





Authentication of Tokaj wine (Hungaricum) with the Electronic Tongue and Near Infrared Spectroscopy

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Abstract: Tokaj wines (Hungaricum) are botrytized wines acknowledged for the unique organoleptic properties bestowed by botrytized grape berries during production. Excluding these berries during wine production or manipulating the sugar content of low-grade wines to imitate high-grade wines are some recent suspicious activities that threaten the wine quality. Advanced methods such as spectroscopy and sensor-based devices have been lauded for rapid, reliable, and cost-effective analysis, but there has been no report of their application to monitor grape must concentrate adulteration in botrytized wines. The study aimed to develop models to rapidly discriminate lower grade Tokaj wines, “Forditas I” and “Forditas II,” that were artificially adulterated with grape must concentrate to match the sugar content of high-grade Tokaj wines using an electronic tongue (e-tongue) and two near infrared spectrometers (NIRS). Data were evaluated with the following chemometrics: principal component analysis (PCA), discriminant analysis (LDA), partial least square regression (PLSR), and aquaphotomics (a novel approach). There was a noticeable pattern of separation in PCA for all three instruments and 100% classification of adulterated and nonadulterated wines in LDA using the e-tongue. Aquagrams from the aquaphotomics approach showed important water absorption bands capable of being markers of Tokaj wine quality. PLSR models showed coefficient of determination (R^2CV) of 0.98 (e-tongue), 0.97 (benchtop NIRS), 0.87 (handheld NIRS), and low root mean squared errors of cross-validation. All three instruments could discriminate, classify, and predict grape must concentrate adulteration in Tokaj with a high accuracy and low error. The methods can be applied for routine quality checks of botrytized wines.

Keywords: adulteration, aquaphotomics, botrytized wine, chemometrics, sensors, transfectance

Practical Application: Tokaj wines (Hungaricum) are botrytized wines acknowledged for the unique organoleptic properties bestowed by botrytized grape berries during production. Excluding these berries during wine production or manipulating the sugar content of low-grade wines to imitate high-grade wines are some recent suspicious activities that threaten the wine quality. Using advanced instruments, the electronic tongue, benchtop near infrared spectroscopy, and a handheld near infrared spectroscopy, we could discriminate, classify, and predict grape must concentrate adulteration in Tokaj with a high accuracy and low error. The models in our study can be applied for routine quality checks of botrytized wines.

Introduction

Tokaj wines are Hungarian wines produced from noble rotten berries or botrytized berries. They are required to be free from any type of sweeteners and grape concentrate (Magyar, 2011; Magyar & Soos, 2016). Tokaj wine specialties are regarded as a national treasure for their historical significance, unparalleled sensory attributes, and organoleptic properties. The wines are produced in the Tokaj region of Hungary, a declared UNESCO World Heritage Site since June 2002 (Makra et al., 2009) for its unique landscape and climate (World Heritage Committee, 2002), that are believed to render some agricultural benefits to the crops in the area. The climate and the grape varieties of Tokaj contribute to a special process called “noble rot” of the grapes. This involves

a partial infection of the berries by the mold *Botrytis cinerea*, combined with physical dehydration due to evaporation, leading to the shriveled state that makes them desirable for Tokaj wine production. The noble rotten berries have high sugar content and a unique chemical composition of acids, nitrogenous compounds, polyphenols, aroma compounds, and so on (Magyar, 2011; Magyar & Soos, 2016). Several types of Tokaj wine exist depending on the class (level of shriveling) of the berries used or the method of production. Among the Tokaj wine specialties are Tokaj Aszu, Tokaj Szamorodni, Tokaj Maslas, and Tokaj Forditas. The principle of production for the different specialties is basically a skin contact (maceration) between the botrytized berries and a base wine/grape juice to extract the sugars and aromatic substances (Torino, 2016). Extensive details about the compositional quality of different Tokaj wines have been reported by Kerényi (2013) and the effects of noble rotted berries on wine quality have also been detailed by Magyar (2011). The ratio of the botrytized grapes to the extracting wine/juice, the duration of maceration (mostly between 12 and 48 hr), and residual sugar content are contributing factors in defining the type of specialty being produced (Magyar

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& Soos, 2016). These factors, with many other parameters, are strictly regulated by law. The volumes of production, however, are subject to market demand and consumer preference. Similarly, to the production of other great wines of the world, this might lead to fraudulent adulteration practices for commercial purposes.

In 2009 alone, more than 1 million adulterated Amarone wine bottles were sold in Italy (Versari, Laurie, Ricci, Laghi, & Parpinello, 2014). In Asia, anthocyanins are reportedly extracted from black rice (mainly located in the husk) and used as correctors for wine color (Ferrari, Foca, Vignali, Tassi, & Ulrici, 2011). Wines can also be spiked with controlled amounts of alcohols (methanol or ethanol), for a deceptive alcoholic content or with other wines of inferior quality but mostly of the same color, to increase the volume (Penza & Cassano, 2004). Such malpractices have been tracked with diverse types of chromatography (Sagandykova, Alimzhanova, Nurzhanova, & Kenessov, 2017; Selih, Šala, & Drgan, 2014; Serrano-Lourido, Saurina, Hernández-cassou, & Checa, 2012), descriptive sensory analysis (Vidal et al., 2017), and other advanced tools (Kutyła-Olesiuk, Wawrzyniak, Jańczyk, & Wróblewski, 2014; Petropoulos et al., 2017) but controversial forms of adulteration continue to evolve. Addition of natural sweeteners to wine is sometimes accepted when the grapes do not accumulate enough sugars due to inappropriate weather conditions but this remains a relatively controversial topic because the legality of this procedure varies by country, region, and even wine type (Regulation [EU] No. 1308, 2013). Addition of any kinds of sugars, including concentrated juice, is strictly forbidden during the production of Tokaj wine specialties. Notably, a partial replacement of noble rotted berries with grape must concentrate (GMC) occasionally might be an illegal practice that devalues the wine, puts its reputation at stake, and affects consumer trust in the product. With the wine currently penetrating the international markets with the prestige of the country on its shoulders, meticulous controls are required to guarantee the quality of the wine through emerging advanced methods such as spectroscopy and biosensor devices (electronic tongue) that are capable of giving a complete overview of variation in food constituents. The Intl. Union of Pure and Applied Chemistry defines the electronic tongue (e-tongue) as “a multisensor system consisting of a number of selective sensors and uses advanced mathematical procedures for signal processing based on pattern recognition and/or multivariate data analysis” (Vlasov, Legin, Rudnitskaya, Di Natale, & D’Amico, 2005). Spectroscopy is an interaction between light and an analyte in a defined wavelength to give a compositional overview of the analyte. The near infrared spectroscopy (NIRS) region provides vibrational information in the form of overtones and combination bands at a wavelength range of 750 to 2,500 nm (13,000 to 4,000 cm) (Kagaya & Miyamoto, 2017). In spite of the low intensity, the band shape often defines a single compound or group of compounds, making this technique suitable for quantification purposes.

No reagents are required for both e-tongue and NIRS analyses; therefore, issues of waste management are very limited and make them cost effective. Experiments can also be conducted with higher sample sizes for quantification and qualification purposes with low sophistication (Dutta, Hines, Gardner, Udrea, & Boilot, 2003). The NIRS presents extra and nondestructive or noninvasive advantages (Bevilacqua et al., 2017). Both e-tongue and NIRS rely heavily on an arsenal of chemometrics tools for rapid real-time signal interpretation and results. Chemometric models from one spectrometer can sometimes be calibrated across multiple instruments in what is often referred to as a “calibration transfer”

(Yang et al., 2019). Calibration transfer can be time-saving and cost-effective but it can also be a rather complex process involving advanced mathematical technicalities (Folch-Fortuny, Vitale, de Noord, & Ferrer, 2017). Spectrometers are reported to give diverse responses/signal due to issues of sensitivity, even those that are very similar and can complicate the calibration transfer process (Yang et al., 2019). Significant differences were observed in predicted results after calibration transfer between parent and child spectrometers (Workman, 2018). Owing to these challenges, models are often built for specific instruments. NIRS has been used for geographical identification of wine (da Costa, Llobodanin, de Lima, Castro, & Barbosa, 2018), assessment of metals in Tokaj wine (Murányi & Kovács, 2000), and phenolic compound quantification (Alexandre-Tudo, Nieuwoudt, Alexandre, & du Toit, 2018). The e-tongue has been used for on-site quantification of ethylphenol metabolites (González-Calabuig & del Valle, 2018), quantification of polyphenols (Ce & Ceto, 2012), storage experiments (Rudnitskaya et al., 2017), and geographical classification (Lozano et al., 2006) of wines, and so on. González-Álvarez, Noguerol-Pato, González-Barreiro, Cancho-Grande, and Simal-Gándara (2014) reported on the variation of sweet wines obtained by the winemaking procedures of botrytization and fortification but they only used descriptive sensory methods in their study. Multisensor arrays have also been used to investigate wine adulteration (Penza & Cassano, 2004) in which ethanol and methanol were the adulterants to manipulate the alcoholic content of the beverage. Compositional evaluation of botrytized Tokaj wine was also performed, but with gas chromatography (Sass-Kiss, Kiss, Havadi, & Adányi, 2008) and recently with mass spectrometry (Negri et al., 2017). New scientific fields, such as aquaphotomics, have become a method of choice for many researchers dealing with aqueous systems (Bazar, Kovacs, & Tsenkova, 2016). It revolves on the principle of using water as a holistic marker to extract information about many different water molecular conformations and their interaction with surrounding solutes by means of their absorbance bands and a light-water phenomenon (Tsenkova, Munčan, Pollner, & Kovacs, 2018). Aquaohotomics has been used for nondestructive quality-monitoring applications (Kovacs et al., 2016), noninvasive bio diagnosis (Jinendra et al., 2010), measuring low concentrations of sugar in water (Bázár et al., 2015), and investigation of honey adulteration (Bázár et al., 2016).

This study aimed to develop rapid techniques for the discrimination of Tokaj forditas wine adulteration with GMC using the e-tongue and NIRS as advanced tools, in conjunction with chemometrics and the aquaphotomics approach.

Materials and Methods

Sample acquisition

For the purposes of this study, “Ford” implies Tokaj Forditas wines. Four Tokaj wines of different quality grade (in increasing order), Ford_{II}, Ford_I, Aszu_{II}, and Aszu_I, and GMC were obtained from experts at the winemaking Tokaj region of Hungary. The wines were produced according to the standard requirements of Tokaj wine production as described: maceration of first-class botrytized berries with base wine (fermented grape juice) to get Tokaj Aszu I wine and maceration of second-class botrytized berries with base wine to get Tokaj Aszu II wine. Similarly, Tokaj Ford I and Ford II wines were prepared by reusing the botrytized berries from Tokaj Aszu I and Aszu II wine production for a second maceration with base wine, which is the normal practice in making Ford. The wines had a maceration period of 48 hr

Table 1—List of samples showing the nonadulterated Tokaj wine, adulterated Tokaj wine, and their corresponding sugar concentrations.

Sample number	Tokaj wines	Adulterated Tokaj wines	Sugar concentrations (g/L)
1	Ford_II		98.9
2	Ford_I		130.2
3		Ford_II.C1	130.2
4	Aszu_II		168.2
5		Ford_II.C2	168.2
6		Ford_I.C1	168.2
7		Ford_I.C2	203.5 ^a
8		Base_Sugar	238.8
9		Ford_II.C3	238.8
10		Ford_I.C3	239.6 ^b
11	Aszu_I		254.5
12		Ford_II.C4	254.5
13		Ford_I.C4	254.5

^aThe value is derived from (Ford_I + Base_Sugar)/2.

^bThe value is derived from (Aszu_I + Base_Sugar)/2.

and resulted in diverse sugar concentrations (Table 1) that were determined by high-performance liquid chromatography at the Dept. of Oenology, Szent Istvan Univ.

Research approach and sample preparation

The determined sugar concentrations of Ford I and Ford II wines were manipulated with GMC of 775.3 g/L sugar concentration to mimic the sugar concentrations of nonadulterated Tokaj wines. This was done in steps, and in total, four different adulteration levels (C1 to C4) were obtained, covering the range of sugar concentration generally existing in Tokaj wines of different quality. This is shown in Table 1. The purpose of this artificial adulteration was to monitor the possibility of producing wines of similar quality to the Tokaj wines by sugar manipulation. Also included was a complex wine referred to as “base_sugar” in this study. This wine contained sucrose during its refermentation and was not macerated with botrytized berries. It was meant to represent complex forms of adulteration.

Three repeats of 50 mL each were prepared for each sample after 50% dilution as described by Soós et al. (2015). Equation (1) was used to calculate the required volume of wine and Eq. (2) for the required volume of adulterant.

$$V_{Ford} = (C_{con} - C_{tcon}) / (C_{conc} - C_{Ford}) \times V_{req} \quad (1)$$

$$V_{conc} = V_{req} - V_{Ford} \quad (2)$$

V_{Ford} : volume of ford wine required for adulterated mixture.

C_{con} : concentration of GMC.

C_{tcon} : targeted content (Sugar concentration of non-adulterated wine).

C_{Ford} : concentration of ford wine.

V_{req} : final volume of mixture (50 mL).

V_{conc} : volume of GMC.

Instrumental analysis

E-tongue analysis. The Alpha Astree potentiometric e-tongue with Ag/AgCl reference electrode and chemically modified field-effect transistor sensors from Alpha MOS (Toulouse, France) were used to discriminate the different wines (both adulterated and nonadulterated) based on pattern recognition. The principle of measurement for the e-tongue is based on the difference in potential changes of several working electrodes against a

reference electrode in zero-current conditions (Ciosek, 2011). According to the manufacturer's recommendations, the instrument was conditioned in two phases: with 0.01 N HCl and with mixture of the wine samples under study, before the analysis to reduce sensor drift. For the analysis, 90 mL (after 50% dilution) of the three repeats were each randomly (to reduce drift) measured in four sequences for 120 s each. The last 10 s of the sensor signals, representing stabilized and optimal sensitivity of the different sensors, were exported for statistical evaluations in R project statistical software.

NIRS analysis. NIRS and aquaphotomics offer the possibility of extracting hidden information in the spectra when conventional data evaluation methods are used. The concept utilizes changes of the water structure as a result of the interaction with the measured solute at specific molecular vibrations of water bands (Bazar et al., 2016). In our study, near infrared technique and aquaphotomics are applied for nondestructive discrimination of adulterated wines based on the measurement of vibrational frequencies from chemical bonds in the wine samples. The metri analyzer from Metrika Inc., Florida (benchtop spectrometer) and the DLP NIRscan Nano from Texas instruments, Texas (handheld spectrometer) device were used for spectra collection. Transflectance spectra were collected using a cuvette providing 0.4-mm layer thickness of the tested liquid sample. Three consecutive scans of all the three repeats were taken for both the benchtop and handheld devices while using Milli-Q purified water (MQ) as a control in a spectral step of 3 nm. Spectral acquisition of all the solutions was performed at room temperature that was monitored using the Voltcraft DL-121TH multi-data logger from Voltcraft, Hungary. Data analysis was done at the spectral range of 1,300 to 1,600 nm; this range is believed to contain active water bands (Tsenkova, 2009). The spectra were pretreated with Savitzky–Golay smoothing filter using second-order polynomial and pretreated with multiplicative scatter correction (MSC). Spectral analysis for aquagram was done in accordance with the aquaphotomics approach (Tsenkova et al., 2018). Regression vectors of the calibration models were studied to make possible correlations with characteristic water bands and water matrix coordinates (WAMACs). WAMACs are spectral ranges in which specific water absorbance bands related to specific water molecular conformations (water species, water molecular structures) are found with the highest probability (Kinoshita et al., 2012). For the first overtone of water (1,300 to 1,600 nm), 12 WAMACs have been experimentally discovered and confirmed by overtone calculations of already-reported water bands in the infrared range (Tsenkova et al., 2018). All data analysis was done in R project was used for spectral analysis.

Chemometrics and statistical evaluations

Principal component analysis (PCA) was performed to detect outliers and identify interrelationships between the samples. It is an unsupervised method in the sense that no grouping of the data has to be known before the analysis (Granato et al., 2018). Discriminant analysis (LDA) was used for multiclass classification of the different wine samples. LDA is a supervised method; the class membership has to be known for the analysis (Granato et al., 2018). Partial least squares (PLS) regression was used to derive the models to predict GMC in Tokaj wine after the detection of outliers in PCA. Threefold cross-validation (CV) was used to test the predictive significance of the results in LDA and also in partial least square regression (PLSR) to test the predictive significance of the regression. The statistical parameters used to evaluate the performance of the PLSR models were the root mean square error of

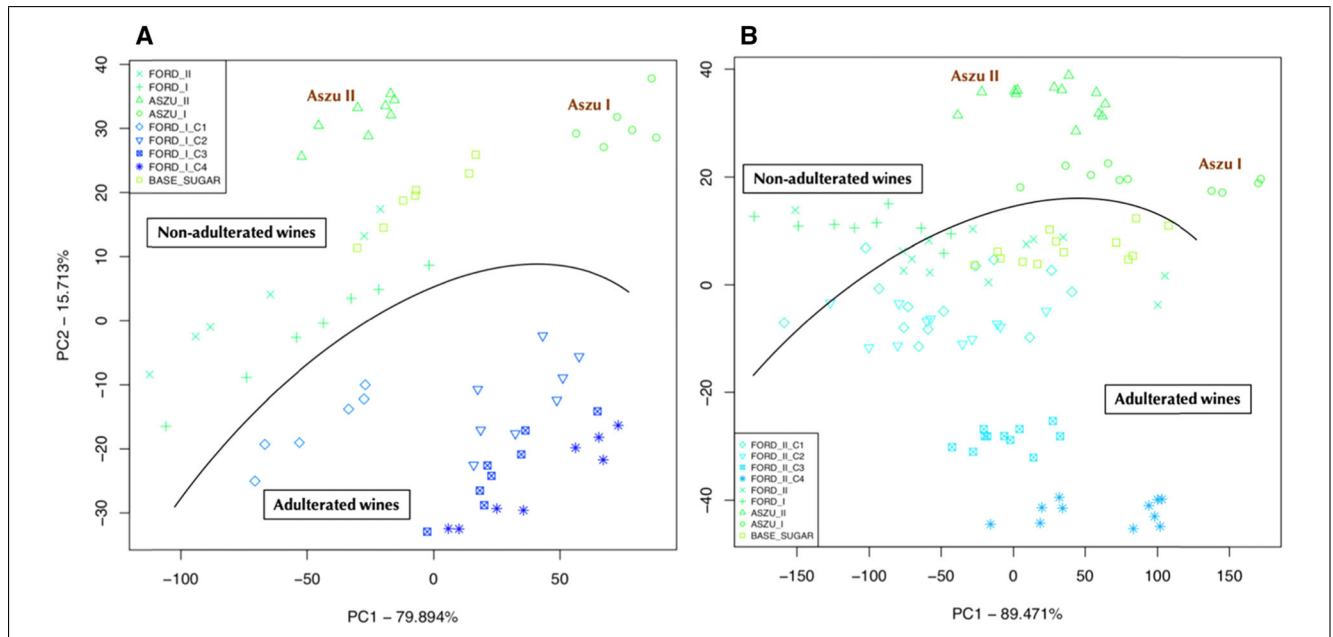


Figure 1—Principal component analysis (PCA) score plots for Ford I wine adulteration (A) and PCA for Ford II wine adulteration (B) with the electronic tongue.

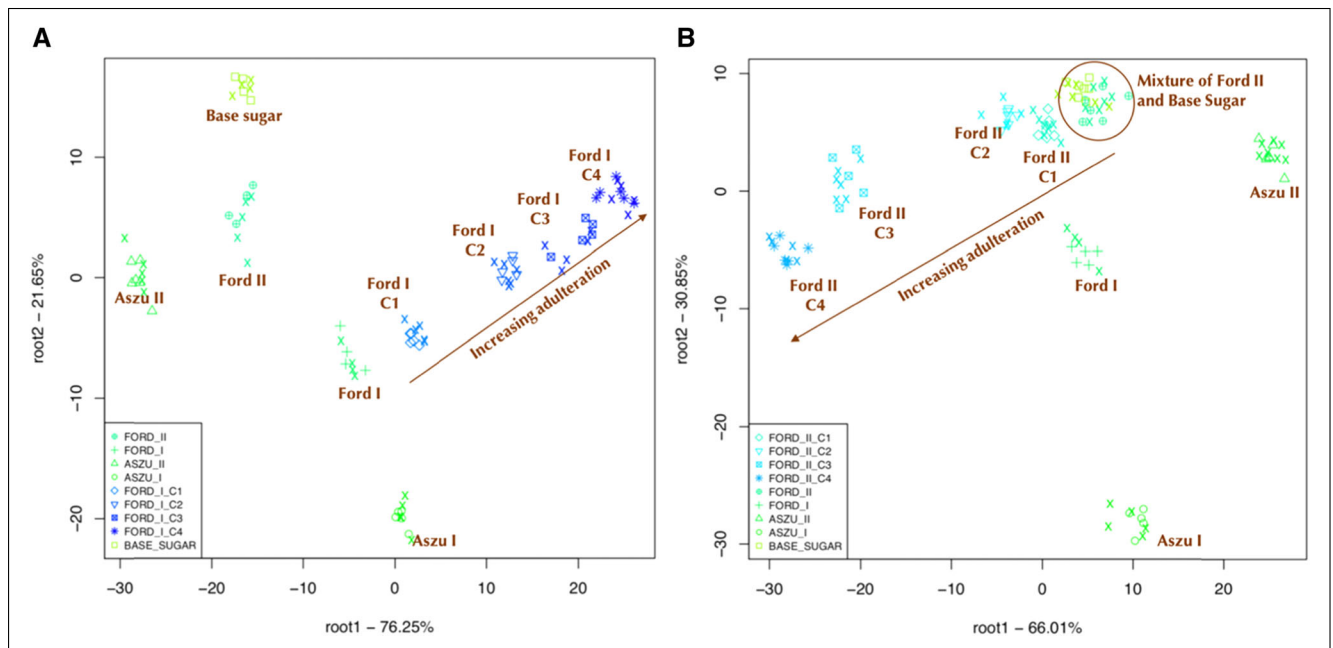


Figure 2—Discriminant analysis plots for Ford I wine adulteration with 100% classification (A) and Ford II wine adulteration with 100% classification (B) with the electronic tongue.

calibration (RMSEC) and the coefficient of determination (R^2C); in cross-validation (RMSECV, R^2CV). The optimum number of latent variables was determined based on the minimum RMSECV value.

Results and Discussion

E-tongue evaluation of Ford I and Ford II wine adulteration with GMC

From the PCA evaluation of both Ford I and Ford II adulterated wines, a pattern of separation was observed with the nonadulter-

ated wines (upper part of Figure 1A and 1B) and adulterated wines (lower part of Figure 1A and 1B), although the wine sample adulterated with sugar before fermentation (base sugar) appeared to be closer to the nonadulterated wines. Kang, Lee, and Park (2014) also reported a good separation of Korean wines (*makgeolli*) using the e-tongue. PCA provides first clues about the major directions and sources of variation in the dataset. It can therefore be concluded from the PCA that, although there was a good separation between the adulterated and nonadulterated wines, the results also suggest the potential of the fermentation process to mask Ford wine adulteration with sucrose if it was added before refermentation.

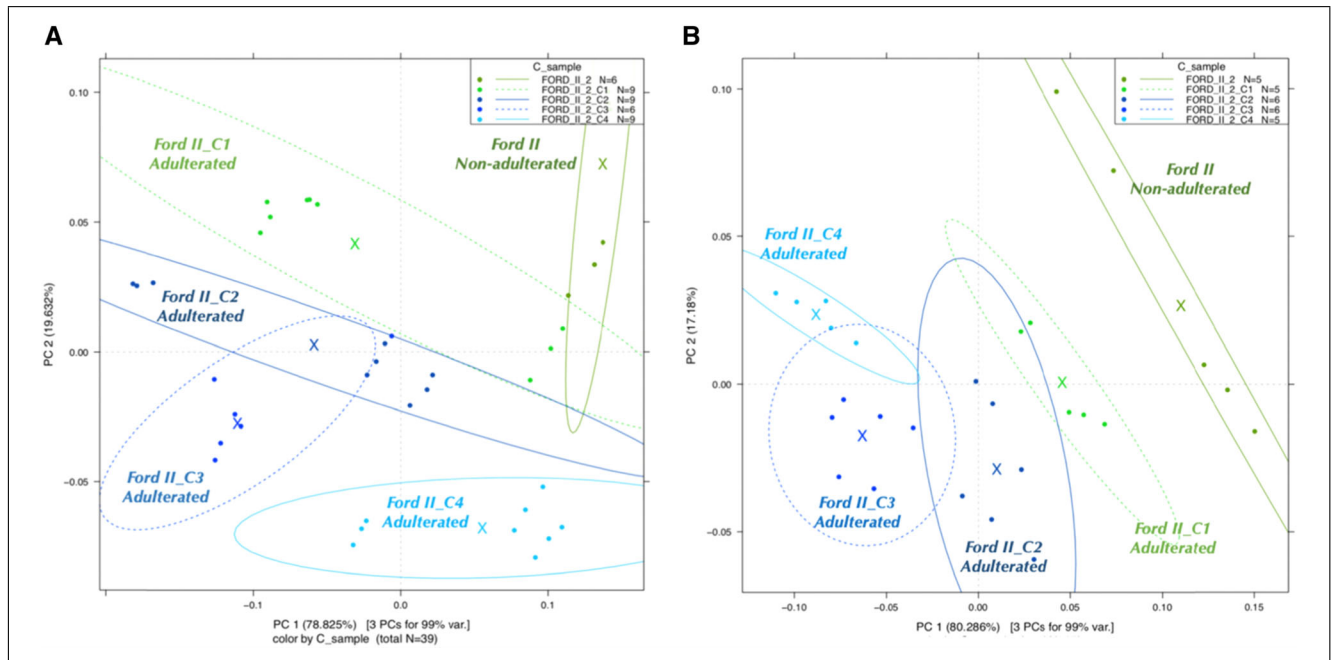


Figure 3—Principal component analysis (PCA) score plots for Ford II wine adulteration with the handheld near infrared spectrometers (NIRS) (A) and PCA for Ford II wine adulteration with the metri NIRS (B) after pretreatment with Savitzky–Golay smoothing filter (second-order polynomial) and multiplicative scatter correction at spectral range of 1,300 to 1,600 nm.

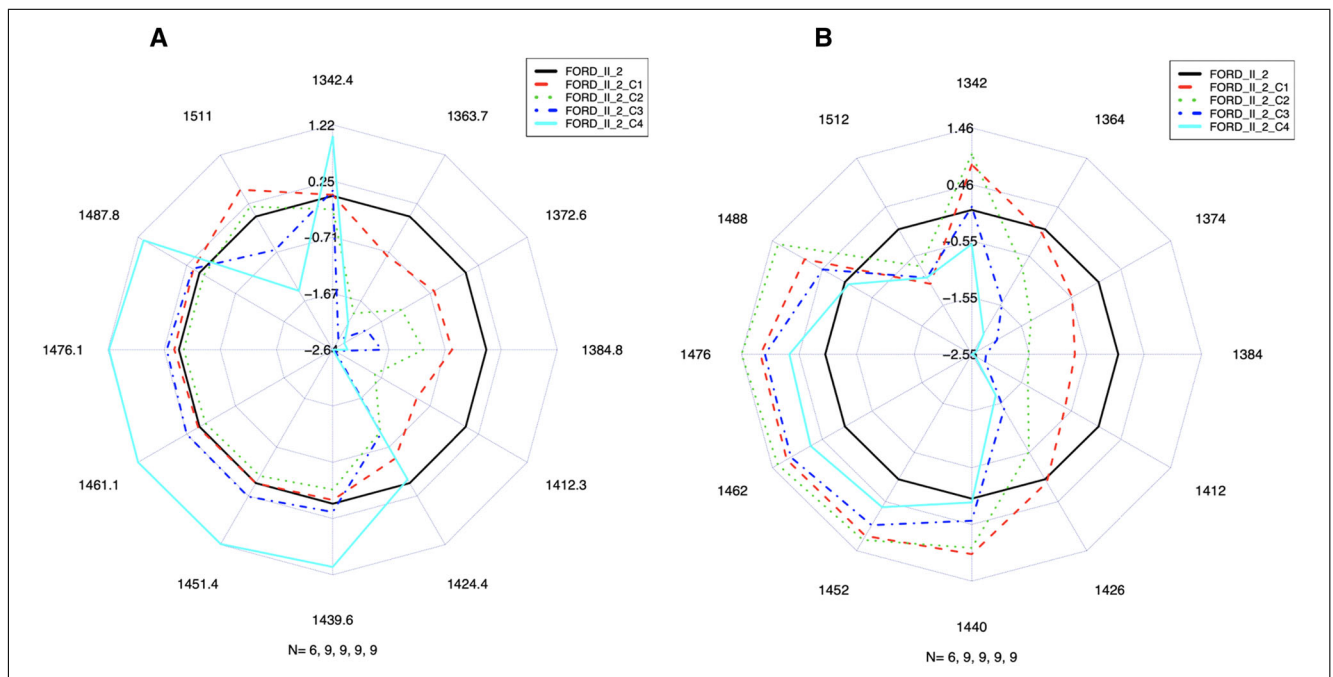


Figure 4—Aquagram plots for Ford II adulterated wines with the handheld near infrared spectrometers (NIRS) (A) and aquagram for Ford II adulterated wines with the metri NIRS (B) after pretreatment.

This makes it a potent or suitable method to deceive unsuspecting consumers. In Figure 1B, Ford_II_C1 and Ford_II_C2 wines were overlapped with nonadulterated Ford I and Ford II wines.

Using LDA, there was a 100% correct classification for all the samples after a threefold CV for Ford I adulterated wines and 98.5% correct classification for Ford II adulterated wines. This was a confirmation of the separation observed in the PCA results. The

LDA model could accurately classify GMC adulteration in Ford I and Ford II wines with high accuracy when the data were divided into a training and validation set. Classification was also observed in a linear pattern in both Ford I adulterated wines and Ford II adulterated wines from C1 to C4 concentration of adulteration (Figure 2). Base sugar adulterated wine was classified closely to Ford II nonadulterated in Figure 2B but was accurately classified in Figure 2A.

NIRS evaluation of Ford II wine adulteration with PCA and aquagram

PCA score for both the benchtop and handheld spectrometers showed a good separation of Ford II wine adulteration as shown in Figure 3. In Figure 3A (handheld NIRS), a decreasing pattern of quality from the nonadulterated wine (Ford_II) to the highest level of adulterated wine (Ford_II_C4) was observed from left to right. The same pattern was observed in Figure 3B (metri NIRS, benchtop) but from right to left. More than 78% of the data variation was expressed in principal component (PC1) for both instruments. The variation in the PCA between the two instruments may, however, be due to difference in sensitivity as a result of the scanning positions. The Merri NIRS (benchtop) always had a fixed scanning position by design but the samples had to be always manually placed on the light source of the handheld instrument. This may have accounted for the difference in repeatability of the samples and hence the variation in the PCA plots. Both instruments were nonetheless sensitive enough to distinguish the samples based on their possible clusters.

The bands assigned—in the first overtone region of –OH bonds (1,300 to 1,600 nm)—by the qualitative and quantitative analyses of the wine samples using PCA and PLSR, respectively, showed high consistency with previously published WAMACs (Tsenkova, 2009). This observation implies that the variation in absorbance values at these bands describes the water spectral pattern (WASP) of the wine samples and can be used to understand the change in the water conformation caused by the adulteration. Aquagrams used to visualize the WASP of Ford II sample (in the center) and its adulterated counterparts are shown in Figure 4A and 4B calculated based on the spectra acquired by the handheld scanner and by the benchtop instrument, respectively.

There was a decreasing pattern of adulteration from C4 adulterated wines to C1 adulterated wines in the free –OH regions (1,322 to 1,326 nm and 1,358 to 1,366 nm). Broadly speaking, the range between 1,342 and 1,385 nm represents none or less H-bonded water in which signals of free –OH vibrations dominate (Xantheas, 1995), but this spectral range can also hold information about highly organized water in water solvation shell (Headrick et al., 2005), and free –OH in water clusters (Mizuse & Fujii, 2012). It can therefore be said that the molecular constituent of the adulterated wines is highly related to these bands in the dynamic water structure; more solutes (sugar) implies less free water.

Absorption around 1,412 nm refers to weakly H-bonded water molecules, and with the increasing wavelength, the increase of the number of H-bonds can be followed (Segtnan, Šašić, Isaksson, & Ozaki, 2001). The interval between 1,441 and 1,470 nm was assigned to the water dimers, trimers, and tetramers, that is, water molecules having H-bonds with one, two, or three other water molecules, respectively (Luck, 1998). Wavelengths at the top left part of the aquagram, that is, 1,488 and 1,511 nm represent highly organized water structures with strong H-bonds, that is, ice-like structures of liquid water with more stable clusters having less free –OH. This structure of water is expected around the hydrated macromolecules (Giangiacomo, 2006).

The aquagrams calculated based on the spectra obtained by the two different spectrometers present very similar patterns (Figure 4). Namely, wine samples with added GMC show mainly lower absorbance values at wavelengths between 1,364 and 1,426 nm, but higher absorbance values in the wavelength range of 1,440 to 1,488 nm compared to the nonadulterated Ford II

Table 2—PLSR results for e-tongue and both NIRS instruments.

Instrument	Wine type (N)	Outliers	Latent variable	R ² CV	RMSECV (g/L)
E-tongue	Ford I (45)	3	3	0.978	4.984
	Ford II (45)	3	4	0.987	5.943
Benchtop (metri NIRS)	Ford II (45)	4	5	0.976	9.311
Handheld (NIRS)	Ford II (45)	6	3	0.870	20.183

Notes: NIRS, near infrared spectrometers; PLSR, partial least square regression; R²CV: coefficient of determination after threefold-cross-validation; RMSECV, root square error of cross validation.

wine sample. Furthermore, the increasing concentration of GMC results in the decrease of absorbance values at shorter wavelengths, which means they contain less water molecules with free OH bond. On the other hand, the pattern observed in the range between 1,440 and 1,488 nm interval suggests that the water dimers, trimers, and tetramers, that is, water molecules having H-bonds with one, two, or three other water molecules, respectively, are formed as a result of the addition of GMC to the wine. The tendency at 1,512 nm representing highly organized water structures with strong H-bonds shows GMC diminishes the ice-like structure of water in wine. Bands above 1,500 nm have been related to aqueous solutions of fructose (1,583 nm), sucrose (1,584 nm), and glucose (1,587 nm) (de Almeida, de Andrade Silva, Lima, Suarez, & da Cunha Andrade, 2018). This may explain the tendency in shift by the adulterated wines (containing more sugar) toward those bands. The aquagrams presented demonstrates the capability of aquaphotomics in discriminating wines of different qualities based on their dynamic water structure.

Regression models from e-tongue and NIRS analysis to predict Ford I and Ford II adulteration

PLSR models for the e-tongue had coefficient of determination: 0.97 and 0.98 for Ford I and Ford II adulterated wines, respectively (Table 2). An R² close to 1 is a necessary condition for a good model (Alexandre-Tudo et al., 2018) but this may not be the only requirement. The errors in calibration: RMSECV explains the fit of the observations to the model in both calibration and validation steps. It is a measure of the average difference between the values determined by the reference methods and those predicted by the model (Ramírez-Morales, Rivero, Fernández-Blanco, & Pazos, 2016). RMSECV was 4.89 and 5.94 g/L for Ford I and Ford II wines, respectively, with the e-tongue. These values show the capability of the model to predict adulteration of Ford II wine with a good accuracy. Similarly, good models were also developed for the benchtop and handheld NIRS instrument as shown in Table 2 but they were relatively weak compared to the e-tongue models. In comparison, Ford II wine could be predicted with a better accuracy than both NIRS instruments. This may be due to the several conditions that often influence spectral data acquisition. Nonetheless, the regression models can be used to predict GMC adulteration in Tokaj Ford wine from good to acceptable accuracy using e-tongue and benchtop or handheld spectrometers, respectively.

Conclusion

Ford I (produced with first-class noble rotten berries) and Ford II (produced with second-class noble rotted berries) Tokaj wines

adulterated with various levels of GMC were rapidly discriminated and classified with 100% accuracy in LDA with the e-tongue. This was in agreement with the PCA results. Notably, base sugar adulteration (adulteration with sucrose before refermentation) was always separated and classified closely to the nonadulterated wines and proved to be a potent form of adulteration for unsuspecting consumers. The wines were also separated in the PCA plots of a benchtop and handheld NIRS instruments after Savitzky–Golay smoothing filter using second-order polynomial and MSC. Important absorption bands in aquagrams elucidated the interaction of water and the wine constituents with a decreasing tendency of less bound water that was directly proportional to an increasing adulteration level. The e-tongue produced the best PLSR model for predicting the adulteration of Tokaj Ford with a coefficient of determination ($R^2 = 0.977$) after threefold CV and the lowest RMSECV (4.98 g/L). It was more generally, more effective in predicting Ford II wine. LDA proved to be the most effective in classifying adulterated and nonadulterated wines. The e-tongue and NIRS present viable and capable sensitivities for monitoring sugar concentration manipulation of Tokaj Ford wine with accurate predictive functions when chemometrics is employed. More studies would, however, be required to build stronger models with defined limits of detection that can be adopted by regulatory authorities.

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Author Contributions

John-Lewis Zinia Zaukuu, Zoltan Kovacs, Soos Janos, and Zsanett Bodor designed and performed experiments. John-Lewis Zinia Zaukuu, Zsanett Bodor, and Zoltan Kovacs performed data analysis. John-Lewis Zinia Zaukuu, Zoltan Kovacs, Ildiko Magyar, and József Felföldi interpreted results and wrote the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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