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# AN IMPROVED DIFFERENTIAL SCANNING CALORIMETRY STUDY FOR THERMAL PROPERTIES OF PEKMEZ SAMPLES ADULTERATED WITH SUGAR SYRUP

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## ABSTRACT

This research was carried out to determine the pH, titratable acidity, ash, specific gravity, color (L*, a*, b*), water activity, electrical conductivity, glass transition temperature ($T_g$) and melting characteristics of grape and mulberry pekmez samples adulterated with different levels (10%, 30%, 50%) of high fructose corn syrup (HFCS). Ash, titratable acidity and electrical conductivity values have decreased significantly ($P$<0.05) with the level of adulteration and determined that these properties can be used as a criterion in the determination of adulteration. Two glass transition temperatures occurring between -25.64°C to -32.58°C ($T_{g1}$) and 23.29°C to 31.22°C ($T_{g2}$) were detected in all pekmez samples. The single glass transition temperature was determined in the pekmez samples diluted with water, and both the glass transition temperatures and the onset, peak, end temperatures and enthalpy values of the melting peaks increased significantly with the increase in the amount of adulteration ($P$<0.05).

**Keywords:** Pekmez, differential scanning calorimetry, glass transition temperature, adulteration, sugar syrup

# ŞEKER ŞURUBUYLA TAĞŞİŞ EDİLEN PEKMEZ ÖRNEKLERİNİN TERMAL ÖZELLİKLERİ İÇİN GELİŞTİRİLMİŞ BİR DIFFERENTIAL SCANNING CALORIMETRY ÇALIŞMA

## ÖZ

Bu araştırma, farklı seviyelerde (%10, %30, %50) yüksek fruktozlu mısır şurubu (HFCS) ile tağşiş edilmiş üzüm ve dut pekmezlerinin pH, titre edilebilir asitlik, kül, özgül ağırlık, renk (L*, a*, b*), su aktivitesi, elektriksel iletkenlik, camsı değişim sıcaklığı ($T_g$) ve erime özelliklerinin belirlenmesi amacıyla yürütülmüştür. Tağşiş seviyesi arttıkça kül, titre edilebilir asitlik ve elektriksel iletkenlik değerlerinin önemli derecede (P<0.05) azaldığı ve bu özelliklerin tağşişin belirlenmesinde kriter olarak kullanılabileceği belirlenmiştir. Pekmez örneklerinin tamamında -25.64°C ile -32,58°C ($T_{g1}$) ve 23.29°C ile 31.22°C ($T_{g2}$) arasında oluşan iki camsı geçiş sıcaklığı tespit edilmiştir. Su ile seyreltilen pekmez örneklerinde tek camsı geçiş sıcaklığı belirlenmiş olup, tağşiş miktarının artmasıyla hem camsı değişim sıcaklıkları hem de erime piklerinin başlangıç, pik, bitiş sıcaklıkları ve entalpi değerleri önemli derecede artış göstermiştir (P<0.05).

**Anahtar kelimeler:** Pekmez, differential scanning calorimetry, camsı değişim sıcaklığı, tağşiş, şeker şurubu

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## INTRODUCTION

In general, pekmez is the name given to sweet syrups concentrated with long shelf life, obtained by crushing and boiling of fruits with possessing high sugar content without adding sugar or other additives (Erbil, 2020). It is commonly produced from grapes, mulberry and carob, and is named after the fruit from which it is obtained. Production processes of pekmez vary according to origin of fruits used in production (Karababa and Isikli, 2005). The use of any additives, mixing of different fruits, dilution and/or reproduction with commercial glucose, sucrose and high fructose corn syrups are prohibited in pekmez standards (Anonymous, 2017). However, today, the high competition in the food sector causes the production of adulterated products in pekmez, as in other food groups, and a growing problem in the global market (Yılmaz, 2012). One of the adulterations made in pekmez is to add cheap sugar syrups in order to reduce the cost. For this purpose, the amount is increased by adding glucose, sucrose and high fructose corn syrups at different ratios during or after production. Even worse, sugar syrup is produced by imitating the sugar profile, color, structure and taste of pekmez with additives such as sugar syrups, coloring, flavoring, but it is sold under the name of pekmez (Tosun, 2014).

Various techniques have been used to determine adulteration in pekmez samples until today. Different characteristics are taken into account in the techniques used. For example, corn and sugarcane are C4 plants, and their photosynthesis pathways differ from those of C3 plants such as wheat, rice, sugar beet, grape, apple, and mulberry. For this reason, $^{13}C/^{12}C$ ($\delta^{13}C$) value is measured with Isotope Ratio Mass Spectrometry (IR-MS) and it can be determined whether sugar cane and corn-based syrup is added to pekmez (Tosun, 2014, Erbil, 2020). Since sugar beet uses the same photosynthesis pathway as fruits, adulteration made by adding syrup from sugar beet or different fruit/fruit pekmez samples cannot be determined. Determination of the 2H/1H ratio in Site-Specific Natural Isotope Fractionation-Nuclear Magnetic Resonance (SNIF-NMR) is used for this purpose (Yılmaz and Afsar, 2012). In addition, if the sugar obtained from beet is inverted and the fructose/glucose ratio is not adjusted to the legal limit, this type of adulteration can be detected by analyzing the sugar components in HPLC (El Darra et al., 2017). Attenuated total reflectance (ATR)-Fourier Transformed Infrared (FTIR) Spectroscopy along with chemometric methods is used for determination of pekmez samples adulteration with glucose syrup (Yaman, 2019).

Although there are various national and international laws for supervising the quality and safety of food products, pekmez adulteration is still widespread. Therefore, effective supervision is very important for ensuring the suitable development of the food industry and accurate, effective, reliable and rapid detection techniques are needed. There has been no research on the DSC characteristics such as glass transition temperature of pekmez samples. The glass transition temperature, a characteristic property of amorphous materials, is a second-order time-temperature dependent transition (Roos, 2010). The electrical, mechanical, physical and thermal properties of a material exhibit discontinuity at this temperature. It can be defined as the temperature at which a material changes from a glassy state to a rubbery state (Roos, 2010). It is a highly importance in determining of the storage temperatures and processability of amorphous materials. If any material is stored at a temperature lower than the glass transition temperature, it can be stored for a long time without any deterioration, because the viscosity is very high ($10^{12}$ Pa.s) at the glass transition temperature and the molecular mobility is restricted (Le Meste et al., 2002). The aim of this research was to determine various physicochemical properties such as pH, color, specific gravity, electrical conductivity, glass transition temperature and melting thermograms of grape and mulberry pekmez samples, and to determine whether there is any change in the properties indicated by adulteration with high fructose corn syrup.

## MATERIALS AND METHODS

### Materials

Grape pekmez samples were obtained from Atatürk Orman Çiftliği Fruit Juice and Honey Factory (Ankara, Turkey). Mulberry pekmez samples were obtained from a local producer (Baldağı, Ankara, Turkey). HFCS was obtained from Sunar Mısır Company (Adana, Turkey).

The dextrose and fructose content of the HFCS specified by the company were 21-25 and 29-35, respectively. The pH, ash, specific gravity, water activity and electrical conductivity of HFCS were 4.22±0.01, 0.03±0.01%, 1.38±0.02, 0.740±0.02 and 0.16±0.02 mS/cm, respectively.

### Preparation of adulterated pekmez samples using HFCS

Adulterated pekmez samples were prepared using HFCS. For this purpose, HFCS was heated to 70°C in a water bath and mixed with grape and mulberry pekmez samples at 10%, 30% and 50% by weight of pekmez, and the mixtures were kept at room temperature overnight. Considering the grape-mulberry pekmez codex and the brix analysis of the pekmez samples obtained from the market, the brix values of pekmez samples adulterated with HFCS at 10%, 30% and 50% was adjusted to 72. All analyzes were carried out on pekmez samples with a brix value of 72.

### Methods

*Physicochemical analyses of pekmez samples*

pH, titratable acidity, soluble dry matter and ash were determined according to the standard method AOAC (2000). pH values were determined by using pH metre (PL- 700PV, Taipei, Taiwan). Before the measurements, the calibration of the pH meter was made using buffer solutions of 4 and 7.

Titratable acidities of the samples were determined by titration with 0.1 NaOH to pH 8.1 using a pH meter (PL- 700PV, Taipei, Taiwan), and expressed as percentage of citric acid.

Solubles dry matter was determined with an Abbe Refractometer (JK-ARM, Shanghai Jingke Scientific Instrument Co., Ltd., Shanghai, China). The ash contents were determined by incinerating the sample in a muffle furnace at 600°C for 18 hours.

Specific gravities were determined at 20°C by using 25 mL pycnometer.

Water activity ($a_w$) values of samples were determined using an $a_w$ instrument (Novasina AG, LabMaster $a_w$, Switzerland). The instrument was calibrated with six different salt solutions at 25°C before using.

L*, a* and b* values of the pekmez samples were determined by using a colorimeter (Konica Minolta Chroma Meter CR-400, Osaka, Japan). For color analysis, the instrument was calibrated with a white calibration plate before measurements. The color values were expressed in terms of the L* value (lightness), a* value (redness), and b* value (yellowness) according to the system of the International Commission of Illumination (CIE). Using the average of the experimental data obtained, the color difference (ΔE) was calculated according to equation 1.

$$\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (L^* - b_0^*)^2} \quad (1)$$

Electrical conductivities of pekmez samples were determined by HQ40d Multi conductivity measuring device (HACH, Colorado, USA). For the measurement, 20% (w/w) solution of each pekmez sample was prepared with ultrapure water. Conductivity measurements in prepared solutions were made at 20°C and the results were expressed as mS/cm.

*Determination of $T_g$*

$T_g$ values were determined using DSC (DSC 6000, Perkin Elmer, USA) equipped with a intracooler cooling accessory. The DSC was calibrated using indium and mercury standards, with onset temperatures of 156.6°C and -38.87°C, respectively. Pekmez samples were weighed 10 mg into DSC hermetic pans (product number 03190029, Perkin Elmer, USA), that is then hermetically sealed, and put into the DSC at room temperature. An empty pan was used as reference. Samples were then cooled from 20°C to -80°C at

5°C/min, held for 30 min, and then scanned from -80°C to 60°C at 5°C/min. All experiments were carried out in nitrogen atmosphere at a flow of 30 mL/min. Each shift on DSC curve was analyzed for the onset ($T_{go}$), mid ($T_{gm}$), and end of glass transition ($T_{ge}$). $T_g$ is reported as the midpoint of the step.

*DSC thermograms of diluted samples*
Since the melting endotherm could not be determined in either undiluted non-adulterated or undiluted adulterated pekmez samples, it was aimed to reveal the differences that may occur as a result of dilution of pekmez samples in these measurements. For this purpose, pekmez samples of 10 mg were weighed into hermetic pans and diluted by one third with distilled water using a micro syringe and pans sealed. Sealed pans were left at room temperature for 24 h to allow for equilibration of moisture. An empty pan was used as reference. Samples were then cooled from 20°C to -80°C at 5°C/min, held for 30 min, and then scanned from -80°C to 60°C at 5°C/min. All experiments were carried out in nitrogen atmosphere at a flow of 30 mL/min. The glass transition temperature ($T_g$) from the step on the DSC curve, the onset ($T_o$), peak ($T_p$), end temperatures ($T_e$) and enthalpy values ($\Delta H$) from the melting peaks were determined.

**Statistical analysis**
In this study, adulterated grape and mulberry pekmez samples with the addition of HFCS at three different concentrations (10%, 30% and 50%) and non-adultered grape and mulberry samples were used. In addition, DSC analyzes were carried out by diluting both non- adulterated and adulterated pekmez samples by one third. The experiment was set up according to a completely randomized design and all analyses were performed at least three times to obtain the average data with acceptable standard deviations. Results are expressed as mean of three replications ± standard deviation. The statistical analysis was performed with SPSS (version 22 for Windows, SPSS Inc.). One-way analysis of variance (ANOVA) was conducted, followed by Duncan's multiple range test to compare treatment means. Differences were considered to be significant at $P<0.05$. Correlations were obtained using Pearson's correlation coefficient.

## RESULTS AND DISCUSSIONS

**Physicochemical properties of pekmez samples**
The pH values of pekmez samples are shown in Table 1. The pH value of pekmez samples may vary depending on the type of fruit, the time of harvest, the climate, the characteristics of the soil in which it is grown, and the process conditions. According to legal regulation by the Republic of Türkiye, the pH range should be 5.0–6.0 in grape and mulberry pekmez (Anonymus, 2011, 2017). Considering the specified limits, it could be stated that all pekmez samples complied with the standards. The pH values obtained in the study were similar to the findings obtained in the studies conducted by several researchers (Şimşek and Artık, 2002; Kaya et al., 2012; Karataş and Şengül, 2018). Compared with the non-adulterated pekmez samples, pH values of mulberry pekmez samples containing HFCS were significantly decreased with the increase in syrup concentration (Table 1). This situation may be due to the low pH value of HFCS used in the adulteration of pekmez samples.

Electrical conductivity values of pekmez samples are given in Table 1. As can be seen in Table 1, the electrical conductivity values of both grape and mulberry pekmez samples were decreased significantly with the addition of HFCS. This decrease in electrical conductivity could be considered as a criterion in determining adulteration in pekmez samples. Electrical conductivity of foods is closely related to physicochemical properties such as pH, brix value, protein, phenolic substance, organic acid and mineral content (Lee et al., 2013). Since the electrical conductivity value of high fructose corn syrup is 0.16 mS/cm, it causes a decrease in the conductivity of pekmez samples to which it is added (Tosun and Keleş, 2012). Pearson correlation analysis showed that there was a positive correlation between the electrical conductivity value and the ash content of both grape and mulberry pekmez samples (for grape pekmez samples 0.987, $P<0.01$; for mulberry pekmez samples 0.986, $P<0.01$).

Table 1. Physicochemical properties of pekmez samples non-adulterated and adulterated with high fructose corn syrup.

| Sample | pH | Ash (%) | Titratable acidity (g/100g) | $a_w$ | Specific gravity |
|---|---|---|---|---|---|
| GP | 5.53±0.03ab | 1.74±0.01d | 0.22±0.01d | 0.700±0.01a | 1.367±0.01a |
| GP + 10% HFCS | 5.50±0.01a | 1.60±0.01c | 0.19±0.01c | 0.708±0.01b | 1.366±0.01a |
| GP + 30% HFCS | 5.54±0.01b | 1.18±0.12b | 0.15±0.01b | 0.712±0.01b | 1.366±0.01a |
| GP + 50% HFCS | 5.55±0.01b | 0.83±0.05a | 0.12±0.01a | 0.721±0.01c | 1.366±0.01a |
| MP | 5.77±0.09d | 2.58±0.05d | 0.46±0.01d | 0.699±0.01a | 1.376±0.01b |
| MP + 10% HFCS | 5.73±0.01bc | 1.94±0.02c | 0.35±0.01c | 0.700±0.01a | 1.379±0.01c |
| MP + 30% HFCS | 5.66±0.02ab | 1.73±0.10b | 0.33±0.01b | 0.714±0.01b | 1.370±0.01a |
| MP + 50% HFCS | 5.61±0.04a | 1.10±0.14a | 0.28±0.01a | 0.738±0.01c | 1.375±0.01b |

| Sample | Electrical conductivity (mS/cm) | L* | a* | b* |
|---|---|---|---|---|
| GP | 3.42±0.01d | 19.29±0.01a | -0.29±0.02a | 1.89±0.01a |
| GP + 10% HFCS | 3.10±0.01c | 19.33±0.01b | -0.28±0.03a | 1.88±0.01a |
| GP + 30% HFCS | 2.46±0.01b | 19.35±0.01c | -0.30±0.01ab | 1.94±0.01b |
| GP + 50% HFCS | 1.81±0.01a | 19.36±0.01c | -0.34±0.03b | 1.93±0.01b |
| MP | 4.06±0.01d | 19.45±0.01a | -0.32±0.03a | 2.13±0.01a |
| MP + 10% HFCS | 3.43±0.01c | 19.50±0.01b | -0.30±0.03a | 2.18±0.01b |
| MP + 30% HFCS | 3.16±0.01b | 19.52±0.01c | -0.32±0.02a | 2.20±0.01b |
| MP + 50% HFCS | 2.33±0.01a | 19.60±0.01d | -0.29±0.02a | 2.26±0.02c |

[a-d] Means ± standard deviation in the same column, values in a column with the different letters are significantly different ($P$<0.05). GP, Grape pekmez, MP, Mulberry pekmez, HFCS, High fructose Corn Syrup.

The ash contents determined in pekmez samples that are non-adulterated comply with the standards. The ash contents of grape and mulberry pekmez samples should be at most 2.5% and 4%, respectively (Anonymous, 2011, 2017). Similar to the electrical conductivity, the ash content of pekmez samples also decreased significantly with increasing HFCS concentration (Table 1, $P$<0.05). These decreases in ash values could be perceived as signs of adulteration made with different sugar syrups. A similar result was found in the samples prepared by adding 10%, 30% and 50% sucrose syrup, glucose syrup and high fructose corn syrup to three different mulberry pekmez to determine adulteration (Tosun and Keleş, 2012).

The titratable acidity values of the non-adulterated and adulterated pekmez samples are given in Table 1. The highest titratable acidity was found in non-adulterated MBP. In the standards, it is emphasized that the titratable acidity of mulberry pekmez should be between 0.12 and 0.9, and there is no value for grape pekmez (Anonymous, 2011, 2017). From the values determined in mulberry pekmez samples in this study, it is possible to state that non-adulterated mulberry pekmez samples comply with the standards. The titratable acidity value in each sample group decreased significantly with the increase in the amount of HFCS($P$<0.05). A similar situation was determined as a result of the research conducted by Tosun and Keleş (2012).

While the water activity values in grape and mulberry pekmez samples increased with the increase in the amount of HFCS. There was a negative correlation between the water activity-electrical conductivity and water activity-ash content of both grape and mulberry pekmez samples (for grape pekmez samples -0.953, $P$<0.01, -0.927, $P$<0.01; for mulberry pekmez samples -0.943, $P$<0.01, -0.901, $P$<0.01). Yaman (2019) determined that the water activity values of grape, mulberry and carob pekmez adulterated with glucose syrup were not statistically different from the water activity values of non-adulterated pekmez. Water activity is an important parameter for the Maillard reaction, which is one of the browning reactions in pekmez samples. Fellows (2000) reported that the Maillard reaction occurred at the highest level at a water activity value of 0.6.

Considering the specific gravity values of the samples, it was determined that adulteration made with HFCS did not make a significant difference in grape pekmez samples but caused an increase in mulberry pekmez samples (Table 1). Tosun and Keleş (2012) determined that the specific gravity value of mulberry pekmez samples adulterated with corn syrup with high fructose content decreased.

Color values of pekmez samples are shown in Table 1. With the increase in HFCS, L* values were increased in grape and mulberry pekmez samples. L* value, which expresses the brightness in the pekmez color, decreases in parallel with the increase in the amount of water-soluble dry matter during the concentration process. The time and temperature of the concentration process have a significant influence on the L* value. There was a negative correlation between the L* values and the ash content of both grape and mulberry pekmez samples (for grape pekmez samples -0.820, $P<0.01$; for mulberry pekmez samples -0.974, $P<0.01$). A positive a* value indicates redness, and a negative a* value indicates greenish. With the increase in the amount of HFCS, the greenish value of grape pekmez samples were increased significantly, but no statistically significant difference was found in mulberry pekmez samples (Table 1, $P>0.05$). The positive b* value, which is an indicator of yellow color, showed a partial increase with the addition of HFCS to grape and mulberry pekmez samples. The color values measured in non-adulterated pekmez are similar to the results determined by Özesmer (2021). Depending on the increasing levels of HFCS, the color difference in grape pekmez samples was determined 0.042, 0.079 and 0.095, while in mulberry pekmez samples was found 0.073, 0.099 and 0.201. The results obtained showed that HFCS creates more color difference in mulberry pekmez samples.

**$T_g$ of pekmez samples**

Figure 1 shows typical DSC thermograms of non-adulterated and adulterated pekmez samples. Two glass transition temperatures occurring between -25.64°C to -32.58°C and 23.29°C to 31.22°C were detected in all pekmez samples (Table 2). This shows that all of the pekmez samples are amorphous character. The first transition corresponds to the glass transition of the branched chains or mobile components, and the second transition refers to the backbone of a large polymer or less mobile components. Similar observations were also reported by Ahmed et al., (2005), Guizani et al., (2010) and Sadeghi et al., (2016) for different date varieties. Al-Farsi et al., (2018) detected multiple glass transition temperatures in crystallized date-syrups with moderate water content. Researchers explained this situation with the natural heterogeneity caused by molecular incompatibility and phase separation in the complex matrix. Considering the obtained midpoints values of the transitions (Table 2), while the glass transition temperatures of adulterated grape pekmez samples were higher than that of non-adulterated grape pekmez samples, it was decreased in mulberry pekmez samples. Luyet and Rasmussen (1968) and Rasmussen and Luyet (1969) reported that $T_g$ values of carbohydrate solutions vary depending on concentration and cooling rate. Also, Roos and Karel (1991a) stated that $T_g$ values of sucrose solutions initially decreased with increasing sucrose concentration but increased again at high sucrose concentrations.

**DSC thermograms of diluted pekmez samples**

Figure 2 shows typical DSC thermograms of non-adulterated and adulterated pekmez samples in diluted samples. In general, grape pekmez samples containing HFCS had significantly higher $T_g$ values than samples without HFCS (Table 3, $P<0.05$). A shoulder was determined at the beginning of the melting peaks of all pekmez samples (Figure 2). The onset, mid, and end temperatures of these shoulders were differed significantly from each other and increased with increasing amount of HFCS (Table 3, $P<0.05$). Obtained values show that non-adulterated pekmez samples have lower $T_o$, $T_p$ and $T_e$ values than adulterated pekmez samples. This could be due to the minerals and different nature of water binding with varied solutes. Similar characteristic properties were determined in crystallized date syrup by Al-Farsi et al., (2018). In general, the enthalpy values of ice melting were increased with the increasing of HFCS content (Table 3). This may be due to the compatibility of the polymer with sugars or sugar mixtures. A similar situation was determined by Singh and Roos (2005, 2010) and Roos and Karel (1991b) in mixed sugar-polymer systems, and researchers attributed this to the compatibility of the polymer with sugars or sugar mixtures.

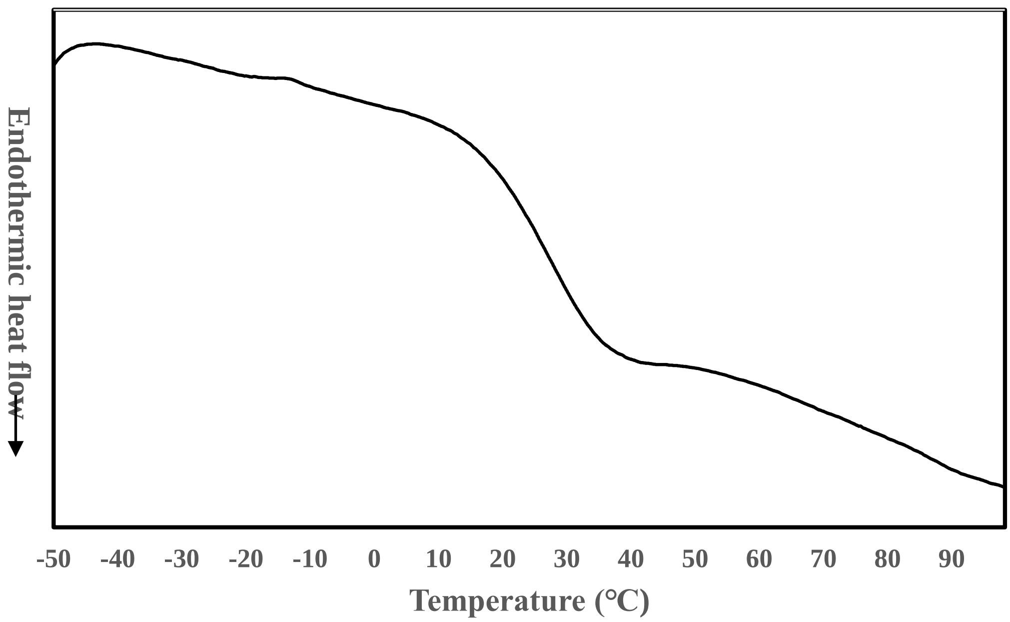


Figure 1. Representative DSC thermograms of non-diluted pekmez samples

Table 2. Glass transition temperatures of non-diluted pekmez samples.

| Sample | $T_{g1o}$(°C) | $T_{g1m}$(°C) | $T_{g1e}$(°C) |
|---|---|---|---|
| GP | -43.60±0.21a | -32.58±0.69c | -17.56±0.16a |
| GP + 10% HFCS | -43.82±0.53a | -28.35±0.42a | -17.45±0.37a |
| GP + 30% HFCS | -43.71±0.96a | -30.50±0.32b | -17.72±0.75a |
| GP + 50% HFCS | -44.35±0.53a | -31.99±0.74c | -17.09±0.84a |
| MP | -35.33±0.59a | -25.64±0.84a | -17.35±0.01a |
| MP + 10% HFCS | -41.53±0.59b | -27.20±1.41b | -17.91±1.04a |
| MP + 30% HFCS | -41.10±1.51b | -27.48±0.52b | -16.99±0.15a |
| MP + 50% HFCS | -44.08±0.05c | -25.82±0.96a | -17.38±0.34a |
| Sample | $T_{g2o}$(°C) | $T_{g2m}$(°C) | $T_{g2e}$(°C) |
| GP | -16.44±0.96a | 26.60±1.60a | 44.24±0.10a |
| GP + 10% HFCS | -16.01±0.31aa | 28.94±0.01b | 44.02±0.59a |
| GP + 30% HFCS | -16.38±0.58a | 30.11±0.32bc | 44.87±0.17a |
| GP + 50% HFCS | -15.80±0.74a | 31.22±0.16c | 48.54±0.22b |
| MP | -17.35±0.01b | 32.71±0.40c | 49.85±0.65c |
| MP + 10% HFCS | -16.43±0.37a | 24.51±1.58ab | 45.29±0.37b |
| MP + 30% HFCS | -16.99±0.15b | 23.29±0.43a | 42.41±1.11a |
| MP + 50% HFCS | -17.38±0.34b | 25.93±1.06b | 45.99±1.17b |

[a-d] Means ± standard deviation in the same column, values in a column with the different letters are significantly different (*P*<0.05). GP, Grape pekmez, MP, Mulberry pekmez, HFCS, High fructose Corn Syrup.

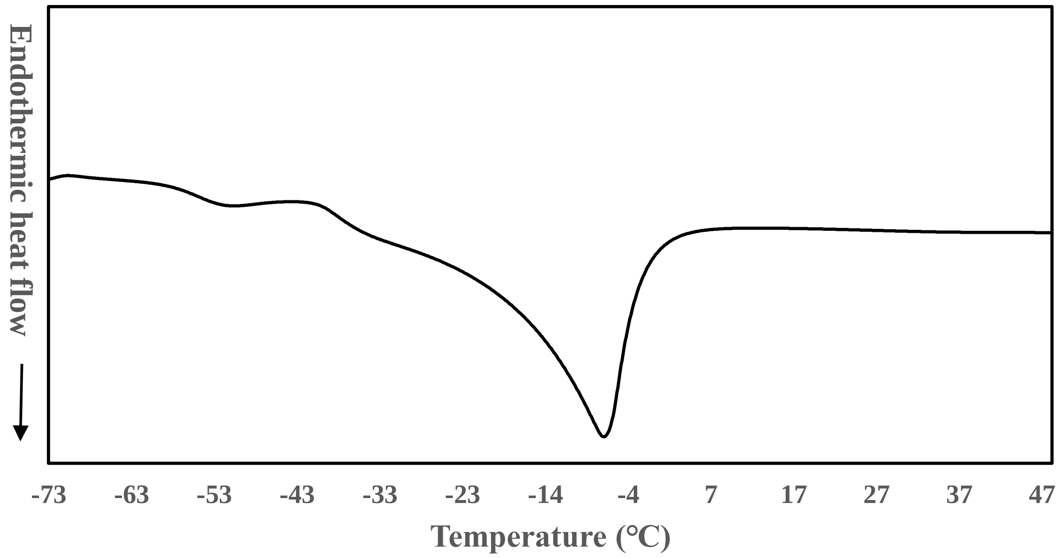


Figure 2. Representative DSC thermograms of pekmez samples diluted with water

Table 3. DSC results of pekmez samples diluted with water.

| | Glass Transition | | | Shoulder of melting endotherm | | |
|---|---|---|---|---|---|---|
| Sample | $T_{go}$(°C) | $T_{gm}$(°C) | $T_{ge}$(°C) | $T_{so}$(°C) | $T_{sm}$(°C) | $T_{se}$(°C) |
| GP | -64.07±0.41a | -55.20±0.01c | -50.67±0.09c | -43.94±0.08c | -38.35±0.16c | -31.38±0.10d |
| GP + 10% HFCS | -63.03±0.99a | -54.63±0.14b | -50.04±0.24b | -43.54±0.12b | -38.06±0.23c | -31.07±0.01c |
| GP + 30% HFCS | -64.06±0.17a | -54.50±0.29ab | -50.01±0.25b | -43.28±0.20b | -37.12±0.30b | -30.16±0.22b |
| GP + 50% HFCS | -63.85±0.55ba | -54.19±0.07a | -49.07±0.04a | -42.36±0.13a | -35.91±0.01a | -29.00±0.18a |
| MP | -62.98±0.52b | -53.60±0.16a | -48.90±0.11b | -42.64±0.01c | -37.55±0.14c | -30.57±0.27c |
| MP + 10% HFCS | -62.92±0.07b | -53.65±0.03a | -48.93±0.13b | -42.46±0.01bc | -36.53±0.01b | -29.53±0.01a |
| MP + 30% HFCS | -62.62±0.05b | -53.40±0.08a | -48.69±0.04b | -42.18±0.03a | -36.49±0.04b | -29.84±0.09b |
| MP + 50% HFCS | -61.87±0.40ba | -53.45±0.20a | -48.31±0.19a | -42.30±0.23ab | -35.92±0.17a | -29.47±0.15a |

| | Melting Endotherm | | | |
|---|---|---|---|---|
| Sample | $T_o$(°C) | $T_p$(°C) | $T_e$(°C) | ΔH (J/g) |
| GP | -19.73±0.13c | -6.52±0.19c | -1.61±0.06a | 90.77±0.05a |
| GP + 10% HFCS | -19.26±0.01c | -6.03±0.12bc | -1.24±0.14a | 89.76±0.27a |
| GP + 30% HFCS | -18.50±0.70b | -5.82±0.53b | -1.33±0.40a | 95.29±3.13b |
| GP + 50% HFCS | -17.67±0.01a | -4.82±0.02a | 0.25±0.02b | 96.94±1.27b |
| MP | -19.53±0.13c | -6.47±0.01c | -1.63±0.21a | 86.64±2.15a |
| MP + 10% HFCS | -18.04±0.18b | -5.35±0.10b | -0.82±0.09b | 96.04±2.52bc |
| MP + 30% HFCS | -18.02±0.11b | -5.33±0.11b | -0.65±0.20b | 95.01±0.54b |
| MP + 50% HFCS | -17.30±0.01a | -4.40±0.07a | 0.85±0.28c | 101.05±3.78c |

[a-d] Means ± standard deviation in the same column, values in a column with the different letters are significantly different (*P*<0.05). GP, Grape pekmez, MP, Mulberry pekmez, HFCS, High fructose Corn Syrup.

**CONCLUSIONS**

As a result of the analysis carried out using HFCS at different levels, it was determined that there were significant decreases in ash and electrical conductivity values. Thus, these two criteria have potential to be taken into account in the determination of adulteration in pekmez samples. The addition of HFCS provided significant changes in the thermal properties of the particularly diluted pekmez samples compared to the non-adulterated pekmez samples. The $T_o$, $T_p$ and $T_e$ values of the melting peaks were increased significantly depending on the amount of HFCS, and $T_e$ values changed from negative to positive values in samples containing 50% HFCS. This parameter could also be taken into account in determining whether pekmez samples are adulterated or not. Based on these differences, it is possible to state that DSC can be used to determine adulteration in pekmez samples.

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**CONFLICTS OF INTEREST**
The author declare that there is no conflict of interest.

**REFERENCES**
Ahmed, J., Ramaswamy, H.S., Khan, A.R. (2005). Effect of water activity on glass transitions of date pastes. *Journal of Food Engineering*, 66: 253–258. https://doi.org/10.1016/j.jfoodeng.2004.03.015

Al-Farsi, K.A., Al-Habsi, N.A., Rahman, M.S. (2018). State diagram of crystallized date-syrup: Freezing curve, glass transition, crystals-melting and maximal-freeze-concentration condition. *Thermochimica Acta*, 666: 166–173. https://doi.org/10.1016/j.tca.2018.06.003

Anonymous (2011). TS 12001 Dut Pekmezi Standardı, TSE, Ankara.

Anonymous (2017). Türk Gıda Kodeksi Üzüm Pekmezi Tebliği (No:2017/8). Tarım ve Orman Bakanlığı. 30 Haziran 2017 tarih ve 30110 sayılı Resmi Gazete, Ankara.

AOAC (2000). Official Methods of Analysis AOAC INTERNATIONAL, 17th Edition, Washington DC, USA.

El Darra, N., Rajha, H.N., Saleh, F., Al-Oweni, R., Maroun, R.G., Louka, N. (2017). Food fraud detection in commercial pomegranate molasses syrups by UV-VIS spectroscopy, ATR-FTIR spectroscopy and HPLC methods. *Food Control*, 78: 132-137. https://doi.org/10.1016/j.foodcont.2017.02.043

Erbil, D. (2020). Endüstriyel ve geleneksel yöntemlerle üretilmiş farklı pekmez çeşitlerinin bazı fizikokimyasal ve kalite özelliklerinin belirlenmesi. İstanbul Teknik Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı Yüksek Lisans Tezi, İstanbul, Türkiye, 115 s.

Fellows, P.J. (2000). *Food processing technology principles and practice*. 2nd Edition, Woodhead Publishing Ltd, Cambridge, England, 575 p.

Guizani, N., Al-Saidi, G.S., Rahman, M.S., Bornaz, S., Al-Alawi, A.A. (2010). State diagram of dates: Glass transition, freezing curve and maximal-freeze-concentration condition. *Journal of Food Engineering*, 99: 92–97. https://doi.org/10.1016/j.jfoodeng.2010.02.003

Karababa, E., Isikli, N.D. (2005). Pekmez: A traditional concentrated fruit product. *Food Review International*, 21: 357-366. https://doi.org/10.1080/87559120500222714

Karataş, N., Şengül, M. (2018). Effect of storage on some chemical and physical properties, antioxidant activity of mulberry pekmez. *Turkish Journal of Agricultural and Natural Sciences*, 5: 34-43. https://dergipark.org.tr/en/pub/turkjans/issue/34475/381429

Kaya, C., Akaydın, M.D., Esin, Y. (2012). Chemical properties of some commercial liquid and solid grape pekmez products. *Academic Food Journal*, 10: 32-39. https://dergipark.org.tr/en/download/article-file/1189202

Le Meste, M., Champion, D., Roudaut, G., Blond, G., Simatos, D. (2002). Glass transition and food technology: A critical appraisal. *Journal of Food Science*, 67: 2444-2458. https://ift.onlinelibrary.wiley.com/doi/epdf/10.1111/j.1365-2621.2002.tb08758.x

Lee, J.H., Choi, K.H., Kim, S.H., Park, K.S., Park, S.H., Kim, J.S., Jang, K.H. (2013). Physicochemical characteristics and electric conductivity of various fruit wines. *International Food Research Journal*, 20: 2987-2993. http://www.ifrj.upm.edu.my/20%20(06)%202013/2%20IFRJ%2020%20(06)%202013%20Jang%20331.pdf

Luyet, B., Rasmussen, D. (1968). Study by differential thermal analysis of the temperatures of instability of rapidly cooled solutions of glycerol, ethylene glycol, sucrose and glucose.

*Biodynamica*, 10: 167-191. https://pubmed.ncbi.nlm.nih.gov/5725455/

Özesmer, B. (2021). Geleneksel ve endüstriyel yöntemlerle üretilen bazı üzüm pekmezlerinin fizikokimyasal ve duyusal özelliklerinin karşılaştırılması. Kahramanmaraş Sütçü İmam Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı Yüksek Lisans Tezi, Kahramanmaraş, Türkiye, 65 s

Rasmussen, D., Luyet B. (1969). Complementary study of some non-equilibrium phase transitions in frozen solutions of glycerol, ethylene glycol, sucrose and glucose. *Biodynamica*, 10: 319-331.

Roos, Y.H. (2010). Glass transition temperature and its relevance in food processing. *Annual Review of Food Science and Technology*, 1: 469-496. https://www.annualreviews.org/doi/pdf/10.1146/annurev.food.102308.124139

Roos, Y.R., Karel, M. (1991a). Amorphous state and delayed ice formation in sucrose solutions. *International Journal of Food Science and Technology*, 26: 553-566. https://doi.org/10.1111/j.1365-2621.1991.tb02001.x

Roos, Y.R., Karel, M. (1991b). Water and molecular weight effects on glass transitions in amorphous carbohydrates and carbohydrate solutions. *Journal of Food Science*, 56: 1676-1681. https://doi.org/10.1111/j.1365-2621.1991.tb08669.x

Sadeghi, M., Mehryar, E., Razavi, J., Mireei, S.A. (2016). Moisture sorption isotherm and glass transition temperature of date powder in terms of various model systems. *Journal of Food Process Engineering*, 39: 61-68. https://onlinelibrary.wiley.com/doi/epdf/10.1111/jfpe.12199

Singh, K.J, Roos, Y.H. (2005). Frozen state transitions of sucrose-protein-cornstarch mixtures. *Journal of Food Science*, 70: 198–204. https://ift.onlinelibrary.wiley.com/doi/epdf/10.1111/j.1365-2621.2005.tb07136.x

Singh, K.J., Roos, Y.H. (2010). Physical state study of (sugar mixture)-polymer model systems. *International Journal of Food Properties*, 13: 184–197. https://doi.org/10.1080/10942910802259184

Şimşek, A., Artık, N. (2002). Studies of compositions of concentrates from different fruit. *Gıda*, 27: 459-467. https://dergipark.org.tr/tr/pub/gida/issue/6961/92812

Tosun, M. (2014). Detection of adulteration in mulberry pekmez samples added various sugar syrups with 13C/12C isotope ratio analysis method. *Food Chemistry*, 165: 555-559. https://doi.org/10.1016/j.foodchem.2014.05.136.

Tosun, M., Keleş, F. (2012). Testing methods for mulberry pekmez adulterated with different sugar syrups. *Academic Food Journal*, 10: 17-23. https://dergipark.org.tr/en/download/article-file/1189287

Yaman, N. (2019). Dut, keçiboynuzu ve üzüm pekmezlerine glukoz şurubu katılarak yapılan tağşişin fourier dönüşümlü kizilötesi (FTIR) spektroskopisi ile tespiti. Tekirdağ Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı Yüksek Lisans Tezi, Tekirdağ, Türkiye, 75 s.

Yılmaz, M. (2012). Pekmez ve pekmeze benzer gıdalarda taklit, tağşiş ve coğrafi köken tayini araştırması. Yıldız Teknik Üniversitesi Fen Bilimleri Enstitüsü Kimya Anabilim Dalı Kısaltılmış Doktora Tezi. İstanbul Sanayi Odası, İstanbul, Türkiye. 63 s.

Yılmaz, M., Afsar, H. (2012). An approach to determination of geographical origin and authenticity of grape and some grape products using SNIF NMR. *Journal of Engineering and Natural Sciences Sigma,* 30: 102–112. https://sigma.yildiz.edu.tr/storage/upload/pdfs/1636107910-tr.pdf