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THE DEVELOPMENT OF CALORIMETER FOR THE STUDY OF BOUND MOISTURE IN HETEROGENEOUS MATERIALS

РОЗРОБЛЕННЯ КАЛОРИМЕТРА ДЛЯ ДОСЛІДЖЕННЯ ЗВ'ЯЗАНОЇ ВОЛОГИ В НЕОДНОРІДНИХ МАТЕРІАЛАХ

Ivanov S.O. / Іванов С.О.
researcher, c.t.s. /н.с., к.т.н.
ORCID: 0000-0002-2722-7323
SPIN: 0000-0000-8855-0141
Institute of Engineering Thermophysics of NAS of Ukraine, Kyiv, Zhelyabova str. 2a, 03057
Інститут технічної теплофізики НАН України, Київ, вул. Желябова, 2а, 03057
Roman T.O. / Роман Т.О.
assistant /асистент
Ivanchenko M.H. / Іванченко М.Г.
lead engineer / Провідний інженер
National university of food technologies, Kyiv, Volodymyrska str. 68, 01601
Національний університет харчових технологій, Київ, вул.Володимирська 68, 01601

Abstract. *The paper devoted to problem of developing a specialized device that allows to investigate the ratio of free and bound moisture of a wide range of heterogeneous materials. The analysis of the main methods and devices which allow to define the number of bound moisture and also the existing normative documents allowed to formulate requirements to development of a specialized device. Considering features of the studied materials the concept of a new low-temperature calorimeter is presented that investigates energy of phase transition of moisture in heterogeneous material. Phase transition is provided by deep freezing of a sample with the subsequent increase in its temperature with a constant speed. The main design features of the device are given in work that the direction of development of work gives an idea about further.*

Key words: *bound moisture, heterogeneous materials, calorimetry, DSC, measurement, liquid nitrogen.*

Introduction.

All the moisture which is a component of any damp material divide into free and bound. Such division related with the fact that parameters and properties of water in material significantly differ depending on presence of bound moisture in material and to kind of bond. For example, density of bound moisture considerably differs from the recommended for water values, and is 1130...1740 kg/m^3; temperature of crystallization can reach 75 °C below zero; bound moisture loses solvent properties and acquires dielectric ones, etc. [1].

The ratio of free and bound moisture is one of important factors which needs to be considered when choosing parameters of storage of goods. It is also necessary to calculate and optimize of fuel consumption on raw materials drying processes. This problem is especially relevant for the food industry because of investigated materials is usually a non-uniform on structure heat-labile ones, which properties change under the influence of temperature, time, enzymatic and microbiological influence, etc. Owing to a large number of factors of influence, the ratio of bound moisture in such material can lead to considerable errors by analytical calculation. Given this, the most appropriate way to obtain the correct data is experimental research.

Overview

Experimental methods of a research of a condition of water in materials differ in variety of approaches and means that they are realized. The most widespread is [2]:

• *Differential scanning calorimetry method*: based on the difference in freezing temperature of free water and bound one;

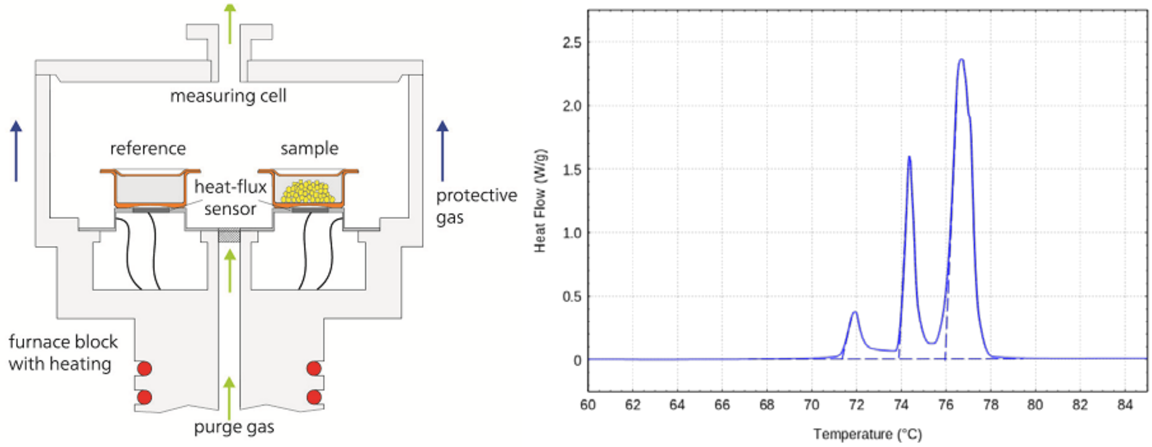
• *Dielectric measurements*: the dielectric constant of bound moisture is significantly different from the free one;

• *Thermogravimetric method*: based on the difference in drying rate of free and bound moisture;

• *Heat capacity measurement*: based on the difference in heat capacity of free and bound water;

• *Nuclear magnetic resonance method*: based on the difference of water mobility in a fixed matrix, which results in different lines of the spectrum;

The DSK method is one of the most expedient ways of obtaining quantitative information on a condition of water in material. According to this method, a sample of material of known mass is placed in one of the crucibles of the differential calorimeter. (pic.1, a) then temperature of crucibles decreases to cryogenic values. Researches the ratio free and bound moisture in material occurs by measurement of a difference of heat fluxes of a sample and the reviewer at a constant speed temperature increase.



a) b)

Pic. 1. Block diagram of heat flux DSC (a) and phase transition graph (b)

Source: [3, 4]

Phase transitions that will occur in a sample at temperature increase, will bring to deviations on graphics of heat fluxes (pic.1, b). The area of peak is proportional to energy of phase transition, and indicates the direction on ordinate axis reaction type (exothermic or endothermic).

Many international companies and research institutes around the world are engaged in development and creation of devices of DSC (tab. 1).

Wide temperature range, presence of two identical holders of a sample in a zone of carrying out experience and small volume of the holder of a sample is joint features of the given calorimeters. Two identical holders of a sample measurements, necessary for realization of a differential method. In one crucible the sample is

Table 1

Modern DSC devices to measure the amount of bound moisture

Title,	Manufacturer	Heat range, °C	Accuracy, %	DSC crucible vol_{max}, µl
DSC 214 Polyma [3]	Netzsch (Germany)	-150…600	±2	75
DSC-60 Plus [5]	Shimadzu (Japan)	-140…600	±2	110
DSC 3 [6]	Mettler Toledo (Switzerland)	-150…700	±3%	160
Discovery DSC 25 [7]	TA Instruments (USA)	-180…725	±1	100

Source: [3, 5-7]

placed, and the second remains empty that allows to reduce an error and to enter the amendment on the thermal capacity of the crucible. Wide temperature range and small volume of a crucible is explained by a scope of calorimeters: researches of pure uniform substances (metals, solutions, polymers, etc.). Small volume of cells allows to increase speed of a measuring system and to increase measurement accuracy, however an opportunity to correctly investigate samples of materials, non-uniform on structure, is lost. The impossibility to investigate a ratio free and bound moisture in a representative sample of non-uniform material in holders of a sample of the existing calorimeters indicates the need creations of a specialized measuring instrument for these purposes.

Concept.

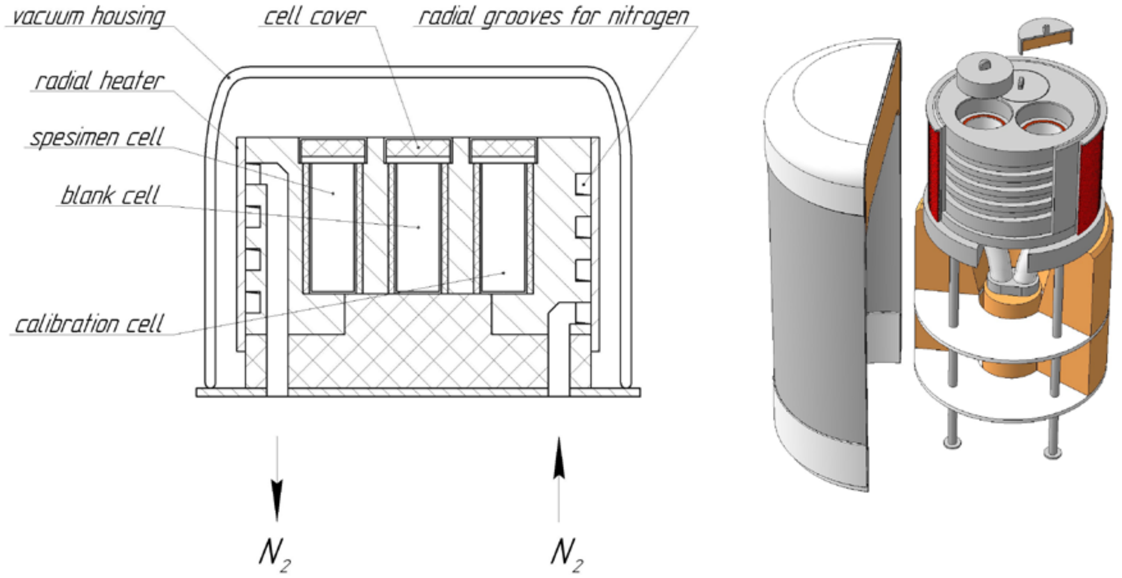
On the basis of the analysis of the existing measuring instruments requirements to development of a specialized calorimeter for a research a ratio free and bound moisture in non-uniform materials are formulated:

- the possibility of cooling the sample to at least 80°C below zero;
- the presence of at least three identical cells;
- large volume of cells to accommodate a representative heterogeneous sample;
- implementing a low rate of cell heating;
- convenience of device preparation for measurement;
- convenience of sample preparation for measurement;

Considering requirements, the concept of a specialized low-temperature calorimeter is presented (pic.2).

Thermal part of a calorimeter represents a cylinder from material with high heat conductivity. The outer surface of a cylinder has spiral grooves which are intended for circulation liquid-gas nitrogen mix. Supply of nitrogen proceed thru the chokes in the lower part of a cylinder by means of the automatic system of circulation directly from a vessel of the Dewar.

From the outside a grooves are closed by a cylindrical ring with an electro heater that turns flutes into closed channels, and allows to regulate temperature of all cylinder. Thermophysical and geometrical parameters of a cylinder have to provide



Pic. 2. Generalized concept of low-temperature calorimeter

Author's design

the uniform temperature field in three cells which are built in in the form of cylindrical openings in the center of a cylinder.

Each cell of the device is equipped with a cover and the cylindrical sensor of a heat flux which covers a cell along walls. The presence of three cells in the calorimeter is associated with the recommendations of existing measurement standards DSC [8]. According to the standard, each DSC measurement consists of three steps with the same scanning speed:

- a blank stage - empty pans in sample and reference holders;
- a calibration stage - calibration material in sample holder pan and empty pan in reference holder;
- a specimen stage - specimen in sample holder pan and empty pan in reference holder.

Three identical cells, one of which is intended for placement of a sample, the second - for calibrating material, and the third (remains empty), allow three stages of DSC measurement. It will not only three times reduce time of carrying out experience, but also will reduce uncertainty of experience owing to non-idealism of reproduction of temperature condition.

Calculation of a mass fraction of bound moisture in the simplified form looks:

$$m_{bound} = m_w - m_{ref} \cdot \sum \frac{\int \left(Q_{sample} - Q_{blunk}\right) d\tau}{\int \left(Q_{ref} - Q_{blunk}\right) d\tau} \cdot K(T) \pm f(T,\tau) \qquad (1)$$

where: m_{bound} - mass fraction of bound moisture; m_w - the full mass of moisture in a sample (is defined separately); m_{ref} - mass of reference substances (the distilled water); Q_{sample}, Q_{ref}, Q_{blunk} - heat flux through a cell with the studied material, a standard and through an empty cell respectively; $K(T)$ - the multiplicative amendment on influence factors; $\pm f(T,\tau)$ - the additive amendment on influence factors.

The advantages of the proposed design include increasing the speed and comparing the data with the standard during each experiment due to the use of three cells, a wide range of investigated materials due to the configuration of the holder of the sample, the ability to fully automate the measurement process and minimize the operator's influence. Possible disadvantages: high inertia of temperature control due to the mutual location of the heater and nitrogen channels, as well as the high cost of secondary equipment.

The following step of further development of research is modeling of the thermal modes for the purpose of material selection of a thermal part of the device and justification of their configuration. It is supposed that use of such calorimeter together with the system of definition of warmth of evaporation and thermal capacity [9] will allow to conduct a complex research of non-uniform materials for the purpose of obtaining full information as about parameters and a condition of moisture in material, and to develop the correct modes of the technological processing and storage of investigated raw materials.

Conclusions.

The analysis of methods and means of experimental determination of the ratio of free and bound moisture in materials on the basis of which formulated the requirements for the development of a specialized calorimeter capable of investigating non-uniform materials. The concept of a new calorimeter is presented, its characteristic features, as well as the principle of operation and processing of data. The analysis of the advantages and disadvantages of the design and the tasks for further work are done. The prospect of use of a calorimeter as the making system of the deep analysis of a condition of liquid in non-uniform materials will have broad application in food and chemical industry, pharmaceutics, the construction industry, etc.

Література:

1. Кузнецова Т.В., Кудряшов Т.В., Тимашев В.В. Физическая химия вяжущих материалов: Учебник для вузов. М.: Высшая школа, 1989, 384 с.

2. Wertz, J.L., Mercier, J.P., & Bedue, O. (2010). Cellulose Science and Technology (1st ed.). Lausanne, Switzerland: EFPL Press

3. DSC 214 Polyma, NETZSCH, URL: https://www.netzsch-thermal-analysis.com/en/products-solutions/differential-scanning-calorimetry/dsc-214-polyma/

4. Hexatriacontane dsc phase transitions, Wikipedia, URL: https://commons.wikimedia.org/wiki/File:Hexatriacontane_dsc_phase_transitions.svg

5. DSC-60 Plus Series, Shimadzu Corporation, 2015, URL: https://www.ssi.shimadzu.com/sites/ssi.shimadzu.com/files/Products/literature/thermal/C160-E013B.pdf

6. DSC 3 Differential Scanning Calorimetry for Routine Analysis, Mettler-Toledo, 2015, URL: https://www.mt.com/dam/Analytical/ThermalAnalysi/TA-PDF/DSC3_Brochure_en_30247073A_V05.15_Original_38549.pdf

7. Discovery DSC Brochure, TA Instruments, 2019, URL: https://www.tainstruments.com/wp-content/uploads/Discovery-DSC-Brochure.pdf

8. ISO 11357-4:2005(E) Plastics - Differential scanning calorimetry (DSC) Part 4: Determination of specific heat capacity;

9. Дмитренко Н.В. Дослідження впливу попередньої гігротермічної обробки на теплові характеристики та ефективність процесу сушіння паренхімних тканин картоплі / Н.В. Дмитренко, С.О. Іванов, Л.В. Декуша, Ю.Ф. Снєжкін // Наукові праці Одеської національної академії харчових технологій. – 2014. – Вип. 45, Т.2. – С. 162-166.

References:

1. Kuznetsova T.V. (1989). Fizicheskaja himija vjazhushhih materialov: Uchebnik dlja vuzov. [Physical chemistry of binding materials: Textbook for universities]. Moscow: Vysshaja shkola. 383 P.

2. Wertz, J.L., Mercier, J.P., & Bedue, O. (2010). Cellulose Science and Technology (1st ed.). Lausanne, Switzerland: EFPL Press

3. DSC 214 Polyma, NETZSCH, URL: https://www.netzsch-thermal-analysis.com/en/products-solutions/differential-scanning-calorimetry/dsc-214-polyma/

4. Hexatriacontane dsc phase transitions, Wikipedia, URL: https://commons.wikimedia.org/wiki/File:Hexatriacontane_dsc_phase_transitions.svg

5. DSC-60 Plus Series, Shimadzu Corporation, 2015, URL: https://www.ssi.shimadzu.com/sites/ssi.shimadzu.com/files/Products/literature/thermal/C160-E013B.pdf

6. DSC 3 Differential Scanning Calorimetry for Routine Analysis, Mettler-Toledo, 2015, URL: https://www.mt.com/dam/Analytical/ThermalAnalysi/TA-PDF/DSC3_Brochure_en_30247073A_V05.15_Original_38549.pdf

7. Discovery DSC Brochure, TA Instruments, 2019, URL: https://www.tainstruments.com/wp-content/uploads/Discovery-DSC-Brochure.pdf

8. ISO 11357-4:2005(E) Plastics - Differential scanning calorimetry (DSC) Part 4: Determination of specific heat capacity;

9. Dmytrenko, N., Ivanov, S., Snezhkin, Y., & Dekusha, L. (2018). Research of Thermal Characteristics of Willow Shoots by Devict of Synchronous Thermal Analysis. *Thermophysics and Thermal Power Engineering*, *37*(2), 77-84. https://doi.org/10.31472/ihe.2.2015.09

Анотація. *В роботі розглядається проблема розроблення спеціалізованого засобу вимірювання, що дозволяє досліджувати співвідношення вільної та зв'язаної вологи широкого кола неоднорідних матеріалів. Аналіз основних методів та приладів, що дозволяють визначити кількість зв'язаної вологи, а також діючих нормативних документів, дозволив сформулювати вимоги до розроблення спеціалізованого засобу вимірювання. Враховуючи особливості досліджуваних матеріалів представлено концепцію нового низькотемпературного калориметра, що досліджує енергію фазового переходу вологи в матеріалі. Фазовий перехід забезпечується шляхом глибокого заморожування зразка з подальшим підвищенням його температури з постійною швидкістю. В роботі наведено основні конструктивні особливості приладу, що дає уявлення про подальший напрям розвитку роботи.*

Ключові слова: *зв'язана волога, неоднорідні матеріали, калориметрія, ДСК, вимірювання, рідкий азот.*

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