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Comparison of butter quality parameters available on the Czech market with the use of FT NIR technology

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Abstract

NIR spectroscopy offers very wide opportunities in the food quality control. This method allows measuring of the samples with minimal usage of chemicals. We used the NIR spectroscopy for the quality control of butters available on the Czech market. Creating a methodology to measure the butter, build calibration models for the fat content and dry matter and verify their functionality. We used 26 samples of butters, of which 13 came from the Czech production and 13 came from abroad. Using reference and instrumental methods were determined the contents of fat, dry matter and acid number. Samples were measured using a FT NIR Antaris spectroscope in reflectance mode on the integrating sphere. The results demonstrated that FT NIR could divide the measured samples of butters into two classes according to their origin. Statistical progressing of the results did not confirm conclusive differences in the amount of the measured components between Czech and foreign butters. Functionality of the calibration models for the fat content and dry matter was demonstrated, while the calibration model for the assessment of the acid number was unreliable.

Key words: fat, dry matter, near infrared spectroscopy

Introduction

Butter is a traditional natural food used worldwide and is essential for human nutrition. Due to its high fat content, it is an important source of energy and contains many other nutritionally important components, such as minerals and fat-soluble vitamins (Procházková et al., 2009). The main parameters that characterize butters in terms of their quality, are water content and fat content. These two ingredients are the most important in terms of butter adulteration because the manufacturers may add some kinds of vegetable fats at the expense of milk fat. The Ministry of Agriculture Decree No. 77/2003 Coll. as amended defines the butter as a milk product containing only milk fat in the form of an emulsion of fat and water. The butter must contain at least 80 % (but less than 90 %) of milk fat, up to 16 % water and 2 % non-fat milk components in dry matter (Council Regulation (EC) No. 1308/2013). Other important parameters in terms of shelf life and spoilage of butter are acid number and evidence of aldehydes and peroxides. Nowadays, there are many sophisticated methods to evaluate the chemical composition of the butter. Conventional analytical methods are time-consuming, expensive and require highly skilled workers, and therefore these methods are not sufficiently effective in meeting the current needs of the food industry. Recently, Fourier transform near-infrared spectroscopy (FT NIR) is used in food quality control because it is possible to introduce this method into

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the production on-line. This technique is an attractive tool for measuring different types of samples and it is used in a number of areas such as food, agriculture, chemicals, pharmaceuticals, textiles, polymers, cosmetic industry and medicine (Šustová, 2007). Quantitative measurements by NIR are usually based on a correlation between the absorption of light of different wavelengths in the NIR and the composition of the sample (Procházková et al., 2009). The primary outcome for the analysis is the interferogram which is mathematically modified with the computer software to the absorptive infrared spectrum (Fig. 1). This process is known as Fourier transformation (Klouda, 2003). The energy of infrared radiation is not large enough to be able to achieve the changes of the electronic states but it is causing a change of vibrational and rotational states in molecules. Infrared spectroscopy covers a portion of the electromagnetic spectrum in the interval from 0.78 to 1000 μm, which corresponds to wavelengths in the range from 12800 to 10 cm^{-1}. The near-infrared spectroscopy (NIR) is widely used in the food applications, because the radiation in this area has the ability to penetrate deeper to the structure of the sample and offers a wide range of use in quality control of food and food ingredients. It is a method that allows measurement of samples without or with minimal use of chemicals (Šustová, 2007).

The goal of the study was to evaluate the using of near infrared spectroscopy to compare the parameters of chemical composition of Czech and foreign butters, set appropriate measurement conditions and create a function to verify the accuracy of the calibration models.

Material and methods

A reference and instrumental analysis of a total of 26 samples was conducted. All butters were unsalted. We used 13 butter samples produced in the Czech Republic and 13 foreign butters produced in Germany, France, Belgium, Poland and Ireland. The percentages of water contents were analyzed for all samples in accordance with ČSN EN ISO 3727-1 (2003). The determination of fat content was carried out using the Gerber traditional procedure by Doležálek et al. (1963). The acid number was determined according to ČSN EN ISO 660 (2009). The butter samples were measured twice with the device Antaris FT NIR (ThermoNicolet Corp., USA, Fig. 2) in parallel with chemical analysis. FT NIR Antaris uses a tungsten-halogen lamp as a radiation source and a beam splitter which is made from KBr. Helium-neon laser acts as a comparative beam.

A computer connected to the spectroscope is equipped with software "Result integration" (ThermoNicolet Corp., USA). We used the control program TQ Analyst (ThermoNicolet Corp., USA), which creates the average spectrum from the two measurements of one sample. The program subsequently uses this spectrum for the evaluation. The samples were assessed at room temperature. No additional treatment of samples was necessary before the measurement. Samples were produced by cutting the butter in to slices with a thickness of 1 cm from the center of the whole cube. Subsequently, the spectrometer panned these prepared samples in reflectance mode at integrating sphere through the polyethylene bag at 80 scans with a resolution 4.

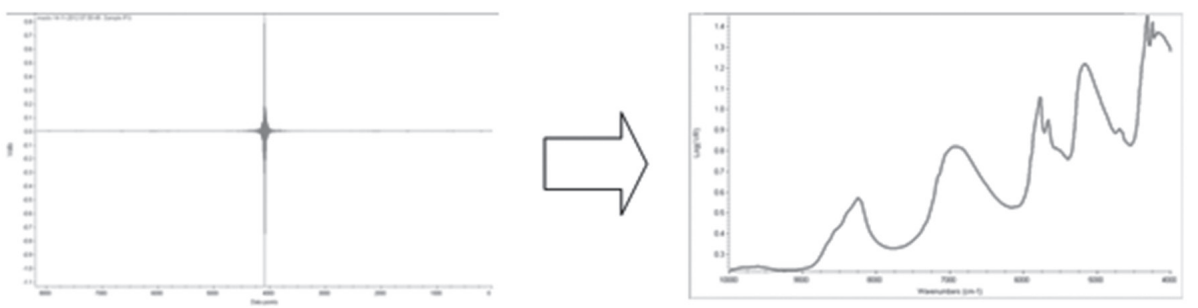


Figure 1. Transfer of the interferogram of the butter to the infrared spectrum using Fourier transformation

The samples were overwrapped with an aluminum foil before the measuring (Fig. 3). Subsequently, the butters were re-packaged and stored in the refrigerator at 8 °C and after the expiration of shelf life of butters were butters measured again for acid number.

The predicted values of measured components using FT NIR were obtained from the measured results utilizing TQ Analyst function of PLS (Partial Least Squares - method of least squares). The cross-validation was carried out and used for the diagnostics of PRESS function (Predicted Residual Error Sum of Squares). The PLS factors used in the calibration model simultaneously include the spectral and concentration information. The high number of PLS factors reduces the predict ability because the PRESS also includes the spectral noise while the optimum value of PLS factors ranges from 2 to 15 and an important aspect is to achieve the declining character of PRESS curve in the reliability assessing (Nicolet.cz. 2007). The number of PLS factors are calculated by evaluation software. Statistical differences for the comparing of results of butter acid values after purchase and after the expiration were evaluated by a paired t-test at a significance level of $\alpha=0.05$.

Table 1. Calibration values for content components of butter

Parameter	$a \pm bx_i$	SEC (%)	CCV(%)	R^2
Fat (%)	0.946x+4.375	0.859	1.054	0.947
Moisture (%)	0.957x+3.569	1.34	1.614	0.956
Acid number (mg * g^{-1})	1.001x+0.002	0.14	15.945	0.790

$a \pm bx_i$ - calibration parameters of the regression line, R^2 - correlation coefficient of calibration, SEC - standard error of calibration, CCV - calibration coefficient of variation

Table 2. Validation values for content components of butter

Parameter	$a \pm bx_i$	SEP (%)	PCV(%)	Rv^2
Fat (%)	0.881x+9,718	1.16	1.397	0.903
Moisture (%)	0.802x+16,54	2.08	2.446	0.908
Acid number (mg * g^{-1})	0.475x+0,444	0.299	35.808	0.279

$a \pm bx_i$ - validation parameters of the regression line, Rv^2 - correlation coefficient of validation, SEP - standard error of prediction, PCV - prediction coefficient of variation

Figure 2. Assembly of PC and FT NIR Antaris

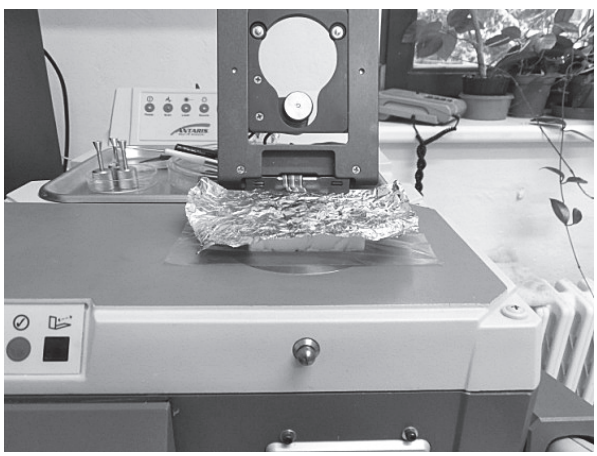


Figure 3. The methodology of measurement - reflectance mode on the integrating sphere

Results and discussion

The quality of the calibration model can be judged by the SEC (standard error of calibration). To compare the reliability of the calibration for the various components the CCV (calibration coefficient of variation), can be calculated expressing the SEC as a percentage of average laboratory values. The advantage of CCV against SEC is independence of the used units. Good calibration has the CCV below 5 %, but the model is still usable to 10 % of CCV (Čurda et al., 2002). Characteristic reliability data of the obtained calibration models are listed in Table 1. The accuracy of the created calibration model was assessed using a cross-validation, which was implemented by the program TQ Analyst.

Validation was performed on the same samples as a calibration and the validation values are presented in Table 2. The model for fat determination had high value of the correlation coefficient (R^2 = 0.947), but its standard deviation reached low level (SEC = 0.859 %). This model was described by a high reliability (CCV = 1.054 %). Correlation coefficient for the determination of moisture reached value of 0.956. Low standard deviation was obtained (1.34 %), as for the fat determination, and this model also was described high reliability (CCV = 1.614 %). The biggest difference of the correlation coefficients was observed for determination of the acid number (0.790). Value of the CCV (15.945 %) shows that the model is unreliable and therefore unusable.

The obtained calibration models were analyzed PRESS function, which had in the case of calibration models for fat and dry matter decreasing character (Fig. 4 and 5). The calibration model for measuring the acid number in this study is shown to be unreliable (Fig. 6). Hermida et al. (2001) obtained the calibration with a lower error of calibration (SEC = 0.192 %) for the determination of water content, but they analysed more samples in their experiment. Simultaneously, they achieved a lower coefficient of correlation (R^2 = 0.90) than was achieved in our work. Furthermore, they reduced errors of calibration for the determination of the fat content (SEC = 0.168 %), but also in this case achieved a lower coefficient of correlation (R^2 = 0.94) than we did. This fact affected the validation results as Hermida et al. (2001)

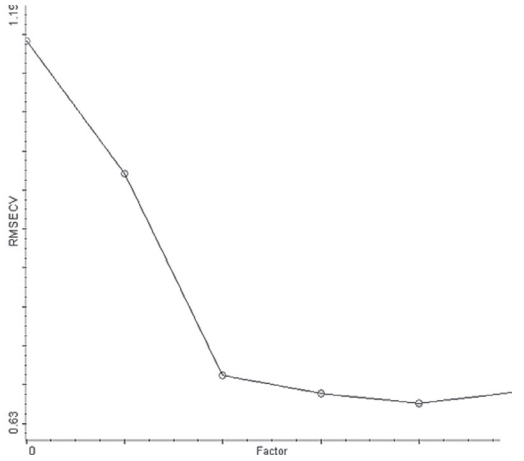


Figure 4. PRESS Diagnostics function for model calibration fat content

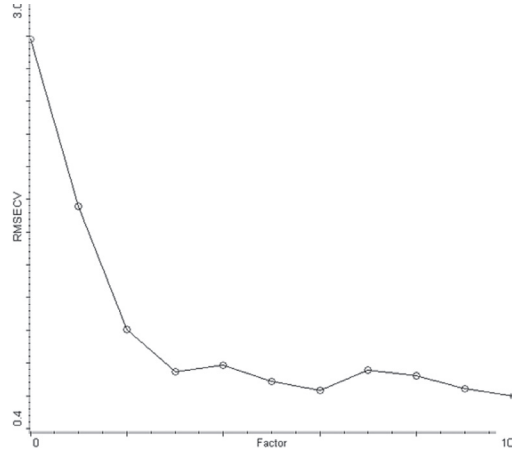


Figure 5. PRESS Diagnostics function for the calibration model of moisture content

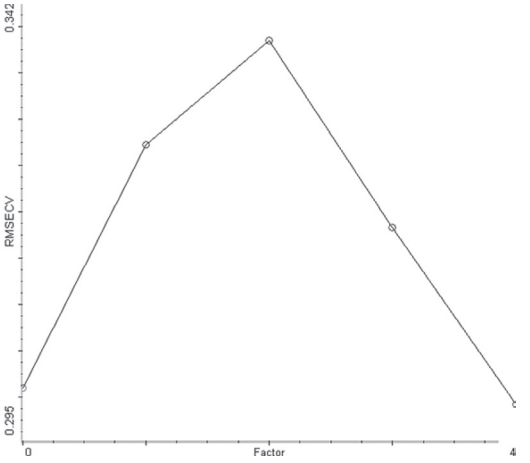


Figure 6. PRESS Diagnostics function for calibration model of acid number

obtained a lower prediction errors (SEP = 0.071 %) again but reached lower coefficients of correlation (R^2 = 0.83). By determining the acid number in their work also dealt Hrnčířová (2009). In his work, he came to very similar conclusions when obtained for calibration model numbers acidity value of the correlation coefficient R^2 = 0.961, but the value of SEC (0.355 %) and the calculated value of the indicator reached CCV inadequate reliability of the calibration function model (CCV>10 %).

We found with the traditional method according to Gerber that the average of fat content of Czech butter was 83.42 % and butters from EU countries had 82.7 %. This difference, however, in the statistical testing revealed as inconclusive, which was subsequently confirmed also with the analysis carried out on FT NIR because we obtained very similar numbers as the reference method. Council Regulation (EC) No. 1308/2013 establishing a common organization of agricultural markets and on specific provisions for certain agricultural products indicates the minimum of fat content of butter 80 %. The producers themselves guarantee this fact on the packaging with the inscription either min. 80 % or interval from 80 to 82 % of fat. One of the Czech butters slightly deviated from this fact because we found the fat content of 79.63 % with the reference method, but using FT NIR was found the fat content of 80.1 %. The package Farmers butter declared minimum fat content of 85 %, upheld in both ways. Both methods showed around 85 % of the dry matter. There is not a statistically significant difference

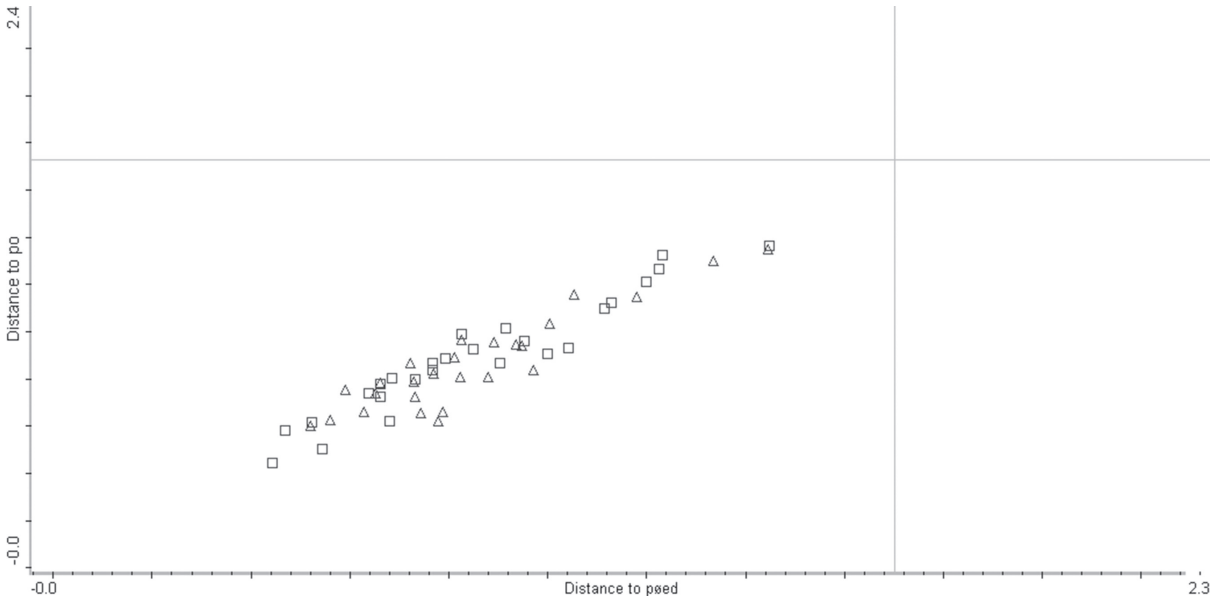
Table 3. Values of acid number (mg*g^{-1}) measured after the butter purchase and the shelf life expiration

Basic statistical characteristics	Acid number (after purchase)	Acid number (the expiration of shelf life)	Difference
	0.81	0.83	+0.02
	0.91	0.94	+0.03
	0.63	0.65	+0.02
	0.6	0.63	+0.03
	0.51	0.53	+0.02
	1.24	1.27	+0.03
	0.45	0.5	+0.05
	0.54	0.59	+0.05
	1.27	1.32	+0.05
	0.69	0.70	+0.01
	0.54	0.55	+0.01
	0.63	0.65	+0.02
	0.75	0.77	+0.02
	1.18	1.2	+0.02
	0.63	0.64	+0.01
	1.12	1.14	+0.02
	0.69	0.7	+0.01
	0.75	0.76	+0.01
	1.51	1.53	+0.02
	0.33	0.34	+0.01
	1.39	1.41	+0.02
	0.63	0.67	+0.04
	1.06	1.1	+0.04
	1.18	1.23	+0.05
x_p	0.835	0.860	+0.025
S_x (%)	0.320	0.323	+0.03
Min/Max	0.45/1.51	0.5/1.53	-

x_p - average, S_x - standard deviation, Min/Max - minimal and maximal obtained value

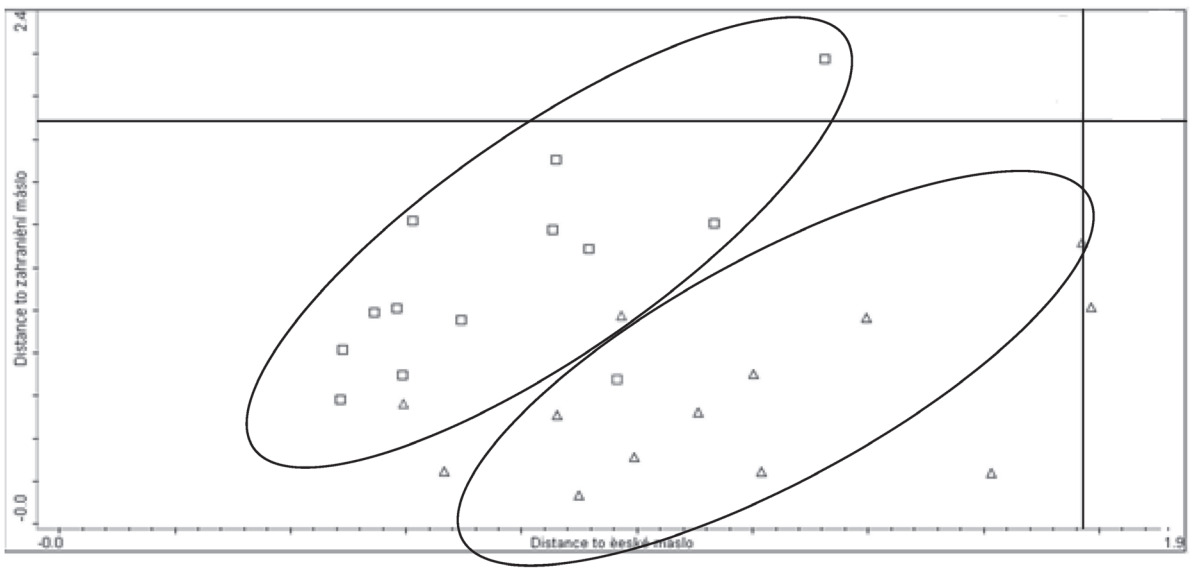
in the values of dry matter content. ČSN 46 7092-8 (1998) defines an acid number as the amount of extractable acidic characters predominantly free carboxylic (fatty) acids in 1 g of fat extracted with appropriate extractant, eventually fat itself, expressed in mg of potassium hydroxide (0,1 M) which are necessary to neutralize them. Czech butters exhibited the lower acid number (0.69 mg*g^{-1}) at the reference method than butter from EU countries (0.98 mg*g^{-1}).

It was found that butter fat was not subject to significant changes during the guaranteed period of durability during the transport and storage conditions. This was determined by measuring the acid number of butter after purchase and after their expiration (Table 3). The calibration model for determining of acid number proved unreliable. This was due to the fact of a very low variability between the measured values, which were then focused into a cluster of values for the calibration straight line leading to a



□ - The value after purchase △ - values at the end of life

Figure 7. Discriminant analysis of acid number values after purchase butters and at the expiration of shelf life



□ - Czech butters △ - foreign butters

Figure 8. Evaluation of butters groups after testing for FT NIR using discriminant analysis

high error calibration. The method of discriminant analysis was used for the determination of changes in the chemical composition of the butter during the storage, in which was evaluated the value of acid number obtained during the sample measuring at the beginning and end of the expiration period (Fig. 7). It was found that values of acid number after purchase butters and at expiration of shelf life were not significantly different, leading to a cluster of values that have not been separated by discriminatory cross. The discriminant analysis was also used to detect the differences in the composition between domestic and foreign butters. On the figure, it can be seen that the FT NIR Antaris spectroscope was able to detect the differences between the domestic butter and butter from EU countries (Fig. 8). It is obvious that the butters were differentiated by the origin. However, there was no absolute differentiation because two samples belonged to a group of domestic butters by its composition. Whereas, one sample from domestic butters rather fell into the group of butters from EU countries. The differences in the composition may be due to different butter production techniques or storage conditions.

Conclusion

The results show that FT NIR Antaris is able to divide the measured samples of butters into two classes according to their origin. Statistical differences of the obtained results were not confirmed between Czech and foreign butter. The functionality for calibration models for fat content and dry matter was proven, calibration model for determining the acid number was unreliable. Considering the obtained results in this experiment, FT NIR technology is reliable and suitable technique for the butter analysis.

Acknowledgement

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Usporedba parametara kvalitete maslaca na češkom tržištu FT NIR tehnologijom

Sažetak

NIR spektroskopija otvara niz mogućnosti u kontroli kvalitete hrane, jer omogućava analizu uzorka uz minimalno korištenje kemijskih reagencija. U ovom radu NIR spektroskopija korištena je za kontrolu kvalitete maslaca na češkom tržištu. Analizirano je 26 uzoraka maslaca, od kojih je 13 proizvedeno u Češkoj, a 13 u inozemstvu. Korištenjem referentnih i instrumentalnih metoda određena je koncentracija masti, suhe tvari i kiselinski broj. Uzorci su analizirani FT NIR Antaris spektroskopijom. Rezultati pokazuju da se uzorci maslaca mogu podijeliti u dvije kategorije s obzirom na porijeklo. Statistička analiza rezultata nije potvrdila razlike u koncentraciji mjerenih parametara između maslaca proizvedenih u Češkoj i inozemstvu. Utvrđena je funkcionalnost kalibracijskih modela za koncentraciju masti i suhe tvari, ali ne i za kiselinski broj.

Ključne riječi: mast, suha tvar,
infracrvena spektroskopija

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