FOOD and HEALTH

FOOD and HEALTH
E-ISSN 2602-2834

Food Health 9(3), 184-192 (2023) • https://doi.org/10.3153/FH23017 *Research Article*

A comparative analysis of ten milk samples with differential scanning calorimetry and Fourier transform infrared spectroscopy

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Cite this article as:
Dinç, B., Üstünsoy, R. Ertaş, T., Şen, E. (2023). A comparative analysis of ten milk samples with differential scanning calorimetry and Fourier transform infrared spectroscopy. *Food and Health,* 9(3), 184-192. https://doi.org/10.3153/FH23017

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Submitted: 14.01.2023
Revision requested: 01.03.2023
Last revision received: 07.03.2023
Accepted: 13.03.2023
Published online: 14.05.2023

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Available online at
http://jfhs.scientificwebjournals.com

ABSTRACT

Milk proteins occupy a prominent place in the nutrition of adults and children. Generally, some commercial dairy contains proteins, lactose, other sugar derivatives, and additives. The proportions of the components that make up the milk are different in commercial milk. For this reason, analyzing milk correctly is essential for determining these contents. In this research, analyses of the milk were made by taking differential scanning calorimetry measurements (DSC), and Fourier transform infrared spectrophotometer (FTIR) measurements. Specific heat values and specific values of temperature peaks were examined for ten kinds of milk. DSC curves revealed triacylglycerol dissolution, lactose crystallization, and protein denaturation peaks. Wide variations were observed with the same fat content from 10 milk powders. Most characteristic peaks were not observed when the samples were re-measured after a year at -20°C. The powder samples were compared in terms of protein, fat, lactose content, whey protein casein, and caseinate contents according to differences in FTIR spectra. The FTIR results confirm the DSC curves for most of the analyzed milk types.

Keywords: Differential Scanning Calorimetry, FTIR, Milk quality, Storage effect, Freeze-Drying

Introduction

More than six billion people worldwide consume milk and milk products. Cheese consumption for breakfast and yogurt consumption for other meals are common in Türkiye. Today nearly all commercial milk is being produced by using milk powders. More economical transportation, extended storage conditions, and ease of use make milk powder indispensable for manufacturing businesses. Milk powder is created simply by drying methods such as evaporating water from condensed milk. Milk components' chemical and physical characteristics undergo modifications during the drying process. These are the Maillard reaction, protein denaturation, protein-protein aggregation, protein-fat aggregation, and changes in protein-carbohydrate bonds. Additionally, physical results such as lactose crystallization, stickiness, precipitation, and retention of undesirable aroma (Kaur et al., 2021) are also in these modifications. The occurrence of these adverse modifications, which can damage the milk quality, may depend on many factors, such as the processes applied to milk and their storage conditions. These modifications may be due to the changes in lactose, fat, and protein structure, depending on the storage conditions of the milk (Tsourouflis et al., 1976).

Lactose, a disaccharide, ensures the quality of milk and its long-term healthy preservation. Lactose is generally observed as amorphous glass and is stable under the glass transition temperature (T_g) (Herrington, 1934). The T_g value of lactose was determined as 101°C (Roos & Karel, 1990). The amorphous glass structure of lactose is hygroscopic, i.e., it attracts and accumulates water and could lead to plasticization and a decrease in T_g value (Slade et al., 1991). Amorphous lactose above the T_g increases molecular mobility and lowers the viscosity of milk, which can result in stickiness, molding, and crystallization (Roos & Karel, 1990).

The protein and fat content in milk is also significant for the quality of the milk. These components are very active in determining milk's physical and chemical properties, such as water absorption, glass transition temperature, and crystallization (Shrestha et al., 2007). Jouppila et al. (Jouppila & Roos, 1994) demonstrated that proteins in milk powder may impede the crystallization of lactose, placing a limit on it. In addition, the denaturation and aggregation of proteins create endothermic and exothermic peaks, respectively, that can be determined by differential scanning calorimetry (DSC) measurements (Phosanam et al., 2020). Milk fat, on the other hand, is characterized mainly by triglycerides and produces endothermic peaks that can vary between -40 and +40°C, which can be seen in DSC curves (Kim et al., 2005). In one- or two-component systems, transition links to molecular modification can be analyzed more quickly than in multi-element compounds. Still, the transitions of substances with many components, such as milk powder, can be more complex and challenging to understand. This situation is because the exchange transitions between the substances in the complex compounds may overlap (Rahman et al., 2012). For the analysis of these thermal transitions, the temperature range set by the DSC must be well defined; it can be concluded that this temperature should be below 150°C to gain information about the water content of milk (Jouppila & Roos, 1994). However, to determine the additives in milk, this temperature should be measured at temperatures above 200°C. Potassium nitrate and sodium nitrate are additives in milk, and the DSC peaks of these substances are at temperatures above 200°C, even though chemical additives are becoming increasingly restricted (Smid & Gorris, 2020). Determining the lower limit can also aid in optimizing the sensitivity of the DSC measurement. Setting the lower limit near the sample's glass transition temperature (Tg), for example, can improve measurement sensitivity by maximizing the heat capacity change that occurs in glass transition (Trachenko & Brazhkin, 2011). In addition, the peak size also gives us the amount of content information. For this reason, the differential scanning calorimetry (DSC) system is a method recommended to be used frequently in the quality assessment of foods (Raemy, 2003). In addition, DSC is a highly effective method for detecting physical changes in milk dehydration and storage stages (Vuataz, 2002).

Pellegrino (Pellegrino, 1994) stated that milk oil reduces heat transfer during heat treatment and has a protective effect on the components. The shelf life is prolonged with the participation of various preservatives in the milk, and the essential condition for using these presents is to be unharmful to health. Each country has set a severe limit by making legal regulations regarding the type and quantity of these protectors. In Türkiye, protective use is not alprohibiteheat-treatedated (Güven, 1998). For this reason, it is very important to trace these additives with different chemical analysis methods.

Another important point concerning the storage conditions of milk is that different storage temperatures and times change the protein structures of milk powders (Anema et al., 2006; Howard et al., 2015; Tunick et al., 2016). This research also evaluated this situation by making DSC measurements of milk powders stored at -20 °C for 12 months under the same conditions.

Methodologically, FT-IR spectroscopy is one of the routine methods that can be used in milk analysis and the determination of additives that impair the purity of milk. Infrared spectroscopy is recommended as a unique detection method for determining additives in liquid milk (Ali et al., 2020).

This report aims to understand the effect of storage conditions on milk powders and their composition. Ten different kinds of milk sold in the markets were freeze-dried. Then their components, such as fat, protein, and lactose, were analyzed with DSC, and the same procedure was applied after 12 months. Different amounts of fat and protein were also analyzed and characterized spectrally.

Materials and Methods

Materials

The cow milk of ten well-known brands of UHT milk sold in the market was chosen as samples in this study. The fat, protein, and carbohydrate values given on the milk labels are shown in Table 1.

Table 1. Fat, milk, and protein ratios of milk (grams/100mL)

	Fat	Protein	Carbohydrate
LM1	3.0	2.9	4.7
LM2	3.3	2.8	4
LM3	2.5	3	4.6
LM4	3.3	3	4.7
LM5	3.0	3.1	4.5
LM6	3.4	3.1	4.7
LM7	3.1	2.9	4.7
LM8	3.0	3.0	4.6
LM9	3.0	2.3	8.0
LM10	3.0	1.5	6.9

After the milk was purchased, it was stored at +4°C for three days before freeze-drying; 10 samples were placed in falcon tubes with a capacity of 15 mL, each of 10 mL, under a laminar flow cabinet to avoid contamination.

Freeze-Drying

Freeze-drying was performed at -40°C and 0.05 mBar pressure using a 24 h Lobcanco freeze drier. After the samples were stored at -20°C for 24 hours, the measurements were carried out.

DSC Analysis

DSC measurement was performed with the DSC 60 Plus Shimadzu. Before the measurements, the instrument was calibrated with indium (Melting point 156.6 °C). All samples for DSC analysis were weighed as 10 mg. As a DSC procedure, the reference cell was left empty, and the sample container was placed in the appropriate places in aluminum containers with a closed mouth. The measurement was made between 30°C and 300°C. Studies in the literature take these measurements between -100°C and 250°C (Pugliese et al., 2019). If potassium nitrate is added to milk, a peak specific to this substance may occur above 200°C. Accordingly, measurements were made up to 300°C. The DSC temperature increasing rate is adjusted to 5°C per minute. Measurements were made in an inert nitrogen environment.

FTIR Analysis

FTIR measurements were performed with the ATR FTIR system, Shimadzu IRAffinity-1S, by taking percent transmittance measurements in the wavenumber range of 400-4000 cm^{-1}. Measurements were taken from powder samples.

Results and Discussion

DSC Results

DSC is an instrument that allows measuring the specific heat capacity depending on the temperature and evaluating the phase transitions and enthalpy changes. It can be used in the pharmaceutical industry to examine protein-ligand interactions, determine protein folding and mutations, and define temperature-dependent phospholipid changes (Chiu & Prenner, 2011). For this reason, it is used to examine the protein and lipid structure changes of milk powders and other milk-derived products. Measurements with DSC were used in the 1950s to determine the polymorphism of milk fat due to rapid and slow cooling (Ten Grotenhuis et al., 1999).

Thermal measurement values of fats reveal results depending on fatty acids and triacylglycerol components. Differential scanning calorimetry measurement results in Figures 1 and 2 revealed different fat, lactose, and protein content ratios. The peaks at the beginning of the curves in the range of 11.51 ±0.2

K and 69.97 ±0.35 °C in DSC curves match the cascade melting of triacylglycerol groups dispersed in the lipid droplet (Zouari et al., 2021).

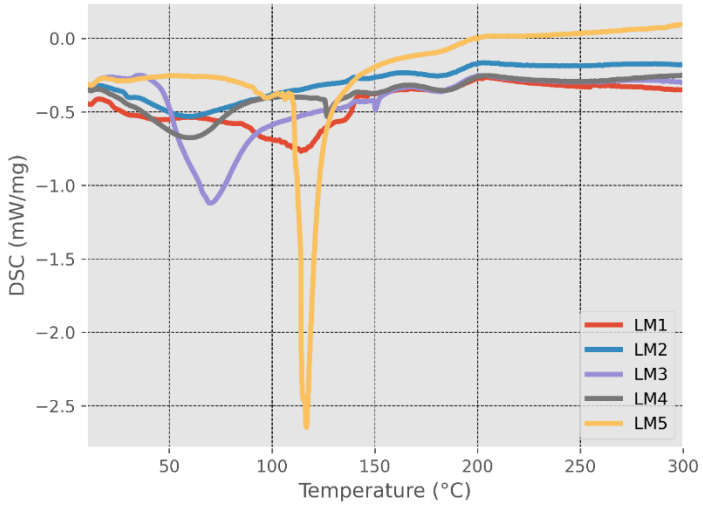

Figure 1. DSC curves of LM1-LM5

While the peaks of fatty acids were prominent in the milk LM3, LM4, LM7, LM8, LM9, and LM10, it was observed that the peaks of fatty acids were not significant in other milk, especially in the follow-on milk LM10 (Figure 1, Figure 2). Interestingly, when the values given on the label are examined, the milk with the least fat ratio is given as LM3. The highest fat-containing milk is LM2, LM4, LM6, and LM7. The values are given on the milk labels, and the values appearing on the DSC curves are different from each other.

The peak of LM10 at -23 °C ±0.33 indicates the polymorphic transition of milk fat from alpha to beta (Ten Grotenhuis et al., 1999). This is because some milk fat still exists in liquid form despite freeze-drying. Additionally, compared to other milk powders, it was in a sticky form, an observation further indicating the presence of polymorphic transition in LM10. These peaks, around -20ºC, are seen in all samples except LM9. The peaks at 11.2°C ±0.21 given by LM7 and LM9 milk in the DSC curves are the first onset temperature peaks and the starting temperature of alpha crystallization. The peaks between 110 and 116 °C are the peaks of lactose, and the highest lactose fraction among these 3 milk powder samples is found in LM9 milk. The peaks of LM2, LM4, and LM8 milk between 204 °C and 205 °C are α-lactose melting peaks. According to Buckton et al., these peaks are due to released water in the collapsed structure of lactose (Buckton et al., 1998). Here the dissolution of crystalline lactose is uneven. The peaks that LM2, LM3, LM4, and LM7 milk give between 140-150 °C are due to the presence of α-lactose monohydrate (Figure 1, Figure 2). The peaks seen here are endothermic (Thomas et al., 2004). On the other hand, determining glass transition temperature effectively determines additives' structural and physiochemical effects in food samples (Cordella et al., 2002).

DSC also determines milk adulteration (Poonia et al., 2017). The glass transition temperature was observed to increase depending on the amount of water added to the milk. The different glass transition temperatures seen between 90 and 120°C are due to the different proportions of water in the milk. The pure milk's glass transition (Tg) value in the previous measurements was 89.2°C. The Tg value was revealed at temperatures varying between 114 and 118°C depending on the amount of water added (Poonia et al., 2017). All the milk except LM3 and LM4 revealed Tg values in this range.

Today, most of the milk is produced from milk powder. Besides, milk powder is used in many products in the food sector, such as cheese, and is stored for months for later usage. During this storage, the physicochemical properties of milk powder change, and its quality decreases (Haque et al., 2010). For this reason, we have stored milk powders for a year at -20°C in closed tubes. When we analyzed the contents of the stored milk powders, we observed that the fat, protein, and lactose peaks of the milk powders disappeared. Only triacylglycerol groups and aquatic peaks were apparent at low amplitude in LM3 and LM9, respectively (Figure 3, Figure 4).

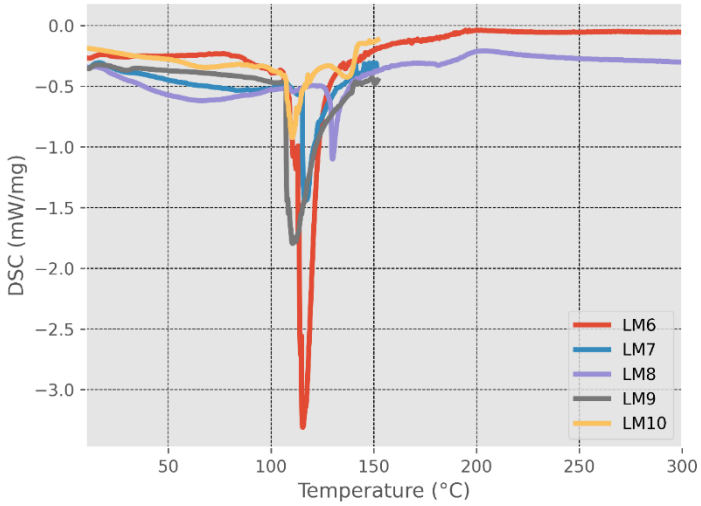

Figure 2. DSC curves of LM6-LM10

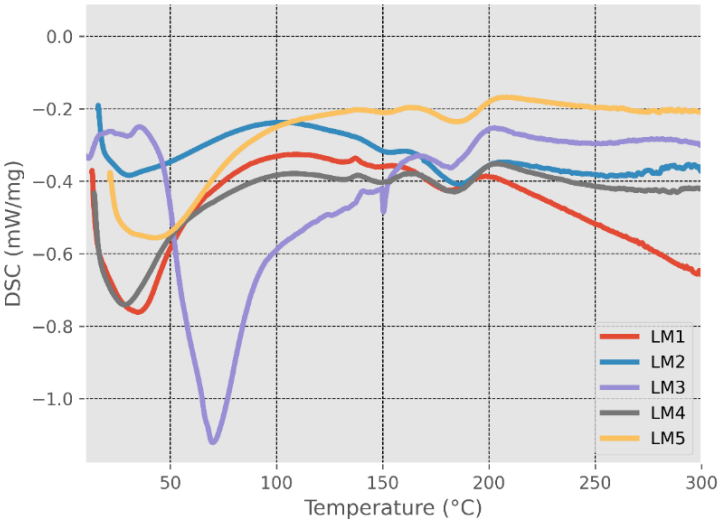

Figure 3. DSC curves of LM1-LM5 after 12 months

During storage, the tendency of milk powder to absorb moisture from the environment creates a bridge between the particles. This causes protein denaturation (Liu & Chaudhary, 2011). From this information, we can say that protein denaturation has occurred, and the physicochemical properties of milk powders have changed. On the other hand, Lactose crystallizes during storage because of the rearrangements of protein-lactose bonds. If amorphous lactose that binds to the active sites of proteins is reduced, it causes destabilization of the proteins (Buera et al., 2005). ΔH values were found by calculating the area of the peak of lactose in LM1 and LM5-10 coded milk. Lactose peaks were not observed in LM2, LM3, and LM4. Looking at the enthalpy values, the milk with the highest lactose content is LM5 and LM9, which have values of 503 and 433 J/g, respectively. Peaks observed in LM2, LM3, and LM4, 59, and 69 have been attributed to the casein glassy transition. It is most significant in the LM4 with a ΔH value of 310 (Table 2) (Jouppila & Roos, 1994; Morgan et al., 2005; Vuataz, 2002).

FTIR spectrums

Examination of the FTIR spectra is also used to determine the differences between milk ingredients. In milk production, protein ratios and nitrogen content are controlled. Adding melamine to milk increases the nitrogen content (Balabin & Smirnov, 2011). In determining melamine contamination, amide I and amide II regions revealed fingerprints in proteins at intervals of 1700-1400 cm^{-1} (Balabin & Smirnov, 2011). In the study of Jawaid et al. on the melamine additive to milk, characteristic peaks were observed between 851-798 cm^{-1} for pure melamine (Jawaid et al., 2013). These peaks are not included in our milk samples. 1800-700 cm^{-1} corresponds to the absorption peaks of carbonyl bonds, which are seen in milky lipids. In addition, the absorption bands between 3000 and 3050 cm^{-1} correspond to olefinic double bonds (-HC=CH-) of unsaturated fatty acids (Araki et al., 2015). Follow-on milk fats showed major peaks in the 753-756 cm^{-1}. Strong absorption of oils and fats are bands between 3000-2800 cm^{-1} caused by stretching vibrations in C-H groups.

One of the amide groups' peaks, visible at 1500 cm^{-1}, disappears in the follow-up milk LM9. The characteristic peaks of C-O vibrations in carbohydrates between 800-1200 cm^{-1} seem to form more and higher bands in follow-up milk LM9 and LM10 compared to the bands of other types of milk (Figure 5, Figure 6).

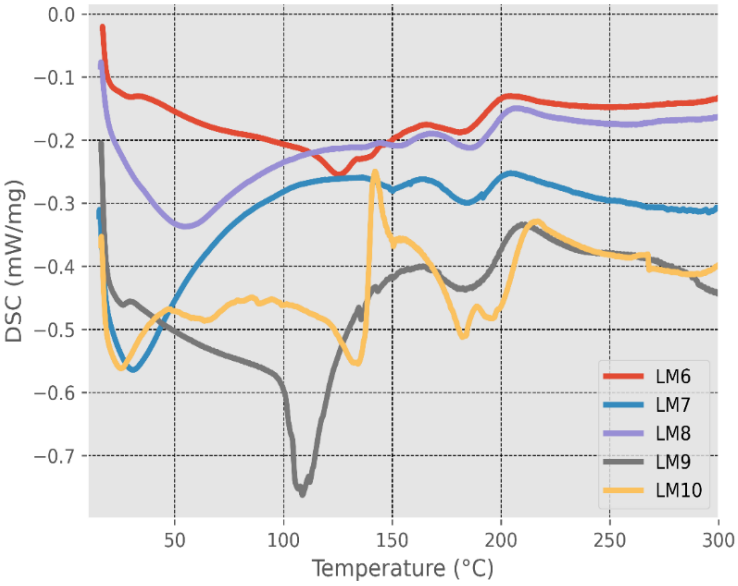

Figure 4. DSC curves of LM6, LM7, LM8, LM9, and LM10 after 12 months

Like DSC curves, FTIR peaks of fatty acids (Rachah et al., 2021) at 1747-1750 cm^{-1} of LM3, LM4, LM7, LM8, and LM9 are evident. The fatty acid peak was not marked in LM10 in DSC curves. Similarly, no peak was observed in LM10 in this band range.

The absorption at 2950 cm^{-1} matches that of C-H (CH_3). The bands at 2915 and 2848 cm^{-1} correspond with -C-H (CH_2) (Dutta et al., 2013). The bands in 1744 and 3004 cm^{-1} belong

to the C=O stretching vibrations of aliphatic esters and C–H stretching vibrations of the cis-CH out-of-plane vibration, respectively (Koca et al., 2010). The wavenumbers at 1320 and 1145 cm^{-1} shows the C–C(=O)–O and O–C–C of the C–O bonds of the esters and the bending vibrations of some methylene groups. The absorption peaks observed at 1467, 1382, 1150, 1117, 1097, and 1057 cm^{-1} are expressing C–H–CH_2, C–H–CH_3, =C–H– (cis), –C–H-bending, –C–H–, and –C–O–CH_2– functional groups, respectively (Figure 5, Figure 6). The bands 753-756 cm^{-1} can be considered an important region for the distinction between bovine and buffalo milk fat fractions and infant formula fat. The differences in the milk fat percentages of follow-on milk, observed in the spectral regions of milk fat, can be attributed to differences in the composition of these fat fractions concerning chain length and degree of unsaturation. It was observed that the total number of bands and their positions were similar in oils obtained from buffalo and bovine milk examined before (Antony et al., 2018).

Table 2. Data are reported as the mean of three replicates ± standard deviation. Tp/ C is the peak temperature of transition. ΔH (Jg-1):change in enthalpy

	>-50 (T_p/°C)	> 10 (T_p/°C)	>20 (T_p/°C)	40-70 (T_p/°C)	105-150 (T_p/°C)	> 150 (T_p/°C)	> 200 (T_p/°C)
LM1	-48.8 ±1.3	11.5 ±0.2	27.25 ±1.5	45.4 ±1.6	114 ΔH= 93 ±24	181.8 ±1.1	254.6 ±1.5
LM2	-30.6 ±1.8	11.6 ±1.5	28.7 ±1.03	59.6 ±1.4 ΔH= 291 ±7.1	140.5 ±1.8	179.8 ±2.6	
LM3		11.5 ±0.5	29.6 ±1.7	69.9 ±0.35 ΔH= 594 ± 2	150.3 ±1.4	181.7 ±1.2	
LM4	-30.4 ±1.6	11.8 ±1.8		59 ±0.7 ΔH= 310 ±3.1	147.8 ±2.8	183.8 ±2	204 ±2.7
LM5	-21.8 ±2.4	11.8 ±1.2			116.7 ±1.3 ΔH= 503 ±13		
LM6	-19.4 ±2.5	17.3 ±1.3			115.4 ± 1.4 ΔH= 43 ±13		
LM7		11.2 ±2.1 16.5 ±1.4			106.1 ±1.2 113.2 ±0.4 ΔH= 113 ±11		
LM8	-31.6 ±1.2 -7.1 ±4.3	11.2 ±0.21			110.8 ±1.8 129.9 ±0.7 ΔH= 42 ±15.4	181.2 ±1.2	204.3 ±1.3
LM9		11.0 ±0.9	29.4 ±1.08		110.4 ±0.6 ΔH= 433 ±16		
LM10	-23 ±0.3			67.7 ±2	110.3 ±2.3 ΔH= 93 ±15 137 ±2.5		

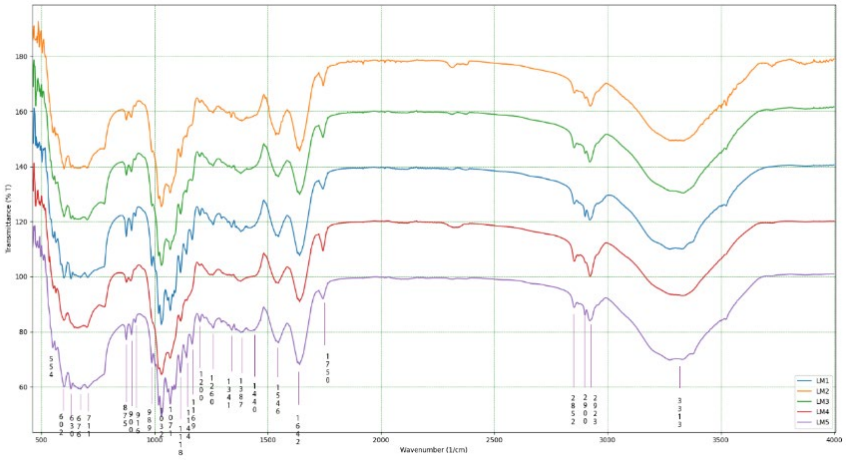

Figure 5. FTIR spectrums of LM1-LM5

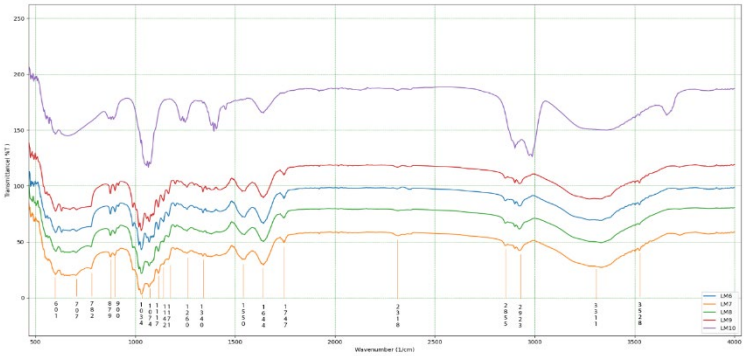

Figure 6. FTIR spectrums of LM6-LM10

Conclusion

Different components added to milk not only reduce milk quality but may also pose a danger to consumers. For example, milk mixed with whey can cause serious problems for people allergic to this substance. For this reason, research on milk content has an important place in the literature. This study identified different water ratios, lactose ratios, protein content, and carbon groups via DSC analysis and FTIR spectra in ten commercial milk brands. The percentages of fat, protein, and carbohydrates in most of the milk sold in the markets should be given on the labels correctly. For this reason, when calculating milk's fat, protein, and carbohydrate content, DSC and FTIR studies should be added to the analysis methods of the brand thanks to their fast, responsive, and accurate analysis. Milk quality also decreases as storage time intervals exceed about 12 months. In markets, packaged foods containing milk are stored at -20°C. For example, ice creams and pastry products using dairy products are stored and sold in the freezer at -20°C in Türkiye. These products are sold with an expiration date of at least one year. However, during this period, the physicochemical structure of milk powder deteriorates, and its nutritional value decreases. These products should not be the priority when purchasing.

Compliance with Ethical Standards

Conflict of interests: The author declares that for this article, they have no actual, potential, or perceived conflict of interest.

Ethics committee approval: Authors declare that this study includes no experiments with human or animal subjects.

Funding disclosure: -

Acknowledgments: -

Disclosure: -

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