STUDY ON IDENTIFYING BUTTER FAKING BY SUBSTITUTION WITH PORK FAT OR WITH MARGARINE

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Abstract: Experimental study's objective is to set the relevant parameters that allow the identification of the presence of animal or nonanimal fat substitutes in butter as a fake by substitution, but also the indication of butter subtituient dose in faked sample. Evaluated parameters for comparative study of the characteristics of the original butter - butter blank and the ones of the faked by substitution with pork fat at different rates were: changes in the melting point of the glycerides (after Bomer - Limprick), refractive index, iodine index, Reichert Meissl and Polenske index. In the second part of the experimental study, for the category of falsified butter by adding margarine, the parameters evaluated for comparative study of the characteristics of original butter - blank, falsified by the addition of margarine, in various percentages, and margarine were: Reichert Meissl index and iodine index. Of all parameters, iodine index varies not relevanly for the purpose of identification or dosing of mix-ups pork fat and butter rates. Iodine index varies relevanlyt for identification or dosing the margarine sustitute in butter. Iodine index varies relevanlyt for the purpose of identification or dosing mix-ups with margarine. Since that can not be considered a single parameter determining the dose of substitutes, the subsequent research will be able to establish a mathematical model, with the variables comprising the parameters settled to be relevant and sufficient to indicate the dose of substitution, applicable to both categories of fakes by substitution used in the experimental study.

Key words: *melting point, refractive index, iodine index, Reichert Meissl index*

Introduction

Of animal fat, butter is the most exposed to fraudulent practices by partial substitution with various types of low-value fat, animal (pork or beef fat) or vegetable fat as margarine or seeds oil [1]. Value given by cow's milk fat parameters are conditioned by the presence of lower saturated fatty acids with 4 to 10 carbon atoms, absent from other fat, and by the low share of fatty acids with a large number of carbon atoms [2].

Identifying butter faking by substitution with pork fat is based on changes in the melting point of glycerides and fatty acids in falsified samples. The constant value of the melting point of the sample fat is due to the relatively constant of the chemical composition (nature and proportion of acylglycerols and fatty acids) of an animal fat [3]. The melting point can be considered as a criterion for checking the purity of fat.

Margarines are fatty food products, containing min 80% fat, obtained by mixing fluid oil, hydrogenated and solid or semisolid (vegetable or animal) and the aqueous phase (dispersed) up to 16.6%. Margarine also contains a number of additives: emulsifiers, vitamins, flavoring and preservatives [4]. With a similar composition to that of butter, margarine is a potential alternative, frequently used in faked butter. Since natural fatty acids are normally found in the cis form, by hydrogenation are partly converted as trans form, their presence in butter is a proof of faked butter by substitution with margarine or other hydrogenated fats [5].

Sensory analysis is not always relevant; whereas faked butter may contain a number of compounds apparently natural $(\beta$ -carotene, diacetyl, acetic acid) giving the sensory qualities similar to original butter, so only the physical-chemical analysis is capable to certify and identify faked butter [6].

Both determining the nature and structure of acylglycerols and fatty acids as well as the indices characterizing the fat phase, particularly saponification indices. Reichert - Meissl and Polenske indices. provides the most secure information for deceleration faking, other indices (melting point, refractive index, index iodine) gives only helpful information, because margarines value depends mainly on the degree of hydrogenation of fats [7].

Experimental

For the experimental study on the identification of butter faking bv substitution with pork fat were made determinations on 6 samples of butter (unfaked and faked at different rates of fat substitution). Evaluated pork parameters for comparative study of the characteristics of the original butter - butter blank and the samples of falsified butter by substitution with pork fat at different rates were: changes in the melting point of the glycerides (after Bomer - Limprick), refractive index, iodine index, Reichert Meissl and Polenske indeces.

In the second part of the experimental study, for the category of falsified butter by adding margarine, parameters evaluated for comparative study of the characteristics of original butter - blank, falsified by the addition of margarine, in various percentages, and margarine were: Reichert Meissl index, and iodine index.

Falsifications were applied by dosing and mixing in BAGMIXER.

To identify the presence of pork fat in butter *Bomer - Limprick method* was used based on differentiation of melting points; it involves sample crystallization with anhydrous acetone and ether, to determine the melting point of the glycerides and to separate and determine the melting point of fatty acids.

Butter is the only animal fat that contains volatile lower saturated fatty acids with 4-10 carbon atoms (butyrate, caproate, caprylic, caprynic). The first two may be charged with water vapor (butyrate, caproate), while the other two (caprylic, caprynic) may be charged with water vapor, but are insoluble in it. These qualities are prerequisites to determine Reichert-Meissl index and Polenske index. According to the data presented in the literature, the index correlated with butyric acid content and caproate - Reichert Meissl index, at cow fat (21 - 36) indicates a higher content of these fatty acids comparatively with caprylic and caprynic, insoluble in water, represented by Polenske index (1.5 - 3.5). In pork fat four volatile lower saturated fatty acids with 4-10 carbon atoms (butyrate, caproate, caprylic, caprynic) are found in reduced content, as revealed by Reichert Meissl index (0.3 to 0.9) and Polenske index (max 0.5). Therefore, for detection of butter faking by substituting with pork fat. in the experimental study we considered it relevant to determine Reichert - Meissl index

Reichert - Meissl index (index of soluble volatile fatty acids) is the number of mg of potassium hydroxide required to neutralize the volatile fatty acids, soluble in water, from 1g fat and **Polenske index** (index of insoluble volatile fatty acids) is the number of mg of potassium hydroxide required to neutralize the volatile fatty acids, insoluble in water, from 1g fat.

Validation of these two indices is the basic criterion for assessing the authenticity of butter or milk fat, so a reliable means to detect substitution of foreign fat. If partial substitution, the values of these two indices will fall below the lower limits of normal, and if the total substitution these values tend towards zero.

Melting point of fat, determined by

capillary method, depends on the length of the fatty acids components carbohydrate chain and on the degree of unsaturation. Thus, the values of the melting point of saturated fatty acids increase as the carbohydrate chain length increases. The presence of one or more double bonds decreasing melting leads to point (introduction of a double bond to C 18:0 leads decreasing melting point from 69.6 ° C to 13.4 $^{\circ}$ C). Steric configuration is also extremely important; cis type double bonds have a weaker crystal setting density and melt at a lower temperature than the trans forms.

Refractive index determination is a reliable method that could indicate the origin of fat, but is rather uncertain in case of fat mixture. Refractive index is changed when a higher water content than the maximum allowed as for grease alteration. Determination was made with Abbe-Zeiss refractometer.

lodine index, determined by Hanus method, is the chemical principle of fatty acids to react with halogens, whom addition to double links. Depending on the degree of unsaturation, unsaturated fatty acids are additional 2, 4 or 6 halogen atoms, while saturated fatty acids behave differently. *The iodine index* means the quantity of iodine, in grams, which may be additioned to fatty acids from 100 g fat.

Saponification index identifies possible fraud, but is also used to determine molecular weight fatty acids. The amount of KOH needed for saponification is variable, depending on the molecular weight of fatty acids components of fat. The higher molecular weight will be, the less will be needed KOH to neutralize and saponificate, as the number of acid molecules contained in one gram of fat will be lower.

Results and Discussion

For the experimental study on the identification of butter faking by

substitution with pork fat were made determinations on 6 samples of butter, according to Table 1.

Falsifications were applied by dosing and mixing in BAGMIXER (for samples with substitution). Evaluated parameters for comparative study of the characteristics of unfaked butter - blank and faked by the substitution with pork fat at different rates, were: changes in the melting point of the glycerides (after Bomer - Limprick), iodine index, Reichert Meissl index and Polenske index (represented in Figure 1) and refractive index (represented in Figure 2).

Table 1

Evaluated samples for identification of butter faking by substitution with pork fat

Evaluated samples	Percentage of pork fat substitution
No pork fat content butter sample (unfaked butter) (Blank)	-
Faked by substitution sample (P1)	4%
Faked by substitution sample (P2)	8%
Faked by substitution sample (P3)	12%
Faked by substitution sample (P4)	16%
Faked by substitution sample (P5)	20%

To determine the melting point variation of glycerides and fatty acids, 50g fat from subjected each sample were to crystallization(5successive crystallization). Melting points of glycerides increase with increasing rate of substitution of butter with pork fat. Chemical composition of animal fat is relatively constant (nature and proportion acylglycerols and fatty acids), so the melting point of fat has constant values, which is a criterion for checking the purity of fat.

An 8% substitution percentage sample has a variation of the melting point of glycerides and fatty acids significantly (66.6) compared with blank sample (61.5) and even with the sample with 4% rate of substitution (63.6) indicating that any substitution of a higher percentage than 4% is identifiable with the relevant parameter variation of the melting point of glycerides and fatty acids. *Iodine index* values are not relevant for

dosing or identification purpose of butter substitution with pork fat.



Figure 1: Changes in parameters of evaluation and identification of falsifications by substituting butter with pork fat

Data represented in figure 1, indicate the correlation with butyric acid content and caproate - Reichert Meissl index; if unfaked butter, indicates higher content of these acids (34) than samples of faked butter (26), corresponding to the maximum percentage of substitution (20%).

Expressed by the refractive index, refraction can be the basis for assessing

the origin of fat, is a reliable method if relates to one fat and relatively uncertain if fat mixture. Refractive index is a relevant parameter identifying butter faking by substitution with pork fat.

Refractive indices of samples submitted evaluations to identify faked butter by substitution with pork fat in different percentages are represented in Figure 2:



Refractive index of butter - the blank is 1.4524. Faked butter with 8% substitution with pork fat, with refractive index 1.4530, is slightly detectable by determining this parameter. Maximum rate of substitution of sample 6 shows a refractive value index 1.4540. For the experimental study on the identification of faked butter by substitution with nonanimale fat (margarine) were assessed 4 samples of butter and margarine, according to Table 2:

Tabelul 2

Evaluated samples for identification of butter faking by substitution with margarine

Evaluated samples	Percentage of substitution with margarine
No margarine content butter	-
sample (unfaked butter)	
(Blank)	
Faked by substitution sample	30%
(P1)	
Faked by substitution sample	60%
(P2)	
Margarine (P3)	100%

Evaluated parameters for comparative study of the characteristics of unfaked butter blank, faked butter by substitution with margarine and margarine were iodine index and Reichert Meissl index.

Iodine index of butter - blank is 34 and easy detectable by determining the iodine index is faking with 30% margarine subsitute, sample in which iodine index is 68. Maximum rate of substitution of sample 3 shows an iodine value index 128.

According to the data represented in Figure 3, Reichert Meissl index if unfaked by substitution butter with margarine, indicates higher content of these acids (34) compared with samples of faked butter (13), according to the percentage of substitution (60%) and minimum value, 0.6, corresponding to maximum percentage of substitution (100%).



Percentage of substitution with margarine



Figure 3: Changes in parameters of evaluation and identification of falsifications by substituting butter with margarine

Conclusion

Sample with 8% percentage of substitution of butter with pork fat indicates a significant variation of the melting point of higher than 4% percentage is identifiable with the relevant variation of the point of melting of glycerides and fatty acids.

Refractive index of evaluated blank butter is 1.4524. Faked butter with 8% percentage of substitution with pork fat is slightly detectable by determining the refractive index (1.4530). Maximum rate of substitution of sample 6 shows a maximum value for refractive index.

Reichert Meissl index, if unfaked butter indicates higher content of butyric acid content and caproate compared with index values at samples of faked butter by substitution with pork fat, corresponding to the maximum percentage of substitution (20%).

Of all parameters, iodine index varies not relevantly for the purpose of identification or dosing of mix-ups pork fat and butter rates. Since this is the same type of animal fat, this parameter can not be very closely related to faking by substitution of butter with pork fat.

Iodine index varies relevant for identification or dosing the margarine sustitute in butter. Iodine index varies relevant for the purpose of identification or dosing mix-ups with margarine. Iodine index of butter - blank is 34 and easy detectable by determining the iodine index is faking with 30% margarine subsitute, sample in which iodine index is 68. Maximum rate of substitution of sample 3 shows an index of iodine 128.

The index which is correlated with butyric acid content and caproate – Reichert

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Since that can not be considered a single parameter determining the dose of substitutes, the subsequent research will be able to establish a mathematical model, the variables comprising with the parameters settled to be relevant and sufficient to indicate the dose of substitution, applicable to both categories of fakes by substitution used in the experimental study.

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