

CHEMICAL INHOMOGENEITY OF MATERIALS AND ITS DETERMINATION. COMPACT MATERIALS

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Received May 30th, 1975

With the aid of the methods described in this paper one is able to determine, or at least to estimate, the contribution of inhomogeneity of the material to the overall variance of the results of analyses carried out in the compact material (spectroscopic methods). One is also able to determine the inhomogeneity variance of single-particle samples of a granular material prepared from the given compact material the use of this method for the determination of inhomogeneity of granular materials will be dealt with in the next paper).

The possibility of separating individual components of the inhomogeneity variance may be put to use in the choice of technological schemes leading to the improved homogeneity of materials.

Chemical inhomogeneity of materials due to nonuniform distribution of the analyzed element is the cause of a part of the scatter of the results of chemical analyses or physical measurements depending on composition. This extra variance increases with decreasing amount of the analyzed sample (*i.e.* the amount of material subjected to a single analysis, characterized by the size, shape and orientation within the material). As far as the compact materials are concerned the problem of inhomogeneity arises in connection with the advent of modern spectroscopic analytical methods working with relatively small amounts of materials. Accordingly, the requirements on the homogeneity, particularly that of the reference materials used for calibration, are extremely stringent¹.

In papers dealing with quantum spectrometry² and emission spectrometry³ the effect of inhomogeneity of compact materials on the results of analyses has been examined by analysis of variance. In the reference⁴ the inhomogeneity of a material is characterized by the variance of the results measured by a microprobe. Electron microprobe appears to be well suited for the study of the distribution of an element in the material, particularly if the variance of the measuring method is negligible in comparison with the variance due to the inhomogeneity of the material. The variance of the results measured by microprobe, however, does not provide sufficient information about the contribution of inhomogeneity to the variance of the results obtained with the same material by other methods working with samples of different volume and shape than the microprobe itself.

The aim of this work is to find parameters necessary to fully characterize inhomogeneity of compact materials, suggest means of determination of these parameters

(by microprobe if possible) and work out mathematical procedures for the assessment from the measured parameters of the effect of inhomogeneity on the variance of the results for various methods of chemical analysis or measurement of physical quantities depending on composition.

DEFINITION OF PRINCIPAL NOTIONS

In order to be able to describe fluctuation of the concentration in a material we shall make use of certain notions from the theory of probability and mathematical statistics. The mean of a random variable ξ shall be designated by $E(\xi)$. Its variance, defined as $E\{[\xi - E(\xi)]^2\}$ shall be designated by $D^2(\xi)$. The random variable ξ depending on a parameter τ constitutes a random (stochastic) process. The correlation function of the process $\xi(\tau)$ is defined by: $R(\tau', \tau'') = E\{[\xi(\tau') - E(\xi(\tau'))] \cdot [\xi(\tau'') - E(\xi(\tau''))]\}$.

We shall be making use of the comparison of the course of concentration with the stationary random processes, for which the mean and the correlation function are invariant with respect to the translation: $\tau^* = \tau + \text{const.}$; the mean is thus independent of the parameter τ and the correlation function depends only on the difference $t = \tau' - \tau''$.

For a measure of the effect of inhomogeneity we shall take⁵ the inhomogeneity variance defined as follows: If Δc is a random variable describing the deviations of the measured concentrations from the mean, δe its part due to the error of measurement, and δc the part due to the true fluctuations of the concentration ($\Delta c = \delta e + \delta c$) then with respect to the statistical independence of δe and δc we may write for the appropriate variances the relation: $D^2(\Delta c) = D_e^2(\delta e) + D_c^2(\delta c)$. $D^2(\Delta c)$ is the variance of the results of measurement, $D_e^2(\delta e)$ is the variance of the measuring method proper and $D_c^2(\delta c)$ is the inhomogeneity variance (in addition to the designation $D_c^2(\delta c)$ or

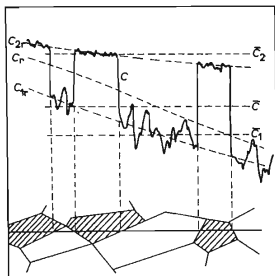


Fig. 1

Course of Concentration in a Two-Phase Material

\bar{c}_1, \bar{c}_2 Mean phase concentrations, \bar{c} mean overall concentration, c_{1r}, c_{2r}, c_r are concentrations estimated by regression.

D_j^2 we shall also use the notation $D_j^2(\omega)$, $D_j^2(V)$ in order to stress that we are dealing with a set of samples ω , or to stress the dependence of the variance on the volume V , etc.).*

The variance D_j^2 generally characterizes the inhomogeneity of distribution of not only the analyzed element but also that of the factors¹ interfering with the analysis. In this paper, however, we shall assume that the effect of the interfering factors has been eliminated and hence that the variance D_j^2 is solely due to the nonuniformity of the distribution of the analyzed element.

Typical course of concentration detected by a microprobe along a given direction in a compact material containing grains of two phases is shown in Fig. 1. $\bar{c} = E(c)$ is the mean concentration of the analyzed element; c_1 and c_2 are mean concentrations in the phases 1 and 2. The symbols c_{1r} and c_{2r} designate the regression courses of phase concentrations while c_r designates the regression course of the overall concentration.

The principal task, *i.e.* the derivation of the inhomogeneity variance $D_j^2(\omega)$ for samples ω greater than the sample for the microprobe, shall be developed gradually for phase-homogeneous materials with stationary course of the concentration ($c_r \equiv \bar{c}$), for heterogeneous materials with stationary course of concentration ($c_r \equiv \bar{c}$, $c_{1r} \equiv \bar{c}_1$, $c_{2r} \equiv \bar{c}_2, \dots$), and, finally, for materials with instationary course of concentration.

STATIONARY COURSE OF CONCENTRATION

In the study of the stationary courses of concentration we shall use some of the results of Chinchin's⁶ correlation theory of stationary random processes. The correlation function, $R(t)$, of a stationary random process depending on a single parameter t may be split into two parts⁶: $R(t) = R_n(t) + R_p(t)$. The former part satisfies the condition $\lim_{t \rightarrow \infty} (1/t) \int_0^t [R_n(t')]^2 dt' = 0$, the latter is a quasi-periodic function given by $R_p(t) = \sum_{j=1}^s R_{pj} \cos(2\pi t/\alpha_j)$, where R_{pj} are amplitudes and α_j periods of individual oscillations.

Random processes depending on several parameters are more often referred to as stochastic fields. Stationary course of the concentration c shall be regarded as a stationary stochastic field depending on three parameters – the coordinates. Its correlation function depends also on three parameters – the components of the vector \mathbf{x} : If $\delta c(A)$ is the deviation of concentration from the mean at an arbitrary point A within the material and if $\delta c(A + \mathbf{x})$ is the deviation at a point at the distance \mathbf{x} from A , then the corresponding correlation function is given by $R(\mathbf{x}) = E[\delta c(A) \cdot \delta c(A + \mathbf{x})]$. For $\mathbf{x} = 0$ we have $R(0) = E\{(\delta c)^2\}$, which, according to the definition, is the inhomogeneity variance $D_j^2(\delta c)$.

The correlation function $R(\mathbf{x})$ may be determined from measurements by microprobe along the straight lines in the direction of the vector \mathbf{x} in various cuts through

the material. The problem simplifies if the stochastic field of the deviations δc is isotropic. If this is the case, the correlation function is independent of the direction of the vector \mathbf{x} and depends on its magnitude $|\mathbf{x}| = x$ only.

PHASE-HOMOGENEOUS MATERIALS

Apart from the random ("noise") component the fluctuating concentration in phase-homogeneous compact materials may exhibit also periodic components associated with the different concentration of the analyzed element within the core and the shell of the grain, or associated with a fibrous structure of the material formed during solidification, *etc.*

If we detect by the microprobe the course of the concentration fluctuations δc along the direction \mathbf{x} within the material and calculate from the detected course the correlation function $R(\mathbf{x})$ the periodic components of the fluctuating concentration (summarily designated as δc_p) will have their corresponding periodic components in the correlation function (summarily designated as $R_p(\mathbf{x})$); the noise component of the fluctuating δc_n will have its corresponding non-periodic part in the correlation function $R_n(\mathbf{x})$. The expression for the deviations: $\delta c = \delta c_n + \delta c_p$ thus has an analogue in terms of the correlation function: $R(\mathbf{x}) = R_p(\mathbf{x}) + R_n(\mathbf{x})$ which is in accord with ref.⁶. Substituting $\mathbf{x} = 0$ we achieve an analogous partition of the inhomogeneity variance $D_J^2(\omega_1) = R(0)$ of the samples ω_1 analyzed by the microprobe into the periodic part $D_p^2(\omega_1) = R_p(0)$ and the non-periodic part $D_n^2(\omega_1) = R_n(0)$ ($D_J^2(\omega_1) = D_p^2(\omega_1) + D_n^2(\omega_1)$). In the calculation of the periodic and non-periodic part of the inhomogeneity variance of samples greater than those for the microprobe we shall start from the functions $R_p(\mathbf{x})$ and $R_n(\mathbf{x})$ respectively. For the sake of unambiguity and feasibility of the calculation we shall confine ourselves to the following rather simplistic model of the field of the deviations δc formulated mathematically in such a manner as to allow the results to be used for the general case at least as an estimate.

From the various possibilities of spatial distribution of the periodic component we shall choose a rather simple case of an oscillating field whose principal directions of periodicity are parallel to the axes of the rectangular system of coordinates x_1, x_2, x_3 :

$$\delta c_p(x_1, x_2, x_3) = A \cos(2\pi x_1/\alpha_1) \cos(2\pi x_2/\alpha_2) \cos(2\pi x_3/\alpha_3) \quad (1)$$

The random deviations δc_n are assumed to be normally distributed (Gaussian distribution); the set is then in the statistical sense fully determined by its mean $E(\delta c_n) = 0$ and its correlation function $R_n(\mathbf{x})$. The correlation function is assumed to be a non-increasing function satisfying in an arbitrary direction the Chinchin's relations:

$$\lim_{x \rightarrow \infty} (1/x) \int_0^x [R_n(x')]^2 dx' = 0.$$

The periodic part of the inhomogeneity variance. The periodic part, D_p^2 , of the inhomogeneity variance depends on the size and shape of the samples and their orientation in the fluctuation field simulated by Eq. (1). We shall confine ourselves now to the simple case of the samples ω being in the form of a parallelepiped whose edges b_1, b_2, b_3 are parallel to the axes of periodicity x_1, x_2, x_3 .

Let the center of the sample parallelepiped be at a general point (x_1, x_2, x_3) of the oscillating field (1). The concentration in the parallelepiped then differs from \bar{c} by a deviation denoted $\delta_{\omega}c_p(x_1, x_2, x_3)$ which can be computed from the relation:

$$\delta_{\omega}c_p(x_1, x_2, x_3) = (1/b_1 b_2 b_3) \int_{x_1 - b_1/2}^{x_1 + b_1/2} \int_{x_2 - b_2/2}^{x_2 + b_2/2} \int_{x_3 - b_3/2}^{x_3 + b_3/2} \delta c_p(x'_1, x'_2, x'_3) \cdot dx'_1 dx'_2 dx'_3 = AJ_1 J_2 J_3 \quad (2)$$

where for $J_i (i = 1, 2, 3)$ we may write

$$J_i = (1/b_i) \int_{x_i - b_i/2}^{x_i + b_i/2} \cos(2\pi x'_i/\alpha_i) dx'_i = (\alpha_i/\pi b_i) \sin(\pi b_i/\alpha_i) \cos(2\pi x_i/\alpha_i).$$

Let us denote further by B_1, B_2, B_3 the dimensions of the material (or that part whose inhomogeneity is being assessed) in the direction of the axes x_1, x_2, x_3 . (If the material is not shaped as a parallelepiped the symbols B_1, B_2, B_3 will refer to the principal dimensions in the directions of the axes x_1, x_2, x_3 .) As follows from the text below the quantities B_i serve only as auxiliary quantities which need not be determined very precisely. The variance corresponding to the deviations $\delta_{\omega}c_p$ may be calculated in the usual manner:

$$D_p^2(b_1 b_2 b_3) = (1/B_1 B_2 B_3) \int_0^{B_1} \int_0^{B_2} \int_0^{B_3} [\delta_{\omega}c_p(x_1, x_2, x_3)]^2 dx_1 dx_2 dx_3 = A^2 K_1 K_2 K_3 \quad (3)$$

where

$$K_i = (1/B_i) \int_0^{B_i} J_i^2 dx_i = (\alpha_i/\pi b_i)^2 \sin^2(\pi b_i/\alpha_i) \frac{1}{2} [1 + (\alpha_i/4\pi B_i) \sin(4\pi B_i/\alpha_i)].$$

Let us note that Eqs (1) and (3) describe respectively a stratified structure (unidimensional periodicity: if *e.g.* $\alpha_2 \rightarrow \infty, \alpha_3 \rightarrow \infty$ then $\delta c_p(x_1, x_2, x_3) = A \cos(2\pi x_1/\alpha_1)$ and we have that $J_2 = J_3 = K_2 = K_3 = 1$) and a fibrous structure (periodicity in two dimensions: if $\alpha_3 \rightarrow \infty$ then $\delta c_p(x_1, x_2, x_3) = A \cos(2\pi x_1/\alpha_1) \cos(2\pi x_2/\alpha_2)$ and we have that $J_3 = K_3 = 1$).

For practical reasons it may more convenient to use instead of Eq. (3) the estimate $D_{p0}^2(b_1, b_2, b_3)$. This estimate is obtained by substituting into the expression for K_i instead of the functions of the type $\sin y/y$ a function $f(y)$ which equals unity for $0 \leq y \leq 1$ and equals $1/y$ for $y > 1$. The estimate $D_{p0}^2(b_1, b_2, b_3)$ is then given by

$$D_{p0}^2(b_1 b_2 b_3) = A^2 K_{10} K_{20} K_{30}, \quad (4)$$

where $K_{i0} = C_i$ for $b_i \leq \alpha_i/\pi$, $K_{i0} = C_i(\alpha_i/\pi)^2 (1/b_i)^2$ for $b_i > \alpha_i/\pi$ and $C_i = 1$ for $\alpha_i \geq 4\pi B_i$, $C_i = 1/2(1 + \alpha_i/4\pi B_i)$ for $\alpha_i < 4\pi B_i$.

For the purpose of determining the amplitude A it is assumed that the measurement by the microprobe is carried out along the axis x_1 and that the dimensions of the sample for the microprobe are sufficiently small in comparison with the periods α_i . The periodic part of the measured correlation function then takes generally the form $R_p(x_1) = R_p(0) \cos(2\pi x_1/\alpha_1)$. Its course may be computed from:

$$\begin{aligned} R_p(x_1) &= (1/\alpha_1) \int_0^{\alpha_1} A^2 \cos(2\pi x'_1/\alpha_1) \cos(2\pi(x'_1 + x_1)/\alpha_1) dx'_1 = \\ &= \frac{1}{2} A^2 \cos(2\pi x_1/\alpha_1). \end{aligned}$$

A comparison yields $A = \sqrt{[2R_p(0)]}$ ($R_p(0)$ designates the periodic part of the inhomogeneity variance of the samples ω_1 analyzed by the microprobe: $R_p(0) = D_p^2(\omega_1)$, thus $A = D_p(\omega_1) \sqrt{2}$).

The course of the deviations δc_p need not be generally given by a single frequency, as in Eq. (1), but may be represented by a sum of s frequencies:

$$\delta c_p = \sum_{j=1}^s A_j \cos(2\pi x_1/\alpha_{1j}) \cos(2\pi x_2/\alpha_{2j}) \cos(2\pi x_3/\alpha_{3j}). \quad (5)$$

For a material of infinitely large size individual periodic components are orthogonal and hence the corresponding correlation function measured in the direction of the axis x_1 takes the form: $R_p(x_1) = \sum_{j=1}^s R_{pj}(0) \cos(2\pi x_1/\alpha_{1j})$. From the amplitudes $R_{pj}(0)$ we could again determine the amplitudes of the oscillations A_j using the relations $A_j = \sqrt{[2R_{pj}(0)]}$, and, from the parameters $A_j, \alpha_{1j}, \alpha_{2j}, \alpha_{3j}$, calculate the periodic part of the inhomogeneity variance $D_{pj}^2(b_1, b_2, b_3)$ of the set of samples ω_1 (parallelepipeds) for each oscillation separately from Eq. (3). The deviations δc_p then exhibit the following variance:

$$D_p^2(b_1 b_2 b_3) = \sum_{j=1}^s D_{pj}^2(b_1 b_2 b_3). \quad (6)$$

For materials of finite dimensions we may use the foregoing procedure only for the oscillations whose periods are sufficiently small in comparison with the dimensions of the material. The oscillations whose periods are comparable with the dimensions of the sample material will not be dealt with in this paragraph. Their contribution will be assessed by the method described in the paragraph concerning the nonstationary course of concentration.

Non-periodic part of the inhomogeneity variance. In this paragraph it will be assumed that the samples ω_1 analyzed by the microprobe (in the following: basic set of samples) are truly cubic with the edge of the cube being denoted by a . (The real shape is rotationally symmetric; the correction on the error committed by the assumption of cubic samples will be made later). From the cubes (a^3) we shall make up larger samples $\omega_k \equiv (ka^3)$. The non-periodic part of the correlation function measured by the microprobe (designated by $R_n(\mathbf{x}; a^3)$; $R_n(0; a^3 \equiv D_n^2(a^3))$) will serve to calculate the non-periodic part of the correlation function of the larger samples $R_n(\mathbf{x}; ka^3)$. Thus we also determine the non-periodic part of their inhomogeneity variance $D_n^2(ka^3) \equiv R_n(0; ka^3)$. Now we denote by X_1, \dots, X_k the positions of the cubes (a^3) within the larger sample (ka^3), $\bar{x}_{ij} = X_i - X_j$ ($i, j = 1, 2, \dots, k$) using corresponding position vectors. The random component of the fluctuating concentration for the larger samples $\delta_k c_n$ is the mean of the random deviations $\delta_1 c_n$ of the cubes of the basic set:

$$\delta_k c_n = (1/k) [\delta_1 c_n(X_1) + \delta_1 c_n(X_2) + \dots + \delta_1 c_n(X_k)]. \quad (7)$$

The non-periodic part of the correlation function of the larger set may then be computed from the definition relation:

$$R_n(\mathbf{x}; ka^3) = E\{(1/k) [\delta_1 c_n(X_1) + \dots + \delta_1 c_n(X_k)] (1/k) [\delta_1 c_n(X_1 + \mathbf{x}) + \dots + \delta_1 c_n(X_k + \mathbf{x})]\} = k^{-2} \sum_{i=1}^k \sum_{j=1}^k R_n(\mathbf{x}_{ij} + \mathbf{x}; a^3). \quad (8)$$

The non-periodic part of the inhomogeneity variance of the larger samples is thus given by:

$$\begin{aligned} D_n^2(ka^3) &= k^{-2} \sum_{i=1}^k \sum_{j=1}^k R_n(\mathbf{x}_{ij}; a^3) = \\ &= D_n^2(a^3) k^{-1} [1 + 2k^{-1} \sum_{i=1}^{k-1} \sum_{j=i+1}^k r_n(\mathbf{x}_{ij}; a^3)] \end{aligned} \quad (9)$$

where the normalized correlation function $r_n(\mathbf{x}_{ij}; a^3)$ is given by: $r_n(\mathbf{x}_{ij}; a^3) = R_n(\mathbf{x}_{ij}; a^3) / D_n^2(a^3)$.

Practical calculations following Eq. (9) are usually feasible only with the aid of a computer. Sometimes, however, we may do with a mere estimate derived on the assumption that the stochastic field of the deviations δ_{1,c_n} is isotropic. From the procedure, however, it will be patent that eventual correlation anisotropy would not markedly affect the result.

By the range of a correlation we shall term such a distance Za (a is the edge of the cube of the basic set) for which on $0 \leq x < Za$ we may write $r_n(x; a^3) > 0$ while for $z \geq Za$ $r_n(x; a^3) = 0$. If the dimensions of the sample (ka^3) are greater than $2Za$, the expression $\sum_{j=i+1}^k r_n(\mathbf{x}_{ij}; a^3)$ in Eq. (9) has the same value C for all i referring to the cubes (a^3) appearing within the sample (ka^3) at the distance Za from the edge. For the remaining values of the index i we have $\sum_{j=i+1}^k r_n(\mathbf{x}_{ij}; a^3) \leq C$. Thus Eq. (9) may be further arranged to the form:

$$\begin{aligned} D_n^2(ka^3) &\leq D_n^2(a^3) [1 + (2/k)(k-1)C] k^{-1} < D_n^2(a^3) (1 + 2C) k^{-1} = \\ &= D_n^2(a^3) k_0/k. \end{aligned} \quad (10)$$

The right hand side of Eq. (10) is an estimate of the variance $D_n^2(ka^3)$. This estimate will be designated as $D_{n0}^2(ka^3)$. Thus:

$$D_{n0}^2(ka^3) = D_n^2(a^3) k_0/k. \quad (11)$$

The constant $k_0 = (1 + 2C)$ is obtained by integrating the function $r_n(x; a^3)$ over the region extending from the i -th cube up to the distance Za , while the beginning of the coordinate system is at the point of the i -th cube ($r_n(x_{ii}; a^3) = r_n(0; a^3) = 1$). For linear samples the integration extends over the line segment of length $2Za$, for the surface samples over the circle of radius Za and for three-dimensional samples the integration domain is a sphere of radius Za . The constant k_0 thus depends on the shape of the sample.

The function $r_n(x; a^3)$ determined experimentally may be approximated by a single or several (m) functions of a simple, easily integrable form. Expressing $r_n(x; a^3)$ as a sum: $r_n(x; a^3) = \gamma_1 r_{n1}(x; a^3) + \gamma_2 r_{n2}(x; a^3) + \dots + \gamma_m r_{nm}(x; a^3)$, where $\gamma_1, \gamma_2, \gamma_m$ are constants for which $\gamma_1 + \gamma_2 + \dots + \gamma_m = 1$, then in view of the linearity of Eq. (9) we may write for the constant k_0 the relation: $k_0 = \gamma_1 k_{01} + \gamma_2 k_{02} + \dots + \gamma_m k_{0m}$ where the constant k_{01} corresponds to the function $r_{n1}(x; a^3)$ of range of correlation $Z_1 a$, k_{02} corresponds to the function $r_{n2}(x; a^3)$ on the range of correlation $Z_2 a$, etc.

For the approximation of the experimental correlation function we may, for instance, use the function of the form (q_i are positive constants):

$$r_{ni}(x; a^3) = \begin{cases} 1 - (x/Z_i a)^{q_i} & \text{for } 0 \leq x < Z_i a \\ 0 & \text{for } x \geq Z_i a. \end{cases} \quad (12)$$

For the linear samples (cube a^3 form a column of a^2 cross sectional area) we find by integration of the function (12): $k_{0i} = Z_i 2q_i / (q_i + 1)$. For surface samples (formed by a single layer of the cubes a^3) we obtain $k_{0i} = Z_i^2 \pi q_i / (q_i + 2)$. Finally, three-dimensional samples $k_{0i} = Z_i^3 \frac{4}{3} \pi q_i / (q_i + 3)$.

For illustration we have evaluated the dependence of the variance $D_n^2(ka^3)$ and its estimate $D_{n0}^2(ka^3)$ on the size and shape of the samples (ka^3) from Eqs (9) and (11) for the correlation function (12) of the range $4a$ ($Z = 4$) and of a linear form ($q = 1$; for linear samples $k_0 = Z = 4$; for surface samples $k_0 = 1/3\pi Z^2 = 16.75$ and for three-dimensional samples $k_0 = 1/3\pi Z^3 = 67.02$). The results are shown in logarithmic coordinates in Fig. 2. The lines 1–3 were computed from Eq. (9), the lines 4–6 from Eq. (11). The lines 1 and 4 correspond to the samples in the form of cubes of the size $a^3 \sqrt{k}$. The lines 2 and 5 correspond to surface samples of the form of parallelepipeds of the dimensions $a \sqrt{k}, a \sqrt{k}, a$. The lines 3 and 6 correspond to the samples in the form of columns of the dimensions ka, a, a .

From Fig. 2 it is apparent that the estimate (11) is good for $k > k_0$. For $1 \leq k \leq k_0$ the variance $D_n^2(ka^3)$ can be estimated better from the expression for $D_n^2(a^3)$ so that instead of Eq. (11) we use for the estimation of $D_{n0}^2(ka^3)$ the relation:

$$D_{n0}^2(ka^3) = \begin{cases} D_n^2(a^3) & \text{for } 1 \leq k \leq k_0 \\ D_n^2(a^3) k_0/k & \text{for } k > k_0. \end{cases} \quad (13)$$

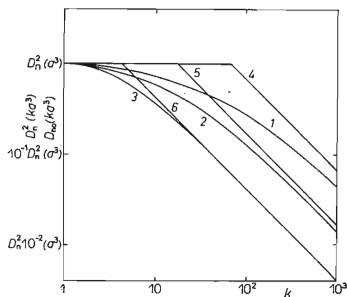


FIG. 2

The Variance $D_n^2(ka^3)$ and Its Estimate $D_{n0}^2(ka^3)$ in Dependence on Size of the Sample (ka^3)

Samples as a column 3, 6, slab 2, 5 and cube 1, 4.

Note: $R_n(\mathbf{x}; a^3)$ have been assumed to be non-increasing functions. This means that for each direction \mathbf{x} when $x_1 < x_2$ we may write $R_n(\mathbf{x}_1; a^3) \geq R_n(\mathbf{x}_2; a^3)$. This assumption, which helps us divide the experimental correlation function into the periodic $R_p(\mathbf{x}; a^3)$ and the non-periodic part $R_n(\mathbf{x}; a^3)$, can be substantiated by means of the following example: The correlation function $R_n(\mathbf{x}; a^3)$ of the set of cubes (a^3) is chosen in the form depicted in Fig. 3 and is assumed to be isotropic at least in the plane (x_1, x_2) of the rectangular system of coordinates x_1, x_2, x_3 . The columns of length $6a$ placed in parallel to the axis x_2 have in the direction x_1 the correlation function $R_n(x; 6a^3)$ as follows from Eq. (8) ($R_n(x; 6a^3) = (1/36) \sum_{i=1}^6 \sum_{j=1}^6 R_n(x_{ij}; a^3)$ where $x_{ij}^* = \sqrt{(x^2 + x_{ij}^2)}$ and x_{ij} is the distance between the i -th and the j -th cube (a^3) in the column). This function is shown also in Fig. 3. As may be seen for $x = 10$ $R_n(10; 6a^3) = 0.5$, while $R_n(0; 6a^3) \approx 0.3$. The result is thus at odds with the basic tenet of the correlation function in that for $x > 0$ $R(x)$ is always smaller or equal than $R(0)$. The function $R_n(\mathbf{x}, a^3)$ satisfies the Chinchin's condition: $\lim_{x \rightarrow \infty} (1/x) \int_0^x [R_n(x'; a^3)]^2 dx' = 0$. The additional assumption, that the function $R_n(\mathbf{x}; a^3)$ is a non-increasing one, removes the above discrepancy.

Generally, the course of the correlation function in an isotropic stochastic field is delimited^{7,8} by the relation

$$R_n(x) = \int_0^\infty (\sin \lambda x / \lambda x) dG(\lambda), \quad (14)$$

where $G(\lambda)$ is a bounded non-decreasing function. The general equation (14) admits, apart from the non-decreasing functions $R_n(\mathbf{x})$, also some other types of functions (damped oscillations). In order to facilitate practical utilization (partition of the correlation function $R(\mathbf{x})$ into $R_p(\mathbf{x})$ and $R_n(\mathbf{x})$) we have confined ourselves in this paper to non-decreasing functions $R_n(\mathbf{x})$ (combination of this assumption with the Chinchin's condition yields $R_n(\mathbf{x}) \geq 0$). The experimental correlation functions of the concentration deviations which we have thus far encountered have fully met this simplified assumption.

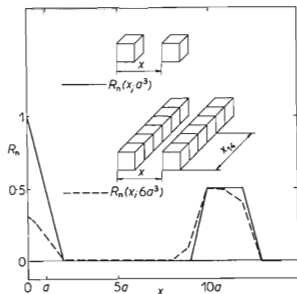


FIG. 3

Selected Correlation Function $R_n(x; a^3)$ of Samples (a^3) in the Form of a Cube and the Correlation Function $R_n(x; 6a^3)$ Derived for Direction Perpendicular to the Longest Edge of Sample Parallelepipeds ($6a^3$)

Correction on non-cubic shape of the sample analyzed by the microprobe. In a homogeneous material the sample analyzed by the microprobe is rotationally symmetric. The error committed by the assumption of cubic sample shall be corrected in the following manner: As a first approximation we shall assume that the sample analyzed by the microprobe is a cylinder (radius r , height h) and compare the correlation function of cylindrical samples with those of cubic shape for the same isotropic field of deviations δc_n . Both shapes of the samples may be thought to consist of a large number of much smaller cubes whose edge equals unity. From the non-periodic part of the correlation function $R_n(x; 1)$ we shall calculate using Eq. (8) the non-periodic part of the correlation function of the cubic, $R_{cn}(x; V)$, and the cylindrical, $R_{vn}(x; V)$, samples.

The comparison was made for the correlation function $R_n(x; 1)$ of the form (12), linear ($q = 1$) with the range $Z = 22, 55, 220$ and 550 . $R_{cn}(x; V)$ were computed for cubes of the length of the edge equal 5, 6, 7, 8, and 10. $R_{vn}(x; V)$ were computed for cylinders of the volume between 49 and 343 with the ratio $2r/h$ between 0.1 and 7.9. It turned out that the correlation function $R_{vn}(x; V)$ for cylinders of volume V has practically the same course as the correlation function $R_{cn}(x; \varepsilon V)$ for the cube of the volume εV . ε depends only on the shape of the cylinder ($2r/h$). It depends neither on the volume V nor the parameter Z of the correlation functions. The dependence of the correction coefficient ε on $2r/h$ is shown in Fig. 4. For a known volume V analyzed by the microprobe and the ratio $2r/h$ we take into the calculation the volume of the cubes of the basic set $a^3 = \varepsilon V$.

Heterogeneous Materials

In heterogeneous materials we cannot expect the random component δc_n of the concentration deviation from the mean concentration to be normally distributed

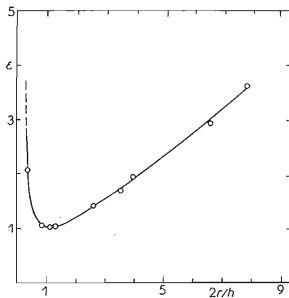


FIG. 4

Dependence of the Correction Coefficient ε on the Ratio of the Diameter $2r$ of the Sample Cylinder to its Height h

as was the case of phase-homogeneous materials. The calculation of the inhomogeneity variance thus has to be corrected.

Let the material contain grain of m phases. Let us denote by $c(\omega)$ the weight concentration of the analyzed element in the sample ω . $g_i(\omega)$ is the weight concentration of the i th phase in ω and $c_i(\omega)$ is the concentration of the analysed element in the part of the i -th phase belonging to the sample ω . The corresponding means are $E[c(\omega)] \equiv \bar{c}$, $E[c_i(\omega)] \equiv \bar{c}_i$, $E[g_i(\omega)] \equiv \bar{g}_i$.

Let us assume that the fluctuations of concentration within the phase about the mean phase concentration c_i are stationary and satisfy also additional assumptions given above for the phase-homogeneous materials. The stationarity is assumed also for the deviations $\delta g_i = g_i(\omega) - \bar{g}_i$ which are due to the nonuniformity of distribution of the grains of different phases on one hand and due to inhomogeneity proper on the other hand.

For $c(\omega)$ we may write generally:

$$c(\omega) = \sum_{i=1}^m g_i(\omega) c_i(\omega). \quad (15)$$

Upon looking on the whole material ω as a sample ($\omega \rightarrow M$), Eq. (15) applies also to the quantities $c(M)$, $g_i(M)$, $c_i(M)$. It can be easily shown that Eq. (15) remains valid also for the mean values \bar{c} , \bar{g}_i , \bar{c}_i by proving the relations $\bar{c} = c(M)$, $\bar{g}_i = g_i(M)$ and $\bar{c}_i = c_i(M)$. Designating, for instance, the weight of the sample ω by $G(\omega)$ (the samples ω of the same set has the same shape and volume), $G_i(\omega)$ the weight of the i -th phase in ω , then $g_i(\omega) = G_i(\omega)/G(\omega)$ and we may write $\bar{g}_i = \sum_{\omega} g_i(\omega) G(\omega) / G(M) = g_i(M)$, where \sum_{ω} designates summation over all samples compounding the material M . Analogous is true for \bar{c}_i and \bar{c} .

More easily accessible to measurement than $g_i(\omega)$ is the volume concentration of the i -th phase $v_i(\omega)$ related to $g_i(\omega)$ by the expression: $g_i(\omega) = v_i(\omega) s_i(\omega) / s(\omega)$. $s_i(\omega)$ is the specific weight of the i -th phase in ω , $s(\omega) = \sum_{i=1}^m v_i(\omega) s_i(\omega)$ is the specific weight of the sample. Among the mean values \bar{g}_i , \bar{v}_i , \bar{s}_i , \bar{s} there exist the same relations; the proof is similar as that for \bar{g}_i , \bar{c}_i , \bar{c} .

The effect of heterogeneity of the material on the inhomogeneity variance of the samples ω will be examined in terms of the quantity $c_h(\omega)$ indicating the concentration of the analyzed element in the sample ω provided the concentration in the phases are at their mean values \bar{c}_i . Thus $c_h(\omega) = \sum_{i=1}^m g'_i(\omega) \bar{c}_i$, where $g'_i(\omega) = v_i(\omega) \bar{s}_i / (\sum_{j=1}^m v_j(\omega) \bar{s}_j)$. (For a sample ω which is entirely from the i -th phase we have $c_h(\omega) = \bar{c}_i$). The deviations of the concentrations $c(\omega)$ from \bar{c} shall be divided into two parts:

$$\delta c = c(\omega) - \bar{c} = [c(\omega) - c_h(\omega)] + [c_h(\omega) - \bar{c}] = \delta c_f + \delta c_h. \quad (16)$$

The deviations $\delta c_h = c_h(\omega) - \bar{c} = \sum_{i=1}^m [g'_i(\omega) - \bar{g}_i] \bar{c}_i$ reflect the nonuniformity of the presence of the phases in the samples ω ; corresponding variance shall be termed the heterogeneity variance and designated by $D_h^2(\omega) \equiv D^2(\delta c_h)$. The deviations $\delta c_f = c(\omega) - c_h(\omega) = \sum_{i=1}^m [(g_i(\omega) - g'_i(\omega) \bar{c}_i + g_i(\omega) \delta c_i)]$ depend on one hand on concentration fluctuations within the phases (if in all phases $\delta c_i \equiv c_i(\omega) - \bar{c}_i = 0$ then $\delta c_f = 0$), and, on the other hand, on the presence, $g_i(\omega)$, of the phases in the samples. Corresponding variance $D_f^2(\omega) \equiv D^2(\delta c_f)$ shall be termed the intraphase variance. Generally speaking, the deviations δc_h , δc_f are not statistically independent. Thus for the inhomogeneity $D_J^2(\omega) \equiv D^2(\delta c)$ we may write:

$$D_J^2(\omega) = D_f^2(\omega) + D_h^2(\omega) + 2D_f(\omega) D_h(\omega) \varrho(\delta c_f, \delta c_h). \quad (17)$$

The correlation coefficient $\varrho(\delta c_f, \delta c_h)$ may generally take values between -1 and $+1$. $D_J^2(\omega)$ thus ranges between the limits $(D_f(\omega) - D_h(\omega))^2$ and $(D_f(\omega) + D_h(\omega))^2$ which are of the same order of magnitude at sufficiently different values $D_f(\omega)$ and $D_h(\omega)$. A surplus of the analyzed sample in a certain point gives rise on solidification of a compact material to preferential formation of the phases with higher phase concentration than the mean concentration. This means that at this point we may also write $\delta c_h > 0$ and $\delta c_f > 0$ (see the definition of the deviations in this paragraph). Analogously at points of instantaneous shortage of the analyzed element we may write the relations $\delta c_f < 0$ and $\delta c_h < 0$. It may thus be expected that the correlation coefficient $\varrho(\delta c_h, \delta c_f)$ will not take negative values. $D_J^2(\omega)$ then falls between $(D_f^2(\omega) + D_h^2(\omega))$ and $(D_f(\omega) + D_h(\omega))^2$ (the upper limit is at most twice the lower limit). In the following text we shall usually confine ourselves to the expression of the inhomogeneity variance of a heterogenous materials from:

$$D_J^2(\omega) = D_f^2(\omega) + D_h^2(\omega). \quad (18)$$

Intraphase variance. For the calculation of the intraphase variance $D_f^2(\omega)$ of samples ω greater than those for the microprobe from the deviations δc_f found by the microprobe we have at our disposal the approach outlined in the foregoing paragraphs. However, the field of the deviations δc_f is different from the deviations δc of a single phase material. The samples analyzed by the microprobe are in various phases different and hence cannot be used to make up larger samples. Theoretically, one can use in each phase a different accelerating voltage in order to make the analyzed sample equally large. In practice, however, it is more likely that we use the following procedure: The measurement is carried out at the same accelerating voltage. From the analyzed samples (a_i^3) we then find the maximum one (designated a_0^3) and calculate from the phase correlation functions $R_i(\mathbf{x}; a_i^3)$ (calculated from the deviations

c_f in individual phases; $R_i(0; a_i^3) \equiv D_{fi}^2(a_i^3)$ are intraphase variances) using Eq. (9) the variances $D_{fi}^2(a_{fi}^3)$. The deviations δc_f in each phase are then transformed using: $\delta_1 c_f = \delta c_f D_{fi}(a_0^3) / D_{fi}(a_i^3)$. The field of the deviations $\delta_1 c_f$ corresponds to the samples of identical size a_0^3 .

The formation of the larger samples ω from k cubes of the basic set (size a_0^3) leading to summation of the non periodic parts $\delta_1 c_{fn}$ of the deviations $\delta_1 c_f$ various densities of the phases apply. Thus instead of Eq. (7) we have to use the following, more general expression:

$$\delta_k c_{fn} = (1/k) \sum_{j=1}^k [s(X_j)/s(\omega)] \delta_1 c_{fn}(X_j), \quad (19)$$

where $s(X_j)$ is the specific weight of the j -th cube of the volume a_0^3 in the sample ω (of volume ka_0^3) and $s(\omega) = (1/k) \sum_{j=1}^k s(X_j)$. The samples for the microprobe (a_0^3) are currently much smaller than the grain of individual phases and, consequently, the cubes forming the samples may be regarded as phase-homogeneous. Just as in Eq. (7) it was assumed that the density of individual cubes equals the mean density of the single-phase material, \bar{s} , we shall now assume that in Eq. (19) each density $s(X_j)$ equals some of the mean phase-densities, \bar{s}_i .

If the samples ω are large enough for we could with sufficient accuracy write $s(\omega) = \bar{s}$, the deviations $\delta_1 c_f$ may be multiplied in each phase by the corresponding ratio \bar{s}_i/\bar{s} . For the non-periodic parts $\delta'_1 c_{fn}$ of the resulting deviations $\delta'_1 c_f = \delta_1 c_f \cdot \bar{s}_i/\bar{s}$ we have again Eq. (7). For $\delta'_1 c_{fn}$, however, it is not realistic to expect the normal distribution unless the phase variances $D_{fi}^2(a_0^3) = (\bar{s}_i/\bar{s})^2 D_{fi}^2(a_i^3)$ are equal in all phases (even though in individual phases the deviations $\delta'_1 c_{fn}$ are normally distributed). Therefore we transform the deviations $\delta'_1 c_f$ in individual phases to the common unit variance by the transformations $\delta_1^* c_f = \delta'_1 c_f / D_{fi}(a_0^3)$.

The field of the deviation $\delta_1^* c_f$ is no longer sufficiently representative for the calculation of the intraphase variance $D_f^2(\omega)$ but we may still apply the procedure derived for single-phase materials and the variance $D_f^2(\omega)$ can be at least estimated. From the deviations $\delta_1^* c_f$ we then calculate the normalized correlation function $r^*(\mathbf{x}; a_0^3)$ and from this in turn the variance $d^{*2}(\omega)$ corresponding to the samples ω in the field of the deviations $\delta_1^* c_f$. On multiplying each deviation $\delta_1^* c_f$ by the maximum standard phase deviation $D'_{fi}(a_0^3)$ (designated D'_{\max}), the samples in this field of deviations will have their corresponding variance $D'^2_{\max} d^{*2}(\omega)$ which is the upper limit for the true value of the intraphase variance $D_f^2(\omega)$; analogously the lower bound is $D'^2_{\min} d^{*2}(\omega)$. Roughly we may estimate $D_f^2(\omega)$ by $D_{f0}^2(\omega)$ determined from the following relation:

$$D_{f0}^2(\omega) = d^{*2}(\omega) \sum_{i=1}^m \bar{v}_i D_{fi}^2(a_0^3). \quad (20)$$

This estimate is substantiated by the following property: If some of the phases in the material dominates (e.g. $\bar{v}_1 \approx 1$ and hence for $i = 2, \dots, m$ then $\bar{v}_i \approx 0$). The estimate in Eq. (20) approaches the true value of the intraphase variance ($D_{f0}^2(\omega) \approx \approx D_{f1}^2(\omega) \approx D_f^2(\omega)$). The estimate (20), in addition, always satisfies the condition $D_{\min}^2 d^{*2}(\omega) \leq D_{f0}^2(\omega) \leq D_{\max}^2 d^{*2}(\omega)$.

If the samples ω are not large enough as to encompass a sufficient number of grains of different phases and the condition $s(\omega) \approx \bar{s}$ for the transformation $\delta_1 c_f \rightarrow \rightarrow \delta'_1 c_f$ is not fulfilled, we may take larger samples ω' , for which the above procedure applies; $D_f^2(\omega)$ or $D_{f0}^2(\omega)$ is then determined by interpolation. On the side of smaller samples than ω we find the intraphase variance of the samples for the microprobe (a_0^3) from the expression $D_f^2(a_0^3) = \sum_{i=1}^m \bar{v}_i D_{fi}^2(a_0^3)$. The same formula may be used to estimate also the intraphase variance up to the size of the samples (ω'') approaching the size of phase-homogeneous grains: $D_f^2(\omega'') = \sum_{i=1}^m \bar{v}_i D_{fi}^2(\omega'')$ where the variances $D_{fi}^2(\omega'')$ are computed from the intraphase correlation functions by a similar procedure leading to $D_{fi}^2(a_0^3)$.

Heterogeneity variance. For direct calculation of variance due to heterogeneity, $D_h^2(\omega)$ from the deviations $\delta c_h = \sum_{i=1}^m (g'_i(\omega) - \bar{g}_i) \bar{c}_i$ we would have to find in each set of the samples ω the volume phase concentrations $v_i(\omega)$. We would thus be confined to the samples whose thickness corresponds to the thickness of the layer analyzed by the microprobe.

Of more general use for larger samples is the following method based on the procedure outlined in the preceding paragraphs. This method, however, works with samples ω_1 of the basic set which are not in the form of cubes but rather parallelepipeds: On a photograph of a material cut we shall draw a set of parallel lines of length L representing parallelepipeds of square cross section (samples ω_1). The depth of the sample equals the thickness of the layer analyzed by the microprobe (and hence is usually smaller than the size of the grains). If the parallelepiped intersects with the grains of the i -th phase on a total length L_i then $v_i(\omega_1) = L_i/L$. For the parallelepipeds we calculate the concentrations $c_h(\omega_1)$ and from the deviations $\delta c_h = c_h(\omega_1) - \bar{c}$ the correlation function $R(\mathbf{x}; \omega_1)$ for the direction perpendicular in the plane of the thin cut to the drawn lines. The variance $D_h^2(\omega)$ of the samples ω formed by the parallelepipeds can then be computed as outlined in the previous paragraphs. From the conditions of the normal distribution of the non-periodic parts δc_{hn} of the deviations δc_h there follows the necessity that the length of the parallelepipeds be large enough for they could intersect with a sufficient number of grains of different phases. The use of this method is limited to samples considerably larger than the size of the phase-homogeneous parts of the material.

For samples ω smaller than the size of the grain the heterogeneity variance $D_{\bar{c}}^2(\omega)$ may be computed in the following manner: Let us designate by S_{ij} the magnitude of the interfacial area between the i -th and the j -th phase related to a unit volume and by b the size of the samples ω in direction perpendicular to S_{ij} (the shape of ω is approximated by a cube of the size b). Because the probability that a random sample ω in the material will have its center in the i -th phase is \bar{v}_i , we may write for the variance due to heterogeneity the relation:

$$D_{\bar{c}}^2(\omega) = \sum_{i=1}^m (\bar{v}_i - \sum_{j=1}^m 1/2bS_{ij}) (\bar{c}_i - \bar{c})^2 + \sum_{i=1}^m \sum_{j=1}^m S_{ij} \int_0^{b/2} (c_{ij}(x) - \bar{c})^2 dx. \quad (21)$$

The first sum in Eq. (21) expresses the contributions of the samples coming all from a single phase. The second sum is a contribution of the samples encompassing two phases; the contributions of the samples encompassing three or more phases are neglected. $c_{ij}(x)$ is the concentration c_b in the sample whose center lies in the i -th phase at the distance x ($x < b/2$) from the interface between the i -th and j -th phase (Fig. 5). On designating by $V_i(x)$ or $V_j(x)$ the volume of that part of the sample coming from the i -th or the j -th phase ($V_i(x) + V_j(x) = V(\omega) = \text{const.}$) then we may write for $c_{ij}(x)$ the relation:

$$c_{ij}(x) = (V_i(x) \bar{s}_i \bar{c}_i + V_j(x) \bar{s}_j \bar{c}_j) / (V_i(x) \bar{s}_i + V_j(x) \bar{s}_j). \quad (22)$$

In the following we shall confine ourselves to the estimate $D_{\bar{c}}^2(\omega)$ based on the assumption that the course of concentration in the transition layer adhering to the interface is linear ($c_{ij}(x) = 1/2(c_i + c_j) + (c_i - c_j)(x/b)$). Eq. (21) can then be rearranged to a simpler form:

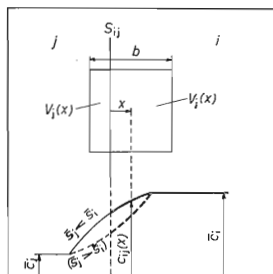


FIG. 5

Course of Concentration $c(\omega) = c_{ij}(x)$ in Samples ω -Cubes (b^3) in the Neighbourhood of Interface S_{ij}

$$D_h^2(\omega) = D_h^2(0) - \sum_{i=1}^{m-1} \sum_{j=i+1}^m b S_{ij} \frac{1}{6} (\bar{c}_i - \bar{c}_j)^2, \quad (23)$$

where $D_h^2(0) = \sum_{i=1}^m \bar{v}_i (\bar{c}_i - \bar{c})^2$ is the heterogeneity variance of infinitesimal samples ω ($b \rightarrow 0$). With increasing b the value of $D_h^2(\omega)$ decreases from $D_h^2(0)$ the faster the larger the surfaces S_{ij} , i.e. the finer the dispersion of individual phases and hence the lower the heterogeneity.

The mentioned isometricity of the samples ω (cubic shape of the samples ω) is not a necessary condition. Eq. (23) shall be generalized for the cases that the principal directions of shape anisotropy of the samples ω and the grains in the material are identical with the axes of a rectangular coordinate system x_1, x_2, x_3 : On approximating the shape of the sample and the grain by parallelepipeds and on designating the edges of the sample-parallelepipeds parallel to x_1, x_2, x_3 by b_1, b_2, b_3 and the surface of the interfaces (per unit volume) parallel to the planes $(x_2x_3), (x_1x_3), (x_1x_2)$ by the symbols $S_{ij1}, S_{ij2}, S_{ij3}$, Eq. (23) changes into:

$$D_h^2(\omega) = D_h^2(0) - \sum_{i=1}^{m-1} \sum_{j=i+1}^m (b_1 S_{ij1} + b_2 S_{ij2} + b_3 S_{ij3}) \frac{1}{6} (\bar{c}_i - \bar{c}_j)^2. \quad (24)$$

The parameters $S_{ij1}, S_{ij2}, S_{ij3}$ may be measured as the length of the interfaces on planes cut through the material parallel to the planes $(x_2x_3), (x_1x_3), (x_1x_2)$. Examining the cut parallel to the plane (x_2x_3) , then according to our notation the interfaces S_{ij2} and S_{ij3} are perpendicular to the surface (cut). On designating by l_{ij2} (or l_{ij3}) the length of the limits between the i -th and the j -th phase perpendicular to the axis x_2 (or x_3) in a unit area of cross section, then the magnitude of the interface in the volume of the surface shell of thickness dh below a unit area of the surface are given by $l_{ij2} dh$ or $l_{ij3} dh$. For a unit volume we thus may write $S_{ij2} = l_{ij2}$ and $S_{ij3} = l_{ij3}$. S_{ij1} is determined from the cut parallel to the plane (x_1x_3) or (x_1x_2) .

On the cut we can also measure the mean volume concentrations of the phases, \bar{v}_i . If on a cut of area S parallel to the plane (x_2x_3) the surface occupied by the i -th phase is S_i , then in the layer of thickness b_1 analyzed by the microprobe the volume concentration of the i -th phase is given by $v_i = (S_i b_1) / (S b_1) = p_i$, where $p_i = S_i / S$ is the surface concentration of the i -th phase on the surface of the cut. If the spatial arrangement of the grain of the i -th phase in the direction perpendicular to the surface of the cut (i.e. in direction x_1) is stationary, we find on a set of cuts parallel to the plane (x_2x_3) the surface concentrations p_i which are estimates of the mean value $\bar{p}_i = \bar{v}_i$.

NON-STATIONARY COURSE OF CONCENTRATION

Non-stationary course of concentration means that either \bar{c} or $R(\mathbf{x})$ are not invariant with respect to translation. Thus either the mean course of concentration depends on some of the direction (or directions) in the material, or, eventually, the correlation function $R(\mathbf{x})$ is not the same in all parts of the material.

The mean course of concentration found either graphically or by regression is designated by c_r (Fig. 1); the index x refers to regression estimates of also additional quantities: g_{ir} , c_{ir} , v_{ir} , s_{ir} , s_r . Among c_r , g_{ir} , c_{ir} there exist again the following relationship: $c_r = \sum_{i=1}^m g_{ir} c_{ir}$ (Eq. (15) and the text below).

The deviation of concentration of the analyzed element in the sample can be again divided into two parts:

$$\delta c = c(\omega) - \bar{c} = [c(\omega) - c_r] + [c_r - \bar{c}] = \delta c_s + \delta c_r. \quad (25)$$

Owing to the statistical independence of δc_s and δc_r (following from the definition of c_r) we may write for the corresponding variances:

$$D_c^2(\omega) = D_s^2(\omega) + D_r^2(\omega). \quad (26)$$

The variance $D_r^2(\omega) \equiv D^2(\delta c_r)$ shall be termed the regression variance. For the samples ω it can be computed from the equation:

$$D_r^2(\omega) = (1/V(M)) \int_{V(M)} (c_r - \bar{c})^2 dV, \quad (27)$$

where $\int_{V(M)}$ designates triple integral over the volume of the material $V(M)$.

Eq. (27) is based on the usual expression for the variance: $D^2 = \sum_i (c_i - \bar{c})^2 v_i$, where the relative frequency v_i is replaced by the probability $dV/V(M)$ of the event that the center of the sample ω will appear in the element dV . On the other hand in the calculation of the mean weight concentration \bar{c} , the contribution of a part of material of volume ΔV_i is proportional to its relative weight $G_i/G(M)$. For integration this can be replaced by the expression $s_r dV/(\bar{s}V(M))$: $c = \sum_i c_{ri} G_i/G(M)$, or $\bar{c} = (\bar{s}V(M))^{-1} \int_{V(M)} c_r s_r dV$.

The symbol c_r in Eq. (27) stands for the value of the regressed concentration in the center of the sample ω for which the difference $c_r - \bar{c}$ is being calculated. Strictly speaking, we should also consider the dependence of c_r on ω : Designating by $c_r(d\omega)$ the course of regressed concentration following from the analyses carried out for infinitesimal samples $d\omega$ then the values $c_r(\omega)$ would represent the mean concentrations

$c_r(d\omega)$ in the samples ω : $c_r(\omega) = (V(\omega) s_r(\omega))^{-1} \int_{V(\omega)} c_r(d\omega) s_r(d\omega) dV$, while between the regression specific weight $s_r(\omega)$ of the sample ω of the volume $V(\omega)$ and the regression specific weight $s_r(d\omega)$ of the samples $d\omega$ of volume dV there would exist a similar relationship: $s_r(\omega) = (1/V(\omega)) \int_{V(\omega)} s_r(d\omega) dV$. Of course, usually the concentrations $c_r(d\omega)$ and $c_r(\omega)$ differ so little that we shall do with Eq. (27).

The deviations δc_s represent the fluctuations of the concentration about the mean value c_r . Formally, at least within each volume dV this oscillations satisfy the condition of stationarity utilized in the preceding paragraphs. Accordingly, the corresponding variance $D_s^2(\omega) \equiv D^2(\delta c_s)$ shall be called stationary part of the inhomogeneity variance.

According to the preceding paragraphs we may in each region of stationarity dV divide the deviations δc_s into the intraphase part $\delta c_f = [c(\omega) - c_{hr}(\omega)]$ and the heterogeneous part $\delta c_h = [c_{hr}(\omega) - c_r]$, where $c_{hr}(\omega) = \sum_{i=1}^m g_i''(\omega) c_{ir}$, $g_i''(\omega) = v_i(\omega) \cdot s_{ir} / \sum_{j=1}^m v_j(\omega) s_{jr}$ and calculate (from the measurements with the microprobe) corresponding variance $D_f^2(\omega; dV)$ and $D_h^2(\omega; dV)$. From these by integrating over the whole volume of the material $V(M)$, we can in turn calculate the intraphase variance $D_f^2(\omega)$ and heterogeneity variance $D_h^2(\omega)$ from the relations:

$$\begin{aligned} D_f^2(\omega) &= (1/V(M)) \int_{V(M)} D_f^2(\omega; dV) dV, \\ D_h^2(\omega) &= (1/V(M)) \int_{V(M)} D_h^2(\omega; dV) dV. \end{aligned} \quad (28)$$

As long as the conditions of stationarity are satisfied in the whole material, or at least in finite volumes V_j ($j = 1, 2, \dots, w$; $\sum_{j=1}^w V_j = V(M)$), integrals in Eq. (28) changes into summations and the variances $D_f^2(\omega)$ and $D_h^2(\omega)$ of the samples may be computed from:

$$\begin{aligned} D_f^2(\omega) &= (1/V(M)) \sum_{j=1}^w D_{fj}^2(\omega) V_j, \\ D_h^2(\omega) &= (1/V(M)) \sum_{j=1}^w D_{hj}^2(\omega) V_j, \end{aligned} \quad (29)$$

where $D_{fj}^2(\omega)$ and $D_{hj}^2(\omega)$ designates the intraphase variance and the heterogeneity variance in the j -th volume. The variance $D_s^2(\omega)$ is then found from Eq. (18): $D_s^2(\omega) = D_f^2(\omega) + D_h^2(\omega)$. Hence the inhomogeneity in materials with instationary course of concentration is given by:

$$D_j^2(\omega) = D_r^2(\omega) + D_f^2(\omega) + D_h^2(\omega). \quad (30)$$

CONCLUSION

The main problem we tried to solve was to estimate the inhomogeneity variance for methods analyzing compact samples and working with materials of various shapes and sizes. For this purpose it was assumed that the initial information about the distribution of the analyzed element in the material is obtained by means of a microprobe.

It turned out that the inhomogeneity variance $D_j^2(\omega)$ of the set of samples ω is a sum of three components of which the first, the regression variance $D_r^2(\omega)$, is due to the deviation of the regression course of concentration from the mean. The second part, the heterogeneity variance, is associated with the size, shape and non-uniformity of distribution of the grains of various phases within the material while the third part, the intraphase variance $D_f^2(\omega)$, reflects the fluctuation of concentration of the analyzed element within the phases. The principal parameters that must be measured analyzed element within the phases.

The principal parameters that must be measured in order that we may be able to determine the inhomogeneity variance and its components are concentrations of analyzed element within the phases c_i and volume concentrations v_i . The course of c_i can be measured by the microprobe, v_i can be determined from photographs of various cuts through the material. From the course of c_i and v_i within the material and from the course of additional parameters derived from c_i and v_i we are in turn able to determine the inhomogeneity variance following the procedure outlined in the above text for the set of samples of chosen size and shape.

With the aid of the methods described in this paper one is able to determine, or at least to estimate, the contribution of inhomogeneity of the material to the overall variance if the results of analyses carried out in the compact material (spectroscopic methods). One is also able to determine the inhomogeneity variance of single-particle samples of a granular material prepared from the given compact material (the use of this method for the determination of inhomogeneity of granular materials will be dealt with in the next paper).

The possibility of separating individual components of the inhomogeneity variance may be put to use in the choice of technological schemes leading to the improved homogeneity of materials.

Thanks are due to Dr K. Rohlena and Dr L. Lejček, Physical Institute, Czechoslovak Academy of Sciences, for their invaluable comments which helped me complete this work.

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Translated by V. Staněk.