A CALORIMETRIC METHOD OF MEASURING LOW WATER CONTENTS IN WATER-SOLUBLE POWDERS

A. E. Sogin, V. L. Tatievskii,
M. V. Venediktov, and N. M. Rudnyi

UDC 53.093.083

The theory is considered for the calorimetric method of [2]. Experimental and theoretical derivations are given for the temperature of the material as a function of time in terms of the initial water content when the pressure is released. A description is given of the device for determining small water contents in water-soluble powders.

It is often necessary to monitor small (~0.02 kg/kg) and very small (~0.003 kg/kg) water contents in the production of powder materials; gravimetric, chemical, and electrical methods of moisture determination are largely unsuitable for this purpose [1].

If a thin layer of the moist material is placed in a closed volume and this is evacuated, one gets rapid evaporation of water from the material, which is accompanied by absorption of heat, which is absorbed to overcome the interaction of the water molecules with those of the material (r_W) and for a phase transition of this water (r) [3]. This leads to a sharp fall in the temperature of the specimen. The temperature rises again by heat transfer with the surroundings, so the temperature-variation curve has a pronounced minimum, whose depth is proportional to the initial water content u_0.

As u_0 and the thickness of the layer are small, while the pressure reduction is rapid, the temperature minimum is reached in 20-50 sec and may be 3-4°C.

These statements can be demonstrated by considering the heat and mass transfer within the moist material on pressure release. These processes are of complex character, and so there are considerable difficulties in exact solution [4]; however, the basic laws may be derived as a first approximation via the equations for the heat balance.

In Part I we consider a simplified solution, while in Part II we consider the more complete solution, and in the concluding section we analyze and compare the results.

I. An unbounded layer of material is exposed to vacuum; the thickness of the material is about $2 \cdot 10^{-3}$ m, so that the temperature distribution in the layer is neglected. The heat transfer with the environment is subject to Newton's law $\alpha_t(t_c - t_s)$, while the temperature of the specimen is measured during the initial pressures at reduction; in this time the temperature variation and change in water content are small, and therefore α_t may be considered as constant. The loss of water from the specimen is described in terms of a continuously distributed negative heat source.

The following is [5, 6] the differential equation for the heat balance:

$$q_u + \alpha_t (t_c - t_s) - \lambda (\nabla t)_n = c\gamma R_v \frac{\partial t}{\partial \tau} + \alpha' (P_s - P_c) r \frac{P_0}{P}, \tag{1}$$

where q_u, $\alpha_t(t_c - t_s)$, $-\lambda(\nabla t)_n$ are respectively the heat fluxes due to radiative heat transfer, convection, and thermal conduction. The heat received by the body goes to heat the material $c\gamma R_v(\partial \bar{t}/\partial \tau)$ and to evaporate water $\alpha'(CP_s - P_c)r(P_0/P)$ (internal negative heat source).

If appropriate measurement conditions are used, q_u and $\lambda(\nabla t)_n$ may be made zero and (1) may be simplified; (1) becomes

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 20, No. 1, pp. 105-113, January, 1971. Original article submitted October 16, 1969.

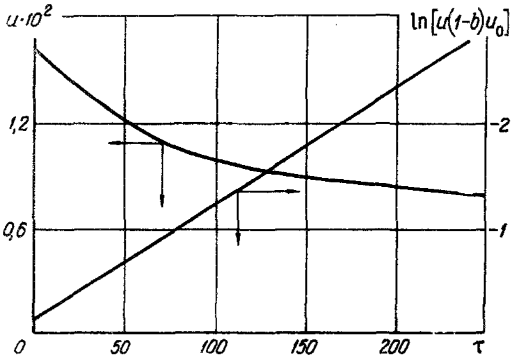

Fig. 1

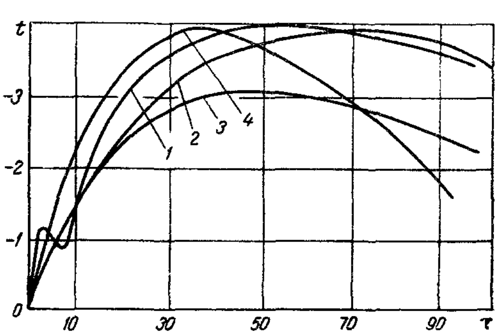

Fig. 2

Fig. 1. Moisture drift u(kg/kg) versus time τ (sec) at pressure drop for NH_4NO_3.

Fig. 2. Temperature material t(°C) versus time τ (sec): 1) experimental curve at $R_V = 3 \cdot 10^{-3}$ m; 2) calculation from (17) at $R_V = 4 \cdot 10^{-3}$ m; 3) calculation from (17) at $R_V = 2 \cdot 10^{-3}$ m; 4) calculation from (6) at $R_V = 2 \cdot 10^{-3}$ m.

$$\alpha_t (t_c - t_s) = c\gamma R_V \frac{\partial t}{\partial \tau} + \alpha' (P_s - P_c) r \frac{P_0}{P} . \tag{2}$$

The coefficient α_t for the materials may be found from published sources [7] or determined by independent experiment [8], e.g., for ammonium nitrate with 0.003-0.02 kg/kg the α_t is 58.0 W/m²·deg. The second term on the right in (2) takes account of the phase transition of the water and may be put as

$$\alpha' (P_s - P_c) r \frac{P_0}{P} = r\gamma R_v \frac{\partial \bar{u}}{\partial \tau} . \tag{3}$$

Equation (2) finally becomes

$$\alpha_t (t_c - t_s) = c\gamma R_v \frac{\partial \bar{t}}{\partial \tau} + r\gamma R_v \frac{\partial \bar{u}}{\partial \tau} . \tag{4}$$

To integrate (4) we need to know $u = u(\tau)$, which has been determined in our measurements; a cell containing the moist material was suspended on a sensitive strain gage system having special temperature-compensating devices, and the readings of the strain gages were recorded with an ÉPP-09 potentiometric recorder. The response for a load of $5 \cdot 10^{-3}$ kg was $1.5 \cdot 10^{-3}$ m/kg. We found that the change in water content on reducing the pressure is described quite accurately by an exponential law:

$$u(\tau) = u_0 (1 - b) + b u_0 \exp(-\alpha_p \tau), \tag{5}$$

where b and α_p are coefficients to be determined by experiment. We substitute (5) into (4) and integrate with zero initial conditions to get

$$\begin{aligned} t(\tau) &= -u_0 \frac{rb\alpha_p}{c\left(\frac{\alpha_t \cdot}{R_v c\gamma} - \alpha_p\right)} \left[\exp(-\alpha_p \tau) - \exp\left(-\frac{\alpha_t}{R_v c\gamma} \tau\right)\right] \\ &= -u_0 \frac{rb}{c} \exp(-\mathrm{Pd}\,\mathrm{Fo}) \frac{(\alpha_p R_v c\gamma - 1)}{\alpha_t} \left[1 - \exp\left(\mathrm{Pd} - \frac{\alpha_t R_v}{ac\gamma}\right) \mathrm{Fo}\right] . \end{aligned} \tag{6}$$

It follows from (5) that not all the water is removed from the material on a reasonably prolonged evacuation, which may be explained because the rapid evaporation from the surface produces a crust of dry material which prevents evaporation from the deeper layers.

The observed $t(\tau)$ on pressure release is shown by Fig. 1 to agree closely with the theoretical relationship of (6); in the calculations we used the measured α_p and b, which for ammonium nitrate are 0.034 sec^{-1} and 0.45 respectively.

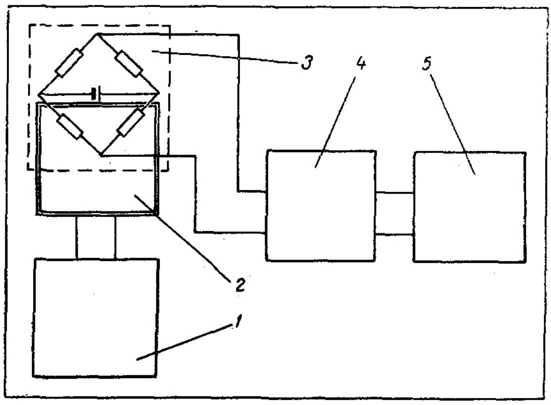

Fig. 3. Block diagram of measuring device: 1) preliminary vacuum pump; 2) vacuum chamber; 3) dc bridge; 4) dc accelerator; 5) registering device ÉPP-09.

The curve of (6) has a turning point at

$$\tau_{\max} = \frac{1}{\alpha_p - \dfrac{\alpha_t}{R_v c\gamma}} \ln \frac{\alpha_p R_v c\gamma}{\alpha_t} . \tag{7}$$

II. An unbounded layer of moist material is 6-8 · 10^{-3} m thick or more. In this case we have to take account of the temperature distribution within the material.

The differential equation for the heat balance in dimensionless form is [9]

$$\frac{\partial T(X,\ \mathrm{Fo})}{\partial \mathrm{Fo}} = \frac{\partial^2 T(X,\ \mathrm{Fo})}{\partial X^2} - u_0 \frac{r\alpha_p b R_v^2}{c(t_c - t_0)} \exp(-\mathrm{Pd}\,\mathrm{Fo}), \tag{8}$$

where

$$T(X,\ \mathrm{Fo}) = \frac{t(X,\ \mathrm{Fo}) - t_0}{t_c - t_0} . \tag{9}$$

The initial conditions are

$$T(X,\ 0) = 0, \tag{10}$$

and the boundary conditions are

$$-\frac{\partial T(1,\ \mathrm{Fo})}{\partial X} + \mathrm{Bi}\,[1 - T(1,\ \mathrm{Fo})] = 0, \tag{11}$$

$$\frac{\partial T(0,\ \mathrm{Fo})}{\partial X} = 0, \text{where } \mathrm{Bi} = \frac{\alpha_t R_v}{\lambda} . \tag{12}$$

The solution to (8) subject to (10) and (11) is

$$T(X,\ \mathrm{Fo}) = \frac{t(X,\ \mathrm{Fo}) - t_0}{t_c - t_0} = -u_0 \frac{rba}{c} \left[\left(1 - \frac{\cos\sqrt{\mathrm{Pd}}\,X}{\cos\sqrt{\mathrm{Pd}} - \dfrac{1}{\mathrm{Bi}}\sqrt{\mathrm{Pd}}\sin\sqrt{\mathrm{Pd}}} \right) \exp(-\mathrm{Pd}\,\mathrm{Fo}) \right.$$

$$\left. - \sum_{n=1}^{\infty} \frac{\mathrm{Pd}}{\mathrm{Pd} - \mu_n^2} A_n \cos\mu_n \exp(-\mu_n^2\,\mathrm{Fo}) \right] + \left[1 - \sum_{n=1}^{\infty} A_n \cos\mu_n X \exp(-\mu_n^2\,\mathrm{Fo}) \right], \tag{13}$$

where

$$A_n = \frac{2\sin\mu_n}{\mu_n + \sin\mu_n \cos\mu_n} ;$$

$$\mu_n \text{ are the roots of } \operatorname{ctg}\mu = \frac{1}{\mathrm{Bi}}\mu. \tag{14}$$

The change in the temperature at the middle of the layer (X = 0) is

$$t(0,\ \mathrm{Fo}) - t_0 = -u_0\,\frac{rab}{c}\left[\left(1 - \frac{1}{\cos\sqrt{\mathrm{Pd}} - \frac{1}{\mathrm{Bi}}\sqrt{\mathrm{Pd}}\sin\sqrt{\mathrm{Pd}}}\right)\exp(-\mathrm{Pd}\,\mathrm{Fo}) - \sum_{n=1}^{\infty}\frac{\mathrm{Pd}}{\mathrm{Pd}-\mu_n^2}\exp(-\mu_n^2\,\mathrm{Fo})\right] + (t_c - t_0)\left[1 - \sum_{n=1}^{\infty}A_n\exp(-\mu_n^2\,\mathrm{Fo})\right]. \tag{15}$$

We see from (15) that the first term is proportional to the initial water content and the second to the temperature difference ($t_c - t_0$); if these temperatures are equal ($t_c = t_0$), the second term becomes zero, and therefore the temperature at the middle of the layer is dependent only on the initial water content.

The latter assertion is correct also for $t_c \neq t_0$, but in that case one must place within the vacuum chamber a second (compensating) cell containing the dry material and measure its temperature on reducing the pressure, as we now show.

Consider the temperature change at the middle of the layer of dry material (compensation cell). The heat balance equation (8) in this case will not contain a second term on the right, since there is no internal heat source; then the solution to (15) with the same initial and boundary conditions of (10) and (11) is

$$t_{\mathrm{dry}}(0,\ \mathrm{Fo}) - t_0 = (t_c - t_0)\left[1 - \sum_{n=1}^{\infty}A_n\exp(-\mu_n^2\,\mathrm{Fo})\right]. \tag{16}$$

If we subtract (16) from (15) we get on the right only a term dependent on the initial water content; the final solution is

$$t(0,\ \mathrm{Fo}) - t_0 = -u_0\,\frac{rba}{c}\left[\left(1 - \frac{1}{\cos\sqrt{\mathrm{Pd}} - \frac{1}{\mathrm{Bi}}\sqrt{\mathrm{Pd}}\sin\sqrt{\mathrm{Pd}}}\right)\exp(-\mathrm{Pd}\,\mathrm{Fo}) - \sum_{n=1}^{\infty}\frac{\mathrm{Pd}}{\mathrm{Pd}-\mu_n^2}\exp(-\mu_n^2\,\mathrm{Fo})\right]$$

$$= -u_0\,\frac{rb}{c}\exp(-\mathrm{Pd}\,\mathrm{Fo})\left[\frac{a\left(\mathrm{Bi}\cos\sqrt{\mathrm{Pd}} - \sqrt{\mathrm{Pd}}\sin\sqrt{\mathrm{Pd}} - \mathrm{Bi}\right)}{\mathrm{Bi}\cos\sqrt{\mathrm{Pd}} - \sqrt{\mathrm{Pd}}\sin\sqrt{\mathrm{Pd}}} - \sum_{n=1}^{\infty}\frac{a\,\mathrm{Pd}}{\mathrm{Pd}-\mu_n^2}\exp(\mathrm{Pd}-\mu_n^2)\,\mathrm{Fo}\right]. \tag{17}$$

Equation (17) contains an infinite series, but it is convenient for practical use, because even for Bi = 1 (in practice, Bi ≪ 1) the series can be restricted to four terms. We see on comparing (6) and (17) that they are the same general type; Figure 2 compares (6) and (17) with experiment.

Solutions to (16) form the basis of a method of determining small water contents. The water content is measured by recording the maximum temperature difference between two transducers filled with the moist and dry materials when the pressure is reduced; it follows from (6) and experiment that this difference is proportional to the initial water content, but is independent of the density of the material and the thickness of the layer, as well as of any presence of water-soluble chemical compounds and the initial temperature.

The time taken by a single measurement is 20-25 sec. The method is of good accuracy and it can be recommended for rapid analysis, as well as for direct measurements in a flow system.

This method is the basis of our device for measuring small water contents (Fig. 3), which consists of a transducer, a measurement circuit, a recording system, and a rotary vacuum pump. The pressure is reduced by the pump, and the two transducers are lucite cells of size 0.06 × 0.06 × 0.004 m, to the bottom of which are attached resistance thermometers and which are suspended within the vacuum chamber. The resistance change in the material is

$$\Delta R = R_0\beta\,[t(0,\ \mathrm{Fo}) - t_0]. \tag{18}$$

The two sensing elements are connected in opposite arms of a dc bridge working near balance. The out-of-balance voltage passes to a dc amplifier employing an F 117 photoelectric amplifier and thence to an ÉPP-09 recorder.

The output voltage is [10]

$$\Delta U(\mathrm{Fo}) = \frac{E_0}{z_{\mathrm{red.}}}R\,\Delta R(\mathrm{Fo}) = \beta E_0\,\frac{R_0}{z_{\mathrm{red.}}}[t(0,\ \mathrm{Fo}) - t_0]. \tag{19}$$

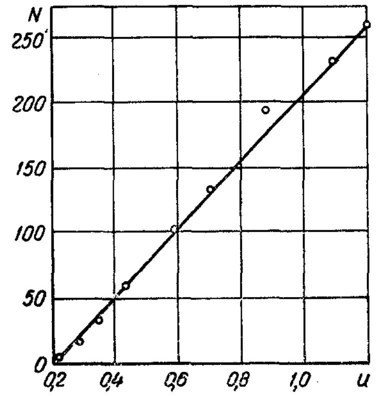

Fig. 4. Grading curve for NH_4NO_3.

This shows that the output voltage is proportional to the supply voltage, but this does not lead to an error, because: 1) the supply may be taken from a KBS stabilized power supply; 2) the time of measurement is so small that E_0 does not have a chance to vary; 3) one can adjust E_0.

The device can work with one sensing element (the dc bridge contains only the thermometer attached to the moist material) or with two sensing elements (as described above). The latter mode of connection eliminates transients arising in the chamber that are unrelated to the humidity of the material (this makes it possible to get a zero temperature change for $u = 0$), and it also eliminates the bridge unbalance due to $(t_c - t_0)$. As the dry material one can use either previously dried material with $u \cong 0$ or material that has been dried for 5-10 min in a vacuum chamber $u_{res} \neq 0$ (in the latter case, since the residual water is not removed, it behaves like the dry material on pressure reduction).

We see from (19) that in the nearly balanced state and with r = constant (heat of evaporation constant throughout the range of water contents) the out-of-balance voltage is linear in ΔR, and consequently in the initial water content.

Now we consider the main source of error in this device. This comes from the error of converting the water content to a temperature difference, because current measuring techniques enable one to record the temperature very accurately.

The instrument was calibrated by preparing specimens of material (granulated NH_4NO_3) with water contents of 0-1.2% by steps of 0.1%, which were kept for over three months at a constant temperature to obtain a uniform water distribution in the material, which for this purpose was periodically stirred. As a check method we used the State Standard (No. 2-65) for drying.

The water content of each prepared sample was measured 20-25 times with the apparatus: in all we made more than 200 measurements.

Figure 4 shows the relationship between the water content as determined by drying and the mathematically expected values read from the scale of the device; the relationship is close to linear, and the parameters may be determined by least squares [11]. The result is $N = 260u - 51$.

The soundest measure of the error is the entropy error calculated from the information theory principle; this is given by [12]:

$$\Delta = \frac{n}{10^{\frac{1}{n}\sum_{=1}^{n} n_i \lg n_i}} \cdot \frac{d}{2} = \pm 17.0 \text{ mm}. \tag{20}$$

Then the relative error of conversion is

$$\delta_{tr} = \frac{\Delta}{X_{sc}} = \frac{17.0}{270.0} = 6.3\,\%.$$

The total error of the device, incorporating the temperature-measurement error (~1%) is

$$\delta_{dev} = \sqrt{\delta_{tr}^2 + \delta_{meas}^2} = 6.4\,\%.$$

The time for one measurement is 20-30 sec.

NOTATION

u	is the moisture content of material, kg/kg;
u_0	is the initial moisture content, kg/kg;
τ	is the time, sec;
Fo	is the Fourier number;
Pd	is the Predvoditelev number;
X	is the reduced coordinate;

T	is the dimensionless temperature;
t_M	is the material temperature, °C;
t_s	is the temperature of material surface, °C;
t_{dry}	is the temperature of dry material, °C;
t_c	is the temperature of medium, °C;
P	is the total pressure of vapor–gas mixture, mm Hg;
P_s	is the partial pressure of vapor at material surface, mm Hg;
P_c	is the partial pressure of vapor in medium, mm Hg;
μ_n	are the roots of characteristic equation;
A_n	is the initial thermal amplitude;
α_t	is the heat transfer coefficient, W/m^2 · deg;
α'	is the mass transfer coefficient at normal pressure, kg/m^2 g · mm Hg;
λ	is the thermal conductivity, W/m · deg;
a	is the thermal diffusivity, m^2/sec;
c	is the specific heat of material, J/kg · deg;
α_p	is the coefficient for rate of moisture removal from material at pressure drop, 1/sec;
b	is the dimensionless coefficient;
r	is the heat phase transformation, J/mole;
r_w	is the heat for overcoming forces of water bond with material, J/mole;
γ	is the density of material, kg/m^3;
ΔU	is the out-of-balance bridge voltage, V;
R_0	is the initial value of resistance, ohm;
ΔR	is the change of resistance, ohm;
β	is the temperature coefficient of resistance, 1/deg;
E_0	is the voltage of bridge feed, V;
$z_{red\cdot}$	is the reduced resistance, ohm;
R_V	is the characteristic dimension, m;
N	is the readings of moisture meter, mm;
Δ	is the entropy error, mm;
δ_{tr}	is the relative error of transformer, %;
δ_{meas}	is the relative error of temperature measuring, %;
δ_{dev}	is the relative error of moisture meter, %;
X_{sc}	is the length of register scale, mm;
n	is the total number of measurements;
m	is the number of divisions within error range;
n_i	is the number of errors per i-th section of divisions;
d	is the width of fracture band, mm.

Subscripts

c	refers to the medium;
M	refers to the material;
dry	refers to dry material;
sc	refers to scale.

LITERATURE CITED

1. M. A. Berliner, Electrical Measurements, Automatic Monitoring, and Humidity Adjustment [in Russian], Énergoizdat, Moscow–Leningrad (1965).
2. M. V. Venediktov, N. M. Rudnyi, A. E. Sogin, and V. L. Tatievskii, Authors' Certificate No. 198012, Byull. No. 13 (1967).
3. O. Krisher, Scientific Principles of Drying Technology [Russian translation], IL (1961).
4. A. V. Lykov and Yu. A. Mikhailov, Theory of Heat and Mass Transfer [in Russian], Gosénergoizdat, Moscow–Leningrad (1963).
5. M. I. Verba, Coll.: Drying in the Food Industry [in Russian], Profizdat (1958).
6. A. V. Lykov, Theory of Drying [in Russian], Énergiya, Moscow (1968).
7. A. A. Gryaznov, Coll.: Drying in the Food Industry [in Russian], Profizdat (1958).
8. I. S. Mel'nikova, Coll.: Heat and Mass Transfer in Evaporation Processes [in Russian], Izd. AN SSSR (1958).

9. A. V. Lykov, Theory of Thermal Conduction [in Russian], Izd. Vysshaya Shkola (1967).
10. A. D. Nesterenko, Calculation Principles for Balanced Measuring Circuits [in Russian], Izd. AN UkrSSR (1960).
11. A. N. Zaidel', Elementary Estimates of Errors of Measurement [in Russian], Nauka, Leningrad (1968).
12. P. V. Novitskii, Principles of the Information Theory of Measuring Devices [in Russian], Énergiya, Leningrad (1968).