

APPLICATION OF THE SIMILARITY METHOD TO
A STUDY OF HYGROTHERMAL EQUILIBRIUM IN
CAPILLARY-POROUS COLLOIDAL MATERIALS

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UDC 620.193.19.001.5

A method is shown of constructing a universal sorption (desorption) isotherm for hygroscopically similar capillary-porous materials. It is shown to be feasible to ascertain the similarity of hygroscopic properties on the basis of a limited number of test points.

Hygrothermal equilibrium in materials can be quantitatively characterized by the specific moisture content u [1], the dependence of which on the temperature t and the relative air humidity φ can be determined from test data. As we know, the thermodynamic properties of substances are often analyzed by the similarity method, by which certain parameters of new test materials can be calculated and the amount of testing can thus be reduced [2].

The authors will discuss here certain aspects of calculating the moisture content by the similarity method, namely in capillary-porous materials of plant origin: wood, jute, cereals, and various garden crops.

Similar hygroscopic materials will be called materials whose equilibrium moisture contents, within the similarity range at equal t and φ , satisfy the following relation

$$\frac{u_{1;\varphi_i;t_j}}{u_{2;\varphi_i;t_j}} = \text{const.} \quad (1)$$

Hygroscopic similarity is found, above all, between materials of a not very different physicochemical constitution [3, 4].

In order to average out the many test data and to construct the universal sorption (desorption) isotherm for hygroscopically similar substances, we propose to introduce a dimensionless parameter: the referred moisture content

$$w = \frac{u}{u_{0S}}, \quad (2)$$

where u_{0S} denotes the equilibrium moisture content at $\varphi = 100\%$ and $t = 0^\circ\text{C}$. It follows from (1) and (2) that the value of w should be the same for hygroscopically similar materials at the same equilibrium air humidity and that any individual differences of moisture content u in real materials are accounted for by u_{0S} .

In order to compile tables of equilibrium moisture contents [5] or to derive the equations of sorption (desorption) isotherms [6, 7], one often constructs average isotherms $u = u(\varphi)$ on the basis of many test data for a given kind of material without taking into account individual internal differences. One assumes either that the internal differences do not exceed the limits of test accuracy or that they do not have a significant effect on the final results. The internal differences in terms of moisture content can be estimated from the ratio $u_{\text{max}}/u_{\text{min}}$, both at the same t and φ . Our calculations have shown that this ratio is equal to 2.9 for wood fiber, 1.3 for rice, 1.15 for coffee, and 1.45 for sunflower seeds. With such a scatter of u values, a construction of the universal isotherm $w = w(\varphi)$ ensures that the trend of the sought relation

Institute of Maritime Engineers, Odessa. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 26, No. 4, pp. 673-677, April, 1974. Original article submitted July 5, 1973.

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TABLE 1. Universal Referred Desorption Isotherm for Vegetable Seeds, $t = 20^{\circ}\text{C}$

$\varphi, \%$	Watermelon		Tomatoes				Cucumbers			w for the universal referred isotherm
	$u_{\text{test}}, \%$	$\frac{u_{\text{test}}}{w_{\text{std}} = 30,02}$	$u_{\text{test}}, \%$	u_{test}	w_{std}	$\frac{u_{\text{test}}}{w_{\text{test}} = 33,58}$	$u_{\text{test}}, \%$	$\frac{w_{\text{std}}}{w_{\text{test}}}$	$\frac{u_{\text{test}}}{w_{\text{test}} = 30,66}$	
10	3,00	0,0999	4,05	40,54	0,1206	3,42	34,23	0,1115	0,1110	
20	4,44	0,1479	5,22	35,29	0,1554	4,85	32,79	0,1581	0,1538	
30	5,45	0,1815	6,18	34,05	0,1840	5,68	31,29	0,1852	0,1835	
40	6,42	0,2138	7,16	33,49	0,2132	6,63	31,01	0,2162	0,2144	
50	7,36	0,2452	8,20	33,44	0,2442	7,46	30,42	0,2433	0,2445	
60	8,40	0,2798	9,23	32,99	0,2749	8,38	29,95	0,2701	0,2750	
70	9,74	0,3244	10,75	33,14	0,3201	9,51	29,32	0,3102	0,3181	
80	11,57	0,3854	12,78	33,16	0,3806	11,13	28,87	0,3630	0,3764	
90	15,41	0,5133	16,96	33,04	0,5051	14,12	27,51	0,4605	0,4935	
100	30,02	1,0000	37,98	—	—	27,04	—	—	1,0000	
				$u_{20,s} = 33,58$			$u_{20,s} = 30,66$			

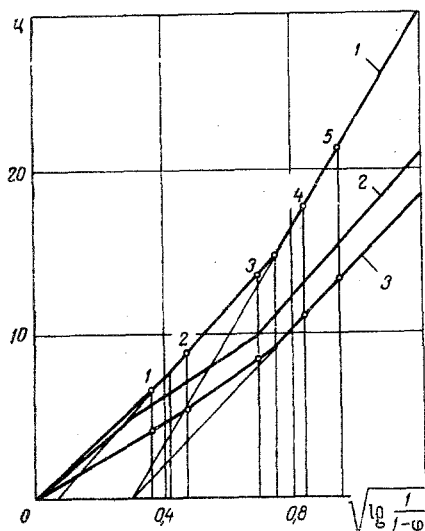


Fig. 1. Isotherms for capillary-porous colloidal materials: 1 and 3) sorption isotherms for hygroscopically similar jute and cotton; 2) desorption isotherm for tomato seeds; moisture content u (kg moisture per kg dry mass, %), temperature $t = 20^{\circ}\text{C}$.

here the value of u_s at $t = 20^{\circ}\text{C}$ without affecting the validity of the method within the given range of the universal isotherm for some fixed temperature. In this case, when a family of universal isotherms for various temperatures is to be constructed, it may be worthwhile to use u_s at $t = 0^{\circ}\text{C}$ in the denominator.

The resulting referred base isotherm is then used for refining the values of $u_{20,s}$ for other seeds. As is well known, an exact determination of u at $\varphi = 100\%$ is difficult and, according to G. A. Egorov [6], even impossible in the case of such materials as grains and seeds. For this reason, the values of u_s obtained by extrapolation, in most cases, are only rough. In order to eliminate the effect of errors in estimating $u_{20,s}$ on the subsequent calculations, in our method $u_{20,s}$ for the basic material is taken from reference sources, as in the case of watermelon seeds, or is calculated from available empirical equations [1, 6]. The values of $u_{20,s}$ for other materials in the test group are determined from the basic isotherm according to the formula

$$u_{0s} = \sqrt{\frac{1}{n} \sum \left(\frac{u_{\text{test}}}{w_{\text{std}}} \right)^2}, \quad (3)$$

where n denotes the number of test points.

will be more correctly represented, will help to reveal random deviations in individual tests, also that such a curve and the test data will supplement one another so as to make it feasible to extend the range of humidity variation.

The reasons for using the maximum hygroscopic moisture content in the denominator of (2) relate to the concepts on the basis of which A. V. Lykov has adopted this quantity and constructed with it an experimental scale for the moisture-transport potential [1]. The first grid of universal w -values was calculated for the 30-100% range of humidity φ and the -40 to $+40^{\circ}\text{C}$ range of temperature t , on the basis of test data for wood with a density varying from 300 to 700 kg/m^3 [8]. These data were used for plotting the curve for wood fibers [9]. Calculations have confirmed the similarity of hygroscopic properties in the case of wood with varying density over the test range of t and φ . The mean-squared relative error at all test points did not exceed 1%. Analogous w -grids were also plotted for rice, coffee, sunflower seeds, and several other capillary-porous colloidal materials.

We will now discuss the procedure for constructing the universal referred isotherm for the seeds of some vegetables with a known moisture content at $t = 20^{\circ}\text{C}$, according to the measurements by A. I. Chuprin [10]. Among the seeds which he has studied, we select watermelon seeds as the basic standard material, and with $u_{20,s} = 30.02\%$ we calculate w_{std} (see Table 1, column 3). It is to be noted that, in view of the lack of data on the maximum hygroscopic moisture content at $t = 0^{\circ}\text{C}$, we use

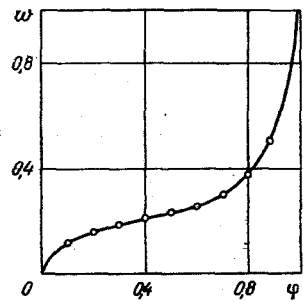


Fig. 2. Comparison between test data on the equilibrium moisture content of carrot seeds [10] and the universal referred desorption isotherms for vegetable seeds at $t = 20^{\circ}\text{C}$. The points represent test values.

A preliminary analysis of measured isotherms [10] has shown that tomato and cucumber seeds are closest to watermelon seeds in terms of hygroscopic properties. Calculated values pertaining to the construction of the universal referred desorption isotherm ($t = 20^{\circ}\text{C}$) for watermelon, tomatoes, and cucumbers are given in Table 1. Having determined the values of $u_{20,S}$ for cucumber and tomato seeds, we calculate w_{test} (columns 6 and 9) with the aid of formula (2). From w_{std} values for watermelon and w_{test} values for tomatoes and cucumbers, furthermore, we determine the numerical values of the referred moisture content (column 10).

The mean-squared relative deviation of all reliable u_{test} values from those calculated on the basis of the universal referred isotherm is 2.3% for watermelon, 1% for tomatoes, and 2% for cucumbers. The similarity of hygroscopic properties, in the case of these seeds, is confirmed also by analogous calculations made on the basis of the test data in [11] and [12].

The universal referred isotherm can be used for calculating the equilibrium moisture content in a new material which belongs to a given group of hygroscopically similar ones, and for doing this on the basis of just the one test point from which u_{0S} has been calculated according to formula (3). This, then, is the basic practical advantage of the proposed method.

Important aspects of the similarity method are the classification of materials into groups of hygroscopically similar ones, that it pinpoints the similarity criterion, and that it establishes a relation between u_{0S} and the physicochemical constitution parameters which affect the hygroscopic properties. Unfortunately, in most cases the researchers have not paid enough attention to this problem, making it difficult to elaborate these aspects of the similarity method on the basis of available test data.

The analysis in [7] has shown that the isotherm for capillary-porous colloidal materials in u , $[\log 1/(1-\varphi)]^{1/2}$ coordinates, can be accurately enough approximated by three straight lines with different slopes.

The relative position of the sorption isotherms for two hygroscopically similar materials, namely jute and cotton, is shown in Fig. 1. It follows from the geometrical concepts that a similarity of hygroscopic properties is maintained along the entire isotherm, if

$$\frac{u_{g1}}{u_{x1}} = \frac{u_{g2}}{u_{x2}} = \frac{u_{g3}}{u_{x3}} = \frac{u_{g4}}{u_{x4}} = \frac{u_{g5}}{u_{x5}} \quad (4)$$

Consequently, in order to ascertain whether a new material is similar to an already known one whose complete isotherm is available, it suffices to measure the equilibrium moisture content at five values of φ selected so that one point will lie on the initial segment of the isotherm and two each on the second and third segments. In this case, when a comparison is made with the universal referred isotherm $w = w(\varphi)$, it is necessary to use the relation

$$\frac{u_{\text{test}1}}{w_1} = \frac{u_{\text{test}2}}{w_2} = \frac{u_{\text{test}3}}{w_3} = \frac{u_{\text{test}4}}{w_4} = \frac{u_{\text{test}5}}{w_5} = u_{0S} \quad (5)$$

Calculations according to Eq. (5) were made for carrot seeds [10]. From the test data in [10] and guided by the graph in Fig. 1, we took the values of u_{test} corresponding to $\varphi = 10, 20, 60, 80$, and 90% . The calculations have shown that equality (5) is valid and that $u_{20,S} = 33.28\%$. Consequently, carrot seeds are hygroscopically similar to watermelon, tomato, and cucumber seeds. This conclusion is supported by the data in Fig. 2, where the position of all test points converted according to the formula $w_{\text{test}} = u_{\text{test}}/33.28$, is shown relative to the universal referred desorption isotherm.

This study has demonstrated the advantages of using the similarity method for an analysis of hygrothermodynamic equilibrium in capillary-porous colloidal materials.

NOTATION

u	is the specific moisture content, kg moisture per kg dry mass, %;
t	is the temperature, °C;
φ	is the relative air humidity, %;
w	is the referred moisture content;
u_s	is the maximum hygroscopic moisture content;
u_{0s}	is the maximum hygroscopic moisture content at $t = 0^\circ\text{C}$;
$u_{20,s}$	is the maximum hygroscopic moisture content at $t = 20^\circ\text{C}$.

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