NÖHÜ Müh. Bilim. Derg. / NOHU J. Eng. Sci., 2025; 14(4), 1530-1541
Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi
Niğde Ömer Halisdemir University Journal of Engineering Sciences
Araştırma makalesi / Research article
www.dergipark.org.tr/tr/pub/ngumuh / www.dergipark.org.tr/en/pub/ngumuh

Quantification of phenolics and antioxidant properties in dried grape pomace by near infrared spectroscopy

Kurutulmuş üzüm posasında fenoliklerin ve antioksidan özelliklerin yakın kızılötesi spektroskopisi ile belirlenmesi

Huseyin Ayvaz[1,*], Muhammed Ali Dogan[2]

[1,2] *Department of Food Engineering, Faculty of Engineering, Canakkale Onsekiz Mart University, Canakkale, 17020, Türkiye*

Abstract

This study evaluated the potential of near-infrared (NIR) spectroscopy, combined with partial least squares regression (PLSR) to quantify bioactive properties in dried grape pomace powders. Twenty-four samples of red-pink and purple-black grapes were examined for total monomeric anthocyanins, phenolics, flavonoids, proanthocyanidins, and antioxidant capacity utilizing CUPRAC (cupric reducing antioxidant capacity) and DPPH (2,2-diphenyl-1-picrylhydrazyl) assays. Chemical analyses verified higher phenolic and antioxidant contents in purple-black pomace than red-pink. PLSR models from NIR spectra produced promising results, showing strong calibration and cross-validation for all analytes. These outcomes indicate that NIR spectroscopy provides a simple, nondestructive, and eco-friendly alternative to conventional wet chemistry methods. Moreover, the approach offers potential for monitoring bioactive compounds in grape pomace, thereby supporting the valorization of agro-industrial residues as sustainable sources of phenolics and antioxidants for food, nutraceutical, and cosmetic applications.

Keywords: Grape pomace, Near-infrared spectroscopy, PLSR, Phenolics, Antioxidant activity

Öz

Bu çalışmada, kurutulmuş üzüm posası tozlarında biyoaktif özelliklerin belirlenmesinde, yakın kızılötesi (NIR) spektroskopisi ile kısmi en küçük kareler regresyonunun (PLSR) potansiyeli değerlendirilmiştir. Kırmızı–pembe ve mor–siyah üzümlerden elde edilen 24 örnek, toplam monomerik antosiyaninler, fenolikler, flavonoidler, proantosiyanidinler ve antioksidan kapasite açısından CUPRAC (cupric reducing antioxidant capacity) ve DPPH (2,2-difenil-1-pikrilhidrazil) yöntemleriyle analiz edilmiştir. Kimyasal analizler, mor–siyah üzüm posasında fenolik ve antioksidan düzeylerinin daha yüksek olduğunu göstermiştir. NIR spektrumlarından elde edilen PLSR modelleri, tüm parametreler için güçlü kalibrasyon ve çapraz doğrulama ile umut verici sonuçlar ortaya koymuştur. Bulgular, NIR spektroskopisinin geleneksel ıslak kimya yöntemlerine basit, tahribatsız ve çevre dostu bir alternatif sunduğunu göstermektedir. Ayrıca bu yaklaşım, üzüm posasında biyoaktif bileşiklerin izlenmesini sağlayarak tarımsal-endüstriyel yan ürünlerin sürdürülebilir biçimde değerlendirilmesine katkı sunabilir.

Anahtar kelimeler: Üzüm posası, Yakın kızılötesi spektroskopi, PLSR, Fenolikler, Antioksidan aktivite

1 Introduction

Grapes (*Vitis spp*., family Vitaceae) are among the most extensively cultivated fruit crops globally, encompassing roughly 60 recognized species and hybrids [1]. During grape processing, such as juice making, substantial amounts of solid by-products, collectively referred to as grape pomace, are generated. This material, primarily consisting of skins and seeds, is produced in enormous quantities across grape-producing regions [2–4]. Türkiye ranks among the leading grape producers, with almost 4 million tons harvested in 2022 [5]. The chemical complexity renders disposal expensive and, if neglected, may lead to environmental issues.

Polyphenols are secondary metabolites found in diverse plant tissues such as fruits, stems, leaves, flowers, roots, bark, and are acknowledged for their capacity to mitigate cardiovascular diseases, degenerative disorders, and specific cancer types. They also influence the sensory attributes of food, including bitterness, color, taste, and pungency [6]. Grapes are notably abundant in antioxidants, exhibiting antithrombotic, antiallergenic, anticarcinogenic, cardioprotective, and hair-stimulating properties. Phenolic chemicals in grape extracts confer health advantages and safeguard the plant from light-induced stress, with their concentrations affected by grape variety and cultivation conditions [7]. Incomplete extraction during food processing leaves grape pomace with significant quantities of phenolic compounds, making it a useful source of bioactive chemicals [8-9]. Although considered as waste, grape pomace possesses significant nutritional value. Approximately seventy-five percent of its mass comprises skins and seeds rich in micronutrients and bioactive substances [10]. The composition of pomace fluctuates based on grape variety, pressing conditions, and fermentation processes;

* Sorumlu yazar / Corresponding author, e-posta / e-mail: huseyinayvaz@comu.edu.tr (H. Ayvaz)
Geliş / Received: 29.08.2025 Kabul / Accepted: 23.09.2025 Yayımlanma / Published: 15.10.2025
doi: 10.28948/ngumuh.1773992

nevertheless, grape skins generally constitute 20–30% of the initial fruit weight and provide pigments like anthocyanins.

The phenolic component of grapes is crucial for assessing the organoleptic characteristics of wines. Anthocyanins change the color of wine directly, while flavonols provide astringency and bitterness. Both of these compounds additionally assist in maintaining the color of wine stable as it ages [11-14]. Kataria and Shaikh [15] stated that the maximum drying temperature for grapes should be 65°C. High-temperature drying causes a significant decrease in the level of extracted polyphenols and antioxidant activity.

Due to increasing consumer demand and rising interest in sustainable agricultural practices, grape pomace has been utilized in food processing (biosurfactants), cosmetics (grape seed oil and antioxidants), functional foods (dietary fiber and polyphenols), pharmaceuticals, and as a source of additives like grape skin powder [16-18]. Compounds in grape seeds are particularly significant to the food industry since they have their anti-aging, anti-carcinogenic, anti-mutagenic, anti-inflammatory, anti-ulcer, anti-atherogenic, and antibacterial properties [19]. As a functional food ingredient due to its richness in bioactive compounds, grape pomace has been incorporated into meat products, pasta, baked goods, and dairy products to improve nutritional and functional qualities, extend shelf life, and enhance antioxidant and antimicrobial properties [20-23]. Such applications demonstrate the potential of grape pomace valorization in diverse sectors, ranging from food preservation to health promotion.

Quantitative analysis of grape pomace composition often utilizes standard methods such as high-performance liquid chromatography (HPLC), gas chromatography (GC), and spectrophotometric assays [24]. Despite their efficacy, these processes are labor-intensive and expensive, and they produce chemical waste, hence constraining their feasibility for large-scale applications. Consequently, there is a necessity for fast, reliable, economical, and chemical-free techniques to measure essential metabolites [25]. Spectroscopic methods, including nuclear magnetic resonance (NMR), infrared (IR), and Raman spectroscopy, in conjunction with multivariate data processing, offer rapid, nondestructive, and eco-friendly alternatives that yield accurate results at a comparatively low expense [25–27]. NIR spectroscopy has attracted interest among IR approaches for its rapidity, nondestructive characteristics, and capacity to penetrate food matrices, making it a valuable instrument for compositional assessment [26]. NIR spectroscopy provides rapid, non-destructive detection of phenolics and other bioactives in foods [28-29]. Applications include the determination of flavonoids in grape seeds [30], quality-related polyphenols in grapes and wines [31-32], procyanidins in cocoa [33] and total polyphenol content in green tea [34]. These studies highlight the relevance of NIR as a sustainable tool for monitoring phenolics in grape-derived matrices.

Thus, the aim of this study was to establish a rapid and eco-friendly analytical approach for quantifying total monomeric anthocyanins, total phenolics, total flavonoids, proanthocyanidins, and antioxidant capacity in red-pink and purple-black dried grape pomace using NIR spectroscopy coupled with PLSR, with implications for its valorization in the food, cosmetic, and pharmaceutical sectors as well as for reducing food waste. Unlike earlier studies in the field, the PLSR models developed in this work used dried grape pomace powders from both red-pink and purple-black samples and simultaneously evaluated multiple phenolic groups and antioxidant assays.

2 Material and methods

2.1 Grape samples and their preparation

Nine pink/red and 15 purple/black fresh grape samples (a total of 24 samples), each weighing approximately 1 kg, were purchased from local markets and small producers in the Canakkale region of Türkiye in the harvest year of 2024. The grapes were washed, cleaned, and carefully destemmed prior to processing.

Figure 1 summarizes the preparation procedures of grape pomace. To replicate grape processing and acquire pomace, the grapes were subjected to pressing with a manual fruit juicer to extract maximum juice and free water, resulting in solid residue. The resultant pomace was uniformly distributed on stainless-steel trays and dehydrated in a laboratory oven at 60°C. Once dried, the material was ground into a fine powder using a laboratory-scale grinder. The powder was then passed through a sieve to separate larger fragments from the fine particles. The fine fraction was collected and transferred into 50 mL centrifuge tubes. The powdered pomace was stored at –18°C until analysis.

Samples were then divided into two sets: one designated for NIR measurements and the other for chemical reference analyses. For NIR analysis, the dried powders were used directly as they are, while for chemical assays, the powders were extracted in duplicate with 80% ethanol acidified with 0.01% HCl (v/v) to obtain phenolic-rich extracts.

Figure 1. Flowchart of grape pomace preparation from fresh grapes to the final powdered form

2.2 Reference analyses

2.2.1 Total monomeric anthocyanins

Samples obtained using 80% ethanol acidified with 0.01% HCl (1:10, v/v) were diluted with buffer solutions at pH 1.0 and 4.5. Absorbance was measured at 520 and 700 nm utilizing a UV–Visible spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan). The difference of absorbances between the two pH settings was used to determine the monomeric anthocyanin content, expressed as mg cyanidin-3-glucoside (cyn-3-glu) equivalents per 100 g of sample [35].

2.2.2 Total phenolic content

The Folin–Ciocalteu (FC) technique was used to calculate the extracts' total phenolic content [36]. The experiment works by having phenolic chemicals reduce the Folin–Ciocalteu reagent in an alkaline solution, resulting in a blue-colored complex. For extraction, samples were prepared in 80% ethanol acidified with 0.01% HCl (1:10, w/v).

Following a two-hour incubation period at room temperature, aliquots from the extracts were successively mixed with 0.2 N Folin–Ciocalteu reagent and 7.5% sodium carbonate solution. Following incubation, absorbance was measured at 765 nm utilizing a UV–Visible spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan). The total phenolic content was quantified as mg of gallic acid equivalents (GAE) per 100 g of sample, applying a calibration curve constructed from gallic acid standards.

2.2.3 Total flavonoids

The aluminum chloride colorimetric technique was used to determine the extracts' total flavonoid content [37]. In summary, 100 µL of 1 M potassium acetate, 100 µL of 10% aluminum nitrate, and 4.4 mL of 96% ethanol were added to the extracts. Following a 40-minute incubation at room temperature in darkness, absorbance was assessed at 415 nm utilizing a UV–Visible spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan). Results were reported as milligrams of quercetin equivalents (QE) per 100 grams of material.

2.2.4 Proanthocyanidins

The butanol–HCl test was used to assess the proanthocyanidin content [38]. For each reaction, 0.25 mL of extract was combined with 2.5 mL of butanol containing 5% HCl and 50 µL of ferrous sulfate solution. The mixtures were incubated either in darkness for 30 minutes or at 92°C for 1 hour, followed by cooling in an ice-water bath. Absorbance was subsequently quantified at 550 nm utilizing a UV–Visible spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan). Results were quantified as cyanidin per 100 g of material.

2.2.5 CUPRAC (Cupric-Ion- reducing antioxidant capacity-copper reducing antioxidant capacity)

As the chromogenic reagent, neocuproine (Nc) was used in the cupric ion reducing antioxidant capacity (CUPRAC) test [39]. This approach involves the reduction of the Cu(II)–Nc complex to the Cu(I)–Nc chelate, resulting in an absorbance maximum at 450 nm. For the reaction, 0.01 M $CuCl_2$, Nc, and 1 M ammonium acetate buffer (pH 7.0) were added to the extracts and incubated for 30 minutes at ambient temperature. Absorbance was subsequently quantified at 450 nm utilizing a UV–Visible spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan), with antioxidant capacity represented as mg Trolox Equivalents (TE) per 100 g of material.

2.2.6 DPPH (2,2-Diphenyl-1-picrylhydrazyl) radical scavenging capacity)

The DPPH radical scavenging test was used to evaluate the extracts' antioxidant properties [40]. This method depends on measuring the decrease in absorbance of the pink DPPH radical at 517 nm. In the process, 300 µL of 1 mM DPPH solution was combined with 100–500 µL of sample extract, and the total volume was adjusted to 3 mL using solvent. The mixtures were incubated at ambient temperature for 15 minutes, following which absorbance was measured at 517 nm using a UV-Visible spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan). Radical scavenging activity was quantified as the effective concentration (IC_{50}, mg extract/mL) necessary to block 50% of the DPPH radicals.

2.3 NIR spectra collection

NIR spectra of grape pomace powders were obtained employing an FT-NIR Nicolet iS50 Flex Gold spectrometer (Thermo Fisher Scientific, Madison, WI, USA). The system had a Ge-coated KBr beamsplitter and an Indium Gallium Arsenide (InGaAs) detector, with spectra acquired in reflection mode. During measurement, the rotating sample holder of the NIR module was used to obtain representative spectrum across the entire sample surface.

Approximately 10 g of the powdered sample was placed in a glass Petri dish for each analysis. A total of 64 scans were collected in the 10,000–4,000 cm^{-1} range at a spectral resolution of 4 cm^{-1}. Background spectra were recorded before each measurement using an empty Petri dish. For each sample, two independent spectra were recorded. Between successive measurements, the portion of the powdered sample (~10 g) placed in the Petri dish was replaced to ensure representative spectral acquisition. The Petri dish was rinsed with distilled water and cleaned with 70% ethanol/water (v/v) in between measurements. All spectra were acquired and analyzed with Omnic 9 software (Thermo Fisher Scientific, Madison, WI, USA).

2.4 Statistical analysis

SPSS software was used to perform statistical analyses (IBM SPSS Statistics, Armonk, NY, USA). Prior to testing, the data were evaluated for normality and homogeneity of variances. Then, an independent two-sample *t*-test was applied to compare the groups. A significance threshold of $p < 0.05$ was considered for all statistical evaluations.

2.5 Chemometrics

Spectral data were processed and subjected to chemometric analysis using Pirouette 4.5 (Infometrix, Inc., Bothell, WA, USA). PCA Principal Component Analysis (PCA) is a multivariate method frequently employed to diminish the dimensionality of extensive datasets. It converts the original variables into a new collection of uncorrelated variables, called principal components, which are expressed as linear combinations of the original data. These components capture the highest achievable variance in the dataset using the minimal number of factors. PCA is most effective when the variables in the dataset exhibit strong positive or negative correlations, enabling the method to reduce the data into fewer significant dimensions.

PCA, being an unsupervised method, is frequently employed prior to calibration modeling to find outliers, detect spectra influenced by unidentified errors, and analyze natural clustering within the data [41]. This study employed PCA to investigate whether samples of grape pomace powder displayed any intrinsic grouping and to determine the parameters responsible for such clustering before performing PLSR analysis.

2.5.1 PLSR

Partial Least Squares Regression (PLSR) is a supervised multivariate analytical method that integrates elements of both Principal Component Analysis (PCA) and Multiple Linear Regression (MLR). PLSR models the link between spectral data and reference values, accommodating variability from both instrumental measurements and reference assays. Due to its capacity to manage highly collinear and high-dimensional data, it has emerged as a standard instrument in both academic research and industrial applications for quantitative model building [42]. Instead of using thousands of spectral variables directly, PLSR extracts a limited number of latent variables, called PLS factors, which capture the relevant information needed to explain the variation in the dataset and to predict the reference parameters [43]. In most cases, fewer than 10 PLS factors are sufficient to build robust models.

In this study, calibration models were developed using all 24 grape pomace powder samples (48 spectra). Model performance was evaluated using internal cross-validation with the leave-one-out approach. In this procedure, the spectrum of one sample was excluded from the calibration set, and its reference value was predicted using the remaining 47 samples. This process was repeated until every sample had been left out once, allowing for the calculation of cross-validation statistics, including the standard error of cross-validation (SECV) and the correlation coefficient of cross-validation (rCV).

Complete NIR spectral region (10,000–4,000 cm^{-1}) was first incorporated in the model building. Regions with insufficient signal-to-noise ratios or absent pertinent spectral information were eliminated to enhance robustness. The evaluation of model performance was conducted using calibration statistics (SEC, rCal), cross-validation statistics (SECV, rCV), and diagnostic instruments, including loading plots and leverage values, to identify probable outliers. Outlier samples exhibiting high leverage were re-evaluated, and models were recalibrated as necessary. The precision of the calibration models was also assessed by correlation coefficients: Values ranging from 0.50 to 0.65 signify the capacity to differentiate between high and low concentrations, 0.66 to 0.81 imply approximate quantitative predictions, 0.82 to 0.90 indicate acceptable quantitative accuracy, and values exceeding 0.91 exhibit exceptional predictive capability [44].

3 Results and discussions

3.1 Reference analyses

The results of the reference chemical analyses for the 24 grape extracts (9 from red/pink grapes and 15 from purple/black grapes) are shown in Table 1. All measurements were performed in duplicate, and the data are reported with mean±standard deviations per sample as well as minimum, maximum, and average values for the groups of red/pink and purple/black grape groups.

Anthocyanins are water-soluble flavonoids responsible for the red to blue pigmentation in many fruits and are valued not only as natural colorants but also for their strong antioxidant and therapeutic properties [45]. In grapes, these compounds are concentrated mainly in the skins, while other phenolics such as proanthocyanidins and flavonols are also present in skins and seeds [46]. In this study, the monomeric anthocyanin content of grape pomace extracts ranged from 7.44 to 144.0 mg cyn-3-glu/100 g (Table 1). Red–pink grapes contained considerably lower anthocyanin levels compared with purple–black grapes, which is consistent with their pigmentation ($p < 0.05$). Documented values in the literature exhibit considerable variability in specific red varieties [47], underscoring the impact of grape cultivar and extraction techniques. Statistical analysis confirmed that the differences observed between red–pink and purple–black grapes were significant ($p < 0.05$).

The total phenolic content of the grape pomace extracts is presented in Table 1. Values ranged from 1115 to 4813 mg GAE/100 g DM across all samples. The mean phenolic content of red–pink grape pomace (≈1586 mg) was statistically lower than that of purple–black pomace (≈2485 mg), indicating a significant difference between the two groups ($p < 0.05$). This color-dependent variation aligns with the increased accumulation of polyphenols, particularly anthocyanins, in darker grape cultivars. In comparison to prior investigations, the phenolic levels recorded in this research were lower than the level reported by Hubner [7], who measured 141.1 mg GAE/g DM in Cabernet Sauvignon pomace. On the other hand, our results were higher than that of reported by Zhao [48]. In that study, the total phenolic content of red grape pomace was reported as 757.36 mg/GAE per 100 g. This discrepancy among studies may be attributed to grape cultivar, agronomic circumstances, harvest ripeness, and methodological variations in extraction and analysis.

Flavonoids are a heterogeneous collection of low molecular weight secondary metabolites characterized by potent antioxidant properties and other biological effects, including anti-inflammatory, antibacterial, and anticancer

activities [49-50]. In grapes, soluble phenolics are predominantly found in the skins, seeds, and stems, constituting one of the most concentrated natural sources [51]. The total flavonoid content of grape pomace extracts in the present study varied from 8.05 to 40.75 mg QE/100 g DM (Table 1). Red–pink grape samples had lower flavonoid levels than purple–black samples, yet the difference was not statistically significant. Prior research has indicated a diverse spectrum of flavonoid concentrations in grape pomace and associated matrices. Iora et al. [52] quantified 21.21 mg of catechin per gram in Merlot, 16.48 mg of catechin per gram in Tannat, and 29.83 mg of catechin per gram in Cabernet Sauvignon pomace. Makris et al. [53] reported 52.89 mg of catechin per gram in red grape pomace, whereas Yılmaz [54] recorded 17.59 mg of catechin per gram in mixed grape pomace. In other matrices, Darıcı [55] documented quercetin concentrations ranging from 58.95 to 135.72 mg/L in red wine, whereas Kasırga [56] noted 2.44 mg quercetin per 100 mL in black grape pomace extracts. In comparison to these findings, the flavonoid levels identified in the current research align with the extensive range published in the literature, despite some values varying remarkably. These variances are likely attributable to changes in grape cultivar and maturity, climatic and agronomic circumstances, and differences in extraction or analytical methodologies.

According to our results, the proanthocyanidin content of grape pomace extracts ranged from 326 to 1890 mg cyanidin equivalents/100 g DM (Table 1). On average, red–pink grape samples contained lower levels than purple–black samples.

Antioxidants are compounds present in small amounts in foods that can prevent, delay, or control the oxidation of food constituents, thereby reducing spoilage and extending shelf life [57]. Phenolic chemicals in plant-based extracts are the primary contributors to antioxidant activity, as they may neutralize free radicals and limit lipid oxidation in food [58-59]. The DPPH test is one of the most frequently utilized procedures due to its sensitivity and simplicity. This approach involves the reduction of the deep purple DPPH radical to a pale yellow hydrazine upon reaction with an antioxidant that can donate a hydrogen atom. This study evaluated the antioxidant activity of grape pomace extracts utilizing DPPH and CUPRAC tests. The IC_{50} values for DPPH varied between 0.44 and 1.39 mg/mL. Red-pink grape extracts had values comparable to those of purple-black grapes, with no statistically significant difference between the two groups. For CUPRAC, results ranged from 3576 to 13279 mg TE/100 g, with red–pink grape extracts typically demonstrating decreased antioxidant capacity compared to purple–black grapes. In this case, statistical analysis confirmed a significant difference between the two groups (p <0.05). When compared with literature values, our findings fall within the broad range reported for grape pomace and related products. Yılmaz [54] measured IC_{50} values of µg/mL in grape pomace, and Rockenbach et al. [60] reported 188–505 µmol/g in Bordeaux, Merlot, Cabernet Sauvignon, and Isabel red grape pomace. Luchian et al. [61] recorded quantities ranging from 98.1 to 144.9 µg/mL in red grape pomace extracts, whereas Bozan et al. [62] documented amounts between 2.71 and 4.62 µg/mL in grape seeds. Although some of our findings were inferior to previously recorded values, the general trends corresponded with established research, suggesting that darker-hued grapes generally had superior antioxidant properties due to their higher amounts of phenolics and anthocyanins.

In light of the reference data, pomace samples in this study were dried at 60°C to provide stable and uniform powders appropriate for grinding and NIR analysis. This method ensures microbiological safety, consistent particle size, and reliable spectral measurements; however, it is important to recognize that extended drying at elevated temperatures may result in the partial degradation of heat-sensitive compounds, notably anthocyanins and specific flavonoids. The quantified phenolic content and antioxidant capacity may reflect diminished values compared to those found in fresh pomace. Nonetheless, this processing step was essential to provide uniformity in sample handling and to enable reliable chemometric modeling.

3.2 NIR spectra of the samples

The overlaid NIR spectra of grape pomace powders exhibited several characteristic absorption bands consistent with previous reports on pomace matrices [63-65]. In the high-wavenumber region (9000–8000 cm^{-1}), absorptions were associated with the second overtone of –CH, $–CH_2$, and $–CH_3$ vibrations, reflecting contributions from carbohydrates and lipids. A broad band between 7622 and 6507 cm^{-1} corresponded to the second overtone of –OH stretching, mainly attributed to water and hydroxyl groups in phenolic compounds. Distinct absorptions between 6000 and 5600 cm^{-1} were assigned to the first overtones of –CH, $–CH_2$, and $–CH_3$, again linked to carbohydrates and lipids. The band at 5350–5000 cm^{-1} was related to the overtone and combination modes of –OH vibrations from water molecules. In the region between 5000 and 4500 cm^{-1}, the absorptions originated from –NH, –CHO, and –NH/–CH combination bands, indicating the presence of proteins and carbohydrate structures. Finally, the intense features between 4400 and 4200 cm^{-1} were attributed to –CH, $–CH_2$, and $–CH_3$ combination bands, which are also characteristic of lipids and carbohydrates. Collectively, these spectral classifications emphasize the chemical complexity of grape pomace, illustrating the roles of water, phenolics, carbohydrates, proteins, and lipid components.

Following normalization and SNV transformation, baseline variation in grape pomace spectra was reduced, thereby enhancing the visibility of minor compositional differences among samples. Significant differences were observed in particular spectral regions. Variability in the second overtone of –CH, $–CH_2$, and $–CH_3$ vibrations was observed in the high-wavenumber region (9000–8000 cm^{-1}), indicating differences in carbohydrate and lipid content among samples. Further separation was observed between 7622 and 6507 cm^{-1}, indicative of the second overtone of –OH stretching, which demonstrates variability in moisture content and hydroxyl groups derived from phenolics.

Table 1. Results of the reference chemical analyses of the samples

Sample	Color	Total Phenolics (mg GAE/100 g)	Total Flavonoids (mg QE/100 g)	Monomeric Anthocyanins (mg cyn-3-glc/100 g)	Proanthocyanidins (mg CE/100 g)	DPPH (EC_{50}. mg/ mL)	CUPRAC (mg TE/100 g)
G1		1744.51±31.26	12.21±0.22	23.12±3.87	685.30±1.06	0.68±0.01	6116.83±37.18
G2		2653.11±29.77	40.75±0.18	38.53±0.22	1252.33±1.13	0.61±0.00	9568.87±108.48
G3		2124.70±27.32	11.24±0.32	27.95±0.61	980.86±6.42	0.66±0.00	8682.75±122.35
G4		1717.07±37.46	12.92±0.10	12.92±2.61	661.86±9.76	0.68±0.00	6729.41±143.58
G5	Pink/Red	1189.74±21.66	10.29±0.30	7.93±1.36	499.50±7.53	0.73±0.01	4132.21±4.41
G6		1409.36±36.68	12.11±0.07	14.43±0.61	598.12±13.23	0.65±0.01	5086.26±50.86
G7		1195.82±60.34	8.05±0.19	7.44±1.11	537.41±6.26	0.67±0.01	3970.53±18.83
G8		1121.23±60.06	15.25±0.27	8.87±2.00	358.42±0.20	1.03±0.00	3575.69±7.95
G9		1115.52±60.06	12.96±0.12	8.93±2.37	325.49±6.25	1.04±0.02	3812.47±144.29
MIN.		1115.52	8.05	7.44	325.49	0.61	3575.69
MAX.		2653.11	40.75	38.53	1252.33	1.04	9568.87
MEAN		1585.673**A**	15.09	16.68**A**	655.48	0.75	5741.67**A**
G10		2164.25±37.42	28.46±0.47	97.97±0.10	736.42±5.79	0.70±0.01	6611.17±129.07
G11		3892.82±42.93	27.30±0.41	143.99±0.25	1457.71±13.75	0.48±0.00	11868.10±161.99
G12		1832.74±74.68	26.97±0.12	127.19±0.08	1630.30±19.12	0.48±0.00	12257.10±230.29
G13		3634.23±0.83	27.35±0.71	119.78±4.43	1317.35±19.57	0.61±0.01	13278.54±64.28
G14		2178.88±66.99	17.89±0.37	65.88±2.46	699.86±1.95	0.69±0.00	6668.40±3.05
G15		4813.00±42.59	37.82±0.48	93.95±1.35	1890.08±1.37	0.44±0.00	12112.34±98.37
G16		3692.94±2.80	18.01±0.11	25.55±2.49	1321.23±18.10	0.70±0.01	10351.03±27.88
G17	Purple/Black	2302.55±39.04	16.64±0.67	98.13±0.49	789.74±13.33	0.73±0.02	7458.80±80.52
G18		1182.04±78.41	19.20±0.15	95.94±6.90	938.71±0.54	0.74±0.01	8758.48±34.38
G19		2233.90±48.83	19.44±0.00	57.48±0.43	888.37±12.10	0.95±0.01	8739.86±104.35
G20		2878.32±66.92	12.75±0.38	34.92±2.96	432.55±6.54	0.90±0.02	4340.65±38.23
G21		1492.66±51.73	12.42±0.14	46.31±5.50	487.96±3.47	0.68±0.01	3956.67±122.70
G22		1772.49±35.84	14.54±0.45	47.61±0.52	619.62±4.20	1.39±0.01	6111.18±66.85
G23		1316.51±25.47	25.24±0.52	88.00±2.16	1042.82±8.99	0.73±0.01	9136.27±164.06
G24		1888.18±41.83	12.86±0.21	59.19±1.34	647.77±5.04	0.98±0.00	6015.80±71.89
MIN.		1182.04	12.42	25.55	432.55	0.44	3956.67
MAX.		4813	37.82	143.99	1890.08	1.39	13278.54
MEAN		2485.034**B**	21.13	80.13**B**	991.366	0.75	8510.96**B**

Note: Different superscript letters within the same column indicate statistically significant differences ($p < 0.05$).

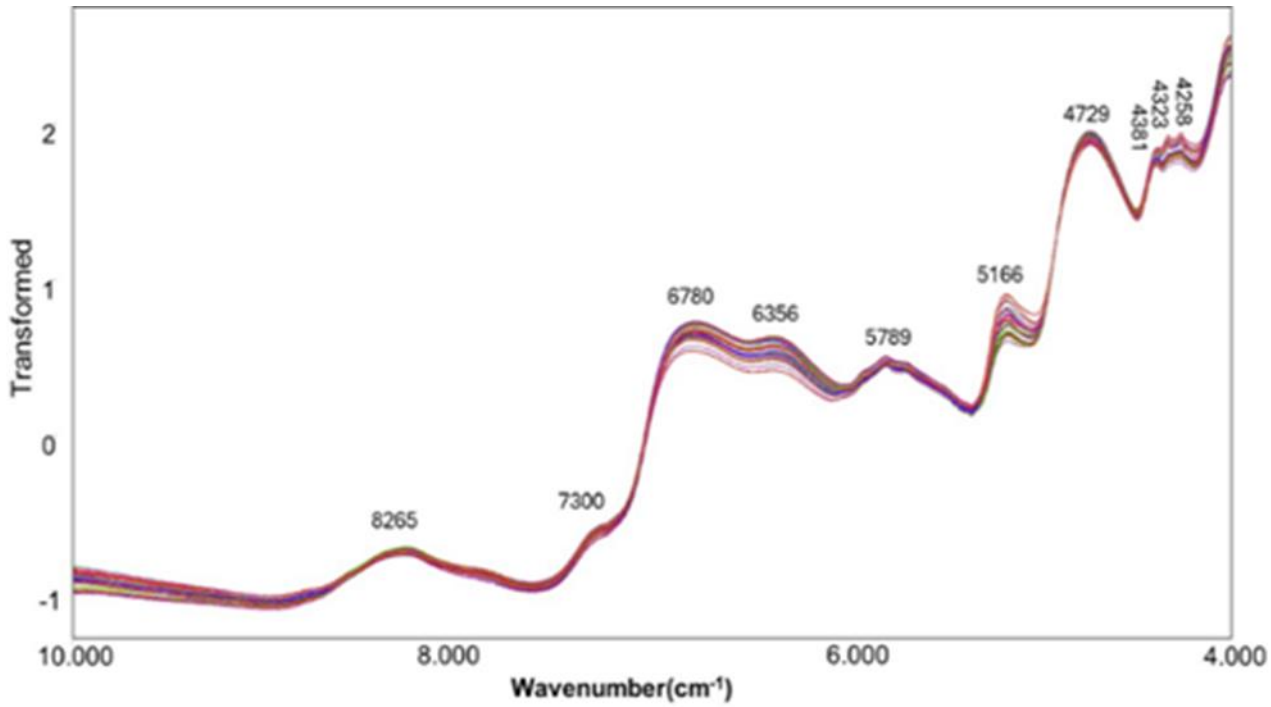

Figure 2. Overlaid mean-centered and Standard Normal Variate (SNV)-corrected NIR spectra of all grape pomace samples

Divergence was observed in the 6000–5600 cm^{-1} region, attributed to the first overtones of CH, $–CH_2$, and $–CH_3$, indicating variations in sugar- and lipid-related constituents. Detectable variations were noted in the 5350–5000 cm^{-1} band, attributed to –OH overtones from water molecules, and in the 5000–4500 cm^{-1} region, linked to –NH, –CHO, and –NH/–CH combinations that indicate the presence of proteins and carbohydrate structures. Differences between 4400 and 4200 cm^{-1}, which correspond to –CH, $–CH_2$, and $–CH_3$ combination bands, also contributed to the clustering of samples. The variations collectively highlight the natural diversity of grape pomace regarding water, phenolics, carbohydrates, proteins, and lipid fractions [63-65].

3.3 PCA Analysis

PCA was utilized to illustrate the variation in NIR spectra of grape pomace powders. The first three principal components represented 95.1% of the total variance, with PC1 contributing 73.4%. The PCA score plot (Figure 3) demonstrated a distinct separation between samples from pink/red grapes and those from purple/black grapes. The clustering indicates that spectral variability is significantly affected by grape color, aligning with variations in anthocyanin concentration and overall phenolic composition. The distinct grouping pattern indicates that PCA can effectively capture natural chemical variation within grape pomace samples and serves as a useful preliminary step before quantitative PLSR modeling.

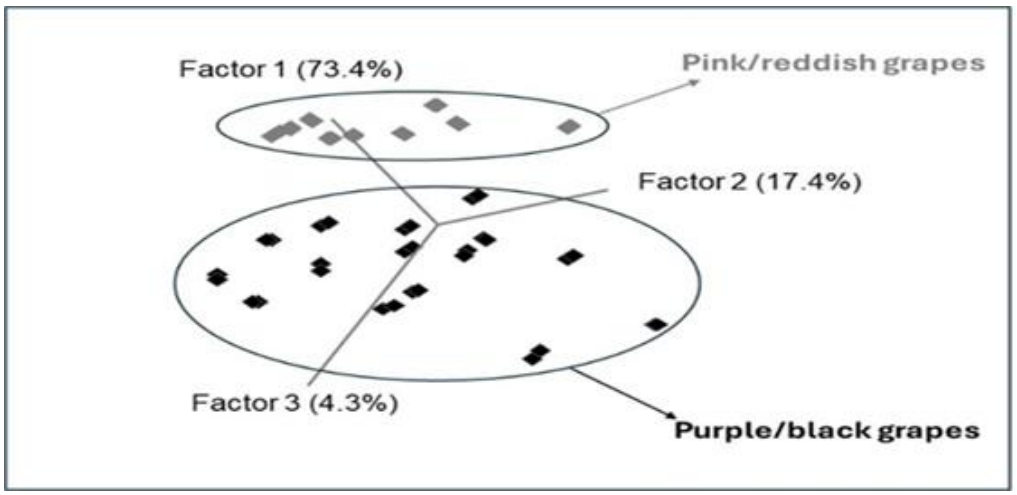

Figure 3. PCA Scores of all grape pomace samples

3.4 PLSR models

The PLSR calibration models constructed from NIR spectra of grape pomace powders demonstrated strong predictive performance across all bioactive compounds investigated (Table 2). Y-plots for the developed PLSR models are also shown in Figure 4, indicating the good correlations between the results of the reference analyses and NIR-predicted levels of the parameters of interest. The total monomeric anthocyanins varied from 7.44 to 144 mg cyn-3-glu/100 g. The models demonstrated a strong fit, with calibration and cross-validation coefficients of 0.99 and prediction errors of SEC = 1.42 and SECV = 5.29 mg cyn-3-glu/100 g. The total phenolic content ranged from 1115 to 4813 mg GAE/100 g and was accurately predicted, achieving rCal = 0.99 and rCV = 0.95, with a SEC of 118 and a SECV of 293 mg GAE/100 g. Total flavonoids and proanthocyanidins were modeled with significant predictive accuracy, exhibiting rCV values of 0.95 and 0.98, respectively, along with relatively low error rates.

Antioxidant capacity assays produced some of the strongest results: CUPRAC, which varied from 3576 to 13279 mg TE/100 g, achieved rCal = 0.99, rCV = 0.98, and SECV = 548 mg TE/100 g, while DPPH provided near-perfect performance (rCV = 0.99; SECV = 0.020 mg IC_{50}). Together, these results confirm that NIR–PLSR can be used as an alternative tool to predict phenolic and antioxidant properties in grape pomace.

When compared with previous research, our findings are largely consistent with earlier reports on grapes and winemaking by-products. Ferrer-Gallego et al. [66] utilized NIR spectroscopy in conjunction with modified PLSR on whole grapes and grape skins, achieving high coefficients of determination ($R^2 > 0.95$) for anthocyanins, flavonols, and total phenolics. Consistent with their findings, the models in this study likewise demonstrated robust calibration and validation, utilizing dried pomace powders instead of fresh fruits.

While they observed better models for intact grapes than isolated skins, our work shows that even processed pomace retains sufficient spectral information for accurate phenolic prediction. Comparable trends have been noted in vineyard applications. Rouxinol et al. [31] indicated that portable NIR instruments effectively predicted anthocyanins, tannins, and berry ripeness indices; however, their models for total phenolics and flavonoids exhibited lower performance (R^2 = 0.7). In contrast, the benchtop FT-NIR analyses of pomace powders in this work produced significantly more robust models (rCV > 0.95). The elevated concentration and uniformity of dried pomace, along with the superior resolution of the benchtop instrument relative to the handheld device, clearly enhanced this performance.

Our results align with the conclusions of Cozzolino et al. [67], who examined the application of NIR spectroscopy throughout the grape and wine production chain and highlighted PLSR as the favored chemometric method for compositional analysis. Their review emphasized the effective applications of sugars, acids, anthocyanins, and other principal components in grapes and wines, while also identifying problems associated with matrix variability, water absorption, and sample presentation. This study centered on grape pomace powders, a more uniform and concentrated matrix, which likely enhanced the robust calibration and validation performance noted for phenolics and antioxidant activity. Our results support the view stated by Cozzolino and colleagues [67] that vibrational spectroscopy offers great promise as a rapid, cost-effective, and versatile tool not only for traditional wine quality assessment but also for the valorization of processing side streams.

Direct comparisons with pomace studies further reinforce our conclusions. Páscoa et al. [65] revealed that ground pomace yielded more robust PLSR models for total phenolics and anthocyanins (R^2 reaching 0.97) in contrast to raw pomace, highlighting the significance of sample uniformity. Our use of dried powders aligns with their findings and may explain the high predictive performance observed. More recently, Páscoa et al. [65] applied NIR–PLS to olive pomace and achieved strong models for compositional traits but weaker predictions for antioxidant capacity (R^2 of ≈ 0.5–0.6), requiring the use of PLS-DA for classification. In contrast, our study achieved high predictive accuracy for both phenolics and antioxidant assays using PLSR alone, suggesting that grape pomace is a more favorable substrate for spectroscopic prediction than olive pomace, where oil content and cultivar variability complicate modeling.

Overall, these comparisons show that our results not only confirm earlier evidence for the feasibility of NIR–PLSR in its applicability to grape pomace, supporting its valorization as a sustainable source of phenolic compounds and antioxidants.

Table 2. Overview of the prediction performance of the developed PLSR models

Analyte	Concentration Range	Spectral Range (cm^{-1})	Factor	rCal	SEC	rCV	SECV
Total Monomeric Anthocyanins (mg cyn-3-glu/100 g)	7.44-144	10,000-4,000	11	0.99	1.42	0.99	5.29
Total Phenolics (mg GAE/100 g)	1115-4813	10,000-4,000	10	0.99	118	0.95	293
Total Flavonoids (mg QE/100 g)	8.05-40.7	10,000-4,000	11	0.99	0.76	0.95	2.32
Proanthocyanidins (mg CE/100 g)	325-1890	10,000-4,000	11	0.99	29.3	0.98	77.4
CUPRAC (mg TE/100 g)	3576-13279	10,000-4,000	11	0.99	226	0.98	548
DPPH (mg IC_{50})	0.44-1.39	8,384-4,101	10	0.99	0.011	0.99	0.020

SEC (Standard error in calibration), SECV (Standard error in cross-validation), SEP (Standard error in external validation), rCal (Correlation coefficient in calibration), rCV (Correlation coefficient in cross-validation

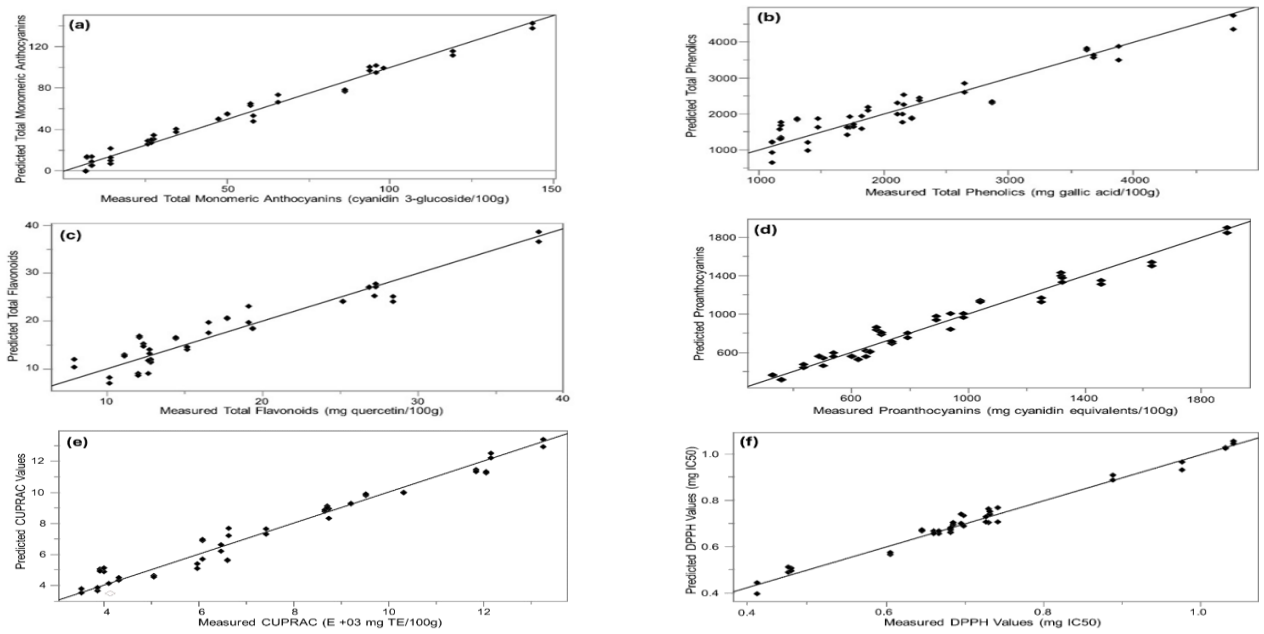

Figure 4. Y Plots of the PLSR models for benchtop FT-NIR detection of **(a)** total monomeric anthocyanins, **(b)** total phenolics, **(c)** total flavonoids, **(d)** proanthocyanidins, **(e)** CUPRAC and **(f)** DPPH values

4 Conclusions

This study demonstrated that NIR spectroscopy combined with PLSR can be effectively applied to quantify phenolic compounds and antioxidant capacity in grape pomace powders. Robust calibration and validation outcomes were achieved for total phenolics, flavonoids, proanthocyanidins, anthocyanins, and antioxidant tests (CUPRAC and DPPH), substantiating the efficacy of this methodology as a quick and non-invasive substitute for traditional chemical techniques. These findings emphasize the significance of grape pomace as a valuable source of bioactive chemicals, supporting its utilization in food, nutraceutical, and cosmetic applications.

Nonetheless, certain limits should be recognized. The quantity of samples, especially the ratio of pink/red to purple/black grape pomaces, should be increased in further investigations. This will facilitate the creation of distinct calibration models for each group, offering insights into the impact of grape color on prediction accuracy, and permit the incorporation of an independent external validation set to further evaluate model robustness and generalizability. This investigation involved drying pomace samples at 60°C to produce stable and uniform powders for NIR measurements. Although this assured microbiological safety, consistent particle size, and reproducible spectra, extended drying at high temperatures may have partially degraded heat-sensitive chemicals, such as anthocyanins and flavonoids, resulting in reduced observed values relative to fresh pomace. Subsequent studies should thus integrate both fresh and fermented pomace, along with ethanolic extracts, to assess potential variations in spectral behavior and model efficacy. Furthermore, integrating NIR with supplementary techniques like MIR spectroscopy could enhance the prediction of bioactive substances.

Collectively, these findings demonstrate the potential of NIR spectroscopy as a sustainable and scalable method for valorizing grape by-products, while also setting up opportunities for further model development through expanded sample sizes, diverse pomace types, and multi-spectral techniques.

Acknowledgement

This work was supported by the COST Action CA22134 (Sustainable Network for Agrofood Loss and Waste Prevention, Management, Quantification and Valorisation (FoodWaStop)) through a Short-Term Scientific Mission (STSM), which provided financial and institutional support for the implementation of this study. During the preparation of this work, the authors used Chat GPT/OpenAI for language editing and improvement purposes only. After using these tools, the authors carefully reviewed and manually edited the content as needed and take full responsibility for the content of the publication.

Conflict of interest

The authors declare that there is no conflict of interest.

Benzerlik oranı (iThenticate): 13%

References

[1] J. Wen, Vitaceae. In: K. Kubitzki (Ed.). The Families and Genera of Vascular Plants. Volume IX: Flowering Plants-Eudicots, 467-479. Springer-Verlag, Berlin, 2007.

[2] M. J. Abarghuei, Y. Rouzbehan and D. Alipour, The influence of the grape pomace on the ruminal parameters of sheep. Livestock Science, 132, (1-3), 73-79, 2010. https://doi.org/10.1016/j.livsci.2010.05.002.

[3] K. L. Christ and R. L. Burritt, Critical environmental concerns in wine production: an integrative review.

Journal of Cleaner Production, 53, 232-242, 2013. https://doi.org/10.1016/j.jclepro.2013.04.007.

[4] P. Cuccia, Ethics+ economy+ environment= sustainability: Gambero Rosso on the front lines with a new concept of sustainability. Wine Economics and Policy, 4 (1), 69-70, 2015. https://doi.org/10.1016/j.wep.2015.05.003.

[5] TÜİK, Meyveler, içecek ve baharat bitkileri üretim miktarları. https://data.tuik.gov.tr/Bulten/Index?p=Bitkisel-Uretim-Istatistikleri-2022- 45504, (Erişim Tarihi: Temmuz, 2023).

[6] A. Cerda-Carrasco, R. Lopez-Solis, H. Nunez-Kalasic, A. Pena-Neira and E. Obreque-Slier, Phenolic composition and antioxidant capacity of pomaces from four grape varieties (*Vitis vinifera* L.). Journal of the Science of Food and Agriculture, 95 (7), 1521-1527, 2015. https://doi.org/10.1002/jsfa.6856.

[7] A. Hubner, F. Sobreira, A. Vetore Neto, C. Pinto, M. F. Dario, I. Díaz, F. R. Lourenço, C. Rosado, A. R. Baby and E. M. Bacchi, The synergistic behavior of antioxidant phenolic compounds obtained from winemaking waste's valorization, increased the efficacy of a sunscreen system. Antioxidants, 8, (11), 530, 2019. https://doi.org/ 10.3390/antiox8110530.

[8] A. R. Fontana, A. Antoniolli and R. Bottini, Grape pomace as a sustainable source of bioactive compounds: extraction, characterization, and biotechnological applications of phenolics. Journal of Agricultural and Food Chemistry, 61 (38), 8987-9003, 2013. https://doi.org/ 10.1021/jf402586f.

[9] M. Bordiga, F. Travaglia and M. Locatelli, Valorisation of grape pomace: an approach that is increasingly reaching its maturity. International Journal of Food Science and Technology, 54 (4), 933-942, 2019. https://doi.org/ 10.1111/ijfs.14118.

[10] R. Marchiani, M. Bertolino, S. Belviso, M. Giordano, D. Ghirardello, L. Torri, M. Piochi and G. Zeppa, Yogurt enrichment with grape pomace: Effect of grape cultivar on physicochemical, microbiological and sensory properties, Journal of Food Quality, 39 (2), 77-89, 2015. https://doi.org/10.1111/jfq.12181.

[11] S. Kallithraka, J. Bakker and M. N. Clifford, Evidence that salivary proteins are involved in astringency. Journal of Sensory Studies, 13, 29-43, 2007. https://doi.org/10.1111/j.1745-459X.1998.tb00073.x.

[12] R. Boulton, The copigmentation of anthocyanins and its role in the color of red wine: a critical review. American Journal of Enology and Viticulture, 522 (2), 67-87, 2001. https://doi.org/10.5344/ajev.2001.52.2.67.

[13] M. Gómez-Míguez, S. González-Manzano, M. T. Escribano-Bailón, F. J. Heredia and C. Santos-Buelga, Influence of different phenolic copigments on the color of malvidin 3-Glucoside. Journal of Agricultural and Food Chemistry, 54 (15), 5422-5429, 2006. https://doi.org/ 10.1021/jf0604586.

[14] S. Preys, G. Mazerolles, P. Courcoux, A. Samson, U. Fischer and M. Hanafi, Relationship between polyphenolic composition and some sensory properties in red wines using multiway analyses. Analytica Chimica Acta, 563 (1), 126-136, 2006. https://doi.org/10.1016/j.aca.2005.10.082.

[15] S. Kataria and F. I. Shaikh, Design of drying chamber for grape drying and drying process. Bav Food World, 34, 56–60, 2007.

[16] K. Dwyer, F. Hosseinian and M. R. Rod, The market potential of grape waste alternatives. Journal of Food Research, 3 (2), 91-91, 2014. https://doi.org/10.5539/jfr.v3n2p91.

[17] A. Rózek, I. Achaerandio, C. Güell, F. López and M. Ferrando, Use of commercial grape phenolic extracts to supplement solid foodstuff. LWT-Food Science and Technology, 43 (4), 623-631, 2010. https://doi.org/10.1016/j.lwt.2009.11.002.

[18] F. B. Shinagawa, F. C. D. Santana, L. R. O. Torres and J. Mancini-Filho, Grape seed oil: a potential functional food. Food Science and Technology, 35 (3), 399-406, 2015. https://doi.org/10.1590/1678-457X.6826.

[19] J. Shi, J. Yu, J. Pohorly, J. C. Young, M. Bryan and Y. Wu, Optimization of the extraction of polyphenols from grape seed meal by aqueous ethanol solution. Food, Agriculture & Environment, 1 (2), 42-47, 2003.

[20] M. M. Selani, C. J. Contreras-Castillo, L. D. Shirahigue, C. R. Gallo, M. Plata-Oviedo and N. D. Montes-Villanueva, Wine industry residues extracts as natural antioxidants in raw and cooked chicken meat during frozen storage. Meat Science, 88, 397–403, 2011. https://doi.org/10.1016/j.meatsci.2011.01.017.

[21] M. Hayta, G. Özuğur, H. Etgü and I. T. Şeker, Effect of grape (Vitis vinifera L.) pomace on the quality, total phenolic content and anti-radical activity of bread. Journal of Food Processing and Preservation, 38 (3), 980-985, 2014. https://doi.org/ 10.1111/jfpp.12054.

[22] V. Sant'Anna, F.D.P. Christiano, and L.D.F. Marczak, The effect of the incorporation of grape marc powder in fettuccini pasta properties, LWT-Food Science Technology 58 (2), 497–501, 2014. https://doi.org/10.1016/j.lwt.2014.04.008.

[23] C. Beres, G. N. S. Costa, I. Cabezudo, N. K. da Silva-James, A. S. C. Teles, A. P. G. Cruz, C. Mellinger-Silva, R. V. Tonon, L. M. C. Cabral and S. P. Freitas, Towards integral utilization of grape pomace from winemaking process: A review. Waste Management, 68, 581–594, 2017. https://doi.org/10.1016/j.wasman.2017.07.017.

[24] J. Herrera, A. Guesalaga and E. Agosin, Shortwave near infrared spectroscopy for non-destructive determination of maturity of wine grapes. Measurement Science and Technology, 14 (5), 689-697, 2003. https://doi.org/10.1088/0957-0233/14/5/320.

[25] V. González-Caballero, M-T. Sánchez, M-I. López and D. Pérez-Marín, First steps towards the development of a non-destructive technique for the quality control of wine grapes during on-vine ripening and on arrival at the winery. Journal of Food Engineering, 101 (29, 158-

165, 2010. https://doi.org/10.1016/j.jfoodeng.2010.06.016.
[26] B. M. Nicolaï, K. Beullens, E. Bobelyn, A. Peirs, W. Saeys, K. I. Theron and J. Lammertyn, Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: A review. Postharvest Biology and Technology, 46 (2), 99-118, 2007. https://doi.org/10.1016/j.postharvbio.2007.06.024.
[27] K. Ali, F. Maltese, A. M. Fortes, M. S. Pais, Y. H. Choi and R. Verpoorte, Monitoring biochemical changes during grape berry development in Portuguese cultivars by NMR spectroscopy. Food Chemistry, 124 (4), 1760-1769, 2011. https://doi.org/10.1016/j.foodchem.2010.08.015.
[28] M. Blanco, and I. Villarroya, NIR spectroscopy: A rapid-response analytical tool. Trends in Analytical Chemistry, 21 (4), 240–250, 2002. https://doi.org/10.1016/S0165-9936(02)00404-1.
[29] C. M. McGoverin, J. Weeranantanaphan, G. Downey and M. Manley, Review: the application of near infrared spectroscopy to the measurement of bioactive compounds in food commodities. Journal of Near Infrared Spectroscopy, 18 (2), 87-111, 2010. https://doi.org/10.1255/jnirs.874.
[30] R. Gallego-Ferrer J. M. Hernandez-Hierro, J. C. Rivas-Gonzalo and M. T. Bailon-Escribano, Feasibility study on the use of near infrared spectroscopy to determine flavanols in grape seeds. Talanta 82 (5), 1778–1783, 2010. https://doi.org/10.1016/j.talanta.2010.07.063.
[31] M. I. Rouxinol, M. R. Martins, G. C. Murta, J. M. Barroso and A. E. Rato, Quality Assessment of RedWine Grapes through NIR Spectroscopy. Agronomy, 12 (3), 637, 2022. https://doi.org/10.3390/agronomy12030637.
[32] R. N. M. J. Pascoa, S. Machado, Magalhaes, L. M. Magalhaes and J. A. Lopes, Value Adding to Red Grape Pomace Exploiting Eco-friendly FT-NIR Spectroscopy Technique, Food Bioprocess Technology, 8, 865–874, 2014. https://doi.org/10.1007/s11947-014-1454-z.
[33] E. Whitacre, J. Oliver, R. van den Broek, P. van Engelen, B. Kremers and B. van der Horst, Predictive analysis of cocoa procyanidins using nearinfrared spectroscopy techniques. Journal of Food Science, 68, 2618-2622, 2006. https://doi.org/10.1111/j.1365-2621.2003.tb05779.x.
[34] Q. Chen, J. Zhao, M. Liu, J. Cai and J. Liu, Determination of total polyphenols content in green tea using FT-NIR spectroscopy and different PLS algorithms. Journal of Pharmaceutical and Biomedical Analysis, 46, 568-573, 2007. https://doi.org/10.1016/j.jpba.2007.10.031.
[35] M. M. Giusti and R. E. Wrolstad, ‘’Unit F1.2. Anthocyanins Characterizition and Measurement with UV-Visible Spectroscopy’’. R.E. Wrolstad and S.J. Schwartz (Eds) In: Current Protocols in Food Analytical Chemistry. (pp 1-13), John Wiley & Sons: New York, 2001.
[36] V. L. Singleton and J. A. Rossi, Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. American Journal of Enology and Viticulture, 16, 144-158, 1965. https://doi.org/10.5344/ajev.1965.16.3.144.
[37] C. C. Chang, M. H. Yang, H. M. Wen and J. C. Chern, Estimation of total flavonoid content in propolis by two complementary colorimetric methods, Journal of Food and Drug Analysis. 10 (3), 178-182, 2002. https://doi.org/10.38212/2224-6614.2748.
[38] T. Froehlicher, T. Hennebelle, F. Martin-Nizard, P. Cleenewerck, J-L. Hilbert, F. Trotin and S. Grec, Phenolic profiles and antioxidative effects of hawthorn cell suspensions, fresh fruits, and medicinal dried parts. Food Chemistry, 115 (3), 897– 903, 2009. https://doi.org/ 10.1016/j.foodchem.2009.01.004.
[39] R. Apak, K. Güçlü, B. Demirata, M. Özyürek, S. E. Çelik, B. Bektaşoğlu, K. I. Berker and D. Özyurt, Comparative evaluation of various total antioxidant capacity assays applied to phenolic compunds with the CUPRAC assay. Molecules, 12 (7), 1496-1547, 2007. https://doi.org/ 10.3390/12071496.
[40] S. Benvenuti, F. Pellati, M. Melegari and D. Bertelli, Polyphenols, anthocyanins, ascorbic acid and radical scavenging activity of rubus, ribes and aronia. Journal of Food Science, 69 (3), 164–169, 2006. https://doi.org/10.1111/j.1365-2621.2004.tb13352.x.
[41] I. T. Jolliffe and J. Cadima, Principal component analysis: a review and recent developments. *Philosophical transactions of the royal society A: Mathematical,* Physical and Engineering Sciences, 374 (2065), 20150202, 2016. https://doi.org/10.1098/rsta.2015.0202.
[42] S. Dejong, PLS fits Closer Than PCR. Journal Of Chemometrics, 7, 551–557, 1993. https://doi.org/10.1002/cem.1180070608.
[43] L. Moseholm, Analysis of air-pollution plant-exposure data-the softindependent modeling of class analogy (SIMCA) and partial least-squares modeling with latent variable (PLS) approaches. Environmental Pollution, 53 (1-4), 313–331, 1988. https://doi.org/10.1016/0269-7491(88)90043-7.
[44] P. C. Williams, Near-Infrared technology getting the best out of light. a short course in the practical İmplementation of Near Infrared Spectroscopy for the user. Canada, Nanaimo, 109, 2003.
[45] P. Denev, M. Ciz, G. Ambrozova, A. Lojek, I. Yanakieva and M. Kratchanova, Solid-phase extraction of berries’ anthocyanins and evaluation of their antioxidative properties, Food Chemistry, 123 (4), 1055-1061, 2010. https://doi.org/10.1016/j.foodchem.2010.05.061.
[46] C. Xu, Y. Zhang, L. Cao and J. Lu, Phenolic compounds and antioxidant properties of different grape cultivars grown in China, Food Chemistry, 119 (4), 1557-1565, 2010. https://doi.org/10.1016/j.foodchem.2009.09.042.
[47] M. Özden and H. Vardin, Şanlıurfa koşullarında yetiştirilen bazı şaraplık üzüm çeşitlerinin kalite ve

fitokimyasal özellikleri. Harran Üniversitesi Ziraat Fakültesi Dergisi, 13 (2), 1-27, 2009.
[48] X. Zhao, H. Zhu, G. Zhang and W. Tang, Effect of superfine grinding on the physicochemical properties and antioxidant activity of red grape pomace powders, Powder Technology 286, 838–844, 2015. https://doi.org/10.1016/j.powtec.2015.09.025.
[49] V. Georgiev, A. Ananga and Tsolova, Recent advances and uses of grape flavonoids as nutraceuticals. Nutrients, 6 (1), 391-415, 2014. https://doi.org/10.3390/nu6010391.
[50] M. J. Cho, L. R. Howard, R. L. Prior and J. R. Clark, Flavonoid glycosides and antioxidant capacity of various blackberry, blueberry and red grape genotypes determined by high-performance liquid chromatography/mass spectrometry. Journal of the Science of Food and Agriculture, 84 (13), 1771-1782, 2004. https://doi.org/10.1002/jsfa.1885.
[51] C. Conde, P. Silva, N. Fontes, A. C. P. Dias, R. M. Tavares, M. J. Sousa, A. Agasse, S. Delrot and H. Gerós, Biochemical changes throughout grape berry development and fruit and wine quality. Food, 1 (1), 1-22, 2007.
[52] S. R. F. Iora, G. M. Maciel, A. A. F. Zielinski, M. V. Silva, P. V. Pontes, C. W. I. Haminiuk and D. Granato, Evaluation of the bioactive compounds and the antioxidant capacity of grape pomace. International Journal of Food Science & Technology, 50, 62-69, 2014. https://doi.org/ 10.1111/ijfs.12583.
[53] D. P. Makris, G. Boskou and N. K. Andrikopoulos, Polyphenolic content and in vitro antioxidant characteristics of wine industry and other agri-food solid waste extracts. Journal of Food Composition and Analysis, 20 (2), 125-132, 2007. https://doi.org/10.1016/j.jfca.2006.04.010.
[54] B. Yılmaz, Üzüm posası ekstraktının nanofiber film üretiminde kullanım olanaklarının araştırılması. Yüksek Lisans Tezi, Erciyes Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı, Kayseri, Türkiye, 2024.
[55] B. Darıcı, Şarap üretiminde kükürtdioksite alternatif olabilecek farklı bitkisel ekstraktların şarap kalitesine etkileri. Yüksek Lisans Tezi, Ege Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı, İzmir, Türkiye, 2019.
[56] K. Kasırga, Karadut ve siyah üzüm posası katkılı sığır burgerlerin raf ömrü süresince kalite parametrelerindeki değişimin belirlenmesi. Yüksek Lisans Tezi, Selçuk Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı, Konya, Türkiye, 2024.
[57] A. Zeb, Concept, mechanism, and applications of phenolic antioxidants in foods. Journal of Food Biochemistry, 44 (1) 13394, 2020. https://doi.org/10.1111/jfbc.13394.
[58] G. Soudad, M. A. E. Faten, M. H. Emad and H. Doha, Antioxidant activity of phenolic compounds from different grape wastes. Food Processing and Technology, 5 (52), 100296, 2014. https://doi.org/10.4172/2157-7110.1000296.
[59] K. J. Olejar, A. Ricci, S. Swift, Z. Zujovic, K. C. Gordon, B. Fedrizzi, A. Versari and P. A. Kilmartin, Characterization of an antioxidant and antimicrobial extract from cool climate, white grape marc. Antioxidants, 8 (7), 232, 2019. https://doi.org/10.3390/antiox8070232.
[60] I. I Rockenbach, E. Rodrigues, L. V. Gonzaga, V. Caliari, M. I. Genovese, A. E. S. S. Gonçalves and R. Fett, Phenolic compounds content and antioxidant activity in pomace from selected red grapes (Vitis vinifera L. and Vitis labrusca L.) widely produced in Brazil. Food Chemistry, 127 (1), 174-179, 2011. https://doi.org/10.1016/j.foodchem.2010.12.137.
[61] C. E. Luchian, V. V. Cotea, L. Vlase, A. M. Toiu, L. C. Colibaba, I. E. Raschip, G. Nadaş, A. M. Gheldiu, C. Tuchiluş and L. Rotaru, Antioxidant and antimicrobial effects of grape pomace extracts. BIO Web of Conferences, 15, 04006, 2019. https://doi.org/10.1051/bioconf/20191504006.
[62] B. Bozan, G. Tosun and D. Özcan, Study of polyphenol content in the seeds of red grape (Vitis vinifera L.) varieties cultivated in Turkey and their antiradical activity, Food chemistry, 109 (2), 426-430, 2008. https://doi.org/ 10.1016/j.foodchem.2007.12.056.
[63] B. Muik, B. Lendl, A. Molina-Díaz, L. Pérez-Villarejo and M. J. Ayora-Cañada, Determination of oil and water content in olive pomace using near infrared and Raman spectrometry. A comparative study. Analytical and Bioanalytical Chemistry, 379 (1), 35-41, 2004. https://doi.org/10.1007/s00216-004-2493-5.
[64] A. S. Barros, A. Nunes, J. Martins and I. Delgadillo, Determination of oil and water in olive and olive pomace by NIR and multivariate analysis. Sensing and Instrumentation for Food Quality and Safety, 3 (3), 180-186, 2009. https://doi.org/10.1007/s11694-009-9083-3.
[65] R. N. Páscoa, M. A. Nunes, F. Reszczyński, A. S. Costa, M. B. P. Oliveira and R. C. Alves, Near infrared (NIR) spectroscopy as a tool to assess blends composition and discriminate antioxidant activity of olive pomace cultivars. Waste and Biomass Valorization, 12 (9), 4901-4913, 2021. https://doi.org/10.1007/s12649-021-01386-1.
[66] R. Ferrer-Gallego, J. M. Hernández-Hierro, J. C. Rivas-Gonzalo and M. T. Escribano-Bailón, Determination of Phenolic Compounds of Grape Skins during Ripening by NIRSpectroscopy. LWT- Food Science and Technology, 44 (4), 847-857, 2011. https://doi.org/10.1016/j.lwt.2010.12.001.
[67] D. Cozzolino, R. G. Dambergs, L. Janik, W. U. Cynkar and M. Gishen, Analysis of grapes and wine by near infrared spectroscopy. Journal of Near Infrared Spectroscopy, 14 (1), 279-289, 2006. https://doi.org/10.1255/jnirs.679.