ANALYSIS OF HEAT AND MASS TRANSFER PROCESSES IN SYSTEMS OF DYNAMIC THERMOVACUUM HYDROMETRY

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UDC 681.542.4

A theoretical model of the process of moisture desorption in evacuation of a sample of moist material is proposed. An interrelationship between the operating conditions of the process and the material characteristics is shown. A new method of thermovacuum hydrometry that makes it possible to improve the rapidity of measurements and to significantly extend the measurement range for the moisture content of loose materials is described.

One of the most promising current mass-transfer methods for measurement of the moisture content of loose materials is the thermovacuum method (TV method), whose main idea is in the following [1, 2]. If a thin uniform-in-thickness layer of material is placed in a hermetic object and evacuated, as a result of intense energy absorption in the phase transition of water to vapor, the material temperature will begin to decrease. As the water evaporates desorption intensity reduces and the material temperature, as a result of heat exchange with the ambient medium, will begin to increase to the temperature of the chamber walls. The temperature change will have an extreme whose magnitude depends on the moisture content. The value of the maximum change in temperature or the difference in the temperatures of the tested and dry standard samples usually serves as the parameter measured.

A mathematical model of this process is described by a system of differential equations in partial derivatives for the temperature, pressure, and potential of mass transfer. In the general case, the differential equations will be nonlinear, since the transfer coefficients are functions of these quantities.

In [2], a solution of the problem for the one-dimensional case is given under the assumption that moisture evaporation occurs uniformly throughout the entire volume of material and the heat- and mass-transfer coefficients do not change in the process of moisture desorption. The effect of the vessel boundaries was not allowed for, and consideration was given to only the second period of drying, which is justified only for low moisture contents. The authors of [3] refined the mathematical model and obtained a solution under the assumption of the distributed character of moisture transfer as well as for the case of high moisture contents, when the first period of drying must also be allowed for.

When solving the problem we need to know the law of variation of moisture content U with time t. For this purpose, the experimentally derived dependence [1, 4]

$$U(t) = U_0(1 - b) + U_0 b \exp(-\alpha_u t), \tag{1}$$

was employed, where b and α_u are empiricially determined coefficients. The first coefficient shows the completeness of moisture extraction in vacuum; the second characterizes the desorption rate. For water-insoluble materials, $b \approx 1$, for water-soluble materials, $b = 0.3 - 0.9$. The quantity α_u is the main parameter of the process that characterizes the rate of moisture desorption.

In [5], α_u is noted to be governed by the moisture content and the volume of the sample in the chamber, the vacuum-pump capacity, and the character of the cohesion between the moisture and sample particles. In the

same work, α_u is shown to have a constant value in the region of low moisture content; the limits of the applicability of this assumption are not indicated and the character of the dependence of α_u on the above factors is not revealed.

The main advantages of the TV method are high accuracy that is comparable with the accuracy of a thermogravimetric method as well as a possibility to measure small (~0.02 kg/kg) and very small values (~0.003 kg/kg) of moisture content, i.e., in those cases when all other indirect methods for determining moisture content are of little use.

Along with the enumerated advantages, this approach to the determination of moisture content has a number of fundamental drawbacks that often make it impossible to obtain highly accurate measurements for the following reasons.

1. The measurement time is sometimes several minutes [2, 5]; during this period, additive and multiplicative errors occur because of unstable characteristics of the electronic circuit, vacuum pump, and other elements of the vacuum system (valves, pipelines, seals of the measuring chamber's cover).

2. A prolonged time of moisture-content measurement involves, in addition to sample cooling, cooling of the entire structure of the primary transducer (the walls of the measuring vacuum chamber, vessel walls); this leads to a change in the temperature difference between the sample and the ambient medium, i.e., the conditions of heat transfer are altered, which induces a significant error, whose magnitude varies and is accumulated in the subsequent measurements [5, 6].

3. In the case of a sufficiently high content of moisture in the specimen, it self-freezes during measurement, which makes it impossible to obtain reliable results in measuring.

4. In sample evacuation, along with the outflow of heat due to moisture evaporation, there are convective and radiant components of the heat flux to the specimen that are characterized by the overall heat-transfer coefficient, which is not constant in measuring, because of the change in the temperatures of the elements of the measuring system and the sample, fluctuations of the pressure and moisture content of the specimen in measuring, evacuation dynamics, and a number of other factors.

5. In a number of cases, the accuracy of measurement is affected by thermal noise due to adiabatic expansion of the vapor-air mixture in the chamber at the initial moment of evacuation, which induces parasitic sample cooling (in the literature on TV hydrometry, this phenomenon is called the Joule-Thomson effect [5].

The indicated drawbacks of the existing procedure for moisture-content determination in TV hydrometry, where the extremum of the temperature curve is used as the informative parameter that is related to the moisture content, can be overcome by developing a rapid dynamic thermovacuum method for measurement of the moisture content of loose and liquid materials (DTV method). It enables us to substantially extend the measurement range for moisture content, to improve accuracy, and to decrease measurement time.

The essence of the DTV method is that α_u is used as the informative parameter related to the moisture content. In the initial time interval, the heat exchange of the sample with the medium can be disregarded, as a result of which the equation of the thermogram will take the form

$$T_0 - T(t) = \Theta(t) = \frac{brU_0}{c}(1 - \exp(-\alpha_u t)), \qquad (2)$$

where T is the sample temperature; r is the heat of vaporization; c is the specific heat of the sample.

The performed investigations showed that the parameter of the rate of moisture desorption α_u decreases as U_0 increases [8]. To find α_u as a function of U_0, let us use the relation that is obtained in statistical physics for two systems of microparticles with different energies in a state of thermodynamic equilibrium. If the liquid in the pores of material and the vapor phase above the sample in the chamber are taken as these systems, the formula for the molecular concentrations n_1 and n_2 will be written as

$$\frac{n_2}{n_1} = \exp\left(-\frac{r}{RT}\right), \qquad (3)$$

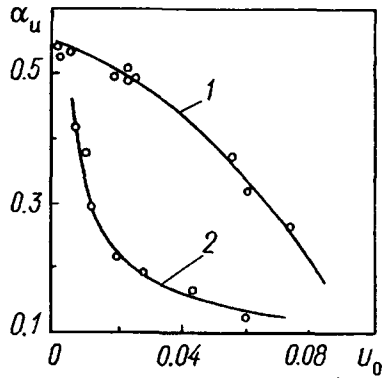where R is the universal gas constant.

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Fig. 1. α_u (sec^{-1}) as a function of initial moisture content for nitroammophoska (1) and quartz sand (2).
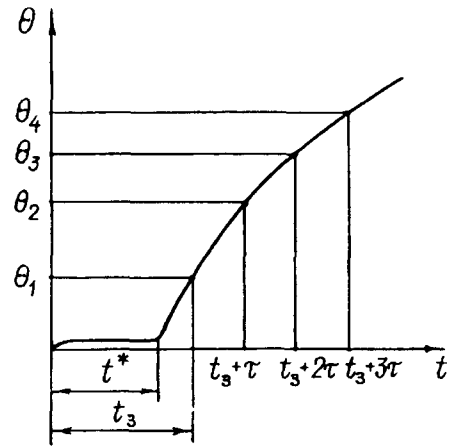
Fig. 2. Change in sample temperature in the initial time interval.

Knowing the pump capacity S and the liquid density γ_{liq} and allowing for the law of conservation of mass, we can write

$$n_1 \frac{m_{\text{dr}}}{\gamma_{\text{liq}}} dU = - n_2 S dt, \tag{4}$$

from which, in view of (3),

$$\frac{dU}{dt} = - \frac{S\gamma_{\text{liq}}}{m_{\text{dr}}} \exp\left(- \frac{r}{RT}\right), \tag{5}$$

where m_{dr} is the mass of the material charge in the dry state.

On the other hand, the rate of change for the moisture content can be determined by differentiating (1):

$$\frac{dU}{dt} = - \alpha_u b U_0 \exp\left(- \alpha_u t\right). \tag{6}$$

Employing (5) and (6), for the initial instant we have:

$$\alpha_u = - \frac{S\gamma_{\text{liq}}}{m_{\text{dr}} b U_0} \exp\left(- \frac{r}{RT}\right). \tag{7}$$

Thus, we have derived a relation that relates the parameter of the rate of moisture desorption in vacuum α_u to the moisture content of the sample U_0. The inversely proportional relationship between them confirms the results of earlier experimental investigations (Fig. 1) [9].

Due to the fact that the process of intense moisture evaporation from the sample begins within the time t^* after the beginning of pumping, formula (2) will take the form

$$\Theta(t) = \frac{b r U_0}{c} \left(1 - \exp\left(- \alpha_u \left(t - t^*\right)\right)\right). \tag{8}$$

Time t^* is required for the vapor pressure in the chamber to decrease to the required level in pumping.

In Fig. 2, relationship (2) is shown graphically. The measurement of θ is performed starting at the instant t_{del} with time-scanning step τ. The delay time t_{del} is chosen from the condition $t_{\text{del}} > t^*$.

We can make the processing of measurement results substantially easier by reducing expression (8) to the form

$$y = A \exp (Bx).$$ (9)

Let us determine an increment in temperature in the time τ:

$$\Theta_i - \Theta_{i-1} = \frac{brU_0}{c} \exp [\alpha_u (t_{\text{del}} - t^*)] (1 - \exp (- \alpha_u \tau)) \exp [- \alpha_u (i - 1) \tau].$$ (10)

We introduce the notation: $y_i = \Theta_i - \Theta_{i-1}$, $x_i = (i - 1)\tau$. Comparing (9) and (10), we obtain

$$A_i = \frac{brU_0}{c} \exp (- \alpha_u (t_{\text{del}} - t^*)) (1 - \exp (- \alpha_u \tau)),$$

$$B = - \alpha_u.$$ (11)

It is evident that the uncertainty of t^* that is due to the moment of the beginning of intense evaporation being affected by a rather large number of factors is built into the scale factor A_i. This improves the accuracy of determining U_0 by the t^*-independent parameter α_u in the exponent.

From the theory of regression analysis, it is known that the parameter B for a relationship of the form (11) is determined in the following manner [10]:

$$B = \frac{\sum\limits_{i=1}^{k} x_i \ln y_i - \frac{1}{k} \sum\limits_{i=1}^{k} x_i \sum\limits_{i=1}^{k} \ln y_i}{\sum\limits_{i=1}^{k} x_i^2 - \frac{1}{k} \left(\sum\limits_{i=1}^{k} x_i\right)^2}.$$ (12)

For example, if k is taken equal to 4, employing (10)-(12), we obtain

$$\alpha_u = - B = \frac{0.3 \ln \dfrac{y_4}{y_1} + 0.1 \ln \dfrac{y_3}{y_2}}{\tau}.$$ (13)

Since $\alpha_u \sim 1/U_0$, we can finally write

$$U_0 \sim \frac{\tau}{0.3 \ln \dfrac{y_4}{y_1} + 0.1 \ln \dfrac{y_3}{y_2}}.$$ (14)

The degree of the cohesion of water molecules with the surface of dispersed-material particles governs evaporation energy losses and depends on the magnitude of adsorption forces; therefore, in formulas (3)-(7) in the exponent, it would be more correct to use $r + E_{\text{coh}}$, where E_{coh} is the energy of the cohesion of the water molecules with the material surface.

Employing (5) and (6) with allowance made for E_{coh}, let us find the ratio of the derivatives of u for the instants t_1 and t_2 $(t_2 - t_1 = \tau)$, which finally yields

$$\overline{E}_{\text{coh}} = \frac{\alpha_u \tau}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} - r,$$ (15)

$$\overline{E}_{\text{coh}} = \frac{1}{\tau} \int\limits_{t_1}^{t_2} E_{\text{coh}} (t) \, dt.$$ (16)
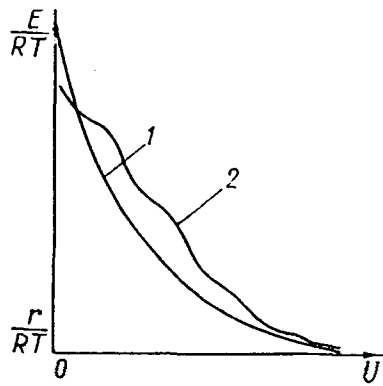
Fig. 3. Dimensionless power complex versus moisture content of material: 1) ideal case calculated by formula (19); 2) real dependences for materials with a complicated cohesion energy.
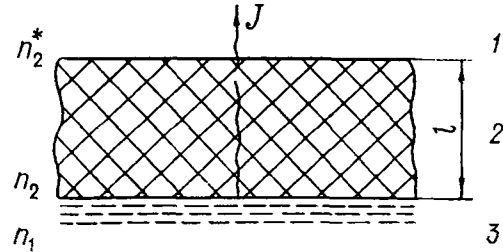
Fig. 4. Derivation of basic relations for dried layer: 1) vapor phase, 2) dried layer, 3) moist layer.

It is evident that α_u characterizes the specific energy losses in moisture desorption. It becomes possible, by measuring the sample temperature with the interval τ at different instants, to find the energy of the cohesion of the moisture with the material and its time history. No expensive equipment is required, and the cohesion energy is rapidly determined in the region of room temperatures, which is currently quite an urgent problem [11, 12].

To find E_{coh} as a function of U, let us use the Rebinder equation [12, 13]:

$$E_{coh} = - RT \ln \varphi ,$$ (17)

where φ is the relative humidity of the air above the liquid surface and the sorption-desorption isotherms $U = U(\varphi)$.

The theoretical dependences $U = U(\varphi)$ are obtained only for the simplest types of isotherms which is due to a great complexity of sorption-desorption processes in real materials. The theory is unable to analytically describe these processes as yet with allowance made for all the inherent basic phenomena. Sorption-desorption processes are described most completely in the theory of polymolecular adsorption [14, 15]. Employing Eq. (29) or experimental dependences, we can express the relative air humidity φ in terms of U and substitute it into (17). Thus, α_u is one of the basic informative parameters in the thermovacuum method; with it, we can determine both the energy of the cohesion of moisture with material and the moisture content of the sample.

As an example, let us use the simplest form of the dependence of the sorption isotherm, i.e., the Henry law [16]

$$U = k\varphi ,$$ (18)

that is a particular case of the equation of polymolecular adsorption. This dependence holds true for $\varphi \leq 50\%$ for a wide class of materials [16, 17]. For large φ, the relationship between the moisture content of the material and the partial pressure of the vapor becomes nonlinear; this is induced by the fact that, in this case, the moisture exchange of the material occurs with the adsorbed-moisture film formed on the surface, rather than with the vapor around the material. In view of (17) we obtain

$$\frac{E}{RT} = \frac{r}{RT} - \ln \frac{U}{k} ,$$ (19)

where E is the total energy loss by moisture evaporation.

Similarly, we can derive the dependences $E(U)$ by employing the Langmuir monomolecular-adsorption equation and the equation of polymolecular adsorption.

Experiments on materials with a complicated character of the cohesion energy [13] showed that the real dependences have a more intricate form (Fig. 3).

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Let us consider the effect of a dried layer (DL) on the process of moisture desorption in sample evacuation. To obtain estimation results, let us use the same approach which was used earlier.

Because of the presence of the DL the vapor concentration near the material surface will become $n_2^* < n_2$ (Fig. 4). This, in turn, leads to an increase by E^* in the cohesion energy. Thus,

$$n_2^* = n_2 \exp \left(- \frac{E^*}{RT} \right). \tag{20}$$

The vapor flow through the DL, for its small thickness l, is equal to

$$J = \frac{n_2 - n_2^*}{l} D_{por} M_{mol} F, \tag{21}$$

where $M_{mol} = 3.0 \cdot 10^{-26}$ kg is the mass of a water molecule; F is the sample surface area.

The diffusion coefficient for water vapor in a porous body D_{por} is calculated by the formula [16-20]

$$D_{por} = \frac{D}{\mu}. \tag{22}$$

The coefficient of diffusion resistance μ depends on both the porosity of the material m and its structural parameters (pore crookedness, the fraction of "dead ends" of the cluster of porous space, etc.). In a number of works, various relations to calculate μ are given; in particular, in [21], based on an electrodiffusion analogy in combined breaking of an elementary cell of a structure with interpenetrating components a formula is proposed that is in good agreement with experimental data:

$$\mu = 1 + \frac{G}{(1 - G)^2}, \tag{23}$$

the parameter G is determined by solution of the cubic equation [22]:

$$m = 2G^3 - 3G^2 + 1. \tag{24}$$

An expression for J can also be written in the form

$$J = Sn_2^* M_{mol}. \tag{25}$$

Setting (21) equal to (25) and allowing for (22), we obtain

$$E^* = RT \ln \left(1 + \frac{Sl\mu}{DF} \right). \tag{26}$$

Due to the fact that, in sample evacuation, the bulk of moisture evaporates from a drying front that moves deep into the material, in view of (1), we can write

$$l(t) = L(1 - \exp(-\alpha_u t)), \tag{27}$$

where L is the thickness of the material charge. On this basis, we have:

$$E^* = RT \ln \left(1 + \frac{\mu SL(1 - \exp(-\alpha_u t))}{DF} \right). \tag{28}$$

Thus, we have derived an expression that relates sample drying to time and multiplicative addition into the formula for dU/dt
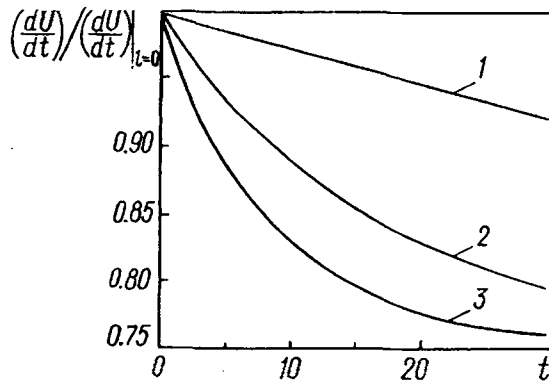
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Fig. 5. Relative variation in rate of moisture desorption for drying of upper layer of sample with time ($\alpha_u = 0.01$ sec^{-1} (1), 0.05 sec^{-1} (2), 0.1 sec^{-1} (3)). t, sec.

$$\frac{dU}{dt} = - \frac{S\gamma_{liq}}{m_{dr}} \frac{\exp\left(-\dfrac{r + E_{coh}}{RT}\right)}{1 + \dfrac{\mu SL\,(1 - \exp\,(-\alpha_u t))}{DF}},$$ (29)

that can significantly alter the result.

Figure 5 gives the variations in the rate of moisture desorption as functions of time when a DL forms for different values of α_u. We used the following values of the quantities: $F = 25$ cm^2, $L = 5$ mm, $D = 3.2 \cdot 10^{-3}$ m^2/sec, $S = 0.1$ liter/sec, and $\mu = 5.3$. From Fig. 5, it is evident that, for small values of α_u (curve 1) that correspond to high moisture contents, the effect of DL is insignificant. If 0.05 sec$^{-1} < \alpha_u < 10$ sec^{-1}, it is appropriate to measure in an interval of 5 to 10 sec, when the rate of moisture desorption decreases by no more than 20%. Therefore, for low moisture contents, it is appropriate to take advantage of the traditional TV method to measure moisture content by the extremum temperature in desorption Θ_{ext}, the following relation

$$U_0 \sim \Theta_{ext}$$ (30)

holding true for different U_0 ranges.

From what has been said, we can propose a measurement procedure for moisture content when both algorithms are fed into the instrument, the information being processed automatically by either depending on the character of the thermogram.

A dynamic thermovacuum method to measure the moisture content of loose materials is used as the basis of the AKVATERM moisture meter developed by the authors.

The algorithm of moisture-meter operation is presented in Fig. 6. When powered the unit of control and computational operations (UCCO) enters the mode of initial data input. The operator keyboards a delay time for the beginning of measurements and a time interval between measurements for algorithm No. 1. Once the program is started the sensor of chamber interlock is polled. If the chamber is not hermetically sealed the lockout is displayed and UCCO enters the mode of data input, the data being stored in random-access memory. For a restart, we need to close the chamber's cover and to start the program. If the chamber is closed, the interlock is polled about the power supply of the pump. If power is not applied to the pump, the interlock is displayed and UCCO enters the mode of initial data input. If power is applied, the roughing pump is started. Depending on the moisture content of material, the UCCO chooses a variation algorithm and by it measures the moisture content. Upon calculation and display of the moisture content a single-chip computer gives an instruction to the inlet valve of the chamber and goes into the keyboard mode.

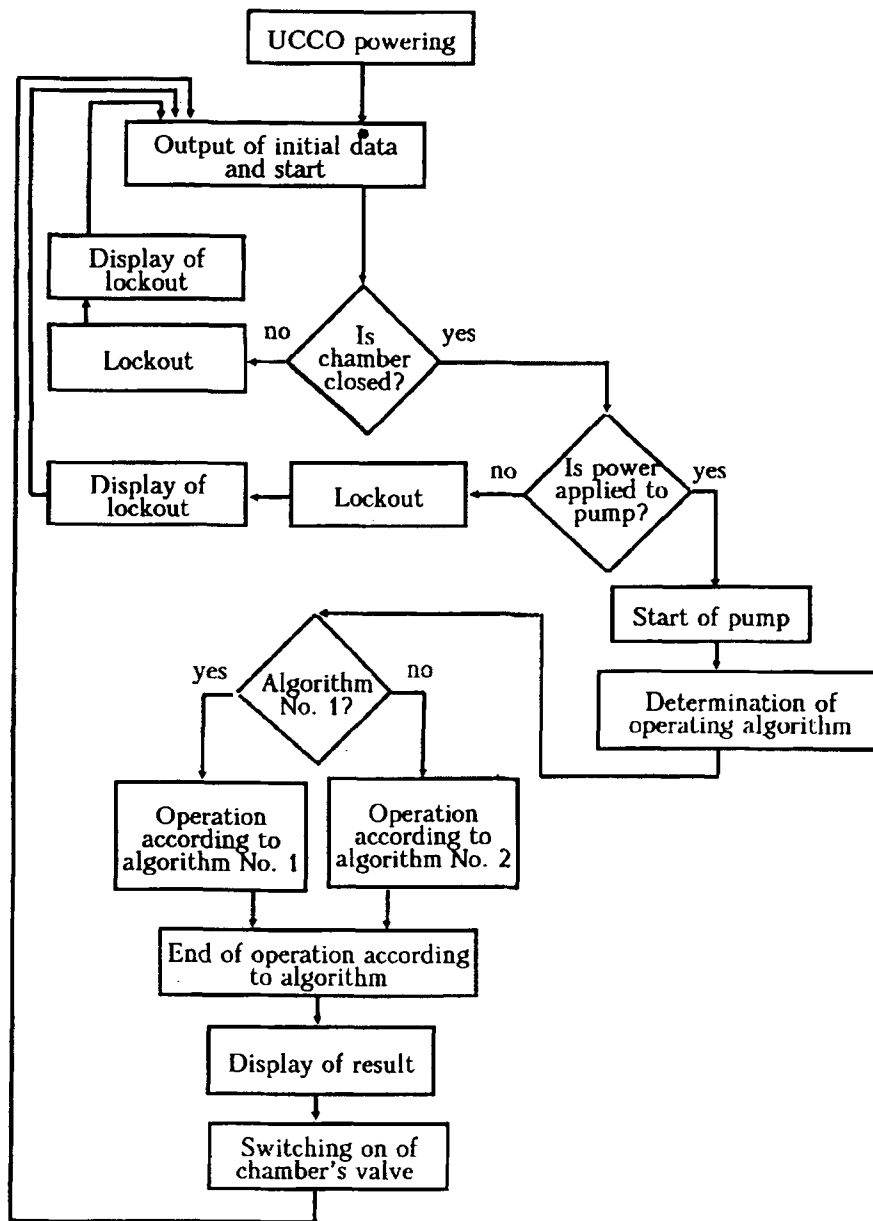From what has been said, we can make the following conclusions.

Fig. 6. Algorithm of AKVATERM moisture meter operation.

1. The use of the parameter α_u as the informative parameter in determining U_0 enables us to significantly decrease the effect of a number of errors that are additive and multiplicative in character and are due, for example, to the initial temperature difference, change in the conditions of heat transfer for large measurement times, etc.

2. In the case of a sufficiently high moisture content in the specimen, in the period of measuring by the experimental method the water self-freezes, which interferes with the completion of measurements, since frozen moisture clogs pores in the specimen and water evaporation from it ceases. In this connection, it is possible to determine U_0 of these materials in thermovacuum hydrometry only by a dynamic method, i.e., by the rate of change in temperature in the transition period.

3. The dynamic thermovacuum method is much faster than the extremum one.

4. When analyzing a thermogram in the process of moisture desorption, it becomes possible to estimate the power characteristics of the cohesion of water with a material.

5. For low moisture contents, it is preferable to employ the extremum method, since a dried layer begins to form for small U_0 already in the very beginning of evacuation, due to which determination of U_0 using α_u becomes inaccurate.

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NOTATION

U_0, U, initial and current moisture contents, kg/kg; α_u, coefficient of the rate of moisture desorption, $\sec^{-1}$; b, coefficient of the completeness of moisture extraction; T_0, T, initial and current sample temperatures, K; Θ_{ext}, Θ, maximum and current variations in the sample temperature with time, K; c, specific heat of sample, J/(kg·K); n_1, n_2, molecular concentrations in the 1st and the 2nd phases, m^{-3}; R, universal gas constant, J/(mole·K); r, heat of vaporization, J/mole; S, vacuum-pump capacity, $m^3/\sec$; γ_{liq}, liquid density, kg/m^3; m_{dr}, sample-charge mass in dry state, kg; t^*, t_{del}, time of the beginning of moisture desorption from the sample after switching on the vacuum-pump and the delay time for the beginning of measurement, sec; τ, step of time scanning, sec; φ, relative humidity of air above the liquid surface, %; E_{coh}, E, energy of the cohesion of water molecules with the material carcass and the total energy expended on moisture desorption, J/mol; F, sample surface area, m^3; J, vapor flow, kg/sec; D, D_{por}, coefficient of water-vapor diffusion in air and in porous body, $m^2/\sec$; M_{mol}, mass of water molecule, kg; μ, coefficient of diffusion resistance for vapor in porous body; m, material porosity; L, material-charge thickness, m.

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