7. E. Holleran, "A dimensionless constant characteristic of gases, equations of state, and intermolecular potentials," J. Phys. Chem., 73, No. 1, 167-172 (1969).
8. V. I. Nedostup, "Use of the ideal gas curve in thermodynamic studies," Zh. Fiz. Khim., 44, No. 9, 2203-2206 (1970).
9. J. O. Hirschfelder, C. Curtis, and R. Bird, Molecular Theory of Gases and Liquids, Wiley (1974).
10. D. Douslin, R. Harrison, and R. Moore, "PVT-relations in the methane—tetrafluoromethane system," J. Phys. Chem., 71, No. 11, 3477-3488 (1967).
11. A. Michels and G. W. Nederbragt, "Thermodynamical properties of methane under pressures up to 400 atmospheres and temperatures between 0 and 150°C," Physica, 3, No. 7 (1936).
12. Sh. D. Zaalishvili, "The second virial coefficient for pure gases," Usp. Khim., 24, No. 6, 759-778 (1955).
13. S. D. Hamann, J. A. Lambert, and R. B. Thomas, "Intermolecular forces and the virial coefficients," Austral. J. Chem., 8, No. 2, 297-303 (1955).
14. R. D. Goodwin, "Thermophysical properties of methane from 90 to 500°K at pressures to 700 bar," Nat. Bur. Stand. (U.S.) Tech. Note, No. 563 (1974).
15. R. Olds, H. Reamer, B. Sage, and W. Lacey, "The n-butane—carbon dioxide systems," Ind. Eng. Chem., 41, No. 3, 475-482 (1949).
16. A. Isikhara, Statistical Physics [in Russian], Moscow (1973).
17. J. S. Rowlinson, "Determination of intermolecular forces from macroscopic properties," Disc. Farad. Soc., No. 30, 19-26 (1965).
18. G. C. Maitland and E. B. Smith, "Direct determination of potential energy functions from second virial coefficients," Mol. Phys., 24, No. 6, 1185-1201 (1972).

A METHOD OF STATISTICAL MODELING TO ESTIMATE THE ERROR IN DETERMINING THE COEFFICIENT OF MOISTURE DIFFUSION

N. I. Gamayunov, R. A. Ispiryan, and A. A. Sheinman

UDC 536.2.083

A method is considered which connects errors in the measurement of moisture content with the determination of the diffusion coefficient.

The majority of known methods of experimental determination of the coefficient of moisture diffusion require, during their practical implementation, creation in test special conditions such as, e.g., constant moisture content or flux of moisture on the surface, semi-finiteness of the medium, and uniformity of the initial distribution. In addition, as is mentioned in [1,2], during the solution of inverse problems insufficient attention is devoted to the error estimate. Often, incorrectly, the errors of direct and inverse problems are taken as identical.

Since existing methods of measurement of moisture fields give large errors, there arises need to work out methods of analysis of experimental data.

The essence of the method being proposed here consists of the following. Let there exist a testpiece of the material in which, as a result of external action, there is created a one-dimensional isothermal process of moisture transfer. We assume that at two points with the coordinates $x = 0$ and $x = l$ we know the dependence of moisture content on time $u(0, \tau) = f_1(\tau)$ and $u(l, \tau) = f_2(\tau)$, and also the distribution $u(x, 0) = g(x)$, referred to a time instant which conditionally is taken as the zero instant.

Usually in a real process the diffusion coefficient varies with time as a consequence of variation of the structure of the material. However, if we choose small time intervals and a thin layer l of the testpiece, then the moisture diffusion coefficient a within this layer can be considered as constant.

Kalinin Polytechnical Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 709-715, April, 1980. Original article submitted June 14, 1979.

With the assumptions just made taken into account, the process of moisture transfer within a thin layer of the testpiece for each time interval will be analogous to the process of transfer in an infinite plate of thickness l with boundary conditions of the first kind:

$$\frac{\partial u(x,\tau)}{\partial \tau} = a\frac{\partial^2 u(x,\tau)}{\partial x^2},\ u(x,\ 0) = g(x),$$

$$u(0,\ \tau) = f_1(\tau),\ u(l,\ \tau) = f_2(\tau).$$

Let at the point $x = l/2$ there be also known the dependence of moisture content on time $u(l/2,\ \tau) = f_3(\tau)$. Then, using the Laplace transform, we find the solution of the problem thus formulated in terms of transforms, and then we stipulate that it would be satisfied at the point $x = l/2$. As a result, we obtain the equation

$$\frac{[\hat{f}_1(s)+\hat{f}_2(s)] - [v(0,\ s,\ a) + v(l,\ s,\ a)]}{2\,\mathrm{ch}\,(l\sqrt{s/a}/2)} + v(l/2,\ s,\ a) - \hat{f}_3(s) = 0, \tag{1}$$

where $\hat{f}_1(s)$, $\hat{f}_2(s)$ and $\hat{f}_3(s)$ are the transforms of the boundary conditions and the auxiliary function, respectively; $v(x,\ s,\ a)$ is the particular solution of the differential equation undergoing Laplace transformation; it is chosen in accordance with the form of the initial distribution.

For the majority of practical problems, the initial moisture distribution can be approximated by the parabolic relation

$$g(x) = \delta_0 + \delta_1 x + \delta_2 x^2. \tag{2}$$

Then the particular solution, which is chosen by the method of undetermined coefficients, has the form

$$v(x,\ s,\ a) = \frac{1}{s}\,[2\delta_2 a/s + g(x)]. \tag{3}$$

With relations (2) and (3) taken into account, Eq. (1) is transformed into

$$\delta_2 l^2(\mathrm{ch}\,\gamma - 1) + \gamma^2 s\,[A(s) - 2B(s)\,\mathrm{ch}\,\gamma] = 0, \tag{4}$$

where

$$A(s) = \hat{f}_1(s) + \hat{f}_2(s) - [g(0) + g(l)]/s; \tag{5}$$

$$B(s) = \hat{f}_3(s) - g(l/2)/s; \tag{6}$$

$$\gamma = (l/2)\sqrt{s/a}. \tag{7}$$

The diffusion coefficient a can be determined directly from Eq. (4), without bringing it into the domain of transforms, but solving for a certain real positive value of the Laplace transform parameter $s = s_0$.

When choosing s_0 it is necessary to proceed from the following. In the process of the experiment we obtain the relations $f_i(\tau)$ ($i = 1,\ 2,\ 3$) for finite time instants. Therefore, replacement of the infinite limit of integration by a finite one in the Laplace transform leads to an error whose magnitude will depend on the parameter s_0. An analysis showed that the choice of the quantity s_0 from the condition $s_0 \geq 10/\tau_m$, where τ_m is the value of the time interval, leads to negligibly small errors.

Thus, as is seen from expression (4), for the determination of the diffusion coefficient of moisture in the course of the experiment it is necessary to determine the time dependence of moisture content for three sections of the testpiece, two of which (the boundary sections) stand at equal distance from the third (the middle one). As an analysis of the experimental data shows, for monotonic processes of mass transfer the variation of moisture content with time is well approximated by parabolic relations. Having divided the entire time of observation into a series of small intervals, we smooth the data thus obtained in each interval by polynomials of the second degree [3]:

$$f_i(\tau) = \beta_{i0} + \beta_{i1}\tau + \beta_{i2}\tau^2,\ i = 1,\ 2,\ 3. \tag{8}$$

Then parameters $A(s)$ and $B(s)$ are found from expressions (5) and (6):

$$A(s) = \beta_{10}/s + \beta_{11}/s^2 + 2\beta_{12}/s^3 + \beta_{20}/s + \beta_{21}/s^2 + 2\beta_{22}/s^3 - (2\delta_0 + \delta_1 l + \delta_2 l^2)/s, \tag{9}$$

$$B(s) = \beta_{30}/s + \beta_{31}/s^2 + 2\beta_{32}/s^3 - (\delta_0 + \delta_1 l/2 + \delta_2 l^2/4)/s. \tag{10}$$

TABLE 1. Dependence of Moisture Diffusion Coefficient on Moisture Content for Sand

Range of variation of moisture content Δu, %	2,6—9,0	2,6—4,5	4,5—6,0	6,0—7,5	7,5—9,0
Diffusion coeff. and confidence interval $(\tilde{a}\pm 3\sigma(a))\cdot 10^8$, m²/sec	1,163±0,114	0,745±0,096	0,905±0,102	1,421±0,198	1,469± 0,174

Equation (4) is functional, although implicit relative to the sought coefficient. However, such an equation is of statistical interest, since parameters A(s) and B(s) entering into it depend on the error of measurement of the field.

Let this error have a normal distribution with zero mathematical expectation and the variance $\sigma^2(\varepsilon)$, i.e.,

$$\varepsilon \sim N(0,\ \sigma^2(\varepsilon)). \tag{11}$$

Here the residual variance is determined for each of parabolas (8) by the relation

$$S_i^2 = \left[\sum_{j=1}^{n}(u_{ij} - b_{i0} - b_{i1}\tau_j - b_{i2}\tau_j^2)^2\right] / (n-3),\ \ i = 1,\ 2,\ 3, \tag{12}$$

where u_{ij} is the value of moisture content for the i-th coordinate point at the j-th time instant; b_{ik} (k = 0, 1, 2), estimates of coefficients of the i-th parabola; τ_j, value of the j-th time instant; n, number of time instants at which measurements have been carried out. The quantity S_i^2 is the estimate of the variance of error $\sigma^2(\varepsilon)$.

With (11) taken into account, each of the coefficients β_{ik} entering into (9) and (10) has a normal distribution with an estimate of the mathematical expectation b_{ik} and an estimate of the variance $\sigma^2(\beta_{ik})$. Then, according to [4], the parameters $A(s_0)$ and $B(s_0)$ also have a normal distribution, i.e.,

$$A(s_0) \sim N(m_A,\ \sigma^2(A)),\ B(s_0) \sim N(m_B,\ \sigma^2(B)), \tag{13}$$

where m_A, m_B, $\sigma^2(A)$, $\sigma^2(B)$ are the corresponding mathematical expectations and variances. Since the coefficients of the parabolas are correlated with one another, the quantities $\sigma^2(A)$ and $\sigma^2(B)$ are computed with covariances taken into account. At the same time, we assume that the coefficients of different parabolas are not connected with one another. Then

$$m_A = \frac{b_{10}}{s_0} + \frac{b_{11}}{s_0^2} + \frac{2b_{12}}{s_0^3} + \frac{b_{20}}{s_0} + \frac{b_{21}}{s_0^2} + \frac{2b_{22}}{s_0^3} - \frac{1}{s_0}(2\delta_0 + \delta_1 l + \delta_2 l^2), \tag{14}$$

$$\sigma^2(A) = \sigma^2(\beta_{10}) + \sigma^2(\beta_{11}) + 4\sigma^2(\beta_{12}) + \sigma^2(\beta_{20}) + \sigma^2(\beta_{21}) + 4\sigma^2(\beta_{22}) +$$
$$+ 2\,[\mathrm{cov}(\beta_{10},\ \beta_{11}) + 2\mathrm{cov}(\beta_{10},\ \beta_{12}) + 2\mathrm{cov}(\beta_{11}, \beta_{12})] + 2\,[\mathrm{cov}(\beta_{20},\ \beta_{21}) + 2\mathrm{cov}(\beta_{20},\ \beta_{22}) + 2\mathrm{cov}(\beta_{21},\ \beta_{22})], \tag{15}$$

$$m_B = \frac{b_{30}}{s_0} + \frac{b_{31}}{s_0^2} + \frac{2b_{32}}{s_0^3} - \frac{1}{s_0}\left(\delta_0 + \frac{1}{2}\delta_1 l + \frac{1}{4}\delta_2 l^2\right), \tag{16}$$

$$\sigma^2(B) = \sigma^2(\beta_{30}) + \sigma^2(\beta_{31}) + 4\sigma^2(\beta_{32}) + 2\,[\mathrm{cov}(\beta_{30},\ \beta_{31}) + 2\mathrm{cov}(\beta_{30}, \beta_{32}) + 2\mathrm{cov}(\beta_{31},\ \beta_{32})]. \tag{17}$$

In relations (15) and (17) the fact that δ_0, δ_1 and δ_2 are deterministic and have zero variance is taken into account.

Thus, as a result of processing of the data of the experiment we have obtained relations for statistical modeling, which are implemented as follows. By means of a transducer of random numbers (TRN) distributed according to a normal law, we generate a sequence $\{z_\mu\}$ ($\mu = 1,\ 2,\ \ldots$), this sequence being a normed sequence [5].

In the case being considered it is necessary to obtain two sequences of normally distributed random numbers having parameters m_A, $\sigma^2(A)$ and m_B, $\sigma^2(B)$. This is achieved by repeated recourse to the TRN and subsequent transformation of the normed random quantities $z_{\mu 1}$ and $z_{\mu 2}$:

TABLE 2. Experimentally Obtained Dependence of Moisture Content on Time for Three Sections of Specimen

Section	$\tau_1=0$	$\tau_2=4$	$\tau_3=8$	$\tau_4=12$	$\tau_5=16$	$\tau_6=20$	$\tau_7=24$	$\tau_8=28$
$x=0$	11,203	9,561	8,677	6,792	6,252	4,482	5,086	3,987
$x=\frac{l}{2}$	9,010	8,840	5,610	6,086	4,879	4,689	3,519	2,514
$x=l$	6,293	6,708	4,458	3,612	3,459	2,397	2,690	2,793

$$A_\mu = m_A + z_{\mu 1}\sigma(A), \tag{18}$$

$$B_\mu = m_B + z_{\mu 2}\sigma(B), \tag{19}$$

where A_μ and B_μ are the μ-th realizations of the random parameters $A(s_0)$, $B(s_0)$; $z_{\mu 1}$ and $z_{\mu 2}$ are the μ-th realizations of the normed random quantity as a result of the first and second address to the TRN, respectively. We note that repeated addressing of the TRN is carried out in order to avoid correlation between $A(s_0)$ and $B(s_0)$.

After obtaining a pair of A_μ and B_μ we solve Eq. (4); as a result, we find the value of γ_μ and, consequently, a_μ in the μ-th realization. Having repeated modeling M times, we obtain a selection of the coefficient a from which we can find the estimate of the mean $\tilde{a}$ and the variance $\sigma^2(a)$. Here the law of distribution of the sought coefficient will differ from a normal law, since Eq. (4) is nonlinear. The number of realizations M is determined from the absolute value of the maximum deviation from the mean [6].

Since the estimate of the error of measurement of the moisture content is given by expression (12), we consequently obtain a statistical connection between the input and output errors. At the same time, according to the Chebyshev inequality [6], in the interval $\tilde{a} \pm 3\sigma(a)$ at least 89.9% of coefficients thus obtained are located.

To verify the method proposed, tests were carried out on isothermal drying of sand with particle size from $0.25 \cdot 10^{-3}$ to $0.5 \cdot 10^{-3}$ m at 348°K. Drying was carried out in columns of length 0.15 m and diameter 0.02 m. Measurement of moisture content was carried out by the weight method.

As a result of processing of experimental data, we obtained the diffusion coefficients and the confidence intervals for various moisture contents presented in Table 1. The value of the parameter s for each interval of time was taken equal to unity, since the length of each of them was not less than 12 h.

To clarify the method being proposed, we present an example of processing of experimental data in a range of moisture content from 2.6 to 9.0%. The duration of the experiment was 28 h, the thickness of the layer of specimen was 0.02 m, measurements were carried out after each 4 h. The experimental data are presented in Table 2.

We first estimate the coefficients of the parabolas approximating experimental data, variances of the coefficients, and covariances. For this we use the matrix form of the least-squares method, and represent the following quantities, e.g., for the coordinate x = 0: the vector of observations

$$\mathbf{U}_1 = (11{,}203;\ 9.561;\ 8.667;\ 6{,}792;\ 6{,}252;\ 4.482;\ 5{,}086;\ 3.987)^{\mathrm{T}},$$

where T is the transposition sign; the given matrix of time instants at which observations were carried out:

$$\boldsymbol{\Theta} = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 4 & 16 \\ 1 & 8 & 64 \\ \cdot & \cdot & \cdot \\ 1 & 28 & 784 \end{pmatrix}$$

and finally, the transposed matrix

TABLE 3. Dependence of the Coefficient of Thermal Diffusivity on Temperature for a Biomass (solution of albumen in sodium sulphocyanate with concentration 18%)

Range of temp. variation, °K	263—273	273—293	293—313	313—333
Coeff. of thermal diffusivity and confidence interval, $\times 10^7$ m²/sec	2,562±0,213	2,788±0,246	3,113±0,294	3,425±0,336

$$\Theta^{\mathrm{T}} = \begin{pmatrix} 1 & 1 & 1 \dots & 1 \\ 0 & 4 & 8 \dots & 28 \\ 0 & 16 & 64 \dots & 784 \end{pmatrix}.$$

Multiplication of Θ^{T} by Θ gives the square matrix

$$\Theta^{\mathrm{T}}\Theta = \begin{pmatrix} 8 & 112 & 2240 \\ 112 & 2240 & 50176 \\ 2240 & 50176 & 1197056 \end{pmatrix}.$$

The system of equations for determining the vector of estimates of the coefficients has the form

$$(\Theta^{\mathrm{T}}\Theta)\,\mathbf{b}_1 = \Theta^{\mathrm{T}}\mathbf{U}_1,$$

where $\mathbf{b}_1 = (b_{10}, b_{11}, b_{12})^{\mathrm{T}}$ is the vector of estimates of the coefficients. Hence

$$\mathbf{b}_1 = (\Theta^{\mathrm{T}}\Theta)^{-1}\Theta^{\mathrm{T}}\mathbf{U}_1 = \mathbf{Y}\Theta^{\mathrm{T}}\mathbf{U}_1,$$

where $\mathbf{Y}$ is the information matrix.

Inversion of the matrix $\Theta^{\mathrm{T}}\Theta$ by the Jordan method gave

$$\mathbf{Y} = \begin{pmatrix} 0.708 & -0.938\cdot 10^{-1} & 0.260\cdot 10^{-2} \\ -0.938\cdot 10^{-1} & 0.197\cdot 10^{-2} & -0.651\cdot 10^{-3} \\ 0.260\cdot 10^{-2} & -0.651\cdot 10^{-3} & 0.233\cdot 10^{-4} \end{pmatrix}.$$

Multiplying Y by Θ^{T}, and then by U_1, we obtain $\mathbf{b}_1 = (11.266;\ -0.426;\ 0.006)^{\mathrm{T}}$.

Next by means of expression (12), with i = 1 and n = 8, we find the estimate of the residual variance $S_1^2 = 0.220$.

To determine the covariance matrix we have to multiply all elements of the matrix $\mathbf{Y}$ by the value of residual variance S_1^2. Then

$$\mathbf{Z} = \begin{pmatrix} 0.156 & -0.206\cdot 10^{-1} & 0.572\cdot 10^{-3} \\ -0.206\cdot 10^{-1} & 0.432\cdot 10^{-2} & -0.143\cdot 10^{-3} \\ 0.572\cdot 10^{-3} & -0.143\cdot 10^{-3} & 0.511\cdot 10^{-5} \end{pmatrix}.$$

The elements of the principal diagonal constitute the estimate of variances of the coefficients of the parabola, while the elements above the diagonal constitute the estimate of covariances [3], i.e., $\sigma^2(\beta_{10}) = 0.156$, $\sigma^2(\beta_{11}) = 0.432\cdot 10^{-2}$, $\sigma^2(\beta_{12}) = 0.511\cdot 10^{-5}$, $\mathrm{cov}(\beta_{10}, \beta_{11}) = -0.206\cdot 10^{-1}$, $\mathrm{cov}(\beta_{11}, \beta_{12}) = 0.572\cdot 10^{-3}$, $\mathrm{cov}(\beta_{10}, \beta_{12}) = -0.143\cdot 10^{-3}$.

Analogously, we can carry out calculations for the points $x = l/2$ and $x = l$. The initial distribution is approximated by the relation (2) and has the form $g(x) = 10.45 - 0.98\cdot x - 0.52\,x^2$.

For statistical modeling we calculate according to the expressions (14)-(17) the mathematical expectations and variances of the parameters A(s) and B(s). Here we put $s_0 = 1$, since $\tau_m = 28$ h. As a result,

$$A(1) \sim N(0.560;\ 0.317),\quad B(1) \sim N(-0.131;\ 0.308).$$

The statistical modeling was carried out on an M-222 computer by means of a standard program for obtaining normed normally distributed numbers. Equation (4) was solved on the computer for each realization by means of dichotomy [7]. Here the μ-th realization of the parameters $A(s_0)$ and $B(s_0)$ was calculated according to expressions (18) and (19).

In the role of the maximum deviation from the mean value, we took the quantity $\omega = 0.005$ at the 5% significance level. As a result of modeling, the absolute value of the maximum deviation became less than ω for M = 59. By sampling from 59 values of the diffusion coefficient a we find the estimate of the mean value $\tilde{a} = 1.163 \cdot 10^{-8}$ m²/sec and the mean-square deviation $\sigma(a) = 0.038 \cdot 10^{-8}$ m²/sec. Thus, in the interval $a = (1.163 \pm 0.114) \cdot 10^{-8}$ m²/sec there are at least 89.9% of all coefficients.

Concluding, we note that the method presented above can be applied for experimental determination of the coefficient of thermal diffusivity, since the mathematical models describing the processes of heat and mass transfer are identical. In particular, we determined the coefficients of thermal diffusivity of biomasses used in the production of synthetic fibers. The results of one of the experiments are presented in Table 3.

NOTATION

u, moisture content, %; l, thickness of specimen layer, m; a, diffusion coefficient, m²/sec; ε, error of measurement of moisture content.

LITERATURE CITED

1. A. A. Aleksashenko, "Analytical method of determining nonlinear thermophysical parameters without linearizing the equations of thermal conduction," Izv. Akad. Nauk SSSR, Energ. Transport, No. 1, 112-136 (1978).
2. A. A. Aleksashenko, "Investigation of errors in solving certain inverse problems," Teplofiz. Vys. Temp., 13, No. 5, 1023-1028 (1975).
3. N. Draper and H. Smith, Applied Regression Analysis, Wiley (1966).
4. G. J. Hahn and S. S. Shapiro, Statistical Models in Engineering, Wiley (1967).
5. V. F. Demin, L. V. Dobrolyubov, and V. A. Stepanov, Programming Systems in ALGOL [in Russian], Nauka, Moscow (1977).
6. E. S. Venttsel', Probability Theory [in Russian], Nauka, Moscow (1969).
7. N. N. Kalitkin, Numerical Methods [in Russian], Nauka, Moscow (1978).