Development of methodological approaches for DSC control of palm oil content in a mixture with milk fat

I A Saranov1, O B Rudakov2, K K Polyanskiy 3, I V Sergienko3, A V Vetrov1 and A V Skrypnikov 1

1 Voronezh State University of Engineering Technologies, 19, Revolutsii Ave., Voronezh, 394036, Russia
2 Voronezh State Technical University, 84, 20 let Oktyabrya st., Voronezh, 394006, Russia
3 Voronezh Branch of the Plekhanov Russian University of Economics, 67, Karl Marx Str., Voronezh, 394030, Russia

E-mail: mr.saranov@mail.ru

Abstract. It is shown that the DSC method allows one to control the palm oil content in the milk fat both qualitatively and quantitatively. This method of palm oil identification as an additive in milk fat and allowing to determination of the amount of this additive by the DSC melting curves for milk fat and its mixtures is applicable for the range of 2÷30 mass percentage of the PO in the fat. The ratio of the temperature extremum of the melting curves and the peak area of milk fat endothermic effect are proposed as an analytical signal. It was found that the minimum temperature in the range of 9.1÷11.0 °C shifts towards higher temperature with an increase of PO additive in milk fat up to 50%, while the maximum temperature falls in the range of 13.2÷17.0 °C. The DSC method is more sensitive to changes in the triglyceride composition of fat than chromatographic methods.

1. Introduction
Butter and cheeses are quite expensive products, and unfair manufacturers seek to partially or completely replace the milk fat with not declared margarine and other substitutes (SMF). A palm oil (PO) is about 5 times cheaper than milk fat and often used for its replacement.

The current State Standard (GOST) allows one to confidently detect the butter and cheese fat falsification just by 15–20%. "Roscontrol", the expert center of the Union of Consumers regularly publishes data on the detection of falsified products such as butter [1] and cheeses [2].

Therefore, innovations in the fat phase quality control remain relevant.

The DSC method has long been used in the fats study [3–9], but its potential is far from fully realized in the analytical practice of oil and fat products quality monitoring.

The DSC method allows one to register the energy necessary to equalize the temperatures of the test and standard samples, depending on temperature or time. A scanning calorimeter measures the absolute temperature of the sample and the temperature difference arises between the sample and the standard, proportional to the difference in heat flux between them. Thus, the DSC method registers the changes occurring in a substance while heating or cooling. Experimental thermograms represent the dependence of
the heat flux on temperature. The temperature change or heat melting and the fat phase crystallization easy distinguishes the pure milk fat from milk fat substitutes (SMF) or milk and non-milk fats mixtures [3–9].

DSC thermograms record endo- and exothermic processes associated with melting, crystallization, structural phase transitions, evaporation, etc. DSC curves demonstrate analytical signals such as peaks, local maximum and extremum.

DSC instruments show a high baseline reproducibility, accurately calibrate by temperature or enthalpy and help to accurately determine the heat of reactions and specific heat. Modern calorimeters are characterized by rapid heat transfer, a small instrument time constant and a small effect of convection and radiation. A high cost of serial DSC devices is the reason for their rare use. They are designed for universal thermal measurements at –180 ÷ +900 °C, while a much narrower range (–100 ÷ +100 °C) is sufficient to control solid and liquid fats at room temperature.

2. The purpose of the study

The work aims the new DSC method development to control the palm oil content in the milk fat both qualitatively and quantitatively by the analytical signals-ratios of such thermophysical parameters of DSC melting curves and peak areas.

3. The object of the study, Materials and methods

Figure 1 shows thermograms samples of milk fat isolated butter «Traditional» with a 82.5% of fat mass fraction [10], manufacturer - a branch of PJSC «Milk plant «Voronezh»), quality examined in accordance with [11], and refined, deodorized and bleached palm oil [12] obtained on a NETZSCH STA 449 F3 Jupiter device. This device combines the advantages of a highly sensitive thermal balance and a differential scanning calorimeter. DSC melting curves were recorded at temperatures from −40 to +50 °C with a heating rate of 3 deg / min in oxidized aluminum crucibles in a medium of especially pure nitrogen. The fat phase was separated from butter according to [11].

![DSC thermogram of melting butter fat (1) and palm oil (2)](image)

4. Discussion of the results

DSC thermograms of milk fat and its mixtures with palm oil have already been studied [7-9]. It is shown that the PO addition to milk fat leads a melting curve change, the peaks areas change, shift the points on the axis maximum temperatures.

The results of thermal effects measurement and the PO content in the mixture are highly correlated ($R > 0.95$). The DSC method is to quantitatively detect milk fat falsification by palm oil and SMF on its basis.

In research [2], the thermograms of 17 vegetable oils samples were studied by DSC. All of them differ from each other and DSC showed reliable identification. DSC data are chromatographic methods with pulsed NMR spectrometry. DSC data comparison with the triglyceride composition fatty acid samples defined a thermal effects of oils with the saturated acids a high content in melting and crystallization points with a higher temperature than highly unsaturated samples. It was shown in [6] that the DSC method allows one to easily control the margarine and beef fat content in milk fat up to
10 – 20 mass %. To control the hydrogenated cotton and coconut oils content in milk, a similar study was conducted [5].

It is known the triglycerides melting points with the rest of trans-unsaturated fatty acid are higher than cis-isomeric fatty acids triglycerides with the same number of carbon atoms. This means that a noticeable number of trans-isomeric fatty acids and a low fat content thermograms are differ. Thus, the DSC method can be informative in quality control direction and oil and fat products safety. It makes sense to start studying the trans fatty acids effect on DSC curves.

Figure 2 shows milk fat and PO mixtures of DSC thermograms (all dependences along the DSC axis start at one point, and for clarity, are spaced relative to each other, the DSC axis only for the PO content is 0 %).

Figure 2. Melting milk fat and PO mixtures of DSC thermograms with 2 to 30% palm oil

Figure 3 shows the DSC milk fat melting curves extremum and peak areas, which are analytical signals. Earlier research [7–9] discussed the temperatures at the endothermic peaks areas maximum as quantitative characteristics of milk fat and PO mixtures, gave the satisfying measurements reproducibility. The fact of how much the sample weights are taken equally is a certain issue in the thermophysical measurements characteristics reproducibility. In this regard, the present workout proposes to use not the absolute values of the DSC curves controlled parameters, but their ratio. Another innovation of this workout is the use of not only temperatures at the thermal effects extremum, but also in the curves kinks areas (“troughs”) at the peaks base. The obtained DSC data analysis showed the prospect of the PO content quantity control in milk fat at the ratios $t_3$ to $t_2$ and $S_2$ to $S_1$ (Figure 3).

Figure 3. The DSC melting curves of milk fat thermophysical characteristics: the temperature extremums $t_1, t_2, t_3, t_4, t_5$, peak areas $S_1, S_2$ and $S_3$
Table 1 shows the $t_2$ and $t_3$ values, as well as the $t_3/t_2$ ratio, depending on the PO content and provides the area values $S_1$ and $S_2$, as well as the $S_2/S_1$ ratio, depending on the palm oil content.

**Table 1.** The $t_2$ and $t_3$, $t_3/t_2$ values depending on the PO content in the butter fat and $S_1$ and $S_2$ areas values and $S_2/S_1$ ratio, depending on the PO content in the butter fat

| PO content, % | $t_2$, °C | $t_3$, °C | $t_3/t_2$ | $S_1$, J/g | $S_2$, J/g | $S_2/S_1$, |
|--------------|-----------|-----------|-----------|------------|------------|-------------|
| 0            | 9,10      | 16,98     | 1,86      | 5,32       | 20,91      | 3,93        |
| 2            | 9,18      | 16,58     | 1,80      | 6,25       | 21,52      | 3,44        |
| 5            | 9,52      | 16,33     | 1,71      | 6,40       | 19,46      | 3,04        |
| 10           | 10,21     | 16,62     | 1,62      | 5,90       | 15,65      | 2,65        |
| 15           | 10,24     | 16,02     | 1,56      | 7,34       | 10,91      | 1,49        |
| 20           | 10,70     | 16,31     | 1,52      | 7,49       | 5,63       | 0,75        |
| 25           | 11,03     | 14,09     | 1,30      | 9,84       | 3,09       | 0,31        |
| 30           | 11,09     | 14,00     | 1,26      | 10,88      | 3,15       | 0,29        |
| 50           | 10,97     | 13,22     | 1,20      | 18,91      | 3,96       | 0,21        |

Figure 4 illustrates the ratio $t_3/t_2$ dependence on the PO mass fraction (%), which is to determine the PO quantitative content in milk fat in the range from 0 to 30 mass. % according to calibration function $t_3/t_2=1,847-0,020\times SPM$ with the approximation degree $R^2=0,970$, where SPM is the PO mass fraction (%).

**Figure 4.** The temperatures $t_3$ to $t_2$ ratio dependence of the DSC melting curve on the PO content in the butter fat phase of (wt.%)

**Figure 5.** The DSC $S_2$ to $S_1$ melting curve peak areas ratio dependence on the PO content (%) in the butter fat phase in the butter fat phase of (wt.%)

It has got the form $S_2/S_1 = 3,845-0,147\times S_{PM}$ and a high approximation degree $R^2=0,986$. While PO increasing above 25%, the saturation effect of the $S_2/S_1$ dependence on the PSD is observed. In general, the observed thermal effects dependences on the PO mass fraction in the range from 0 to 100 % are nonlinear.

It is known the milk fat is a multicomponent mixture of more than two hundred triglycerides, which varies in certain ranges [12]. These compositional variations depend on the cows breed, on the season, on the food supply, etc.

Fusible fractions contain unsaturated and shorter chain fatty acid residues, and refractory fractions contain saturated triglycerides with the highest molecular weights. The more refractory triglycerides dissolve in triglycerides melts with a lower melting point. Therefore, the peaks observed for thermal effects are only a peaks superposition characterizing the milk fat or its mixtures melting with SMF various fractions. Thus, the DSC melting curves geometric parameters proposed as analytical signals are being considered as integral analytical indicators that only indirectly indicate the fractional triglycerides composition in a fat sample.
5. Conclusion
Modern instruments for differential scanning calorimetry demonstrate a high potential in the quality control of butter and other fat and oil products. Investigated results confirmed that the DSC method allows one to identify the palm oil content in milk fat by melting curves in the temperature range from -40 to +50 °C with palm oil concentrations from 2 to 30 mass. % The palm oil detection limit in milk fat is about 5 %, which fails falsification revelation while controlling the fatty acid composition by gas chromatography. The palm oil content in milk fat quantitative analysis method, presented in this workout, is a loan prospect for laboratory practice. The proposed method provides the preliminary fat phase separation from the product samples according to standard sample preparation methods, which allows to use it in combination with chromatographic, NMR and IR spectrometric methods for fats quality indicators monitoring.

6. Acknowledgments
The studies were carried out on STA 449 F3 Jupiter, a synchronous thermal analysis instrument, in the collective use center laboratory "Control and Management of Energy Efficient Projects" of Voronezh State University of Engineering Technologies within the grant of the President of the Russian Federation, № MK-590.2020.8.

References
[1] Expert center of the Union of Consumers, available at: https://roscontrol.com/journal/tests/roskontrol-podvel-itogi-proverki-slivochnogo-masla/
[2] Wxpert center of the Union of Consumers, available at: https://roscontrol.com/journal/news/v-rossiyu-kontrabandoy-vvezli-ogromnuyu-partiyu-sirnogo-falsifikata/
[3] Tan C P and Che Man Y B 2000 Differential scanning calorimetric analysis of edible oils: comparison of thermal properties and chemical composition Journal of the American Oil Chemists' Society 77(2) 143-155
[4] Aktaş N and Kaya M 2001 Detection of beef body fat and margarine in butterfat by differential scanning calorimetry Journal of Thermal Analysis and Calorimetry 66(3) 795-801
[5] Shen Z, Birkett A, Augustin M A, Dungey S and Versteeg C 2001 Melting behavior of blends of milk fat with hydrogenated coconut and cottonseed oils Journal of the American Oil Chemists' Society 78(4) 387-394
[6] Tomaszewska-Gras J 2013 Melting and crystallization DSC profiles of milk fat depending on selected factors Journal of Thermal Analysis and Calorimetry 113 (1) 199-208
[7] Tomaszewska-Gras J 2016 Rapid quantitative determination of butter adulteration with palm oil using the DSC technique Food Control 60 629-635
[8] Rudakov O B, Saranov I A and Poliansky K K 2018 Thermal analysis in the quality control of butter Dairy industry 11 38-40
[9] Rudakov O B, Saranov I A and Poliansky K K 2019 Control of palm oil content in the mixtures with milk fat by the Differential Scanning Calorimetry (DSC) 23(1) 127-135
[10] GOST 32261-2013 2019 Butter. Technical conditions (Moscow: Standartinform) (In Russ.).
[11] GOST 31647-2012 2013 Refined deodorized palm oil for food industry. General specifications. (Moscow, Standartinform)
[12] Rudakov O B, Ponomarev A N, Poliansky K K and Lyubar A V 2005 Fats. Chemical composition and quality examination (M.: Delhi Print)