American Journal of Food Technology

ISSN 1557-4571

Academic Journals Inc.

www.academicjournals.com

American Journal of Food Technology 3 (3): 154-163, 2008
ISSN 1557-4571

Changes in the Acid Value of Butter During Storage at Different Temperatures as Assessed by Standard Methods or by FT-IR Spectroscopy

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Abstract: Three different types of polish commercial butters, namely: light, regular and high fat content were under study. Studied samples were stored at two different temperatures (5 or 20°C) for a period of 8 weeks. Measurements of the content of fat, water, Acid Value (AV) and Peroxide Value (PV) were determined in the fresh butter and at one week interval. The AV and PV were determined by the conventional titrimetric method. IR spectra of every sample were registered. The relation between the AV values obtained by titration and by spectral measurements were studied by the Partially Least Square (PLS) regression, to built a statistical model for rapid determination of acid value. Two independent models, one for light type butters (model I) and the second one for regular and high fat content butters (model II) were calibrated. The characteristic parameters of the models are: $R^2 = 0.97$, PRESS (Prediction Residual Error Sum of Squares) = 2.91, factors number = 5 and $R^2 = 0.84$, PRESS = 3.64, factors number = 6, for model I and model II, respectively. The developed models correctly predict acid values of unknown samples of different types of butters.

Key words: Butter, acid value, peroxide value, FT-IR spectroscopy, PLS regression

INTRODUCTION

The general characterization of butter and the monitoring of modification it may undergo during processing or storage are important relative to its quality, functionality and economic value. Typical analyses that are important include iodine value (degree of unsaturation), saponification number (average molecular weight), moisture content, cis-trans fatty acids ratio, peroxide value and anisidine value (the level of hydroperoxides and carbonyls content), acid value (the level of free fatty acids) and thiobarbituric acid number (Ismail *et al*., 1993).

The determination of acid value is one of the more common analyses that fats are subjected to in terms of evaluating lipolysis after extraction and of defining and monitoring refining procedures (Ismail *et al*., 1993). The acid value is defined, as the amount of free acids present in fats as measured by the milligrams of potassium hydroxide needed to neutralize them (PN-EN ISO 660:2005). The acid content in a alimentary fat or oil is given by the quantity of free fatty acids deriving from the hydrolytic deterioration (ranciding) of the triacylglycerols. This alteration occurs under unsuitable conditions of treatment and preservation of the fats and thus the acidity represents a basic indicator of the genuineness of the product. Fats with high water content, such as butter, are more susceptible to hydrolysis and they can alter more easily, assuming the typical unpleasant smell and taste.

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The oxidation of fats is an important deteriorative reaction with significant commercial implications in term of product value. The initial oxidation products that accumulate are hydroperoxides, which may subsequently break down to form lower-molecular weight compounds such as alcohols, aldehydes, free fatty acids and ketones, leading to autoxidative rancidity. The peroxide content present in alimentary fats attests to its state of primary oxidation and thus its tendency to go rancid. Unsaturated fatty acids, in fact, react with oxygen forming peroxides, which determine a series of chain reactions whose end result is volatile substances having the characteristic smell of rancidness. These reactions are accelerated by high temperatures and by exposure to light and oxygen (Yildiz *et al*., 2002). The lower the peroxide and acid values, the better the quality of the alimentary fats and their state of preservation.

Although simple, procedures of AV or PV determination are cumbersome, destructive to the sample, costly, require potentially hazardous solvents, substantial personnel time, glassware and accurate preparation of reagents and are dependent on a visual endpoint (Ismail *et al*., 1993; Van de Voort *et al*., 1994).

Recently, the determination of PV in commercial oils was assessed by the modern Infrared Spectroscopy (IR) (Yildiz *et al*., 2002); which can also be extended to the determination of AV in butter. The theoretical principle of IR had been reported earlier (Koczoñ *et al*., 2001, 2003, 2006) and the technique finds application in the food analysis (Ismail *et al*., 1993; Chippie *et al*., 2002; Guillen and Cabo, 2002; Tay *et al*., 2002; Van de Voort *et al*., 2004) and significantly less number for monitoring of chemical changes in foods (Quilitzsch *et al*., 2005).

In this study, we have monitored characteristic parameter, namely acid value and peroxide value during butter storage at 5 or 20°C. Whereby, the acid value and peroxide value, were assessed by the conventional method and the FT-IR spectra were registered for each sample. The correlation of tested parameters as the quality status of the butter with IR spectral data was the aim of this study.

MATERIALS AND METHODS

Butter

Four commercial brands were purchased from local supermarkets in Warsaw, Poland to achieve representativeness. The dates of sell by of all samples were available from packaging information and care was taken to purchase samples of close to each other sell by dates.

The samples were distributed into 18 portions of equal weight. Nine portions were stored in the refrigerator (5°C); whereas, the other 9 portions were stored at room temperature (20°C). To avoid any influence of light on butter, which might effect in the rate of chemical reactions, samples stored at room temperature were wrapped up in a paper and placed in a dark place on the table. Although storage of butter under such conditions is out of common home practice, the procedure of long storage of butter samples at 20°C, allowed us to obtain number of data of high values of AV and PV to be included in model creation. Therefore, one of the aims of this study, that is the robust model creation, have been realised. Extreme temperatures (5 and 20°C) and long time of storage involved in experiment provided us with high number of data of range from 0.1 up to 13.8 (Table 1).

Sampling for wet chemical as well as spectral measurements took place at 0, 1, 2, 3, 4, 5, 6, 7 and 8 weeks of storage.

Analytical Methods

All reagents and solvents were purchased from Merck or Sigma.

Fat Content

Before analysis all dishes used were dried to constant weight. The ammonium hydroxide solution (%) was added to butter sample (ratio w/v) and mixed thoroughly. The ammonium hydroxide (PN-EN

Table 1: Mean acid value (AV) followed by standard error in low, regular and high fat butter before and after storage for 8 weeks at 5 or 20°C. Pairs of $p<0.05$ are listed

		Acid value [mg KOH/1 g of fat]					
Butter		Storage 5°C			Storage 20°C		
the percentage	Storage						
of fat and water	weeks	Mean	St. Error	p<0.05	Mean	St. Error	p<0.05
Low fat	0	0.700	0.023	0 - 3,4,5,6,7,8	0.700	0.023	0-2,3,4,5,6,7,8
Fat	1	0.900	0.029	1 - 3,4,5,6,7,8	1.280	0.031	1-3,4,5,6,7,8
55.8%	2	1.113	0.047	2 - 4,5,6,7,8	1.617	0.044	2-3,4,5,6,7,8
Water	3	1.873	0.087	3 - 5,6,7,8	2.700	0.058	3-4,5,6,7,8
43.0%	4	2.633	0.120	4 - 5,6,7,8	3.880	0.091	4-5,6,7,8
	5	4.523	0.139	5 - 7,8	5.233	0.145	5-6,7,8,
	6	5.200	0.231	6 - 7,8	7.333	0.203	6-7,8
	7	8.400	0.173	7 - 8	10.500	0.265	7–8
	8	10.200	0.404		13.797	0.286	
Regular fat	0	0.425	0.048	0 - 5,6,7,8	0.425	0.048	0- 5,6,7,8
Fat	1	0.525	0.025	1 - 5,6,7,8	0.650	0.050	1- 5,6,7,8
74.3%	2	0.675	0.075	2 - 6,7,8	0.900	0.071	2-6,7,8
Water	3	0.975	0.085	3 - 6,7,8	1.300	0.212	3-7,8
24.7%	4	1.375	0.180	4 - 7,8	1.825	0.214	4-7,8
	5	1.800	0.311	5 – 8	2.400	0.404	5-8
	6	2.300	0.363		3.050	0.450	
	7	2.775	0.403		3.875	0.708	
	8	3.350	0.403		5.225	0.654	
High fat	0	0.450	0.050	0 - 5,6,7,8	0.450	0.050	0-4,5,6,7,8
Fat	1	0.475	0.063	1 - 5,6,7,8	0.575	0.063	1-5,6,7,8
82.9%	2	0.575	0.063	2 - 6,7,8	0.750	0.065	2-5,6,7,8
Water	3	0.750	0.096	3 - 6,7,8	0.925	0.103	3-5,6,7,8
15.8%	4	0.950	0.126	4 - 6,7,8	1.425	0.229	4-6,7,8
	5	1.325	0.202	5 - 7,8	1.875	0.295	5-7,8
	6	1.850	0.236	6 - 8	2.500	0.316	6-8
	7	2.375	0.275		3.300	0.216	
	8	2.925	0.239		4.125	0.214	

ISO 660:2005). After that ethyl alcohol was added and the mixture was shaken for 1 minute. The fat was extracted from the butter sample three times using the mixture of ethyl ether: petroleum ether in appropriate proportions After extraction procedure the solvents were evaporated. The increase in the weight of the container represented the fat, which was expressed as %.

Water Content

Weighed samples (5±0.2 g) were dried to constant weight in a vacuum oven at 102±2°C, for 3 h. Afterwards they were cooled in an efficient desiccator for 30 min and weighted. Constant weight was attained when successive 1 h drying periods showed additional loss ≤0.05%. (Polish Standard - PN-EN ISO 3727-1:2004).

Acid Value

The acid values of fats extracted from butters were determined according to Polish Standard (PN-EN ISO 660:2005). Weighed samples of around 20 g were dissolved in 100 cm^3 of ethanol: diethyl ether mixture (1:1, v/v) and titrated with 0.1 N potassium hydroxide solution using phenolphthalein as an indicator. Analyses were carried out in triplicate the acid value is the mg KOH used to neutralize 1.0 g of butter. Results were used as reference data for model building.

Peroxide Value

Weighed sample of around 20 g were dissolved in 100 cm^3 of a mixture of chloroform: acetic acid (2:3, v/v) followed by the addition of saturated potassium iodine solution. The mixture was agitated and kept in darkness for 5 min. Distilled water was added and the released iodine was titrated with

0.001 M sodium thiosulphate, using 1% starch solution as an indicator. The analyses were carried out in duplicate and blank was run in parallel. to obtain the net sodium thiosulfate necessary for titrating the PV of the butter.

The content of peroxides (LOO), expressed in mmol of active oxygen per 1 kg of fat was calculated according to the formula:

$$LOO = (V - V_0) \times c/m$$

where,

$V\ (cm^3)$ = The volume of $Na_2S_2O_3$ solution used for fat sample titration.
$V_0\ (cm^3)$ = The volume of $Na_2S_2O_3$ solution used for blank sample titration.
c [1 mmol L^{-1}] = $Na_2S_2O_3$ solution concentration.
m [g] = Fat sample mass.

FT-IR spectra scanning

A Perkin Elmer System 2000 spectrometer, equipped with HATR accessory and managed by GRAMS AI 8.0 software was used throughout the present study. Background spectrum of empty HATR was registered once (14 scans) at the beginning of measurements in a given week. Then, reflectance spectra were registered within spectral range of 9000-400 cm^{-1} in the absorbance (log 1/transmitance) format, with resolution set to 4 cm^{-1}. Measurements were carried out at room temperatures (20°C). Butter samples were placed on KRS crystal, to cover whole crystal space. When measurement had been done, crystal was washed out carefully with butyl alcohol twice to completely remove fat and then with distilled water and dried out with a soft cotton. Spectrum of empty HATR accessory was registered to ensure the lack of any remainders and pollution on the plate. When registration of spectrum of empty HATR plate produced straight, horizontal line without any absorption bands, the next butter sample was placed on the crystal and its spectrum was registered. The spectrum of each butter sample was obtained by collecting and averaging 14 individual scans.

Modelling and Statistics

GRAMS AI 8.0 software with PLS plus/IQ supplement running on Windows XP platform was used to search for best statistical model correlating spectral and chemical data. Cross validation diagnostic with one-left-out procedure was used to validate a model. Spectra under calculations were automatically normalized and mean centre data preparation was done. Maximal number of 3 and 20 factors were set for model 1 and model 2, respectively. Spectral ranges for model 1 were: 1040-1020 cm^{-1}, (21 points altogether) while for model II: 7099-7008, 3507-3338, 1774-1712, 1686-1607, 1473-1452, 1425-1412 and 760-680 cm^{-1} (528 points altogether). The sample storage time of eight weeks, which is surely high above practical time of butter home-storage, especially in room temperature, was applied in this experiment, to create the model containing samples of distinct AV values. Obtained AV values covered the level of AV values of practically home-stored butters, as well as higher levels. This allowed us to built a model, in which AV values of practically stored butters are located far enough from the model limits. All statistics were performed using XLSTAT version 2007.6 software.

RESULTS AND DISCUSSION

The mean AV and PV values of three types of commercial butters with low (55.8%), medium (74.3%) and high (82.9%) fat contents are shown in Table 1 and 2, respectively. Data for light butter were obtained by measuring butter from the same producer in triplicate, while data for regular

Table 2: Mean peroxide value (PV) followed by standard errors in low, regular and high fat butter before and after storage for 8 weeks at 5 or 20°C. Pairs of $p<0.05$ are listed

		Acid value [mg KOH/1 g of fat]					
Butter		Storage 5°C			Storage 20°C		
the percentage	Storage						
of fat and water	weeks	Mean	St. error	p<0.05	Mean	St. Error	p<0.05
Low fat	0	0.297	0.009	0 - 5,6,7,8	0.297	0.009	0 - 3,4,5,6,7,8
Fat	1	0.390	0.021	1 - 5,6,7,8	0.490	0.038	1 - 4,5,6,7,8
55.8%	2	0.493	0.023	2 - 6,7,8	0.880	0.093	2 - 4,5,6,7,8
Water	3	0.597	0.043	3 - 6,7,8	1.467	0.145	3 - 4,5,6,7,8
43.0%	4	0.797	0.055	4 - 7,8	2.800	0.379	4 - 6,7,8
	5	0.880	0.070	5 - 7,8	3.700	0.321	5 - 6,7,8
	6	1.130	0.091	6 - 8	5.467	0.186	6 - 7,8
	7	1.457	0.137	7 - 8	5.467	0.186	7 - 8
	8	1.933	0.203		9.733	0.384	
Regular fat	0	0.175	0.025	0-3,4,5,6,7,8	0.175	0.025	0-2,3,4,5,6,7,8
Fat	1	0.200	0.041	1 - 4,5,6,7,8	0.400	0.041	1 - 3,4,5,6,7,8
74.3%	2	0.325	0.025	2 - 4,5,6,7,8	0.800	0.041	2 - 4,5,6,7,8
Water	3	0.400	0.041	3 - 5,6,7,8	1.225	0.063	3 - 4,5,6,7,8
24.7%	4	0.550	0.065	4 - 6,7,8	2.125	0.103	4 - 5,6,7,8
	5	0.675	0.048	5 - 6,7,8	3.050	0.096	5 - 6,7,8
	6	0.925	0.048	6 - 7,8	3.950	0.119	6 - 7,8
	7	1.150	0.050	7 - 8	5.150	0.132	7 - 8
	8	1.400	0.058		6.625	0.180	
High fat	0	0.175	0.025	0 - 5,6,7,8	0.175	0.025	0 - 4,5,6,7,8
Fat	1	0.275	0.025	1 - 5,6,7,8	0.275	0.025	1 - 4,5,6,7,8
82.9%	2	0.325	0.048	2 - 6,7,8	0.475	0.063	2 - 5,6,7,8
Water	3	0.425	0.048	3 - 6,7,8	1.075	0.232	3 - 6,7,8
15.8%	4	0.550	0.065	4 - 7,8	1.950	0.206	4 - 6,7,8
	5	0.700	0.082	5 - 7,8	2.675	0.272	5 - 7,8
	6	0.900	0.122	6 - 8	3.650	0.323	6 - 8
	7	1.200	0.108		4.850	0.538	
	8	1.450	0.132		5.800	0.627	

and high fat butters were obtained by measuring butters from four different producers, each sample in triplicate. Means in both Table 1 and 2 are followed by standard errors. Next column lists those pairs of weeks, between which statistically significant difference exists.

Table 1 shows that the initial mean AV were close to each other in the three types of butter samples and ranged between 0.3 and 0.7, for AV.

The mean AV values increased at a slower rate when samples were storage in the refrigerator (5°C) compared to the respective changes in AV, when the storage was at 20°C. Turkey test showed, that statistically significant difference ($p<0.05$) between AV's in low and room temperatures occurs in weeks 3-8, 1-8, 4-8, for light, regular and high butters, respectively. So that, for regular butter, out of three studied butter types, the temperature of storage is most important parameter due to AV change.

Light butter undergoes changes effected in increase of AV and PV to a higher degree compared to other butter types, as there are statistically significant differences between data for light and other butter types, after eight week of storage in both temperatures. After eight weeks of storage at room temperature AV increased up to 13.8 and PV up to 9.9 and when storage in refrigerator, they increased up to 10.2 and 1.9, respectively. For regular butter samples after eight weeks of storage AV value were 3.350 and 5.255 for low and room temperatures, respectively and PV values were 1.400 and 6.625, for low and room temperatures, respectively. For high butters AV values after eight weeks of storage were 2.925 and 4.125, for low and room temperatures, respectively and PV values were 1.450 and 5.800, for low and room temperatures, respectively. There is statistically significant difference between AV values for regular and high butters after 8 week of storage at room temperature, while no difference was observed when samples were storage in low temperature.

Table 3 presents ANOVA analysis for samples studied in this study.

The results of the IR measurements of butter samples before and after storage for 1, 5 and 8 week of storage in room temperature is shown in Fig. 1. Spectral regions (1040-1020 cm^{-1}) involved in creation of statistical model for light type butters (model I) are marked. The sample spectra of butter samples with regular and high fat content stored for three weeks are shown in Fig. 2. Spectral regions involved in creation of statistical model for regular and high fat content (model 2) are marked.

Table 3: Analysis of variance (ANOVA) attributed to butter, temperature and duration of storage

Source	Type III SS	df	MS	F	Prob.
Acid value (AV)					
Butter	330,314	2	165,157	689,761	0,000
Storage	784,969	8	98,121	409,792	0,000
Temperature	29,953	1	29,953	125,096	0,000
Butter×storage	269,074	16	16,817	70,235	0,000
Butter×temperature	5,515	2	2,757	11,516	0,000
Storage×temperature	21,124	8	2,641	11,028	0,000
Peroxide value (PV)					
Butter	18,454	2	9,227	78,300	0,000
Storage	215,980	1	215,980	1832,771	0,000
Temperature	394,018	8	49,252	417,947	0,000
Butter×storage	8,576	2	4,288	36,388	0,000
Butter×temperature	15,108	16	0,944	8,013	0,000
Storage×temperature	187,597	8	23,450	198,990	0,000

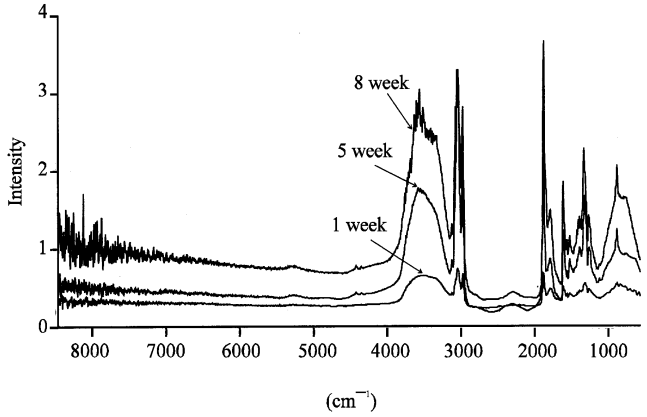

Fig. 1: The spectra of light butter samples after 1, 5 and 8 weeks of storage at room temperature (20°C)

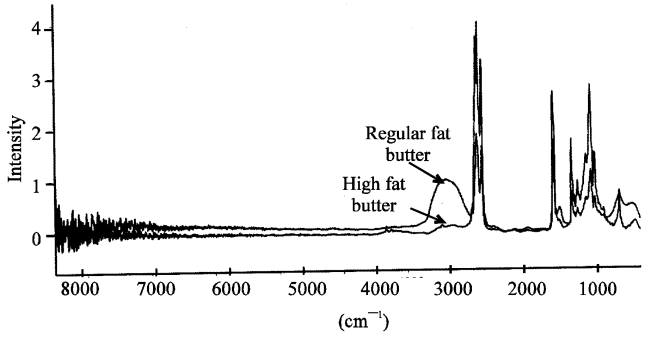

Fig. 2: The spectra of regular and high fat butters samples in the 3rd week of storage at room temperature (20°C)

Table 4: Parameters characteristic for obtained models

	Factor No.	PRESS	R^2 (actual versus predicted)	Spectral range
Model 1	5	2.91	0.97	1020-1040 cm^{-1}
Model 2	6	3.64	0.84	7099-7008; 3507-3338; 1774-1712; 1686-1607; 1473-1452;1425-1412; 760-680 cm^{-1}

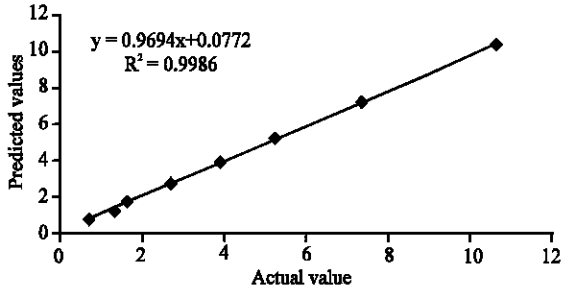

Fig. 3: Actual versus predicted acid values of light butter samples storage at room temperature (20°C)

Samples in calibration /validation set are of slightly different chemical composition due to changes taking place within the time. Those are rather quantity than quality changes, as spectral variation is observed mainly as absorbance increase/decrease at a given spectral range. Shifts, appearance or disappearance of spectral bands within time intervals were not observed. In other words, main differences between spectra of studied butters are express as an different area under appropriate absorption bands.

Optimal calibration equations were explored using PLS-1 regression. Optimal number of factors in model is very important as if too few of them are used to construct the model (so called underfit model), the prediction accuracy for unknown samples will suffer since not enough terms are being used to express all the spectral variations that influence the AV. On the other hand, adding too much contribution (more factors) which might come from the noise (so called overfit model) will also decrease the model prediction strength. Therefore, it is very important to define a model that consists of proper number of vectors to properly model the AV. The optimal number of PLS factors to include in a calibration was evaluated by comparing correlation coefficients (R^2) between actual and predicted values (those included in calibration set) and PRESS. It is to say, that PRESS is a special case of cross validation approach to assessing statistical prediction. This well-known parameter was proved to be important as measure in statistic researches in general (Nguyen, 1988; Qing-Song *et al*., 2001) and very recently for various food analysis (García-Jares and Bernard, 2006; Martín-del-Campo *et al*., 2007; López-Feria *et al*., 2007).

The models of minimal PRESS and maximal R^2 with a given number of factors were selected. In the Table 4 parameters characteristic for models I and II are gathered. For model I there are 5 factors, R^2 is 0.97 and PRESS is 2.91, while for model II there are 6 factors, $R^2 = 0.84$ and PRESS = 3.64.

Nine out of 18 spectra and results of standard AV measurements of light type butters with the mean of actual AV values M = 4,16 and standard deviation SD = 3,41 were involved in model I calibration and validation. Remaining samples with the mean of actual AV values M = 4.22 and standard deviation SD = 3.11 were used for model testing. Those are independent samples not included in any way in model creation. That means those could be any sample purchased in any shop and in any time. AV values of those samples were first assessed with created model and than actual values were measured by standard method, than predicted with the model and actual values were correlated. There is the linear correlation between actual and predicted AV values of 9 samples included in cross-validated model, with correlation coefficient $R^2 = 0.97$ and PRESS = 2.91. The Fig. 3 shows

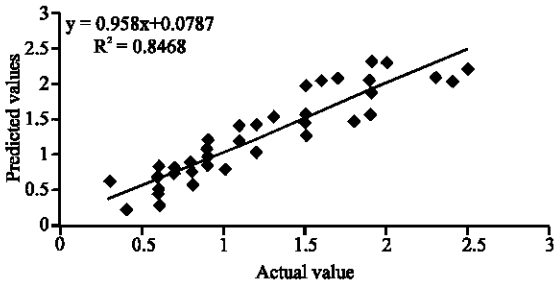

Fig. 4: Actual versus predicted acid value of regular and high fat content randomly selected butter samples storage at 20°C (room temperature) and at 2°C (refrigerator)

linear correlation between actual and predicted AV values of 9 remaining samples, not included in model calibration or validation. There is very good conformity between two data sets with correlation coefficient $R^2 = 0.99$ and slope S = 0.97. Spectral region of 1020-1040 cm^{-1}, was selected for model I calibration. Within region selected, there was 21 spectral data points taken into regression analysis.

Spectra and results of standard AV measurements of 63 randomly selected samples of two (regular and high content) butter types (butters of eight different fat contents) after different time storage at room temperature were randomly selected into two groups. The first group of 36 samples altogether with the mean of actual AV values M = 0.50 and standard deviation SD = 0.26 was used for cross-validation model 2. The second group of 27 spectra altogether, with the mean of actual AV values M = 1.09 and standard deviation SD = 0.49, as well as next 17 spectra randomly selected from refrigerator storage samples with the mean of actual AV values M = 1.32 and standard deviation SD = 0.35 were both used for testing the model II. That means those are independent samples and any sample, purchased anywhere at any time could take place of one of this samples. AV values of those samples were first assessed with created model and than actual values were measured by standard method, than predicted with the model and actual values were correlated There is correlation between actual and predicted AV values of 36 samples included in cross-validated model, with correlation coefficient $R^2 = 0.84$ and PRESS = 3.91. There is the linear relation between actual and predicted AV of 44 samples both from refrigerator and room temperature, not included in the model II calibration and validation presented in Fig. 4. There is a very good conformity between two data sets with correlation coefficient $R^2 = 0.85$ and slope S = 0.96. Spectral regions of 7099-7008, 3507-3338, 1774-1712, 1686-1607, 1473-1452, 1425-1412 and 760-680 cm^{-1}, were selected for model II calibration. Within region selected, there was 528 spectral data points taken into regression analysis.

The data of all butter types were initially included into one set used for calibration, however, during cross-validation procedure light type butter samples were rejected as outliers from that calibration set. Therefore, two separate models described above were created (Table 4). Obtained characteristics R^2 and PRESS describe precision and accuracy of developed model. Both values are well known statistical parameters discussed in the literature of this area. R^2 is used by another Authors for evaluations models developed for foods (Mirghani *et al*., 2002). The increase of R^2 the increase of model precision. Obtained here values of R^2 are of the same range as this parameter found by another researchers (Yildiz *et al*., 2002; Mirghani *et al*., 2002; Peña *et al*., 2005). Similarly PRESS values is used for evaluating precision of the model. The lower values of PRESS the better model precision. For fats analysis PRESS or equivalent statistical values were used also by Naczk *et al*., (2002) and López-Feria *et al*., (2007). Their values were at the same level as PRESS values obtained within our approach.

In this study the second parameter of studied butters monitored within the time by standard method was peroxide value PV (Table 1 and 2). There is a relatively strong co-linearity between those

data sets of those two parameters (AV and PV), which prohibits to create one model for both of them. If the value of two important parameters in the calibration samples is always present in the same ratio, the model will only detect one variation, not two. As far as the model is concerned, all the absorbance related to parameter 1 (AV) increases or decreases when parameter 2 (PV) also increases or decreases and vice versa. Therefore, only one variation is detected. So that, it is very important, that the calibration data have values of the individual parameters present in evenly and randomly distributed ratios. That is the reason why models for only one parameter were created.

Only five butters of different fat/water content were studied, therefore building the IR/PLS model for those components was pointless.

CONCLUSIONS

FT-IR spectroscopy is precise, sensitive, rapid, not expensive, non destructive and easy-to-perform both in laboratory and in manufacture (on line) method for monitoring acid value of butters, which is an parameter characteristic for butter quality.

Most literature provide data on usage of NIR for food measurements, as there is a less number of bands occurring in this region, mainly first and second overtones and therefore the spectral assignment is easier and more precise, despite bands are of rather low intensity. The apparatus of NIR spectral range are only seldom available, as more expensive. Herein, we involved mainly MIR (middle infrared region) region for calibration/validation models. Applied procedure produced satisfactory results. Regions involved in model I are 1020-1040 cm^{-1} and regions involved in the model II are 7099-7008, 3507-3338, 1774-1712, 1686-1607, 1473-1452, 1425-1412 and 760-680 cm^{-1} which means that first tones (MIR) and some overtones (NIR) are incorporated in model 2.

Although the MIR region is full of bands generated from vibrations of various bonds, careful selection extracts the regions related to AV and might be used for measurement of this important parameter. It is to say, that each of regions extracted within this paper applied separately to calibrate a model, generated a correlations of lower R^2 or higher PRESS's in comparison with model presented in Table 4.

ACKNOWLEDGMENT

This research was financially supported by the University Grant 504 09 270015.

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