\sqrt{\Lambda} - 1) + 1}$	$1 - \frac{1}{[1 + M_5 (\sqrt{\Lambda} - 1)]^2}$	$\frac{\Lambda [M_5^2 (\sqrt{\Lambda} - 1) + 2M_5]}{(\sqrt{\Lambda} + 1) [M_5 (\sqrt{\Lambda} - 1) + 1]^2}$	$\frac{M_5 (\sqrt{\Lambda} - 1) + 1}{\sqrt{\Lambda}}$	$\frac{\sqrt{\frac{ \Sigma_g }{ S }} - 1}{\sqrt{\frac{ \Sigma_g }{ \Sigma_r }} - 1}$

Table 2--Cont Inued

M_1	M_2	M_3	M_4	M_5
$1 - M_6$	$1 - M_6^2$	$\frac{1 - M_6^2}{1 - \frac{1}{\Lambda}}$	$\frac{1}{\sqrt{\Lambda} M_6}$	$\frac{1 - M_6}{M_6 (\sqrt{\Lambda} - 1)}$
$1 - \exp [M_7^2 \ln \frac{1}{\sqrt{\Lambda}}]$	$1 - \exp [M_7^2 \ln \frac{1}{\Lambda}]$	$\frac{1 - \exp [M_7^2 \ln \frac{1}{\Lambda}]}{1 - \frac{1}{\Lambda}}$	$\frac{1}{\sqrt{\Lambda} \exp [M_7^2 \ln \frac{1}{\sqrt{\Lambda}}]}$	$\frac{\exp [M_7^2 \ln \sqrt{\Lambda}] - 1}{\sqrt{\Lambda} - 1}$
$M_8 (1 - \frac{1}{\sqrt{\Lambda}})$	$1 - [1 - M_8 (1 - \frac{1}{\sqrt{\Lambda}})]^2$	$\frac{1 - [1 - M_8 (1 - \frac{1}{\sqrt{\Lambda}})]^2}{1 - \frac{1}{\Lambda}}$	$\frac{1}{\sqrt{\Lambda} - M_8 (\sqrt{\Lambda} - 1)}$	$\frac{M_8}{\sqrt{\Lambda} - M_8 (\sqrt{\Lambda} - 1)}$
$1 - \sqrt{M_9}$	$1 - M_9$	$\frac{1 - M_9}{1 - \frac{1}{\Lambda}}$	$\frac{1}{\sqrt{\Lambda} M_9}$	$\frac{1 - \sqrt{M_9}}{\sqrt{M_9} (\sqrt{\Lambda} - 1)}$
$1 - \frac{M_{10}}{\sqrt{\Lambda}}$	$\frac{M_{10}^2}{\Lambda} - 1$	$\frac{1 - M_{10}^2/\Lambda}{1 - 1/\Lambda}$	$\frac{1}{M_{10}}$	$\frac{\sqrt{\Lambda} - 1}{M_{10} \frac{\sqrt{\Lambda} - 1}{\sqrt{\Lambda} - 1}}$

Table 2--Continued

M_6	M_7	M_8	M_9	M_{10}
M_1	$1 - M_1$	$\frac{1}{1 - \frac{1}{\sqrt{\lambda}}}$	$(1 - M_1)^2$	$\sqrt{\lambda}(1 - M_1)$
M_2	$\sqrt{1 - M_2}$	$\frac{1}{1 - \sqrt{1 - M_2}}$	$1 - M_2$	$\sqrt{\lambda}(1 + M_2)$
M_3	$\sqrt{1 - M_3(1 - \frac{1}{\lambda})}$	$\frac{1 - \sqrt{1 - M_3(1 - \frac{1}{\lambda})}}{1 - \frac{1}{\sqrt{\lambda}}}$	$1 - M_3(1 - \frac{1}{\lambda})$	$[\lambda - M_3(\lambda - 1)]^{\frac{1}{2}}$
M_4	$\frac{1}{\sqrt{\lambda} M_4}$	$\frac{1}{1 - \frac{1}{\sqrt{\lambda}}}$	$\frac{1}{\lambda M_4^2}$	$\frac{1}{M_4}$
M_5	$\frac{1}{M_5(\sqrt{\lambda} - 1) + 1}$	$\frac{\sqrt{\lambda} M_5}{M_5(\sqrt{\lambda} - 1) + 1}$	$\frac{1}{(M_5(\sqrt{\lambda} - 1) + 1)^2}$	$\frac{\sqrt{\lambda}}{1 + M_5(\sqrt{\lambda} - 1)}$

Table 2--Continued

	M_6	M_7	M_8	M_9	M_{10}
M_6	$\frac{\sqrt{ \Sigma }}{\sqrt{ \Sigma_s }}$	$\sqrt{\frac{\ln M_6}{\ln \frac{1}{\sqrt{\Lambda}}}}$	$\frac{1 - M_6}{1 - \frac{1}{\sqrt{\Lambda}}}$	M_6^2	$\sqrt{\Lambda} M_6$
M_7	$\exp \left[M_7^2 \ln \frac{1}{\sqrt{\Lambda}} \right]$	$\sqrt{\frac{\ln \Sigma_s - \ln \Sigma }{ \Sigma_s - \ln \Sigma_r }}$	$\frac{1 - \exp \left[M_7^2 \ln \frac{1}{\sqrt{\Lambda}} \right]}{1 - \frac{1}{\sqrt{\Lambda}}}$	$\exp \left[M_7^2 \ln \frac{1}{\sqrt{\Lambda}} \right]^2$	$\frac{\frac{1}{2}}{\exp(M_7^2 \ln \Lambda)}$
M_8	$1 - M_8 \left(1 - \frac{1}{\sqrt{\Lambda}} \right)$	$\frac{\ln \left[1 - M_8 \left(1 - \frac{1}{\sqrt{\Lambda}} \right) \right]}{\ln \frac{1}{\sqrt{\Lambda}}}$	$\frac{\sqrt{ \Sigma_s } - \sqrt{ \Sigma }}{\sqrt{ \Sigma_s } \sqrt{ \Sigma_r }}$	$\left[1 - M_8 \left(1 - \frac{1}{\sqrt{\Lambda}} \right) \right]^2$	$\sqrt{\Lambda} \left[1 - \frac{1}{\sqrt{\Lambda}} \right]$
M_9	$\sqrt{M_9}$	$\sqrt{\frac{\ln \sqrt{M_9}}{\ln \frac{1}{\sqrt{\Lambda}}}}$	$\frac{1 - \sqrt{M_9}}{1 - \frac{1}{\sqrt{\Lambda}}}$	$\frac{ \Sigma }{ \Sigma_s }$	$\sqrt{\Lambda} M_9$
M_{10}	$\frac{M_{10}}{\sqrt{\Lambda}}$	$\sqrt{\frac{\ln \Lambda - 2 \ln M_{10}}{\ln \Lambda}}$	$\frac{1 - \frac{M_{10}}{\sqrt{\Lambda}}}{1 - \frac{1}{\sqrt{\Lambda}}}$	$\frac{M_{10}^2}{\Lambda}$	$\frac{\sqrt{ \Sigma }}{\sqrt{ \Sigma_r }}$

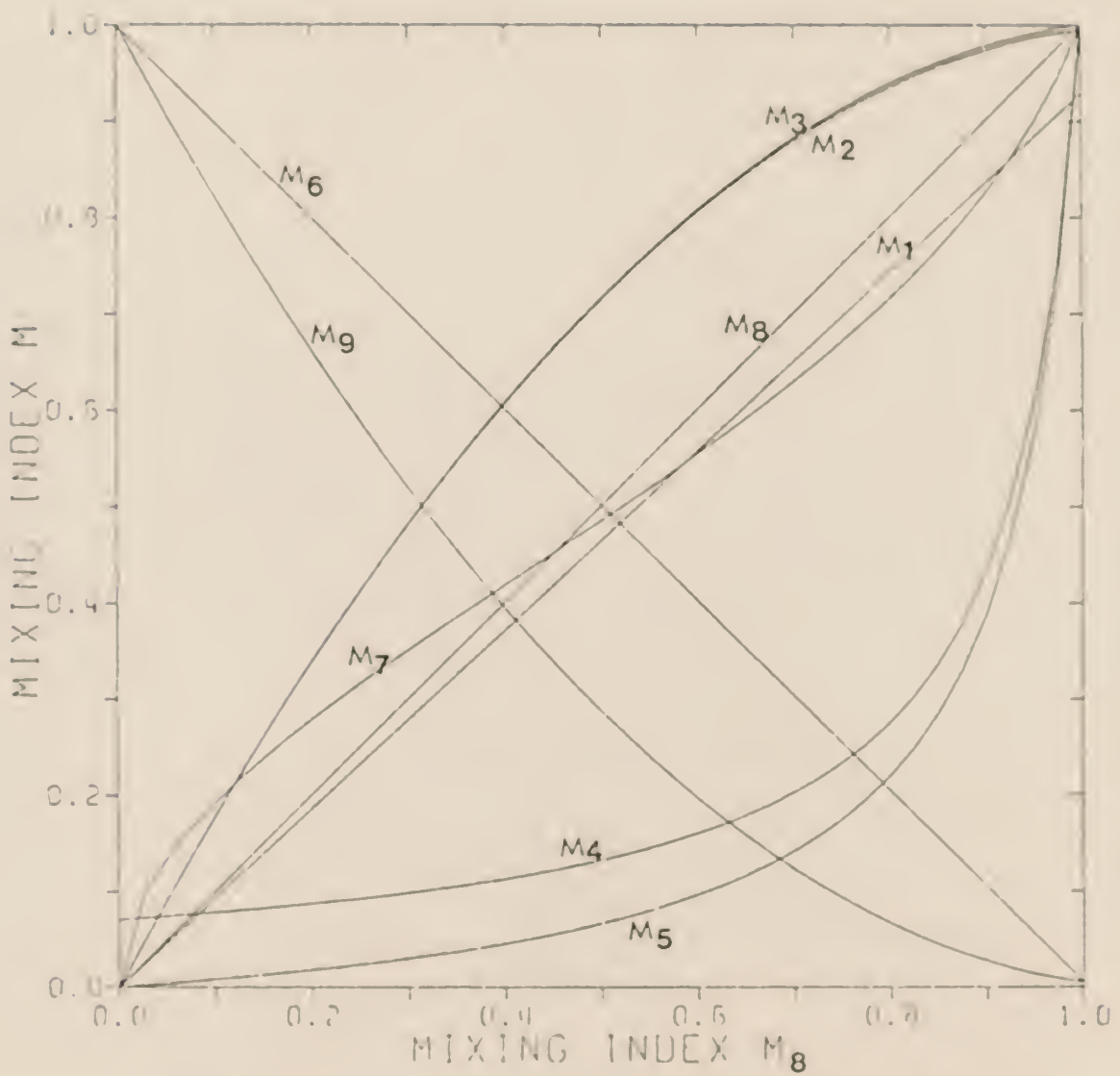


Fig. 3 Comparison of mixing indices based on the 3rd approach (the determinant of the covariance matrix) for sample size of 20.

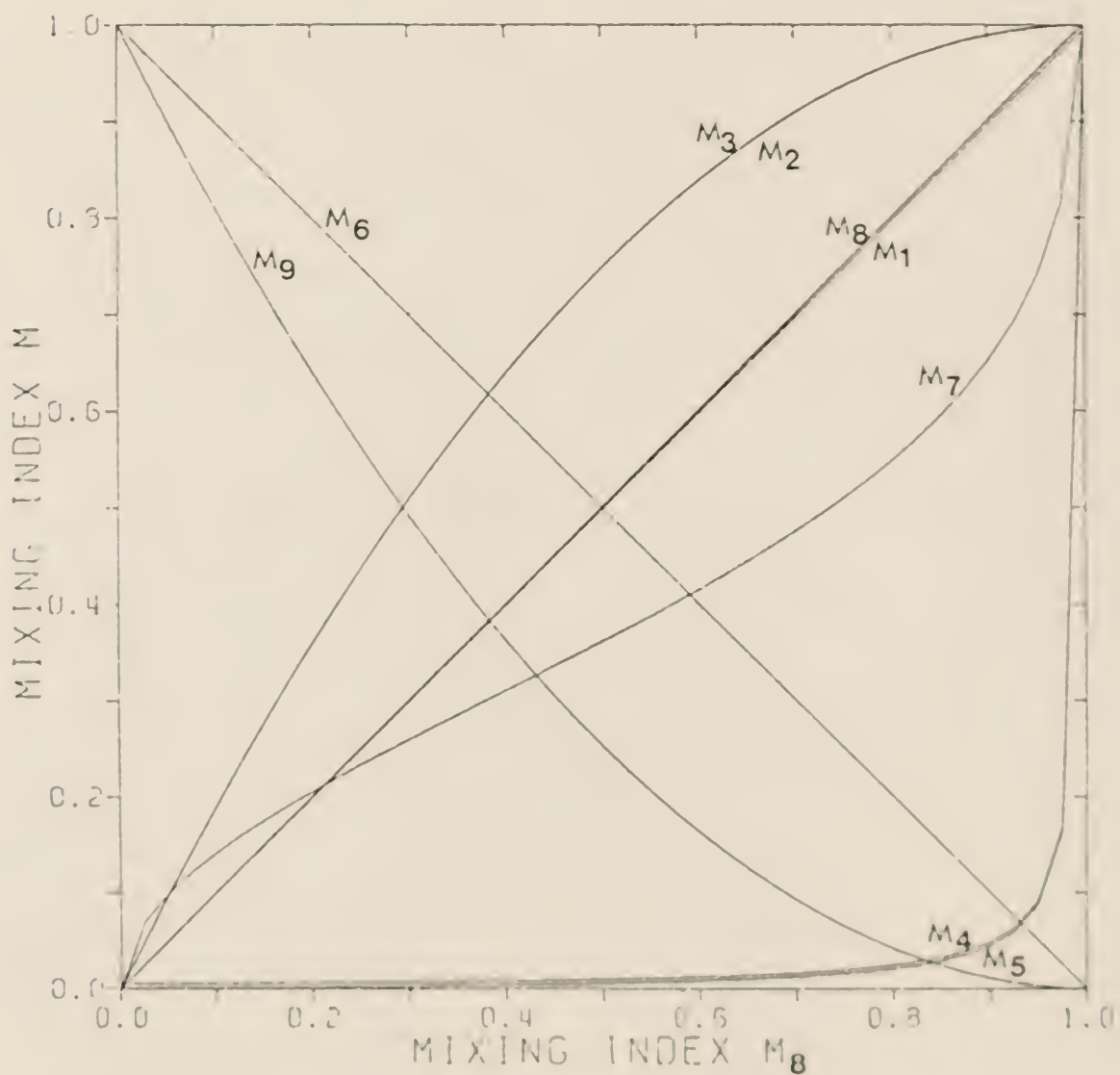


Fig. 4 Comparison of mixing indices based on the 3rd approach (the determinant of the covariance matrix) for sample size of 200.

spot sample of constant weight, W , and q_i is the volume fraction of the i -th component.

The variances and covariances of weight fractions of components in a multicomponent mixture, having this probability density function, are derived, respectively, as [see Appendix C]

$$\text{Var}[x_i] = \frac{\bar{w}}{W} \cdot \frac{c}{\rho_i} p_i (1 - \frac{c}{\rho_i} p_i), \quad i = 1, 2, \dots, k \quad (40)$$

and

$$\text{Cov}[x_i, x_l] = \frac{\bar{w}}{W} \cdot \frac{c^2}{\rho_i \rho_l} p_i p_l, \quad i, l = 1, 2, \dots, k \text{ and } i \neq l \quad (41)$$

This establishes the variance-covariance matrix for a multicomponent mixture in the completely mixed state, \underline{I}_m . Similarly, the variances and covariances of the weight fractions of the components in a multicomponent mixture in the completely segregated state are given, respectively, by [see Appendix D]

$$\text{Var}[x_i] = \frac{c}{\rho_i} (1-p_i)^2 p_i + p_i^2 (1 - \frac{c}{\rho_i} p_i), \quad i = 1, 2, \dots, k \quad (42)$$

and

$$\text{Cov}[x_i, x_l] = p_i p_l [1 - \frac{c}{\rho_i} - \frac{c}{\rho_l}], \quad i, l = 1, 2, \dots, k \text{ and } i \neq l \quad (43)$$

This establishes the variance-covariance matrix for a multicomponent mixture in the completely segregated state, \underline{I}_s . Notice that the variances and covariances for a heterogeneous system are reduced to those for a homogeneous system by setting

$$\rho_1 = \rho_2 = \dots = \rho_k$$

and

$$\bar{w}_1 = \bar{w}_2 = \dots = \bar{w}_k.$$

3.4. Sample Mean of an Individual Component

Akao et al. [18] have proposed a mixing index based on the contact number as

$$\begin{aligned} M_{11} &= \frac{\hat{C} - C_s}{C_r - C_s} \\ &= \frac{\hat{C}}{C_r} \end{aligned} \quad (44)$$

where \hat{C} is an estimator of the population contact number for a mixture in an arbitrary state, C_r and C_s are mean contact numbers of the mixtures in the completely mixed state and completely segregated state, respectively. This mixing index, M_{11} , eqn. (44), takes the value of 0 in the completely segregated state, a value between 0 and 1 in an incompletely mixed state, and 1 in the completely mixed state. Recently, Shindo et al. [19] proposed a beta-binomial model to describe the mixture in an incompletely mixed state. They have shown that the parameter, τ , which is unique, can be employed to define the mixing index

$$M_{11} = \frac{\tau}{\tau+1} \quad (45)$$

It has been shown that this definition can be extended to the multicomponent system to define the mixing index as [20]

$$M_{11} = \frac{\tau}{\tau+1} \quad (46)$$

The relative standard error of the mean contact number estimator has been shown to be smaller than that of the variance estimator of spot samples [20].

Similarly, the mixing index may be defined by using the sample mean of each individual component instead of the variance which is conventionally used to define the mixing index. For instance, the following expression can be used as a mixing index for a binary mixture;

$$M_{12} = 1 - \frac{\sum_{j=1}^m |x_{1j} - P_1|}{mP_1 \left[\frac{c}{c_1} (1 - P_1) + \left(1 - \frac{c}{c_1} P_1 \right) \right]} \quad (47)$$

The denominator of this equation is the total sum of the absolute differences between the sample concentrations and the population concentration among the spot samples from a mixture in the completely segregated state [See Appendix E]. In case the population mean is not specified, it can be replaced by its sample mean. The concentration of the perfect mixture throughout the whole system is exactly equal to the theoretical value, and therefore, the mixing index of the perfect mixture is 1 according to eqn. (47). If a mixture is in the completely segregated state, its mixing index is 0. Therefore, the mixing index, eqn. (47), always takes a value between 0 and 1 for a mixture in an arbitrary state. This definition can also be extended to a multicomponent system as

$$M_{12} = 1 - \frac{\sum_{i=1}^k \left(\sum_{j=1}^m |x_{ij} - P_i| \right) P_i}{m \sum_{i=1}^k P_i \left[\frac{c}{c_i} (1 - P_i) + \left(1 - \frac{c}{c_i} P_i \right) \right]} \quad (48)$$

4. COMPARISON OF DIFFERENT DEFINITIONS OF MIXING INDICES

To minimize computational effort, a ternary particle system was chosen to demonstrate the use of the proposed mixing indices for multicomponent mixtures. The values of the degree of mixedness evaluated according to different definitions were compared.

An actual mixture was generated by a drum mixer which was constructed from a lucite tube with a diameter of 7 cm and a length of 38 cm and fitted with two lucite end flanges, each with a diameter of 12.7 cm. Particles of three different types were used. Their physical properties are summarized in Table 3.

component	material	color	particle		density (gr/cm ³)	average (gr.) weight \bar{w}_f
			diameter in. (cm)	diameter in. (cm)		
1.	steel	silver	0.1875 (0.4763)		7.60	3.438
2.	lucite	red	0.1819 (0.4620)		1.18	0.487
3.	lucite	white	0.1618 (0.4110)		1.18	0.343

Table 3. Physical characteristics of particles

Prior to mixing, two thin semi-circular partitions were placed between two ends of the mixer, normal to the mixer axis. They divided the mixer into three compartments of equal length. Two hundred grams of component 1 and one hundred and fifty grams of each of components 2 and 3 were loaded in the middle, right and left compartments, respectively. Then the bed was leveled, the partitions were removed, the cover was put in place, and the mixer rotated. The speed of the mixer was set at 30 r.p.m. for this experiment and sampling was carried out at interval of 10 minutes after the onset of rotation. A sample divider was employed to divide the mixture into ten sections. Each sample obtained from each section contained 20 grams of particles. Mixing indices were calculated from the experimental data, which are summarized in Table 4. The procedures are briefly described as follows:

(1) Pseudo-binary mixture

Particles of type 1 was assumed as the key component, and particles of types 2 and 3 were jointly considered as the pseudo-component. The particle weight and density of this pseudo-component were calculated from eqns. (12) and (13), respectively. The mixing indices were calculated according to ten of the more frequently used criteria given in Table 1, and the resultant values of indices are listed in Table 4.

(2) Pooled variance

The pooled variance of weight fractions of the components in a multi-component mixture was calculated from eqn. (14). The variance for the multicomponent mixture in the completely mixed state, c_T^2 , and that for the mixture in the completely segregated state, c_0^2 , were calculated according to eqns. (15) and (16), respectively. Mixing indices were computed by substituting the variances, c_T^2 and c_0^2 , in the expressions in Table 1. Results are also tabulated in Table 4.

component sample	1	2	3
1	0.345	0.450	0.205
2	0.450	0.075	0.457
3	0.410	0.150	0.440
4	0.390	0.275	0.335
5	0.475	0.275	0.250
6	0.565	0.225	0.210
7	0.520	0.295	0.185
8	0.610	0.250	0.140
9	0.575	0.325	0.100
10	0.355	0.585	0.060

Experimental data expressed in weight fraction

mixing index	Approach 1	Approach 2	Approach 3
M ₁	0.775	0.742	0.937
M ₂	0.949	0.934	0.996
M ₃	0.964	0.957	0.996
M ₄	0.541	0.605	0.343
M ₅	0.477	0.532	0.329
M ₆	0.225	0.258	0.063
M ₇	0.842	0.880	0.958
M ₈	0.882	0.880	0.958
M ₉	0.051	0.066	0.040
M ₁₀	1.848	1.653	2.915

Note: Approach 1 - pseudo binary mixture

Approach 2 - pooled variance

Approach 3 - determinant of covariance matrix

Table 4. A ternary mixture and resultant values of mixing indices of this mixture according to approaches 1, 2 and 3.

(3) Determinant of the sample covariance matrix

The matrices, \underline{S} , \underline{I}_r and \underline{I}_s , were constructed and their determinants were then evaluated. According to the definitions listed in Table 1, the indices were determined. The results are also tabulated in Table 4.

(4) Sample mean of an individual component

The sample mean of each individual component was calculated. Then, the total sum of the differences between sample concentrations and sample mean was determined. According to eqn. (46), the mixing indices was computed as 0.699 for this mixture.

5. CONCLUDING REMARKS

To assess the quality of a mixture is one of the most important aspects in the investigation of solids mixing. The concept of homogeneity of dispersed (or heterogeneous) particle systems is useful for the examination of the mixing and dispersion process and for the elucidation of problems which are of practical significance.

Although much effort has been expended on this subject, it still lacks generally accepted indices to assess the homogeneity of a heterogeneous multicomponent mixture. Four approaches, which have been proposed in this study, are of universal applicability. The approximate joint distribution of random vector $[Y_1, Y_2, \dots, Y_k]$ for a multicomponent mixture in the completely random state has been derived. The use of various mixing indices for multicomponent mixtures has been shown through a ternary mixture over a wide range of physical properties.

The proposed expressions of mixing indices for multicomponent mixtures reduce to those for a binary mixture. Any mixing index for a homogeneous system is a special case of that for a heterogeneous system.

The choice of a mixing index depends on the application of mixing processes. The relationships among the ten most frequently used indices based on the second and third approaches are also evaluated. The mixing index defined by each sample mean may have smaller relative standard error.

In the future, we shall study the feasibility of extending the mixing index, as defined by chi-square [6], to a universal index for a heterogeneous multicomponent mixture.

NOTATIONS

A	N^{k-1}
\hat{C}	estimation of the population contact number
C_r	mean contact number in the completely random state
C_s	mean contact number in the completely segregated state
$\text{Cov} [Y_i, Y_j]$	covariance between the random variables Y_i and Y_j
$E [Y_i]$	expected value of the random variable Y_i
k	no. of components
M	mixing index
m	no. of spot samples
N	no. of particles in a spot sample
N^*	expected number of particles in a sample of constant weight, W .
n_j	no. of particles of component j in a spot sample
P_j	weight proportion of component j
q_j	volume fraction of component j
\underline{S}	sample variance-covariance matrix
$SP_{x_i x_i}$	sum of cross products of x_i and x_i
SS_{x_i}	sum of squares of x_i
\bar{s}_j	standard deviation of particle weight of component j
s_{ii}	variance of x_i
s_{ij}	covariance between x_i and x_j
T	total weight of the mixture
V	total net volume of solid particles in the mixture
$\text{Var} [Y_i]$	variance of the random variable Y_i

w	weight of a spot sample
\bar{w}_j	mean particle weight of component j
x_i	a random variable denoting the weight fraction of component i in a sample
x_{ij}	weight fraction of component i in the j -th spot sample
\bar{x}_i	sample mean of component i
y_j	a random variable denoting the number of particles of component j in a spot sample

Greek

ρ	mean density
ρ_i	density of component i
$\bar{\Sigma}_r$	variance-covariance matrix of a mixture in the completely mixed state
$\bar{\Sigma}_s$	variance-covariance matrix of a mixture in the completely segregated state
c^2	sample variance of weight fraction
c_0^2	variance of a mixture in the completely segregated state
τ_p^2	variance of a perfect mixture
c_r^2	variance of a mixture in the completely mixed state
τ	a parameter as defined in [19]

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Appendix A. Derivation of Equation (7)

Before mixing starts, a mixture is assumed to be in the completely segregated state. Among the n spot samples taken, m_1 samples contain only particles of component 1, and the remaining $(n-m_1)$ contain only particles of component 2. Assume that the probability of taking a particle of a given component is proportional to its volume fraction, i.e.,

$$m_1 = nq_1 \quad (A-1)$$

The sample variance can be obtained from eqn. (1), in which

$$\bar{x}_1 = P_1$$

Thus,

$$\begin{aligned} c_0^2 &= \frac{1}{n} \sum_{i=1}^n (x_{1i} - \bar{x}_1)^2 \\ &= \frac{1}{n} \sum_{i=1}^n (x_{1i} - P_1)^2 \\ &= \frac{1}{n} \left[\sum_{i=1}^{m_1} (x_{1i} - P_1)^2 \Big|_{x_{1i}=1} + \sum_{i=1}^{n-m_1} (x_{1i} - P_1)^2 \Big|_{x_{1i}=0} \right] \\ &= \frac{1}{n} [(1 - P_1)^2 m_1 + P_1^2 (n - m_1)] \quad (A-2) \end{aligned}$$

Since

$$\begin{aligned} m_1 &= nq_1 \\ &= n \left(\frac{V_1}{V} \right) \\ &= n \frac{c}{c_1} \cdot \frac{V_1 c_1}{V c} \\ &= n \frac{c}{c_1} P_1 \quad (A-3) \end{aligned}$$

we have

$$c_0^2 = \frac{1}{n} \left[(1 - P_1)^2 n \cdot \frac{c}{c_1} P_1 + P_1^2 \left(1 - \frac{c}{c_1} P_1 \right) n \right]$$

$$= \frac{c}{c_1} (1 - p_1)^2 p_1 + p_1^2 \left(1 - \frac{c}{c_1} p_1\right) \quad (7)$$

Similarly, we may also derive the variance of weight fraction for component 2 as

$$c_0^2 = \frac{c}{c_2} (1 - p_2)^2 p_2 + p_2^2 \left(1 - \frac{c}{c_2} p_2\right)$$

Since

$$\rho = \frac{\rho_1 \rho_2}{p_1 \rho_2 + p_2 \rho_1} ,$$

the variances of components 1 and 2 are identical.

Appendix B. Derivation of Equation (11)

Consider a mixture of two components, 1 and 2, which are present in the weight proportion, P_1 and P_2 ($P_1 + P_2 = 1$). Suppose that components 1 and 2 have particle densities ρ_1 and ρ_2 , respectively, and also suppose that the weight and volume of the mixture are T and V , respectively. Note that the volume, V , is the net volume of solids, and not the total apparent volume of the mixture mass including the space between the particles.

Therefore, V can be expressed as

$$V = \frac{P_1 T}{\rho_1} + \frac{P_2 T}{\rho_2} \quad (B-1)$$

The mean particle density, ρ , can be defined as

$$\begin{aligned} \rho &= \frac{T}{V} \\ &= \frac{\rho_1 \rho_2}{P_1 \rho_2 + P_2 \rho_1} \end{aligned} \quad (B-2)$$

When sampling, the probability of taking a particle is proportional to the volume fraction of that component. Particles in the completely mixed state are assumed to be distributed according to the binomial distribution with parameters N^* and q_1 , where N^* is the expected number of particles in a sample of constant weight, W , q_1 is the volume fraction of component 1.

The variance of weight fraction of component 1 can be expressed as

$$\begin{aligned} \sigma_v^2 &= \text{Var}[x_1] \\ &= \text{Var}\left[\frac{Y_1 \cdot \bar{w}}{W}\right] \\ &= \frac{\bar{w}^2}{W^2} \cdot \text{Var}[Y_1] \\ &= \frac{\bar{w}^2}{W^2} \cdot N^* q_1 (1 - q_1) \end{aligned}$$

$$= \frac{\bar{w}_1^2}{\bar{w}^2} \cdot \frac{\bar{w}_2}{\bar{w}_1} \cdot \frac{c}{c_1} v_1 \cdot \frac{c}{c_2} v_2$$

Thus,

$$c_2 = \frac{v_1 v_2}{\bar{w}} \cdot \frac{c^2}{c_1 c_2} \cdot \frac{\bar{w}_1 \cdot \bar{w}_2}{(v_1 \bar{w}_2 + v_2 \bar{w}_1)} \quad (11)$$

Appendix C. Derivation of Equations (40) and (41)

Consider a multicomponent mixture having k components for which we defined the following for $i = 1, 2, \dots, k$:

ρ_i = density of component i

\bar{w}_i = particle weight of component i

P_i = weight proportion of component i

q_i = volume fraction of component i

Under the assumption as described in subsection 3.3, particles taken from a spot sample are distributed approximately according to the multinomial distribution with parameters N^* and q_i . Therefore, the variance of weight fraction of component i is [15]

$$\begin{aligned} \text{Var}[x_i] &= \text{Var}\left[\frac{Y_i \bar{w}}{W}\right] \\ &= \frac{\bar{w}^2}{W^2} \text{Var}[Y_i] \\ &= \frac{\bar{w}^2}{W} N^* q_i (1 - q_i) \\ &= \frac{\bar{w}^2}{W^2} \cdot \frac{\bar{w}}{W} \frac{\rho}{\rho_i} P_i (1 - \frac{\rho}{\rho_i} P_i) \end{aligned}$$

Thus,

$$\text{Var}[x_i] = \frac{\bar{w}^2}{W} \frac{\rho}{\rho_i} P_i (1 - \frac{\rho}{\rho_i} P_i), \quad i = 1, 2, \dots, k \quad (40)$$

The covariance of weight fractions between the i -th and j -th component can be expressed as [15]

$$\begin{aligned} \text{Cov}[x_i, x_j] &= \text{Cov}\left[\frac{Y_i \bar{w}}{W}, \frac{Y_j \bar{w}}{W}\right] \\ &= \frac{\bar{w}^2}{W^2} \text{Cov}[Y_i, Y_j] \end{aligned}$$

$$= \frac{\bar{w}_i^2}{w^2} (-N^* a_i a_j)$$

$$= \frac{\bar{w}_i^2}{w^2} \left(-\frac{\bar{w}_i}{w}\right) \frac{p_i}{p_i} p_i \cdot \frac{p_j}{p_j} p_j$$

Thus,

$$\text{Cov}[x_i, x_j] = -\frac{\bar{w}_i}{w} \cdot \frac{p_i^2}{p_i p_j} p_i p_j, \quad (41)$$

$i, j = 1, 2, \dots, k$ and $i \neq j$

Appendix D. Derivation of Equation (42)

For a multicomponent mixture in the completely segregated state, the derivation of the variance of weight fraction for each component is similar to that for a binary mixture (see Appendix A). Thus, we have

$$\text{Var}[x_i] = \frac{c}{c_i} (1 - P_i)^2 P_i + P_i^2 (1 - \frac{c}{P_i} P_i), \quad (42)$$

$$i = 1, 2, \dots, k$$

Under the assumption as described in Appendix A, we have

$$m_i = m q_i \quad (D-1)$$

and

$$m_i = m q_i \quad (D-2)$$

where m_i denotes the number of samples containing only particles of component i and m_i that of component i . The covariance of weight fractions between components i and k is expressed as

$$\begin{aligned} \text{Cov}[x_i, x_k] &= \frac{1}{m} \sum_{j=1}^m (x_{ij} - \bar{x}_i)(x_{kj} - \bar{x}_k) \\ &= \frac{1}{m} \sum_{j=1}^m (x_{ij} - P_i)(x_{kj} - P_k) \\ &= \frac{1}{m} \left[\sum_{j=1}^{m_i} (x_{ij} - P_i)(x_{kj} - P_k) \Big|_{x_{ij} = 1, x_{kj} = 0} \right. \\ &\quad \left. + \sum_{j=1}^{m_k} (x_{ij} - P_i)(x_{kj} - P_k) \Big|_{x_{ij} = 0, x_{kj} = 1} \right. \\ &\quad \left. + \sum_{j=1}^{m - m_i - m_k} (x_{ij} - P_i)(x_{kj} - P_k) \Big|_{x_{ij} = 0, x_{kj} = 0} \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{m} [m_i(1 - p_i)(-p_i) + m_l(-p_i)(1 - p_l) \\
&\quad + (m - m_i - m_l) p_i p_l] \\
&= \frac{1}{m} [m p_i p_l - m_i p_l - m_l p_i] \\
&= p_i p_l - q_i p_l - q_l p_i
\end{aligned}$$

Thus,

$$\text{Cov}[x_i, x_l] = p_i p_l \left[1 - \frac{c}{r_i} - \frac{d}{r_l}\right], \quad (42)$$

$$i, l = 1, 2, \dots, k \text{ \& } i \neq l$$

Appendix E. Sum of the Absolute Differences between the Sample Concentrations and its Population Concentration

For a binary mixture in the completely segregated state, we assume that m_1 samples contain only particles of component 1 among the m spot samples to be taken. Under the same assumption imposed in Appendix A, we have

$$m_1 = m q_1$$

Therefore, the sum of the absolute differences between the sample concentrations and its population concentration is

$$\begin{aligned} \sum_{j=1}^m |x_{ij} - P_1| &= \sum_{j=1}^{m_1} |x_{ij} - P_1| \Big|_{x_{ij}=1} + \sum_{j=1}^{m-m_1} |x_{ij} - P_1| \Big|_{x_{ij}=0} \\ &= (1 - P_1)m_1 + P_1(m - m_1) \\ &= (1 - P_1)m q_1 + P_1 m (1 - q_1) \\ &= (1 - P_1)m \frac{c}{\rho_1} P_1 + P_1 m \left(1 - \frac{c}{\rho_1} P_1\right) \\ &= m P_1 \left[\frac{c}{\rho_1} (1 - P_1) + \left(1 - \frac{c}{\rho_1} P_1\right) \right] \end{aligned} \quad (E-1)$$

If the system is a homogeneous system, this equation reduces to

$$\sum_{j=1}^m |x_{ij} - P_1| = 2m P_1 (1 - P_1) \quad (E-2)$$

Equations (E-1) and (E-2) are employed in deriving eqn. (47).

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes significant conclusions of this work and gives several recommendations for further studies.

1. CONCLUSIONS

- (1) The concept of the contact number to estimate the mixing index is successfully extended to multicomponent mixtures. Such an application has been employed only for the mixing of binary mixtures [1]. The multinomial model is proposed to describe a multicomponent mixture in the completely mixed state. Numerical experiments have been performed to verify the theoretical expressions of the distribution of the contact number. The mean contact numbers and their precision from the computer simulations of mixtures with regular packing arrangement are reported.
- (2) A theoretical model, namely, the Dirichlet-multinomial model, is derived to describe a multicomponent mixture in an incompletely mixed state. This model contains parameter τ that defines uniquely the mixing index based on the contact number. An estimate of this parameter, τ , is derived and the precision of the estimated population mean contact number is assessed. Computer simulations are included to demonstrate the effectiveness of the derived model. The relative standard error of the mean contact number estimator has been shown to be smaller than that of the variance estimator of spot samples. Therefore, the precision of the mixing index based on the mean contact number estimator is superior to that conventionally based on the variance estimator.

(3) Literature on the assessment of mixture quality is very scarce, as this topic still lacks generally accepted principles, in spite of its practical significance. This is especially true for multicomponent solids mixing. Several approaches to assess the homogeneity of a multicomponent solids mixture have been proposed in Chapter V. An approximate distribution of a heterogeneous mixture in the completely mixed state is also reported. The mixing indices proposed here are estimated on the basis of the

- (a) pseudo binary mixture concept,
- (b) pooled variance of the whole system,
- (c) determinant of the sample covariance matrix, or
- (d) sample mean of each component in the mixture.

2. RECOMMENDATIONS

- (1) The non-ideal mixing behavior of cohesionless solid particles in a horizontal drum mixer has been modeled by a continuous Markov process [2]. The Markov chain may also be applied to simulate the non-ideal mixing behavior of solids particles in a drum mixer.
- (2) Lai and Fan [3] proposed a discrete steady-state Markov chain model for the mixing process of a multicomponent homogeneous particle system in a motionless mixer. Wang and Fan [4] also proposed a Markov chain model for axial segregation of binary solid particles. It is recommended that this model may be extended to multicomponent heterogeneous particles blended by a motionless mixer.
- (3) Other types of stochastic models, e.g., the birth-death model [5,6] and the restricted random walk model [7,8], may be employed to simulate solids mixing and demixing.

- (4) Multivariate analysis is an effective tool to deal with multi-component solids mixing problems [9,10,11]. Since the variables are statistically dependent among themselves, we can not single out one from the others for treatment in bulk sampling of a multi-component heterogeneous mixture. The variables must be considered jointly. Thus, the following multivariate statistical methods may be exploited to analyze sampling results:
- (a) multivariate analyses of variance and covariance,
 - (b) multiple, partial, and canonical correlation techniques,
 - (c) discriminant and classification analysis,
 - (d) factor analysis and canonical analysis.
- (5) Nonparametric statistical tests can be performed on the data with different scales of measurement, such as nominal, ordinal, interval or ratio, without knowing the distribution of the population [12]. The distributions of the components during mixing are usually unknown, and therefore, nonparametric statistical tests should be effective tools to analyze the sampling results of solids mixing. Applicability of these tests on solids mixing of binary mixtures was demonstrated [13]. Naturally, these tests can be extended to multicomponent mixtures and mixing.

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STUDIES ON MULTICOMPONENT SOLIDS MIXING AND MIXTURES

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ABSTRACT

The concept of the contact number is extended to a multicomponent solids mixture in the completely mixed state. Chapter 3 presents an estimation of the mean contact number by measuring the concentration of particles by spot sampling. This chapter also reports the mean contact numbers and their precision determined from the computer simulation of mixtures with regular packing arrangements at different concentrations of the key component. The number of spot samples necessary for a specified value of the relative standard error is also derived. All equations derived here are reduced to the corresponding expressions for two-component mixtures.

A theoretical model, namely, the Dirichlet-multinomial model, is derived for the distribution of (Y_1, Y_2, \dots, Y_p) in a spot sample of size n of a multicomponent mixture in an incompletely mixed state, where Y_j denotes the number of particles of component A_j . This model contains the parameter, \mathcal{T} , that defines uniquely the mixing index based on the contact number. Estimate of this parameter, \mathcal{T} , is derived and the precision of the estimated population mean contact number is assessed. Computer simulation is included to support the effectiveness of the derived model.

The literature on the assessment of the quality of solids mixtures is very scarce. This is especially true for multicomponent mixtures. Four approaches to assess the homogeneity of a multicomponent solids mixture have been proposed in this study. The mixing indices proposed are estimated on the basis of the

- (a) pseudo binary mixture concept,
- (b) pooled variance of the whole system,
- (c) determinant of the sample covariance matrix, or
- (d) sample mean of each component in the mixture.

The use of various mixing indices for multicomponent mixtures has been shown through two ternary mixtures.

