1. Introduction

A comprehensive study of the properties of materials, including their thermophysical properties, in particular, thermal conductivity, necessitates the development of effective research methods and techniques. The thermal conductivity coefficient is an important indicator of various thermal processes. The most effective methods for determining the thermal conductivity coefficient include non-destructive testing. With their help, it is possible to obtain information on thermal conductivity of the studied material with maximum preservation of its natural structure. In addition, non-destructive methods allow achieving the highest measurement efficiency since these methods do not require laborious preparation of the materials to be studied. The measurement of TPP of substances is used to determine their composition. The method of thermal non-destructive testing, in particular, “thermal conductivity method”, is used to determine the thermal conductivity coefficient of various materials.
termine the composition of gas mixtures in process mixtures of different composition [1] in gas analyzers with the aim of developing modern innovative cooling liquids (nano-liquids) [2], nondestructive testing of the binder liquid content in polymer-composite materials at the stage of their manufacture [3]. Also, the “thermal conductivity method” is used to measure the content of water and ethanol in mixtures [4], to determine the presence and degree of immunological reaction [5], to determine the surface heating temperature of an ultrasonic emitter [6], etc.

It is important to develop new methods and instruments based on them, which greatly simplifies the process of measuring the thermal conductivity of materials by the non-destructive method. Importantly, it is possible to simultaneously measure several samples with improved efficiency (provided that the time of measuring multiple samples is shortened) and given accuracy of measurements.

2. Literature review and problem statement

In [7], the results of the studies to determine the thermal conductivity of substances are presented. Most of the existing thermal conductivity measurement methods have a number of disadvantages. The issue of the bulkiness of heat measuring systems remains unresolved. This places increased demands on experimental conditions. At the same time, the measurement time is increased and the problem of conducting studies of several samples simultaneously is unresolved. A way to overcome these difficulties can be mathematical processing of thermistor heating thermograms during the heating pulse. But the issue of using this method for measuring over a wide temperature range remains unresolved. The reason for this is the nonlinear dependence of the thermistor resistance on its temperature and the change in thermistor power during heating, which leads to an increase in measurement error. An option to overcome such difficulties may be to introduce appropriate adjustments in the calculation formula.

This approach is used in [7]. However, this paper does not address the issue of changes in the operating modes and parameters of the measuring bridge to ensure a minimum error in determining the thermal conductivity coefficient. This suggests that it would be advisable to conduct a study for measuring the thermal conductivity coefficient in a wide temperature range under the appropriate operating modes and parameters of the measuring bridge.

Thus, a detailed analysis of methods for measuring the TPP of biological substances and analysis of studies made by various researchers was carried out in [8]. The author concluded that the most appropriate method of measuring the TPP of biological materials is the method of pulse heating of the thermistor.

In [9–11], the results of the studies on determining the thermal conductivity coefficient by the heating temperature of the thermistor having thermal contact with the studied substance are presented. In [12, 13], the results of the studies on determining the thermal conductivity coefficient by the mathematical processing of thermistor heating thermograms during the heating pulse are given. In [14], the results of the studies on determining the thermal conductivity coefficient by comparing the temperature of thermistor heating in the studied substance and the temperature of thermistor heating in the reference substance are presented. However, the published results of [9–14] left the problem of applying a large number of correction coefficients in mathematical models for determining the thermal conductivity of substances (mixtures), which significantly increases the measurement error for a number of studies. It should be noted that this approach is impractical for accurate determination of thermal conductivity, since it will not be possible to determine the TPP of mixtures with a small difference in thermal conductivity values of substances.

It should be noted that a fairly simple method of analyzing the mixture composition is often used to determine the distribution of gas mixtures and solutions. This method is based on the dependence of the thermal conductivity coefficient on the concentration of mixture components (“thermal conductivity method”) [15–18]. The application of the thermistor direct heating method to determine the composition of substances (mixtures) by measuring the coefficient of their thermal conductivity allows creating a simple express method of determining the composition of substances [18].

It is highly demanded to develop effective methods of measuring the thermal conductivity of substances in order to determine their thermophysical properties and to analyze the composition of mixtures based on the determination of their TPP. The need to control the TPP of substances at all stages of production leads to the search for and improvement of the means of non-destructive testing of thermal conductivity of materials.

Based on the above, it can be concluded that an effective method for examining substances is based on the determination of their TPP, in particular, thermal conductivity. But there is no clear description of thermophysical mechanisms that occur during short-term heating of various substances by a small heat source. Therefore, an important factor for reliable determination of the composition of substances is their TPP as the main properties of substances.

The instruments used to determine the composition of substances by their TPP are complex to implement, require long-term studies, impose increased requirements on experimental conditions, require a long calibration process, are characterized by the design complexity of the measuring cell, have limited sensor sensitivity and require a large volume of the test substance. All of the above results in a significant measurement error. This substantially limits the capabilities of the method of determining the substance composition by the value of thermal conductivity for practical use in biomedical, food and mixture composition research.

3. The aim and objectives of the study

The aim of this study is to investigate the possibility of determining the composition of solutions, biological materials and foodstuffs by their thermophysical characteristics using the thermistor direct heating method based on their thermophysical properties in different temperature ranges. In particular, the study of the possibility of using this method to determine the composition of the mixture by its thermal conductivity coefficient.

To achieve the aim, the following objectives were set:
- to substantiate the possibility of using the thermistor direct heating method to determine the thermal conduc-
tery coefficient of various substances – mixtures;
- to develop the principles of constructing the device for implementing the proposed method in different temperature ranges;
- to give the necessary mathematical dependence, which explains the process of determining the thermal conductivity of substances on the basis of the obtained data of thermistor heating temperature;
- to carry out studies to determine the thermal conductivity of solutions, biological materials and foodstuffs and to evaluate the error in determining the data obtained.

4. Materials and methods of studies to determine the thermal conductivity coefficient of substances

To determine the thermal conductivity coefficient of substances, the simplest method is thermistor direct heating, which uses the ability of the thermistor to self-heat when an electric current flows through it. The heating temperature of the thermistor depends on the temperature of the medium in which the thermistor is located, that is, on the thermophysical characteristics of the test substance with which the measuring element (thermistor) has thermal contact.

Ideally, when the thermistor is shaped like a ball of radius \( r \), under the condition of ideal thermal conductivity \( \lambda > 10 \text{ W/m·K} \) and the thermal energy spreads uniformly from it to all directions. Thus, there is thermal contact (no thermal resistance) at the boundary between the thermistor and the medium, the value of the thermal conductivity coefficient \( \lambda \) of the surrounding test substance is determined by the formula [9, 19, 32]:

\[
\lambda = \frac{P_t}{4\pi r^2 \Delta T},
\]

where \( \lambda \) is the thermal conductivity coefficient of the test substance, \( W/(m·K) \); \( P_t \) is the thermistor power, \( W \); \( r \) is the thermistor radius, \( m \); \( \Delta T \) is the thermistor heating temperature, \( K \).

Thus, to determine the value of the thermal conductivity coefficient by the thermistor direct heating method, it is sufficient to directly measure the heating temperature of the thermistor in the test substance.

4.1. Device for measuring the thermal conductivity of substances

Measurement of the temperature of thermistor heating in the test substance at different temperatures is carried out using a measuring device, the simplified block diagram of which is shown in Fig. 1.

The thermistor \( R_t \) is included in one of the arms of the measuring bridge. The resistance value of the other three resistors \( R_m \) is the same and depends on the temperature range of the measurement. In this case, the RH16-3G202FB “MITSUBISHI MAT. CORP.” thermistor (Japan), which at +25 °C has a resistance of 2 kOhm ±1 % was used. If the measurement is carried out in the temperature range from +30 °C to +70 °C, probe No. 2 with \( R_m = 1.15 \text{ kOhm} \) is used and the bridge is balanced at +40 °C. The device for measuring in different temperature ranges has two parallel measured channels with different probes. For simultaneous measurement of thermal conductivity of several test substances, the measuring device has two probes the unbalance of the bridges of which is measured by the same ADC. Measured signals from different probes are fed to the ADC via a multiplexer.

If the measurement is carried out in the temperature range from +18 °C to +48 °C, probe No. 1 with \( R_m = 1.87 \text{ kOhm} \) is used and the measuring bridge is balanced at +27 °C. The presence of two different probes for measurement in different temperature ranges is due to the need to ensure the accuracy of measurement of the thermal conductivity coefficient of the test substances, provided that the relative measurement error does not exceed 3 % and a resolution of 0.0006 °C of temperature measurement in each of the ranges. The voltage in the bridge diagonal is amplified by the amplifier and fed through the divider to the analog-to-digital converter (ADC). The voltage divider is required to match the voltage range at the amplifier output, which is from 0 to +15 V with the maximum allowable voltage at the ADC input, which varies from 0 to +2.5 V. At the ADC output we get a binary code whose value is proportional to the bridge unbalance voltage. This unbalance is measured by the microcontroller at the beginning of the current pulse flowing in the thermistor under the influence of voltage \( U_{oc} \) and at its...
end, and transmitted through the interface to the personal computer (PC), and the resulting data set is stored as a text file. In this case, Wi-Fi modules are used to connect the meter to the PC. According to the obtained data of thermistor heating under the action of current pulse stored in the file (the N value at the beginning of the pulse and at its end), the thermistor heating temperature is determined. The switch position sets the required pulse amplitude \( U_{cc} - 12 \) V for Probe No. 2 or 15 V for Probe No. 1 to provide the same thermistor power in different temperature ranges.

The presented device is improved on the basis of the device developed earlier by the authors [7, 18, 19]. The improved device is used to determine thermal conductivity at different temperature ranges. It differs from the previously developed device in that different circuit solutions are used for different thermistor probes, and the amplitude of the heating pulse is changed to set the same thermistor power in variable temperature ranges.

### 4.2. Substantiation of the mathematical dependence of the thermal conductivity coefficient on the measured thermistor heating temperature

The presented mathematical dependence of the process of measuring the thermal conductivity of various substances, in contrast to the existing ones, takes into account a number of conditions that reduce the measurement error and the time required to prepare samples for measurements and to conduct research directly.

Thus, thermistor resistance is calculated by the formula [20]:

\[
R_t = R_{25} \cdot e^{\left(\frac{1}{729} + \frac{1}{298} T\right)},
\]

where \( R_t \) is the thermistor resistance, Ohm; \( R_{25} \) is the thermistor resistance at +25 °C, Ohm; \( B \) is the process factor, dependent on the thermistor material, 1/K; \( T \) is the thermistor temperature, K.

In this case, at the ambient temperature \( T_{amb} = +25 \) °C, the thermistor power is:

\[
U_t = U_{cc} \cdot R_{25} \cdot e^{\left(\frac{-1}{729} + \frac{1}{298} T\right)},
\]

Then:

\[
R_t = R_{25} \cdot e^{\left(\frac{1}{729} \cdot \frac{1}{298} T\right)},
\]

where \( U_t \) is the heating pulse amplitude, V; \( U_{cc} \) is the heating pulse amplitude, V.

Current \( I_t \) flowing through the thermistor:

\[
I_t = \frac{U_t}{R_t + R_{25} \cdot e^{\left(\frac{1}{729} \cdot \frac{1}{298} T\right)}},
\]

where \( I_t \) is the current flowing through the thermistor, A.

Thermistor power \( P_t \):

\[
P_t = U_t \cdot I_t,
\]

where \( P_t \) is the thermistor power, W.

Given that at different temperatures the thermistor resistance is different in probes No. 1 and No. 2, the thermistor power will be different at the same heating pulse amplitude. To equalize the thermistor power of probes No. 1 and No. 2, it is necessary to use different heating pulse amplitudes \( U_{cc} \). Thus, for probe No. 1, the heating pulse amplitude is +15 V, and for probe No. 2 – +12 V. The graphs of Fig. 2 show the temperature dependence of the thermistor power for probes No. 1 and No. 2.

![Fig. 2. Temperature dependence of thermistor power for probes No. 1 and No. 2](image)

The thermistor heating temperature \( \Delta T \) is determined by the thermistor resistance, which depends on its temperature. In turn, the thermistor resistance determines the unbalance voltage of the measuring bridge in one of the arms of which the thermistor is included. If the measurement of the unbalance voltage of the measuring bridge is carried out by the ADC, then this voltage will be represented by the value at the ADC output, that is, the binary code of number \( N \). Determination of the thermal conductivity coefficient by the measured value of \( N \) is carried out by software implemented on the PC.

To determine the dependence of the binary code of number \( N \) at the ADC output on the thermistor temperature for both probes, we consistently determine the voltage dependence on the elements of the block diagram.

Voltage in the bridge diagonal \( U_{c} \):

\[
U_c = U_t - \frac{U_{cc}}{2},
\]

where \( U_t \) is the thermistor voltage, V; \( U_{cc} \) is the heating pulse amplitude, V.

Amplifier output voltage \( U_a \):

\[
U_a = K_a \cdot U_c + U_{ref},
\]

where \( U_{ref} \) is the reference voltage of the differential amplifier, V; \( K_a \) is the gain of the differential amplifier.
ADC input voltage $U_{\text{adc}}$:

$$U_{\text{adc}} = \frac{U_0}{K},$$  \hspace{1cm} (8)

where $K$ is the divider ratio.

Then the numerical value at the ADC output, i.e. the binary code of number $N$, $N_{\text{adc}}$:

$$N_{\text{adc}} = U_{\text{adc}} \cdot \frac{N_{\text{adc max}}}{U_{\text{adc max}}},$$  \hspace{1cm} (9)

where $N_{\text{adc max}}$ is the maximum numerical value at the ADC output, c. u.; $U_{\text{adc max}}$ is the maximum voltage at the ADC input, V.

This uses the dependence of numerical values at the ADC output $N$ on the thermistor temperature in the temperature range from $+18^\circ$C to $+48^\circ$C for bridge No. 1 with $R_0=1.87$ kOhm and in the temperature range from $+30^\circ$C to $+70^\circ$C for bridge No. 2 with $R_0=1.15$ kOhm. The functions of the dependence of the numerical value at the ADC output on the thermistor temperature are calculated according to the actual electric characteristics of the measuring channel of the device and are shown in Fig. 3.

The heating temperature of the thermistor, due to the passage of an electric current pulse through it, is proportional to the difference in numerical values at the ADC output at the end of the pulse (the end heating point) and at its beginning (the starting heating point). It should be noted that the thermistor has a shell of glass or epoxy resin, and there is an error in determining the thermistor resistance and the nonlinear nature of the temperature dependence of thermistor resistance. Therefore, it is necessary to introduce additional proportionality coefficients into the calculation formula (1), which are determined by testing on reference fluids with known TPP [21, 22].

Given the nonlinear nature of the dependence given in Fig. 3, to adjust it to linear, when performing the calculations of the thermal conductivity coefficient, we introduce appropriate corrections. Then the formula (1) for determining the thermal conductivity coefficient at temperature $T$ will take the following form:

$$\lambda_{t,s} = \frac{P_r \cdot K_{\text{prop}}}{4\pi r \left[\left(N_{\text{end}} - N_{\text{start}}\right) - \left(N_{T_s} - N_{\text{corr}}\right) \cdot K_{\text{diff}} - K_{\text{comp}} \cdot \frac{T_{\text{ref}} - T_r}{N_{\text{ref}} - \Delta T}\right]},$$  \hspace{1cm} (10)

where $\lambda_{t,s}$ is the thermal conductivity coefficient of the test substance, $W/(m\cdot K)$; $P_r$ is the thermistor power, $W$; $r$ is the thermistor radius, m; $\Delta T$ is the additional thermistor heating temperature, caused by the presence of the thermistor shell and measured by calibration of the device using reference substances, K; $K_{\text{prop}}$ is the proportionality factor, which is also determined by the calibration of the test meter using reference substances. This factor characterizes the sensitivity of the thermistor probe to the value of the thermal conductivity coefficient of the test substance in which the measuring probe is located; $N_{\text{end}}$ is the numerical value at the end heating point of the thermistor measured by the thermistor probe; $N_{\text{start}}$ is the numerical value at the starting heating point of the thermistor measured by the thermistor probe; $K_{\text{corr}}$ is the coefficient that adjusts the measured value of the thermal conductivity coefficient depending on the error of measuring the temperature of the analysed sample by the thermistor probe (error of temperature measurement by the thermistor probe before thermistor heating); $K_{\text{diff}}$ is the coefficient that adjusts the dependence of the difference $N_{\text{end}} - N_{\text{start}}$ measured by the thermistor probe on the temperature of the test sample; $K_{\text{comp}}$ is the coefficient that determines the sensitivity of the thermistor probe (compensates for the error of the difference $N_{\text{end}} - N_{\text{start}}$ measured by the thermistor probe to the average value for all probes); $T_r$ is the thermistor temperature equal to $+40^\circ$C; $T_s$ is the thermistor temperature at which $N_{\text{ADC}} = 0$; $N_{\text{ref}}$ is the numerical value at the ADC output at probe temperature $+25^\circ$C for probe No. 1 and at probe temperature $+40^\circ$C for probe No. 2, $N_{T_s}$ is the numerical value at the ADC output at probe temperature $T$ (in this case the thermal conductivity coefficient was determined at sample temperatures of $+25^\circ$C and $+40^\circ$C), calculated under the condition of linear dependence $N=f(T)$.

The values of the coefficients $\Delta T_s$, $K_{\text{prop}}$, $K_{\text{corr}}$, $K_{\text{diff}}$, $K_{\text{comp}}$ should be determined during the investigations individually for each probe during calibration testing using reference fluids with known TPP. These coefficients are the characteristics of the thermistor probe. It is also necessary to analyze the uncertainty of the coefficients $\Delta T_s$, $K_{\text{prop}}$, $K_{\text{corr}}$, $K_{\text{diff}}$, $K_{\text{comp}}$, thermal conductivity coefficient of reference liquids with known TPP, which were used in the calibration. This is necessary to determine the measurement accuracy of the thermal conductivity coefficient of the device.

![Fig. 3. Temperature dependence of the numerical value at the ADC output](image-url)
The results of measurements of the thermal conductivity coefficient of sugar, glycerol, aqueous ethanol solutions, biological materials (human blood and human blood plasma, milk of different fat content, egg white and yolk) are considered. Measurements of the thermal conductivity coefficient of food-related substances (lemon, banana, orange) were also made.

Although the thermal conductivity coefficient is not constant for many substances but depends on temperature \( T \), the measurements were carried out at +25±2 °C using probe No. 1 and at +40±2 °C using probe No. 2. Such data are necessary for objective evaluation of thermal conductivity measurement results and creation of a model of the temperature dependence of thermal properties. The dependence in temperature ranges can be approximated by a linear function, for example [23]:

\[
\lambda(T) = \lambda_0 [1 + \alpha_0 (T - T_0)].
\]  

(11)

where \( \lambda_0 \) is the value of the thermal conductivity coefficient at temperature \( T_0 \); \( \alpha_0 \) is an empirical constant [11], determined by comparing the measured value of the thermal conductivity coefficient at different temperatures of the test samples; \( T \) is the temperature of the medium.

The proposed mathematical dependence of the thermal conductivity coefficient on the measured thermistor heating temperature, in contrast to the existing ones, takes into account the conditions of thermal energy propagation from the sensing element when measuring the temperature of the test sample, the change of the thermistor power during heating and the sensitivity of the thermistor probe to the thermal conductivity value of the test substance.

4.3. Design features of the developed meter for determining the TPP of substances

Measurements of the thermal conductivity coefficient were carried out using the system shown in Fig. 4 and the probe design shown in Fig. 5. The thermistors are attached to the end of the cone-shaped measuring probes.

To measure liquids with probe No. 1 in the thermistor temperature range from +18 °C to +48 °C, a hole of the corresponding diameter from +18 °C to +48 °C, a hole of the corresponding diameter was created in the material, and then a probe was installed into this hole. Fig. 7, a–d show examples of probe placement.

To measure liquid materials with probe No. 2 in the thermistor heating temperature range from +30 °C to +70 °C, an 8 mm diameter test tube of 350–450 μl was filled with the test material using the batcher (Fig. 6, a) and placed in the cartridge, and the cartridge was installed in the thermostat. The thermostat (Fig. 6, a) heated the test samples to +40±2 °C to stabilize the temperature during the measurement session.

Prior to the measurement, the calibration of the meter using reference liquids with known thermal conductivity coefficients was carried out. The unit has two measuring probes, measuring unit and additional thermostat (Fig. 6). The measurement results are processed using a PC connected to the developed measuring device. To conduct the measurement session, the operator immerses the probes into the test sample and then starts the measurement procedure on the PC using the appropriate software.

At the beginning and end of heating, the values at the ADC output are recorded in the memory of the measuring device microcontroller and then transferred to the external PC, where the measurement data file is formed. According to these measurements, the temperature of thermistor self-heating is determined. The heating time of the thermistor should be greater than the time constant of the thermistor. In this case, for the RH15 thermistor, the time constant is 6 s, so the heating time should be more than 6 s. The duration of the pause between the pulses to effectively cool the thermistor must exceed the duration of the heating pulse by more than 4–5 times.

Fig. 5. Design of the measuring probe of the device

To measure the thermal conductivity of food products, banana, lemon, orange were used as the test substances using probe No. 1. In the thermistor heating temperature range from +18 °C to +48 °C, a hole of the corresponding diameter was created in the material, and then a probe was installed into this hole. Fig. 7, a–d show examples of probe placement.

8 mm diameter test tube of 350–450 μl was filled with the test material and placed in a container at a temperature of +25±2 °C. The container is shown in Fig. 6.

Fig. 7. a–d show examples of probe placement.
Calculation of the thermal conductivity coefficient by measuring the heating temperature of the thermistor having thermal contact with the test material is carried out by the formula (10).

The proposed design of the meter for determining the TPP of substances, in comparison with the existing ones, allows simplifying the design of the device, reduces the requirements for experimental conditions, which, in turn, reduces the time of research. In this case, the process of calibration of thermistor probes is also simplified, since the proposed mathematical dependence of the thermal conductivity coefficient on the measured thermistor heating temperature takes into account the measurement error of the thermistors. It should also be noted that the specified meter allows measuring the TPP of small amounts of substances, up to 0.2 μl, which greatly expands the application of the thermistor direct heating method in various industries.

5. Results of studies on thermal conductivity of solutions, biological materials and foodstuffs

Before carrying out the studies to determine the coefficients Δλ, kprop, kcorr, kemp, calibration of the measuring device was carried out for each of the probes (i – probe number), which consisted in control measurements of the thermistor heating temperature in reference liquids with known TPP. Distilled water, 85 % glycerol solution in purified water and 96 % aqueous ethanol solution were used as reference liquids. The procedure for determining the coefficients Δλ, kprop, kcorr, kemp, kemp is given in [7].

To check the error of determining the proportionality coefficients and thermal conductivity coefficient of the test substances of the measuring device, a control study of the thermal conductivity of the reference liquids was performed:
- distilled water;
- 85 % glycerol solution in purified water (85 % skin solution, medical);
- 96-Extra medical ethanol (96 % aqueous ethanol solution).

The results of the studies are given in Table 1.

These and subsequent thermal conductivity measurements of the test materials were carried out in 10 min sessions (number of sessions – 10) upon reaching the temperature of the test samples +25 °C (for probe No. 1) and +40 °C (for probe No. 2).

Calculation of the thermal conductivity coefficients at these temperatures was carried out using the formula (10) according to the measurement data and, respectively, N(T) values at the probe temperatures T = +25 °C and +40 °C, calculated from the linear dependence of the numerical value at the ADC output (N) on temperature (T).

To check the adequacy of the developed mathematical dependence in determining the thermal conductivity coefficient of the investigated substances, the results of the measurements were used, and the results are given in Table 1. It is found that by the F-test the obtained dependence is adequate with a confidence probability of 0.95. The estimated value of the criterion F0, which is 1.12261825, does not exceed the table (critical) value of Ftable, which is 1.8307 at the level of significance α=0.05 and the number of degrees of freedom f1=10 and f2=990.

### Table 1

| Test substance                     | Temperature, °C | Mathematical expectation, W/(m·K) | Standard deviation, σ, W/(m·K) | Relative error, % | Reference data, W/(m·K) | Data of other researchers* |
|------------------------------------|-----------------|----------------------------------|---------------------------------|--------------------|--------------------------|---------------------------|
| Distilled water                    | +25 °C          | 0.611                            | 0.006                           | 1.57               | 0.609                    | [24]                      |
|                                    | +40 °C          | 0.629                            | 0.007                           | 1.11               | 0.628                    | [24]                      |
| Medical ethanol (96 % aqueous     | +25 °C          | 0.332                            | 0.005                           | 1.92               | 0.33                     | [24]                      |
| ethanol solution)                  | +40 °C          | 0.337                            | 0.005                           | 1.65               | 0.336                    | [24]                      |
|                                    | +40 °C          | 0.180                            | 0.003                           | 1.87               | 0.178                    | [24, 25]                  |
|                                    | +40 °C          | 0.174                            | 0.003                           | 1.80               | 0.175                    | [24, 25]                  |

Note: * – the ‘Source of information’ column of Table 1 shows the measured values of the thermal conductivity coefficient of substances, solutions, given in the directories. The square brackets provide a reference to the source of information and the parentheses indicate the sample temperature at which the value is given.

As is known, substances can change their properties over time and when their temperature changes, so the study of their characteristics must be carried out taking into account these circumstances.

Measured values of thermal conductivity, measurement error and empirical coefficient of the temperature dependence of thermal conductivity are given in Table 2.

Measurements of the thermal conductivity coefficient of biological materials were carried out in order to investigate their properties and to create a basis for further development of various research methods in the field of medicine. Measurements of the thermal conductivity of some foodstuffs were carried out in order to investigate their properties and evaluate the applicability of the method of TPP studies of foodstuffs.

In order to establish the uncertainty of thermal conductivity measurement, 10 measurements were performed in 10 min sessions for the test samples of substances, solutions, mixtures, some foodstuffs, biological materials.

The arithmetic mean (mathematical expectation) of the thermal conductivity coefficient $\bar{\lambda}_{ts}$ of each test sample is determined by the formula:

$$\bar{\lambda}_{ts} = \frac{1}{n} \sum_{i=1}^{n} \lambda_{ts,i},$$

where $\lambda_{ts,i}$ is the result of the i-th measurement, W/(m·K); n is the number of measurements of each of M test substances.

The results of the calculations are given in Table 1.

The total standard error is determined by the formula:

$$\Delta \lambda_{ts} = \sqrt{\Delta \lambda_{ts,\text{corr}}^2 + \Delta \lambda_{ts,\text{sys}}^2},$$

where $\Delta \lambda_{ts,\text{corr}}$ is the estimate of the random error of the measurement result and with the value of confidence $p=0.95$; $\Delta \lambda_{ts,\text{sys}}$ is the systematic error (the difference between the value obtained as a result of the measurement (the average of all measurements in the series) and the reference value – the table value taken from the directories.
### Table 2

Results of thermal conductivity measurement of solutions, biological substances and some food products

| Biological material          | Probe No. | Measured data | Empirical constant $\alpha$, 1/°C | Data of other researchers* |
|-----------------------------|-----------|---------------|-----------------------------------|-----------------------------|
|                             |           | Thermal conductivity coefficient, W/(m·K) (temperature, °C) | Relative error, %           |                             |
| 20 % sugar solution         | 1         | 0.540 (+25 °C) | 2.4                                | 0.00125                     |
|                             | 2         | 0.564 (+40 °C) | 2.2                                | 0.535(20 °C) [25] 0.56(40 °C) [25] |
| 40 % sugar solution         | 1         | 0.475 (+25 °C) | 2.3                                | 0.0011                       |
|                             | 2         | 0.495 (+40 °C) | 2.1                                | 0.47(20 °C) [25] 0.49(40 °C) [25] |
| 60 % sugar solution         | 1         | 0.407 (+25 °C) | 2.5                                | 0.0007                       |
|                             | 2         | 0.423 (+40 °C) | 2.3                                | 0.405(20 °C) [25] 0.419(40 °C) [25] |
| 20 % ethanol solution       | 1         | 0.477 (+25 °C) | 1.8                                | 0.00095                      |
|                             | 2         | 0.495 (+40 °C) | 1.7                                | 0.47(20 °C) [24] 0.49(40 °C) [24] |
| 40 % ethanol solution       | 1         | 0.368 (+25 °C) | 1.6                                | 0.00045                      |
|                             | 2         | 0.371 (+40 °C) | 2.0                                | 0.364(20 °C) [24] 0.373(40 °C) [24] |
| 60 % ethanol solution       | 1         | 0.277 (+25 °C) | 2.3                                | 0.00015                      |
|                             | 2         | 0.276 (+40 °C) | 2.2                                | 0.276(20 °C) [24] 0.279(40 °C) [24] |
| 80 % ethanol solution       | 1         | 0.210 (+25 °C) | 2.3                                | -0.00015                     |
|                             | 2         | 0.205 (+40 °C) | 2.1                                | 0.212(20 °C) [24] 0.209(40 °C) [24] |
| Ethanol                    | 1         | 0.166 (+25 °C) | 2.1                                | -0.00025                     |
|                             | 2         | 0.164 (+40 °C) | 2.2                                | 0.167(20 °C) [24] 0.162(40 °C) [24] |
| 20 % glycerol solution      | 1         | 0.527 (+25 °C) | 1.8                                | 0.00125                      |
|                             | 2         | 0.545 (+40 °C) | 1.7                                | 0.522(20 °C) [24] 0.547(40 °C) [24] |
| 40 % glycerol solution      | 1         | 0.452 (+25 °C) | 1.9                                | 0.00095                      |
|                             | 2         | 0.474 (+40 °C) | 1.7                                | 0.452(20 °C) [24] 0.471(40 °C) [24] |
| 60 % glycerol solution      | 1         | 0.390 (+25 °C) | 1.8                                | 0.0006                       |
|                             | 2         | 0.397 (+40 °C) | 1.9                                | 0.387(20 °C) [24] 0.399(40 °C) [24] |
| 80 % glycerol solution      | 1         | 0.332 (+25 °C) | 2.1                                | 0.0003                       |
|                             | 2         | 0.334 (+40 °C) | 2.0                                | 0.33(20 °C) [24] 0.336(40 °C) [24] |
| Cow’s milk 1.0 %            | 1         | 0.542 (+25 °C) | 1.9                                | 0.0008                       |
|                             | 2         | 0.577 (+40 °C) | 1.6                                | 0.544(27 °C) [26]           |
| Cow’s milk 2.5 %            | 1         | 0.558 (+25 °C) | 1.95                               | 0.0006                       |
|                             | 2         | 0.561 (+40 °C) | 1.7                                | 0.554(20 °C) ±7.9 % [26] 0.612(80 °C) ±7.9 % [26, 28] |
| Cow’s milk 3.2 %            | 1         | 0.547 (+25 °C) | 1.96                               | 0.0009                       |
|                             | 2         | 0.565 (+40 °C) | 1.7                                | 0.56(40 °C) [21]           |
| Chicken egg (yolk)         | 1         | 0.338 (+25 °C) | 2.6                                | 0.0006                       |
|                             | 2         | 0.349 (+40 °C) | 2.4                                | 0.357(7.8 °C) [28] 0.337(19.4 °C) [28] 0.383(31.3 °C) [28] 0.34 |
| Chicken egg (white)        | 1         | 0.577 (+25 °C) | 2.5                                | -0.0005                      |
|                             | 2         | 0.567 (+40 °C) | 2.2                                | 0.5(78 °C) [28] 0.383(19.4 °C) [28] 0.577(31.3 °C) [28] 0.56 |
| Blood (whole)              | 1         | 0.494 (+40 °C) | 2.7                                | -                             |
|                             | 2         | 0.567 (+40 °C) | 2.6                                | 0.506(38.1 °C) [29]          |
| Blood (plasma)             | 1         | 0.51 (+25 °C)  | 3.0                                | -                             |
|                             | 2         | 0.567 (+40 °C) | 2.6                                | 0.581(36.4 °C) [29]          |
| Red apple                  | 1         | 0.418 (+25 °C) | 2.9                                | -                             |
|                             | 2         | 0.376 (+25 °C) | 2.6                                | 0.46(23 °C) [30]            |
| Green apple                | 1         | 0.418 (+25 °C) | 2.9                                | -                             |
|                             | 2         | 0.376 (+25 °C) | 2.6                                | 0.43(27 °C) [30]            |
| Orange                     | 1         | 0.424 (+25 °C) | 2.9                                | -                             |
|                             | 2         | 0.424 (+25 °C) | 2.9                                | 0.392(28 °C) [31]           |
| Lemon                      | 1         | 0.51 (+25 °C)  | 3.0                                | -                             |
|                             | 2         | 0.567 (+40 °C) | 2.6                                | 0.388(28 °C) [31]           |
| Banana                     | 1         | 0.424 (+25 °C) | 2.9                                | -                             |
|                             | 2         | 0.424 (+25 °C) | 2.9                                | 0.498(27 °C) [31]           |

Note: * – the “Publications data” column of Table 2 shows the measured values of the thermal conductivity coefficient of substances, solutions, mixtures, some foodstuffs, biological materials conducted by other researchers. The square brackets provide a reference to the source of information and the parentheses indicate the sample temperature at which measurements were made.

Then, for the significance level $\alpha$, which corresponds to the confidence probability $p=1-\alpha$, the measurement result differs from the true one by a value not exceeding $\Delta \lambda_{\alpha}$.

Thus, it is possible to determine the range of the measured value $\left[\bar{\lambda}_{s} \pm \Delta \lambda_{s}, \bar{\lambda}_{s} + \Delta \lambda_{s} \right]$, which is the confidence interval.

The half-width of the confidence interval is defined as:

$$\Delta \lambda_{s, \text{rel}} = t_{\alpha/2} S$$  \hspace{1cm} (14)

where $t_{\alpha/2}$ is the table value of the Student’s coefficient taken with the significance level $\alpha$ for the number of degrees of freedom $n$; $S$ is the mean square error of the arithmetic mean.

By the arithmetic mean and the total standard error, the relative error of calculations is defined as:
6. Discussion of the results of studies of thermophysical properties of substances and evaluation of factors influencing measurements

Measurement of the thermal conductivity of the blood plasma was carried out after separation of the liquid portion from the formed elements by the separator. This procedure is implemented by centrifugation of whole blood.

In the study of the thermal conductivity of egg white and yolk, it was found that with increasing temperature from +25 °C to +40 °C, the thermal conductivity of white decreased and the thermal conductivity of yolk increased. The location of the measuring probe in the study of thermal conductivity in test tubes with samples of white and yolk is shown in Fig. 7, a.

In the study of the thermal conductivity of milk with varying fat content, it was revealed that with increasing fat content, the thermal conductivity of milk decreases. The location of the measuring probe in the milk sample tube is shown in Fig. 7, b.

Studies were also carried out to determine the thermal conductivity of fruits such as lemon and banana (Fig. 7, c, d).

In some solutions, heavier enzymes may settle over time, which leads to delamination of the mixture and, consequently, distortion of the measurement results. In such cases, it is necessary to limit the time of mixture preparation for the study and the duration of the measurement procedure. Most of these mixtures are biological fluids, such as human or animal blood.

In the measurement of the thermal conductivity coefficient of multicomponent substances, the content of each component should be determined by introducing additional substances to the solution which, when interacted with the corresponding component, change the TPP of the mixture. An example of such a study is the determination of the presence and degree of immunological response [5, 7] when a liquid allergen is added to the biological fluid (human blood or human blood plasma), which changes the thermal conductivity coefficient of the biological fluid in the presence of the immunological response.

The studies of the thermal conductivity of physiological substances and foodstuffs confirm that for most of the samples studied, the thermal conductivity coefficient \( \lambda \) increases with increasing temperature. Exceptions are the 80 % and 96 % aqueous ethanol solutions and egg white (Table 2), in which the thermal conductivity coefficient \( \lambda \) decreases with increasing temperature (empirical constant \( \alpha_0 \) is negative).

From the thermal conductivity measurements of the solutions, it can be concluded that the content of the dissolved substance can be determined by the measured thermal conductivity coefficient. It is found that the accuracy of determining the volume content depends on the difference in the thermal conductivity coefficients of the components.

In order to observe the required measurement accuracy, it is necessary to choose a research algorithm [21], depending on the values of the difference in the thermal conductivity coefficients of the components.

The studies confirm the efficiency of using the thermistor direct heating method for measuring the thermal conductivity coefficient of various substances – mixtures in different temperature ranges, as well as the possibility to determine the content of dissolved substance by the measured thermal conductivity coefficient. Thus, due to the small size of thermistor probes (Fig. 5), this method allows measurements of the test substances in small volumes (Fig. 7, a, b).

The measurement procedure can take several minutes, since the time constant of a small thermistor is several seconds. A simple design of the device for determining the thermal conductivity coefficient by the thermistor direct heating method (Fig. 1) allows using the proposed method for the simultaneous measurement of several test samples, which significantly reduces the time of research. This is an advantage of this study over similar ones.

The analysis of the given mathematical dependence of determining the thermal conductivity of substances on the basis of the obtained data of thermistor heating temperature (10) shows that to achieve a measurement accuracy of less than 3 % in different temperature ranges, it is necessary to provide the
same thermistor power (Fig. 2). This is explained by the nonlinear dependence of the thermistor resistance on its temperature.

In further applications of the method in practice and theoretical developments, it is necessary to take into account the thermistor characteristics, and for each particular case, thermistors with the corresponding characteristics in the respective operating modes should be applied.

Thus, when measuring over a wide temperature range, it is necessary to change the amplitude of the thermistor heating pulse and apply different thermistor modifications. For example, for measurements at temperatures above 100 °C, thermistors coated with a glass shell must be used.

Further investigations of other substances, mixtures, biological and food materials should take into account not only the problems indicated, but also the properties of the materials themselves, especially when they change over time or under the influence of external factors.

7. Conclusions

1. The data obtained from the studies coincide (the deviation error does not exceed 2.7 %) with the data published in the literature, and the relative error of determining the thermal conductivity coefficient from the measurement data did not exceed 3 %. The results of the studies confirm the possibility of using the thermistor direct heating method for measuring the thermal conductivity coefficient of various substances.

2. The simplicity of the measuring probe and the meter allow the creation of simple measuring instruments for the simultaneous determination of several samples, which significantly reduces the time of research and, thus, improves the measurement efficiency.

3. The mathematical dependence describing the process of determining the TPP of substances, based on the fact that to determine the thermal conductivity coefficient by the thermistor direct heating method, it is sufficient to directly measure the temperature of thermistor heating in the test substance is proposed. The nonlinear nature of the obtained thermistor heating dependence is taken into account, and appropriate corrections are made when performing the calculations of the thermal conductivity coefficient.

4. Measurements of the thermal conductivity coefficient of sugar, glycerol and aqueous ethanol solutions confirm the possibility of applying thermal control using the thermistor direct heating method to determine the composition of different mixtures. The condition for this method is the difference between the thermal conductivity coefficients of the constituent components of the solution. The difference in the thermal conductivity coefficients of the solution components will determine the error when calculating the content of the investigated component in the mixture (solution). In the study of multicomponent substances, the content of each component should be determined by introducing additional substances to the solution which, when interacted with the corresponding component, change the TPP of the mixture.

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