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Analytical Methods

Differentiation of Greek red wines on the basis of grape variety using attenuated total reflectance Fourier transform infrared spectroscopy

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ABSTRACT

Mid-infrared spectroscopy combined with appropriate software was used in an attempt to differentiate Greek red wines of different varietals origin, including the cultivars Agiorgitiko (Nemea-Peloponnesus), Xinomavro (Naousa-Central Macedonia) and Merlot from Greece. Extract of wine phenolic components were investigated by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The wine extracts were obtained by solid-phase extraction with C-18 columns and elution by methanol containing 0.01% hydrochloric acid. Libraries of spectra were created using sample from each wine variety. Spectra of unknown wine extracts were recorded and compared with those of the wine libraries and the rate of affinity (the match value) was measured automatically using the appropriate software (OMNIC ver. 7.3). The spectral region 1800–900 cm^{-1} was used to 'fingerprint' wine on the basis of grape variety. This simple and fast method of analysis showed that wines from different grape varieties can be differentiated between them.

1. Introduction

Wine is a complex mixture of several hundred compounds present at different concentrations. The major ones are water, ethanol, glycerol, sugars, organic acids, salts; aliphatic and aromatic alcohols, amino acids and phenolic compounds are present at much lower concentrations. Chemical analysis of a complex mixture such as wine is becoming of great importance for quality control to both the winemaking industries and the consumers. Particularly, differentiation according to vine variety, geographical origin, and year of production is of great importance. According to Ribéreau-Gayon (1982), the individual phenolic fingerprint (anthocyanins, flavonoids, procyanidins, hydroxycinnamic acids, and their derivatives) is characteristic for any plant. Probably this could hold true for the varieties of each plant also. Analysis of anthocyanins and flavonoids has been used for distinguishing among grape varieties (Berente, De La Calle Garcia, Reichenbächer, & Danzer, 2000; Etievant, Schlich, Bertrand, Symonds, & Bouvier, 1988; Santos et al., 1991).

Reversed phase high pressure liquid chromatography (HPLC) – ultra violet–visible (UV–Vis) methods are commonly used for analysis of phenolic compounds. Also sample preparation, usually isolation of phenolic compounds on C18-RP cartridges before measurements, is necessary. Separation, derivatization and preconcentration in the case of compounds in low concentration are usually common steps in these procedures. Thus, these methods are time consuming. Recently HPLC combined with mass spectrometry was also used for investigating the anthocyanin and flavonoid composition and variety characterisation (Da Costa, Horton, & Margolis, 2000; Heier, Blaas, Dross, & Wittkowski, 2002; Monagas, Suárez, Gómez-Cordovés, & Bartolomé, 2005; Revilla, Perez-Magarino, Gonzalez-SanJose, & Beltran, 1999).

Infrared spectroscopy based methods for analysis of wine and determination of major constituents of the wines are recently emerging because of their versatility, efficiency, being cost effective, fast and non-invasive (Cavinato, Mayes, Ge, & Callis, 1990; Gallignani, Garrigues, & De la Guardia, 1994; Herrera, Guesalaga, & Agosin, 2003; Picque, Lefier, Grappin, & Corrieu, 1993).

Generally, spectroscopic techniques (UV–Vis, IR), where used for analysis of major compounds such as phenolic composition of wines. Near-infrared (NIR) as well as mid-infrared (MIR) spectroscopic techniques combined with multivariate data analysis are very promising in this context. NIR spectroscopy has already found widespread application in quality control and process analysis in wine industry (Dambergs, Kambouris, Francis, & Gishen, 2002; Dambergs et al., 2003).

Also recently the use of NIR for white wine varietals discrimination (Riesling vs Chardonnay) was reported (Cozzolino, Smyth, & Gishen, 2003).

However, due to the fact that NIR absorptions reflect overtones and combination bands of fundamental transitions, NIR spectra are much less distinct than MIR spectra. MIR absorption bands are

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generally well resolved and can be related to defined vibrational transitions. Some researchers tried to exploit mid-infrared transmission spectroscopic studies in brewing industry and they observed strong absorption of water in mid-infrared region that posed problems in spectral analysis. The use of attenuated total reflectance technique is shown to be a far better choice for analyzing biological samples (Bellon, 1993; Nagarajan, Gupta, Mehrotra, & Bajaj, 2006; Picque et al., 1993).

MIR technique was used (Bevin, Ferguson, Perry, Janik, & Cozzollino, 2006) for red wine authenticity confirmation during transport and processing; namely, a wine 'fingerprinting' system. A similarity index (SI) method was used as a tool to classify wine samples on the basis of their spectral data. In five of the six winery data sets, the SI correctly classified 98% of the wines. It was also observed that less than 1% of wines were misclassified between the different wineries investigated.

UV–Vis and MIR spectroscopy, combined with multivariate data analysis, was applied to wine for the whole phenolic fingerprint in order to discriminate wines produced from different cultivars of *Vitis vinifera*. Although the phenolic composition may be influenced by vinification, maturation, and aging, the differences in the overall phenolic fingerprints might still be characteristic for each cultivar (Edelmann, Diewok, Schuster, & Lendl, 2001). Both authentic wines and their phenolic extracts, obtained by solid-phase extraction with C-18 columns and elution by methanol containing 0.01% hydrochloric acid, were investigated the using Attenuated Total Reflectance (ATR)-MIR spectroscopy. Hierarchical cluster analysis was performed with mid-infrared spectra of both wines and extracts, as well as with UV–Vis spectra of the phenolic extracts. However satisfactory classification of 'raw' wines was not achieved, but only after extraction with solid-phase extraction (SPE).

In our study we aim to differentiate Greek red wines and/or Merlot planted in Greece. It is challenging to develop an analytical method which could be used for differentiation of the varieties used for the production of each corresponding wine. Sensory analysis is used in AOC (Appellation Origin Contrôle) regions of Greece (as obliged by European Union regulations) (Commission Regulation, 2002) for controlling the authenticity of the wines. In Greece most of the AOC regions are mono-varietals so the development of such an analytical method for the differentiation of the varieties could be a powerful tool for the protection of the wine quality in the AOC regions. In the present work AOC Nemea and AOC Naousa and their unique Vitis vinifera cv. Agiorgitiko and cv. Xinomavro respectively, were studied, as these AOC are the regions of the best quality red wine appellations in Greece (Chapa, Fallis, & Farrel, 2001).

2. Materials and methods

2.1. Wine samples

Thirty-four red wine samples were collected from collaborating wineries in Peloponnesus (Nemea) and Central Macedonia (Naousa) of Greece. Twenty wine samples (A01–A20) from the variety Agiorgitiko (AOC Nemea), eight (X01–X08) Xinomavro (AOC Naousa) and six (M01–M06) Merlot were used. The above wines were made from 1998 to 2005. According to the wineries the wines were authentic, individually fermented and aged either in new oak or in stainless steel tanks (Table 1).

Table 1
Authentic wines from varieties Agiorgitiko (A01–A20), Xinomavro (X01–X08) and Merlot (M01–M06), year of production and method of ageing

Sample code	Method of ageing	Year of production	Sample code	Method of ageing	Year of production
A01	In stainless steel tank	2005	A18	In stainless steel tank	2003
A02	In stainless steel tank	2005	A19	In new oak barrel	2005
A03	In stainless steel tank	2005	A20	In new oak barrel	2005
A04	In stainless steel tank	2005	X01	In new oak barrel	2005
A05	In new oak barrel	2005	X02	In new oak barrel	2005
A06	In new oak barrel	2005	X03	In new oak barrel	2000
A07	In new oak barrel	2005	X04	In new oak barrel	1999
A08	In new oak barrel	2005	X05	In new oak barrel	2005
A09	In new oak barrel	2005	X06	In new oak barrel	1998
A10	in new oak barrel	2005	X07	In new oak barrel	2004
A11	In new oak barrel	2005	X08	In new oak barrel	2003
A12	In new oak barrel	2005	M01	In stainless steel tank	2005
A13	In new oak barrel	2005	M02	In new oak barrel	2003
A14	In new oak barrel	2005	M03	In new oak barrel	2003
A15	In new oak barrel	2004	M04	In new oak barrel	2003
A16	In stainless steel tank	2005	M05	In new oak barrel	2005
A17	In stainless steel tank	2004	M06	In new oak barrel	2005

2.2. Extract of wine phenolic components preparation

According to Edelmann et al. (2001) every wine sample was filtered through a 0.45 μm porosity filter. Then 3 mL of each filtered sample was diluted with 15 mL distilled water. The solutions (18 mL) passed through a C18 SPE (Bakerbond J.T. Baker SPE C18) under vacuum. The cartridges were preconditioned using 10 mL methanol and 10 mL distilled water for every cartridge. Then the solutions were placed on the cartridges. Every cartridge was washed with 20 mL of distilled water; the extract was removed and dried by means of a vacuum pump. Then the cartridges were washed with 3 mL acidified methanol (0.01% hydrochloric acid) and the fractions were collected (1.5 mL for each one fraction). In the methanolic extract are included flavonoids, procyaninidins, and hydroxycinnamates together with the anthocyanins. The methanolic extracts were measured by FT-IR.

2.3. FT-IR spectroscopic measurements

FT-IR spectra were obtained in the ATR mode using a standard ZnSe 45° flat plate against a ZnSe background on a Nicolet 6700 FT-IR spectrometer (DTGS detector; Nichrome source; KBr beamsplitter), with a total of 100 scans (resolution, 4 cm^{-1}). The ZnSe flat plate was covered four times with 100 μL of methanol extract every time. The sample was air-dried after every covering. After the fourth covering the sample was dried in an oven at 40 °C for 15 min. Spectra were collected and manipulated using the OMNIC (ver. 7.3) software supplied from the manufacturer of the spectrometer. Spectra of each sample were collected in triplicate.

All spectra were smoothed using the 'automatic smooth' function of the above software, which uses the Savitsky–Golay algorithm (95-point moving second-degree polynomial). Then the baseline was corrected using the 'automatic baseline correct'.

Table 2
Comparison of the unknown samples spectra with the library (Lib01) which included three random spectra of each variety

Unknown sample	Match value to Agiorgitiko			Match value to Xinomavro			Match value to Merlot		
	A6	A12	A18	X2	X5	X8	M2	M4	M6
A01	98.94	**99.47**	99.27	93.88	95.27	95.55	97.46	90.10	95.50
A02	94.78	97.27	**97.95**	88.56	92.02	92.49	93.76	87.94	91.07
A03	97.66	97.55	**98.60**	95.48	97.58	97.61	98.55	91.77	95.73
A04	**99.50**	98.21	96.65	94.69	95.16	96.31	95.29	84.32	91.78
A05	**97.22**	97.06	96.03	93.66	90.96	92.10	93.33	85.93	92.22
A06	**100.00**	98.45	97.25	96.20	96.27	96.96	96.73	87.20	93.84
A07	86.18	89.20	**90.48**	78.48	83.63	82.65	87.94	87.47	88.32
A08	98.19	**99.79**	99.03	91.57	93.25	93.59	95.76	87.69	94.21
A09	**99.13**	98.85	98.15	94.23	93.92	94.60	96.59	88.15	94.82
A10	98.78	**99.27**	98.30	94.34	95.45	95.64	96.78	87.75	94.17
A11	**99.49**	98.57	97.49	95.57	95.09	96.01	96.12	86.60	93.48
A12	98.45	**100.00**	99.07	92.46	93.92	94.38	95.84	87.70	94.07
A13	**99.46**	98.46	96.93	94.97	95.45	96.40	95.40	84.27	91.95
A14	98.22	**99.86**	99.11	91.75	93.13	93.50	95.73	87.99	94.30
A15	97.77	**99.50**	99.24	92.50	93.13	93.28	96.19	90.01	95.21
A16	98.39	**99.24**	98.94	93.97	95.74	95.89	97.07	89.08	94.56
A17	**96.82**	96.44	95.82	95.32	92.10	92.66	94.64	88.47	93.33
A18	97.25	99.07	**100.00**	91.80	94.29	94.34	97.38	91.56	96.27
A19	95.74	96.62	**97.65**	91.75	95.82	95.83	96.56	89.60	93.18
A20	98.29	**98.45**	98.06	94.34	92.76	93.31	96.18	89.94	95.40
X01	96.61	92.93	91.57	**99.12**	96.87	97.22	94.79	85.00	90.87
X02	96.20	92.46	91.80	**100.00**	96.84	96.88	95.34	86.56	91.81
X03	95.85	93.25	93.35	97.29	**98.86**	98.35	96.79	87.32	92.60
X04	95.40	93.22	93.05	95.21	**97.59**	97.03	96.44	87.21	92.87
X05	96.27	93.92	94.29	96.84	**100.00**	99.62	97.13	88.29	92.99
X06	**91.14**	89.24	85.68	90.90	89.94	90.96	85.21	74.05	80.31
X07	97.15	94.01	93.36	97.68	98.89	**99.56**	95.37	84.78	90.41
X08	96.96	94.38	94.34	96.88	99.62	**100.00**	96.70	87.06	92.20
M01	92.08	92.30	95.26	88.81	93.31	92.20	**97.80**	95.45	97.62
M02	96.73	95.84	97.38	95.34	97.13	96.70	**100.00**	93.94	98.45
M03	94.02	94.07	96.07	90.18	93.10	92.31	98.56	93.65	**98.71**
M04	87.20	87.70	91.56	86.56	88.29	87.06	93.94	**100.00**	95.71
M05	85.00	84.04	87.09	84.50	90.40	88.63	**92.39**	92.19	91.28
M06	93.84	94.07	96.27	91.81	92.99	92.20	98.45	95.71	**100.00**

Agiorgitiko: A06, A12, A18; Xinomavro: X02, X05, X08; Merlot: M02, M04, M06.

Simultaneously, we calculated and saved the average of three spectra of each sample and they were then used.

Three libraries were created using the OMNIC software. The first library (Lib01) included three random spectra of each variety (Agiorgitiko: A06, A12, A18; Xinomavro: X02, X05, X08; Merlot: M02, M04, M06). The second library (Lib02) included the average of above three spectra sample of each variety. The third library (Lib03) included the average of all spectra of each variety.

Using the 'search' function, the spectroscopic region 1800–900 cm^{-1} was selected and each spectrum of all Greek red wine samples (now called unknown samples) was compared with the spectra of the created libraries. Then, the match value was measured by software automatically and represented in the Tables 2–4. The match value (the rate of affinity) determines how well the library spectrum matches the unknown. A match value of 100 indicates a perfect match. The closer the value is to 100, the better the match.

3. Results and discussion

The method is based on the spectroscopic differences between the wine phenolic extracts. So the polar compounds were removed from the cartridges using distilled water. Then phenolic components were collected using acidified methanol solution (Edelmann et al., 2001).

3.1. FT-IR spectral analysis

Our interest was focused on the 1800–900 cm^{-1} spectral region because in this area characteristic groups absorb and the 'fingerprint' region is included. Consequently in this region any differences between the spectra can be detected.

Fig. 1 shows typical FT-IR spectra of Agiorgitiko, Xinomavro and Merlot wine in the spectroscopic region 1800–900 cm^{-1}. Ten peaks appear. The first peak is centered at 1712–1704 cm^{-1}. It is due to the stretching of carbonyl (C=O) group (Edelmann et al., 2001; Nakanishi & Solomon, 1977; Socrates, 1997). The second and third peaks at 1609–1608 and 1519–1516 cm^{-1} have been assigned to C=C stretching which are typical for aromatic systems (Edelmann et al., 2001; Nakanishi & Solomon, 1977; Socrates, 1997). Generally in the region 1680–900 cm^{-1} bands originating from wine phenols can be found.

The absorption at 1448–1444 cm^{-1} corresponds to the antisymmetric in-plane bending of $-CH_3$ (Nakanishi & Solomon, 1977; Socrates, 1997). Furthermore in the same spectral region the phenyl nucleus (C=C) absorbs and the deformation of $-CH_2-$ appears (Nakanishi & Solomon, 1977; Socrates, 1997). The weak peak at 1376–1373 cm^{-1} is associated with symmetric in-plane bending of $-CH_3$ (Edelmann et al., 2001; Nakanishi & Solomon, 1977; Socrates, 1997). The absorption at 1340–1339 cm^{-1} has been assigned to CH bending and CH_2 wagging (Edelmann et al., 2001; Nakanishi & Solomon, 1977; Socrates, 1997). The peak at 1281–1278 cm^{-1} corresponds to in-plane bending of O–H (Nakanishi & Solomon, 1977; Socrates, 1997). The bands at 1207, 1110–1107, 1068–1062 correspond to stretching vibration of C–O (Edelmann et al., 2001; Nakanishi & Solomon, 1977; Socrates, 1997).

There are minor differences between the phenolic extracts spectra. The main differences are between the height ratio of 1712–1704 and 1609–1608 cm^{-1}. As is shown this ratio is bigger in Xinomavro, afterwards in Agiorgitiko and smaller in Merlot

Table 3
Comparison of the unknown samples spectra with the library (Lib02) which included the average of three spectra sample of each variety

Unknown sample	Match value to Agiorgitiko	Match value to Xinomavro	Match value to Merlot
A01	**99.77**	95.59	96.38
A02	**96.87**	91.64	92.81
A03	**98.46**	97.59	97.40
A04	**99.00**	96.07	92.94
A05	**97.45**	92.96	92.42
A06	**99.45**	97.19	94.89
A07	88.66	82.15	**88.99**
A08	**99.45**	93.47	94.61
A09	**99.39**	94.95	95.30
A10	**99.39**	95.84	95.13
A11	**99.31**	96.27	94.34
A12	**99.64**	94.26	94.61
A13	**99.12**	96.29	93.02
A14	**99.51**	93.46	94.68
A15	**99.23**	93.66	95.63
A16	**99.36**	95.89	95.70
A17	**97.04**	94.12	93.98
A18	**99.06**	94.14	96.89
A19	**97.06**	95.11	95.19
A20	**98.87**	94.20	95.66
X01	94.85	**98.52**	92.60
X02	94.58	**98.72**	93.50
X03	95.04	**98.90**	94.63
X04	94.75	**97.32**	94.49
X05	95.67	**99.53**	95.13
X06	89.74	**91.28**	82.32
X07	95.87	**99.42**	92.72
X08	96.14	**99.52**	94.41
M01	93.52	92.09	**98.37**
M02	97.22	97.11	**99.37**
M03	95.13	92.54	**98.63**
M04	88.99	87.98	**96.96**
M05	85.78	88.46	**93.16**
M06	95.10	93.04	**99.39**

Average Agiorgitiko: A06, A12, A18; Average Xinomavro: X02, X05, X08; Average Merlot: M02, M04, M06

Table 4
Comparison of the unknown samples spectra with the library (Lib03) which included the average of all spectra of each variety

Unknown sample	Match value to Agiorgitiko	Match value to Xinomavro	Match value to Merlot
A01	**99.91**	95.62	95.62
A02	**97.36**	91.85	91.18
A03	**98.59**	97.20	96.13
A04	**98.89**	96.42	91.60
A05	**97.45**	93.11	88.94
A06	**99.22**	97.44	93.33
A07	**90.68**	89.72	82.10
A08	**99.45**	93.75	93.40
A09	**99.37**	94.95	93.67
A10	**99.47**	96.42	93.83
A11	**99.26**	96.37	92.53
A12	**99.61**	94.58	93.04
A13	**99.02**	96.63	91.69
A14	**99.50**	93.73	93.25
A15	**99.34**	93.82	93.60
A16	**99.52**	96.31	94.29
A17	**97.17**	94.22	90.39
A18	**99.12**	95.57	93.75
A19	**97.35**	94.81	94.22
A20	**98.89**	94.11	93.32
X01	94.60	**99.06**	90.56
X02	94.40	**98.59**	91.32
X03	94.92	**98.85**	94.08
X04	94.61	**97.58**	94.44
X05	95.35	**99.02**	94.69
X06	89.62	**94.01**	80.10
X07	95.48	**99.29**	91.36
X08	95.79	**99.20**	93.64
M01	93.55	90.71	**99.52**
M02	97.17	96.27	**98.76**
M03	94.92	91.43	**98.94**
M04	89.30	86.38	**96.29**
M05	86.14	86.97	**96.37**
M06	95.04	91.94	**98.51**

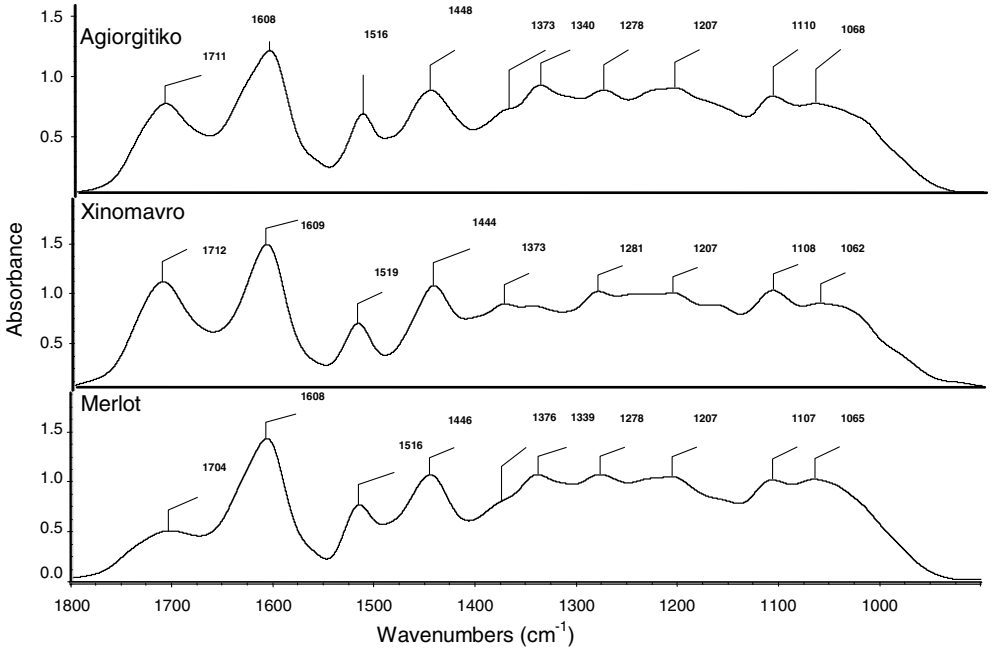

Fig. 1. The spectral region 1800–900 cm^{-1} of FT-IR spectra of standards acidified methanol extracts of Agiorgitiko, Xinomavro and Merlot.

(Fig. 1). Furthermore the 1340 cm^{-1} peak is absent in Xinomavro case.

In our study, the differentiation between wine samples is based on small differences between spectra of their phenolic extracts. An alteration was observed between phenolic wine extract samples in the 1800–1600 cm^{-1} region. Furthermore the spectroscopic region 1500–900 cm^{-1} is the 'fingerprint' area. So the 1800–900 cm^{-1} spectral region has been chosen for the match values (the rate of affinity) measuring.

3.2. Match value

The FT-IR spectra of unknown wines phenolic extracts were compared with the three libraries (Lib01, Lib02, Lib03) using the 'search' function of OMNIC software. The above software determines the minimum match value for searching and displaying results. The match values of the FT-IR spectra of unknown samples are shown in Tables 2–4.

In the case of comparison of unknown samples with Lib01 all Agiorgitiko, all Merlot and almost all Xinomavro samples found have affinity to Agiorgitiko, Merlot and Xinomavro samples of library, respectively. Only, one Xinomavro (X06) found be related to Agiorgitiko (A06). The comparison of unknown samples with Lib02 showed that all Xinomavro, all Merlot and almost all Agiorgitiko samples, found have affinity to Xinomavro, Merlot and Agiorgitiko samples of library. Exception constituted sample A07 which was more affinity to Merlot. Finally, the comparison of unknown samples with Lib03 all Agiorgitiko, all Xinomavro and all Merlot samples found have affinity to Agiorgitiko, Xinomavro and Merlot samples of library, respectively. In this case the similarity of unknown samples with the desirable spectra of library was complete.

It can be concluded from the above results that the classification of wines was better when used the Lib03 (where all unknown samples were correctly discriminated), as compared to Lib01 and Lib02. Despite the small sample number, the promising results of the above method showed that it is possible to discriminate well among the three cultivars of the study. Future work will involve development of a database comprised of more varieties to expand the discriminating options and to predict different blend compositions. If a wine is a mixture of two or three varieties the similarity of this sample with the spectra of library will be at low level due to different phenolic composition.

Overall, these results verified that differences between red wines of different varietal origin might be confirmed using mid-infrared spectra and our method is simpler, fast and accurate in comparison with other methods from bibliography.

4. Conclusion

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) combined with appropriate software have been applied for the discrimination of Greek red wines, including the cultivars Agiorgitiko (AOC Nemea), Xinomavro (AOC Naousa) and Merlot. Our method is based on creation of a mid-infrared spectra data bank. The spectra were recorded from the phenolic extract of authentic wines. Then, the phenolic extract spectra of unknown wines were recorded and compared with the spectra of data base. Thus, using ATR-FTIR spectroscopy, almost complete discrimination of all cultivars investigated was achieved measuring the percentage of similarity with the spectra of data base. However, the method that was described is simple, fast and a very powerful tool for accurate identification on varietal origin of red wines.

References

Bellon, V. (1993). Fermentation control using ATR and an FT-IR spectrometer. *Sensors and Actuators B: Chemical, 12*(1), 57–64.

Berente, B., De La Calle Garcia, D., Reichenbächer, M., & Danzer, K. (2000). Method development for the determination of anthocyanins in red wines by high performance liquid chromatography and classification of German red wines by means of multivariate statistical methods. *Journal of Chromatography A, 871*, 95–103.

Bevin, C., Ferguson, A., Perry, W., Janik, L., & Cozollino, D. (2006). Development of a rapid "fingerprinting" system for wine authenticity by mid-infrared spectroscopy. *Journal of Agricultural and Food Chemistry, 54*, 9713–9718.

Cavinato, A. G., Mayes, D. M., Ge, Z., & Callis, J. B. (1990). Noninvasive method for monitoring ethanol in fermentation processes using fiber-optic near-infrared spectroscopy. *Analytical Chemistry, 62*(18), 1977–1982.

Chapa, R., Fallis, C., & Farrel, P. (2001). *The global encyclopedia of wine*. San Francisco: Wine Appreciation Guild.

Commission Regulation. (2002). Laying down certain rules for applying Council Regulation (EC) No. 1493/1999 as regards the description, designation, presentation and protection of certain wine sector products. EC No. 753/2002 of 29 April 2002. *Official Journal of the European Communities, L, 118*, 1–75.

Cozzolino, D., Smyth, H. E., & Gishen, M. (2003). Feasibility study on the use of visible and near infrared spectroscopy to discriminate between white wine of different varietal origin. *Journal of Agricultural and Food Chemistry, 5*(26), 7703–7708.

Da Costa, C. T., Horton, D., & Margolis, S. A. (2000). Analysis of anthocyanins in food by liquid chromatography, liquid chromatography–mass spectrometry and capillary electrophoreses. *Journal of Chromatography A, 881*, 403–410.

Dambergs, R. G., Cozzolino, D., Esler, M. B., Cynkar, W. U., Kambouris, A., Francis, I. L., Hoj, P., & Gishen, M. (2003). The use of near infrared spectroscopy for grape quality measurement. *Australian and New Zealand Grapegrower and Winemaker, 476 A*, 69–76.

Dambergs, R. G., Kambouris, A., Francis, I. L., & Gishen, M. (2002). Rapid analysis of methanol in grape derived distillation products using near-infrared transmission spectroscopy. *Journal of Agricultural and Food Chemistry, 50*(11), 3079–3084.

Edelmann, A., Diewok, J., Schuster, K. C., & Lendl, B. (2001). Rapid method for the discrimination of red wine cultivars based on mid infrared spectroscopy of phenolic wine extracts. *Journal of Agricultural and Food Chemistry, 49*(3), 1139–1145.

Etievant, P., Schlich, P., Bertrand, A., Symonds, A., & Bouvier, J. C. (1988). Varietal and geographic classification of French red wines in terms of pigments and flavonoid compounds. *Journal of the Science of Food and Agriculture, 42*(11), 39–54.

Gallignani, M., Garrigues, S., & De la Guardia, M. (1994). Derivative Fourier transform infrared spectrometric determination of ethanol in alcoholic beverages. *Analytica Chimica Acta, 287*(3), 275–283.

Heier, A., Blaas, W., Dross, A., & Wittkowski, R. (2002). Anthocyanin Analysis by HPLC/ESI-MS. *American Journal of Enology and Viticulture, 53*(1), 78–86.

Herrera, J., Guesalaga, A., & Agosin, E. (2003). Shortwave near infrared spectroscopy for non-destructive determination of maturity of wine grapes. *Measurement Science and Technology, 14*(5), 689–697.

Monagas, M., Suárez, R., Gómez-Cordovés, C., & Bartolomé, B. (2005). Simultaneous determination of nonanthocyanin phenolic compounds in red wines by HPLC-DAD/ESI-MS. *American Journal of Enology and Viticulture, 56*(2), 139–147.

Nagarajan, R., Gupta, A., Mehrotra, R., & Bajaj, M. (2006). Quantitative analysis of alcohol, sugar, and tartaric acid in alcoholic beverages using attenuated total reflectance infrared spectroscopy. *Journal of Automated Methods and Management in Chemistry, 2006*, 1–5.

Nakanishi, K., & Solomon, P. H. (1977). *Infrared absorption spectroscopy* (2nd ed.). San Francisco: Holden-Day, Inc.

Picque, D., Lefier, D., Grappin, R., & Corrieu, G. (1993). Monitoring of fermentation by infrared spectrometry: alcoholic and lactic fermentation. *Analytica Chimica Acta, 279*(1), 67–72.

Revilla, I., Perez-Magarino, S., Gonzalez-SanJose, M. L., & Beltran, S. (1999). Identification of anthocyanin derivatives in grape skin extracts and red wines by liquid chromatography with diode array and mass spectrometric detection. *Journal of Chromatography A, 847*, 83–90.

Ribéreau-Gayon, P. (1982). The anthocyanins of grapes and wine. In P. Markakis (Ed.), *Anthocyanins as Food Colors* (pp. 209–244). New York: Academic Press.

Santos, C., Munoz, S. S., Gutiérrez, Y., Hebrero, E., Vicente, J. L., Purificación, G., & Rivas, C. (1991). Characterization of young red wines by application of HJ biplot analysis to anthocyanin profiles. *Journal of Agricultural and Food Chemistry, 39*, 1086–1090.

Socrates, G. (1997). *Infrared characteristic group frequencies. Tables and charts* (2nd ed.). Chichester: John Wiley & Sons Ltd.