In conclusion, we suggest that the proposed method of mathematically describing the geometric configuration of high-strength gypsum stone can be easily extended for a description of the geometrical configuration of various polydisperse systems.

NOTATION

a, characteristic dimension of a particle; η, relative characteristic size of a particle; ν, form factor; α_x, α_y, α_z, direction factors of particles; m_1 and m_2, dispersion moduli; N_0, number of solid particles per unit volume; $\langle a \rangle$, mean-integral characteristic dimension; S_0, total area of the inner surface of the solid phase per unit volume; V_0, total volume of the solid phase per unit volume; and $\langle F \rangle$, average area of contact between two particles of the solid phase.

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THERMAL FEATURES OF THE DEHYDRATION TECHNOLOGY OF THERMO- AND MOISTURE-LABILE MATERIALS

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UDC 663.1.047

The relationship between the main thermal parameters of the dehydration process and the technological criteria of the quality of the material is analyzed. The choice of methods and drying modes is justified.

The principles and methods of dehydration are based on a study of the technological properties of the object being investigated. Multicomponent systems with labile centers and bonds, typical representatives of which are materials of biological origin, particularly micropreparations and products of microbe biosynthesis, are especially complex in this plan. The difficulty in developing an optimum drying technology for microbiological materials is due to the large variety of forms characterized by a difference in the physicochemical properties and responses to the action of the surrounding medium [1-3] and also the high initial moisture content of the product (95.0-99.5%). Microbiological materials have not been investigated to any great extent as objects of drying, and investigations in this area, as a rule, have only been of a partial nature [4, 5].

In the present paper we consider a wide spectrum of microbiological materials including objects of different kinds: vegetative cultures, spore-forming bacterial forms, and the products of microbe biosynthesis. The technological criterion (the quality characteristic) of the system is assumed to be the survivability (preservability) of the preparation,

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characterizing the susceptibility of the object being investigated to external or internal inactivation factors, in particular, to the intensity and duration of heating — the thermal stability, the depth and rate of drying — and the moisture stability:

$$B = \frac{N}{N_0}. \tag{1}$$

Microbiological materials can be conventionally divided into two groups. The first consists of microbe preparations, the nature of which is characterized by the presence of living bacterial cells, and the second consists of products of microbe synthesis and biochemical materials. The second group also includes spore-forming bacterial forms, which are those forms of microbe cultures which possess the ability to adapt to extreme external conditions (saturation of the metabolite medium, depletion of feed materials, and also the factor of most interest to us, viz., dehydration).

The quality of microbiological materials, which belong to the second group, when dehydrated is practically independent of the level of residual moisture, since we are here concerned with complex organic compounds (antibiotics, amino acids, and enzymes), where it is mainly irreversible reactions of thermal inactivation that occur [6, 7]. The situation is quite different with microbe preparations of the first group.

The drying of living microbe cells, as is well known [8], transfers them into the so-called state of dry anabiose, in which vital processes occurring in the living organism are inhibited, life is suspended or depressed, but the lethal state has not yet begun, and when favorable conditions are reestablished normal exchange processes can be resumed. Clearly, in this case, the residual moisture of the microbe biomass is a regulator of the intensity of vitally important exchange processes. Consequently, for vegetative bacterial forms the first stage of the development of an optimum drying technology is to determine the permissible residual moisture which enables the microbe cells to remain in the lifelike anabiotic state and which simultaneously ensures the possibility of prolonged storage (conservation) of the microbiological preparation. Unfortunately, often in papers devoted to problems of drying bacterial cultures, attention is given to drying methods (sublimation, spraying, and fluidized bed) and temperature processes without taking into account such an important factor as the residual moisture content, which leads to negative results, i.e., the final product is of low quality in which the bacterial cells are destroyed [9, 10].

We determined the moisture sensitivity of microbe vegetative cultures by sorbtion dehydration of the specimen when the material-sorbent system was in thermodynamic equilibrium [11]. We used inert materials (silica gel and zeolite) as sorbents and also potentially possible components of the drying preparation (peat, meal, etc.). The amount of sorbent was calculated from the relation

$$G_2 = \frac{G_1 \Delta u}{u_k \frac{c_{m_2}}{c_{m_1}}}. \tag{2}$$

In Fig. 1 we show the effect of the residual moisture content on the vital capacity of microbe cells of different kinds. By analyzing the nature of curves 1-3 and the sorbtion isotherms of these preparations 1'-3', we find an interesting behavior. In the range of moisture contents from 50% to 80% (35-45% moisture) there is a sharp loss in the viability of the cells. The moisture content at which mass dying off of the cells begins must be regarded as critical, but it should also determine the limit of dehydration of the material for preserving the desired quality (B = 100%). The value of the critical moisture content corresponds to the value of the maximum hygroscopic moisture content, while the region in which the viability falls coincides with the part of the sorbtion isotherm on which the moisture is mainly capillary. It is obvious that the maintenance of minimum intensity of exchange reactions, inherent in the anabiose state, is only possible when moisture is present in the microcapillaries of the body-biomass. On entering the region of hydration moisture content and changing the form in which the sorbed moisture is bound, the microbe cells, which are individual elements of the structure of the capillary-porous body, are destroyed. This destruction occurs suddenly, which follows from an analysis of curves 1-3. It is obvious that the mechanism by which the cells are destroyed is related to the destruction of the cell membranes, but this problem is the subject of a special investigation.

Hence, the hygroscopic point of the sorption isotherm corresponds to the minimum value of the residual moisture content, for which 100% viable microbe cells can be preserved in

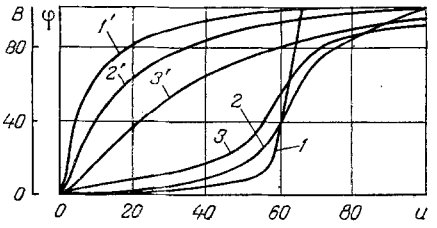

Fig. 1

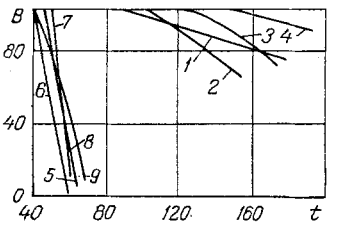

Fig. 2

Fig. 1. Comparison of the effect of residual moisture content on the viability of microbe cells with the sorption isotherms of these materials: 1-3) survival curves, 1'-3') sorption isotherms (1, 1' — a culture of *Lactobacterium plantarum*; 2, 2' — *Rhizobium pisum*; and 3, 3' — *Beauveria bassiana*). B, φ, and u, %.

Fig. 2. Comparative thermal sensitivity of microbiological materials: 1) spore-forming culture of *Bac. thuringiensis*, 2, 3) antibiotics of different kinds — grisine and bacitracine, 4) lysine amino acid, 5-8) vegetative cultures of *Lactobacterium plantarum*, *Rhirobium pisum*, *Lactobacterium avidophilum*, and *Beauvera bassiana*. t, °C.

the biomass, i.e., the sorption isotherm enables one to determine the permissible residual moisture content of the biomass for microbiological materials of the first group, the value of which depends on the choice of the method of dehydration.

When recommending any method of drying it is necessary to specify the temperature mode of the process. In order to intensify heat-mass transfer one should naturally attempt to obtain maximum thermal potential, which in turn determines the limiting temperature of the heating medium, permissible from the point of view of the technological properties of the material. There is a widely held opinion that the temperature of the drying agent when the time of contact with fine particles of the dried material is small can be fairly high, and this has no effect on the quality of thermolabile materials, since the temperature of its surface during the first drying period is taken to be equal to the temperature of a wet thermometer. However, as a whole series of indirect experiments show [12], for very intense drying (spray drying or pneumatic drying) the temperature of the surface of the particles of the material increases from the very beginning of the process. Consequently, the maximum permissible temperature to which the material can be heated for different exposures is the most important technological criterion when developing dehydration technology for microbiological materials.

The thermal stability of microbe preparations was found by a capillary method over a wide temperature range (40-200°C) and over a wide range of exposures (5-900 sec), The method of investigation, viz., practically gradient-free heating of the specimen, enabled us to establish a clear relationship between the intensity and duration of the thermal action on the activation kinetics of the object [13]. From an analysis of the experimental data we can state that there is a sharp difference in the temperature sensitivity of the materials investigated. Figure 2 shows a graphical comparison of the effect of temperature on the viability (preservation) of microbe cells and the product of biosynthesis for a 15-sec exposure to heat. As in the case of the effect of residual moisture, we can here again divide microbiological objects into two groups from the point of view of drying: 1) vegetative bacterial cultures, and 2) the products of microbe biosynthesis and spore-forming microorganisms. For the first group the characteristic feature is the high rate of destruction over a comparatively narrow temperature range (40-60°C) irrespective of the form of the culture. Materials in the second group have a considerably higher thermal stability and a lower rate of inactivation. Thus, in the case considered of short-term heating, the maximum permissible temperature, at which B = 100%, for the first group does not exceed 40-45°C, for spore-forming and antibiotics it is 90-100°C, and for amino acids it is 150°C.

To classify microbiological materials from the point of view of temperature stability we propose the following characteristics:

TABLE 1. Rate Constants and Inactivation Energy of Microbe Biomass

Object	$K \cdot 10^2$, sec^{-1}	E, kJ/mole	K_0, sec^{-1}
Spore-forming bacterial forms (Bac. thuringiensis, Bac. subtilis etc.). Temperature range 80—190°C	0,8—6,2	29,4	30
Vegetative bacterial cultures (Az. chroococcum, Rhizobium pisum, etc.). Temperature range 40—55°C	0,2—10	310	$1 \cdot 10^{48}$
Products of microbiosynthesis (antibiotics – grysine and bacitracine; amino acids – lysine). Temperature range 90-200°C	0,3—0,9	15	0,5—0,6

a) the rate constant of the inactivation process characterizing the kinetics of thermal destruction of the bacteria or disintegration of the biopolymer molecule:

$$K = -\frac{dB/d\tau}{B}. \tag{3}$$

It should be noted that the value of K is only constant over a small range of heating exposures ($\tau \leqslant 60$ sec);

b) the inactivation energy, by the action of which an irreversible change in the material begins to occur (denaturation of albumen, inactivation of enzymes, etc.);

c) the coefficient K_0 characterizing the state of a given object, the presence of labile centers, and their degree of susceptibility to thermal action, i.e., essentially a numerical factor of the nature of the material.

The dependence of the constant of the inactivation process on the nature of the object being investigated and on the temperature, as in chemical kinetics, can be described by Arrhenius's equation

$$K = K_0 \exp(-E/RT). \tag{4}$$

Numerical values of the thermal-stability factors of microbiological materials are given in Table 1.

An increase in the exposure to heat naturally reduces the maximum permissible temperature which enables one to obtain a specified value of the survivability (Fig. 3). A generalization of the experimental data over the whole temperature and time range investigated enabled us to derive a single empirical relationship B = f(t, τ) in the form of a polynomial

$$B = at + b\tau^2 + c\tau + d, \tag{5}$$

where a, b, c, and d are empirical coefficients which depend on the nature of the microbiological material.

From relation (5) one can determine the maximum permissible temperature to which the material can be heated during drying, i.e., the form of thermal processing for which a certain specified survivability of the microbiomass can be preserved:

$$t = \frac{1}{a}(B - b\tau^2 - c\tau - d). \tag{6}$$

The values of the empirical coefficients in relations (5) and (6) are given in Table 2.

TABLE 2. Values of the Empirical Coefficients from Relations (5) and (6)

Object	a	$b \cdot 10^2$	c	d
Spore-forming bacterial forms	—0,3	0,8	—0,9	140
Antibiotics	—0,8	—0,5	—0,4	210
Vegetative cultures	—3,8	0,4	—0,8	290

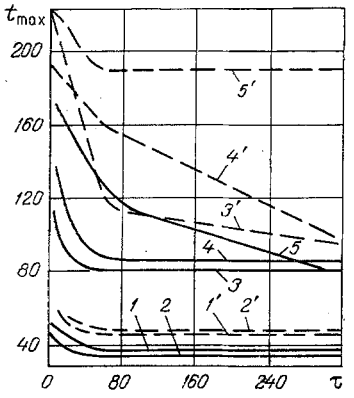

Fig. 3

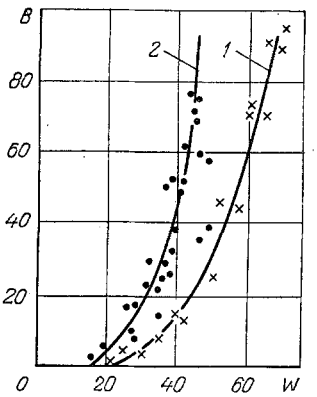

Fig. 4

Fig. 3. Maximum permissible temperature of thermal processing as a function of the exposure to heat: 1, 2) vegetative cultures; 3) spore-forming culture; 4) antibiotic bacitracine; 5) amino acid lysine (1-5 — B = 100%, 1'-5' — 50%). τ, sec.

Fig. 4. Effect of initial moisture content and dehydration intensity on the survivability of the culture *Rhizobium pisum*: 1) W = 70%, 2) 45%.

The thermal processing procedure, as is well known, is characterized not only by the temperature but also by the rate of heating or cooling of the material being processed. However, in this case, as results of a number of experiments carried out with the most thermally sensitive vegetative cultures (*Rhizobium pisum*, *Lactobacterium* plantarum) have shown, a reduction in the intensity of heating and cooling from 50-55 deg/sec to 0.01-0.02 deg/sec has practically no effect on the survivability of microorganisms.

The effect of the rate of dehydration on the quality of the final product of the first group of microbiological materials is quite different. A reduction in $dW/d\tau$ can be achieved by reducing the initial moisture content of the dried biomass by preliminary mixing with sorbent in certain specified ratios. Drying is carried out in the fluidized bed of the sorbent in a temperature mode chosen taking the thermal sensitivity of the bacteria into account, and the temperature of the layer did not exceed 40-45°C. A reduction in the initial moisture content of the biomass from 70% to 45% and subsequent thermal drying of the material to the critical moisture content (40%) enable one to preserve 50-60% of the viable cells (Fig. 4, curve 2), whereas thermal drying without preliminary sorption dehydration worsens the quality of the preparation by a factor of 3.5-4 (B = 15-18%, Fig. 4, curve 1). The rate of dehydration is 4% and 1% per minute, respectively. A reduction in the intensity of the drying of the more moisture-stable culture *Salmonella enteritidis* by a factor of 1.5 enables one to increase the number of living bacterial cells in the final product by a factor of 5. Consequently, a rapid removal of the moisture of a microbiomass has a bad effect on the integrity of a bacterial cell, and hence obviously for the first group of micropreparations it is inadvisable to use very intense methods of dehydration, e.g., spray drying, which contradicts the present methods employed to obtain dry bacterial materials most often used at the present time.

One of the necessary stages in developing material dehydration technology having extremely unstable technological criteria is monitoring their change after the drying process is completed. The logical need for such an investigation is due to the fact that comparatively high quality factors of a dried material obtained directly after traditional methods of dehydration fall sharply after fairly short storage. As an example, Table 3 shows the changes in the survivability of bacterial cultures with time. It should be noted that micromaterials belonging to the first group, viz., moisture-labile materials, possess this capability. Materials of the second group (spore-forming cultures and the products of microbe synthesis) with a low residual moisture content preserve their quality unchanged over a fairly long period of time. The presence of a certain range of moisture contents corresponding to a reduction in the survivability of the cells can be explained by the relaxation of intercell and inner-cell moisture by diffuse moisture transfer, and also by the individual features of

TABLE 3. Change in the Survivability of Vegetative Bacterial Cultures with Time, %

Object	Drying and storage conditions	Storage duration, days								
		Directly after drying	1	2	3	4	5	10	20	60
Lactic acid preparations:	Contact-sorption mass transfer,									
Lactobacterium plantarum	t=20°C W=20%	11,7	8,3	0,63	0,5	0,5	0,4	—	—	—
	t=20°C W=30%	21,6	6,2	6,2	5,1	4,6	4,4	—	—	—
	t=20°C W=40%	100,0	96,2	94,1	93,8	93,6	93,6	93,6	68,9	45,5
Lactobacterium acidophilum	t=40°C W=40%	85,4	58,9	15,8	—	—	—	—	—	—
	t=40°C W=60%	100,0	76,9	47,1	—	—	—	—	—	—
	t=50°C W=40%	20,1	0,01	—	—	—	—	—	—	—
	t=50°C W=60%	29,9	0,02	—	—	—	—	—	—	—
Ethanol-assimilating cultures:	Sublimation and storage in ampules at 5°C									
Akinetic bacteria grade 154		39,0	—	—	—	—	—	1,4	0,2	0,1
grade I72		30,8	—	—	—	—	—	0,7	0,45	0,01

the living organisms (the phase of development and structural-morphological characteristics).

The complexity and interrelationship of the effect of different factors on the technological criteria characterizing the objects considered make it necessary to study each factor separately. An analysis of the results obtained shows that there is no need to derive unique empirical relations describing the change in the technological criteria as a function of the thermal parameters of the dehydration process. In this situation only a multiplan analysis of the experimental data and an estimate of the specific facts enable one to justify the choice of the optimum procedure, which in turn determines the method of dehydration and the constructional form of the technology [12]. Thus, for microbiological materials of the first group (in our proposed classification) the dehydration procedure should be as follows:

1) determination of the value of the critical moisture content;

2) determination of the maximum permissible heating temperature taking into account the exposure characteristic for the dehydration methods which ensure the possibility of controlling the final moisture content of the material (pseudoliquefaction layer, sublimation, contact-sorption drying [14-16]);

3) determination of the sorption and thermodynamic characteristics of the moist material and the possible sorbents, which, according to the technology, are an inseparable part of the finished product (milled peat, wheat bran, etc.);

4) constructional development enabling the above technology to be achieved effectively.

For microbiological materials of the second group (antibiotics, amino acids, means of protecting plants, etc.) the most effective is spray drying, which satisfies the increasing scales of production. In this connection the problem of developing optimum modifications of this method taking into account physical properties of thermolabile microbiological materials is an extremely pressing problem [17, 18].

NOTATION

N_0, N, qualitative characteristics of the object (e.g., the number of viable microbe cells) before and after inactivation respectively; τ, time, sec; t, T, temperature, °C K; R, gas constant; G_1, G_2, absolutely dry mass of material, sorbent; $\Delta u = u_i - u_f$, difference in moisture content; u_i, u_f, initial and final moisture content; c_{m_1}, c_{m_2}, specific mass capacity of the material and sorbent; W, moisture.

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DEFORMATIONS OF THE SOLID PHASE OF DISPERSED SYSTEMS UNDER THE INFLUENCE OF ADSORBED WATER AND ORGANIC COMPOUNDS

P. P. Olodovskii and L. A. Malkova

UDC 541.182

Diffractometric data are used for determining the variation of the volume of the crystal lattice of kaolinite under the simultaneous adsorption of water and organic compounds.

The effect of adsorbed water alone on the variation of the parameters and volume of the crystal lattice of kaolinite was studied in [1]. In what follows, we present the results of further investigations. The techniques and methods of measurement remained essentially the same. We used the method of x-ray diffractometry with a DRON-2.0. All the experimental results are shown in Fig. 1, from which it can be seen that the volume of an elementary cell of kaolinite expands during the hydration process. It should be noted that this expansion is determined by the structure of the organic-compound molecules. This phenomenon can be explained by the following.

Calculation of the Deformations of the Crystal Lattice of Kaolinite. On the basis of [2], for deformations which vary only slightly within the limits of some constants of the lattice, the change in volume can be represented as

$$\frac{\Delta V}{V} = \frac{\Delta E_F}{E_F}, \qquad (1)$$

where E_F is the Fermi energy of the crystal lattice.

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