

CHEMICAL INHOMOGENEITY OF MATERIALS AND ITS DETERMINATION. GRANULAR MATERIALS

P. BOHÁČEK

*Institute of Physics,
Czechoslovak Academy of Sciences, 180 40 Prague 8*

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The dependence of the inhomogeneity variance has been derived in the paper on the size of the sample for granular perfectly mixed materials as well as for imperfectly mixed materials.

Inhomogeneity of granular materials has been treated in a voluminous literature. Heterogeneous powder mixtures have been studied and theoretical relations have been derived for the variance of inhomogeneity due to the fluctuation of the number of particles of different phases in the analyzed sample¹⁻³. The study of the dependence of the inhomogeneity variance on the amount of the sample or the number of particles in the sample has led to equations indicating indirect proportionality between the inhomogeneity variance and the size of the sample or the number of particles composing the sample.

For real granular materials, however, the inhomogeneity variance exhibits higher values in dependence on the size of the sample than those corresponding to the above mentioned dependence⁴⁻⁶. This discrepancy is being explained^{4,7-9} by statistical dependence of composition of neighbouring particles or neighbouring samples.

Statistical dependence of composition of neighbouring samples can be suppressed or eventually eliminated by mixing the material. The state of a perfectly mixed material has been defined in ref.⁵ as one when k random samplings yields the results X_1, \dots, X_k (the deviations of concentration from the mean) as k independent statistical variables with the same normal distribution.

A review of the literature devoted to inhomogeneity of granular materials has been presented in ref.¹⁰. This reference lists also a series of papers dealing with technical aspects of mixing granular materials and the derivation of criteria for a quantitative assessment of the degree of uniformity.

In this paper we shall deal with perfectly mixed materials prepared by crushing compact materials. It will be assumed that the inhomogeneity variance, corresponding to samples equivalent in size to a single particle of the granular material, has been determined from the course of concentration in the compact material using the method

described in ref.⁹. From this basic tenet we shall start in the derivation of the dependence of the inhomogeneity variance on the size of the sample. For imperfectly mixed material we shall investigate the correlation function and in the derivation of the dependence of the inhomogeneity variance on the size of the sample we shall make use of the approach published elsewhere⁹.

THEORETICAL

Perfectly Mixed Materials

The expression for the dependence of the inhomogeneity variance on the size of the sample for a granular material composed of particles of different size and specific weight will be derived by steps. First, we shall assume that all particles in the granular material are of the same size, shape and specific weight s . Let us denote by v volume of the particle, $D^2(v)$ the inhomogeneity variance of a set of single-particle samples (determined in accord with ref.⁹) and let $D^2(kv)$ denote the inhomogeneity variance of a set of k -particle samples. The deviation of the concentration of the analyzed element c from the mean $E(c) \equiv \bar{c}$ equals for the k -particle sample to

$$\delta c(kv) = k^{-1}[\delta c(v, 1) + \delta c(v, 2) + \dots + \delta c(v, k)], \quad (1)$$

where $\delta c(v, i)$ is the concentration deviation from \bar{c} in the i -th particle of the sample.

In k -particle samples taken from perfectly mixed materials the composition of individual particles is statistically independent (this means that for the correlation coefficient $R_{ii'} = E[\delta c(v, i) \delta c(v, i')]$ of an arbitrary pair of particle ($i \neq i'$) $R_{ii'} = 0$; for individual particles ($i = i'$) then $E[\delta c(v, 1)]^2 \equiv R_{11} = E[\delta c(v, 2)]^2 \equiv R_{22} = \dots = E[\delta c(v, k)]^2 \equiv R_{kk} = D^2(v)$). On raising Eq. (1) to the second power and averaging, an expression for the sought variance $D^2(kv)$ is obtained:

$$D^2(kv) = k^{-2}[kD^2(v)] = D^2(v)/k. \quad (2)$$

Further we shall examine granular materials consisting of particles of the same specific weight but different size and shape. The inhomogeneity variance of a set of samples ω of the same weight G_ω (hence the same volume V_ω) composed of different number of particles of various size can be calculated as follows: The particles are divided into w classes depending on their size and shape. Each class of particles identical as to their volume and shape is assigned its single-particle variance $D^2(v_l)$ using the parameters of the compact material. $l = 1, 2, \dots, w$ is the index of the class and v_l is the volume of the particles of the l -th class.

Let in a certain sample ω of volume V_ω be $k_{1\beta}$ particles of the first class (volume v_1), $k_{2\beta}$ of particles of the second class (volume v_2), ..., $k_{w\beta}$ particles of the w -th class

(volume v_w). β is the index of possible alternatives of the ratio $k_{1\beta} : k_{2\beta} : \dots : k_{w\beta}$ of the numbers $k_{l\beta}$ constrained by the condition $k_{1\beta}v_1 + k_{2\beta}v_2 + \dots + k_{w\beta}v_w = V_\omega$. In this sample ω the deviation of concentration from \bar{c} is then given by

$$\delta c_\beta(V_\omega) = V_\omega^{-1} \{v_1[\delta c(v_1, 1) + \dots + \delta c(v_1, k_{1\beta})] + \dots + v_w[\delta c(v_w, 1) + \dots + \delta c(v_w, k_{w\beta})]\}. \quad (3)$$

Let us consider now a set of samples ω such that in each sample the number of particles of the same class is given by the same number $k_{1\beta}$, the number of particles of the second class is given by the same number $k_{2\beta}$, etc. The deviations expressed in Eq. (3) have in this set (see the derivation of Eq. (2) for the deviations (1)) the variance:

$$D_\beta^2(V_\omega) = V_\omega^{-2} \{v_1^2 k_{1\beta} D^2(v_1) + \dots + v_1^2 k_{1\beta} D^2(v_1) + \dots + v_w^2 k_{w\beta} D^2(v_w)\}. \quad (4)$$

In the general case when the number of particles of the same class is not in all samples the same we shall consider a set of N samples of which N_β has the same combination of β numbers $k_{1\beta}, k_{2\beta}, k_{3\beta}, \dots, k_{w\beta}$. Let in this sample be p such combinations ($\beta = 1, 2, \dots, p; \sum_{\beta=1}^p N_\beta = N$). The inhomogeneity variance of this sample is found by determining the deviations δc in individual samples with the aid of the classic expression $D^2(V_\omega) = N^{-1} \sum_{i=1}^N (\delta c_i)^2$. The sum of square deviations $(\delta c_i)^2$ corresponding to the samples of the same combination β can be estimated by the expression $N_\beta D_\beta^2(V_\omega)$ where the variance $D_\beta^2(V_\omega)$ is given by Eq. (4). The inhomogeneity variance of the set of N samples is then given by

$$\begin{aligned} D^2(V_\omega) &= N^{-1} \sum_{\beta=1}^p N_\beta D_\beta^2(V_\omega) = N^{-1} \sum_{\beta=1}^p N_\beta \sum_{l=1}^w (v_l/V_\omega)^2 k_{l\beta} D^2(v_l) = \\ &= \sum_{l=1}^w (v_l/V_\omega)^2 D^2(v_l) \sum_{\beta=1}^p k_{l\beta} N_\beta / N. \end{aligned} \quad (5)$$

The expression $\sum_{\beta=1}^p k_{l\beta} N_\beta / N$ indicates the average number of particles of the l -th class in a single sample of our set of N samples. Let us denote this quantity by k'_l . Thus

$$D^2(V_\omega) = \sum_{l=1}^w (v_l/V_\omega)^2 D^2(v_l) k'_l. \quad (6)$$

The variance (6) thus depends only on the average representation of the classes k'_l in the whole set of samples. On the contrary, the representation of the classes in indi-

vidual samples is immaterial. For example, a set, whose numbers of particles in individual classes are given in each sample (volume V_ω) by the same numbers k'_l , has the same inhomogeneity variance as a set of samples (taken from the same granular material, volume V_ω) in which each sample consists of particles of one class only and number of samples, N_l , consisting of particles of l -th class, is given by $N_l(V_\omega/v_l) = Nk'_l$ (N is the total number of samples in the set).

If we take from the same material instead of the samples ω n -times larger samples of volume nV_ω and denote by K'_l the average number of the particles of the l -th class in the set of these samples the inhomogeneity variance of this set is then given, according to Eq. (6), by:

$$D^2(nV_\omega) = \sum_{l=1}^w [v_l/(nV_\omega)]^2 D^2(v_l) K'_l. \quad (7)$$

The variance $D^2(nV_\omega)$ is n -times smaller than $D^2(V_\omega)$ if for all l we may write $K'_l = nk'_l$. Unless this conditions is fulfilled we may find deviations in the dependence of the inhomogeneity variance on the size of the sample from the curve of the type $1/n$ (for materials perfectly mixed) even for a sufficient number of samples forming the sets. Thus care must be taken to keep the ratio of the numbers $k'_1 : k'_2 : \dots : k'_w$ and $K'_1 : K'_2 : \dots : K'_w$ very close to the ratio valid for the number of particles of individual classes in the bulk material.

In the following part we shall deal with the more general case of granular materials with unequal specific weight of particles. The cause of unequal specific weight may be primarily the unstationary course of concentrations of various elements in the compact materials from which the granular material was prepared. We shall assume that the specific weight of a given particle equals its regression value, s_r , in that point within the compact material where the particle was originally located. Random fluctuation of the real specific weights shall not be considered. (If the particles of the granular material are smaller than the size of the grain of individual phases of the compact material we shall identify s_r with the mean course of the specific weight of the phases — an example of this type is treated in the discussion).

Let us divide the compact material from which our granular material is to be prepared to u regions in such a manner that within each region the regression specific weight, s_r , as well as the regression concentration, c_r , take constant values. Thus in the j -th region ($j = 1, 2, \dots, u$) we have $s_r = s_{rj}$ and $c_r = c_{rj}$. Moreover, the regions are taken such that the fluctuations of the concentration c within the region be stationary. The concentration deviations from the mean, \bar{c}_j , measured in the j -th region of the compact material for the set of samples of identical shape and volume v shall be denoted $\delta c_j(v)$. Corresponding variance of inhomogeneity for this set shall be denoted by $D_j^2(v)$. Let us prepare from the just characterized material a granular material consisting of particles of identical shape and volume (the specific weight of

each particle equals some of the values s_{rj}). The inhomogeneity variance of samples of weight G_ω shall be derived in an analogous manner as Eq. (6). However, instead of the classes of particles of identical size we shall consider classes of particles of identical weight. Instead of Eq. (3) we shall start from

$$\delta c_p(G_\omega) = G_\omega^{-1} \sum_{j=1}^u g_j \sum_{\alpha_j=1}^{k_{j\beta}} \delta c(g_j, \alpha_j), \quad (8)$$

where $g_j = v s_{rj}$ is the weight of a particle from the j -th region.

Analogous arrangements to those leading to Eq. (6) lead also to:

$$D^2(G_\omega) = \sum_{j=1}^u (g_j/G_\omega)^2 D_j^2(v) k'_j. \quad (9)$$

Let us designate by V_M the volume of the compact material crushed to give the studied granular material. V_j is the volume of the j -th region. The ratio $v_j = V_j/V_M$ is then proportional to the number of particles formed by the material from the j -th region.

In the following we shall assume that the numbers k'_j equal their mean values \bar{k}_j . Thus $k'_j = \bar{k}_j = \bar{k} v_j$, where $\bar{k} = \sum_{j=1}^u \bar{k}_j$ is the mean number of particles in the samples of our set. On denoting further by $\bar{g} = G_\omega/\bar{k}$ the mean weight of the particle and by \bar{s} the mean specific weight of the material ($\bar{s} = \sum_{j=1}^u v_j s_{rj}$, $\bar{g} = v\bar{s}$), Eq. (9) may be rearranged to the form:

$$D^2(G_\omega) = \bar{k}^{-1} \sum_{j=1}^u v_j (s_{rj}/\bar{s})^2 D_j^2(v) = \bar{k}^{-1} D^2(\bar{g}). \quad (10)$$

In the calculation of the inhomogeneity variance of granular materials with unequal specific weight of particles the principal datum thus required from the parameters of the compact material⁹ is the modified single-particle variance $D^2(\bar{g}) = \sum_{j=1}^u v_j (s_{rj}/\bar{s})^2 \cdot D_j^2(v)$. The inhomogeneity variance in the set of single-particle samples in the compact material is, of course, given by $D^2(v) = \sum_{j=1}^u v_j D_j^2(v)$. The difference between $D^2(v)$ and $D^2(\bar{g})$ rests in that the variance $D^2(v)$ corresponds to the set of samples of the same volume and shape while the variance $D^2(\bar{g})$ is an extrapolation to $\bar{k} = 1$ of the variance corresponding to the set of equal-weight samples. ($D^2(v)$ thus plays a role in compact materials while $D^2(\bar{g})$ is important for granular materials).

The the general case of a granular material formed by particles of various sizes and

specific weight we may proceed in the derivation of inhomogeneity variance similarly as in the preceding cases: Divide particles to w classes according to their size (and shape) and each size class divide further into u classes according to the specific weight. The final equation we obtain is of the same form as Eq. (6) except that it contains G_ω instead of V and instead of the volume of particles l -th size class, v_l , we have their mean weight $\bar{g}_l = \bar{s}v_l$. Also, instead of the single-particle variance $D^2(v_l)$ the equation contains the modified single-particle variance $D^2(\bar{g}_l) = \sum_{j=1}^u v_j (s_{rj}/\bar{s})^2 D_j^2(v_l)$:

$$D^2(G_\omega) = \sum_{l=1}^w (\bar{g}_l/G_\omega)^2 D^2(\bar{g}_l) k'_l. \quad (11)$$

The variance (11) again does not depend on the representation of the size classes in individual samples but only on their mean representation k'_l in the whole set. About the representation of the different specific weights, s_{rj} , among the particles of the same size class we have assumed in the derivation of Eq. (11) that it is directly proportional to the volume concentration of the regions v_j ($j = 1, 2, \dots, u$).

About the relation between the ratios $k'_1 : k'_2 : k'_3 : \dots : k'_w$ or $K'_1 : K'_2 : \dots : K'_w$ and the dependence of the variance (11) on the size of the sample (G_ω) we may say the same as that mentioned in connection with Eq. (7).

Imperfectly Mixed Materials

For imperfectly mixed materials the modified variance of single-particle samples $D^2(\bar{g})$ is no longer the only determining factor for the course of the dependence of the inhomogeneity variance on the size of the sample. The other factor entering is the statistical dependence of compositions of close particles or samples and also the instationarity of the course of concentration and with it associated regression variance may become effective.

For a quantitative prediction of the effect of inhomogeneity of the material in samples of various sizes it is necessary to know the course of concentration in the bulk of the granular material.

Let us therefore draw from various locations within the material as well as along different directions a set of samples to be analyzed. From the results we determine the regression course of concentration and the correlation function of the deviations of concentration from the regression course.

In order to make distinction from the compact material we shall use the subscripts r' for the regression course of the concentration $c_{r'}$ and its corresponding regression variance $D_{r'}^2$. The deviations of the concentration c in the sample (of weight G_ω) from the regressed value $c_{r'}$ at a sampling point A shall be designated by δc_s or $\delta c_s(G_\omega)$ or $\delta c_s(G_\omega; A)$. The variance corresponding to the deviations δc_s shall be designated

D_s^2 , or $D_s^2(G_\omega)$ and shall be termed the stationary part of the inhomogeneity variance. For the inhomogeneity variance we may write⁹

$$D^2(G_\omega) = D_r^2 + D_s^2(G_\omega). \quad (12)$$

Further we shall designate by $R(\mathbf{x}; G_\omega)$ the correlation function of the deviations δc_s , defined by:

$$R(\mathbf{x}; G_\omega) = E[\delta c_s(G_\omega; A) \delta c_s(G_\omega; A + \mathbf{x})]. \quad (13)$$

The symbol $R(\mathbf{x}; G_\omega)$ shall be used instead of the more simple $R(\mathbf{x})$ in order to distinguish the granular material whose samples ω of the same set exhibit the same weight G_ω , from compact materials for which we have assumed⁹ that the samples ω of the same set have the same volume (and where the corresponding correlation function would be designated $R(\mathbf{x}; V_\omega)$). For $x = 0$ the definition gives, of course, $R(0; G_\omega) \equiv D_s^2(G_\omega)$.

In the calculation of the inhomogeneity variance we shall first assume that the course of concentration is stationary in the whole volume of the granular material, then $c_r \equiv \bar{c}$ and hence $D_r^2 = 0$ and $D^2(G_\omega) = D_s^2(G_\omega)$. The samples analyzed as solutions contain always more than a single particle and thus the concentration fluctuations correspond to the model⁹ valid for phase-homogeneous materials. The correlation function $R(\mathbf{x}; G_\omega)$ is then divided into the periodic part $R_p(\mathbf{x}; G_\omega)$ and the non-periodic part $R_n(\mathbf{x}; G_\omega)$. For a set of k -times larger samples than ω we shall calculate the non-periodic part of inhomogeneity variance from the equation⁹

$$D_n^2(kG_\omega) = k^{-2} \sum_{i=1}^k \sum_{j=1}^{ik} R_n(\mathbf{x}_{ij}; G_\omega), \quad (14)$$

where the vector \mathbf{x}_{ij} is given by the positions of the i -th and j -th sample of weight G_ω . Each of these samples of size kG_ω is thought to be composed in the same manner. For the calculation of the periodic part $D_p^2(kG_\omega)$ the reader is referred to cit.⁹

In compact materials the correlation function $R(\mathbf{x}; V_\omega)$ is determined by analyses made by the microprobe along the line coinciding with the direction of the vector \mathbf{x} . A longer time of analyses in individual locations eliminates the error of the measuring method. The found deviations of the concentration \bar{c} then correspond only to the inhomogeneity of the material and we can calculate directly the correlation function $R(\mathbf{x}; V_\omega)$.

For granular materials analyzed in solutions the experimental error generally cannot be neglected and the found correlation function $R(\mathbf{x}; G_\omega)$ thus differs from the sought correlation function $R(\mathbf{x}; G_\omega)$ corresponding truly to the inhomogeneity

of the granular material. The relation between $R(\mathbf{x}; G_\omega)$ and $R(\mathbf{x}; G_\omega)$ shall be derived as follows: Let us denote by $\Delta c(G_\omega; A)$ the deviation from $\bar{c} (\equiv c_r)$ measured for a sample of size G_ω taken from a point A of the granular material. This experimental deviation consists of the true concentration deviation $\delta c_s(G_\omega; A)$ and experimental error $\delta e(G_\omega; A)$. The correlation function of the found deviations is given by the following definition:

$$R^*(\mathbf{x}; G_\omega) \equiv E[\Delta c(G_\omega; A) \Delta c(G_\omega; A + \mathbf{x})]. \quad (15)$$

Substituting in the last equation the relation $\Delta c(G; A) = \delta c_s(G; A) + \delta e(G; A)$ then, owing to mutual statistical independence of the deviations δe and their independence on the deviations δc_s , the right hand side of Eq. (15) is free of the mean values of the mixed products $\delta e \delta c_s$, and there remains the true correlation function $R(\mathbf{x}; G_\omega)$ given by Eq. (13) and the expression $E[\delta e(G; A) \delta e(G_\omega; A + \mathbf{x})]$, which for non-zero x takes a zero value and for $x = 0$ equals the variance of the measuring method $D^2(\delta e) \equiv D_e^2$. The sought correlation function $R(\mathbf{x}; G_\omega)$ thus differs from the measured correlation function only at $x = 0$ and namely by the variance of the measuring method D_e^2 :

$$\begin{aligned} R^*(\mathbf{x}; G_\omega) &= R(\mathbf{x}; G_\omega), \quad \text{for } x \neq 0; \\ R^*(0; G_\omega) &= R(0; G_\omega) + D_e^2. \end{aligned} \quad (16)$$

The estimate of the variance D_ω^2 may be obtained for the case of analysis in solutions by a series of analyses of the same solution.

For granular materials which do not satisfy the assumption of stationary course of concentration we have to establish first the regression course of the concentration in the bulk of the granular material. The inhomogeneity variance is then given as the sum of the regression variance, D_r^2 , due to the deviation of the regression concentration c_r , from the mean \bar{c} (the calculation of D_r from the course of c_r , is given in ref.⁹), and the stationary component D_s^2 , corresponding to the deviations δc_s , of the concentration c in individual samples from c_r . (The determination of the correlation function $R(\mathbf{x}; G_\omega)$ from the deviations $\delta c_s(G_\omega)$ and the calculation of the variance $D_s^2(kG_\omega)$ has been dealt with previously in the part concerning granular material exhibiting stationary course of concentration). The regression variance is practically independent of the size of the sample. Thus it is necessary in the separation of the smaller portions of the granular material (for instance during filling of the sample flask) to take precautions that the whole separated part M (weight $G(M)$) is not taken all from one location, but, instead, composed of several (p) smaller doses M_i (weight $G(M_i)$, $i = 1, 2, \dots, p$) taken from different points. This should eliminate

the regression variance (if we designate by $c_{r,i}$ the regression concentration at the point where the part M_i was taken, the whole sample should be composed so as to have $\sum_{i=1}^p c_{r,i} G(M_i)/G(M) = \bar{c}$).

After elimination of the regression variance by appropriate sampling technique (M consisting of M_i parts) the inhomogeneity variance $D^2(M)$ caused solely by the variable component of the course of concentration, *i.e.* by the deviations from c_r . Thus, according to Eq. (12), $D^2(M) = D_s^2(M)$. This variable component of concentration is either stationary in the whole volume of the granular material or at least in its parts substantially greater than the amounts M_i . We may thus, according to the preceding text (see the part concerning granular materials with stationary course of concentration), determine from the concentrations measured in the samples G_ω (roughly tenths of a gram) the variances $D_s^2(M_i)$ ($G(M_i)$ roughly tens of grams). The sought variance $D^2(M)$ then follows from the expression for the deviations of concentration in the sample M :

$$\delta c_s(M) = \sum_{i=1}^p \delta c_s(M_i) G(M_i)/G(M). \quad (17)$$

Owing to the spatial separation of the samples M_i the practically important case is that of the mutual statistical independence of the deviations $\delta c_s(M_i)$. From Eq. (17) then follows for the variance $D^2(M) = D_s^2(M)$ corresponding to the deviations $\delta c_s(M)$ the relation:

$$D^2(M) = D_s^2(M) = \sum_{i=1}^p D_s^2(M_i) [G(M_i)/G(M)]^2. \quad (18)$$

DISCUSSION

Correlation coefficients or correlation functions used to express statistical dependence of close particles or samples have been dealt with in the literature in various ways. Landry⁴ (see also ref.⁷) confined himself to expressing statistical dependence in terms of the correlation coefficient, a , characterizing the dependence of composition of neighbouring particles and derived the dependence of the inhomogeneity variance on the size of the sample in the form:

$$D^2(kv) = D^2(v) k^{a-1}. \quad (19)$$

Stange⁸ has also used correlation, similarly as Landry, in order to characterize the imperfectly mixed material. Instead of a single correlation coefficient however, he used correlation function. For two selected types of the correlation function he

found using an expression essentially identical to Eq. (14) of this paper, the inhomogeneity variance of samples of linear shape in dependence on their size.

Experimental results show that a plot of the dependence of the inhomogeneity variance on the size of the sample (in log-log coordinates) exhibits for real materials lower slope and a shift toward greater samples in comparison with perfectly mixed materials. Landry's approach permits the first factor to be accounted for qualitatively (for imperfectly mixed materials, $a > 0$, the slope of the linear dependence of $\ln D^2(kv)$ on $\ln k$ is smaller than that corresponding to perfectly mixed materials, $a = 0$). In order to explain the shift one has to assume agglomeration of particles which need not be realistic. Stange's approach, leading to non-linear dependence (in log-log coordinates) between the variance of inhomogeneity and the size of the sample, a qualitative comparison leads to more adequate results.

Correlation function has been also used in paper⁹, dealing with the inhomogeneity of compact materials. In the same work the limitations of the validity of Eq. (14) have been shown. The correlation function $R(\mathbf{x})$ is divided into the non-periodic part, $R_n(\mathbf{x})$ and the periodic part, $R_p(\mathbf{x})$. The function to be substituted into Eq. (14) is only $R_n(\mathbf{x})$ and there result the inhomogeneity variances (its non-periodic part) for linear, surface and three-dimensional samples. The courses of the functions $R_n(\mathbf{x})$ have been specified to which Eq. (14) is applicable. The periodic part, $R_p(\mathbf{x})$, is processed in a different manner. With the aid of the correlation function the intra-phase component of inhomogeneity variance was determined, and, for samples substantially greater than the size of the phase-homogeneous part in the material, also the heterogeneous component of the inhomogeneity variance. The regression component and the heterogeneous component for samples smaller than the size of the grain were computed without the aid of the correlations.

Wilson² has applied correlation coefficients in his work in a somewhat different manner in order to determine the inhomogeneity variance of a heterogeneous mixture of phase-homogeneous particles. The concentration c_i of the analyzed element in each of the m -phases ($i = 1, 2, \dots, m$) was regarded to be a constant ($c_i = \bar{c}_i$). In the set of samples composed each of k particles the variance of inhomogeneity was due to the nonuniform representation of the phases in the samples. In the calculation of the inhomogeneity variance (or actually its heterogeneous part, see ref.⁹) the author started from a relation analogous to Eq. (14) of this work. The correlation coefficients R_{ij} (in the notation of this paper) described, however, the dependence between the deviations dk_i, dk_j of the number of particles of the i -th and the j -th phase in the sample from corresponding means. A subsequent assumption of multinomial distribution of the deviations dk_i meant actually that the problem was narrowed to one of perfectly mixed materials (for a greater number of particles in the samples, k , and with the assumption of multinomial distribution of the deviations dk_i the distribution of the deviations of concentration from \bar{c} may be approximated by the normal distribution, as required by the definition of the perfect mixture⁵). The

resulting Wilson's formulas, which no longer contain the correlation coefficients thus relate only to perfectly mixed materials. It can be shown that these formulas are particular cases of the equations derived in this paper: Let us denote V_i the volume of the i -th phase and V_M the total volume of the compact material from which the granular material was prepared. $v_i = V_i/V_M$ is the relative number of equally large particles made of the material of the i -th phase, v is the volume of the particle, \bar{s}_i is the specific weight of the i -th phase and \bar{s} is the specific weight of the material. Eq. (5) from ref.² takes the form:

$$D^2(kv) = \frac{1}{2}k^{-1} \sum_{i=1}^m \sum_{j=1}^m [(\bar{c}_i - \bar{c})(\bar{s}_i/\bar{s}) - (\bar{c}_j - \bar{c})(\bar{s}_j/\bar{s})]^2 v_i v_j. \quad (20)$$

A simple rearrangement gives:

$$D^2(kv) = k^{-1} \left\{ \sum_{i=1}^m v_i (\bar{s}_i/\bar{s})^2 (\bar{c}_i - \bar{c})^2 - \left[\sum_{i=1}^m v_i (\bar{s}_i/\bar{s}) (\bar{c}_i - \bar{c}) \right]^2 \right\}. \quad (21)$$

The second term on the right hand side of the last equation, however, vanishes.

Owing to the definition of the mean specific weight ($\bar{s} = \sum_{i=1}^m v_i \bar{s}_i$) and the mean concentration ($\bar{c} = \sum_{i=1}^m v_i (\bar{s}_i/\bar{s}) \bar{c}_i$) we have $\sum_{i=1}^m v_i (\bar{s}_i/\bar{s}) = 1$ and thus $\sum_{i=1}^m v_i (\bar{s}_i/\bar{s}) \bar{c} = \sum_{i=1}^m v_i (\bar{s}_i/\bar{s}) \bar{c}_i$. Eq. (20) thus transform into:

$$D^2(kv) = k^{-1} \sum_{i=1}^m v_i (\bar{s}_i/\bar{s})^2 (\bar{c}_i - \bar{c})^2 \quad (22)$$

which is identical with the Eq. (10) of this work. For the i -th region in the compact material we take the space occupied by the i -th phase and then $c_{ri} \equiv \bar{c}_i$, $s_{ri} \equiv \bar{s}_i$. Because the concentration in the i -th phase, according to the assumption², does not fluctuate the inhomogeneity variance of single-particle samples from the i -th phase, $D_i^2(v)$, equals its heterogeneous component $(\bar{c}_i - \bar{c})^2$.

Equation (10) in comparison with Wilson's equation is somewhat simpler. The main difference rests in that the preliminary assessment of the course of concentration within the phases in the compact material from which the granular material was prepared by means of the microprobe enables the effect of the concentration fluctuation within the phases to be incorporated into the variances $D_i^2(v)$ in Eq. (10) or in its more general form in Eq. (11).

CONCLUSION

The dependence of the inhomogeneity variance has been derived in the paper on the size of the sample for granular perfectly mixed materials as well as for imperfectly mixed materials. For perfectly mixed materials we started from the assumption that in the compact material, from which the granular material was prepared, the course of concentration was known from measurements by the microprobe which permits the determination⁹ of the inhomogeneity variance for samples equivalent in size to a single particle of the granular material. For heterogeneous mixtures of phase-homogeneous particles it is common to assume^{1-3,5}, that the concentration of the analyzed element within in each particle equals the mean value in the corresponding phase; this approach lead to only the heterogeneous component of the inhomogeneity variance. The approach adopted in this work also enables the intraphase component to be determined, given by the fluctuation of concentration within the phases. In addition, the described approach is applicable also to granular materials consisting of phase-inhomogeneous materials (*e.g.* metal chips).

From the single-particle variance, determined from the parameters of the compact material⁹, we have derived the variance of inhomogeneity of samples formed by several particles of equal weight first for the case of perfectly mixed materials composed of equally large particles of the shape same and specific weight and arrived ultimately to the general formula for perfectly mixed material composed of particles of different size, shape and specific weight. The obtained results provide also the practical conclusion that the inhomogeneity variance of a set of samples does not depend on the representation of various size classes in individual samples: Instead, it depends solely on their average representation in the whole set of samples.

For materials imperfectly mixed with a statistical dependence of composition of individual particles or samples, the calculation of the variance of inhomogeneity in dependence on the size of the sample was carried out by the approach⁹ derived for phase-homogeneous compact materials. It has been shown that in the experimental determination of the correlation function its initial value, $R(0)$, increases by the variance of the measuring method D_{ϵ}^2 .

In the discussion the author's approach has been compared with the previously published methods utilizing correlation functions to calculate statistical dependence of composition of close particles or samples on the variance of inhomogeneity of samples of different size.

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