BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 68 (72), Numărul 2, 2022
Secţia
CHIMIE şi INGINERIE CHIMICĂ

EVALUATION OF THE FAT CONTENT OF SPREADABLE FOODS

BY

PAULA SIMIONESCU*, ANAMARIA POROHNIUC, ANIŞOARA AIONESEI, VALENTIN PANAIT and GABRIELA LISA

“Gheorghe Asachi” Technical University of Iaşi, “Cristofor Simionescu” Faculty of Chemical Engineering and Environmental Protection, Iaşi, Romania

Received: March 9, 2022
Accepted for publication: April 20, 2022

Abstract. Differential scanning calorimetry was used to identify the types of fats in spreadable food. Three types of commercial margarine and three types of butter and a homemade product were analyzed. The presence of vegetable oils in two of the types of butter analyzed was identified. In one of the samples of margarine analyzed, the presence of saturated fats was highlighted, although according to the producer, it would contain only unsaturated vegetable fats. It has been shown that the DSC technique can be used to identify adulteration of butter or margarine and this method has the advantage of requiring a very small amount of samples, very good reproducibility and a short time for analysis.

Keywords: DSC, margarine, butter, adulteration of spreadable foods.

1. Introduction

Margarine and butter are spreadable foods that go into the daily diet of most consumers. It is very important for consumers to know information about the quality of the products purchased, respectively the fat content and their type. Differential scanning calorimetry is a technique that can be used to identify the

*Corresponding author; *e-mail*: paula.simionescu@student.tuiasi.ro

types of fats in spreadable foods (Almoselhy, 2020). The price of butter is higher than that of margarine and there is a risk that a number of producers will sell it mixed in various proportions with margarine (Naktiyok and Doğan, 2021). Saturated fats of animal origin may also be included in margarine for economic reasons (Upadhyay *et al.*, 2017; Marikkar *et al.*, 2012; Farah *et al.*, 2018). Upadhyay et al. used the DSC technique to highlight the presence of goat fat and peanut oil in butter used in South Asian cooking (Upadhyay *et al.*, 2017). The melting and crystallization peaks were shifted to higher temperatures for samples containing goat fat, or goat fat and peanut oil than pure butter. This shift has been attributed to an increase in the amount of long chain saturated fatty acids. Contamination of sunflower oil samples with various animal fats (beef, chicken) was highlighted by Marikkar et al. based on the DSC heating curves. In the case of contaminated samples, the presence of peaks in the temperature range between 8 and 43°C was highlighted (Marikkar *et al.*, 2012). The position of the peaks moves from 13.67°C to 17.8°C, with the increase of the fat content of animal origin from 8 to 20%. The presence of chicken fat in butter samples was highlighted by Coni et al. based on the appearance on the crystallization curves of a small peak at a temperature of -12°C (Coni *et al.*, 1994). The area of the peak, respectively the enthalpy of crystallization increased proportionally with the increase of the fat content of chicken in butter. Tomaszewska-Gras J. used the DSC technique to assess the amount of water present in the butter (Tomaszewska-Gras, 2012). He proposed mathematical expressions that correlated the enthalpy of melting ice and the enthalpy of crystallization with the water content of the butter samples. The same author used melting curves to identify the presence of palm oil in various butter samples (Tomaszewska-Gras, 2016). The percentage of palm oil contained in the butter samples was correlated by the multiple linear regression method with the ratio of the height of the peaks on the melting curve and the ratio of the melting heat. Tomaszewska-Gras J. highlighted in this study the advantages of using the DSC technique to identify butter adulteration: very small amount of samples, minimum stages of preparation, no other chemicals that may be harmful are required for testing, the method is not destructive and the analysis time is short (Tomaszewska-Gras, 2016). Contamination of coconut oil samples with animal fats has been demonstrated by the DSC technique of Mansor *et al.* (Mansor *et al.*, 2012). They also used the method of multiple linear regressions to correlate the content of animal fat in coconut oil with the characteristic temperatures on the melting curve and on the crystallization curve.

In this study, the DSC technique was used to evaluate the fat content of spreadable foods. The analysis of the heating and cooling curves allowed the evaluation of the quality of the products, respectively of the presence of water, of saturated and unsaturated fats and of some preservatives.

2. Materials and methods

The spreadable foods used in this study were three commercially available types of butter marked P1, P2 and P3 and a homemade butter P4. We also analysed three types of commercial margarine, two new generation spreads (P5 and P6), and one with a high butter-like consistency, due to a higher vegetable fat content (P7).

The study of the thermal behaviour of different types of margarine and butter was performed with a Mettler Toledo DSC1 differential calorimeter. The thermal behaviour was evaluated in the temperature range -30°C and 22°C, with a heating rate of 10°C/min a cycle consisting of a heating and a cooling. The work was carried out in a nitrogen atmosphere, and the sample mass used was between 4.5 and 9.9 mg.

The processing of the DSC curves aimed at highlighting the melting and crystallization peaks, respectively the determination of the melting and crystallization peaks was performed with the STAR software by Mettler Toledo.

3. Results and discussions

The DSC curves recorded in the heating stage at a speed of 10°C/min are shown in Fig. 1 for the four types of butter (P1, P2, P3, P4), in Fig. 2a for spreadable margarines (P5 and P6) and in Fig. 2b for high consistency margarine (P7). The curve for margarine P7 was shown separately because it has a different behavior from that obtained for the other margarines. Figs. 3 and 4 show the DSC curves obtained in the cooling stage.

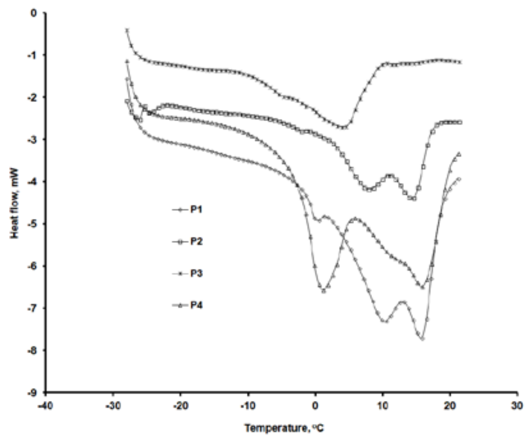
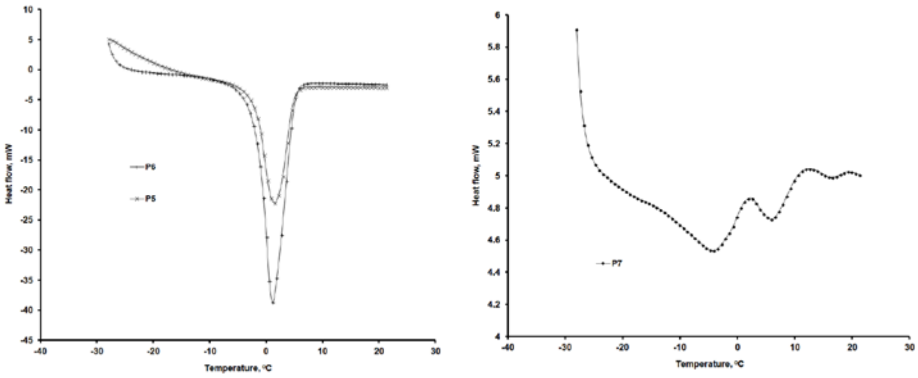


Fig. 1 – Heating curves for butter samples.

Table 1 shows the temperatures for the different types of margarine and butter corresponding to the melting peaks.



a) P5 and P6 b) P7

Fig. 2 – Heating curves for margarine samples.

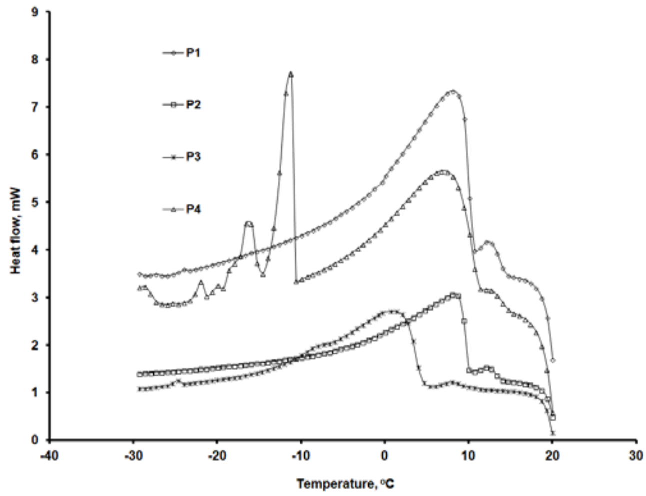
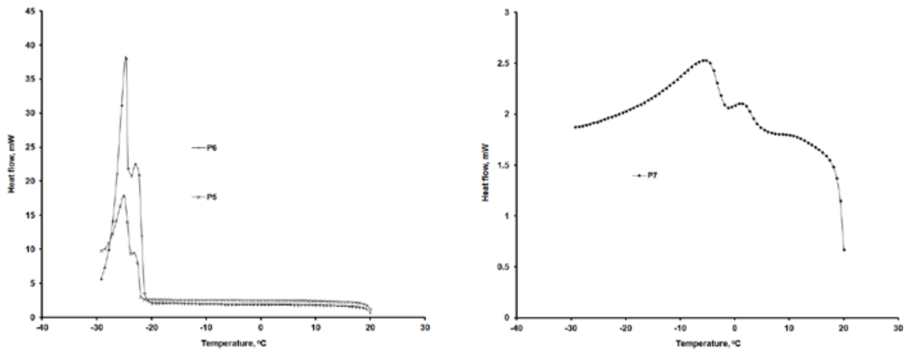


Fig. 3 – Cooling curves for butter samples.

To assess the presence of different types of fat in margarine and butter, Table 2 shows the values calculated with the STAR software for the melting heat corresponding to each peak.

Table 3 shows the crystallization peaks for the different types of margarine and butter. The values of the crystallization heat for each peak are reported in Table 4.



a) P5 and P6 b) P7

Fig. 4 – Cooling curves for margarine samples.

Table 1
Melting peaks

Sample code	T_{peak} (°C)		
	1	2	3
P1	0.05	9.99	15.98
P2	-2.21	7.42	14.75
P3	-5.22	4.43	11.63
P4	1.01	10.86	16.36
P5	1.33	-	-
P6	0.96	-	-
P7	-4.06	6.28	16.28

Table 2
Melting heat

Sample code	ΔH (J/g)		
	1	2	3
P1	0.30	1.11	1.79
P2	0.085	3.46	4.60
P3	0.21	9.52	0.026
P4	8.49	0.32	4.68
P5	102.73	-	-
P6	210.98	-	-
P7	2.33	1.13	0.17

The results obtained and presented in Figs. 1, 2 and Tables 1 and 2 lead us to the following observations regarding the different types of margarine and butter for which the thermal behavior was analyzed. Endothermic peaks with values between about 1 and -5°C are characteristic of water. We observe that the P5 and P6 margarines, which have a high-water content, have higher peaks (Fig. 2), but also a higher value for the melting heat (Table 2). For samples P2, P3 and P7 the peaks obtained for water at negative temperatures, respectively -2.21, -5.22 and -4.06°C indicate the use of salt in their composition. If we analyze the melting heats characteristic of each peak for the different types of butter presented in Table 2, we find that the largest amount of water is found in the homemade butter sample P4 (ΔH melting = 8.49 J/g). If we apply the relation % water = 0.2952·ΔH melting + 4.2981, proposed by Tomaszewska-Gras J. (Tomaszewska-Gras, 2012) the presence of 6.8% water is found for homemade butter.

Table 3

Crystallization peaks

Sample code	T_{peak} (°C)				
	1	2	3	4	5
P1	-	-	8.34	12.60	18.58
P2	-	-	8.57	12.54	18.69
P3	-8.13	1.56	8.03		18.02
P4	-11.34*	-	7.63	12.91	18.33
P5	-24.84	-22.67	-	-	-
P6	-24.65	-22.28	-	-	-
P7	-4.95	1.71	10.88	-	-

**There are less intense peaks at -21.94°C, -19.77°C, -18.09°C, -16.07°C and -14.92°C*

Table 4

Crystallization heat

Sample code	ΔH (J/g)				
	1	2	3	4	5
P1	-	-	-12.48	-0.45	-1.72
P2	-	-	-11.61	-0.46	-2.40
P3	-0.15	-9.81	-0.22		-0.69
P4	-5.85*	-	-11.22	-0.20	-1.74
P5	-21.51	-4.85	-	-	-
P6	-45.46	-22.68	-	-	-
P7	-2.19	-0.48	-0.17	-	-

**Crystallization heat for less intense peaks at -0.21, -0.12, -0.19, -1.05 and -0.095 J/g*

Melting peaks around 15°C are characteristic of saturated fats that are found mainly in different types of butter (Schäffer *et al.*, 2001). Surprisingly, a melting peak near this value is also found in the case of P7 margarine, which according to the manufacturer contains only unsaturated vegetable fats. The amount of saturated fat in this type of margarine is probably small when we compare the value of the melting heat (Table 2) obtained for this type of margarine with that obtained for the various types of butter. A low value for the melting heat corresponding to peak 3 is also found in the case of the P3 butter sample. Also, there is a displacement with 3.6°C of the temperature of peak 3 which according to the literature (Tomaszewska-Gras, 2016) for butter has the value of 16.23°C. This shift may indicate the presence of small amounts of palm oil (Tomaszewska-Gras, 2016) in this butter sample.

The crystallization peaks shown in Figs. 3 and 4, as well as the values of the crystallization heat shown in Table 4, also give us information about the quality of the different types of margarine and butter under analysis. The crystallization peak (Table 3) obtained at 10.88°C confirms the presence of saturated fats in margarine P7, according to the literature (Tasirin and Said, 2012; Fessas *et al.*, 2005). Crystallization peaks obtained at negative values are characteristic of unsaturated fats. Higher crystallization heat values are also observed for P5 and P6 margarines. Crystallization peaks obtained at negative values for samples P3 and P4 may indicate the presence of unsaturated fats. If we analyze the heat of crystallization, we find that in P4 butter we find higher amounts of unsaturated fats that have polymorphism, identifying several peaks of crystallization in the temperature range between -23 and -10°C (Fig. 4).

3. Conclusions

Differential calorimetry studies have shown the presence of different types of saturated and unsaturated fats in butter and margarine samples. The presence of saturated fats in P7 margarine was noted, although according to the manufacturer it would only contain unsaturated vegetable fats. In the P3 butter sample, the presence of small amounts of palm oil was found. In the case of homemade butter, a water content of 6.8% was established and the presence of unsaturated fats was also highlighted. For samples P2, P3 and P7, the analysis of the melting curves showed the presence of salt in their composition.

REFERENCES

Almoselhy R.I.M., *Applications of differential scanning calorimetry (dsc) in oils and fats research. A review*, Am. Res. J. Agric., **6**, *1*, 1-9 (2020).

Coni E., Di Pasquale M., Coppolelli P., Bocca A., *Detection of animal fats in butter by differential scanning calorimetry: a pilot study*, J. Am. Oil Chem. Soc., **71**, *8*, 807-810 (1994).

Farah J.S., Silva M.C., Cruz A.G., Calado V., *Differential calorimetry scanning: current background and application in authenticity of dairy products*, Curr. Opin. Food Sci., **22**, 88-94 (2018).

Fessas D., Signorelli M., Schiraldi A., *Polymorphous transitions in cocoa butter. A quantitative DSC study*, J. Therm. Anal. Calorim., **82**, 691-702 (2005).

Mansor T.S.T., Che Man Y.B., Shuhaim M., *Employment of differential scanning calorimetry in detecting lard adulteration in virgin coconut oil*, J. Am. Oil Chem. Soc. **89**, 485-496 (2012).

Marikkar J.M.N., Dzulkifly M.H., Nor Nadiha M.Z., Che Man Y.B., *Detection of animal fat contaminations in sunflower oil by differential scanning calorimetry*, Int. J. Food Prop., **15**, *3*, 683-690 (2012).

Naktiyok J., Doğan T.H., *A research on the detection of fake butter by traditional and modern methods*, J. Eng. Sci. Des., **9**, *2*, 453-462 (2021).

Schäffer B., Szakály S., Lõrinczy D., Schäffer B., *Melting properties of butter fat and the consistency of butter. Effect of modification of cream ripening and fatty acid composition*, J. Therm. Anal. Calorim., 64, 659-669 (2001).

Tasirin A., Said M., *Potential of a soft spreadable margarine produced from waste chicken fat and corn oil catalyzed by the thermomyces lanuginosus (Tl Im) lipozyme*, Pak. J. Nutr., **11**, *4*, 360-366 (2012).

Tomaszewska-Gras J., *Detection of butter adulteration with water using differential scanning calorimetry*, J. Therm. Anal. Calorim., **108**, 433-438 (2012).

Tomaszewska-Gras J., *Rapid quantitative determination of butter adulteration with palm oil using the DSC technique*, Food Control, **60**, 629-635 (2016).

Upadhyay N., Goyal A., Kumar A., Lal D., *Detection of adulteration by caprine body fat and mixtures of caprine body fat and groundnut oil in bovine and buffalo ghee using differential scanning calorimetry*, Int. J. Dairy Technol., **70**, *2*, 297-303 (2017).

EVALUAREA CONȚINUTULUI DE GRĂSIMI DIN PRODUSE ALIMENTARE TARTINABILE

(Rezumat)

S-a utilizat calorimetria cu scanare diferențială pentru identificarea tipurilor de grăsimi din produse alimentare tartinabile. S-au analizat trei tipuri de margarină și trei de unt din comerț și un produs homemade. S-a identificat prezența de uleiuri vegetale în două dintre tipurile de unt analizate. În una dintre probele de margarină analizate s-a evidențiat prezența de grăsimi saturate, deși conform producătorului aceasta ar conține doar grăsimi vegetale nesaturate. S-a demonstrat că tehnica DSC poate fi utilizată pentru identificarea alterării untului sau margarinei și această metodă prezintă avantajul necesității unei cantități foarte mici de probe, o reproductibilitate foarte bună și un timp scurt pentru analiză.