Journal of Engineering Physics and Thermophysics, Vol. 80, No. 5, 2007

HEAT CAPACITY OF NATURAL FRUIT JUICES AND OF THEIR CONCENTRATES AT TEMPERATURES FROM 10 TO 120°C

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UDC 536.71:536.22:522.14

The heat capacity of natural apple, cherry, and raspberry juices and of their concentrates has been studied at temperatures from 10 to 120°C and pressures of 0.1 and 2 MPa. A setup based on the method of adiabatic calorimeter was assembled to carry out investigations. An estimate of the error of setup operation as well as control measurements on water prove the accuracy of experimental data to be within ±0.8% at the indicated parameters of state. For the heat capacity of juices 175 values have been obtained. Equations that describe experimental data as functions of temperature and content of dry matter have been constructed.

At the present time an important challenge to the foodstuff industry is the improvement of the technology of production of materials and products and, in particular, creation of new methods of processing them that would ensure high qualitative technical and economical characteristics. This, in turn, presupposes construction of new highly productive and highly technological machines and apparatuses, which is unachievable without data on the thermophysical properties of foodstuffs [1, 2]. The information available in the literature shows that despite the intense investigations carried out by experimentalists working in the field [3–10], the thermophysical data have not been systematized for a whole number of substances and sometimes they are accidental in character.

A detailed study of the heat capacity of a grape juice was carried out in [11]. An electrocalorimetric method was used. The working part of the setup was a Dewar vessel placed into an air thermostat the temperature in which was maintained identical with that of the test liquid. Seventy-eight values were obtained by the authors for the heat capacity in the temperature range 20–80°C with a step of 5°C for concentrations of 15, 20, 30, 40, 50, and 58% of grape juice. The results were tabulated.

In [12], some thermophysical characteristics of an orange juice were investigated, including its heat capacity. Measurements were made with the aid of a cell made in the form of coaxial cylinders. The investigations were carried out at temperatures of 0, 5, 8, 18, 27, 47, 53, and 62°C. The concentrations were 0.34, 0.40, 0.44, 0.50, 0.55, 0.59, 0.63, 0.69, and 0.73 of mass fractions to water content. Seventy-two experimental values of heat capacity were obtained. It should be noted that the work presented only graphical information and the equation

$$c_p = 1424.34 + 2673.19X_{\mathrm{w}} + 2.446T\,. \tag{1}$$

According to the authors, the correlation factor was no less than 0.97.

In [13], the heat capacity of a natural grape juice was investigated. The content of dry matter was determined by a refractometer at 20°C. An equation of the type

$$c_p = yc_{p\mathrm{s}} + (1 - y)\,c_{p\mathrm{w}}\,, \tag{2}$$

was compiled, which is valid at 25°C with an error of 2.8%.

In [14], the heat capacity of a guava juice was investigated at 30–80°C. The investigated samples of the juice had a concentration of 10, 15, 20, 25, 30, 35, and 40°Brix. The content of glucose in the juice having a concentration of 10°Brix was 1.38%; 1.66% of fructose, and 0.74% of saccharose. To describe the dependence of the heat capacity on temperature for a juice with 10°Brix the following equation was obtained:

Azerbaijan State Economical University, 6 Istiglaliiyat Str., Baku, AZ1001, Azerbaijan. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 80, No. 5, pp. 192–200, September–October, 2007. Original article submitted May 23, 2006; revision submitted January 22, 2007.

$$c_p = 3.96 + 0.00054T\,. \tag{3}$$

The error was estimated to be within ±0.004 kJ/(kg·K).

In [15], to determine the heat capacity of celery juice a dynamic method was used. Two measuring cells were employed. The rate of change in temperature was 10°C/min. A sample was heated from -40°C to $+20^{\circ}$C. A linear equation was obtained that describes the dependence of the specific heat on concentration at a temperature of 20°C:

$$c_p = 4.22 - 0.03C\,. \tag{4}$$

The correlation factor was equal to 0.958.

There are a number of equations and models available in the literature that were suggested to describe the heat capacity of liquid foodstuffs. A brief review is given below. In [16], an equation was compiled to calculate the heat capacity above the freezing point in the form

$$c_p = 0.837 + 3.349X_{\mathrm{w}}\,. \tag{5}$$

Its application is restricted to a low content of dry matter. In [17], a model that describes the heat capacity of pea-nuts oil is suggested:

for an unhydrated oil at a temperature from 26.84 to 56.84°C

$$c_p = 2.057 + 0.00167T\,, \tag{6}$$

and for a hydrated one at 46.84–76.84°C

$$c_p = 1.97 + 0.00489T\,. \tag{7}$$

In [18], the following expression was suggested, which can be used predominantly for products with a high moisture content (usually, above 50%):

$$c_p = 1.675 + 2.512X_{\mathrm{w}}\,. \tag{8}$$

In [19], a model that represents the contributions of individual components to the heat capacity was suggested:

$$c_p = 2.093X_{\mathrm{f}} + 1.256X_{\mathrm{s}} + 4.187X_{\mathrm{w}}\,. \tag{9}$$

The latter equation was extended to the expression [20]

$$c_p = 1.424X_{\mathrm{c}} + 1.549X_{\mathrm{p}} + 1.675X_{\mathrm{f}} + 0.837X_{\mathrm{a}} + 4.187X_{\mathrm{w}}\,. \tag{10}$$

In [21], an equation of the form

$$c_p = 4.187X_{\mathrm{w}} + (1.373 + 0.0113T)\,X_{\mathrm{s}}\,, \tag{11}$$

is given that describes the heat capacity of milk at contents of solid matter 8–40% within the temperature range 40–80°C. In [22], an equation to calculate the heat capacity of various fruits and juices in a wide range of concentrations is suggested:

$$c_p = 885 + 33.0C_{\mathrm{w}} + 1.6T\left(1 - \frac{C_{\mathrm{w}}}{100}\right). \tag{12}$$

The present work is the continuation of a series of complex investigations into the thermophysical properties: density [23–27], viscosity [24, 26, 28, 29], thermal conductivity [25, 26, 29, 30], thermal diffusivity [25, 29, 31, 32],

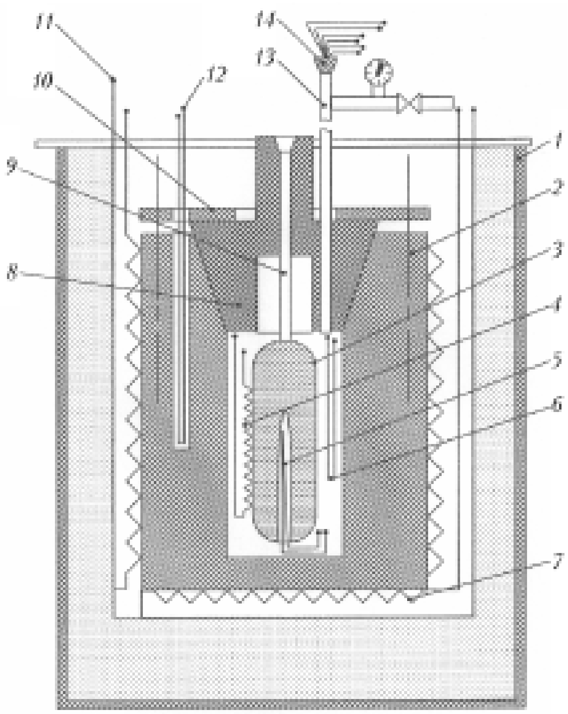


Fig. 1. Schematic diagram of the experimental setup: 1) thermally insulated casing; 2) copper block-thermostat; 3) measuring cell; 4) microheater; 5) thermocouple; 6) differential thermocouple; 7) outer heater (bottom one); 8) cone sealing; 9) pipe for leading out the upper and lower capillaries; 10) cap; 11) outer heater (on the side); 12) resistance thermometer; 13) pipe for leading out wires; 14) funnel.

electrical conductivity [33, 34], and surface tension [35]. The heat capacity is one of the most important characteristics of liquid foodstuffs. The results of its study are given below.

To carry out experimental investigations of the heat capacity of juices a setup was assembled, which implements the method of adiabatic calorimeter. Its schematic diagram is shown in Fig. 1. The setup consists of a thermally insulated casing 1, copper block-thermostat 2, and a measuring cell 3. The measuring cell made from stainless steel is the main element of the setup. The vessel is placed into the thermostat with a small gap from the outer wall. As the thermostat a massive copper envelope is used around which a nichrome heater 11 is wound uniformly over the height. In the lower part of the thermostat there is a bottom heater 7. A fine-regulation heater 4 is wound around the surface of the measuring cell. The copper block is covered by a cap 10 with cone sealing 8 inside which there is a pipe 9 for the output of the upper and lower capillaries. In the upper part of the copper block there is a pipe 13 to lead out wires. The end of the pipe has the shape of a funnel 14 which is filled with resin for air insulation.

The space between the temperature-controlled envelope and the measuring cells is evacuated to sustain adiabaticity. Inside the thermostat there are a thermocouple 5 and a differential thermocouple 6. There is also a socket for a platinum resistance thermometer 12.

The schematic diagram of the measuring cells is shown in Fig. 2. It consists of an ampoule 1, upper capillary 2, pipe 3 for a thermocouple, microheater 4, thermocouple 5, and a lower capillary 6. The cell has a length of 0.095 m, inner diameter 0.020 m, and wall thickness 0.0009 m. The gap between the measuring cell and the envelope is 8–10 mm. Two capillaries (upper and lower) are welded to the measuring ampoule: The lower one is needed for reliable filling of the ampoule with a test liquid 7 without air pockets (it is closed by a valve when the ampoule is filled), and the upper one is connected to the manometer, with the aid of which a pressure is created and measured in the system. In production and processing of liquid foodstuffs a maximum pressure in the apparatuses usually does not exceed 5 MPa. Therefore the construction of the measuring cell was designed precisely for such high pressures. The thickness

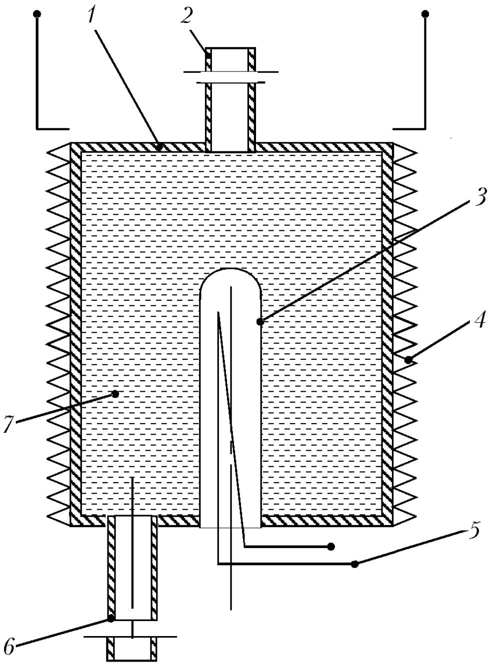


Fig. 2. Schematic of the measuring cell: 1) ampoule; 2) upper capillary; 3) pipe for the thermocouple; 4) microheater; 5) thermocouple; 6) lower capillary; 7) test liquid.

of the ampoule must be minimal to reduce the ballast heat capacity of the ampoule itself. Calculations have shown that such a construction of the cell with the dimensions selected by us allows one to raise the pressure of a test substance up to 10 MPa at temperatures of up to 200°C.

The volume of the inner cavity of the cell was determined by careful calibration with water, and the working volume of the calorimeter at various parameters was found from the equation

$$V = V_0 (1 + 3\alpha (T - 293) + \beta (p - 0.1)) , \tag{13}$$

$$\beta = \frac{2}{(R^2 - r^2) E} \left[(1 - 2\mu) r^2 + (1 + \mu) R^2 \right] . \tag{14}$$

The working formula of the method has the form

$$c_p = \frac{1}{\rho V} \left[\frac{W - A(t)}{b} - c_{\text{am}}(t) \right] [1 + \sigma] . \tag{15}$$

The quantities $A(t)$ and $c_{\text{am}}(t)$ are the functions of temperature; they were determined from calibrating tests with an empty ampoule.

To measure the rate of heating, a higher value of emf than that indicated by a thermocouple is set on the potentiometer. At the instant when the arrow of the device passes zero, the time counter is switched on. The value of emf increases and at the moment of the second passage of zero the timer is stopped. It is from the value of the added emf and the time reckoned that the rate of heating is determined.

The error in determining the temperature of the test liquid is 0.05°C. The accuracy of determining pressure corresponds to the class of the MP-60 piston manometer and is equal to 0.05. The error of finding the mass of the test liquid in the ampoule depends on the accuracy of determining the density and on the measuring volume. The density was determined by us in previous works with the aid of pycnometers of volume 50 cm^3 with an error not exceed-

TABLE 1. Chemical Composition of Apple, Cherry, and Raspberry Juices (%)

Substance	Juice		
	Apple	Cherry	Raspberry
Saccharose	0.52	0.46	1.44
Glucose	1.55	5.28	1.60
Fructose	6.12	4.11	2.50
Pectins	0.58	0.55	1.12
Ocidity	0.62	0.68	1.74

TABLE 2. Heat Capacity of Apple Juice

T, ^{o}C	C, %				
	14.3	25.8	35.2	44.7	51.6
10	3.752	3.539	3.264	2.964	2.761
25	3.776	3.559	3.296	2.999	2.788
35	3.796	3.572	3.323	3.008	2.795
50	3.829	3.605	3.372	3.048	2.827
60	3.846	3.639	3.384	3.071	2.847
70	3.857	3.671	3.413	3.098	2.869
80	3.872	3.698	3.448	3.113	2.868
90	3.882	3.718	3.477	3.157	2.894
100	3.923	3.759	3.496	3.174	2.918
110	3.937	3.787	3.517	3.207	2.968
120	3.987	3.818	3.546	3.259	3.076

TABLE 3. Heat Capacity of Cherry Juice

T, ^{o}C	C, %				
	11.3	18.8	26.3	37.2	48.4
10	3.820	3.592	3.370	3.060	2.760
20	3.850	3.635	3.430	3.130	2.840
30	3.862	3.663	3.458	3.160	2.864
40	3.886	3.691	3.483	3.194	2.904
50	3.910	3.710	3.515	3.218	2.930
60	3.932	3.745	3.538	3.241	2.954
70	3.955	3.780	3.550	3.265	2.975
80	3.972	3.808	3.573	3.274	2.986
90	3.994	3.83	3.592	3.280	3.010
100	4.009	3.857	3.608	3.301	3.024
110	4.014	3.871	3.617	3.318	3.039
120	4.023	3.885	3.631	3.329	3.052

ing 0.05%. At a pressure exceeding the atmospheric one and a temperature above 90^{o}C the density was measured on an experimental setup based on the method of hydrostatic pressure. The error in the determination of density was 0.08% at temperatures of up to 120^{o}C. The error in the determination of the measuring volume does not exceed 0.1%. Thus, the total error does not exceed 1.2% at temperatures of up 200^{o}C. The results of control measurements of the heat capacity of water agree with the reference data within 0.8%.

In the present work, the heat capacity of apple, cherry, and raspberry juices was investigated. The apple juice was investigated for dry matter concentrations of 14.3, 25.8, 35.2, 44.7, and 51.6% at temperatures from 10 to 120^{o}C (all in all 12 isotherms), the cherry juice — for concentrations 11.3, 18.8, 26.3, 37.2, and 48.4% at 25–120^{o}C (10 isotherms), and a black currant juice – for 13.1, 20.6, 29.3, 37. 4, 41.9, and 51.6% at 25–120^{o}C (10 isotherms). At temperatures above the boiling point, i.e., at 100–120^{o}C, the tests were run at a pressure of 2 MPa.

TABLE 4. Heat Capacity of Raspberry Juice

T, ^{o}C	C, %					
	13.1	20.6	29.3	37.5	41.9	51.6
10	3.842	3.652	3.386	3.148	3.075	2.853
20	3.853	3.669	3.426	3.193	3.123	2.891
30	3.871	3.691	3.446	3.276	3.181	2.913
40	3.902	3.742	3.479	3.306	3.217	2.951
50	3.914	3.759	3.506	3.328	3.238	2.964
60	3.932	3.772	3.519	3.358	3.273	3.002
70	3.946	3.792	3.547	3.389	3.295	3.024
80	3.957	3.811	3.578	3.409	3.316	3.042
90	3.974	3.834	3.596	3.424	3.339	3.053
100	3.986	3.851	3.617	3.445	3.36	3.065
110	3.997	3.862	3.64	3.475	3.385	3.085
120	4.009	3.88	3.664	3.491	3.401	3.101

To carry out the investigations, fresh fruits at the stage of biological ripeness were chosen. Juice was squeezed out with the aid of a laboratory press, then was settled and twice filtered. To obtain juice concentrates, a vacuum facility was used, in which the temperature was kept not higher than 50^{o}C during vaporization. After filtration the juice was also subjected to chemical analysis. The results of these investigations are given in Table 1; they agree with average values obtained by other researchers. Experimental data on the heat capacity of the apple, cherry, and raspberry juices are presented in Tables 2–4.

For the convenience of practical application of the results of thermophysical investigations, equations are used that correlate this property with the state parameters. In the first stage the temperature dependence of the heat capacity of the juices was determined. An analysis has shown that this dependence is close to a linear one. The compiled equations of the temperature dependence of the heat capacity at a fixed concentration of dry matter for different juices have the following form:

apple juice

$$C = 14.3\% \,, \quad c_p = 3.722 + 2.010\cdot 10^{-3} T \,; \quad C = 25.8\% \,, \quad c_p = 3.475 + 2.808\cdot 10^{-3} T \,;$$

$$C = 35.2\% \,, \quad c_p = 3.233 + 2.628\cdot 10^{-3} T \,; \quad C = 44.7\% \,, \quad c_p = 2.916 + 2.671\cdot 10^{-3} T \,;$$

$$C = 51.6\% \,, \quad c_p = 2.696 + 2.573\cdot 10^{-3} T \,;$$

cherry juice

$$C = 11.3\% \,, \quad c_p = 3.811 + 1.919\cdot 10^{-3} T \,; \quad C = 18.8\% \,, \quad c_p = 3.58 + 2.702\cdot 10^{-3} T \,;$$

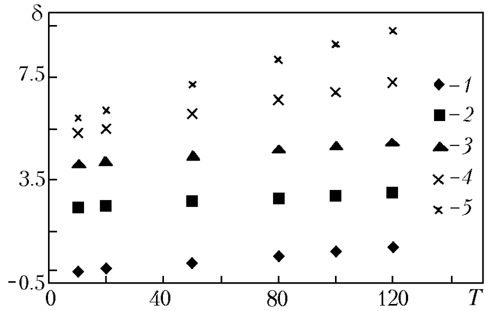
$$C = 26.3\% \,, \quad c_p = 3.386 + 2.215\cdot 10^{-3} T \,; \quad C = 37.2\% \,, \quad c_p = 3.088 + 2.19\cdot 10^{-3} T \,;$$

$$C = 48.4\% \,, \quad c_p = 2.789 + 2.392\cdot 10^{-3} T \,;$$

raspberry juice

$$C = 13.1\% \,, \quad c_p = 3.831 + 1.55\cdot 10^{-3} T \,; \quad C = 20.6\% \,, \quad c_p = 3.640 + 2.098\cdot 10^{-3} T \,;$$

$$C = 29.3\% \,, \quad c_p = 3.374 + 2.451\cdot 10^{-3} T \,; \quad C = 37.5\% \,, \quad c_p = 3.163 + 2.922\cdot 10^{-3} T \,;$$



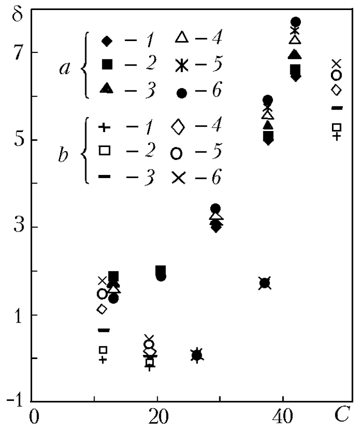


Fig. 3. Error in using a single equation to describe test data on the heat capacity of apple juice depending on temperature at different contents of dry matter: 1) C = 14.3%; 2) 25.8; 3) 35.2; 4) 44.7; 5) 54.6. T, °C.

Fig. 4. Error in using a single equation to describe test data on the heat capacity of raspberry (a) and cherry (b) juices depending on the content of dry matter at different temperatures: 1) T = 10°C; 2) 20; 3) 50; 4) 80; 5) 100, and 6) 120. C, %.

$$C = 41.9\% \,,\quad c_p = 3.084 + 2.819 \cdot 10^{-3} T \,;\quad C = 51.6\% \,,\quad c_p = 2.852 + 2.204 \cdot 10^{-3} T \,.$$

The dependence of the heat capacity of the juices on concentration differs from a linear one; therefore a second-order polynomial was used for its description;

$$c_p = A_1 + B_1 C + D_1 C^2 \,. \tag{16}$$

In a general form the equations for the juices considered are

apple juice

$$c_p = 3.946 - 1.218 \cdot 10^{-2} C - 2.358 \cdot 10^{-4} C^2 + 9.305 \cdot 10^{-4} T + 9.909 \cdot 10^{-5} CT - 1.324 \cdot 10^{-6} C^2 T \,,\quad \delta = \pm 1.2\% \,;$$

cherry juice

$$c_p = 4.138 - 2.991 \cdot 10^{-2} C + 4.279 \cdot 10^{-5} C^2 + 1.845 \cdot 10^{-3} T + 3.0547 \cdot 10^{-5} CT - 4.377 \cdot 10^{-7} C^2 T \,,\quad \delta = \pm 0.8\% \,;$$

raspberry juice

$$c_p = 4.249 - 3.278 \cdot 10^{-2} C + 1.1091 \cdot 10^{-4} C^2 - 3.339 \cdot 10^{-4} T + 1.677 \cdot 10^{-4} CT - 2.2665 \cdot 10^{-6} C^2 T \,,\quad \delta = \pm 1.3\% \,.$$

In the production of juices, great attention is paid to blended juices containing two or more components. Naturally, it is hardly possible to carry out experimental investigations for the entire variety of the juices produced. In our opinion, the sole correct solution seems to be the derivation of a generalized equation that could describe, with an accuracy applicable for industrial purposes, some thermophysical property depending on the parameters of state and content of dry matter. In the present work we have made an attempt to devise such an equation for the heat capacity of fruit juices on the basis of literature data:

$$c_p = 4.115 - 2.56 \cdot 10^{-2} C - 9.5 \cdot 10^{-5} C^2 + 7.727 \cdot 10^{-5} T + 1.5 \cdot 10^{-4} CT - 2.4 \cdot 10^{-6} C^2 T \,. \tag{17}$$

In its derivation the aim was to use as small a number of coefficients as possible.

The influence of temperature on the error in the description of experimental data on the heat capacity of an apple juice by a single equation is shown in Fig. 3. As follows from the calculations, the error increases insignificantly with increase in temperature. This becomes noticeable at high concentrations. The standard error in describing experimental data by the equation is 3.8%, which should be considered satisfactory. However, at a high content of dry matter the error is significant: it reaches 8–9% at temperatures 100–120^{o}C for a maximum concentration.

Figure 4 demonstrates the behavior of the error resulting from the description of experimental data on the raspberry juice (a) and cherry juice (b) by equation (17). In the first case it attained 3.5%, in the second 1.6%. Just as in the case of the apple juice, the error increases insignificantly with temperature and appreciably with an increasing concentration. The maximum errors are equal to 6–7% for the raspberry juice at concentrations of 41.9%. For the cherry juice these errors are equal to 5.0–6.5% for a concentration of 48.4%.

Conclusions. It has been established that the temperature dependence of the heat capacity of the apple, cherry, and raspberry juices and their concentrates is close to linear. The concentration dependence of the heat capacity is well described by a second-order polynomial. A single equation has been suggested that allows one to calculate the heat capacity of various fruit juices with an accuracy sufficient for practical purposes.

NOTATION

$A(t)$, power scattered between the ampoule and envelope at a zero reading of the differential thermocouple, W; A_1, B_1, D_1, coefficients of Eq. (16); b, heating rate, K/sec; C, concentration of dry matter, %; C_{w}, concentration of water, %; $c_{\mathrm{am}}(t)$, heat capacity of the ampoule, kJ/(kg·K); c_p, specific heat, kJ/(kg·K); $c_{p\mathrm{w}}$, specific heat of water, kJ/(kg·K); $c_{p\mathrm{s}}$, specific heat of grape sugars, kJ/(kg·K); E, elasticity modulus of the ampoule material, Pa; p, pressure, Pa; R, outer radius, m; r, inner radius, m; T, temperature, ^{o}C; t, time, sec; V, internal volume of the ampoule, m^3; V_0, volume of empty ampoule at a temperature of 293 K, m^3; W, power of the heater located in the measuring cell, W; X_{a}, fraction of ash; X_{c}, fraction of hydrocarbons; X_{p}, fraction of protein; X_{w}, fraction of water; X_{f}, fraction of fats; X_{s}, fraction of a solid component; y, weight fraction equivalent to saccharose; α, coefficient of linear expansion of the ampoule material, K^{-1}; β, baric coefficient, Pa^{-1}; μ, Poisson coefficient; δ, error; σ, correction for nonlinearity; ρ, density of the substance investigated. Subscripts: a, ash; c, hydrocarbons; f, fats; p, protein; s, solids; w, water; am, ampoule.

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