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Analytical Techniques for the Authenticity Evaluation of Chokeberry, Blackberry and Raspberry Fruit Wines: Exploring FT-MIR Analysis and Chemometrics

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Abstract: The modern analytical technique of Fourier-transform mid-infrared spectroscopy (FT-MIR) has found its place in routine wine quality control. It allows rapid and nondestructive analysis, with easy sample preparation and without the need for chemical pretreatment or expensive reagents. The objective of this research was to apply these advantages to fruit wines in order to create a tool for the authentication of fruit wines produced from different fruit species (chokeberry, blackberry, and raspberry). The aim of this work was to establish a chemometric model from FT-MIR spectra and to find a "fingerprint" of specific fruit wines, enabling the classification of fruit wines by plant species. Physicochemical analysis of 111 Croatian fruit wine samples (38 liqueur fruit wines and 73 fruit wines) revealed content levels of the following parameters: alcoholic strength (5.0–15.2% vol.), total dry extract (60.4–253.3 g/L), total sugars (1.2–229.9 g/L), pH (3.13–4.98), total acidity (4.2–18.3 g/L) and volatile acidity (0.2–1.5 g/L). For statistical data processing, spectral ranges between 926 and 1450 cm^{-1} and between 1801 and 2951 cm^{-1} were used. The first principal component (PC1) explained 70.4% of the observed variation, and the second component (PC2) explained 16.7%, clearly separating chokeberry fruit wines from blackberry and raspberry fruit wines. Soft Independent Modeling Class Analogy (SIMCA) was performed following the development of a PCA model showing that the chokeberry and blackberry wine samples form clearly separated clusters. Key discriminators for classifying chokeberry vs. blackberry wines were identified at 1157, 1304, and 1435 cm^{-1}, demonstrating high discrimination power (DP 26, 17, and 14, respectively). FT-MIR spectroscopy, in combination with chemometric methods, has shown promising potential for the authenticity assessment of fruit wines.

Keywords: fruit wine authenticity; FT-MIR spectroscopy; physicochemical analysis; multivariate data analysis (PCA/SIMCA); chemometric modeling

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1. Introduction

The rights of consumers and food producers regarding food safety and traceability are set out in the European Union Regulation No. 178/2002 (Official Journal of EC, 2002) with the aim to prevent food adulteration and fraudulent or deceptive practices in food processing [1]. Like any other food product, fruit wines can be subject to falsification, such as the addition of exogenous alcohols, including rectified ethyl alcohol of grain origin [2], or by nondeclared or mislabeled fruit species that are cheaper or of poorer quality. It is important to emphasize that food adulteration misleads consumers and constitutes a criminal offense, representing a serious violation subject to legal sanctions. Such actions

not only compromise consumer protection but also undermine the integrity of food safety regulations [3].

Croatian legislation classifies fruit wines and establishes their quality requirements for market placement through the Wine Act [4] and the accompanying Ordinance on Winemaking [5]. These regulations ensure that fruit wines meet specific standards for production, quality, and marketing within Croatia.

In recent decades, traditional methods have been primarily used to control the quality of fruit wines, such as alcoholic strength, total dry extract, sugars, total acidity, volatile acidity, ash, and free and total sulfur dioxide. Moreover, Croatian national regulations mandate that these parameters are measured before releasing fruit wines to the market [5]. Although traditional methods are still used, new approaches that could improve the expensive and time-consuming methodologies are emerging in food authentication applications [6,7].

The authenticity of fruit juices is recognized as a major challenge for a rapidly growing and expanding industry [2,8–12], but research on the authenticity aspects of fruit wines is scarce [13–15] even though fruit wine production has been growing steadily in recent years [16]. The increased interest in human health, nutrition, and disease prevention has also led to a rise in consumer demand for functional drinks based on fruit sources, thus expanding the market for fruit wines [17].

To determine the authenticity of fruit wines, the same principles applied to fruit juices and other commodities can be used, combining chemical and multivariate statistical methods. The main prerequisite for developing robust classification models based on chemometrics is the establishment of larger databases that take into account all sources of variation, such as individual variability, variety or breed, feeding or fertilization practice, geographical location or climate, etc. [18]. To account for variability and obtain models with global applicability, large studies, where sample collection and analysis are conducted over multiple years and across different locations, need to be organized. Only with these databases can relevant compounds be routinely identified or quantified [6].

In recent years, the modern analytical technique FT-MIR (focused mainly on the mid-IR part of the electromagnetic spectrum—MIR) has found its place in the field of routine wine quality control, bringing numerous advantages. It allows for rapid, nondestructive analysis, with minimal sample preparation (only filtration), and requires no chemical pretreatment or expensive reagents. All these advantages can also be applied to fruit wines as well, with the exception of the commercial calibration sets, which have been developed for grape wines but not for fruit wines.

FT-MIR spectroscopy has also demonstrated great potential for various food authentication purposes, particularly in the area of alcoholic beverages and fermented products, milk and dairy products, honey and oil adulteration [6], and fruit juices such as pomegranate concentrate authentication [7].

Fruit wines differ from grape wines in taste and characteristics, often being sweeter and retaining much of the original fruit's aroma and color [19]. In recent years, there has been significant interest in fruit wines, driven by the increasingly diverse consumer demand for wines with various colors, flavors, and nutritional values, made possible by using different types of fruit [20]. In Eastern European countries, certain berry fruits have been of great importance, primarily used for the production of juices, jams, and wines on a large scale and also as a rich source of natural food pigments [21,22]. Berry fruit wines are a natural source of minerals and numerous bioactive plant compounds, such as polyphenols, which have a strong antioxidant potential [22–24]. Croatian fruit wines are available on the market in six categories: fruit wine, fruit wine from mixed fruits, liqueur fruit wine, aromatized fruit wine, sparkling fruit wine, and semi-sparkling fruit wine [5].

This research aims to develop a tool for authenticating fruit wines produced from different fruit species—black chokeberry (*Aronia melanocarpa*), blackberry (*Rubus* L. subgenus *Rubus* Watson), and raspberry (*Rubus idaeus*)—that can be applied to the quality and authenticity control of fruit wine production. The objective of this study was to establish a

model based on FT-MIR spectra in order to find a "fingerprint" of specific fruit wine and enable their classification according to plant species.

2. Materials and Methods

2.1. Samples

The samples investigated in this study were divided into the two most common categories in the Croatian market: fruit wines and liqueur fruit wines. According to the Ordinance on Winemaking [5], fruit wine must have a natural alcoholic strength of not less than 1.2% vol. and not more than 18% vol. The liqueur fruit wine category is characterized by the addition of fruit-derived alcohol and/or fruit brandy, fruit juice, and/or concentrated juice. The actual alcoholic strength of the liqueur fruit wine must be at least 13% vol., and the total alcoholic strength must not exceed 22% vol. [5].

A total of 111 Croatian fruit wine samples (Table 1) were analyzed as a part of the procedure of placing the wine on the Croatian market at the Center for Viticulture, Enology and Edible Oils Analysis within the Croatian Agency for Agriculture and Food (CAAF), the authorized institution responsible for carrying out this procedure in accordance with Croatian legislation. The wines analyzed in this study were those available under the legal framework established by the National Wine Act [4]. The selected set of samples consisted of 22 chokeberry, 84 blackberry, and 5 raspberry fruit wines, produced across eight different harvests (2017–2021) and classified into two product categories/types: liqueur fruit wine (n = 38) and fruit wine (n = 73).

Table 1. Fruit wine samples according to declared product type, fruit species, and vintage.

Wine Type	Species	Vintages					
		2017	2018	2019	2020	2021	Total
Liqueur fruit wine	Chokeberry	1	-	1	-	-	2
	Blackberry	-	2	15	7	7	31
	Raspberry	-	1	3	1	-	5
Fruit wine	Chokeberry	2	3	5	6	4	20
	Blackberry	-	4	19	21	9	53
Total		3	10	43	35	20	111

2.2. Physicochemical Methods

Alcoholic strength (% v/v) was determined by an electronic density meter coupled with a near-infrared (NIR) spectrometer (DMA 4500 and Alcolyzer, Patent Anton Paar® [25]; Anton Paar, Graz, Austria).

The official methods published in the Compendium of International Methods of Wine and Must Analysis (OIV) [26] were used to analyze total dry extract (OIV-MA-AS2-03B: R2012), pH (OIV-MA-AS313-15: R2011), total acidity expressed as malic acid (OIV-MA-AS313-01: R2015), volatile acidity expressed as acetic acid (OIV-MA-AS313-02: R2015), ash (OIV-MA-AS2-04: R2009), free (OIV-MA-AS323-04A1: R2018) and total sulfur dioxide (OIV-MA-AS323-04A2: R2018). Determination of total sugars was performed by the Rebelein method [27] modified for the Mettler Toledo T50 potentiometric titrator with combined platinum electrode for redox systems type DM 140-SC in KCl3 mol L^{-1}/AgCl sat. (Mettler Toledo, Greifensee, Swizterland).

The aforementioned methods were accredited in accordance with HRN EN ISO/IEC 17025:2017 [28], which confirms the laboratory's ability to perform valid and comparable testing results. The control charts of the appropriate reference materials were used throughout the study period to ensure the quality of measurement results.

2.3. FT-MIR Analysis

Each sample was analyzed using the FT-MIR technique, and the obtained spectra were statistically processed. FT-MIR analysis was performed by FT2 Winescan™ (Foss Electric, Hilleroed, Denmark). Sampling was conducted with an autosampler, using about 30 mL of sample for a triple measurement, including pre-flushing of the system. Spectra ranging from 926 to 5012 cm^{-1} (PIN: 240-1299) with a spectral resolution of 14 cm^{-1} were recorded at a sample temperature of 40 °C. Measurements were carried out in transmission at a defined optical path length of 37 µm using a CaF_2 cuvette [29]. The average of three replicates was used for further data processing.

Correction for background effects, such as water vapor in the instrument's optical pathway, was performed by measuring a standard (Zero Liquid Salt, Foss, Hilleroed, Denmark) prior to the sample measurement. The sample transmittance spectrum was then divided by the background transmittance spectrum obtained during the standard measurement. Background measurements were taken automatically against double-distilled water in 20-min intervals following system backflushing or after every set of 15 samples [29].

All spectra were expressed as a set of numerical values, representing a PIN multiplied by a factor of 3858 expressed in cm^{-1} [30]. A dataset from all spectra (cm^{-1}) was exported to Unscrambler 11.0 (64-bit) (Camo AS, Oslo, Norway).

Spectral profiles in the wavenumber range between 1450 and 1800 cm^{-1} and >2950 cm^{-1} did not carry any important information in the context of the wine analysis [31] and were therefore trimmed out.

2.4. Spectral Data Pretreatment

Due to the scattering of electromagnetic radiation in the MIR spectrum, nonlinearities, baseline shifts, and pronounced noise occur, making it necessary to preprocess the spectral data to achieve robust and accurate prediction results (models). The dataset correction was performed via a Multiplicative Scatter Correction (MSC) by Unscrambler 11.0 (64-bit) (Camo AS, Oslo, Norway).

2.5. Multivariate Data Analysis of FT-MIR Spectra

Principal Component Analysis (PCA) and Soft Independent Modeling Class Analogy (SIMCA) were performed by Unscrambler 11.0 (64-bit) (Camo AS, Oslo, Norway).

3. Results

3.1. Physicochemical Analysis

Investigated samples were tested as a part of the quality control procedure for placing fruit wine on the Croatian market, and the obtained results of the physicochemical tests are shown in Table 2. The range of alcoholic strength in all tested samples was between 5.0% vol. and 15.2% vol., with the widest range for chokeberry wines (5.0–13.5% vol.). The total dry extract, or dry matter, was found between 60.4 g/L in chokeberry wine and 253.3 g/L in blackberry wine. Sugars in this research are expressed as total sugars, with results found across a wide range (1.2–229.9 g/L), with the highest level observed in blackberry wine. The acidity of wine is primarily indicated by the pH value, which was found between 3.13 and 4.98. The total acidity (expressed as g of malic acid per L) of the tested samples ranged from 4.2 g/L in chokeberry wine to 18.3 g/L in blackberry wine. Volatile acidity (expressed as g of acetic acid per L) in tested fruit wines ranged between 0.2 g/L and 3.1 g/L, with only one sample exceeding the maximum permissible level of 1.5 g/L [5]. Obtained values of ash were from 1.8 g/L to 7.4 g/L. Sulfur dioxide in all samples was below the maximum permissible amount [5], which is 30 mg/L for free and 200 mg/L for total SO_2.

Table 2. Minimum and maximum values of the physicochemical testing of fruit wine samples (n = 111) according to fruit species.

Parameter	Chokeberry (Min–Max)	Blackberry (Min–Max)	Raspberry (Min–Max)
Alcoholic strength (% vol.)	5.0–13.5	8.7–15.2	13.4–14.6
Total dry extract (g/L)	60.4–247.6	61.6–253.3	99.8–166.8
Total sugars (g/L)	1.2–145.5	26.4–229.9	57.5–117.6
pH	3.64–4.98	3.13–3.65	3.24–3.32
Total acidity (g of malic acid/L)	4.2–8.7	6.2–18.3	8.2–17.6
Volatile acidity (g of acetic acid/L)	0.3–1.5	0.4–3.1	0.2–0.9
Ash (g/L)	2.6–7.4	1.8–5.1	2.0–4.3
Free sulfur dioxide (mg/L)	2–29	0–30	0–16
Total sulfur dioxide (mg/L)	7–135	7–195	26–88

3.2. Fourier-Transform Mid-Infrared Analysis

Samples of interest were analyzed in triplicate (n = 3), and the mean spectrum of each sample was calculated. Since MSC normalizes based on the mean spectrum of a dataset, it is best suited for similar sample sets, as used in this research. MSC is typically used to compensate for additive and/or multiplicative scatter effects in spectral data. A reference spectrum, which is the average of all input spectra, is fitted to each individual spectrum. The offset and slope of this function are used to correct the spectra. Figure 1 shows all collected spectra of the samples. For statistical data processing, the following spectral ranges were used: 926–1450 cm^{-1} and 1801–2951 cm^{-1}. The remaining part of the FT-MIR spectrum is considered irrelevant due to the excessive influence of water molecules on the signal saturation effect, and it was not used for further processing [31].

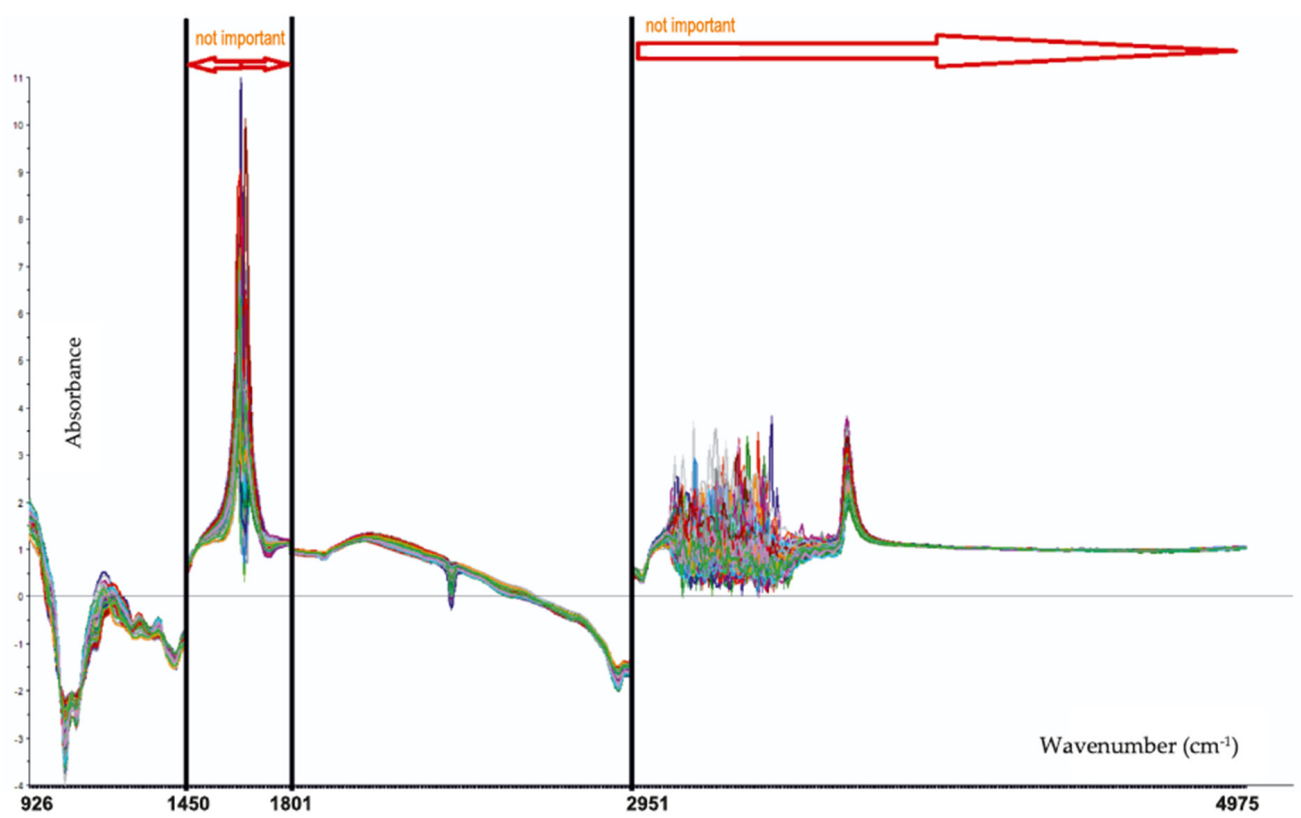

Figure 1. FT-MIR spectra of all samples. Spectral ranges used for statistical processing: 926–1450 cm^{-1} and 1801–2951 cm^{-1}. Different colors represent different samples.

3.3. Principal Component Analysis

Figure 2 shows a two-dimensional scatter plot of the scores for two specified components (PCs) from the PCA. The plot provides information about patterns in the samples. The scores plot for PC1 and PC2 is particularly useful, as these two components summarize more variation in the data than any other pair of components. The first principal component (PC1) explains 70.4% of the observed variation, while the second principal component (PC2) explains 16.7% of the observed variation, showing a noticeable trend in the separation of chokeberry fruit wines from blackberry and raspberry fruit wines.

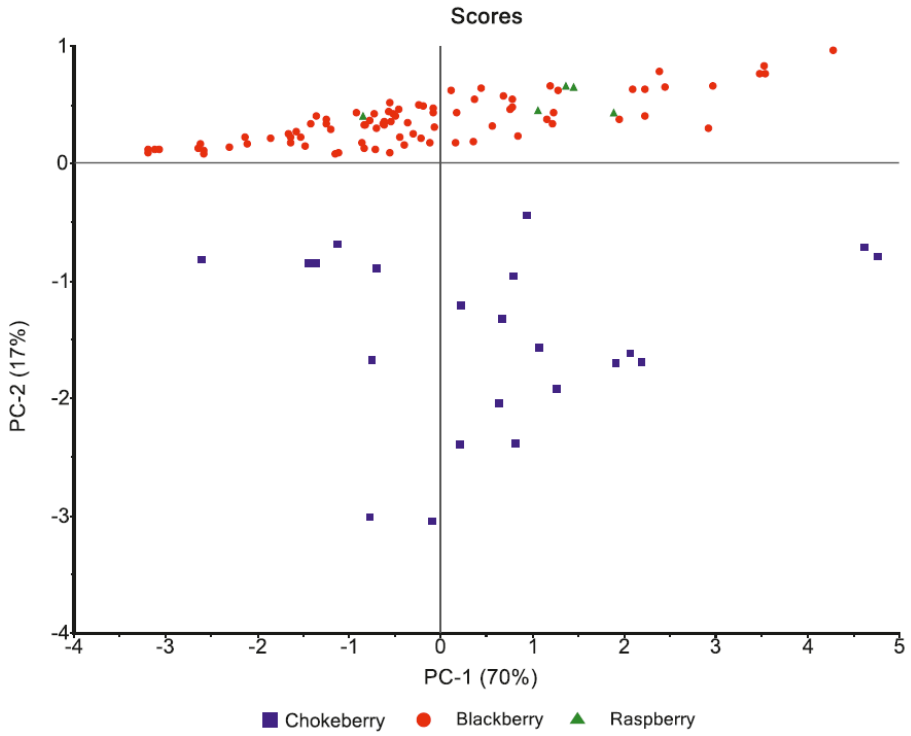

Figure 2. Scatter plot of the scores for two specified components (PC1 and PC2) of the PCA on chokeberry, blackberry, and raspberry samples.

Validation is the only way to ensure that only informative PCs are retained in the model. The validation variance is computed by testing the model on data that were not used in its construction (random method, 20 segments, five samples per segment). The explained variance for both calibration and validation datasets for PC1–PC7 is shown in Table 3.

Table 3. Explained variance of the calibration vs. validation dataset.

	Explained Variance for PC0–PC7						
	PC-1 (70.4%)	**PC-2 (16.7%)**	**PC-3 (5.7%)**	**PC-4 (2.8%)**	**PC-5 (2.3%)**	**PC-6 (0.9%)**	**PC-7 (0.4%)**
Calibration set	70.4	87.1	92.8	95.6	97.9	98.8	99.2
Validation set	69.4	86.2	91.8	94.8	97.5	98.5	99.0

The most important variables, i.e., the absorption bands, were determined using a two-dimensional scatter plot of the X-loadings for the first two specified components from the PCA. This plot is particularly useful for interpreting component 1 vs. component 2, as they represent the largest variations in the X-data. The highest loadings for PC1 were observed at 1045 cm^{-1} and 1153 cm^{-1} (Figure 3).

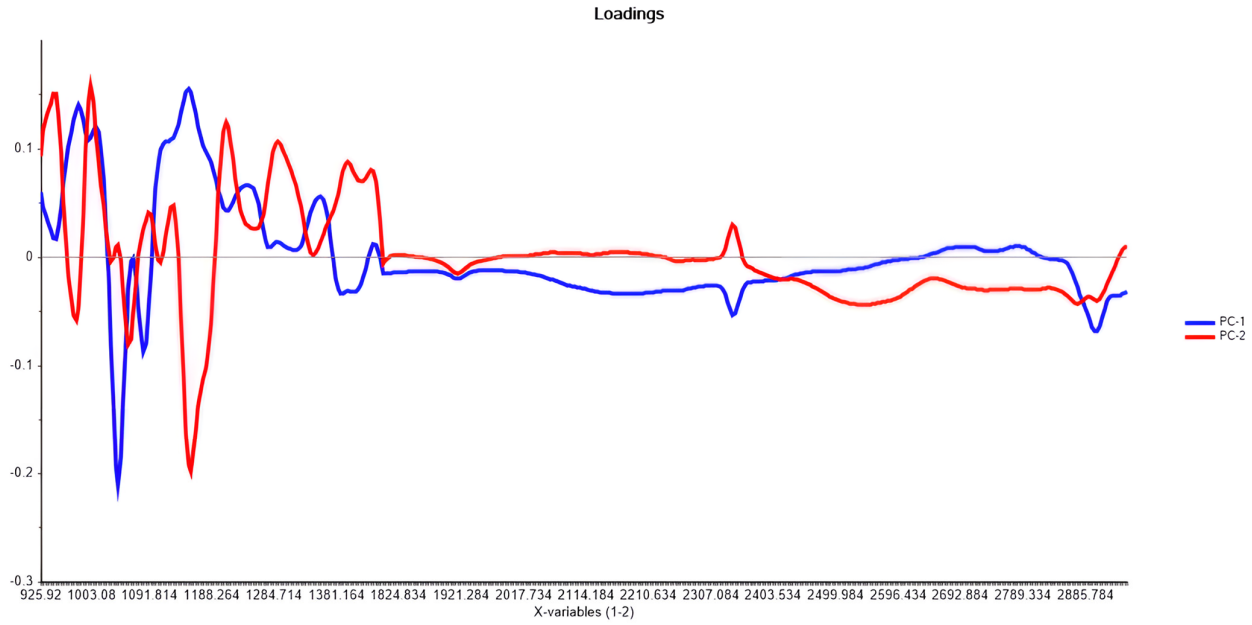

Figure 3. The line plot of the PC1 and PC2 loadings from the PCA on chokeberry, blackberry, and raspberry samples (wavenumber (cm^{-1}).

3.4. Soft Independent Modeling Class Analogy

SIMCA was performed following the development of a PCA model for each class in a defined training set. Unknown samples were then compared to these class models and assigned to classes according to their proximity to the training samples. Using the PCA class model, a Cooman's plot (Figure 4) was constructed to visualize the residual distances of all fruit wine samples to each of the two fruit wine type samples (chokeberry and blackberry), plotted against each other. Samples that form clusters on a Cooman's plot are more similar to each other than those with greater distances between them, hence the chokeberry and blackberry wine samples analyzed here form clearly separated clusters.

Samples that fall within the membership limits of a class are recognized as members of that class. The membership limits (S0) are indicated, reflecting the significance level used in the classification. The significance level for Hi is 5%. S0 for blackberry, chokeberry, and raspberry fruit wine were 1.99, 2.07, and 2.57, respectively.

Figure 5 shows the main discriminators that enabled the classification of chokeberry vs. blackberry fruit wines as a function of their discrimination power (DP). The wavenumbers with the highest discrimination potential, as demonstrated by their discrimination power, are 1157, 1304, and 1435 cm^{-1}, with a DP of 26, 17, and 14, respectively.

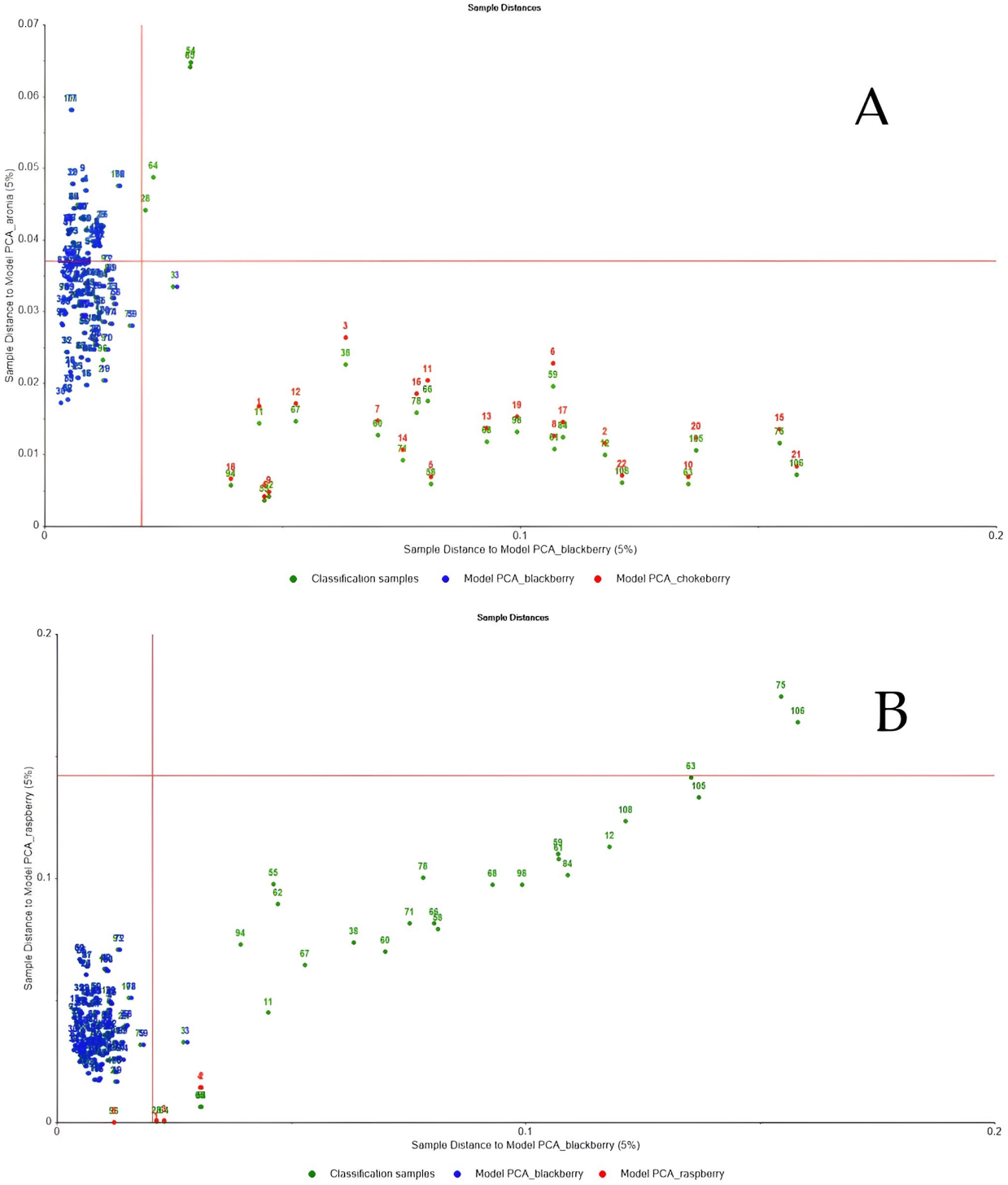

Figure 4. *Cont.*

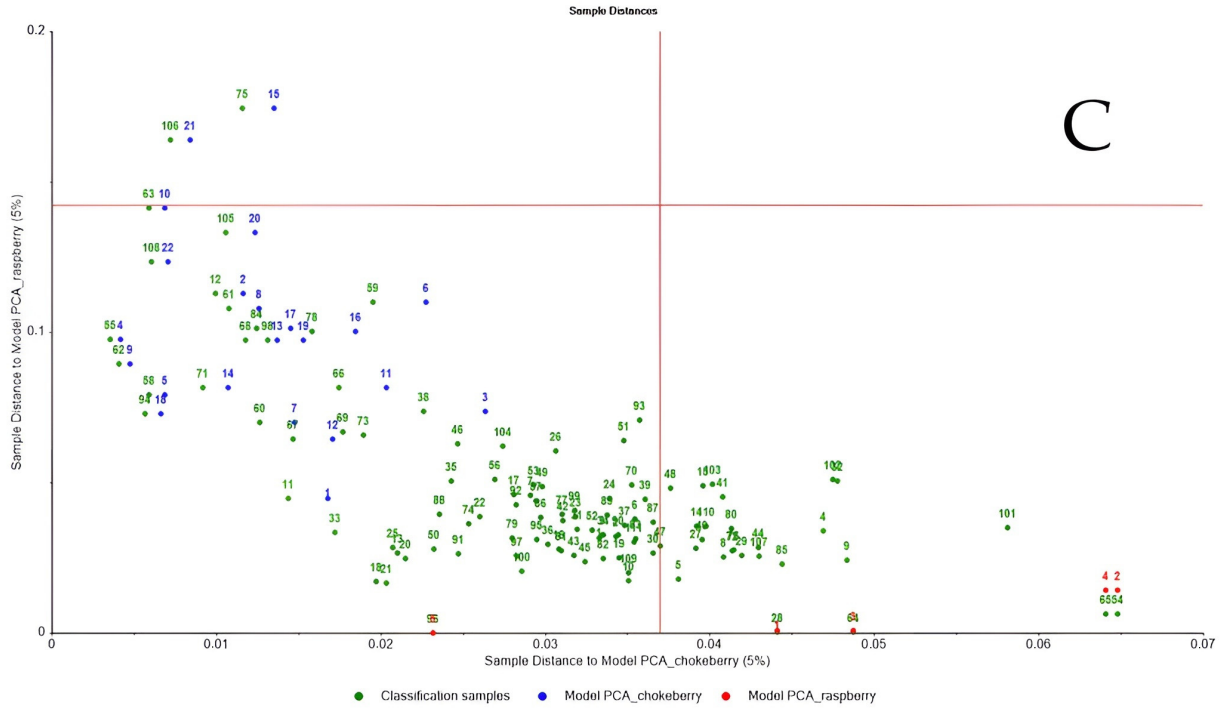

Figure 4. Cooman's plot for chokeberry and blackberry fruit wines (**A**), blackberry and raspberry fruit wines (**B**), and chokeberry and raspberry fruit wines (**C**).

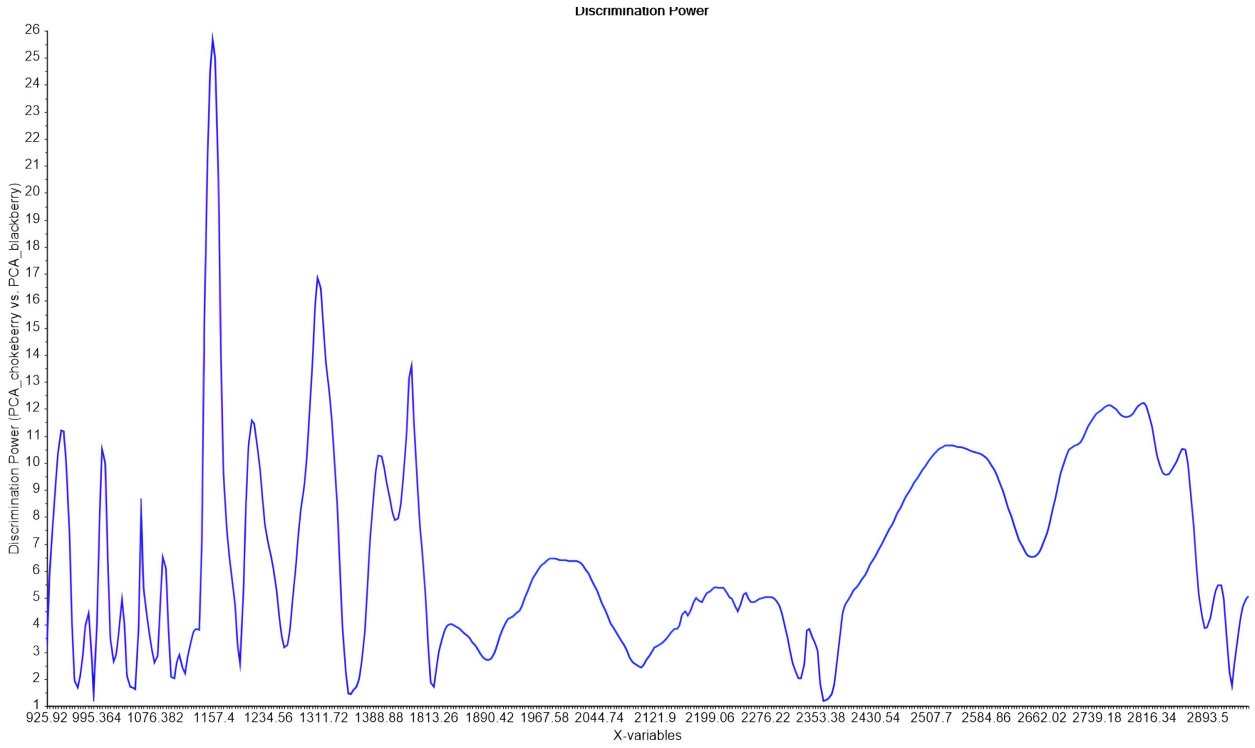

Figure 5. Main discriminators for the classification of the investigated fruit wines as a function of their discrimination power.

4. Discussion

4.1. Physicochemical Quality Parameters

The results of the physicochemical quality parameters showed that all the analyzed wines (except for one that had volatile acidity above the permissible limit) complied with

Croatian national regulations for physicochemical quality parameters of fruit wines [5]: total acidity of at least 3.5 g/L (expressed as g of malic acid per L), volatile acidity no higher than 1.5 g/L (expressed as g of acetic acid per L), and ash content at least 1.0 g/L. Regarding food safety, the concentration of SO_2, the most common allergen used in producing wine and fruit wines [32], in all samples did not exceed the legal limits of 30 mg L^{-1} for free and 200 mg L^{-1} for total SO_2 [5]. The impact of the sensory quality of fruit wines was not investigated in this study.

During wine production, alcoholic fermentation occurs in the fruit must, where sugars, especially hexoses (glucose and fructose), are transformed into ethanol and carbon dioxide along with a variety of minor byproducts [33,34]. The final ethanol concentration in the wine depends on the initial sugar concentration in the must/juice and the conditions prevailing during fermentation [35].

The alcoholic strength in all tested samples ranged from 5.0% vol. to 15.2% vol., while for blackberry wines (8.7–15.2% vol.), it was similar to the findings of Amidžić Klarić et al. (2017) [36]. The most important criterion for distinguishing between two categories—fruit wines and liqueur fruit wines—is the actual alcoholic strength. In the liqueur fruit wines category, the alcohol content must be at least 13.0% vol., and the total alcoholic strength must not exceed 22.0% vol. [5].

The total dry extract, or total dry matter, includes all nonvolatile substances under specified physical conditions [26] and was found to range between 60.4 g/L and 253.3 g/L. The most abundant sugars present in fruit (and, accordingly, in fruit wines) are fructose and glucose, with sucrose also present in some types of fruit [16]. The sugars are expressed here as total sugars, and the results varied widely (1.2–229.9 g/L), with the highest level found in blackberry wine. For fruits with low sugar content, sugar or sugar syrup can be added to the must [37]. According to the Ordinance on Winemaking [5], the addition of sugar to fruit juice and/or concentrated fruit juice is permitted, provided that the actual alcohol content at the time of delivery to the consumer does not exceed 13% vol.

The concentrations of organic acids can vary greatly, depending on the condition and maturity of the fruit, as well as the fermentation process during which many organic acids are formed (e.g., malic, acetic, and succinic acid) [17]. The acidity of wine is primarily indicated by the pH value, which in this study ranged from 3.13 to 4.98. Total acidity (expressed as g of malic acid per L) in the tested samples ranged from 4.2 g/L in chokeberry wine to 18.3 g/L in blackberry wine, similar to the results of Amidžić Klarić et al. (2017) [36]. Volatile acidity (expressed as g of acetic acid per L) ranged between 0.2 g/L and 3.1 g/L. The ash content in all samples ranged from 1.8 g/L to 7.4 g/L. The range for blackberry wines (1.8–5.1 g/L) is comparable to that reported by Amidžić Klarić et al. (2017) [36].

4.2. Fourier-Transform Mid-Infrared Analysis

FT-MIR spectra of the analyzed fruit wines and multivariate statistical methods were employed to determine the criteria for differentiating fruit wines according to their respective fruit types. Figure 1 shows the spectra of the samples that were collected. The main features of the spectra include absorption bands between 926 cm^{-1} and 1450 cm^{-1}, as shown by several studies in beers, wine, and grape juice, confirming that this region carries the most valuable information [31,38–41] and can be recognized as the 'fingerprint' region [42]. It is known that this region contains absorbance bands attributable to water, sugars, and phenolic compounds [40] and results from the stretching and/or bending of CH–OH, C–C, C–O, and C–H bonds [39].

As seen in Figure 2, the 2D display of the samples obtained from the PCA, the sum of the first two components explains 87.0% of the total variation, representing a high portion of the information in the data. The projection of the cases (according to the fruit species) on the factor planes of PC1 vs. PC2 reveals that the blackberry and raspberry wines are positioned mostly on the positive side of PC2, while the chokeberry wines remain on the negative side of the PC2, forming two distinctive groups.

The PCA model was validated by segmented cross validation, and both calibration and validation variance were similar, suggesting the calibration and the test data are representative (Table 1). The line plot of the PC1 and PC2 loadings (Figure 3) highlights the specific wavenumbers (or spectral regions) that contribute most to the variation between the samples. The highest loadings for PC1 were observed at 1045 and 1153 cm^{-1}, and these were identified as the most important variables, i.e., absorption bands. The mentioned spectral profile can be used as a potential marker for classification analysis.

Kumar et al. (2018) [31] reported that all samples belonging to group 1 exhibited a low ratio, while all samples from group 2 showed a high-intensity ratio for the absorption band appearing at 1046 and 1080 cm^{-1}. They also noted that this particular part of the spectral profile can explain the classification of the studied samples. Absorbance between 1045 and 1080 cm^{-1} is usually associated with the C–C and C–OH bonds of primary alcohols (e.g., ethanol), glycerol, and sugars (glucose and fructose) [39,43–46].

PC1 loadings were observed from 1130 to 1150 cm^{-1}, with the latter possibly being characteristic of pyranose sugars [39,42]. This suggests that the variation observed between samples in the first principal component is largely explained by differences in residual sugar and alcohol content. Ethanol had the most significant effect on the PC1 due to the pronounced C–O stretch of the primary alcohol at 1050 cm^{-1} [47].

In this study, PC2 is of particular interest as it differentiates the fruit types used in wine production. The highest loadings for PC2 were observed at 949, 976, 1003, 1157, 1211, 1292, 1400 and 1435 cm^{-1}. Bands between 950 and 1225 cm^{-1} are attributed to aromatic C–H in-plane bending from tannin molecules [41,48] but also to the stretching modes of C–C and C–O [44].

This difference points to the need for further research into the relationship between tannin levels in fruit and corresponding fruit wines, taking into consideration the tannin levels of chokeberry (from 522 to 1000 mg/100 g FW 320/fresh weight/), blackberry (160 mg/100 g FW) and raspberry (120 mg/100 g FW) reported in other studies [49,50]. Proanthocyanidins are the major class of tannins in blueberries and chokeberries, with chokeberries characterized by the highest content of condensed tannins among 100 plant foods investigated [51]. Also, on a fresh weight basis, Chokeberries are among the richest dietary sources of anthocyanins and polyphenols [52,53].

The highest loadings for PC2 observed between 1400 and 1450 cm^{-1} are associated with CO=O and C=C, C–H_2, and C–H_3 are linked to organic acids and aldehydes [46,47]. Additionally, variation in the region between 1420 and 1380 cm^{-1} may be associated with the stretching of C–H bonds from polysaccharides [39].

The PCA revealed a strong influence on the separation of fruit wines according to the fruit species from which they were produced. The distinction between chokeberry fruit wines and blackberry/raspberry fruit wines was explained by the PC2 component, indicating that their separation is influenced primarily by the content of tannins, sugars, organic acids, and aldehydes.

The lack of separation between fruit wines produced from raspberries and blackberries can be explained by their shared genus, *Rubus*. The differences between fruit wines produced from species of the same genus may be too subtle for this statistical model to capture. Additionally, the limited sample size of raspberry wines in the studied harvests suggests the need for further research.

The subsequent statistical model applied was the SIMCA method, which uses the principal component analysis (PCA) to create class models and classify new samples based on their distance from the class centroids [54]. The SIMCA Colman's plot (Figure 4) also showed a very good separation of blackberry and chokeberry fruit wines. In this plot, any sample with a distance to the related centroid greater than the critical distance is considered an outlier and rejected by the specific group [55]. Samples that fall within the membership limit of a class are recognized as members of that class.

The fact that raspberry fruit wine (Figure 4) could not be well classified suggests that additional samples reflecting greater variability are needed to construct a more robust model for this class.

The primary discriminators (Figure 5) enabling the classification of chokeberry vs. blackberry fruit wines, according to their discrimination power (DP), were the signals from the 'fingerprint' region [42]: 983, 1030 and 1088 cm^{-1} (DP 0.3–7.0) than 945, 1003, 1057, 1211, 1389 and 1412 cm^{-1} (DP 7.1–12.0). Based on the literature, these signals can be attributed to tannin content [41,48], primary alcohols (e.g., ethanol), glycerol, and sugars (glucose and fructose) [39,43–47], as well as aromatic groups of phenolics, organic acids, and aldehydes [41,56].

The markers with the highest discrimination power were observed at 1157, 1304, and 1435 cm^{-1} DP with DP 26, 17, and 14, respectively. The main discriminating signal (1157 cm^{-1}) correlates with aromatic C–H in-plane bending from tannin molecules [41,48] and is also explained by the stretching modes of C–C and C–O [44]. The second and third discrimination markers (1304 and 1435 cm^{-1}) are located in the band regions associated with $–CH_2$ deformations, as well as C–C–H and H–C–O deformations [44,45], and are related to CO=O and C=C, $C–H_2$, and $C–H_3$ associated with organic acids and aldehydes [46,47,56].

These results indicate that the SIMCA method effectively enables differentiation between fruit wine types based on their chemical characteristics, with particular attention to specific markers in the 'fingerprint' region. However, to enhance the classification accuracy for all classes, including raspberry, it will be necessary to expand the sample set and include a greater variety of samples in the modeling. This will ensure a more precise and reliable classification of wines according to their specific chemical profiles.

5. Conclusions

This study demonstrates that FT-MIR spectroscopy, combined with PCA and SIMCA, can be effectively utilized as a technique for discrimination between chokeberry, blackberry, and raspberry fruit wines. The analysis of the obtained spectral data (grouped according to fruit species) revealed distinct separation in the PCA and SIMCA models, which could be applied to differentiate chokeberry from blackberry and raspberry wines but was not effective for distinguishing between blackberry and raspberry wines.

When comparing chokeberry with blackberry and raspberry wines, the main spectral differences were observed in two wavenumber regions: 1100–1450 cm^{-1} and 925–1090 cm^{-1}, which enabled the classification of chokeberry wines apart from blackberry and raspberry wines. This distinction is primarily explained by the differences in tannin contents, organic acids, and aldehydes, as well as primary alcohols (e.g., ethanol) and sugars (glucose and fructose) in the fruit wines. Spectroscopic techniques, which measure a large number of chemical components simultaneously, compared to traditional laboratory methods, offer significant opportunities for solving complex problems. In conclusion, infrared spectral profiles can effectively represent the "fingerprint" of fruit wines, and when used in combination with chemometrics, they provide a promising approach for fruit wine authentication.

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