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Kemometrik Veri Analiz Yaklaşımına Dayalı Senkron Floresans Spektroskopi Yöntemi: Mut (Mersin) Yöresi Zeytinyağları ve Rafine Yenilebilir Yağlarda Tağşiş Tespiti

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ÖZ

Bu çalışma, Mut (Mersin) bölgesinden iki farklı hasat döneminde (2019 ve 2020 Ekim) elde edilen ekstra saf sızma zeytinyağı (VOO) ve farklı markalara ait rafine yemeklik yağ numunelerinde tağşiş/sahtecilik durumu hakkında fikir edinmeyi amaçlamaktadır. Araştırmayı gerçekleştirmek için senkron floresans (SyF) spektroskopisine dayalı analitik yaklaşım, PCA ve SIMCA kemometrik veri analiz yöntemi ile kullanılmıştır. SyF verileri 200–800 nm emisyon bölgesinde elde edilmiş ve uyarma/emisyon monokromatörleri senkronize şekilde kullanılmıştır. Saf VOO ve farklı türdeki yağ numuneleri için elde edilen veriler; PCA ve SIMCA çok değişkenli veri modellemeleri ile analiz edilmiştir. Elde edilen PCA skor grafiklerinde; yağ türlerinin ve farklı hasat zamanlarına ait zeytinyağı örneklerinin sınıflandırma yeteneğinin oldukça yüksek olduğu; SIMCA modellemelerinde ise VOO numunelerinin diğer yağ türlerinden %100 farklı bir grupta sınıflandırılabildiği tespit edilmiştir. Sonuç olarak SyF spektroskopisi kemometrik analiz yöntemleri ile birleştirildiğinde hız ve maliyet açısından oldukça avantajlı bir yöntem olup, zahmetli numune ön işlemleri ve kimyasal kullanımını ortadan kaldırarak büyük kolaylık sağlamaktadır.

Synchronous Fluorescence Spectroscopy Method based on Chemometrics: Authentication of Extra Virgin Olive Oils Harvested in Mut (Mersin) Region and Refined Edible Oils

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ABSTRACT

This study aims to gain insights into the prediction for the authentication of extra virgin olive oils (VOOs) from two different harvest terms (2019 and 2020 October) in Mut (Mersin) region and other refined edible oils from different brands. To pursue the research, an analytical approach based on synchronous fluorescence (SyF) spectroscopy combined with chemometrics including PCA and SIMCA was used. The SyF data were gathered in the emission region of 200–800 nm, and the emission/ excitation monochromators were synchronously used. The data of VOO and different types of edible oil samples were analyzed by the multivariate data analysis including PCA and SIMCA. It has been determined that the classification ability of oil types from different harvest terms is quite high by PCA score graphs; and the VOOs could be classified in a 100% different group from other oils by SIMCA. Consequently, the SyF spectroscopy combined with chemometrics is very advantageous methodology in terms of speed and cost, and it provides a great convenience by eliminating the laborious sample pre-treatments and chemical usage.

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INTRODUCTION

Extra virgin olive oil (VOO) is a valuable nutrient that is produced from the fruit of olive tree (*Olea europaea L.*) has a unique taste and smell, and it could be consumed without refining process. The VOO is an important part of the Mediterranean diet due to its dietary and sensory properties, and it has been used as a protective and therapeutically effective nutrient from past to present, especially due to its bioactive components (*fatty acids, mono- and diacylglycerols, aliphatic alcohols and hydrocarbons, sterols, phenolic and volatile compounds, coloring agents and tocopherols, etc.*) and monounsaturated fatty acid (MUFA) profile [1–4]. These components also play an important role in autoxidation and photooxidation reactions. Fatty alcohols and diterpene alcohols in free or ester position are evaluated in aliphatic or aromatic alcohols, tocopherols are considered as compounds effective on the oxidative stability of biological oils, tyrosol and hydroxytyrosol, apigenin, luteolin, caffeic acid, *o*- and *p*-coumaric, ferulic, gallic, vanillic, phydroxybenzoic, protocatechic, syringic acids, oleuropein, pinoresinol and vanillin phenolic compounds provide the oil with bitterness aroma properties. On the other hand, the aromatic compounds play a vital function in determining the oil quality and occur biochemically as a result of controlled oxidation of fatty acids in the presence of various enzymes. To obtain VOO from olive fruit, mechanical or physical methods are generally used at a temperature that will not change its natural properties. The demand for methods such as cold press process, which preserves the bioactive component content of oily fruits, has increased significantly in recent years.Since, cold press is a process without high temperature and chemical application, there is no risk of solvent residue in the final oil product, and so it becomes a safer product [5] and more preferred by consumers. It is known that the bioactive components determined as active ingredients for the usage of VOOs are at a significant level [2,6–9]. Since these oils respond to consumers' search for natural and safe food, they have a commercially widespread consumption rate, although relatively expensive.

As in many foodstuffs, the adulterated extra VOO products are presented to market by unconscious producers for more profit, by adding less costly pomace or refined vegetable oils to expensive extra VOOs. Due to the adulteration, the quality of extra VOO products decreases; it could lead to dangerous health conditions and cause some ethical and moral problems. In proportion to the development of food technology, the variety of adulteration made to extra VOO products increases and its applicability becomes easier, so the analyses and comments on the subject could become more complex and troublesome [1–3,6–9]. Detection and quantification of inexpensive edible oil adulterants in extra VOOs is of great significance to the olive oil sector. The analytical methods used to conclude the quality and quantity of possible adulteration in VOOs are based on the determination of characteristic fluorescent components and ratios such as phenolic substances, fatty acid composition, sterols, triglycerides, etc. However, these analyses require the application of laborious pre-treatments, the use of high-cost systems and chemicals, as well as the expert analysts. In addition to the cost of specified analysis systems, they require long analysis times, making it necessary to develop alternative fast and simple methods [10–17]. For this reason, it is necessary to develop fast, simple, and non-destructive new analytical methods that provide great convenience by eliminating the pre-processes of the analysis, and provide advantages in terms of analysis time, cost, and environmental sensitivity. Several spectroscopic methods combined with chemometrics have been recently reported [10,11,18–22]; however, the findings obtained are limited and not always correctly predicted as methods are developed to a specific set of olive cultivars, harvesting/growing seasons, oil extraction techniques and geographical regions. In the context of the above objectives, herein we aimed to gain insights into the prediction of authentication of extra VOOs in Mut (Mersin) region and other refined edible oils from different brands by using SyF spectroscopy combined with chemometrics. The SyF data were analyzed in detail by multivariate data analysis including PCA and SIMCA.

MATERIALS AND METHODS

Chemicals and samples

The high–purity chemicals and reagents were procured from VWR Chemicals BDH Inc. (West Chester, Pennsylvania, US) and Sigma–Aldrich Inc. (St. Louis, Missouri, US). 60 different VOO samples of known origin

(Supplementary Table 1) and 26 different refined edible oil samples from local markets (Karaman City, Türkiye) were utilized to develop qualitative chemometrics models for the screening of their authentication [4]. The extra VOO samples from two different harvest terms (2019 and 2020 October, "Ayvalık" and "Gemlik") were procured from different local producers in Mut region (Mersin City, Türkiye), and the refined edible oils from different brands. The qualities of samples were all certificated on their labels with their acceptable limits by the related providers. The VOO from harvest term of 2019 October (*n=30; 2019–VOO–1 to 30*), VOO from harvest term of 2020 October (*n=30; 2020–VOO–1 to 30*), refined sunflower oil (SFO)(*n=5; SFO–1 to 5*), refined soybean oil (SBO)(*n=5; SBO–1 to 5*), refined hazelnut oil (HNO)(*n=6; HNO–1 to 6*), virgin olive oil (VOO)(*n=5; VOO–1 to 5*) and refined cottonseed oil (CSO)(*n=5; CSO–1 to 5*) samples were procured and filtered through a 0.45 µm pore size filter before the SyF measurements.

Acquisition of synchronous fluorescence (SyF) spectra

A fluorescence spectrophotometer (Agilent Tech. Cary Eclipse, US) was used to gather spectra at room temperature. The data were obtained in the emission wavelength region of 200–800 nm with λ_{exc}=360 nm; and the monochromators were used synchronously with ten different wavelength intervals ($\Delta\lambda$; $\Delta\lambda$=10 to 80 nm). The integration time, slit widths and acquisition intervals were set as 0.3 s, 5 nm and 1 nm, respectively. The samples were measured with a standard micro plate reader cuvette.

Data sets and chemometrics

The multivariate data analyses were done by Unscrambler®X10.4 (CAMO Software, Oslo, Norway) and Octave v.4.2.1 (GNU General Public License) softwares. The obtained SyF spectral data were subjected to the multivariate supervised [*principal component analysis (PCA)*] and unsupervised [*soft independent modeling of class analogy (SIMCA)*] data analyses. The SyF spectra were analyzed using the data of the full range (200-800 nm) and six different emission bands characterizing natural fluorescence compounds in vegetable oil samples [4]. The spectral data were presented in a matrix consisting of the total number of samples and their replicates in Office-365 (Microsoft Corporation, Redmond, WA), and then they were imported into the chemometric software. The data were schemed by OriginPro 9 (OriginLab, US) software.

RESULTS

SyF spectra of samples

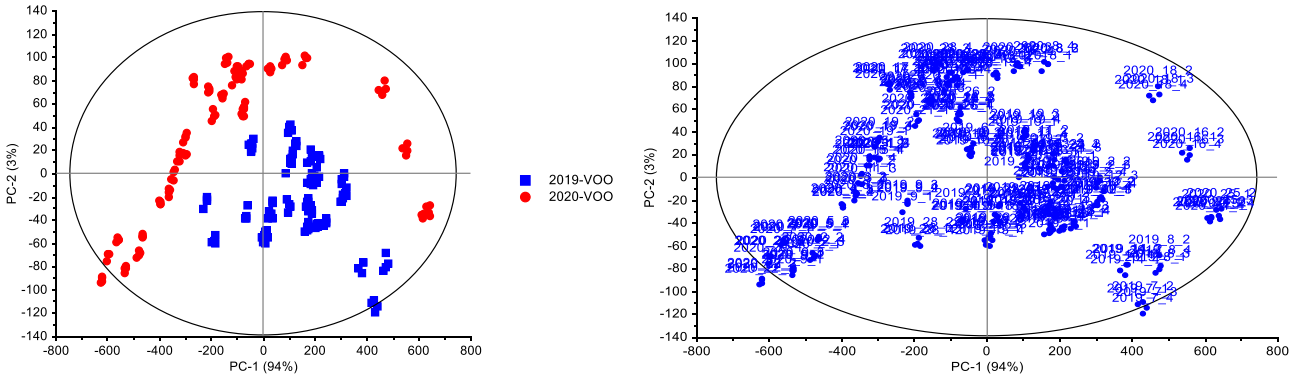
In the first stage of study, the SyF spectroscopy analyzes were performed for the classification of VOOs harvested from "Ayvalık" and "Gemlik" olive trees in the Mut (Mersin) region by cold pressing method and the other vegetable oil samples (*SBO, CSO, SFO, HNO and OO*) from different brands. The SyF spectroscopy analyzes were performed based on the methods recommended in literature [23–26], and the spectra were obtained by scanning the excitation and emission monochromators simultaneously in the wavelength range of 200–800 nm region. The spectra of extra VOO and other edible oil samples are given in Supplementary Figure 1. It has been determined that the $\Delta\lambda$ value applied between the monochromators ($\Delta\lambda$=10-80 nm) is quite effective for the determination of fluorescent compounds. At lower $\Delta\lambda$ values, it is seen that the emission intensities of fluorescent components are higher. It was concluded that when $\Delta\lambda$=10 nm value is applied; the most appropriate data could be obtained. The fluorescent components present in tested samples show characteristic emission bands in the spectrum [23–27]. Based on the strong emission peaks in the spectra, 6 basic regions were constructed, and the evaluations were made by considering these regions. The strong bands; region–I 340–365 nm (*tocopherols and phenolics*), region–II 365–420 nm (*refined/unrefined oil marker*), region–III 420–460 nm and region–IV 460–490 nm (*conjugated diene/trienes, hydrolysis products*), region–V 490–600 nm (*vitamin E) / α–tocopherol and fatty acid oxidation products*) and region–VI 650–700 nm (*pigment compounds such as chlorophyll and carotene*) were detected.

Authentication of VOOs and refined oils by PCA and SIMCA (200–800 nm region's data)

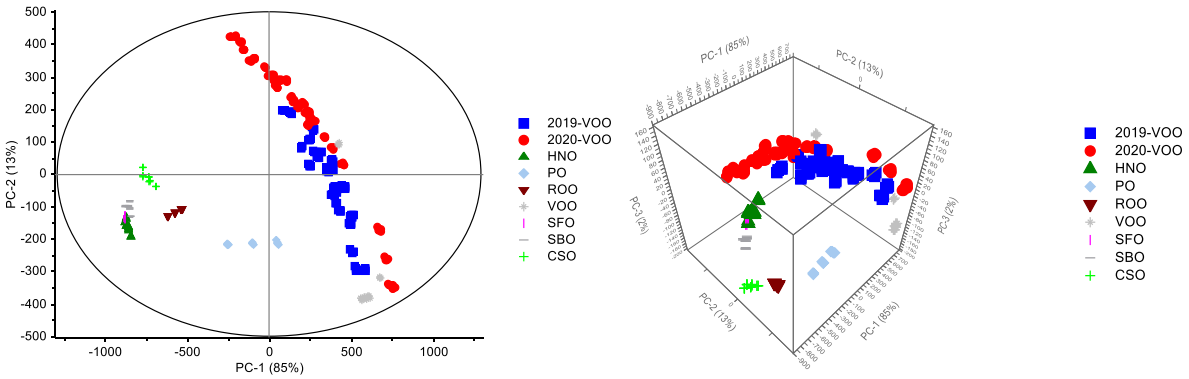
To determine the differences at molecular level in the oil samples and to develop prediction models, the multivariate data analyzes were carried out by processing the spectral data. To determine the adulteration;

qualitative classification/differentiation and quantitative estimation models were constructed. When the results of 60 extra VOO and commercial edible oil samples from 26 different companies are evaluated, it is seen that the spectra are quite similar to each other, and it is not possible to distinguish the oil types (Supplementary Figure 2). The raw data obtained as an Excel file was transferred to the Unscrambler®X10.4 program for the development of chemometrics models (Supplementary Figure 2a). Then, Savitzky–Golay preprocessing (Supplementary Figure 2b) and standard normal variate baseline correction (Supplementary Figure 2c) was applied to the data in order to increase the difference between the bands in spectra.

To examine the classification abilities of VOO samples based on their harvest periods, the PCA score graphs were constructed on 2 coordinates (PC1 & PC2) (Figure 1a) in the region of 200–800 nm. As seen from the score graphs, the extra VOO samples could be classified into distinctly different groups based on their harvest years. There is a quite different location for the VOO samples from the mentioned 2020 harvests [VOO-16 (Erdek), VOO-18 (Erdek), VOO-24 (Delice, Harap) and VOO-25 (Delice, Harap)] (Figure 1a). Apart from these samples, olive oil types could be classified successfully depending on their harvest year. The effect of different wavelength interval values (Δλ=10-80 nm) on classification was also examined in the region of 200–800 nm (Supplementary Figure 3).



(a) PCA score graph_VOO samples harvested in 2019&2020 October _ Full region 200–800 nm_Δλ=10 nm



(b) PCA score graph_VOO samples harvested in 2019&2020 October and other refined edible oil samples_ Full region 200–800 nm_Δλ=10 nm

Figure 1. *PCA 2D and 3D score plots (PC1&PC2&PC3) of* ***a)*** *2019–VOO and 2020–VOO and* ***b)*** *2019–VOO and 2020–VOO and other refined edible oils (Δλ=10 nm), from SyF analysis in the region of 200–800 nm*

As the Δλ value increased, the classification ability of oil types decreased, and the classification based the harvest periods decreased proportionally with the increase of Δλ value. In the PCA score graph (Figure 1a), the eigenvector value was obtained as 97% (PC1=94% and PC2=3%). When the value of Δλ=10 nm was applied, the separation was successfully achieved for the samples from different harvesting periods. In second stage of the study, the classification abilities of extra VOO samples and other oils were investigated by PCA in the region of 200–800 nm. The score graphs were obtained for different wavelength intervals (Δλ=10-80 nm) (Figure 1b and

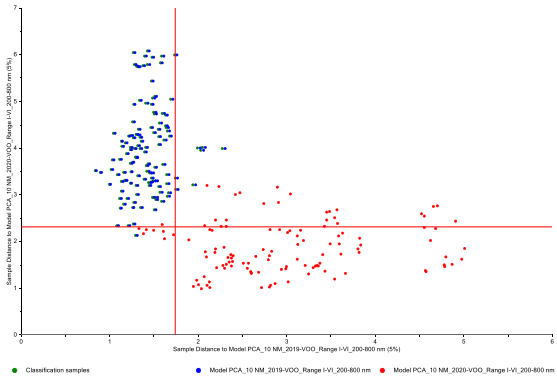
Supplementary Figure 4). It is clearly seen that the best classification was obtained for the Δλ value of 10 nm. In the score graphs visualized on 2 (PC1&PC2) or 3 coordinates (PC1&PC2&PC3), the eigenvector values are 98% (PC1=85%, PC2=13%) and 100% (PC1=85%, PC2=13%, PC3=2%) respectively, (Figure 1b). As the Δλ value increased, the classification ability between oil types decreased (Supplementary Figure 4). When the Δλ value of 80 nm was applied, the discrimination of samples was unsuccessful. The samples of PO, ROO and commercially supplied extra VOO, which are similar in terms of compounds with fluorescent properties, were located closer to the samples from local producers. The refined SFO, SBO, CSO and HNO samples, which have similar properties in terms of fluorescent components, were located in a close region to each other but quite different from the extra VOO samples and could be classified successfully.

In the second part of classification study, the SIMCA, which is an important multivariate data analysis used to decide whether a sample of unknown origin could be accepted into a certain quality class with the F-ratio, was performed at tolerance/confidence level of 95% (Figures 2 and 3). With the Coomans graphs, it was tried to decide whether the examined extra VOO samples could be accepted into the quality class or whether they could be distinguished from commercially supplied vegetable oils (*sunflower, soybean, olive pomace, refined olive oil, cotton and hazelnut oils*). As seen in the Coomans graphs; the VOO samples from both 2019 and 2020 October harvests could be classified in a 100% different group from sunflower, soybean, olive pomace, refined olive oil, cotton and hazelnut oils. In the samples of 2019 and 2020 October harvests with more similar content, this classification could be carried out, but similar types of extra VOO samples obtained from some producers were located in very close regions. Similar to the PCA score graphs, the samples of pomace, refined olive oil and commercially supplied extra VOO that show similarities in terms of fluorescent components (*tocopherols, pigments, phenolic compounds, fatty acid oxidation products, conjugated diene and triene structures*) were located closer to the samples obtained from different manufacturers. Other commercial sunflower, soybean, cotton and hazelnut oils with similar fluorescent components could be classified in a region that is close to each other but quite different from the extra VOO samples. Therefore, it has been observed that more successful classifications could be performed between the oil types by SIMCA.

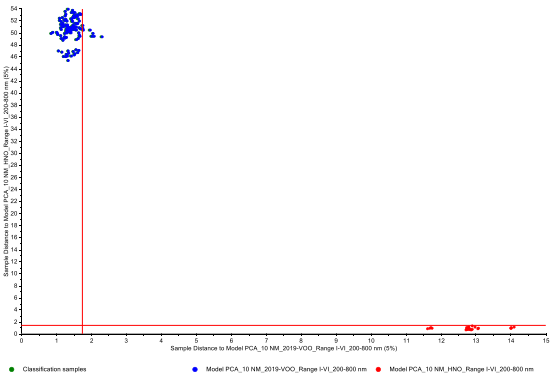
Authentication of VOOs and refined oils by PCA and SIMCA (selected region's data)

The SyF spectra were then analyzed using the data of six different emission bands (*region– I; 200–365 nm, region– II; 365–420 nm, region– III; 420–460 nm, region–IV; 460–490 nm, region–V; 490–600 nm, and region–VI; 600–800 nm*). It is known that the spectrum region of 340–365 nm represents tocols and phenolic components, the spectrum region of 365–420 nm represents the refined/unrefined oils, the 420–460 nm and 460–490 nm represent the conjugated diene/trienes and hydrolysis products, 490–600 nm represents vitamin E (α–tocopherol) and fatty acid oxidation products, and the spectrum region of 650–800 nm represents pigments such as chlorophyll and carotene [23–27]. The PCAs were carried out at Δλ=10 nm using data from these specific regions (Supplementary Figure 5). In the PCA score graphs at Δλ=10 nm; it is seen that the 650-800 nm spectrum region's score graph is the most appropriate for the classification of extra VOOs based on their harvest periods. The eigenvector value was 98% (PC1=95% and PC2=3%) obtained with the data of 650–800 nm region. Similarly, the 490–600 nm region data seems to contain applicable results for the classification of extra VOOs according to their harvest periods, and the eigenvector value in this score graph is 99% (PC1=96%, PC2=3%).

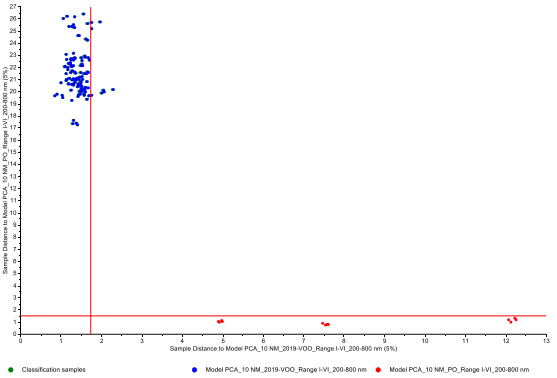
The classification ability of samples (sunflower, soy, olive pomace, refined olive oil, cotton and hazelnut) belonging to different local producers, olive species or brands was also examined by the data from specific regions. The PCA score graphs were constructed for different spectral regions (*region– I; 200–365 nm, region–II; 365–420 nm, region– III; 420–460 nm, region–IV; 460–490 nm, region–V; 490–600 nm, and region–VI; 600–800 nm*) (Supplementary Figure 5). It is seen that the data of 650-800 nm is the most appropriate data for the classification of samples, and the eigenvector value is 99% (PC1=88% and PC2=11%). The samples of PO, refined OO and commercially supplied extra VOO were located closer to the samples from Mut region. The commercial sunflower, soybean, cotton and hazelnut oils were located close to each other but different location from the extra VOO samples and could be classified successfully. Similarly, the data of 490–600 nm region seems to contain applicable results for the classification of samples, and the eigenvector value is 100% (PC1=97% and PC2=3%).



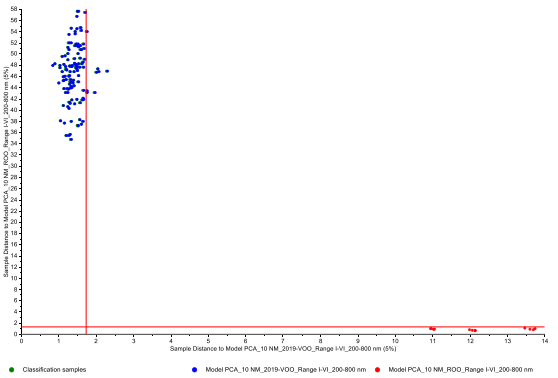
2019–VOO from 2020–VOO_ 200–800 nm_Δλ=10 nm



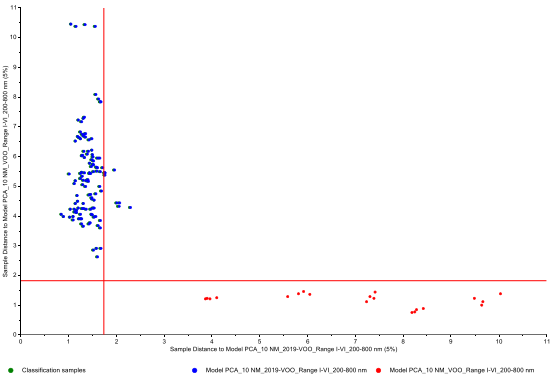
2019–VOO from HNO_ 200–800 nm_Δλ=10 nm



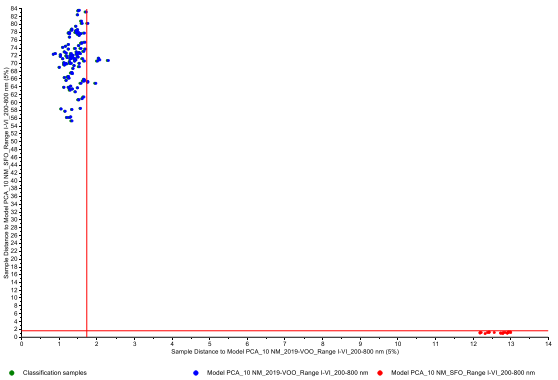
2019–VOO from PO_ 200–800 nm_Δλ=10 nm



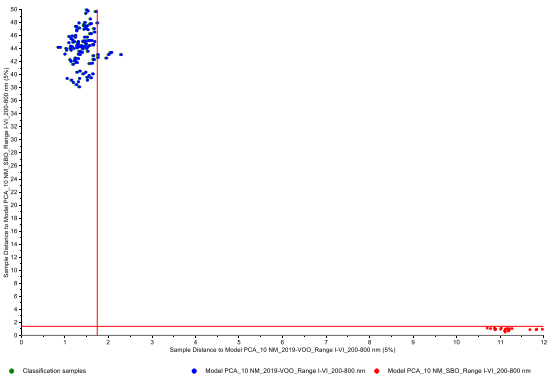
2019–VOO from ROO_ 200–800 nm_Δλ=10 nm



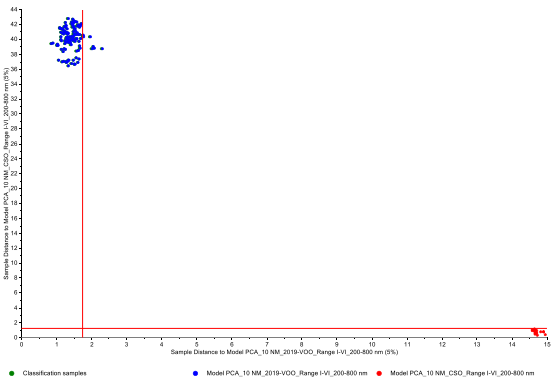
2019–VOO from OO_ 200–800 nm_Δλ=10 nm



2019–VOO from SFO_ 200–800 nm_Δλ=10 nm



2019–VOO from SBO_ 200–800 nm_Δλ=10 nm



2019–VOO from CSO_ 200–800 nm_Δλ=10 nm

Figure 2. *Coomans plots for the classification of 2019–VOO and other edible oils (Δλ=10 nm), recorded in the region of 200–800 nm*

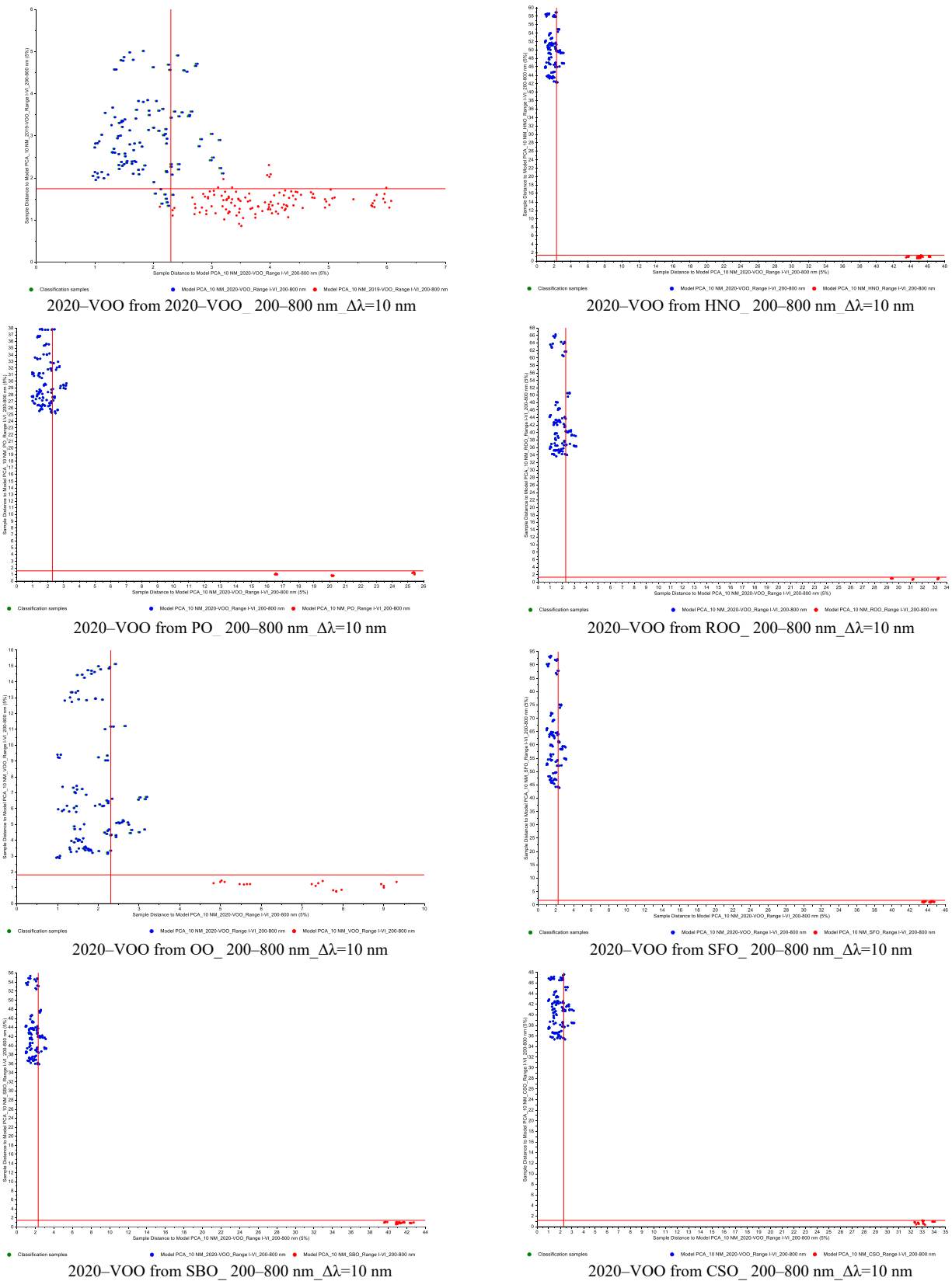


Figure 3. *Coomans plots for the classification of 2020–VOO and other edible oils (Δλ=10 nm), recorded in the region of 200–800 nm*

DISCUSSION AND CONCLUSIONS

In conclusion, the study aimed to gain insights into the classification of olive oils obtained from "Ayvalık" and "Gemlik" olives harvested in Mut (Mersin) region from other edible oils and the development of emission

spectroscopy methodologies based on chemometrics. Different classification methods including unsupervised pattern recognition PCA and supervised pattern recognition SIMCA were applied to the SyF spectral data obtained from oil samples. The qualitative chemometrics models were constructed by evaluating the data from full spectral region (200–800 nm) and different spectral regions. The proposed SyF spectroscopy methods combined with chemometrics are very advantageous in terms of cost and analysis time, and they provide great convenience by eliminating laborious sample pre-treatments. The qualitative determination of possible adulteration to VOOs with inexpensive refined edible oils (*sunflower oil, hazelnut oil, cottonseed oil or soybean oil*) was extensively searched and the findings were well satisfactory.

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REFERENCES

[1] F.N. Arslan, ATR–FTIRspectroscopy combined with chemometrics for rapid classification of extra virgin olive oils and edible oils from different cultivars available on the Turkish markets, *Eskişehir Technical University Journal of Science and Technology A- Applied Sciences and Engineering*. 19 (2018), 926–947. doi:10.18038/aubtda.425374.

[2] I. Gouvinhas, J.M.M.M. De Almeida, T. Carvalho, N. Machado, A.I.R.N.A. Barros, Discrimination and characterisation of extra virgin olive oils from three cultivars in different maturation stages using Fourier transform infrared spectroscopy in tandem with chemometrics, *Food Chemistry*. 174 (2015), 226–232.

[3] G. Yildiz, T. Huseyin, Quantification of soybean oil adulteration in extra virgin olive oil using portable raman spectroscopy, *Food Measurement and Charecterization*. 11 (2017), 523–529. doi:10.1007/s11694-016-9419-8.

[4] İ. Varlı, Development of Simple and Rapid Synchronous Fluorescence Spectroscopy Methods based on Chemometric Data Analysis Approach for the Classification and Adulteration of Olive Oils in Mut (Mersin) Region, Master Thesis, *Karamanoglu Mehmetbey University Institute of Science, Department of Chemistry*, Karaman (2022).

[5] M.K. Demir, N. Bilgiçli, S. Türker, B. Demir, Farklı Stabilizasyon İşlemleri Uygulanmış Buğday Ruşeymlerinin Depolama Özellikleri, *Necmettin Erbakan University Journal of Science and Engineering*. 2 (2019), 67–75.

[6] M. Bevilacqua, R. Bucci, A.D. Magrì, A.L. Magrì, F. Marini, Tracing the origin of extra virgin olive oils by infrared spectroscopy and chemometrics: A case study, *Analytica Chimica Acta*. 717 (2012), 39–51. doi:10.1016/j.aca.2011.12.035.

[7] Lerma-Garcia, G. Ramis-ramos, J.J. Martinez-Tellez, Simo-Alfonso, Authentication of extra virgin olive oils by Fourier-transform infrared spectroscopy, *Food Chemistry*. 118 (2010), 78–83. doi:10.1016/j.foodchem.2009.04.092.

[8] G. Ozulku, R.M. Yildirim, O.S. Toker, S. Karasu, M.Z. Durak, Rapid detection of adulteration of cold pressed sesame oil adultered with hazelnut , canola , and sun fl ower oils using ATR-FTIR spectroscopy combined with chemometric, *Food Control*. 82 (2017), 212–216.

[9] P. De, A. Dominguez-vidal, J.M. Bosque-sendra, A. Ruiz-medina, L. Cuadros-rodríguez, M.J. Ayora-cañada, Olive oil assessment in edible oil blends by means of ATR-FTIR and chemometrics, *Food Control*. 23 (2012), 449–455. doi:10.1016/j.foodcont.2011.08.013.

[10] F. Mabood, R. Boqué, R. Folcarelli, O. Busto, A. Al-harrasi, J. Hussain, Thermal oxidation process accelerates degradation of the olive oil mixed with sunflower oil and enables its discrimination using synchronous fluorescence spectroscopy and chemometric analysis, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 143 (2015), 298–303. doi:10.1016/j.saa.2015.01.119.

[11] A. Dankowska, M. Małecka, W. Kowalewski, Application of synchronous fluorescence spectroscopy with multivariate data analysis for determination of butter adulteration, *International Journal of Food Science and Technology*. 49 (2014), 2628–2634. doi:10.1111/ijfs.12594.

[12] J. Cao, C. Li, R. Liu, X. Liu, Y. Fan, Z. Deng, Combined Application of Fluorescence Spectroscopy and Chemometrics Analysis in Oxidative Deterioration of Edible Oils, *Food Analytical Methods*. 10 (2017), 649–658. doi:10.1007/s12161-016-0587-2.

[13] K. Poulli, N. V Chantzos, G.A. Mousdis, C.A. Gorgiou, Synchronous Fluorescence Spectroscopy : Tool for Monitoring Thermally Stressed Edible Oils, *Journal of Agricultural and Food Chemistry*. 57 (2009), 8194–8201. doi:10.1021/jf902758d.

[14] F.N. Arslan, G. Akin, Ş.N. Karuk Elmas, I. Yilmaz, H.-G. Janssen, A. Kenar, Rapid detection of

authenticity and adulteration of cold pressed black cumin seed oil: A comparative study of ATR–FTIR spectroscopy and synchronous fluorescence with multivariate data analysis, *Food Control*. 98 (2019). doi:10.1016/j.foodcont.2018.11.055.

[15] A. Kenar, B. Çiçek, F.N. Arslan, G. Akin, Ş.N. Karuk Elmas, I. Yilmaz, Electron Impact – Mass Spectrometry Fingerprinting and Chemometrics for Rapid Assessment of Authenticity of Edible Oils Based on Fatty Acid Profiling, *Food Analytical Methods*. 12 (2019), 1369–1381.

[16] G. Akin, Ş.N. Karuk Elmas, F.N. Arslan, İ. Yılmaz, A. Kenar, Chemometric classification and quantification of cold pressed grape seed oil in blends with refined soybean oils using attenuated total reflectance–mid infrared (ATR–MIR) spectroscopy, *LWT - Food Science and Technology*. 100 (2019) 126–137. doi:10.1016/j.lwt.2018.10.046.

[17] F.N. Arslan, F. Çağlar, Attenuated Total Reflectance – Fourier Transform Infrared (ATR – FTIR) Spectroscopy Combined with Chemometrics for Rapid Determination of Cold-Pressed Wheat Germ Oil Adulteration, *Food Analytical Methods*. 12 (2019), 355–370.

[18] A. Sayago, D. Garcia-Gonzalez, M. Morales, R. Aparicio, Detection of the Presence of Refined Hazelnut Oil in Refined Olive Oil by Fluorescence Spectroscopy, *Journal of Agricultural and Food Chemistry*. 55 (2007), 2068–2071.

[19] E. Sıkorska, A. Gliszczynska-Swiglo, I. Khmelinskii, M. Sıkorski, Synchronous Fluorescence Spectroscopy of Edible Vegetable Oils . Quantification of Tocopherols, *Journal of Agricultural and Food Chemistry*. 53 (2005), 6988–6994.

[20] E. Guzmán, V. Baeten, J. Antonio, F. Pierna, J.A. García-mesa, Evaluation of the overall quality of olive oil using fluorescence spectroscopy, *Food Chemistry*. 173 (2015), 927–934. doi:10.1016/j.foodchem.2014.10.041.

[21] P.B. Oldham, M.E. Mccarroll, L.B. Mcgown, I.M. Warner, N. Carolina, Molecular Fluorescence , Phosphorescence , and Chemiluminescence Spectrometry, *Analytical Chemistry*. 72 (2000), 197–210. doi:10.1021/a1000017p.

[22] K.I. Poulli, G.A. Mousdis, C. Georgio, Synchronous fluorescence spectroscopy for quantitative determination of virgin olive oil adulteration with sunflower oil, *Analytical Bioanalytical Chemistry*. 386 (2006), 1571–1575. doi:10.1007/s00216-006-0729-2.

[23] H. Tumay, U. Tamer, A. Berkkan, I. Hakki, Synchronous fluorescence spectroscopy for determination of tahini adulteration, *Talanta*. 167 (2017), 557–562.

[24] B. Li, H. Wang, Q. Zhao, J. Ouyang, Y. Wu, Rapid detection of authenticity and adulteration of walnut oil by FTIR and fluorescence spectroscopy : A comparative study, *Food Chemistry*. 181 (2015), 25–30. doi:10.1016/j.foodchem.2015.02.079.

[25] F. Ge, C. Chen, D. Liu, S. Zhao, Rapid Quantitative Determination of Walnut Oil Adulteration with Sunflower Oil Using Fluorescence Spectroscopy, *Food Analytical Methods*. 7 (2014), 146–150. doi:10.1007/s12161-013-9610-z.

[26] K.I. Poullı, N. V. Chantzos, G.A. Mousdıs, C.A. Georgıou, Synchronous Fluorescence Spectroscopy : Tool for Monitoring Thermally Stressed Edible Oils, *Journal of Agricultural and Food Chemistry*. 57 (2009), 8194–8201. doi:10.1021/jf902758d.

[27] Ş.N. Karuk Elmas, F.N. Arslan, G. Akin, A. Kenar, H. Janssen, I. Yilmaz, Synchronous fluorescence spectroscopy combined with chemometrics for rapid assessment of cold – pressed grape seed oil adulteration : Qualitative and quantitative study, *Talanta*. 196 (2019), 22–31. doi:10.1016/j.talanta.2018.12.026.