



CALORIMETER FOR MEASUREMENT INTERNAL HEAT RELEASE IN FOODSTUFF

Stanislav Proshkin

Department of General and Applied Physics, National Mineral Resources University (Mining University), St.-Petersburg, Russia

E-Mail: stach@mail.ru

ABSTRACT

The article deals with aspects of development features of manifestation and the cause of the emergence of the sources of an internal heat release in foodstuff. The article considers the theory of the method, which allows measuring the sources of internal heat release of various types of objects and also a design of the heat measuring cell created on its basis. Experimental results of measurement of a heat release are given in the sprouting wheat seeds.

Keywords: thermophysics, heat release, calorimeter, foodstuff.

1. INTRODUCTION

It is known that when studying the thermal processes going in biological, food and other objects, it is necessary to consider processes, connected with their own heat release. At the same time it should be noted undoubted complexity of this task. The heat release is determined not only by a concrete type and structure of a product, but also by the conditions under which the process of research is done. The size of a heat flux may be in advance an unknown function of temperature and time of the course of process. For example, the heat which is released when receiving a bioyoghurt possesses a temperature threshold - at lower temperatures the heat release doesn't occur at all as activity of the milk-sour bacteria stops [1].

The heat which is released when carrying out refrigerating processes can include phase transitions water-ice and melting-crystallization of fats. These components of heat usually enter as component parts into a concept of a full enthalpy of a foodstuff and its effective heat capacity [2]. However with it, many types of foodstuff can allocate or absorb additional amount of heat because of the various biochemical processes connected with performance of physiological functions.

For an assessment of processes of an internal heat release two main directions are used: first purely analytical approach using calculation of a heat release in separate biochemical reactions and the second - use of devices for obtaining values of this heat.

The first method has a number of limitations because it requires preliminary knowledge of a chemical composition of a product, kinetics of chemical reactions and conditions under which they are proceed.

The plants have a heat of breath generally connected with oxidation of some hydrocarbons. It is noted in work [3] that data on a heat release at breath of various plants depending on temperature aren't steadily constant even for fruits of the same type, the same maturity. They depend on a number of factors, which are difficult to predict. Therefore, the range of a heat release can be rather wide.

As follows from the analysis of the data provided in the works of I.G. Alyamovski [4, 5], the heat release

depending on a type of a foodstuff can greatly change; at the same time its values are small. Therefore measurement of a heat release by technical devices is rather complicated independent research task.

Furthermore, it is important to note that measurement of the released and absorbed heat is a task not only in refrigerating processes of storage of foodstuff. Similar problems arise in a number of other scientific areas, sometimes not connected with foodstuff technologies at all. For example at cultivation of strains of the bacteria which are used in production of bioyoghurt biochemical exothermic reactions take place. The first works of E. Pratt have proved possibility of identification of micro-organisms on the basis of change of a plot "heat release-time" [6]. He has shown that at identical temperatures of the environment different types of bacteria give various, inherent only to this sort, heat release. Sprouting of seeds of plants is also accompanied by the processes connected with release and absorption of heat.

2. METHOD AND APPARATUS

2.1 Calorimeter for measurement of an internal heat release

We have created the calorimeter for solution of the task (see Figure-1). Thin-walled metal cell of 33, 22 cm³ was filled with the studied sample (1). The mass of a sample didn't exceed 30, 0 g. In the calibration experiment the electric heater (2) was located inside the cell.

In our installation two microthermistors for measurement of temperature cell with a sample (3) and the external block (4) were used. Voltage measured by mikrothermistors in a digital form was brought into the memory of the computer with the help of the controller.

The thermal flux proceeding from the cell with the sample was measured by means of semiconductor thermobatteries (5). Power failure on such thermobattery is proportional to the thermal flux passing through her. This thermal flux in a digital form was also registered in the computer.

Thus, in the memory of the computer was written down information on the values of two temperatures and a thermal flux as a function of time.

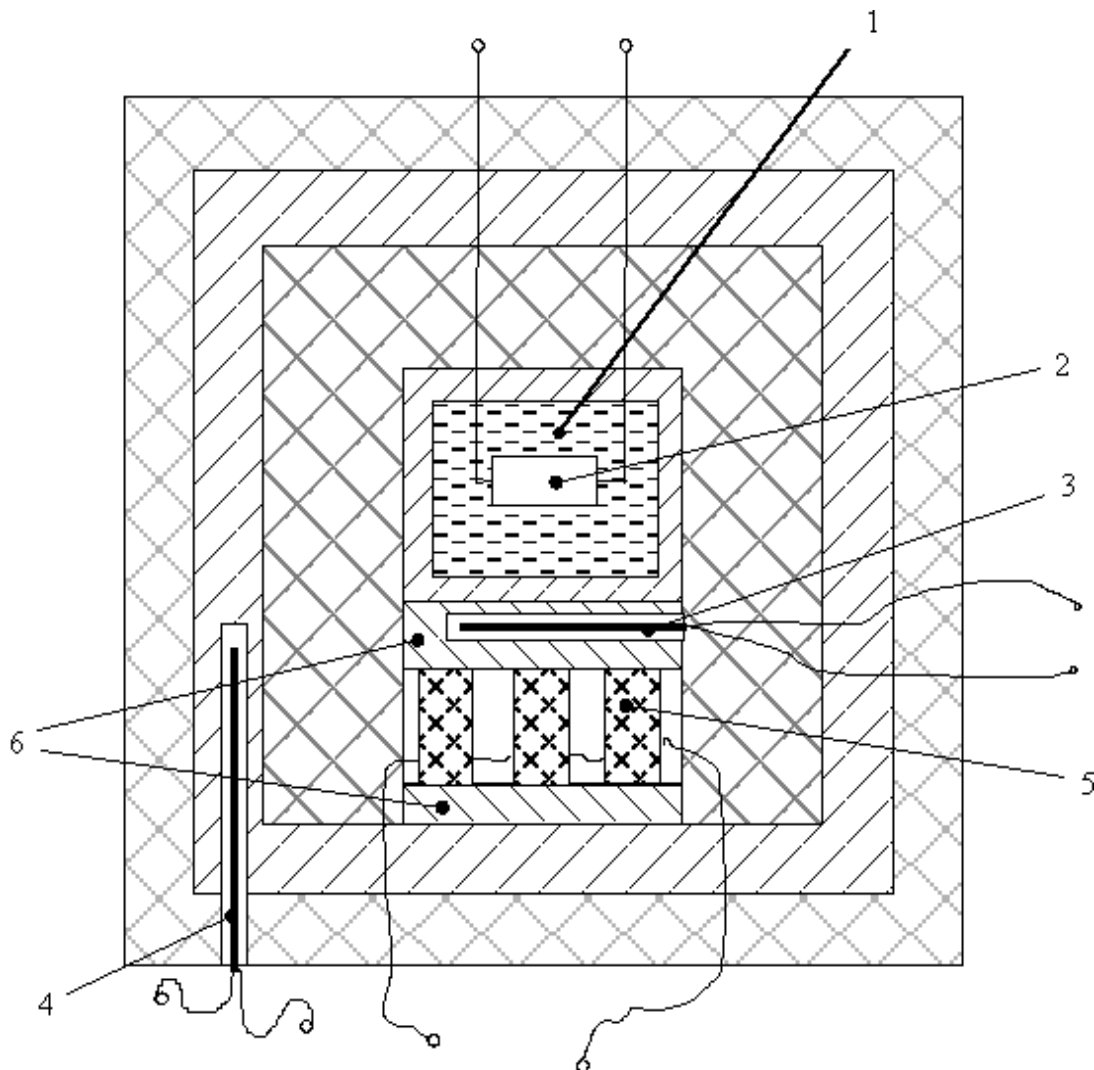


Figure-1. The scheme of a thermal cell for measurement of power of internal sources of a heat release.

1 - the studied substance; 2 - electric heater; 3, 4 - microthermistors; 5 - semiconductor thermobattery; 6 - metal disks.

In our installation we used semiconductor thermobatteries with an area of thermal contact about 1, 00 cm². As the area of the bottom surface cell through which the measured heat flux equalled 16, 61 cm² had to pass; there was a need to use several thermobatteries. We used seven thermobatteries connected in series (heat meter). For alignment of a thermal flux on a contact surface of the cell and the heat meter the latter has been placed between the two thin-walled cylindrical aluminium disks (6). The surface area of these disks coincided with the area of the base of the cell, which was placed on one of them.

The side surface and the upper base of cell have been surrounded with foam plastic isolation. Thickness of foam plastic made 2, 00 cm, and coefficient of heat conductivity of 0,025 W/(m K). Thus as a first approximation we can consider that all thermal flux which is released in a sample passes only through the lower surface and, therefore, it is completely measured by the

heat meter. At the same time the part of a thermal flux is spent for a heating up cell, a sample, the top part of the heat meter and plastic foam isolation. So, it is possible to write the equation of thermal balance for the stationary mode:

$$W + \omega = C_k b_w + K_T N_w + K_\lambda \theta(\tau), \quad (1)$$

where W – the heat flux released by the internal electric heater, W; ω – the measured heat flux which is released because of heat reactions in a sample, W; K_T – coefficient of sensitivity of the heat meter, W/bit; N_w – the size of the heat flux registered by the heat meter in a digital form, measured in bits; C_k – a total full heat capacity cell, a sample, the heater, part of the heat meter and foam plastic isolation, J/K; $b_w = \frac{dI_1(\tau)}{d\tau}$ – speed of



change of temperature of a sample in time, K/sec; K_λ - heat transfer coefficient between cell and foam plastic isolation, W/K; $\theta = t_1(\tau) - t_2(\tau)$ - temperature drop between cell and the block of calorimeter, K.

2.2 Calibration experiment

Follows from the equation (1) that for obtaining value ω it is necessary to know "constants" of the device K_T and K_λ , and also a heat capacity of the studied sample taking into account a heat capacity of cell C_k . We received these values from the calibration experiments made with water. Inside the cell filled with water the heater with the known R resistance was placed. Setting current I through it, it was possible to select various

values of the power, which was released by the heater. Calculation of this power was made by the Joule formula: $W = I^2 R$. The experiment was made in two stages, at first the heater was turned on and the system approached in the mode close to the stationary, then the heater was switched off and the system was cooled in the free mode to a state with constant value of temperature. Calibration experiments were made at several values of power, from 0,008 to 0,52 W.

In Figure-2 typical plots received for the power of the heater of 0, 203 W are shown. Dependence of temperature of the cell with water and the block of calorimeter, and also a thermal flux on time are presented.

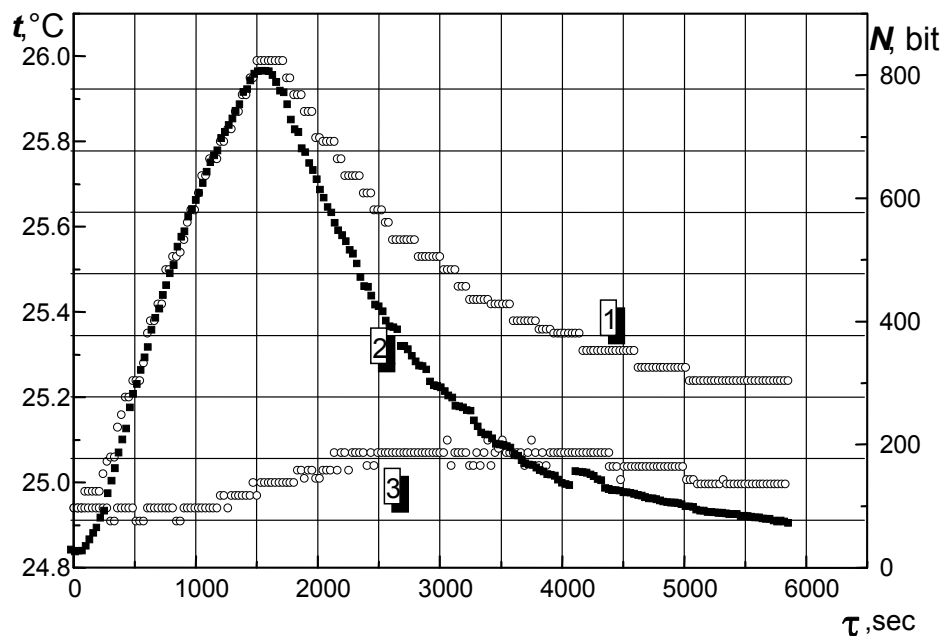


Figure-2. Plots of temporary dependence of temperatures of the cell with water and the block of calorimeter; temporary dependence of a thermal flux.

1 - cell temperature with water; 2 - thermal flux; 3 - temperature of the block of calorimeter.

We shall write down the equations of thermal balance for two sites of both plots:

$$W = C_k b_w + K_T N_w + K_\lambda \theta_w(\tau), \quad (2)$$

$$0 = C_k b_0 + K_T N_0 + K_\lambda \theta_0(\tau), \quad (3)$$

where badges w belong to a heating site, 0 – to cooling.

Now we subtract from (2) (3) and, considering that $\theta_w(\tau) = \theta_0(\tau)$, we receive:

$$W = C_k (b_w - b_0) + K_T (N_w - N_0), \quad (4)$$

where from we get the value of a heat capacity:

$$C_k = \frac{W - K_T (N_w - N_0)}{b_w - b_0}. \quad (5)$$

The last formula includes unknown coefficient K_T . However if we choose two sites of the plots which correspond to the identical values of a flux, then the formula will become simpler:

$$C_k = \frac{W}{b_w - b_0}. \quad (6)$$

In the process of experiment, approximation of temperature plots was made for heating and cooling by means of square dependence. After that the speed of



change of temperature could be calculated analytically for the cell with a sample for two modes. Selecting sites of plots with identical flux, we have calculated a full heat capacity of 183, 35 J/K. Now that a heat capacity is known, it is possible to count:

$$K_T = \frac{W - C_k b_w}{N_w}. \quad (7)$$

The average value of this size for the five calibration experiments has made: $K_T = 0,0001241$ W/bit. The microcircuits of transformation of an analog signal to digital used in the controller allow us to receive the signals corresponding to the maximum flux of 0,127 W. From reference literature it is known that the cranberry possesses the smallest heat of breath among vegetable products. The capacity of our sell being about 30 g, the general flux for cranberry might be 0, 24 W. Thus, the preliminary estimate proves high sensitivity of the created installation.

The fact that several calibration experiments have been made allows us to receive device "constants" in a different way. We will write down the equations of thermal balance for two independent experiments with different powers of the heater:

$$W_1 = C_k b_{w1} + K_T N_{w1} + K_\lambda \theta_{w1}(\tau) \quad (8)$$

$$W_2 = C_k b_{w2} + K_T N_{w2} + K_\lambda \theta_{w2}(\tau) \quad (9)$$

We shall consider on the plots the sites with an equal thermal flux and temperature difference in two experiments, then simple subtraction of these equations gives us value of a heat capacity and coefficient K_T :

$$C_k = \frac{W_1 - W_2}{b_{w1} - b_{w2}} \quad (10)$$

$$K_T = \frac{(W_1 + W_2) - C_k (b_{w1} + b_{w2})}{N_{w1} + N_{w2}}. \quad (11)$$

Finally, we receive the values of "constants" of the device, which differ from the previous ones less than for 1, 0%.

Earlier at a conclusion of formulas equality of thermal overheats in two modes of experiment was supposed: $\theta_w(\tau) = \theta_0(\tau)$ or (at the different powers of the heater): $\theta_{w1}(\tau) = \theta_{w2}(\tau)$. This overheat includes the size of the thermal flux that is lost through foam plastic isolation on a formula:

$$W_{ex} = K_\lambda \theta_w(\tau). \quad (12)$$

We will carry out an assessment of this flux. For this purpose we will calculate a heat transfer coefficient in the equation (12).

As the flux is lost through a side surface of the cell and its top surface, on the whole decision of such task will be rather difficult. Therefore we will replace a surface through which there is a leakage of heat, by an effective surface of a hemisphere. Radius of such a hemisphere can be calculated on the formula:

$$r_{in} = \sqrt{\frac{S_{in}}{2\pi}},$$

where S_{in} – the area of a side surface of the cylindrical cell.

In a similar way we may calculate the external effective radius of a hemisphere which "will replace" an external surface of foam plastic isolation,

$$r_{ex} = \sqrt{\frac{S_{ex}}{2\pi}},$$

where S_{ex} – the area of a cylindrical foam plastic cover.

In the theory of heat conductivity well known is the solution of the problem: the thermal flux going through a hemispherical wall in stationary conditions [7]

$$W_{ex} = \frac{2\pi\lambda}{\frac{1}{r_{in}} - \frac{1}{r_{ex}}} \theta_w(\tau) = K_\lambda \theta_w(\tau).$$

As a result we have received numerical value of coefficient of a heat transfer $K_\lambda = 0,00929$ W/K. In our calibration experiments a difference of temperatures between the cell and the block of a calorimeter didn't exceed 1, 50 °C which gives the maximum value of the lost flux $W_{ex} = 0,014$ W. This value is nearly twenty times less than that assessment, which was given for a "useful" signal.

The heat capacity C_k includes that component of heat, which is spent for a warming up of foam plastic isolation. We will estimate this component on a formula:

$$C_p = c_p \rho_p V_p,$$

where c_p – the specific heat of foam plastic; ρ_p – foam plastic density; V_p – volume of foam plastic isolation. In our installation we used foam plastic with a density of 32, 8 kg/m³. Average value of specific heat capacity for foam plastic isolations of different brands can be taken 1335 J/(kg K). When we have the volume of foam plastic isolation of 2, 6·10⁻⁴ m³, we receive a full heat capacity of foam plastic equal to 10,1 J/K, which makes less than 6,0% of the value of the full heat capacity received in



calibration experiments. Thus, component for the heat absorbed by foam plastic isolation it is possible to neglect. Therefore, assumptions, which were accepted at a conclusion of formulas for the device "constants", may be justified and confirmed.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

Now we will consider a situation when in a cell there is a sample with its own internal heat release. We shall assume that all the volume of a sample is filled with uniformly distributed heat sources.

In this case the equation of thermal balance in this case is the following:

$$\dot{Q} = C_s \dot{h}_w + K_T N_w, \quad (13)$$

where C_s – a full heat capacity of the cell and a sample.

Seeds of the sprouting wheat have been chosen as an object of our research. E. Calvet and H. Prat studied these processes by the help of the microcalorimeter created by them [6]. For their experiments they took 1, 0 g of wheat. This amount of wheat was humidified with 1, 0 ml of distilled water, which resulted in the heat release immediately. The heat release began quickly to increase, reaching a maximum in (20... 40) min that corresponded in their experiences of 1, 40 mW/g. Then the heat release slowly decreased, reaching zero several hours later. The authors called this phase of the described thermal process "a hydrostage", when the sprout could react only to such factor as humidity. Contact of a grain with water is a starting point of the beginning of the seed germination. It is observed that when the hydrostage ended, the follows a considerable time interval (from 5 to 10 hours) without any heat release. Then the heat release has to increase progressively because the physiological processes connected with germination come into effect: rise in intensity of breath, intervention of the enzymes hydrolysing the spare substances of a seed etc. For this stage extremely important is a presence of oxygen, which the seeds didn't need before, and also lighting.

Since in our installation the experiments are made in the opaque and tight metal cell, we have paid the main attention to the research of process of a heat release in wheat seeds for a hydrostage.

For experimental calculation of a heat release of wheat our experiment was made in the following way. The cell was filled with 17, 68 g of dry wheat seeds and the sample was placed in a thermal cell for twenty-four hours. In such a way, it was possible to consider the temperature field in a sample to be stationary and uniform before measurements began. Water, weighing 12, 66 g, in a metal cell was in the same thermal conditions, as a cell with the wheat.

After the wheat was covered with water, the measurement of thermal characteristics in time began. As the process of an initial heat release is fast proceeding, the time step was chosen equal 10 seconds. After the thermal flux, after about half an hour, reached its maximum, the

process of a heat release slowed down. For this stage we chose a time step of 60 seconds.

The unknown heat capacity C_s enters formula (13). It can be defined from experiment. For this purpose in the cell with a sample it is necessary to place the additional electric heater which would be turned on for short period of time after its own heat release of wheat ends (from the plot this state comes approximately after three hours). Unfortunately, in our experiments it isn't possible to carry out this experiment because of a design of a cell, for this reason we have estimated C_s analytically on a formula:

$$C_s = c_x m_x + c_y m_y + C_k,$$

where c_x, c_y – specific heat capacities of wheat and water; m_x, m_y – mass of wheat and water; C_k – heat capacity of cell. The only unknown figure in this formula is the specific heat of wheat. We took it from the data provided in the book [8]. There for the dry wheat the following dependence of specific heat on temperature is offered as follows:

$$c_x = -708 + 7,5 \cdot T, \text{ J/(kg K)}.$$

At an average temperature in our experiments 298 K specific heat of wheat appears to equal 1530 J/(kg K). The heat capacity of cell can be received if to subtract a heat capacity of the water used in calibration experiment from the value of a heat capacity. The above-said has allowed us to estimate an unknown heat capacity of the sample and to accept it equal 76, 3 J/K.

As a result, having used formula (13), we have received the plot of dependence of power of heat release on time (see Figure-3).

Results of our experiments perfectly coincide with those presented in the book of to E. Calvet and H. Prat [6]. In particular, the most heat release in our experiments came 30 min later and equalled 22, 16 mW. As mentioned above, in the book of E. Calvet and H. Prat the maximum corresponded to 1, 4 mW/g; in our experiment mass of wheat of 17,68 g the most heat release must correspond to 24,75 mW.

This coincidence is especially surprising as heat release size in a thermogenesis stage strongly depends on ambient temperature, initial humidity of grain and other factors [9].

Just as shown in work [6] upon the end of the initial stage (approximately after 5, 5 hours) corresponding to swelling of seeds we also observed almost complete cessation of a heat release. Further, after about 7 hours have passed since the beginning of the experiment, growth of a heat release connected with the seed germination begins. The authors of work [6] named these stages "biological termogenes". We didn't begin to study in detail this stage because for its supervision special conditions of



maintenance of temperature, lighting and presence of oxygen are required.

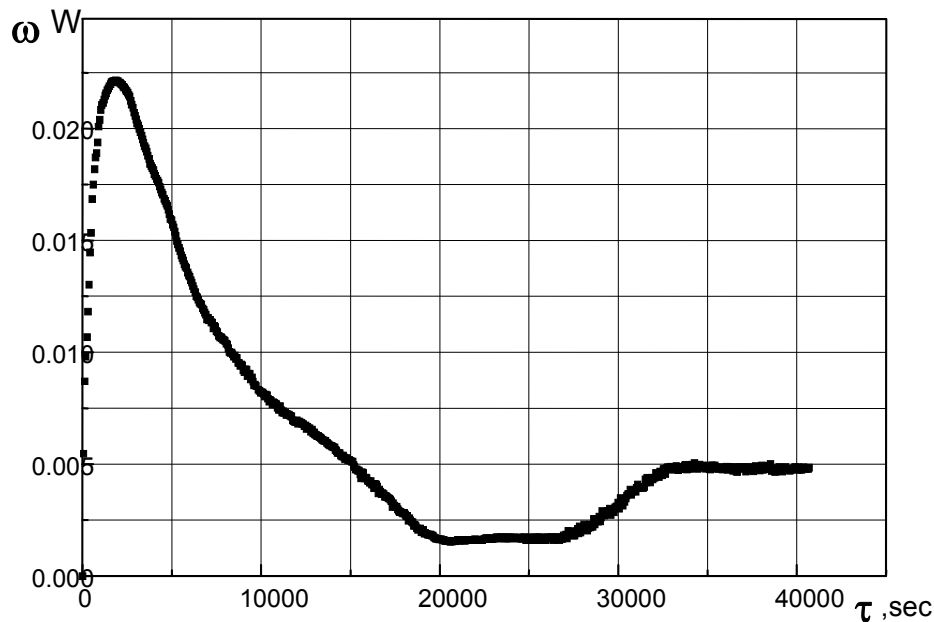


Figure-3. Plot showing dependence of the power of a heat release of the sprouting wheat seeds on time.

Thus, it is possible to state a high sensitivity of the created installation and its high operational opportunities. It should be noted that the minimum heat of breath for cranberry with a mass of our sample corresponds to value of 241 mW [4], i.e. 10 times higher than the values measured by us for wheat.

We emphasize the importance of this installation, as it allows us to measure heat both in exothermic and in endothermic reactions. In the latter in calculated formulas signs for thermal flux will only change.

4. CONCLUSIONS

The method of experimental measurement of power of sources of an internal heat release of various natures in foodstuff is developed and theoretically reasonable.

Analysis of thermal model of the method has allowed us to create a design of a calorimeter. Having carried out the experiments we received basic formulas for calculation of power of an internal heat release and the device "constants" got in the experiment.

The experimental results received for the sprouting wheat seeds prove high sensitivity of the offered method.

REFERENCES

- [1] Andreev E.F., Lebedev D.P., Uvarov V.V. 1986. Microcalorimetry of biological objects. Moscow: Agropromizdat (in Russian).
- [2] Baranov I.V., Proshkin S.S. 2006. A Multifunctional Device for Thermophysical Measurements. Sixteenth Symposium on Thermophysical Properties, Boulder, Colorado, USA, 245-246.
- [3] Chidjov G.B. 1977. Refrigerating engineering of foodstuff. Leningrad: LTI (in Russian).
- [4] Alyamovski I.G. 1967. Temperature dependence of heat release of fruits and vegetables. Journal of Refrigerating Engineering. 6. 41-42 (in Russian).
- [5] Alyamovski I.G. 1969. Calculation of physiological heat in exothermic and in endothermic reactions of fruits and vegetables. Journal of Refrigerating Engineering. 8. 43-44 (in Russian).
- [6] Calvet E., Prat H. 1983. Recent Progress in Microcalorimetry. New York: Pergamon Press.
- [7] Luikov A.V. 1978. Heat and Mass Transfer. Moscow: Energia (in Russian).
- [8] Siebel I. 1982. Specific heat of various products. Ice and Refrigeration. 2(4). 256-257.
- [9] Houška M., Adam M. 1997. Thermophysical and rheological properties of foodstuff. Prague: Institute of Agricultural and Food Information.