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# Cheese quality assessment by use of near-infrared spectroscopy

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**Abstract.** Dairy products are worldwide spread and have great commercial importance. Rapid and reliable analysis of cheese would be highly desirable both for the manufacturers and consumers. The results of experiments, related to the application of near-infrared spectroscopy for cheese quality estimation will be presented. Several kinds of Bulgarian white brine cheese - natural from cow milk, imitation products with vegetable oil, and cheese with different water content were investigated. Fatty acids composition of samples was determined by using gas chromatography and moisture content by the oven-dry method. Spectra of all tested samples were obtained with a scanning NIRQuest 512 (Ocean Optics, Inc.) instrument in the range of 900-1700 nm using a reflection fiber-optics probe. PLS models were developed for quantitative determination and SIMCA for classification. The misclassification rate of the SIMCA model for discrimination of natural cheese and imitation products with vegetable oil was 2.9%. Quantitative determination of water content based on NIR spectra showed high accuracy, Models for classification of cheese samples into 3 groups according to water content achieved 5.64% misclassification rate for the independent test set. Results showed the potential of near-infrared spectroscopy as a non-destructive and rapid screening tool for assessing cheese quality and detecting adulteration.

## 1 Introduction

Dairy products represent an essential and important part of the total variety of food products. Therefore, the questions of their quality assessment and control are of great concern. Traditionally, different types of chemical analyses are used for the quality investigation of dairy products [1]. There should be pointed out the role of the liquid and gas chromatographic technics which are adopted as reference methods in providing precise and reliable information about the qualitative and quantitative content of the products [1]. Another spectroscopic technique in the area of food analysis is nuclear magnetic resonance, especially for the classification of dairy products according to the raw material origin and differentiating milk fat products from vegetable fat substitutes [2,3]. In spite of this, they have some essential disadvantages which make them unusable in the mass production and quality control. These type of analyses requires highly qualified personnel, expensive equipment, expensive and potentially harmful chemical reagents, while being time-consuming. That is why they cannot be used as express analyses. The necessity of quick, relatively cheap, and non-destructive analyses led to the application of different spectroscopic technics for this purpose. The near-infrared spectroscopy (NIRS) combined with proper chemometric methods has an increasing importance in the area of dairy products quality assessment due to its low cost, quick data collection and almost no sample preparation [1, 4, 5, 6]. Spectral differences along with supervised methods for classification allow NIR technologies to be used for the discrimination of cheese samples between different ripening times, brands, storage temperatures etc. In the review paper De Marchi et al. [4] summarized the outcomes from the scientific literature available online between 2013 and 2017 and related to the application of infrared spectroscopy for dairy products analysis. Lei and Sun [5] consider various non-destructive methods, including NIRS, for evaluating the quality attributes of cheeses. The recent application of NIR spectroscopy for dairy products analysis was reviewed by Yakubu et al. [6]. A new powerful tool for data analysis of food products and especially water content and water structure in the foods was introduced through aquaphotomics [7].

There are some investigations in which the authors demonstrate the viability of the NIR spectroscopy for the determination of cheese composition and quality attributes. For instance, Inmaculada Gonzales-Martin et al. [8] prove in their work the ability of the NIRS to provide quick and reliable information on the lipid profiles of cheese samples. David McKenna [9] tries to find a better way to measure the moisture content in cheese.

The selection of food by consumers is based on either lifestyle or health concerns. The presence of adulterants or foreign substances, which are different from those declared in labelled products, is important for consumers, producers, and regulatory agencies. In the last years,

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spectroscopic techniques have become widely used methods in food research for determining the authenticity and detecting adulteration of dairy products [10]. Adulteration of butter with cheaper vegetable fats was investigated by Heussen et al. [11]. The authors stated that the region from 1560 to 1960 nm could be used to detect adulteration of butter. Mabood et al. [12] used the PLSDA model based on NIR spectra of model butter samples adulterated with tallow at a percentage from 1% to 20%. They have a good ability to quantify less than 1.5% of tallow adulteration in clarified butter samples. NIR combined with the partial least square discriminant analysis (PLS-DA) was successfully applied by Visconti et al. [13] for discrimination of the adulterated by the higher level of additives hard cheese.

Technological progress in the development of NIR equipment has made possible the creation of small portable instruments which are of particular interest to the agro-food industry and consumers. Manuelian et al. [14] evaluate the feasibility of a low-cost pocket-sized near-infrared spectrometer to predict cheese chemical composition and ripening index. They obtained an accuracy of determination similar to those with benchtop infrared instruments. The results demonstrated that the miniaturization of the NIR instruments represents an opportunity in the dairy industry.

This work aimed to assess the applicability of portable near-infrared instruments and the Aquaphotomics approach as a non-destructive, fast, and relatively low expensive technique for the authentication of white brine cheese.

## 2 Material and methods

Two experiments with white brine cheese were performed. The samples from various brands and dairies – 86 samples from natural cheese and 47 samples produced with added vegetable oil as declared by producers were collected. Additionally, 118 samples were analysed for water content by the oven-dry method.

NIRQuest 512 (Ocean Optics, Inc.) instrument in the range 900 - 1700 nm was used for spectra acquisition of tested samples using a reflection fiber-optics probe. Two different pieces were used and measured for every sample. The samples were measured as whole pieces. Several measurements were taken from different places of every piece in order to minimize any possible effects of structural variation in the samples. Additionally, samples of pure butter and palm oil were measured.

The spectral data processing was performed with Pirouette 4.5 software (Infometrix, Inc.). Partial least square (PLS) models were compiled for quantitative determination. Soft Independent Modeling of Class Analogy (SIMCA) was used to develop the classification models. In SIMCA each different class was described by its own model, based on principal components analysis (PCA). SIMCA models were developed first for discrimination of natural cheese and cheese produced with added vegetable oil, and second for discrimination of cheese into three groups according to the water content.

Aquagrams, radar charts that display normalized absorbance values at several wavelengths, connected with specific water vibrations - free water, specific water configurations such as dimers, trimers, solvation shells, etc., were calculated [7]. The aquagram values $Aq_\lambda$ are calculated using the equation:

$$Aq_\lambda = \frac{A_\lambda - \mu_\lambda}{\sigma_\lambda} \quad (1)$$

where: $A_\lambda$ is the absorbance at wavelength $\lambda$, $\mu_\lambda$ is the mean value, and $\sigma_\lambda$ is the standard deviation of all spectra at wavelength $\lambda$, respectively.

## 3 Results and discussion

### 3.1 Discrimination of natural cheese and cheese produced with added vegetable oil

Two-thirds of each group of the samples (natural cheese or imitation cheese produced with added vegetable oil) was used as a calibration data set and the remains as a test set. All spectra of measured two different pieces from one cheese sample were included either in calibration or in the test group.

The main differences in the spectra of natural and imitation cheese were observed in the region from 1150-1370 nm. In this spectral range, significant differences are also observed between the spectrum of cow butter and the spectrum of palm oil (Fig. 1). The absorption at these wavelengths might be assigned mainly to C=O and second harmonics for C–H stretching vibrations [15].

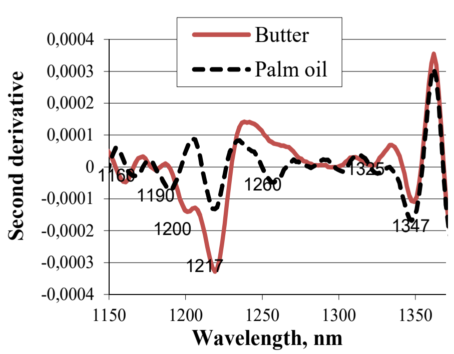


**Fig. 1.** Spectra of cow butter and palm oil

The results of the developed SIMCA models are presented in Table 1. The misclassification rate was 2.9%. Graphical illustrations of the results of SIMCA classification of natural cheese or imitation cheese produced with added vegetable oil are presented in Fig. 2 for the calibration set and Fig. 3 for the test set.

**Table 1.** Results of SIMCA models for discrimination of natural white brine cheese and imitation products with added vegetable oil

| | Calibration set | | Test set | | |
|---|---|---|---|---|---|
| | **Predicted as natural cheese** | **Predicted as imitation cheese** | **Predicted as natural cheese** | **Predicted as imitation cheese** | **No match** |
| Natural cheese samples | 176 | 1 | 80 | 0 | 1 |
| Imitation cheese samples | 0 | 84 | 0 | 54 | 3 |

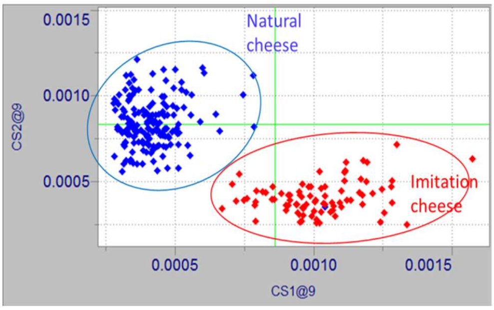


**Fig. 2.** SIMCA classification of natural cheese or imitation cheese produced with added vegetable oil for the calibration set

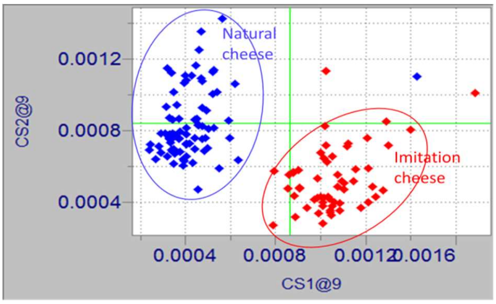


**Fig. 3.** SIMCA classification of natural cheese or imitation cheese produced with added vegetable oil for the test set

From a nutritional point of view, the determination of the fatty acid composition of cheese is important. The results showed very successful discrimination of natural and imitation cheese products based on their near-infrared spectra.

### 3.2 Determination of water content in cheese

Water content in analyzed cheese samples ranged from 48 to 75.82%. The average value was 62.24% and the standard deviation was 8.79. Samples were divided into 3 groups for classification. Cheese with water content from 48 to 54% formed a group with low water content. The threshold of 54% is set according to the requirements of the Bulgarian National Standard for Bulgarian white cheese in brine from cow milk [16]. The middle group formed samples with water content from 59 to 69% and the remaining samples formed a group with high water content (above 69%). Half of each group of the samples was used as a calibration data set and the remains as a test set.

Spectra of cheese samples, transformed as second derivative, are presented in Fig. 4. There are clear differences around 1162, 1218, 1345, 1366, 1417 and 1472 nm. The spectral maximum increased with increasing of water content at 1162 and 1417 nm and decreased at 1218 nm. The absorption at these wavelength regions might be assigned mainly to O–H vibration around 1417 and 1470 nm, N-H vibration at 1472 nm, C=O vibration at 1160 nm, second harmonics for C–H stretching vibrations at 1160, 1218, and 1366 nm [13].

The standard error of calibration and correlation coefficient of the PLS model for the determination of water content was SEC = 1.59 and $R_{cal}$ = 0.98, respectively. The results for the independent test set were standard error of prediction SEP = 1.90 and correlation coefficient $R_{test}$ = 0.97. The slope of the regression line for test set samples was 0.978, very close to 1. The value close to 1 indicates that samples with low and high water contents were determined correctly and not overestimated or underestimated. The ratio of SEP and standard deviation RPD = 4.43. The value of RPD bigger than 3 showed good accuracy of determination of water content in cheese.

The results of developed SIMCA models for the discrimination of cheese samples into three groups according to their water content were presented in Table 2 for the calibration data set and Table 3 for the test set. The models correctly classified all samples from the calibration data set. Misclassification rate for the test set was 5.64%.

**Table 2.** Results of SIMCA models for discrimination of white brine cheese according to water content for the calibration data set

| | **Predicted Low water content** | **Predicted Middle water content** | **Predicted High water content** |
|---|---|---|---|
| Low water content | 32 | 0 | 0 |
| Middle water content | 0 | 65 | 0 |
| High water content | 0 | 0 | 30 |

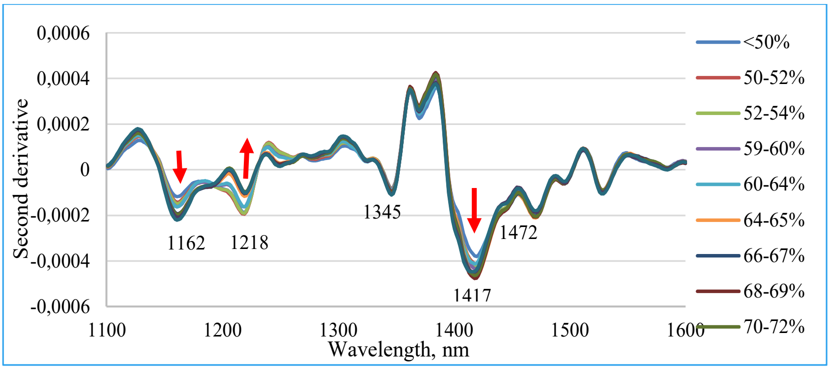


**Fig. 4.** Spectra of cheese samples with different water content

**Table 3.** Results of SIMCA models for discrimination of white brine cheese according to water content for the test data set

| | Predicted Low water content | Predicted Middle water content | Predicted High water content | No match |
|---|---|---|---|---|
| Low water content | 28 | 1 | 3 | 0 |
| Middle water content | 0 | 62 | 2 | 0 |
| High water content | 1 | 0 | 27 | 0 |

Graphical illustrations of the results of SIMCA classification of cheese according to water content were presented in Fig. 5 for the calibration set and Fig. 6 for the test set.

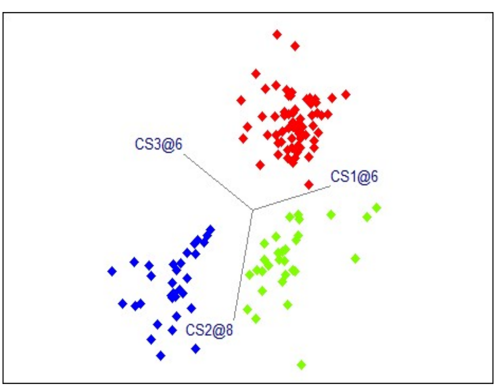


**Fig. 5.** SIMCA classification of cheese according to water content, calibration set (Blue – low water content; Red – middle water content; green – high water content)

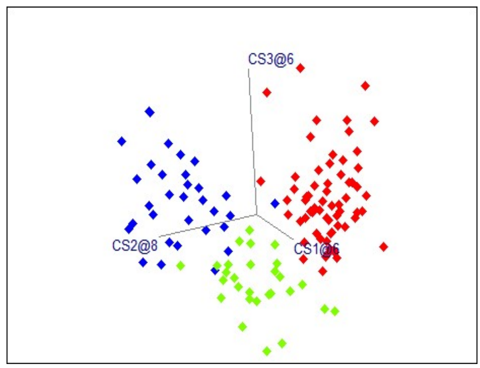


**Fig. 6.** SIMCA classification of cheese according to water content, test set (Blue – low water content; Red – middle water content; green – high water content)

### 3.3 Aquaphotomics for investigation of water structure in cheese

To visualize in detail the changes in water absorbance pattern, a chart termed "Aquagram" is used. The aquagrams, calculated using spectral data of cheese samples, are presented in Fig. 7. Aquagram pattern of cheese samples was changed significantly according to their water content. Aquagrams formed clear 3 groups of samples. The first is cheese with a water content of up to 63%. They have very similar aquagram patterns. Cheeses with a water content of 64 - 65% can also be included in this group. They have lower values of the aquagram coefficients in the range 1334 - 1398 nm, but the shape of the aquagram is similar to that of the first group.

The next group is made up of cheese samples with a water content of 66-70%. For them, a sharp decrease in the values at 1344 nm and an increase in the values from 1398 to 1517 nm were observed. Cheese samples with water content above 70% form the third group.

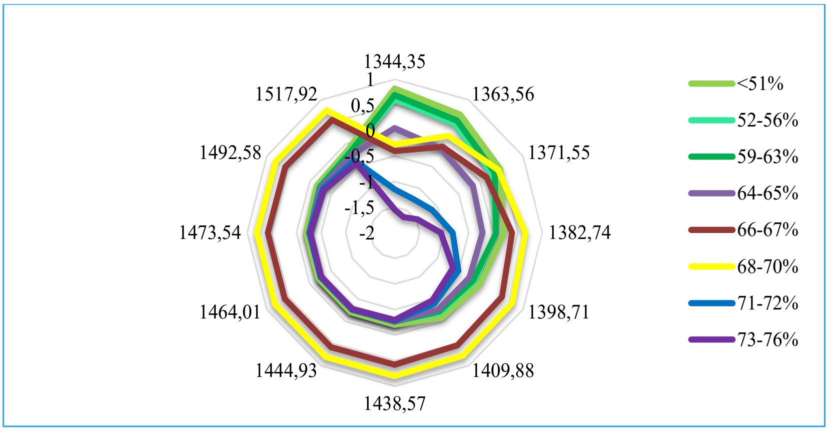


**Fig. 7.** Aquagrams of white brine cheese samples with different water content

According to the Bulgarian standard for white brine cheese produced from cow milk, the water content must be no more than 54%. Increasing of water content in white brined cheese is possible in several ways. One is pasteurization at a higher temperature. The other is the addition of high hydrophilic additives such as E466 (Cellulose gum, or sodium carboxymethyl cellulose). It functions as a moisture binder, thickening, and emulsion stabilizer, and improves the texture of a wide range of food products. The aquagrams clearly distinguish three different water structures in measured cheese samples, probably connected with different techniques of producing cheese and used additives.

Aquagrams confirm that the spectra of cheese, measured non-destructively and without any sample preparation, contain information not only about the total water content, but also about the structure of the water in the cheese, and hence also about the technology of their production.

## 4 Conclusions

Differences between near-infrared spectra of natural cheese and imitation produced with vegetable oil and cheese with different water content were found. SIMCA models based on near-infrared spectra of cheese correctly distinguish between natural cheese and imitation products with vegetable oil. The PLS models for determination of cheese water content and the SIMCA model for discrimination of cheese into three groups according to their water content showed very good accuracy. Near-infrared spectroscopy and Aquaphotomics approaches have a potential as a rapid screening tool for detecting the adulteration of dairy products.

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