ELECTRONICS AND ELECTRICAL ENGINEERING
ISSN 1392 – 1215 2008. No. 1(81)
ELEKTRONIKA IR ELEKTROTECHNIKA

T125 AUTOMATION, ROBOTICS
AUTOMATIZAVIMAS, ROBOTECHNIKA

Research into Correlation of Milk Electrical Conductivity and Freezing Point Depression

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Introduction

Ever increasing number of dairy producers as well as a vast range of dairy production in the modern world is posing a significant task that consists in product quality assurance, which in its turn is essentially dependent on the quality of raw materials (milk). Hence, search for techniques and methods, which employ state-of-the-art technologies and the latest element base, for design of new information systems enabling to perform speedy and accurate analysis on raw material (milk) parameters becomes of utmost necessity and significance.

The equipment item that is currently used for determination of milk freezing point depression is the cryoscope. Due to low analytical capacity this instrument is not suitable for laboratory's routine operation as it is not possible to assure timely performance of analysis of all samples. The cryoscopic method for determination of freezing point depression is not automated; it requires constant human supervision. Necessity to analyse a flow of tens or hundreds of thousands of milk samples per month, triggers an urgent need to create an automated parameter control system that is capable of independent, accurate and fast determination of extraneous water content as well as other relevant parameters in milk, needless of additional human supervision.

Automation of analysis

The measurement speed of freezing point depression using milk cryoscopy is 15...20 samples per hour. In case the load is 800...1000 samples per day this method becomes inappropriate for everyday use because of low speed and high labour expenditures.

An alternative way to evaluate milk freezing point depression is to calculate it out of milk composition parameters. Welboren et al. [1] carried out some research on which milk parameters are significant to evaluate milk freezing point depression. As milk lactose and dissolved salts make the highest influence on freezing point there were experiments to calculate milk freezing point out of milk fat content, milk density and electrical conductivity. Neither methodology nor results were presented in details, the conclusion was that it is possible to determine milk freezing point this way. J.Koops et al. [2] carried out a research if there is correlation between milk freezing point and milk composition parameters (milk fat, protein and lactose content). As a result a following formula was presented (1):

$$T_{uzs} = \sum_{i=1}^{4} a_i x_i \ . \qquad (1)$$

Here T_{uzs} – calculated milk freezing point; a_i – coefficients; x_i – milk fat, protein, lactose content and conductivity values.

Analysis of the results showed that the erroneous result of milk conductivity has the biggest influence on an error of the estimation. The sources of this erroneous result are the temperature of the sample during analysis and the bacterial contamination of the milk.

To evaluate dependency of specific electrical conductivity on temperature an experimental testing trials were carried out [3]. The temperature and specific electrical conductivity of the sample were simultaneously registered. The temperature of the sample is changed (increased) by means of a heater. The heater has a two-way link with the controller, which assures gradual increase of the sample temperature, safeguards from exceeding the maximal allowed temperature value, measures the temperature of the heating element in the heater. The same controller simultaneously registers the readings of the thermometer, which measures temperature in the sample, and the value of specific electrical conductivity.

To conduct this experiment 100 samples of natural milk (devoid of extraneous water) were used. In turn the samples were warmed up till the temperature of 45ºC, with the temperature and specific electrical conductivity being registered with measurement interval of 0.5ºC. The results of an experiment are presented in Fig. 1. The results of only five samples are drawn here, as the other fit between them.

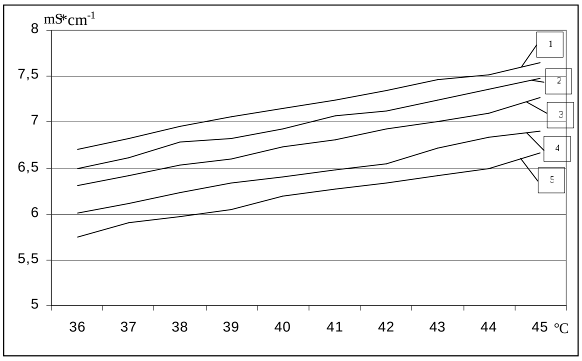

Fig. 1. Dependence of milk conductivity and temperature of the sample

The results show that as the temperature of the sample rises, the milk conductivity rises too. This dependency in the area around +40°C can be described (2):

$$G = G_p * (1 + \alpha \cdot (T - 40)); \qquad (2)$$

where G – specific electric conductivity at temperature T, mS*cm-1; G_p – specific electric conductivity at temperature T=40°C, mS*cm^{-1}; T – temperature, °C; α – temperature coefficient of specific electrical conductivity of milk.

The temperature coefficient of specific electrical conductivity of milk that has been determined during the experiment α=0.015ºC^{-1}. Knowledge of the coefficient enables us to evaluate the influence of the sample temperature on the error of result in determination of freezing point depression of milk.

To analyse the influence of bacterial contamination on specific electrical conductivity of milk an experiment was carried out [4]. More than 30 different milk samples were collected. As they were stored in constant temperature, there electrical conductivity and bacterial contamination was registered. Right after milking until the beginning of the experiment each milk sample was stored at (2...6) °C temperature in order to prevent bacteria from growing. During the experiment the sample was stored at +15°C temperature. Selection of this temperature was determined by the fact that such a temperature is favourable to bacterial growth; besides, there is a high probability that the average temperature of the milk sample since sampling until analysis in the laboratory will not exceed this

During the experiment specific electric conductivity is measured by an analogical measurer, which feeds data through converter analogue – code to a data processor, a PC in our case. Electrical conductivity is recorded at 10-minute intervals, with a few measurements made and their mean value recorded. Duration of one sample analysis is about 30 hours.

To correlate experimental and reference data an exponential model was used. The result (conductivity change in time *t*=0...28 hours) can be presented using (3):

$$\Delta G = 0.95 \cdot e^{0.3(t-38.25)}. \qquad (3)$$

Changes in bacterial contamination (time *t*=0...28 hours) can be presented using (4):

$$\Delta BBU = 0.99 \cdot e^{0.805(t-10)}. \qquad (4)$$

The correlation between total bacterial contamination (ΔTBC=(0...2000)*10^3 CFU/ml) and conductivity change ΔG can be presented (5):

$$\Delta G = 0.00390 \cdot \ln(\Delta TBC) + 0.00543. \qquad (5)$$

As we can see, the results of the experiment indicate that when bacteria count in milk increases >10^6 CFU/ml, i.e. milk is sour or near sour (cannot be analysed by the spectrometer), change in specific electric conductivity ΔC=0.04 mS/cm increases the error of result of the forecast milk freezing point depression till 0.001ºC, which in its turn means error of result of 0.2% in determination of extraneous water. Therefore it is expedient to analyse the sample within less than 20 hours since the time of sampling or estimate the error of result due to bacterial contamination.

Estimation of model parameters

An experiment [5] was carried out to define the expression of milk freezing point depression evaluation (1) once the known error sources have been determined. To conduct the experiment unpreserved milk samples heated up till a temperature of 40°C were analysed. The total of 3588 samples were analysed, 30 of these – repeatedly, in order to analyse the dispersion of the experimental data scattering. The following parameters were registered during the experiment: fat content, %; protein content, %; lactose content, %; specific electrical conductivity, mS*/cm^{-1}; temperature of sample, °C; time-span past sampling until analysis; freezing point temperature obtained by the cryoscope.

To perform correction of specific electrical conductivity, total bacteria count of 50 samples was recorded. Correction of specific electrical conductivity was performed taking into account the temperature of the sample during analysis and time passed after sampling as well. Analysis of the sample consists of the following steps:

1. determination of its composition;
2. registration of its temperature during analysis;
3. evaluation of its specific electrical conductivity;
4. determination of freezing point depression by the cryoscope;
5. correction of specific electrical conductivity when total bacteria count, time past sampling, temperature of sample are given.

Having fulfilled these steps the parameters of the model's (1) coefficients are determined.

For determination of the model's coefficients the least partial squares regression was used, as it enables to perform determination of the parameter values of the model the structure of which has been selected on the basis of the experimental data and allows verification of the model's adequacy.

Prior to determination of the coefficients it is necessary to perform verification if the data is distributed normally as otherwise it is impossible to check the adequacy of the model (1).

For testing normality a Jarque-Bera test [7] was used. The test statistic JB of Jarque-Bera is defined by (6):

$$JB = \frac{n}{6} \times \left(S^2 + \frac{(K-3)^2}{4} \right); \qquad (6)$$

where the sample skewness $S = \hat{\mu}_3 / \hat{\mu}_2^{3/2}$ is an estimator of $\beta_1 = \mu_3 / \mu_2^{3/2}$; the sample kurtosis $K = \hat{\mu}_4 / \hat{\mu}_2^2$ is an estimator of $\beta_2 = \mu_4 / \mu_2^2$. μ_2, μ_3, μ_4 are the theoretical second and third central moments (dispersion, coefficient of asymmetry and excess), respectively, with its estimates:

$$\hat{\mu}_j = \frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^j, \; j = 2,3,4. \qquad (7)$$

JB is asymptotically chi-squared distributed with two degrees of freedom because JB is just the sum of squares of two asymptotically independent standardized normals. That means: null hypothesis has to be rejected at level α , if $JB \geq \chi^2_{1-\alpha,2}$.

The histograms of experimental data are presented in Fig. 2-6.

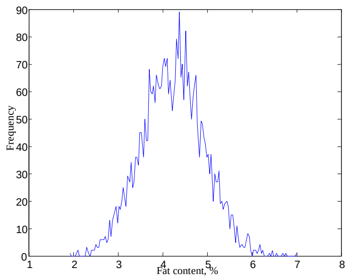

Fig. 2. Distribution of milk fat measurement results

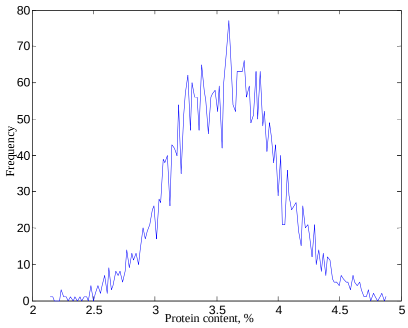

Fig. 3. Distribution of milk protein measurement results

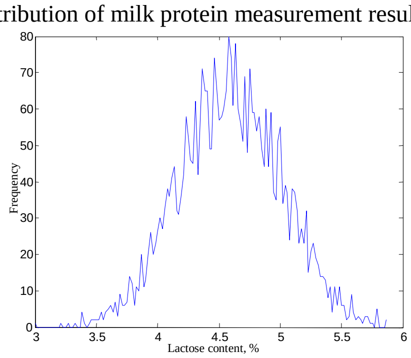

Fig. 4. Distribution of milk lactose measurement results

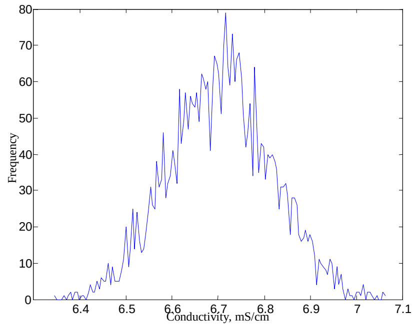

Fig. 5. Distribution of milk conductivity measurement results

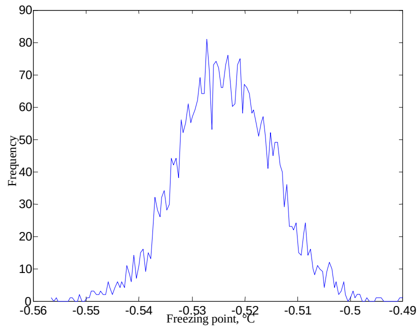

Fig. 6. Distribution of milk freezing point measurement results

The Jarque-Bera test showed that all the independent factors (milk fat, proteins, lactose, conductivity and freezing point) are distributed normally (at level of confidence of 95%). Thus a least squares method can be used to identify the model (1) coefficients. The results are presented in Table 1:

Table 1. Jarque-Bera test results

Factor	Calculated JB value	Critical $\chi^2_{0.95,2}$ value	Result
Fat	0.0794	0.103	Normal distribution
Proteins	0.0512	0.103	Normal distribution
Lactose	0.0841	0.103	Normal distribution
Conductivity	0.0972	0.103	Normal distribution
Freezing point	0.0649	0.103	Normal distribution

A final model (adequacy check passed) to calculate milk freezing point depression out of milk composition parameters and conductivity is presented in (8):

$$T_{uzs} = 0{,}0612 - 0{,}0085 * F - 0{,}0136 * P - 0{,}0641 * L - 0{,}0314 * G . \qquad (8)$$

Uncertainty of measurement system

The uncertainty of a measurement system is calculated out of experimental data (reference data) and freezing point depression data calculated using (8). The uncertainty is expressed as experimental root-mean-square deviation, multiplied by factor 2 (9) [8].

$$UNC = 2 * \sqrt{\sum_i \left(T_{uzsi} - \hat{T}_{uzs} \right)^2 / (n-1)} = 0.0036 \text{ °C}. \qquad (9)$$

Conclusions

1. The research shows that milk freezing point depression can be calculated out of milk composition parameters (milk fat, protein, lactose content) and milk conductivity.

2. The impact of change in bacterial contamination and sample temperature on specific electrical conductivity has been examined. Correlation between changes in specific electrical conductivity also correlation between changes in specific electrical conductivity and samples temperature has been defined. The results obtained allow minimize an error of milks freezing point depression estimation.

3. The research on milk samples parameter distribution shows that they are distributed normally. This allows to evaluate a statistically reliable mathematical model of the system.

4. The experiment shows that it is possible to determine milk freezing point depression using indirect method up to 20 times faster with 0.002°C error. An estimated uncertainty is less than 0.004°C.

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Submitted for publication 2007 11 19

J. Daunoras, A. Knyš. Research into Correlation of Milk Electrical Conductivity and Freezing Point Depression // Electronics and Electrical Engineering. – Kaunas: Technologija, 2008. – No. 1(81). – P. 23–26.

The results on research into correlation of milk conductivity and freezing point depression are presented. In this research the possibility to automate analysis was analysed. The key factors that have influence on conductivity measurement result were determined. The influence of sample's temperature and total bacterial contamination of the sample onto a conductivity value was evaluated. The analytical expressions of these that help minimize the error of conductivity estimation are presented. Also analysis on distribution of milk parameters and uncertainty of the presented system are given. Ill. 6, bibl. 8 (in Lithuanian; summaries in English, Russian, Lithuanian).

Й. Даунорас, А. Кныш. Анализ корреляции специфической электрической проводимости и температуры замерзания молока // Электроника и электротехника. – Каунас: Технология, 2008. - № 1(81). – С. 23–26.

Представлены обобщенные результаты анализа системы, предназначенной для оценки температуры замерзания молока косвенным методом. Рассматривалась возможность автоматизации процесса, определены значительные факторы, имеющие значение для погрешности результата при косвенной оценке. Сделан анализ и дана оценка влияния температуры образца и бактериального загрязнения образца на погрешность измерения специфической электрической проводимости молока. Представлены аналитические выражения, которые позволяют минимизировать погрешность измерения электрической проводимости. Дан анализ результатов измерения параметров молока, оценка закона распределения параметров, а также метрологическая оценка системы. Ил. 6, библ. 8 (на литовском языке; рефераты на английском, русском и литовском яз.).

J. Daunoras, A. Knyš. Pieno savitojo elektrinio laidžio ir užšalimo temperatūros ryšio tyrimas // Elektronika ir elektrotechnika. – Kaunas: Technologija, 2008. – Nr. 1(81). – P. 23–26.

Pateikiami apibendrinti sistemos, skirtos pieno užšalimo temperatūrai nustatyti netiesioginiu būdu, tyrimo rezultatai. Nagrinėta automatizavimo galimybė, apibrėžti reikšminiai faktoriai, turintys įtakos netiesioginio įvertinimo rezultato paklaidai. Išanalizuota ir įvertinta pieno mėginio temperatūros įtaka savitojo elektrinio laidžio įvertinimo tikslumui, mėginio bakterinio užterštumo įtaka, pateikiami tyrimo rezultatai bei analitinės išraiškos, kurias panaudojus minimizuojama savitojo elektrinio laidžio įvertinimo paklaida. Pateikiama pieno mėginio sudėties tyrimo rezultatų analizė, pasiskirstymo dėsnio įvertinimas, pieno užšalimo temperatūros matavimo metrologinis įvertinimas. Il. 6, bibl. 8 (lietuvių kalba; santraukos anglų, rusų, ir lietuvių k.).