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Measurement and Modeling of Thermal Conductivity of Frozen Surimi*

Mjerenje i modeliranje toplinske vodljivosti zamrznutih surimija

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Summary

A design of a system for measurement of thermal conductivity of food by the method of unsteady response from a line heat source is presented. The method is applied for determination of dependence of thermal conductivity of frozen surimi on temperature and cryoprotectant concentration. Measurements were performed in the temperature range from –25 °C to +5 °C. A mathematical model is developed and it is proven that response from a line heat source is defined by the first order exponential integral function $E_1(x)$. The estimated parameter is present in the model as a part of the boundary condition. Data are obtained from responses induced by impulses in the power range 2.25 – 4.2 W m^{-1}, sampled with an A/D converter with the frequency of 3.5 kHz, and are analyzed in the linear range by the least squares method. The effect of cryoprotectant Polydextrose, added in the mass fraction range 0 – 12 % was studied. Data are modeled by the Schwartzberg's model and validated by statistical analysis.

Sažetak

U radu je opisan sustav za mjerenje toplinske vodljivosti hrane primjenom nestacionarnih odziva pobuđenih impulsima topline iz linearnog izvora topline. Postupak je primijenjen za određivanje ovisnosti toplinske vodljivosti zamrznutih »surimija« o temperaturi i masenom udjelu polidekstroze u granicama od 0 do 12 %. Mjerenja su provedena u temperaturnom području od –25 °C do +5 °C. Izveden je matematički model i dokazano je da je odziv mjernog sustava određen eksponencijalno integralnom funkcijom prvog reda $E_1(x)$. Procijenjeni je parametar dio modela rubnih uvjeta. Podaci su dobiveni iz odziva pobuđenih impulsima u području snage od 2,25 do 4,2 W m^{-1}, uzorkovani A/D pretvornikom s frekvencijom od 3,5 kHz, i analizirani u linearnom području primjenom postupka najmanjih kvadrata. Schwartzbergov je model prilagođen izmjerenim podacima, a valjanost procjene parametara provjerena statističkom analizom.

Introduction

For design and control of food production processes, which are based on thermal operations, it is important to determine process parameters involved in heat transfer, especially thermal conductivity which is a function of temperature and complex chemical composition subject to changes during processing *(1)*. There are various methods for the experimental determination of thermal conductivity which may be generally classified as steady state and transient methods *(2)*. For determination of the thermal conductivity parameter k there is no standard method, but most frequently used is the transient method with the thermal conductivity probe and a line heat source *(3)*. The theoretical bases of the method are given by Hooper and Lepper (1950) and Nix *et al.* (1967) *(4)*. The theory *(5)* is based on the fact that temperature rise at a point close to a line heat source, in a semi-infinite solid subject in step change of power of heat source is a function of applied power, time, and the two parameters: thermal conductivity and diffusivity.

For experimental study of cryoprotectant effect on thermal conductivity a measurement system based on online analysis of temperature response was constructed. Due to high sampling frequency, each experiment yields computer files with a large number of data enabling de-

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tailed analysis based on exact mathematical model of heat transfer dynamics and statistical evaluation of residual errors. For modeling functional dependence of thermal conductivity on temperature and cryoprotectant concentration Schwartzberg's nonlinear model is applied *(6)*.

Mixture of sorbitol/sucrose has long been considered as the best cryoprotectant, but the latest investigations show that the same properties are achieved with low-calorie polysaccharides (Polydextrose, Palatanit and Lactitol) which eliminate sweet flavor of final products and stimulate laxative effects *(7–9)*. We have studied the effect of Polydextrose on thermal conductivity of surimi in the mass fraction range 0 – 12 % and at temperatures from –25 °C to +5 °C. Measurement of thermal conductivity in the freezing range can contribute to the understanding of the mechanism of cryostabilization which is a complex process resulting from: 1) dynamics of intermolecular interaction of water-cryoprotectant-protein; 2) intricate process of water-ice phase transformation. As thermal conductivity is a physical parameter, its determination directly reflects the physical state of water; it is especially a function of the ratio of unfrozen and frozen water. Studies of Wang and Kolbe *(6)* show that an increase in cryoprotectant content results in small changes of thermal conductivity in the freezing range, but can be quantified and applied for correction of the parameters in the Schwartzberg's model.

Materials and Methods

Materials

Experiments were conducted with samples of surimi prepared in laboratory from Adriatic pilchard *(Sardina pilchardus)* according to industrial technique described by Lee 1984 *(10)*, Sych *et al. (8)*, with modifications for laboratory preparation *(11)*. Water content was 82.01 %, determined by the AOAC procedure for meat products *(12)*. Polydextrose was added as a cryoprotectant in mass fractions from 0 to 12 %. Total proteins content was 10.95 %, and it was determined in 1 g samples with the method of Kjeldahl *(12)*, (Kjeltec System, model 1002 Distilling Unit). Samples were packaged in polyethylene bags, quickly frozen in liquid nitrogen, and stored at temperature –(25 ± 2) °C. Average storage time of samples before experimental treatment was two weeks.

Initial freezing temperature was determined in separate experiments by the differential temperature analysis (DTA). Water solution of $CaCl_2$, $w(CaCl_2)$ = 30 %, was used *(13)*. Distilled water was used as a calibration substance for static correction of initial freezing temperature and thermal conductivity.

For each experiment, a sample of 5 g of surimi was placed in the measurement tube with careful manipulation to avoid presence of air bubbles in the material. The tube filled with sample was quickly cooled by immersion in liquid nitrogen until the temperature of –40 °C was reached. Upon cooling, the tube was placed in a metal container, insulated from the surroundings, and filled with a mixture of a water and antifreeze at initial temperature of –25 °C. During measurement of thermal conductivity, temperature of sample was continuously monitored and constant rate of temperature increase of 2.5 °C h^{-1} was maintained. Measurement continued until the temperature of +10 °C was reached.

Apparatus for thermal conductivity measurement

For thermal conductivity measurement a laboratory apparatus shown in Fig. 1. was constructed. The construction of the apparatus is based on recommendations from literature *(1,3–6)*. The measurement tube was made of aluminum with diameter of 18 mm and height of 36 mm. The probe is made of a plastic holder which supports a heat source and a thermocouple for measurement of temperature response. The heat source is a stainless steel wire with diameter of 0.1 mm and resistivity of 15.6 Ω m^{-1}. The heat source is connected into electrical circuit with stabilized direct current source (INEL model SI 330/1), potentiometer, milliampermeter, and a mechanical switch. Thermocouple was »in-house« constructed from Chromel and Alumel wires with the diameter of 0.07 mm. The thermocouple wires are placed inside of a steel capillary of diameter 0.1 mm, with the sensor tips extending outward. The distance between the line heat source and the sensor tip is 1.5 mm, while the distance to the tube surface is 7.5 mm, making applicable the assumption of heat transfer in a solid of infinite dimension. The ratio between the diameters of thermocouple wires and the test tube is 1:500, resulting in negligible disturbance of temperature profiles by the presence of the sensor. Time delay in measured responses is avoided by low heat capacity of the sensors. The ratio between the distance between the sensor and heat source to the height of the test tube is 1:20, which enables simplified mathematical analysis of heat transfer as a one-dimensional process in radial direction. The junction of the referent thermocouple was placed in a thermos bottle filled with mixture of fine particles of ice and tap water. Referent temperature of 0 °C was maintained and monitored by a separate digital thermometer during the experiment.

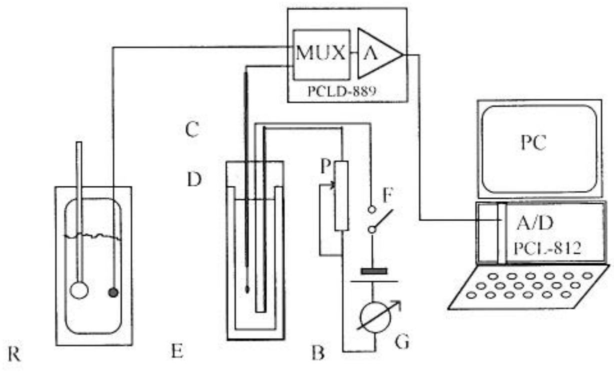

Fig. 1. Measurement system for on-line determination of thermal conductivity. The components are: multiplexer (MUX) with instrumentation amplifier (A) PCLD-889, personal computer (PC), analog to digital converter (A/D) PCL-812, line heat source (B), plastic holder (C), aluminum tube (D), measurement thermocouple (E), mechanical switch (F), milliampermeter (G), potentiometer (P), and referent thermocouple (R).

Slika 1. Mjerni sustav za neposredno (on-line) mjerenje toplinske vodljivosti. Dijelovi su: višepolna elektronička sklopka (MUX) s instrumentacijskim pojačalom (A) PCLD-889, osobno računalo (PC), analogno digitalni pretvornik (A/D) PCL-812, linijski izvor topline (B), plastični nosač (C), aluminijska cijev (D), mjerni termočlanak (E), mehanička sklopka (F), miliampermetar (G), potenciometar (P) i referentni termočlanak (R).

Thermocouples were connected to the on-board multiplexer and their electromotive forces (EMF) were amplified by a high grade instrumentation amplifier (PCLD-889), sampled by a 12 bit A/D converter (PCL-821, Advantech Co., Ltd.) and on-line recorded by a standard PC. The measurement range was calibrated from –25 °C to +10 °C. Standard error in calibration was 50 mK, with achieved resolution of 10 mK. The signals were sampled with the frequency of 3.5 kHz per channel. Each signal was on-line preprocessed for noise rejection. Each package of data was evaluated for its average and standard deviation, and filtering with the 3-standard deviation rule was applied. The reduced package of data was recalculated for improved estimate of average value. The filtered estimates of averages corresponding to intervals of 1 s were recorded as ASCII files on a computer disc, and later imported to standard PC software for mathematical analysis and graphical presentation.

Mathematical model of thermal conductivity measurement

Measurement of thermal conductivity with impulse heat method and line source is based on the mathematical model of transient heat transfer in a test material. The model is based on the heat balance:

$$\frac{\partial T}{\partial t} = \alpha \cdot \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial T}{\partial r}\right) \qquad \alpha(T) = \frac{k}{\rho \cdot c_p} \qquad /1/$$

where α is apparent thermal diffusivity of a sample. Thermal diffusivity is a function of temperature but due to a small heat input during perturbation temperature is assumed constant. The estimated thermal conductivity k is present in the boundary conditions:

$$\lim_{r \to \infty} T(r,t) = 0 \qquad \lim_{r \to 0}\left[2 \cdot \pi \cdot k \cdot r \cdot \frac{\partial T}{\partial r}\right] = Q \qquad /2/$$

where Q is impulse function of dissipated power per unit length of the line source. The corresponding initial condition is:

$$T(r, t = 0) = 0 \qquad /3/$$

The solution is given by the first order exponential integral E_1 *(14)* function of Fourier dimensionless number Fo:

$$T(r,t) = \frac{Q}{4 \cdot \pi \cdot k} \cdot E_1\left(\frac{1}{4 \cdot Fo}\right)$$

$$E_1(x) = \int_x^{\infty} \frac{e^{-t}}{t} \cdot dt \qquad /4/$$

For the estimation is used the least squares method in the linear range of temperature versus $\ln[(t-t_o)/s]$. Thermal conductivity is inverse proportional to the estimated slope *(15)*:

$$k = \frac{Q}{4 \cdot \pi} \cdot \frac{\overline{\{\ln[(t-t_0)/s]\}^2} - \overline{\ln[(t-t_0)/s]}^2}{\overline{T \cdot \ln[(t-t_0)/s]} - \overline{T} \cdot \overline{\ln[(t-t_0)/s]}} \qquad /5/$$

Results and Discussion

A measurement system for determination of thermal conductivity which enables one dimensional treatment of heat transfer was designed. The model is based on two physical parameters: apparent heat diffusivity α, and thermal conductivity k. For the unsteady heat transfer equation /1/ the analytical solution /4/ is derived. Thermal conductivity is estimated from the asymptotic part of the solution (linear in semi-log presentation) by application of the statistical criteria /5/ based on minimization of the variance between an experimental response and the mathematical solution /4/.

Measurements of k were conducted in the temperature range from –25 °C to 10 °C at the rate of thawing of 2.5 °C h^{-1}, and with impulses in the power range per unit length Q, from 2.25 to 4.2 W m^{-1}. Duration of impulses was from 30 to 60 s. Applied power is lower than used by Sweat and Haugh *(3)* and Wang and Kolbe *(6)*, which was enabled by the use of high sensitivity A/D conversion and resulted in reduced disturbance in distribution of unfrozen water in samples.

Maximum amplitude in the temperature was restricted to 0.6 °C in the range below –10 °C, and 0.3 °C in the range from –10 °C to initial freezing temperature T_i. For each sample about 40 experiments were performed and in each experiment 400 data points were taken.

Results of the measurements of k at different cryoprotectant concentrations are presented in Fig. 2. The parameter was determined by linear regression for the temperature range corresponding to /5/, and linearity was checked by determination coefficient (R^2) which was in all experiments in the range 0.97 – 0.99. The result of the test of linearity is in agreement with most of the published data, for example, Sweet and Haugh *(3)* report R^2 values in the range 0.8 – 0.99. In this work better agreement of experimental data with the published result *(5)* is achieved due to improved on-line statistical processing of the measurement signal. Also, by keeping our maximal value of temperature deviation at 0.3 °C, which is lower than the recommended value of 1.5 °C given by Wang and Kolbe *(6)*, we have obtained measurements with minimal disturbances in the temperature range close to the initial freezing points.

The data presented in Fig. 2 were analyzed by the Schwartzberg model *(6)*. The model parameters k_f' and B, were estimated by the least squares method from the linearized model expression given by:

$$\left(k - k_f \cdot \frac{T_i}{T}\right) = k_f' \cdot \left(1 - \frac{T_i}{T}\right) + B \cdot (T_i - T) \qquad /6/$$

In /6/ T_i is determined from DTA as suggested in *(13)*. The initial freezing points were correlated with mass fraction of Polydextrose in surimi samples. A linear model was confirmed. It is shown in Fig. 3 and given by:

$$T_i / K = 272.868 - 0.0368 \cdot w \qquad /7/$$

with the standard error for T_i of 0.032 K, and the determination coefficient $R^2 = 0.95$. The depression of freezing points with an increase in fraction of Polydextrose results from its cryoscopic effect and linearity is in agreement with Rault's law. The Schwartzberg's parameters B

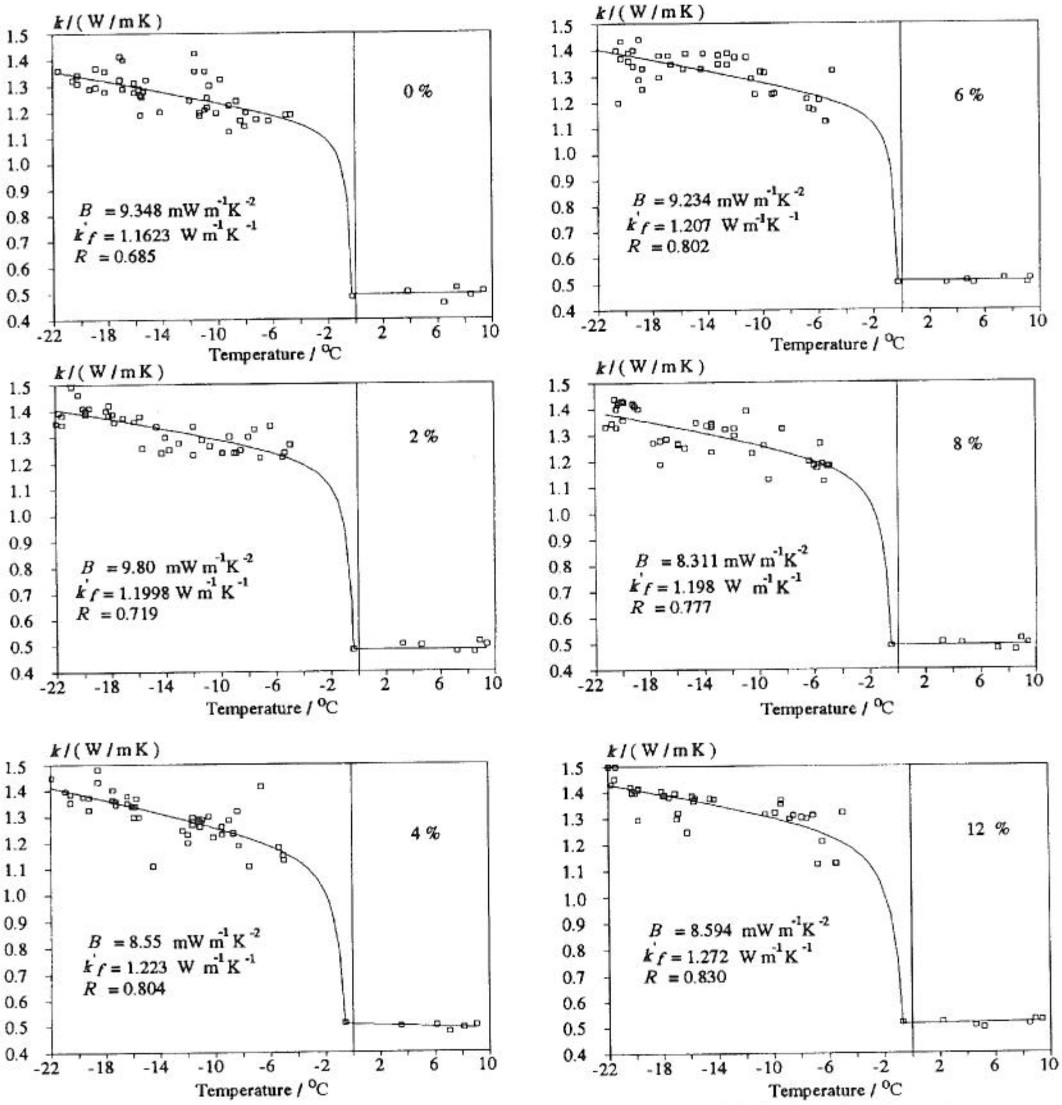

Fig. 2. Graphical presentation of thermal conductivity k (□ experimental and — model data) as function of temperature and mass fraction of Polydextrose w given in %

Slika 2. Grafički prikazi toplinske vodljivosti k (□ eksperimentalni podaci i podaci iz modela —) ovisno o temperaturi i masenom udjelu w polidekstroze izraženim u %

and k_f' were obtained by /6/ for temperatures below the initial freezing points. The mathematical model of thermal conductivity is completed by modeling the dependence of parameters B and k_f' on mass fraction of Polydextrose. A second stage linear regression between each parameter and mass fraction is applied. Experimental values and regression models are presented in Figs. 4 and 5. Each presented value for B and k_f' is the result of 40 separate experiments for which were calculated averages and variances, and taken into account for minimization of weighted variance for model of B:

$$\sigma^2 = \frac{1}{N-2} \cdot \sum_{i=1}^{i=N} \frac{1}{\sigma_i^2} \cdot (B_i - a_0 - a_1 \cdot w_i)^2 \qquad /8/$$

and the same method /8/ is used for the model of k_f'. The obtained results are confirmed by the experiments described by Wang and Kolbe *(6)*. The parameter B, which is related to linear dependence of thermal conduc-

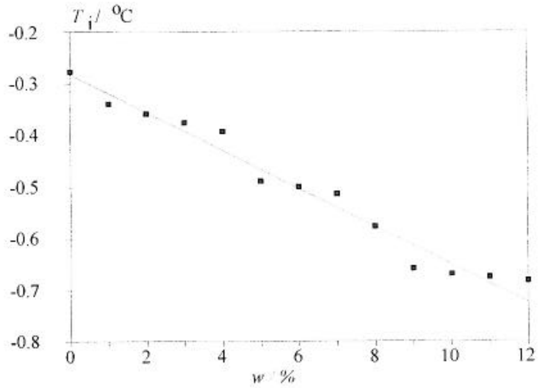

Fig. 3. Dependence of the initial freezing temperature T_i on mass fraction of Polydextrose (■ experimental values, — linear regression model)

Slika 3. Ovisnost početne temperature zamrzavanja T_i o masenom udjelu polidekstroze (■ eksperimentalne vrijednosti, — linearni regresijski model)

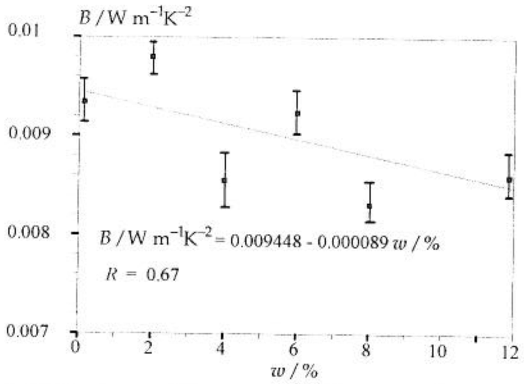

Fig. 4. Dependence of the parameter B on mass fraction of Polydextrose (■ experimental data, — linear regression model, ⊢⊣ are the limits of $\pm\sigma$)

Slika 4. Ovisnost parametra B o masenom udjelu polidekstroze (■ eksperimentalne vrijednosti, — linearni regresijski model, ⊢⊣ granice $\pm\sigma$)

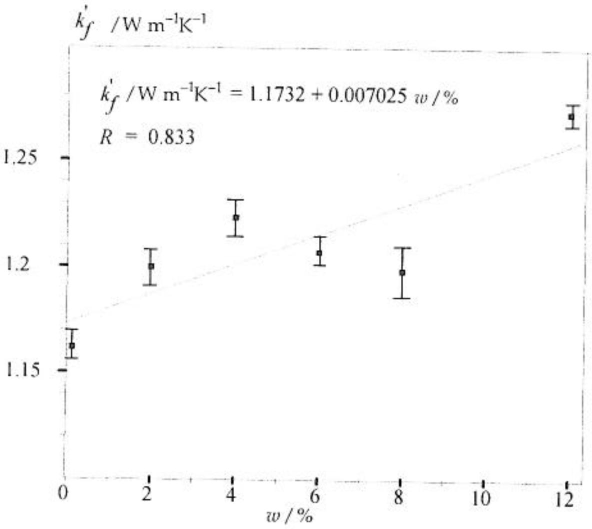

Fig. 5. Dependence of the parameter on mass fraction of Polydextrose (■ experimental data, — linear regression model, ⊢⊣ are the limits of $\pm\sigma$)

Slika 5. Ovisnost parametra o masenom udjelu polidekstroze (■ eksperimentalne vrijednosti, — linearni regresijski model, ⊢⊣ granice $\pm\sigma$)

tivity on temperature, decreases with increasing concenration of Polydextrose due to increase level of bound water, i.e. it is a result of cryoprotectant effect. Presence of bound water limits migration of water molecules from the surroundings of myofibril proteins, slows growth of ice crystals and decreases the amount of frozen water, which is then reflected in thermal conductivity.

Conclusion

A laboratory thermal conductivity probe for thermal conductivity measurements with on-line monitoring and data processing by a standard PC was designed. High sampling rate and applied statistical noise rejection enabled highly reproducible experiments, effective measurement noise rejection, and improved parameter estimation.

The exact mathematical model for heat transfer was derived, based on apparent heat diffusivity, and thermal conductivity was introduced as a parameter in the model of a boundary condition. The data were analyzed from transient response in the linear range.

The method was applied for measurement of thermal conductivity of surimi with addition of Polydextrose as a cryoprotectant in the temperature range from –25 °C to +5 °C. The data for thermal conductivity were confirmed by the linearized form of Schwartzberg's model, and the model parameters were linearly correlated with mass fraction of the cryoprotectant.

The complete model is applicable for the estimation of cryoprotectant function in frozen samples based on thermal conductivity measurement.

List of symbols
Popis oznaka

a_0	$W\,m^{-1}\,K^{-2}$	intercept in Schwartzberg model odsječak na ordinati u Schwartzbergovu modelu
a_1	$W\,m^{-1}\,K^{-2}$	slope in Schwartzberg model koeficijent smjera u Schwartzbergovu modelu
B	$W\,m^{-1}\,K^{-2}$	parameter in Schwartzberg model parametar u Schwartzbergovu modelu
c_p	$J\,kg^{-1}\,K^{-1}$	specific heat capacity at constant pressure specifični toplinski kapacitet pri stalnom tlaku
$E_1(x)$		first order exponential integral function eksponencijalno integralna funkcija prvog stupnja
Fo		dimensionless Fourier variable bezdimenzionalna Fourierova varijabla
k	$W\,m^{-1}\,K^{-1}$	thermal conductivity toplinska vodljivost
k_f, k_f'	$W\,m^{-1}\,K^{-1}$	parameters in Schwartzberg model parametri u Schwartzbergovu modelu
N		number of data broj podataka
Q	$W\,m^{-1}$	power per unit length snaga po jedinici duljine
R		correlation coefficient koeficijent korelacije
r	m	radius radijus
T	K	temperature temperatura
T_i	K	initial freezing point početna temperatura zamrzavanja
t	s	time vrijeme
t_0	s	initial time početno vrijeme
w		mass fraction maseni udio
α	$m^2\,s^{-1}$	apparent thermal diffusivity prividna toplinska difuzivnost
ρ	$kg\,m^{-3}$	density gustoća
σ		standard deviation standardna devijacija
σ^2		variance varijanca

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