Current Extraction and Instrumental Characterization Processes in Vegetable Oil Technology

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Abstract

Food analysis methods are carried out in two ways: classical methods and instrumental methods. While general analyzes can be made in which more dominant components can be determined in terms of quantity in classical methods, it is possible to perform detailed analyzes in which more specific components can be determined precisely in instrumental analyzes. This distinction also comes to the fore in oil technology, and comprehensive analyzes can be made to obtain important data in terms of oil technology with various devices used. These devices are based on transmitting signals to detectors by utilizing the properties of food components such as beam absorption, beam refraction, beam rotation, electric potential, mass/charge ratio by spectroscopic, chromatographic, thermochemical and electrochemical methods, and then presenting data by passing through the signal processor. In this review, information about instrumental analysis techniques, which are frequently used in oil technology, is given under the headings of extraction techniques, spectroscopic techniques and chromatographic techniques. Today, as a result of the developments in all these techniques, the rate of preference in oil technology is increasing due to advantages such as obtaining fast results, using less samples and solvents, and obtaining reliable results.

Keywords: Oil, extraction, spectroscopy, chromatography, characterization, food

Bitkisel yağ Teknolojisinde Güncel Ekstraksiyon ve Enstrümental Karakterizasyon Yöntemleri

Öz

Gıda analiz yöntemleri klasik yöntemler ve enstrümental yöntemler olmak üzere iki şekilde gerçekleştirilmektedir. Klasik yöntemlerde miktar olarak daha baskın bileşenlerin belirlenebildiği genel analizler yapılabilirken, enstrümental analizlerde daha spesifik bileşenlerin hassas bir şekilde tespit edilebildiği ayrıntılı analizlerin yapılabilmesi mümkün olmaktadır. Yağ teknolojisinde de bu ayrım oldukça ön plana çıkmakta ve kullanılan çeşitli cihazlarla yağ teknolojisi açısından önemli veriler elde edilebilecek kapsamlı analizler yapılabilmektedir. Bu cihazlar, spektroskopik, kromatografik, termokimyasal ve elektrokimyasal yöntemlerle

gıda bileşenlerinin ışın absorpsiyonu, ışın kırılması, ışın rotasyonu, elektrik potansiyeli, kütle/ yük oranı gibi özelliklerinden yararlanarak sinyallerin dedektörlere iletilmesi ve daha sonrasında sinyal işlemcisinden geçerek veri sunmasına dayanmaktadır. Bu derlemede yağ teknolojisinde sıklıkla yararlanılan ekstraksiyon teknikleri, spektroskopik teknikler ve kromatografik teknikler başlıkları altında bilgiler verilmektedir. Günümüzde tüm bu tekniklerdeki gelişmeler sonucunda, hızlı sonuç alma, daha az numune ve çözücü kullanımı, güvenilir sonuçlar elde etme gibi avantajlar dolayısıyla yağ teknolojisinde tercih edilme oranları giderek artmaktadır.

Anahtar Kelimeler: Yağ, ekstraksiyon, spektroskopi, kromatografi, karakterizasyon, gıda.

1. Introduction

In the analysis of foods, instrumental analyzes are carried out with various methods such as spectroscopic, electrochemical, chromatographic and thermal analysis methods by using analytical devices. When evaluated in terms of oil technology, the extraction process is at its core. In the realization of this process, many techniques have been used from the past to the present and studies are still continuing to develop these techniques. In the analyzes made with the developments, many advantages can be achieved. Some of these advantages are that the analysis time is significantly reduced compared to the analysis made with classical methods, the amount of solvent to be used is significantly reduced and this reduction has a positive effect on the environment.

Instrumental analyzes come to the fore in processes such as determining the physicochemical properties of the oils obtained after the extraction process or detecting adulteration in many oils produced by various techniquesThe instrumental techniques used in oil technology, together with the selection of the most appropriate method according to certain criteria, enable fast, reliable and sensitive analyzes in terms of quality and quantity.

In this review, it is aimed to define the instrumental analyzes carried out in the field of oil technology by grouping them within the framework of certain techniques, to reveal their advantages and disadvantages, to highlight the advantages they provide and to indicate which properties of the samples can be useful in determining.
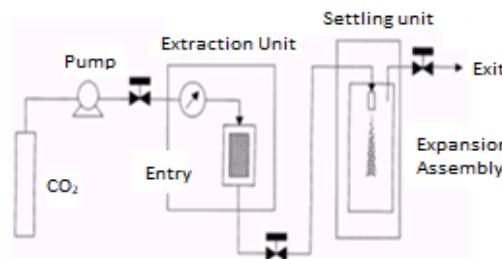
2. Extraction Techniques

Extraction is an inevitable step for research in oil technology [1]. In recent years, with the use of advanced extraction techniques, advantages such as significant reduction in extraction time, amount of organic solvent to be used, environmental pollution and sample preparation cost have emerged [1].

2.1. Supercritical Fluid Extraction

Hannay and Hogarth first stated in 1879 that a solid dissolves in a gas at high pressure and this solid precipitates when the pressure is reduced [2]. Later, Eduard Buchner, as a result of a long-term study, was awarded the Nobel Prize in biochemistry in 1907 by measuring the solubility of naphthalene in Supercritical-Carbon Dioxide (SC-CO2) [2].

The schematic representation of the supercritical fluid extraction (SAE) technique is as in Figure 1. Substances such as carbon dioxide, ethane, ethylene, trifluoromethane, chlorine trifluoride methane, nitrous oxide, ammonia propane, propylene, and hexane can be used as supercritical fluids [3]. The liquid to be used is brought to the appropriate pressure level by means of a fluid pump [4]. It is then sent to the heater where it is heated to the appropriate temperature [4]. In this way, the fluid is sent to the extractor at constant temperature as supercritical [4]. Dissolution occurs by contacting the substance in the extractor and this mixture is sent to the separator [4]. The pressure is reduced in the separator and thus the fluid is separated from the product by losing its dissolving force, and its temperature is lowered in the cooler for recycling and it is fed back to the system. [4]. The product or products obtained are taken from the bottom of the separator [4].

Figure 1. Supercritical fluid extraction system [5].

Several studies have shown that SAE is faster and more efficient than hours-long soxhlet extraction [6]. Ye CL, Lai YF used the supercritical CO2 extraction technique to obtain essential oil from onions; They reported that it is possible to obtain essential oil in high yield with this method by optimizing pressure, temperature and extraction time. Similarly, it has been reported that by optimizing the subcritical extraction process parameters, essential oil is obtained with 90% efficiency in the essential oil extraction from turmeric [8].

In a study, it was determined that the oil extracted from wheat germ with SC-CO2 has a high tocopherol content and that the phospholipid content of this oil is very low, showing that the SC-CO2 extraction method can eliminate the degumming step from oil refining processes [9].

In green coffee oil [10] and in crude palm oil [11] SAE method has been suggested as a preferred purification method in order to obtain an extract rich in the desired components [6].

Pumpkin (Cucurbita maxima) seed oil was extracted using SC-CO2 and the physicochemical properties of the oil showed that this oil could be used as a food oil supplement [12].

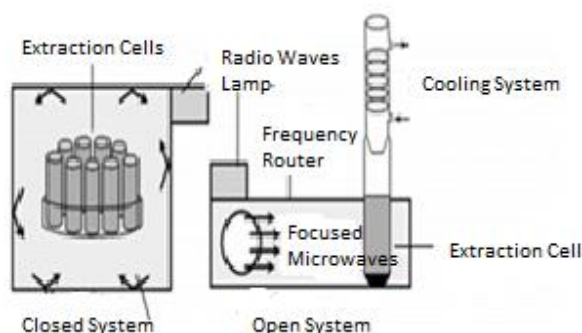## 2.2. Microwave Assisted Solvent Extraction

Microwave assisted extraction (MDE) is a process that separates solutes from a solid matrix with a solvent. The properties of heat and mass transfer are extremely important. Accurate and controlled heat is possible in microwave assisted applications [13]. Therefore, microwave technique can be exploited to obtain compounds of interest in the substrate with a certain strength of electromagnetic energy [13]. The use of this technique results in higher quality products compared to other extraction techniques, with a reduction in production costs due to energy savings and short processing times, and an improvement in product homogeneity and yield [13].

The main advantage of MDE is the ability to rapidly heat the sample and solvent mixture. A typical extraction process takes 15–30 minutes and takes place using 10–30 ml of solvent. This amount is approximately 10 times less than conventional extraction techniques [14]. In addition, the yield is increased as it allows several samples to be extracted at the same time. [14].
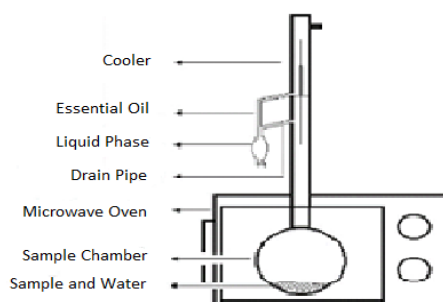
Figure 2. Microwave assisted extraction system [15].

MDE system is of two kinds [6]. One of them is the closed vessel system in which all of the extraction cells are irradiated at the same time, while the other is the open vessel system where the extraction cells are irradiated separately [6]. If we compare these two systems, the temperature can be increased by applying pressure in the closed vessel system and the closed vessel system is more suitable for essential oil extraction [6]. However, when evaluated in terms of time, the extraction time is a little longer since the temperature must be waited for the container to be opened in the closed container system [6].

Figure 3. Closed and open system in MDE [16].

Djemaa-Landri K. Vd. The phenolic contents and antioxidant activities of Vitis vinifera L. leaf extracts were determined by conventional solvent extraction and microwave assisted extraction. The results showed that the samples were rich in phenolic compounds in both techniques applied, but the MDE technique had the highest phenolic content and antioxidant activity with a shorter time and lower solvent consumption.

In another study, physical and chemical changes, fatty acid profile, trans fatty acid content and volatile compounds of oils obtained from avocado pulp were defined by different extraction methods. It was stated that the highest extraction efficiency was achieved in the combined microwave technique [18].

2.3. Ultrasound Assisted Extraction

Ultrasonic sound waves are sound waves with frequencies of 20 kHz and above, above the hearing limit of the human ear [19]. While the generator is responsible for the generation of energy from the systems that play a role in the formation of ultrasonic waves, the transducer provides the conversion of this energy into ultrasonic sound energy [19].

Ultrasound is divided into three groups: high-intensity and low-frequency (20–100 kHz), medium-intensity and intermediate frequency (100 kHz-1 MHz), low-intensity and high-frequency (1-10 MHz). [20], [21].
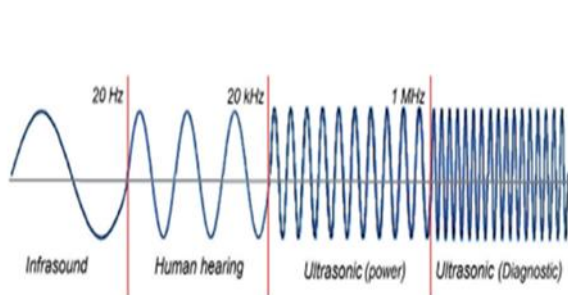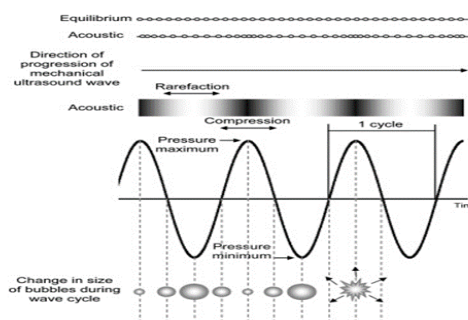

Figure 4 Sound spectrum [22]

Figure 5. Ultrasonic Cavitation [23]

Cavitation caused by the propagation of ultrasound waves in a liquid medium; bubble formation develops in the form of bubble growth and bursting, and as a result of the effect of hydrostatic pressure to strengthen the mass transfer, the efficiency and efficiency of the extraction increase with the realization of more solvent transfer [15]. Molecules in liquids combine under the influence of attractive forces [19]. With the propagation of ultrasound waves, the structural molecules are displaced longitudinally and pressure is created, and the molecules in the liquid substances are separated from the point where they are located under the influence of the pressure and combine with the surrounding molecules [19].

This technique shortens the extraction time and reduces the use of organic solvents, so it is energy and cost efficient [24]. At the same time, it is fast, highly efficient and one of its most important features is that it can be carried out at low temperatures, preventing heat-sensitive samples from being damaged and protecting the properties of bioactive compounds [24]. All these features make it a preferred method for oil technology [24].

Luque-García JL et al. extracted oil from sunflower, soybean and rapeseed seeds using a combination of traditional soxhlet technique and ultrasound. They reported that the extraction took place faster when combined with ultrasound and there was no change in the fatty acid composition.
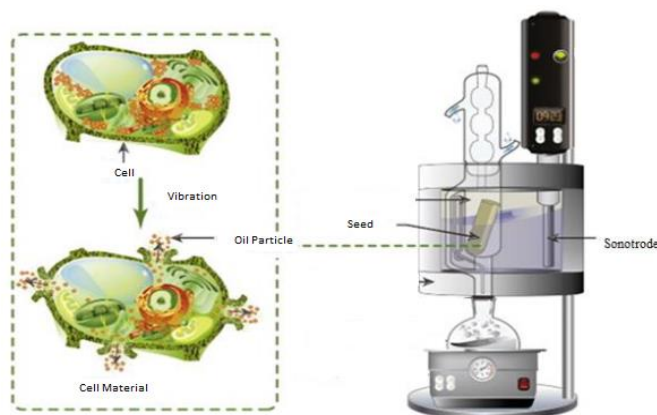

Figure 6. A laboratory-scale ultrasound-assisted extraction for extracting seed oils using the Sokshlet apparatus [26].

In a study, phenolic substance was extracted from the green shell of the walnut by two methods and the total phenolic substance and antioxidant activity kinetics of the obtained extracts were compared [27]. Ultrasonic bath, which is the indirect method, was used in the first extraction method, and ultrasonic probe, which was the direct method, was used in the other [27]. As a result, it has been observed that the use of ultrasonic probes is more effective and the extraction time is greatly reduced. At the same time, the results of this study show that walnut green shell, which is an agricultural waste, can be used as a valuable source for natural antioxidants and phenolic substances [27].

3.Spectroscopic Techniques

Spectroscopic analysis is a technique that utilizes the interaction of electromagnetic radiation with atoms and molecules to provide qualitative and quantitative chemical and physical information contained in the wavelength or frequency spectrum of absorbed or emitted energy [28]. Spectroscopy is examined in two groups as atomic spectroscopy and molecular spectroscopy [29]. These techniques are used in oil technology, especially in the determination of toxic components and adulteration. Generally used spectroscopy techniques; These include inductively coupled plasma, Fourier transform infrared spectrometry and raman spectroscopy.

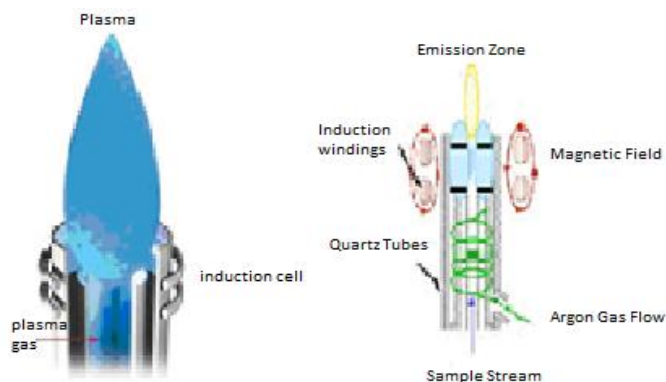### 3.1. Inductively Coupled Plasma

Inductively coupled plasma operating at high temperature at atmospheric pressure was first described and used by Reed (1961). Later, Greenfield et al. (1964) and Wendt and Fassel (1965) followed suit. These studies are used as the basis of the ICP technique today [30].

Plasma is a medium that consists of cations and electrons and enables the conduction of electric current. Since the sum of the negative charges and positive charges in the plasma is equal, its charge is zero. Although the most commonly used plasma type is ICP, the four types of plasma used today are as follows;

1. Plasmas created by direct current (DCP)
2. Microwave-powered plasmas (MIP)
3. Capacitive-coupled microwave plasmas (CMP)
4. Inductively coupled high frequency plasmas (ICP)

In the ICP technique, argon gas is used because of its easily ionizable and inert properties in the formation of plasma. There are three nested torches in the ICP. Argon gas passes between these torches and there is a radio induction coil at the top of the torch. For example, its solution is pumped into the plasma with argon gas through a cylindrical quartz tube as in figure 7 [31].

Various numbers of induction windings are wound on the end of the outer cylinder and these are connected to the radio frequency generator [32]. Argon is ionized by a spark from the tesla coil [32]. These ions interact with the magnetic field windings and begin to flow in the same direction. With the resistance shown to this flow, the ambient temperature reaches a temperature of around 6000-10000ºK. Similar to the transfer of energy from the primary winding to the secondary winding in electrical transformers, the plasma also absorbs energy from the magnetic field [33].

Figure 7. ICP technique [34].

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used in a study to determine toxic metals in unflavored and flavored (mushroom flavor, vegetable flavor and pepper flavor) olive oil samples from Iran and Italy. As a result of this study, a positive correlation was recorded between storage time and heavy metal contents, although it is especially high in Iranian brands. The results of the research show that all the heavy metal contents obtained in the pepper flavored olive oil samples are significantly lower than the other samples. Considering the mushroom-flavored samples, Pb and Cd levels were significantly higher and above the maximum allowable level [35].

In a study on heavy metal determination in aromatic spices by inductively coupled plasma mass spectroscopy (ICP-MS) technique, ICP-MS working conditions; RF power 1500W; plasma gas flow rate 15 L min-1; auxiliary gas flow rate 0.9 L min-1; carrier gas flow rate 1.1 L min-1 ; helium collision gas flow rate 4 mL min-1; spray chamber temperature 2°C; sample depth 9 mm; sample inlet flow rate was determined as 1 mL min-1. As a result, it has been shown that the maximum levels determined by the European directive 88/388/EEC and international organizations are not exceeded in all spice samples. It was also stated that the consumption of spices such as cinnamon, Indian turmeric and ginger from Indonesia and Madagascar does not pose a threat to the health of an adult consumer, but regular consumption of spices such as cinnamon and Japanese ginger from Vietnam may pose a risk to human health [36].

## 3.2. Fourier Transform Infrared Spectrometer

The infrared spectrum gives the fingerprint of the sample with the absorption peaks that indicate the frequencies created by the vibrations of the bonds between the atoms of the substances [37]. Except for optical isomers, each substance has a unique spectrum. Some of these spectra are more detailed and the region where this part is is the fingerprint region where the spectrum is obtained by expanding it twice. Thus, we can have detailed information about the substance [31]. In addition, the fats in the food also establish a relationship between the absorption bands characteristic of the infrared spectrum and the food components [38].

Fourier transform infrared spectrometry (FTIR) is a technique in which the number of waves is determined according to the infrared intensity of light. The infrared region in the electromagnetic light array consists of three regions. These regions are as follows:

1. Near-wavelength infrared (NIR)
2. Medium wavelength infrared (MIR)
3. Far-wavelength infrared (FIR) [32], [39]

FTIR spectroscopy is a measurable control method that has been used to date to authenticate and detect adulteration in many foods [40], [41]. It provides us with information about the biomolecules that make up cells [42].

In order to determine the adulteration in oils with the FTIR technique, the sample oils are generally mixed in certain proportions to observe the differences in their spectra [43]. An exemplary FTIR spectrum and fingerprint region of Sunflower oil mixed with pure olive oil in certain proportions are given in Figure 8.
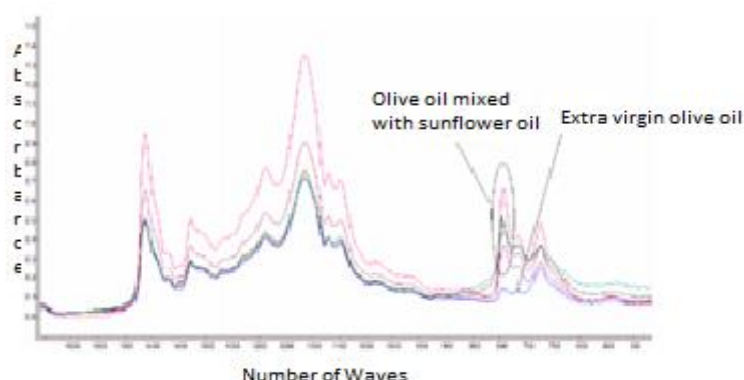
Figure 8. An exemplary FTIR spectrum and fingerprint region of sunflower oil mixed with pure olive oil in certain proportions [44].

The most important advantages of the FTIR technique are the reliability of the analysis results and the ease of calibration [45]. In addition, the fact that it gives fast results with a small sample makes the use of this technique widespread [46].
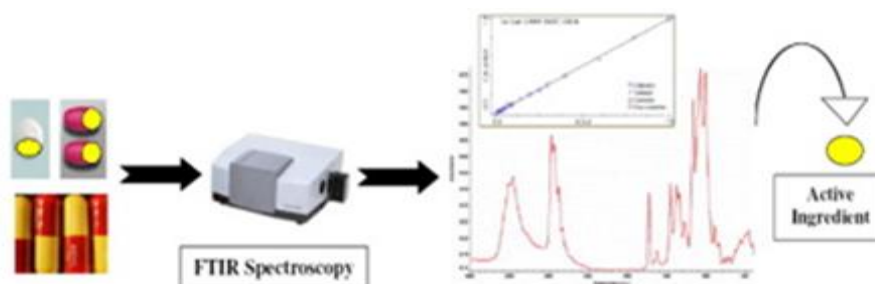
Figure 9. FTIR spectroscopy [47].

Pan M. et al. showed that the SIMCA model based on ATR-FTIR spectra using FTIR spectrometry in extra virgin olive oil mixed with different vegetable oils can detect olive oils mixed with 5% to 10% canola oil, peanut oil, corn oil, soybean oil or sunflower oil. .

In a study conducted by Özülkü G. et al., it was concluded that the FTIR technique can be used as a non-destructive, fast, effective and less time-consuming method from sesame oil in which sesame oil is mixed with different oils such as pure hazelnut, canola and sunflower.

3.3. Raman spectroscopy

Raman spectroscopy was introduced in 1928 by C.V. It was discovered by Raman [50]. Raman spectroscopy is one of four vibrational spectroscopy techniques (near infrared (NIR), mid infrared (MIR), raman spectroscopy and hyperspectral imaging (HSI)) [51]. This technique can provide specific information in the identification of components such as lipids, proteins and carbohydrates and is sensitive to minor components of microorganisms that cause food spoilage [52]. These vibrational spectroscopies are as in Figure 10.
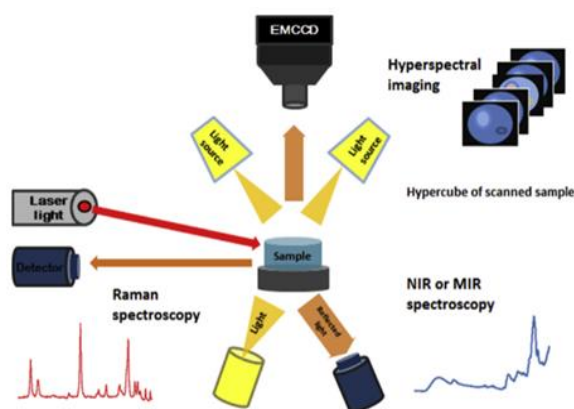

Figure 10. Schematic representation of vibrational spectroscopy techniques [51].

Although both IR and Raman spectroscopy are vibrational spectroscopy, unlike IR absorption, Raman spectroscopy relies on the exchange of light photon energy with a molecule [53]. The Raman effect occurs when the light charge on the molecule interacts with the electron cloud of bonds in the molecule and the photon charge brings the electron to a virtual state [53]. Raman scattering occurs when a molecule is excited from a ground state to a virtual energy state and then relaxes into an excited vibrational state [53].

Interest in Raman spectroscopy has increased as it is a versatile and rapid technique for the analysis of biological samples [54]. As with FTIR, Raman spectroscopy is a non-destructive technique that can be used in food analysis because it requires little pretreatment of samples and simultaneously provides information about different food compounds [54]. Compared to FTIR, it can be performed with less samples, is less costly and portable [54].

Raman and infrared spectroscopies are complementary techniques for food and foodstuff analysis [55]. The main advantages of Raman spectroscopy over NIR and MIR spectroscopy are as follows:

1. No or minimal restriction effect of water
2. Ability to analyze aqueous solutions with no obstruction or minimal effect of water
3. Easier analysis of inorganic substances
4. The ability to analyze samples with glass or polymer packaging [55].

Raman spectroscopy also has some disadvantages [55]. These are as follows:

1. The sample itself or fluorescence of impurities can obscure the Raman spectrum.
2. Due to the intense laser beams increasing the temperature of the sample, the sample may be destroyed or obscure the Raman spectrum [55].

In terms of oil technology, Raman spectroscopy, which is based on the principle of detecting variations in the distribution of unsaturated fatty acids in the content of olive oil and low quality edible oils added to olive oil, can be used to determine especially the adulteration of olive oil [56].

Purity determination in cold press oils using Raman spectroscopy; Almond, black cumin and walnut oils were used as material and adulteration was carried out by deliberately adding 25% and 50% sunflower and corn oil to these oils. The verification of this separation study, which was basically carried out as a result of the differentiation of fatty acids in the structure of oils, affecting Raman signals, was made by gas chromatography. When the findings are examined, it has been revealed that it can be used successfully in the rapid detection of

possible adulteration in cold pressed oils and can replace chromatographic analysis, which is a routine analysis method [57].

For example, the score plot used in the determination of adulterated cold pressed almond oil in this study is as in Figure 11.
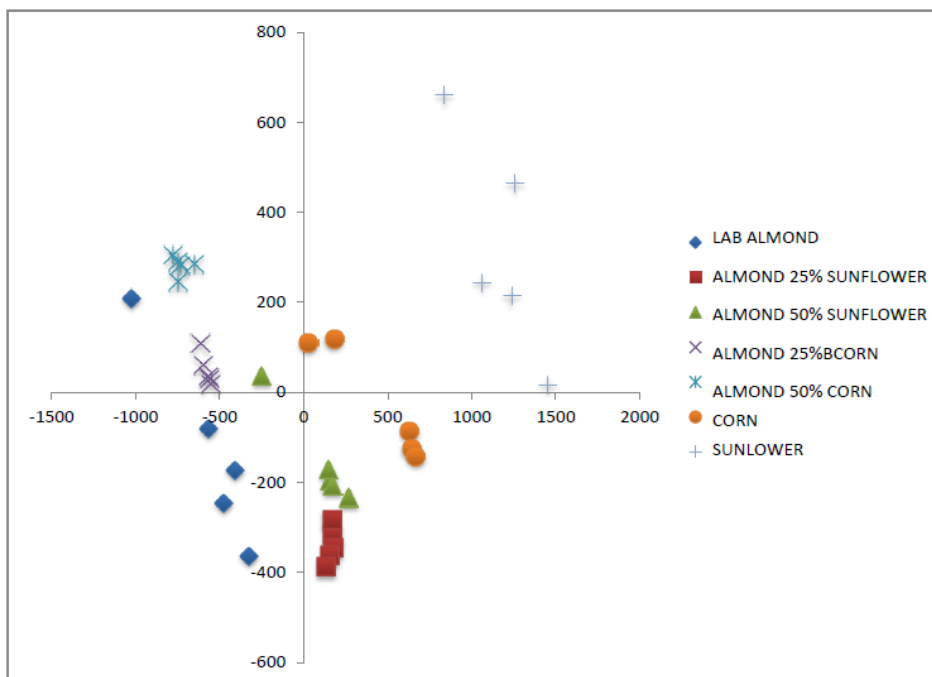

Figure 11. Score plot used to detect adulterated cold pressed almond oil [57].

López-Diez EC. et al. showed that hazelnut oil levels between 0% and 20% of virgin olive oils mixed with hazelnut oils could be successfully detected.

Zou MQ. et al. used a portable Raman spectroscope with intensity ratios of vibrational bands to distinguish between various grades of olive oil and seed oils. He stated that he could reliably distinguish genuine olive oil from other edible oils such as soybean oil, rapeseed oil, sunflower seed oil or corn oil containing 5% (volume percent) or more.

4. Chromatographic Techniques

Chromatography was first used by Mikhail Tswett in 1906 [59]. Chromatography is based on the principle that the components of a mixture added to a solvent medium are dissolved and separated depending on their physical and chemical properties [32]. In oil technology, chromatographic techniques such as high performance liquid chromatography, gas chromatography and thin layer chromatography are widely used for fatty acid composition, phenolic compounds, preservatives and toxic metabolite analysis.

4.1. High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) and LC-MS/MS devices based on liquid chromatography are the most important and widely used devices in chromatography techniques, which are used in many different fields [59]. In HPLC, substances are determined according to the time to leave the column, while in LC-MS/MS, they are determined according to the time to leave the column and the mass/charge ratio [59]. HPLC is one of the most powerful analytical chemistry tools, capable of separating, identifying and quantifying compounds present in any sample that can be dissolved in a liquid [60].

The principle of HPLC is that the sample solution is injected into a column of porous material (stationary phase) and the liquid phase (mobile phase) is pumped through the column at higher pressure [61] The separation principle followed is the adsorption of the solute on the stationary phase due to its affinity for the stationary phase [61]]. Separation by HPLC is heavily dependent on some parameters of the mobile phase such as polarity, flow rate, pH, composition, some inherent properties of the sample matrix and stationary phase, and environmental factors such as temperature, detector type and settings [62]. The HPLC technique, schematized in Figure 12, has the following features [61]:

1. High resolution
2. Small diameter, Stainless steel, Glass column

3. Fast analysis
4. Relatively higher mobile phase pressure
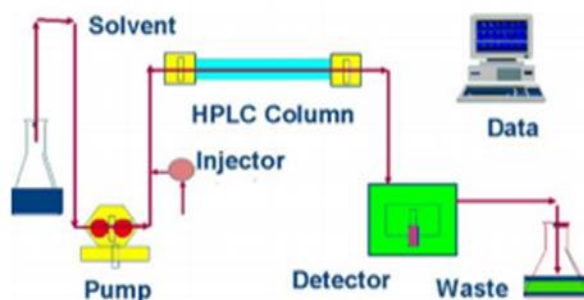5. Controlled flow rate of the mobile phase

Figure 12. Flow chart of HPLC [61].

In the HPLC device, the process begins with the dissolution of the sample to be analyzed in a suitable solvent. The components are then separated in the column, which we refer to as the stationary phase. The dissolved mixture is injected into the column and pressure is applied to move the mixture and mobile phase. Under the influence of this pressure, each component moves at a different speed and leaves the system at a different time. After the separation of the components is achieved, a suitable detector is used for quantification and the chromatograms obtained from this detector are interpreted in computer programs [59].

(63), In the determination of γ tocopherol amounts in dry and fresh walnuts in the Adilcevaz region in the Van Lake area, using the HPLC device, the amount of γ tocopherol was found to be higher than in other regions. He also stated that this technique is one of the techniques successfully applied in tocopherol analysis and that the separation of mixtures, the determination of components and their amounts can be done sensitively and in a short time, and it provides better results than colorimetric and other electrochemical techniques.

(64) They determined the phenolic acid compositions (gallic, protocatechin, p-hydroxybenzoic, vanillic, caffeic, chlorogenic, syringic, p-coumaric, ferulic, Okuric, rosmarinic and trans-cinnamic acids) of some plants collected from Kaz Mountains. Phenolic acid analyzes were performed by reverse phase HPLC in a gradient system, at a wavelength of 280 nm, using propylparaben as an internal standard. As a result, they observed that two species of these plants were quite rich in phenolic acids and they determined that rosmarinic acid was higher than other phenolic acids in terms of both the frequency and amount of presence.

4.2. Gas Chromatography

Gas chromatography (GC) is a unique and versatile technique. In the early stages of development, very volatile components were used in the analysis of gases and vapors. The mixtures to be analyzed and separated by GC may in some cases be gases, liquids or solids [65]. GC requires the analyte to have a significant vapor pressure between 30°C and 300°C [66].

This technique includes column selection (fixed phase and dimensions: column identity, length and film thickness), carrier gas selection (Nitrogen, Helium, flow rate), temperature programming (Initial temperature, initial hold, ramp rate, final temperature and final hold), injector temperature and detector temperature) and the flow diagram of this technique is schematized in Figure 13 [67].
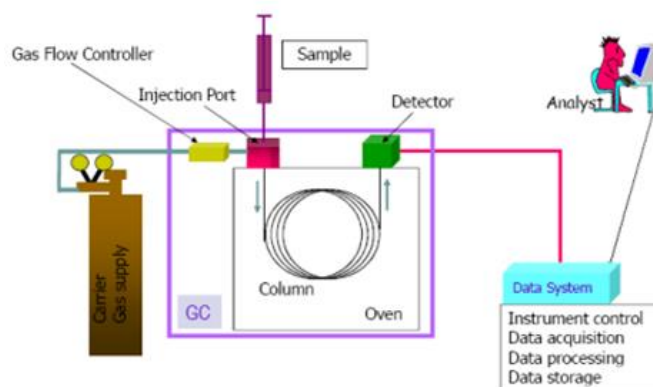

Figure 13. Flow chart of GC [67].

GC systems include an injector, a carrier gas, a column (stationary phase), a heater, a detector, and a recorder or information processor [68]. As carrier gas or mobile phase of GC, gases such as hydrogen, helium and nitrogen are widely used as carrier gas. Considerations such as inertness, oxygen independence, safety, cost and availability should be considered in the selection of carrier gas [68].

Chen Y. et al. studied the optimization of selected parameters for the analysis of rosemary and thyme essential oils using GC and GC&MS techniques, and in this study, different terpene compositions of rosemary and thyme aroma fractions were investigated. The amount of aroma of the plants studied with the obtained optimum method was determined and the functional groups were examined. Obtained essential oil concentration ranges were determined as 0.04-6.6 μg/g for rosemary extracts and 0.04–0.5 μg/g for thyme extracts.

A. Bele and Khale A. analyzed the trans fatty acid profiles of palm oil and chicken fillets fried by gas chromatography technique. As a result of the analysis, good solubility for position and geometric (cis/trans) isomers was obtained for both oleic acid and linoleic acid. In general, minor changes in the formation of trans fatty acids and the composition of fatty acids were observed after 8 hours of frying at temperatures below 200 °C. However, thermal degradation and formation of trans fatty acids in frying oil increased in direct proportion to frying temperature and time. This method has been proven to be precise, accurate and precise. The gas chromatography technique has been proven to be precise, accurate and sensitive in achieving all these results.

4.3. Thin-layer chromatography

Thin layer chromatography (TLC) is a chromatography technique used to separate mixtures. Chromatography was discovered by M. Tswett in 1906 [71]. Thin layer chromatography is recognized as an effective technique for low-cost analysis of samples as it requires minimal sample cleaning and allows reduction in sample preparation steps [72].

TLC is usually performed on a sheet of glass, plastic or aluminum foil coated with a thin layer of adsorbent material such as silica gel, aluminum oxide or cellulose [71]. This adsorbent layer is known as the stationary phase. After the sample is applied to the plate, a solvent or solvent mixture (known as the mobile phase) is prepared [71]. Separation is achieved because different analytes rise to the TLC plate at different rates [71]. The TLC technique can be schematized as in Figure 14 [73].
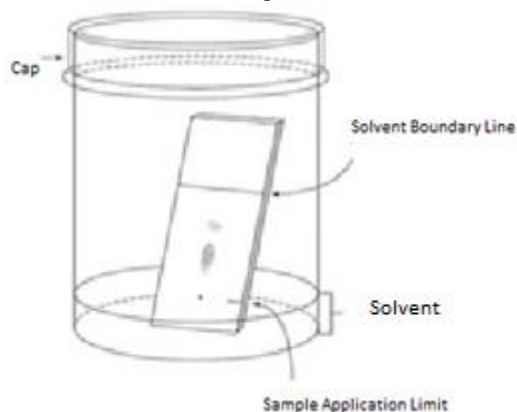
Figure 14 Thin Layer Chromatography Application [73].

The behavior of a single compound in TLC is characterized by a quantity known as R_f and is expressed as a decimal fraction [71]. R_f is calculated by dividing the distance the compound has traveled from its original location by the distance the solvent has traveled from its original location [71]. The R_f value is visually shown in Figure 15 [73].

Figure 15. Calculation of the Rf value on the plate [73].

Schwertner showed that quantitative determination of different fatty acids is possible using this method. Autoxidation products of cholesterol can be identified by TLC [74]. In a study, aflatoxin analysis was performed on figs produced in Aydın. As a result of the study, it was determined that the least common aflatoxin in the samples was Afla G2, the most common one was Afla B1, and it was determined that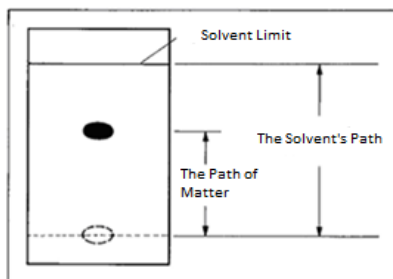 only 2 of 38 randomly selected samples did not contain aflatoxin [75]. In another study, phospholipids, monoglycerides, free fatty acids, cholesterol, 1,2-diglycerides, 1,3-diglycerides, triglycerides and cholesterol esters were determined in milk and egg yolk using thin layer chromatography [73].

5. Results and Discussion

In this study, various instrumental analyzes applied in oil technology were examined. Instrumental analysis using various techniques in oil technology is very important both in obtaining oil and in investigating certain properties of obtained oils or oil-containing samplesSignificant increases in extraction speed are observed by performing extraction with supercritical fluid instead of solvents used in the classical extraction process or by the contribution of various applications such as ultrasound and microwave to the classical extraction process. In addition, as a result of spectroscopic and chromatographic techniques, very low levels of adulteration in oils can be determined and the physicochemical properties of oils can be revealed. In order to carry out these analyzes, the advantages that will emerge with the development of the devices used or the development of new techniques will make significant contributions to the oil technology.

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Mermer Atıklarının Porselen Bünyede Kullanımının Değerlendirilmesi

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Özet

Son zamanlarda sanayi kuruluşlarının gelişmesi ve nüfusun artması ile paralel olarak endüstriyel atık maddelerde artış gözlenmektedir. Bu yüzden atıkların minimizasyonu ve alternatif hammadde olarak kullanılması zorunlu bir hal almıştır. Seramik ve porselen karo fabrikaları üretim miktarları olarak en yüksek hacme sahip endüstriyel faaliyet gösteren sektörler arasındadır. Seramik karo bileşiminde % 30-40 kil, % 10-15 kuvars, % 40-45 oranında feldspat vardır. Bu çalışmada, Bilecik Organize Sanayi Bölgesinde bir firmadan tedarik edilen mermer atıklarının porselen karo bünye içerisinde kullanımı ve porselen karo özelliklerine etkisi incelenmiştir. Porselen karo üretimde kullanılan standart bünye reçetelerindeki farklı hammaddelerin yerine farklı oranlarda mermer atığı ilavesi ile yeni reçeteler oluşturulup porselen karo numuneleri hazırlanmıştır. Hazırlanan numunelerin fiziksel ve mekanik testleri yapılmış, standart numune ile sonuçları kıyaslanmıştır. Yapılan çalışma sonucunda endüstriyel simbiyoz kapsamında mermer atıklarının porselen karo bünyesinde, istenen özellikleri bozmadan kullanılabileceği gibi alternatif bir hammadde olarak da değerlendirilebileceği anlaşılmıştır.

Anahtar Kelimeler: Porselen Karo, Seramik Karo, Mermer Atığı, Endüstriyel Simbiyoz

Evaluation of Usage of Marble Wastes in Porcelain Body

Abstract

Recently, there has been an increase in industrial waste materials in parallel with the development of industrial establishments and the increase in population. Therefore, the minimization of wastes and their use as alternative raw materials have become mandatory. Ceramic and porcelain tile factories are among the industrial sectors with the highest volume of production. There are 30-40% clay, 10-15% quartz, 40-45% feldspar in the composition of ceramic tiles. In this study, the use of marble wastes supplied from a company in Bilecik Organized Industrial Zone in the porcelain tile body and its effect on the porcelain tile properties were investigated. In place of the different raw materials in the standard body recipes used in porcelain tile production, new recipes were created by adding marble waste at different rates and porcelain tile samples were prepared. The physical and mechanical tests of the prepared samples were carried out and the results were compared with the standard sample. As a result of the study, it has been understood that within the scope of industrial symbiosis, marble wastes can be used within the body of porcelain tile without destroying the desired properties, or it can be evaluated as an alternative raw material.

Keywords: Porcelain Tile, Ceramic Tile, Marble Waste, Industrial Symbiosis

1. Giriş

Mermer, $CaCO_3$ (Kalker) ve $CaMg(CO_3)_2$ (Dolomit) bileşenlerine sahip kayaçların basınç ve ısı altında değişime uğrayıp, yeniden kristalleşmesinden sonra yeni bir yapı oluşturması ile meydana gelen kayaç türleridir [1]. Uygun boyutlarda blok verebilen, kesilip parlatılan veya yüzeyi işlenebilen ve taş özellikleri kaplama taşı normlarına uygun olan her türden taş örnek olarak kalker, traverten, kumtaşı gibi tortul; gnays, mermer, kuvarsit gibi metamorfik; granit, siyenit, serpantin, andezit, bazalt gibi magmatik taşlar da mermer olarak isimlendirilmektedir [2]. Mermer imalatı yapan fabrikalarda, mermerin çıkarılması ve işlenmesi aşamalarında üretimin %40-60'ını oluşturacak oranda parça ve toz halinde olmak üzere atıklar oluşmaktadır [3]. Bu atıklar, fabrika içerisinden toplanıp atık sahasında biriktirilmektedir. Mermer imalatlarının fazla olduğu alanlarda bu atıkların biriktirilmesi ile çevre ve ekonomik olumsuzluklar oluşmaktadır [4]. Günümüzde farklı sektörlerde değerlendirilen bu atık malzemeler, hali hazırda kullanılan malzemelerin yerine kullanıldıklarında ve üretilen ürünlerin özellikleri ile aynı sonuçlar alan işletmeler için önemli ekonomik fayda sağlayacaktır [5].

Literatürde çimento bileşimi [6-7], karoyolu inşaatı [8], jeoteknik mühendisliği uygulamaları[9] gibi farklı sektörlerde mermer atıklarının geri dönüşümü ile ilgili çalışmalar bulunmaktadır. Bu atıkların kullanım alanlarından biri de seramik sektörüdür. Seramik alanında, mermer atıkları %5-6 aralığında kullanılmaktadır. Seramik bünye ve sırlarında CaO olarak bünyeye alınan hammadde kaynakları genel olarak; kalsit, dolomit ve mermerdir. Bünyede bulunan CaO, sır içerisindeki SiO_2 ile tepkimeye girerek ara tabaka meydana getirir. Meydana gelen ara tabaka, gerilimleri önleyerek çatlaklardan kurtulmayı sağlar [10-11].

Porselen karolar, düşük su emme ve yüksek mukavemet, aşınma, donma ve kimyasal direnç gibi yüksek teknolojik özelliklere ve geliştirilmiş estetik görünüme sahip olan karolardır. [12-13]. Araştırmalarımıza göre mermer atıklarının porselen karo bünyelerde kullanımına ilişkin çalışma bulunmamaktadır. Yapılan bu çalışma ile mermer atıklarının porselen karo bileşiminde kullanımı değerlendirilecektir. Bu çalışmada, Bilecik Organize Sanayi Bölgesinden (OSB) tedarik edilen mermer atıklarının porselen bünye içerisinde kullanımı ve aynı zamanda porselen karo teknik özelliklerini bozmadan, ithal kil miktarının azaltılması amaçlanmıştır. Böylece hem atığın alternatif hammadde olarak kullanımı sağlanacak, hem de ithal kil kullanım miktarı azaltılacaktır.

2.   Materyal ve Metot

2.1. Mermer Atığı İlavesi

Bilecik OSB'den temin edilen mermer atığına 150ºC'de etüvde kurutma işlemi yapılmıştır. Kurutma işlemi yapılan mermer atıkları Ar-Ge merkezi laboratuvarında bulunan 1 kg'lık jet değirmenlerde 20 dk boyunca öğütme işlemine tabi tutulmuş olup, çamur elek bakiyesi %0,5 olarak belirlenmiştir. Daha sonra tekrar etüvde kurumaya bırakılmıştır. Atık tozun fiziksel ve kimyasal analizi yapılmıştır. Mermer atıklarının etkisini görebilmek için standart reçete içerisine farklı oranlarda mermer atığı ilavesi yapılmış olup, en uygununun %4 ve %5 oranlarda olduğu anlaşılmıştır. Karışım oranları Tablo 3'de gösterilmektedir.

2.2. Deney Numunelerinin Hazırlanması

İlk olarak mevcut porselen bünyesindeki kullanılan masse reçetesi, aynı oranlar ile hassas terazide tartım işlemi yapılarak jet değirmenlerde öğütülmüştür. Hazırlanan reçete 300 gr üzerinden tartılarak 20 dk boyunca öğütülmüştür. Öğütülen karışımlar etüvde 150 ºC'de kurutulmuştur. Kurutulan numuneler porselen seramik havan yardımı ile toz haline gelerek, %5 oranında nemlendirme işlemi yapılmıştır. Toz numuneler, laboratuvarda bulunan 55x110mm ölçülere sahip kalıpta preslenerek 1210ºC ve 57 dk' da endüstriyel pişirme fırınında(Sacmi Marka) pişirilmiştir. Pişme sonrası numunelerin pişme renkleri, mukavemetleri, su emmeleri, pişme küçülmeleri, spesifik yoğunlukları, eğilme dayanımı ve kırılma yükü analizleri yapılarak kıyaslama gerçekleştirilmiştir. Reçetelerde kullanılan hammadde kimyasal içerikleri Tablo 1'de gösterilmektedir.

Numunelerin viskozite, yoğunluk ve spesifik yoğunlukları standart ile kıyaslanmıştır (Tablo 4). Kıyaslama sonucunda ilave edilen mermer atıklarının viskozite değerlerinde önemli bir farklılık oluşturmazken, yoğunluk ve spesifik yoğunluk değerlerini ve pişme küçülmesinin düştüğü tespit edilmiştir. Bilecik OSB'den temin edilen mermer atıklarının Seramik Araştırma Merkezi'nde(Eskişehir Teknik Üniversitesi) yapılan analizlerin fiziksel analiz sonuçları Tablo 2'de gösterilmektedir.

Tablo 1. Reçetelerde kullanılan hammaddelerin kimyasal içerikleri (%)

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3	TiO_2	P_2O_5	A.Z.

Mermer Atığı	1,05	0,73	0,043	0,01	52,03	2,31	0,07	0,02	0,02	43,74
Yerli Kil-1	77,90	12,60	4,75	0,48	0,29	0,26	1,06	-	-	2,52
Yerli Kil-2	64,80	21,00	2,19	0,40	0,18	0,49	1,89	0,98	0,07	8,00
İthal Kil-1	62,10	23,80	1,95	0,71	0,40	0,46	0,98	1,36		8,05
Yerli Kaolen-1	79,80	12,10	0,57	-	0,20	0,16	0,81	0,36	0,10	5,59
Silis Kumu	91,90	4,63	0,27	0,82	0,21	0	0,49	-	-	1,64
Sodyum Feldspat	73,40	15,00	0,19	9,10	0,66	0,27	0,64	0,23	0,18	0,26

Tablo 2. Mermer Atığının Fiziksel Analiz Sonuçları

Fiziksel Analiz	*Sonuçlar*
Nem	% 1 max.
Beyazlık	% 95 min.
Sarılık	% 4 max.
Viskozite (sn)	700 max.
Tane Boyutu < 2 μ	%80 min.
>10 μ	%2 max.
>45 μ	-
Aşındırma (mg)	25 max

Tablo 3. Karışım oranları (%)

Hammadde/Reçete	**Standart**	**Deneme 1**	**Deneme 2**
Yerli Kil-1	4	4	4
İthal kil-1	17	17	17
Yerli Kil-2	17	17	17
Yerli Kaolen-1	11	11	11
Silis Kumu	9	9	9
Sodyum Feldspat	42	42	42
Mermer Atığı	-	5	4

Tablo 4 .Viskozite, Yoğunluk,, Spesifik yoğunluk ve Pişme Küçülme(%) Sonuçları

Reçete/Özellik	*Çamur*	*Çamur*	*Pişmiş*	*Pişme*
Standart	31	1660	2.41	7.96
Deneme 1	28	1647	2.25	7.45
Deneme 2	32	1658	2.26	7.49

Manyezitin yüksek termal kararlığı ve sinterlemeyi iyileştirici özelliği bilinmektedir [14]. Bu nedenle yoğunluk değerlerini ve sinterlemeyi iyileştirmek için manyezit ile birlikte mermer atıklarının bileşimi oluşturan hammaddeler ile farklı kombinasyonları incelenmiştir. Hazırlanan karışım oranları Tablo 5'de sunulmuştur. Atık ve manyezit bileşimde kullanılan killer, silis kumu ve feldspat yerine değişen oranlarda ilave edilmiştir.

Tablo 5. Standart, Deneme 3, Deneme 4, Deneme 5 (%)

	Standart	Deneme 3	Deneme 4	Deneme 5
Yerli Kil-1	4	5	5	5
İthal Kil-1	17	15	15	15
Yerli Kil-2	17	18	18	18
Yerli Kaolen-1	11	8	8	8
Silis Kumu	9	9	9	10
Sodyum Feldspat	42	39	40	39
Mermer Atığı	-	6	5	5
Manyezit	-	2	1	1.5

Manyezit ve mermer atığı ilaveli reçetelerde manyezit oranının yükselmesi ile viskozitenin de artış gösterdiği tespit edilmiştir. Manyezit ilavesi ile viskozite arasındaki ilişki incelendiğinde reolojik açıdan %1,5'a kadar manyezit kullanımının standart ile uyumlu davranış sergilediği tespit edilmiştir. Numunelerin endüstriyel pişirim süreci, süre-sıcaklık grafiği Şekil 1'de gösterilmektedir. Elde edilen grafikte 25 dk ile 35 dk arasında, 10 dk süre boyunca 1210ºC' de bekletme işlemi yapılmıştır. Şekillendirilen numunelerin fırın giriş-çıkış toplam süresi 57 dk sürdüğü gözlemlenmiştir. Fırından çıkış sıcaklığı 80ºC, ön ısıtma sıcaklığı 300 ºC' dir.
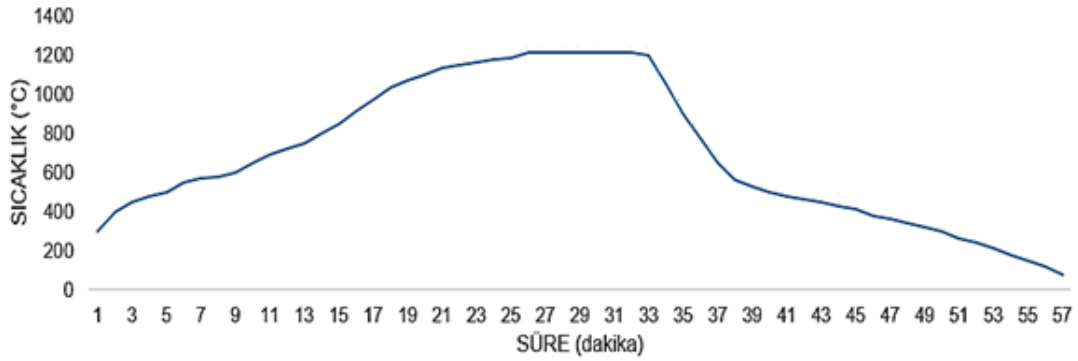
Şekil 1. Pişirme rejim grafiği

3. Bulgular

3.1. Manyezit ve Mermer Atığı İlaveli Numunelerin Analiz Sonuçları

Endüstriyel pişirim sonrası manyezit ve mermer atığı ilaveli numunelerin fiziksel test sonuçları Tablo 6'da verilmiştir.

Tablo 6. Manyezit ve Mermer Atığı İlaveli Numunelerin Analiz Sonuçları

	Çamur Yoğunluk (kg/m3)	Pişmiş Spesifik Yoğunluk (kg/m³)	Pişmiş Eğilme Dayanımı (N/mm2)	Pişmiş Max. Kırılma Yükü (N)	Pişme Küçülmesi(%)	Pişmiş Su Emme (%)
Standart	1660	2.41	44.5	805,66	7.59	0.018
Deneme 3	1704	2.37	41.23	733,33	7.75	0.005
Deneme 4	1703	2.38	42.12	752,84	7.86	0.003
Deneme 5	1670	2.40	43.23	769,59	7.91	0.003

Standart ile kıyaslama yapıldığında spesifik yoğunluk, eğilme mukavemeti, kırılma yükü, su emme değerleri ve pişme küçülmesi açısından Deneme 3-4-5 kodlu numunelerinden olumlu sonuçlar alındığı tespit edilmiştir. Deneme 5 numunesinde ithal kilin %2, yerli kaolen ve Na-feldspatın % 3 oranında azaltılması ile yerine %5 mermer atığı ve %1,5 manyezit ilavesi ile standarda benzer sonuçlar alındığı tespit edilmiştir.

Standart porselen karo bünye ile deneme 5 kodlu numunenin pişme rengi kontrolü Konica Minolta renk ölçüm cihazı ile yapılmış, standart numune ile 5 kodlu numunenin karşılaştırılması Tablo 7'de verilmiştir. Numunelerin görüntüleri Şekil 2'de gösterilmektedir.

Tablo 7. Standart porselen karo bünyesi ile Deneme 5 kodlu numune kıyaslamaları

5x10 Lab Numunesi	*Standart*	*Deneme 5*
L*	71.82	72.13
a*	1.59	0.91
b*	13.55	12.78
ΔE		0.85
Su Emme(%)	0.018	0.030

Şekil 2. Standart ve Deneme 5 numuneleri

3.2. XRF Sonuçları

Standart numunenin ve standart numuneye en yakın olan deneme 5 kodlu numunenin X-ışını floresansı (XRF) ile belirlenen analiz sonuçları Tablo 8'de gösterilmektedir.

Tablo 8. XRF analiz sonuçları (%)

|	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3	TiO_2	P_2O_5	A.Z.
Standart	69,76	19,12	1,120	4,25	0,42	0,20	0,85	0,58	0,12	3,55
Deneme 5	65,27	18,31	1,060	3,59	3,06	0,83	0,81	0,51	0,12	6,33

XRF sonuçları incelendiğinde Deneme 5 kodlu numunenin kimyasal içeriği standart numuneye çok yaklaşmıştır. SiO_2, Al_2O_3 ve Na_2O değerleri birbirine oldukça yakındır. Kimyasal içeriğinin birbirine yakın olması fiziksel ve mekanik dayanımlarının yakın performansı sergileyeceği anlaşılmaktadır.

3.3. X-ışını kırınımı (XRD) Analiz Sonuçları

Standart numune ile manyezit ve mermer atığı ilaveli deneme 5 kodlu numunelerin XRD analiz sonuçları Şekil 3 ve 4'de gösterilmektedir. Elde edilen veriler incelendiğinde numunelerde, kuvars, albit, kaolinit ve illit fazların oluştuğu tespit edilmiştir.
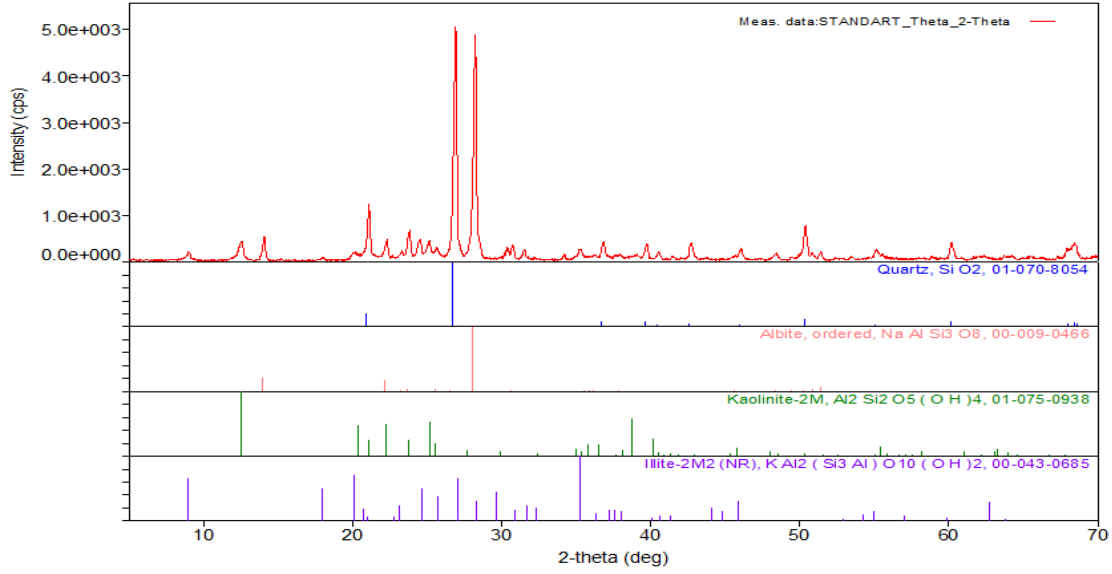
Şekil 3. Standart numunenin XRD analiz sonucu
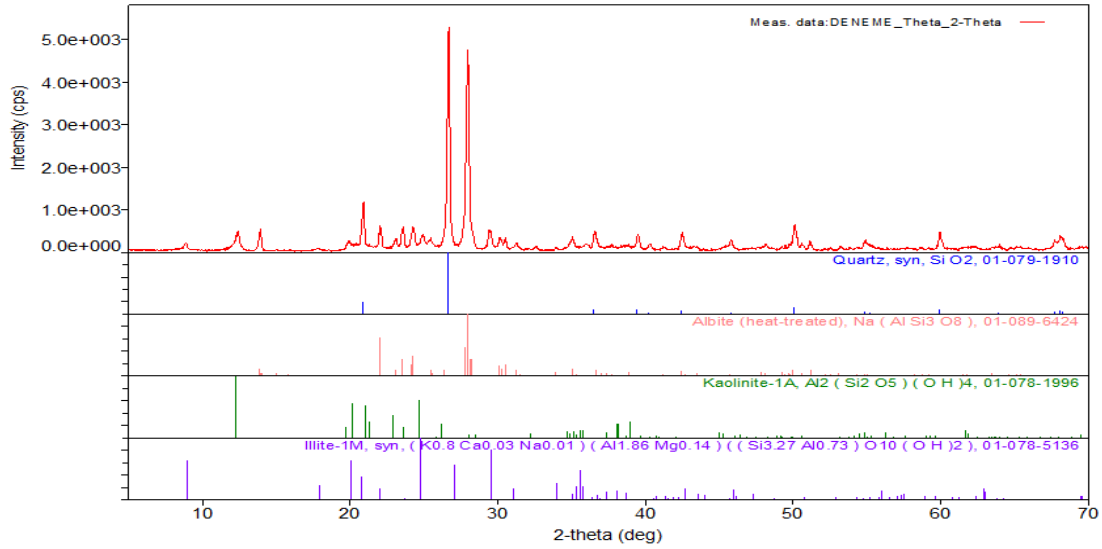
Şekil 4. Deneme 5 kodlu numunenin XRD analiz sonucu

4. Sonuçlar ve Tartışma

Yapılan bu çalışma kapsamında standart reçetede bulunan ithal kil, yerli kaolen ve sodyum feldspatın %2-3 oranında azaltılması ile mermer atığının %5 oranında porselen karo reçetesinde kullanılabileceği belirlenmiştir. Manyezit ve mermer atığı ilaveli numunenin mekanik ve fiziksel özellikleri bozmadan standarttan daha iyi sonuçlar verdiği tespit edilmiştir.

- Reçeteye girilen maksimum mermer oranı %5 olarak belirlenmiştir.
- Atığın manyezit ile birlikte kullanımı çamur reolojisi ve pişme sonrası yoğunluklarda avantaj sağlamıştır.
- Masse reçetesindeki manyezit oranı maksimum %1.5 olarak belirlenmiştir. Manyezit oranı arttıkça çamur viskozitesi artmıştır.
- Pişme rengi açısından ∆E değeri 0,85 çıkmıştır, beyazlık değeri daha yüksek olduğu için kullanımı uygundur.
- Spesifik yoğunluk porselen karo standartları dâhilindedir.
- Mekanik özellikleri (eğilme dayanımı, kırılma yükü) fiziksel özellik (su emme, viskozite, yoğunluk, özgül yoğunluk) testleri standarda yakındır.
- Reçete içerisine %5 mermer atık kullanılması ile ithal kil yaklaşık %12 düşmüş ve birim maliyeti %10 azalmıştır.

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