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EXPERIMENTAL AND ANALYTICAL DETERMINATION OF FREEZING POINT DEPRESSION

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ABSTRACT

The work presents characteristics of determination and prediction of the freezing point of agricultural products and food with some analytical methods. Using 11 models and special software this property was computed including 299 freezing cases of differentiated products. To obtain that the authors experiments (52 products) were made. The data concerning other cases were drawn from literature. Model accuracy was estimated on the basis of results from the statistical analysis of relative error of prediction. The Chang-Tao's method was regarded the best owing to its universality, while Salvadori-Mascheroni's one the least accurate.

Key words: freezing, freezing point, prediction methods

INTRODUCTION

Freezing as an arranged set of processes occurring in product and its surrounding is a result of heat removal from a product under the definite conditions till a technologically programmed temperature has been obtained. Separation and thorough characteristics of each freezing stage course, i.e. chilling, pure freezing and freezing up, is not possible due to among others unsteadiness of the process. Generally, the first stage consists in product temperature reduction to its initial freezing point depression, whereas at the next one -continuation of lowering till a moment when on average 75% of freezable water contained in a product has been crystallized. Theoretically, one can be alluded that product temperature at this stage of the process should maintain at the

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constant level. Practically, owing to the constant heat removal and progressing water -freezing up there is recorded increase of water solution concentration in a product resulting in turn in drop of freezing point value [3]. The following stage – freezing up is continuation of product temperature reduction along with freezing of water contained there and it closes with obtainment of the conditions programmed at the technological process.
Freezing point proves to- be one of the most important properties of agricultural products and food in this process, therefore its appropriate determination, prediction above all, makes a vital problem in the freezing process regarding the multidirectional significance of this property. Its full characteristics is necessary for projects of agricultural products and food freezing as well as design of machines for its realisation [11]. The knowledge on the freezing point is also indispensable for some other reasons, like possibility to determine water activity of products [2].

The objective of the present work was to characterise the selected methods for freezing point prediction of agricultural products and food performed by means of computational analysis in comparison to the authors' own results and the complementary data obtained from the literature.

MATERIALS AND METHODS

The studies focused on the course of full freezing process of 52 products grouped as following: fruits, vegetables, vegetable-fruit juices and meat, including fish. All the products were frozen under natural convection with gravitational air movement at –31.0°C temperature. The course of temperature dependence on the process time was registered by a measuring set including electronic thermometer TA 100 type with thermocuples NiCrNi kit and recording computer (fig. 1). Freezing point was determined each time out of freezing curve diagram by a tangent method of Christodulo-Rjutov [3] (fig. 2). The "solid" products were mostly frozen without any packages according to infinite cylinder model maintaining one-dimensional heat removal from the samples. The "liquid" products were frozen in fit aluminium, cylindrical containers of 0.03 m diameter and 0.04 m height.

Figure 1. Test stand: 1 – digital multi-channel thermometer type TA 100, 2 – thermocouples NiCrNi, 3 – computer PC, 4 – measuring containers, 5 – refrigerating unit type Z-40, 6 – water bath type UL-1, A – thermocouple position in measuring container

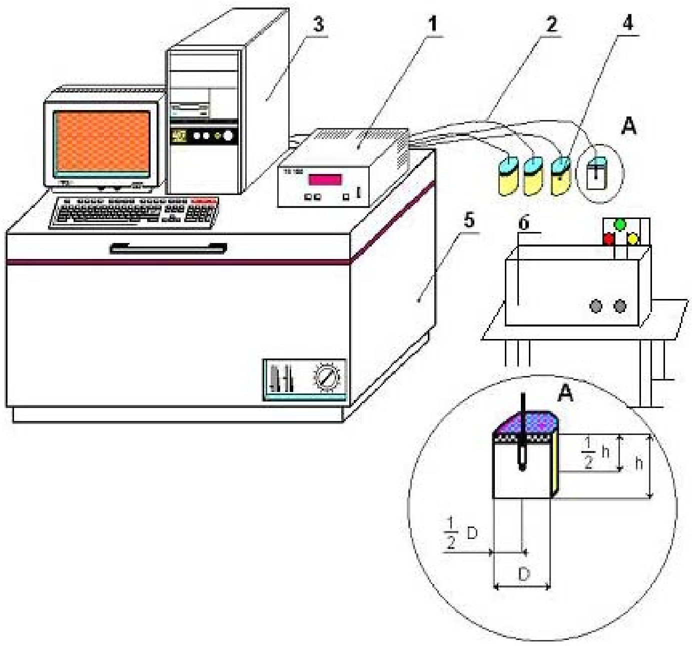
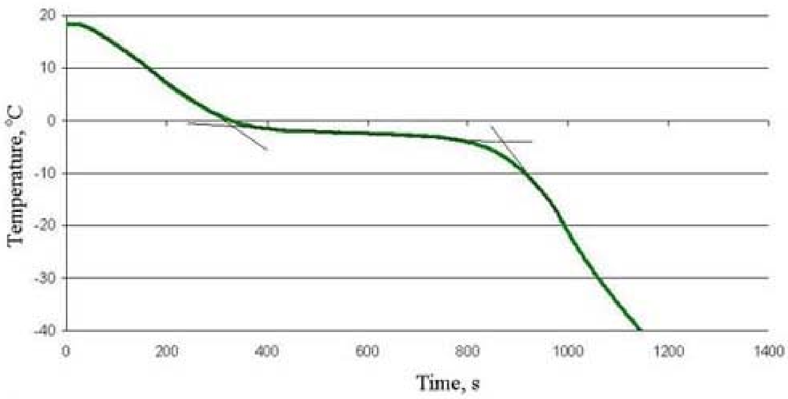


Figure 2. Method of freezing point determination



Structure of a research-measuring stand assured appropriate performance of the process experiments and as for the freezing conditions of samples, their volume was uncomparably smaller than volume of the space where freezing took place. Hence, there were not any difficulties with field temperature stabilization in the system.

In each group a dozen of products were examined changing their moisture and conducting a separate regression analysis of the freezing point depression for each of them in relation to the factors studied every time. Water content in the products was determined with a drier method according to the Polish Standard PN-90/A-75101.

As the input data for analytical simulation of the freezing point depression there were used those obtained by the present authors and supplemented by the results available in literature, that made 299 data altogether (tab. 1).

Table 1. Data used for verification of models for freezing point determination

Group of products	Data amount	Source of data
Vegetables	96	Chang, Tao [1]; Hsieh, Lerew, Heldman [4]; Jankowski [5], Gruda, Postolski [10]; Rjutow [12]; authors own results
Fruits	84	Chang, Tao [1]; Hsieh, Lerew, Heldman [4]; Gruda, Postolski [10]; Rjutow [12]; Wójcik [14]; authors own results
Fruit-vegetable juices	34	Chang, Tao [1]; Hsieh, Lerew, Heldman [4]; Gruda, Postolski [10]; Rjutow [12]; Wójcik [14]; authors own results
Meat	56	Chang, Tao [1]; Hsieh, Lerew, Heldman [4]; Gruda, Postolski [10]; Rjutow [12]; Wójcik [14]; authors own results
Fish	29	Chang, Tao [1]; Hsieh, Lerew, Heldman [4]; Gruda, Postolski [10]; Rjutow [12]; Wójcik [14]; authors own results

The computational analyses were performed evaluating 10 selected models for freezing point determination on the basis of knowledge on a frozen product composition (tab. 2) and the latest method of Schwartzberg modified by Pham

$$T_k = -0.141 - 4.36\frac{x_o}{x_w} - 43.5\frac{x_a}{x_w}$$

where x_w means water mass fraction, x_a – ash mass fraction, x_o – other components mass fraction [9]

Table 2. Mathematical models for determination of foods freezing point (w – water content in product)

Method by	Relation	Application range
Levy [8]	$T_k = -3\cdot(1/w - 1)$	beef and fish
	$T_k = -0.75\cdot(1/w - 1)\cdot 0.5$	mutton
	$T_k = 271.18 + 1.47\cdot w$	meat
Chang and Tao [1]	$T_k = 120.47 + 327.35\cdot w - 176.49\cdot w^2$	fruit and vegetable juices
	$T_k = 287.56 - 49.19\cdot w + 37.07\cdot w^2$	fruit and vegetable
	$T_k = 0.57\cdot w - 2.28$	beef
Levy [7]	$T_k = 1.06\cdot w - 0.175$	pork
	$T_k = 0.337\cdot w - 0.618$	mutton
Lacey and Payne [6]	$T_k = 5.1093\cdot w - 5.7924$	product of moist. > 70%
Salvadori and Mascheroni [13]	$T_k = (1 - w)/(0.06998 - 0{,}4393\cdot w)$	food
Wójcik [14]	$T_k = -122.72\cdot w^2 + 216.98\cdot w - 97.82$	fruit and juices

To perform this temperature computation effectively and competently after the models examined there was worked out an advanced computer program KRIO.EXE. Applying this software, freezing point depression as a result from the selected prediction models was established for the freezing conditions of all the products chosen and those from literature. Thus apart from the experimental data the result base was obtained out of the computation of an examined value under the same conditions.

The mentioned above data bases allowed to perform the estimation of relative error at each freezing point value determination after a method used in relation to the actual values. Thereby the data base was obtained being formed by the results of relative error of freezing point prediction of each product according to the models examined. Prediction relative error was calculated as proportion of a difference between actual value of freezing point and that computed and the actual value of the freezing point depression.

The results of the calculations were analysed with mathematical statistics methods with a special concern to descriptive statistics and regression analysis broadly understood. In order to advance and facilitate the realisation of this stage a statistical project StatGraphics v. 5.0 was applied.

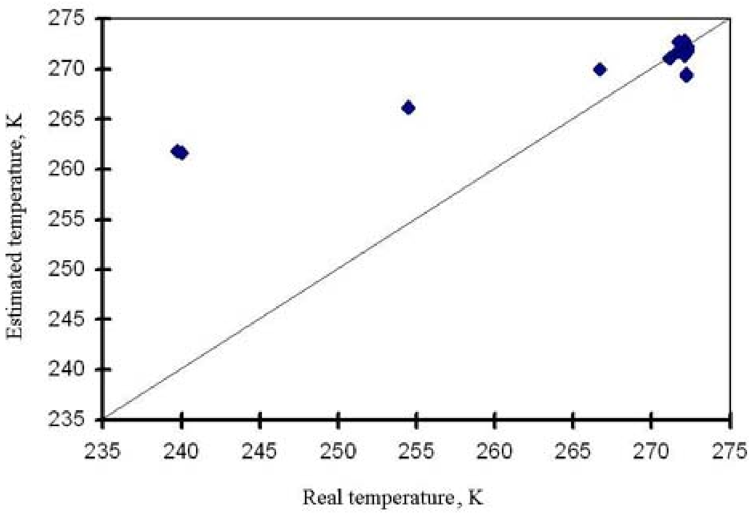
DISCUSSION

The results of the researches made on the experimental unprocessed products and processed ones in form of mousse and fruits have confirmed a possibility of simple dependence of freezing point depression on material water content, as it occurs in the models examined.

Owing to a lack of reliable data containing component mass fractions indispenable to verify Pham's method, it was impossible to check this method efficiency. The author claims that a correlation coefficient between freezing point values obtained from the measurements and the computed ones after his method is equal 91.6%.

The analyses performed in the present work show that an error of freezing point value of meat products, fruits and vegetables as well as fruit-vegetable juices determined acc. to Chang-Tao's model [13] is relatively low (fig. 3). This model application occasionally leads to higher results in relation to the actual cryoscopic temperature of the products examined.

Figure 3. Dependance of freezing point depression fixed after Chang-Tao's method on the actual temperature



Alike all the models, Chang-Tao's model use imposes some restraints. In the case of defining the freezing point depression of fruits, vegetables and such juices this model should not be used if the product moisture exceeds 92%. The freezing point values calculated under these conditions reach the range over 0°C. No such restraints were reported at freezing point estimation in meat products where mean prediction error is 0.23% which is regarded as a very good result (tab. 3).

Table 3. Results of statistical analysis of error of freezing point determination after the selected methods

Method	Size mean	Mean	Standard deviation.	Standard error	Property range
Levy [8]	42	-11.13	25.27	3.9	101.75
Chang and Tao [1] – fruit and vegetable	143	0.49	0.29	0.02	1.42
Chang and Tao [1] – meat	67	0.23	0.27	0.03	1.23
Levy [7]	10	-23.3	31.2	9.86	68.23
Lacey and Payne [6]	252	19.5	80.83	5.09	1024.9
Salvadori and Mascheroni [13]	299	-43.12	63.15	3.94	531.31
Wójcik [14]	54	1.06	14.18	1.93	69.7

A method elaborated by Lacey and Payne [6] can be applied to all the biological products both processed and raw, whose moisture content reaches 70% at least (fig. 4). In comparison to the effects obtained after the other models analysed the results from this method are burdened with a relatively high error. Mean prediction error determined on the grounds of 252 computational results was equal ±19.5% (tab. 3). A range of relative error of freezing point determination after this method is the biggest as against the others and amounts as much as 1024.91%.

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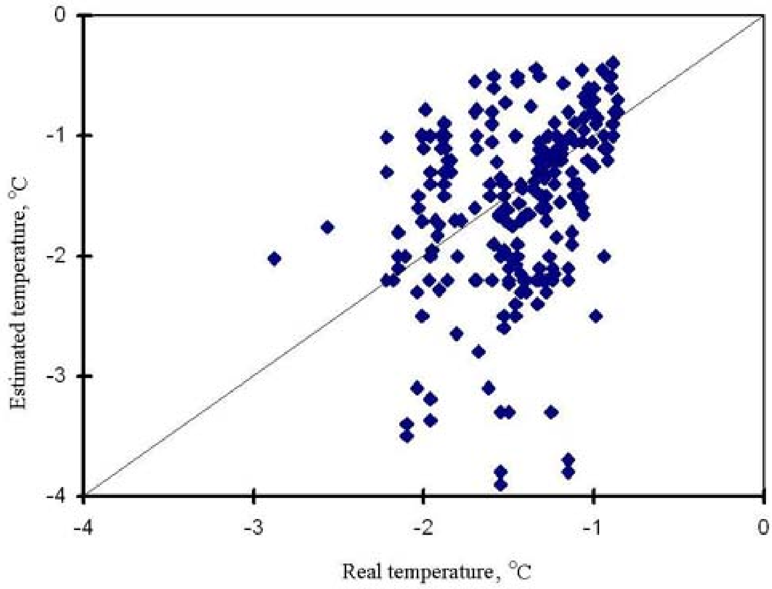
Figure 4. Dependance of freezing point depression determined with Lacey and Payne's method on the actual temperature



A relatively narrow application range is demonstrated by both methods of Levy, one established in 1979 [7] and the other from the year 1984 [8] (figures 5, 6). These methods can be used only for certain products of animal origin e.g. lamb, which deprives them of universal character. The Levy's models tend to underestimate freezing point value in relation to the actual data (tab. 3), whereas the highest mean error (–23.3%) burdens the method from 1984 used to establish this property in pork. This fact can be explained with great scatter of the examined products composition and small size of the data applied (only 10). The other models by this author lead to the results of freezing point computation with a mean error ranging from –5.5 to –11.1%.

Figure 5. Relation between the freezing point of beef and sea fish after Levy's method [8] and the real temperature

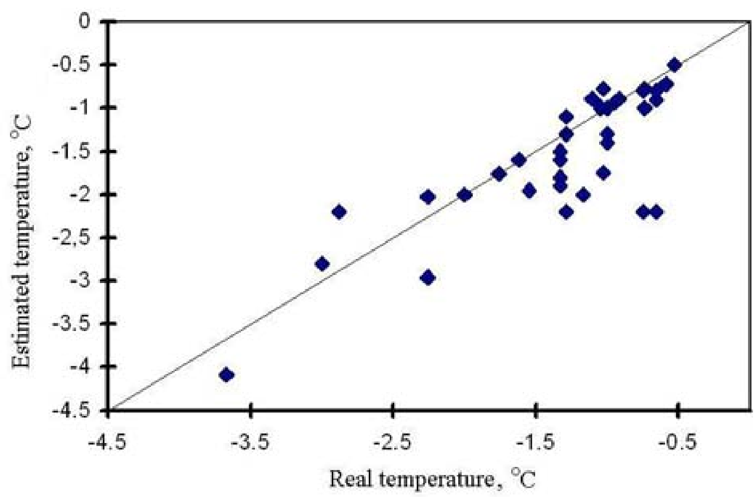


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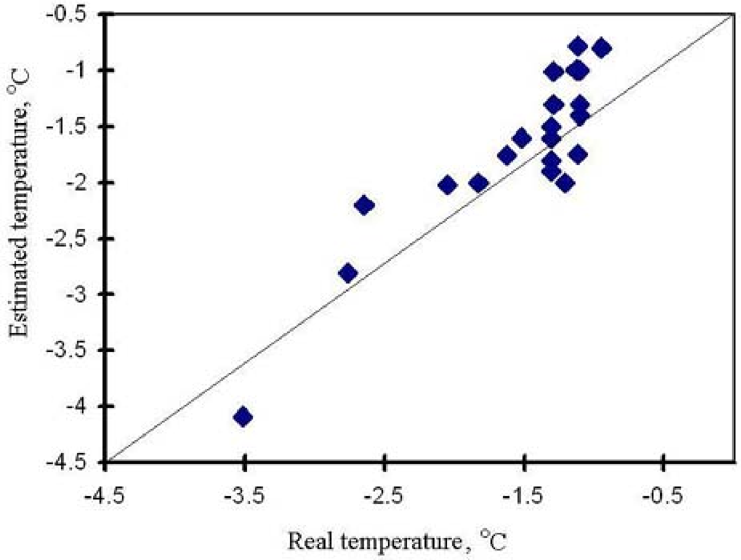
Figure 6. Freezing point of beef fixed after Levy's method [7]



The widest scope of the Salvadori-Mascheroni's model use is combined with the poorest quality of its effects as mean prediction error amounted to –43.1% under the experimental conditions (at the highest experimental data size – 299) (fig. 7, tab. 3). Alike, computational error range proved to be extremely high and reached 531.31%. It indicates little usability of this method in practice.

Figure 7. Cryoscopic temperature of agricultural products fixed after Salvadori-Mascheroni's method in dependance on real temperature

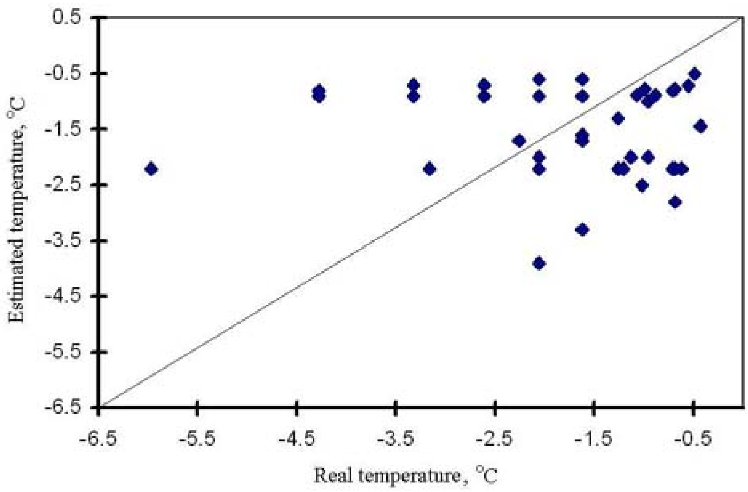


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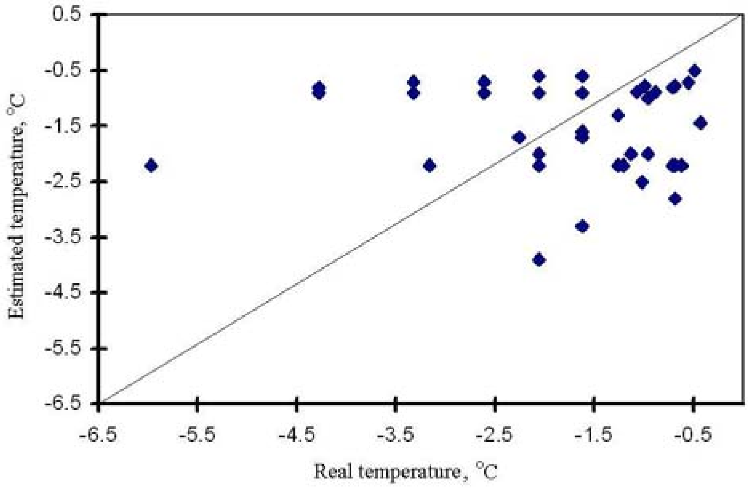
Figure 8. Freezing point depression determined ace. to Wojcik in relation to the actual temperature



The effects of prediction concerning a small group of products and obtained on the basis of the Wojcik's equation are burdened with a relatively low error value that amounts to ±1.06% (tab. 3, fig. 8). However, in this case a trend is evident to obtain the results overestimated in relation to the actual values. Still, calculation error maintains at the average level (69.7%) as against the ranges illustrating the use of the other models analysed.

CONCLUSIONS

1. A comprehensive analysis of the results of the studies carried out proves that the knowledge on foods composition affords possibility to perform computational characteristics of their freezing point depression.
2. In this case the researches on usability of the selected freezing point prediction methods showed that the Chang-Tao's method is most useful for all the product groups involved, hence most universal one.
3. Other methods examined should be applied exclusively for freezing point prediction of these product groups they were elaborated for.
4. The least accurate method under the experimental conditions turned out to be Salvadori-Mascheroni's one. Mean error of freezing point prediction after this method shaped at the level –43.1%.

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