Characterization and Classification of Turkish Wines Based on Elemental Composition

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Abstract: Commercial wines from 13 native and nonnative varieties in Turkey were analyzed for their elemental composition. Wines from four vintages (2006–2009) were analyzed by inductively coupled plasma with atomic emission spectrometry and mass spectroscopy (ICP-AES and ICP-MS) followed by multivariate statistics to study vintage, varietal, and regional differences. According to the partial least squares-discriminant analysis, wines from western regions could be discriminated with their higher Pb content. The red wines of two native grapes, Boğazkere and Öküzgözü, were separated from the remaining varieties based on their high Ca and low B and Cu levels. Öküzgözü wines were different from Syrah and Cabernet Sauvignon wines. Similarly, native Emir wines showed differences from Muscat wines. The effective variables for discrimination analysis were natural minerals (Sr, Li, Al, Ba, and B) and minerals originating from agricultural activities, processing, or pollution (Ca, Cu, Mg, Co, Pb, and Ni). Characteristics of Turkish wines from native and nonnative grape varieties such as Cabernet Sauvignon, Merlot, Syrah, and Chardonnay were defined in terms of their mineral content for the first time.

Key words: geographical classification, grape variety, mineral content, multivariate analysis, wine

The chemical composition and sensory characteristics of wine are highly influenced by geographical origin, grape variety, climatic, vintage, and processing conditions (Marini et al. 2006). In addition to details on wine composition and nutritional value, many wine consumers now expect information on the original territory of wine products, as the geographical origin of a wine can be an important criterion ensuring the quality of product. The label "controlled denomination of origin" indicates recognized winegrowing regions, winemaking practices, and grapes (Martinez-Carrasco et al. 2005) and has been used in many wine-producing countries. The label may appear in different forms, such as denominazione di origine controllata (DOC), appellation d'origine contrôlée (AOC), and denominación de origen (DO) (Castro et al. 2011, Gonzalves et al. 2008, Marengo and Aceto 2003, Martin et al. 2012, Saavedra et al. 2011, Trujillo et al. 2011). The labeling of controlled denomination of origin can help to prevent fraud and protect the origin and quality of the wine.

The minerals in wine originate from the capacity of the vine to take elements from soil (geographical region), climatic factors such as heavy rains, environmental conditions such as pollution, and agricultural applications such as fertilizers and pesticides. The mineral content of red and white wines from the same region can differ due to the impact of the vinification process on the elemental composition, such as the maceration step in red winemaking, where the juice is in longer contact with the skins and flesh of the grapes (Coetzee et al. 2005).

The elemental composition of wine has been useful in characterizing wine samples, identifying wine origin, and assessing the nutritional safety of the product (Fabani et al. 2010, Grindlay et al. 2008, Gonzalves et al. 2009). The latter highly depends on the capacity of vine to uptake toxic elements, which are the consequence of pollution in the soil. Heavy metals, especially lead (Pb), cadmium (Cd), and mercury (Hg), are toxic to humans (Volpe et al. 2009).

Previous studies on wine determined the elemental composition using inductively coupled plasma–atomic emission spectroscopy (ICP-AES) and mass spectrometry (ICP-MS), as well as graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrometry techniques (FAAS), and voltammetry. Wines from many countries have been successfully discriminated according to geographical region using elemental profiling (Angus et al. 2006, Etievant et al. 1988, Fabani et al. 2010, Gomez et al. 2004, Gonzalves et al. 2008, Kment et al. 2005, Moreno et al. 2007, Sperkova and Suchanek 2005, Thiel et al. 2004, Trujillo et al. 2011, Zou et al. 2012). To our knowledge, there are no published reports on the detailed elemental compositions and the classification of Turkish wines using multivariate statistical techniques. The classification of wine samples using multielement content is possible with the use of chemometric tools. Techniques such as principal component analyses (PCA), discriminant analyses (DA), and cluster analysis can be useful in the differentiation of samples according to their geographical origin, harvest year, and grape variety as well as the contribution of each variable to the established models.

Turkey has a long history of grapegrowing, and according to an OIV report on world vitiviniculture (OIV 2013), it had

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the fifth largest vineyard area of all wine-producing countries. The aim of this study was to characterize and classify monovarietal wine samples from grape varieties grown in Turkey based on their multielement composition and according to the geographic regions and grape varieties using multivariate statistical techniques. Significant elements that affected regional and varietal discrimination were also investigated.

Materials and Methods

Wine samples. A total of 116 commercial wine samples from the 2006, 2007, 2008, and 2009 harvest years were collected from local markets and included 66 red, five rosé, and 45 white wines. These wines were produced from 13 different grape varieties in Turkey, eight of which were native (Boğazkere, Öküzgözü, Çalkarası, Kalecik karası, Emir, Narince, Sultaniye and Papazkarası) and five of which were nonnative (Cabernet Sauvignon, Merlot, Syrah, Muscat, and Chardonnay) (Table 1). Information on vineyard and grape variety of the samples was based on the information given on the wine bottles. The grape varieties were cultivated in 10 different regions from three areas of Turkey (Figure 1). All native varieties in this study are used for winemaking. Among them Sultaniye (or Sultani, a seedless white grape) is also used for raisin production and fresh consumption.

Reagents. HNO_3 (suprapur 65%), H_2O_2 (suprapur 30%), multielement standard solution, and rhodium (Rh) were purchased from Merck (Darmstadt, Germany). Multielement standard solution of aluminum (Al), boron (B), barium (Ba), beryllium (Be), bismuth (Bi), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium

Table 1 The varietal, geographical area and region in Anatolia, and harvest year(s) for wine samples.

Varietal	Area	Region	Vintage year	Samples (n)
Red and rosé				
Boğazkere	Eastern	Diyarbakır	2007, 2008, 2009	5
Boğazkere	Central	Cappadocia	2006, 2008	2
Boğazkere	Central	Tokat	2007	1
Cabernet Sauvignon	Western	Izmir	2006, 2007	2
Cabernet Sauvignon	Western	Bozcaada	2007	1
Cabernet Sauvignon	Western	Thrace	2006, 2008	2
Cabernet Sauvignon	Central	Cappadocia	2007, 2008	2
Cabernet Sauvignon	Central	Tokat	2007	1
Çalkarası (red)	Western	Denizli	2008	1
Çalkarası (rosé)	Western	Denizli	2006, 2008, 2009	5
Kalecik Karası	Western	Denizli	2006, 2007, 2008	10
Kalecik Karası	Western	Izmir	2006	1
Kalecik Karası	Western	Thrace	2006	1
Kalecik Karası	Central	Ankara	2006, 2007, 2008	3
Merlot	Western	Denizli	2006, 2007, 2008	4
Merlot	Western	Izmir	2006, 2007, 2009	4
Merlot	Western	Thrace	2007, 2008	2
Öküzgözü	Eastern	Elazığ	2006, 2007, 2008, 2009	9
Öküzgözü	Central	Cappadocia	2006	1
Öküzgözü	Central	Tokat	2007	1
Papazkarası	Western	Thrace	2006	1
Syrah	Western	Denizli	2006, 2007, 2008, 2009	10
Syrah	Western	Manisa	2008, 2009	2
White				
Emir	Central	Cappadocia	2006, 2007, 2008, 0909	10
Muscat	Western	Denizli	2006, 2007, 2008, 2009	5
Muscat	Western	Izmir	2006, 2008, 2009	4
Muscat	Western	Thrace	2006	1
Muscat	Western	Manisa	2008	1
Narince	Central	Tokat	2006, 2007, 2008	5
Narince	Western	Denizli	2006	1
Narince	Western	Manisa	2008, 2009	2
Sultaniye	Western	Denizli	2006, 2007, 2008	5
Sultaniye	Western	Manisa	2006	1
Chardonnay	Western	Denizli	2006, 2007, 2009	3
Chardonnay	Western	Izmir	2007, 2008, 2009	4
Chardonnay	Western	Thrace	2006, 2007	2
Chardonnay	Central	Cappadocia	2008	1

(Ga), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr), tellurium (Te), thallium (Tl), and zinc (Zn) (100 mg/L) was dissolved in 1% HNO_3 (v/v) for external calibration. For ICP-MS analyses, Rh was used as internal standard. The tuning solution of ICP-MS was 1 mg/L Li, yttrium (Y), Co, Tl, and cerium (Ce) mixture (Agilent Technologies, Santa Clara, CA). A certified reference wine sample including Cd and Pb was used for the accuracy of ICP-MS analyses (T0777, FAPAS, York, UK).

Instrumentation. The ICP-MS instrument was an Agilent 7500ce ORS, equipped with a concentric nebulizer, nickel sampling cone, and peristaltic pump (Agilent Technologies). The octopole reaction system (ORS) used in the ICP-MS was FoodORS (library for food analysis) for the wine samples. Helium and no gas ORS modes were used in the method. The ICP-AES instrument was a Varian Liberty Series II with axial viewing plasma type (Varian Inc., Palo Alto, CA) and was used to quantify major elements such as Na, Mg, K, Ca, and Fe. Optimization parameters and operating conditions of ICP-MS and ICP-AES are given (Table 2).

Standards and spikes. The ICP-MS working standard solutions were prepared daily from stock solution using 1% HNO_3 solution. The calibration concentrations (19 points) ranged from 0.01 to 500 µg/L. Rh was used as internal standard in each ICP-MS working standard solution, wine sample, and spiked sample at a concentration of 10 µg/L in final solution. Spiked samples were also studied each time the digestion procedure was run. Trace elements like Be, Co, Ga, Cd, and Tl were spiked at a concentration of 2 µg/L. Li, Pb, Cr, and Ni were spiked at a concentration of 10 µg/L. Two spike concentrations (100 and 1000 µg/L) were used for B, Al, Mn, Cu, Zn, Sr, and Ba, which were present in wine at wider concentration ranges. The eight working standard solutions of ICP-AES (ranging from 0.3 to 60 mg/L) were prepared from the multielement standard using 1% HNO_3 solution with an external calibration technique. Major elements like Na, Mg, K, Ca, and Fe were spiked at 1 and 10 mg/L concentrations.

Sample preparation. The neck of wine bottles was cleaned with 2% HNO_3 solution before opening to prevent contamination by trace metals. Once opened, bottles were treated according to a procedure based on the wet digestion of organic material in an open vessel (Skurikhin 1993). Rh was added as internal standard (ISTD). The solution with ISTD and 10 mL HNO_3 was heated until it evaporated down to a volume of 5 mL. Later, 10 mL HNO_3 and 4 mL H_2O_2 were added. The heating process proceeded to a final volume of 5 mL. The next step was the addition of 5 mL HNO_3, 2 mL H_2O_2, and 10 mL ultrapure water and digestion of sample until the white fume was diminished. Eventually, the solution was diluted to a final volume of 100 mL with ultrapure water. The samples were kept at 4°C for 48 hours. The certified reference wine sample was treated in the same way as the wine samples. Two replicate digestions were made for each sample together with two blanks for every experiment set excluding the sample. The spiked samples were also prepared in an identical way following spiking.

Statistical analyses and method validation. The repeatability was evaluated by calculating the relative standard deviation of replicate measurements. The limit of detection

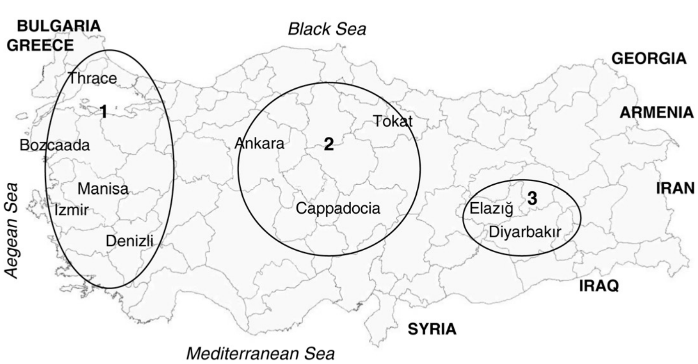

Figure 1 Wine regions in Turkey: (1) western Anatolia (Izmir, Manisa, Bozcaada, Thrace, Denizli); (2) central Anatolia (Ankara, Cappadocia, Tokat); and (3) eastern Anatolia (Diyarbakır, Elazığ).

Table 2 ICP-MS and ICP-AES operational parameters.

Parameter	Value
ICP-MS	
RF power	1550 W
Sampling depth	8–9 mm
Gas	Argon
Carrier gas flow	0.9 L/min
Make-up gas flow	0.15–0.19 L/min
Nebulizer pump	0.1 rps
Octopole reaction system	FoodORS
Interference equation	$^{208}Pb = {}^{208}Pb+{}^{206}Pb+{}^{207}Pb$
Sample and skimmer cones	Nickel
Nebulizer	Concentric
Spray chamber temperature	2°C
Reaction/collision	
He gas flow	4 mL/min
Signal measurement	
Acquisition mode	Spectrum multitune
Acquisition time	174 sec
Calibration	External
Internal standard	^{103}Rh
Repetition	3
Stabilization time	30 sec
ICP-AES	
Power	1.2 kW
PMT voltage	650 V
Gas	Argon
Plasma gas	15 L/min
Auxiliary gas	1.5 L/min
Nebulizer	Concentric
Pump rate	15 rpm
Fast pump	On
Rinse time	10 sec
Sample uptake	30 sec
Integration time	2 sec
Replicates	3
Calibration	External

(LOD) was calculated as three times the standard deviation of the signal of the blank sample (prepared 10 times). The limit of quantification (LOQ) was calculated as 10 times the standard deviation of the signal of the blank sample. Recoveries were calculated based on the difference of spiked and unspiked samples and by taking the ratio of this difference to the assigned value. In general, relative standard deviation <15% was obtained for the most variables. The elements with high relative standard deviations, such as Be, Ga, and Tl, were eliminated from data analysis (although reported in tables).

All data were standardized by subtracting the averages and dividing with the standard deviations. Transformation was used on the variables to minimize skewness. The statistical analysis for some samples having values below the LOD was performed by assigning the corresponding LOD value. The data were statistically evaluated by multivariate statistical analysis using Simca-P (ver. 10.5; Umetrics Inc., Umea, Sweden) and Minitab (ver. 16; Minitab Inc., State College, PA). Principal component analysis (PCA), partial least squares–discriminant analysis (PLS-DA), and hierarchical cluster analysis (HCA) were used to evaluate the effect of growing region and grape variety on wine mineral properties. With PLS-DA, ~80% of the data set was chosen for model development and the remaining 20% constituted the validation set. The model fit and cross-validation statistics of PLS-DA were given in terms of regression coefficients R^2_Y and Q^2, respectively. The significant variables affecting the models were determined with the variable importance plots (VIP) of PLS-DA models created by Simca software. The variables with a VIP >1.0 were taken as the significant ones in the model (Eriksson et al. 2001).

Results

The element concentrations of monovarietal red, rosé, and white wine samples are reported (Table 3, Table 4). The following elements were quantified in the samples: Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, and Zn. The results and recovery (%) values of the certified reference wine sample (contained 69.3 ng/mL Cd and 260 ng/mL Pb element) were 62.01% ± 9.78 and 89% ± 14 for Cd and 280.29% ± 29.36 and 108% ± 11 for Pb. The recovery values of spiked samples ranged from 77 to 120% for all elements except K and Zn (<60% in red wines). Mg in red and rose wines and Ga, Cd, and Tl in white wines produced recoveries >120%. The median values of Ca and Fe were consistent with the data from European viticulture areas and South Africa (Coetzee et al. 2005, Verbeke et al. 2009). The iron contents of red and white wines were also in agreement with data observed elsewhere (Simsek et al. 2008). The median values of Na and Mg contents were slightly greater than European wines, although the minimum–maximum ranges were consistent, and median levels were consistent with the Argentinean and Spanish wines. K levels in Turkish wines were lower than the levels in European wines but consistent with Argentinean wines (Fabani et al. 2010, Gonzalves et al. 2009, Verbeke et al. 2009). The minor elements were similar to those in literature. However, Pb, Cd, and Cu levels were lower than the data observed elsewhere (Simsek et al. 2008). According to the OIV maximum acceptable limits of elements in wine, one white wine sample (Narince variety from the Tokat region) exceeded the Cu limit (1 mg/L). The samples were below the OIV limits for Zn (5 mg/L) and Pb (0.15 mg/L).

The PCA model of all data showed that white and red wines were clearly separated from each other (score plot not shown). In the classification of wine samples, the white and red wines were studied separately in PLS-DA to show more clearly the separation among different red and white wine samples.

Regional discrimination. The PLS-DA models were developed by defining classes of wines with respect to the vineyard location. PLS-DA is a special extension of PLS regression and is used to find different classes of observations by using the information given in a X data matrix (n observations and z quality variables) and a Y matrix, which is a user-defined matrix of dummy variables representing the class of observations. In PLS-DA, among-classes variation is maximized against within-classes variation so that cluster of similar observations becomes apparent (Berrutetaa et al. 2007).

The PLS-DA model for the discrimination of red and rosé wines according to geographic region was developed with eight variables defined by the VIP feature of the Simca software: Sr, Ni, Ca, Cu, Li, Pb, B, and Al. The classes were established for Elazığ and Diyarbakır as class 1 (nine observations), Denizli as class 2 (28 observations), and Izmir, Bozcaada, Manisa, and Thrace as class 3 (13 observations). Wines from central Anatolia (Ankara, Cappadocia [Kapadokya], and Tokat) appeared very scattered within the control ellipse and failed to form a cluster; consequently, the red wines of this region were not included in class models. The model with two principal components produced a regression coefficient of Y matrix (R^2_Y) of 0.451 and a prediction coefficient (Q^2) of 0.275 (Figure 2A). The wine samples in the validation set were tested by the probability of the sample belonging to the model with a value >10% (Simca-P). All wines in the prediction set were correctly classified by the developed calibration model. Red wines of grapes cultivated in western Turkey (Izmir, Bozcaada, Manisa, and Thrace) could clearly be discriminated from those in eastern Turkey (Elazığ and Diyarbakır). The wines from western Anatolia had higher Pb levels than the wines from the east, which may be related to the growing industrial development of western Turkey. According to one study, the major source of lead contamination in table wines is the vinification process (Almeida and Vasconcelos 2003). Pb can also originate from environmental factors such as soil contamination, atmospheric pollution, and fungicidal treatment (Volpe et al. 2009). In our study, the wine samples were from different producers. Regardless of producer, the wines of western regions such as Izmir, Denizli, Manisa, and Thrace had higher Pb levels than the wines of other regions, but still had less than the legal limit set by the OIV (0.15 mg/L).

The PLS-DA model for the discrimination of white wines according to geographic region was developed with eight variables (Sr, Ni, Li, Mg, Ba, Pb, Co, and Al). The model with two principal components produced a regression coefficient of

Table 3 Element concentrations in red and rosé wines, shown as minimum (min), median (med), and maximum (max) values.

	Ca (µg/mL)	Fe (µg/mL)	K (µg/mL)	Mg (µg/mL)	Na (µg/mL)	Sr (ng/mL)	B (ng/mL)	Al (ng/mL)	Ba (ng/mL)	Li (ng/mL)	Cr (ng/mL)	Mn (ng/mL)	Co (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Pb (ng/mL)	Zn (ng/mL)	Ga (ng/mL)	Cd (ng/mL)	Be (ng/mL)	Tl (ng/mL)
Boğazkere																					
min	<LOQ	<LOQ	127	66	8.7	193	3447	163	32	8.93	7.29	0.81	<LOQ	16.56	10.62	0.23	116	0.1038	0.31	0.0578	<LOQ
max	86	3.39	472	152	82.9	652	6831	1556	191	22.99	38.66	1.36	7.3561	61.27	84.48	19.04	464	0.6839	18.33	0.4043	0.4666
med	55	1.18	289	100	14.9	361	4926	654	100	14.99	19.68	1.03	4.1041	37.10	28.32	8.24	249	0.2537	0.68	0.1545	0.2118
Cabernet Sauvignon																					
min	<LOQ	0.68	425	117	6.7	270	5085	243	60	8.12	14.30	0.73	2.4215	29.69	2.67	10.36	157	0.2471	0.16	0.0634	0.1636
max	64	3.46	768	167	44.6	933	8643	1410	255	25.23	28.27	1.50	6.8229	58.87	250.75	26.57	498	0.5848	12.05	0.3203	0.5813
med	53	1.79	542	124	29.6	464	6934	489	139	13.94	19.51	1.30	4.5837	43.47	97.66	14.22	347	0.3838	0.33	0.1692	0.3021
Kalecik Karası																					
min	<LOQ	0.84	182	74	<LOQ	226	4776	165	92	5.63	7.67	0.61	1.5750	10.58	21.13	1.11	115	0.1127	0.04	0.0047	0.0868
max	62	4.61	604	143	52.3	1643	10811	947	207	70.91	31.65	1.19	5.0510	60.64	426.34	33.35	333	0.5956	21.77	0.3265	0.5185
med	47	1.21	416	110	21.2	428	6239	392	128	13.40	15.62	0.96	3.3000	30.14	76.89	6.91	220	0.3082	0.28	0.0937	0.1890
Çalkarası (red)																					
single sample	15	0.91	148	101	4.3	221	5622	400	67	6.55	10.59	0.94	1.2230	23.81	41.62	2.12	185	0.1948	0.07	0.0208	<LOQ
Merlot																					
min	<LOQ	0.91	148	101	4.3	219	5597	294	67	6.55	10.59	0.94	1.2230	23.81	41.62	2.12	185	0.1948	0.07	0.0208	<LOQ
max	61	2.68	591	191	35.2	694	8574	851	195	23.63	22.88	1.56	7.7362	64.63	304.64	23.87	591	0.4383	17.29	0.3721	0.3956
med	50	1.25	373	129	20.1	393	7521	504	113	9.90	17.53	1.06	4.0804	44.99	139.38	10.66	430	0.3499	0.35	0.1163	0.1781
Öküzgözü																					
min	50	0.43	190	83	8.6	398	4310	326	54	8.85	8.92	0.83	<LOQ	10.07	9.70	1.28	81	0.0914	0.11	0.0258	<LOQ
max	89	2.98	497	154	58.9	708	6481	984	147	26.07	28.84	1.13	5.7910	43.42	306.72	27.70	378	0.6192	10.43	0.2619	0.2676
med	66	1.10	240	106	18.4	590	5601	669	107	16.31	17.12	1.04	2.9790	24.99	27.71	6.89	223	0.2998	0.50	0.1229	0.1217
Papazkarası																					
single sample	56	2.59	325	106	31.4	862	6828	1085	151	21.83	22.89	1.27	9.0051	59.94	348.27	22.52	324	0.6249	0.27	0.2500	0.1949
Syrah																					
min	<LOQ	0.50	242	108	7.6	225	4535	293	60	5.31	9.01	0.85	0.6835	22.66	19.80	2.00	262	0.1583	0.18	<LOQ	<LOQ
max	70	2.19	593	201	140.1	946	8727	837	168	34.75	25.05	1.25	5.2045	83.05	656.50	30.35	488	0.5826	20.36	0.2397	0.3603
med	55	1.18	401	127	17.7	353	6803	448	117	8.60	18.18	1.10	4.6817	33.19	141.04	8.60	357	0.3106	0.37	0.0993	0.1523
Çalkarası (rosé)																					
min	<LOQ	0.76	162	85	3.3	207	3759	388	64	8.91	9.59	0.73	2.3763	6.92	15.61	3.90	177	0.3566	0.14	0.0630	0.0652
max	79	1.18	334	112	27.7	266	5749	1208	87	18.63	15.98	1.26	6.0501	63.76	38.58	11.29	419	0.9925	21.18	0.2541	0.3589
med	65	0.88	235	108	8.8	250	4538	452	68	15.55	10.72	1.09	2.7005	16.77	27.78	10.18	211	0.4074	0.31	0.1109	0.2169
LOD	14.96	0.12	0.15	0.24	0.71	0.01	6.13	1.2	0.09	0.06	0.04	0.02	0.003	0.10	0.02	0.05	1.03	0.003	0.01	0.0005	0.001
LOQ	49.86	0.39	0.50	0.79	2.36	0.03	20.44	4.0	0.30	0.19	0.13	0.06	0.010	0.32	0.05	0.16	3.44	0.010	0.02	0.0017	0.002

Table 4 Element concentrations in white wines, shown as minimum (min), median (med), and maximum (max) values.

	Ca (µg/mL)	Fe (µg/mL)	K (µg/mL)	Mg (µg/mL)	Na (µg/mL)	Sr (ng/mL)	B (ng/mL)	Al (ng/mL)	Ba (ng/mL)	Li (ng/mL)	Cr (ng/mL)	Mn (ng/mL)	Co (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Pb (ng/mL)	Zn (ng/mL)	Ga (ng/mL)	Cd (ng/mL)	Be (ng/mL)	Tl (ng/mL)
Emir																					
min	<LOQ	0.40	60	77	9.8	560	3930	242	38	47.07	7.65	0.46	<LOQ	7.44	<LOQ	5.24	185	0.0961	0.12	0.1799	<LOQ
max	93	2.39	416	148	100.1	1264	6705	1661	135	386.37	24.96	0.92	3.9860	117.79	195.20	33.84	648	0.8323	31.40	2.0601	0.2705
med	70	0.64	164	94	21.2	894	5040	428	68	155.92	11.35	0.67	2.3970	16.61	23.41	9.66	307	0.2677	0.69	0.3150	0.0692
Chardonnay																					
min	<LOQ	<LOQ	108	54	<LOQ	178	4104	282	35	3.51	8.37	0.44	0.9850	16.94	18.41	1.85	175	0.1530	0.20	0.0263	<LOQ
max	94	52.77	468	153	29.8	1196	9886	1374	104	119.22	27.11	0.99	5.8394	84.91	467.65	33.76	764	0.4121	36.22	4.1898	1.7700
med	67	0.67	297	110	16.6	266	5221	485	63	13.81	14.09	0.81	3.9225	45.23	91.37	14.34	379	0.2993	0.55	0.2907	0.3196
Narince																					
min	<LOQ	<LOQ	185	70	13.9	164	3357	225	36	9.97	5.81	0.54	0.7000	9.55	6.94	2.02	115	0.1122	0.13	0.0403	<LOQ
max	90	0.88	507	140	44.4	849	5947	1212	101	121.62	40.02	0.94	3.6969	66.96	1055.50	27.33	808	0.4646	8.00	0.4652	0.5336
med	67	0.62	290	90	28.2	639	4511	601	80	24.77	14.15	0.71	2.0579	16.62	52.54	10.97	282	0.3352	0.46	0.3170	0.1171
Muscat																					
min	<LOQ	0.49	26	107	14.7	336	3539	397	46	7.02	7.80	0.68	1.9325	18.78	23.67	18.41	246	0.1521	0.30	0.2835	<LOQ
max	93	2.78	445	181	65.3	609	5967	2708	194	42.75	93.55	2.20	13.0600	115.16	300.50	72.43	663	2.0930	31.65	3.6333	0.8771
med	64	0.82	178	135	28.7	426	4961	672	75	29.40	13.65	1.02	4.7350	43.87	49.95	29.06	417	0.3218	0.69	0.8912	0.4409
Sultaniye																					
min	<LOQ	<LOQ	53	89	10.9	232	3106	234	52	9.69	8.11	0.66	1.1363	8.39	41.04	2.94	153	0.1680	0.10	0.0697	0.0534
max	85	3.47	455	153	47.4	781	10270	753	129	81.24	24.08	0.87	3.8695	30.31	211.09	13.20	509	0.4967	8.50	0.7095	0.3783
med	55	0.89	135	112	31.6	433	4397	473	80	21.04	13.17	0.71	2.7281	24.60	71.31	7.41	262	0.3464	0.32	0.2693	0.1058

Y matrix (R^2_Y) 0.619 and a prediction coefficient (Q^2) of 0.372 (Figure 2B). The regional classes were established for Cappadocia and Tokat wines as class 1 (13 observations) and for Denizli, Izmir, Manisa, and Thrace wines as class 2 (24 observations). Cappadocia and Manisa wines were the richest in Sr and Li contents, despite their different classes. Izmir and Thrace wines were rich in Pb, Co, Al, and Ni contents. Denizli wines were poor in Sr, Li, Ba, and Pb contents. The concentrations of natural minerals such as Ba, B, Li, Al, and Sr do not depend on agricultural and processing activities, and they can play role on the regional discrimination of wine samples. For this study, it was recognized that the farther the distances among the vine growing regions, the better the discrimination. Similar results were reported elsewhere (Capron et al. 2007).

Varietal discrimination. Varietal discrimination was investigated through PLS-DA and HCA. The classes were

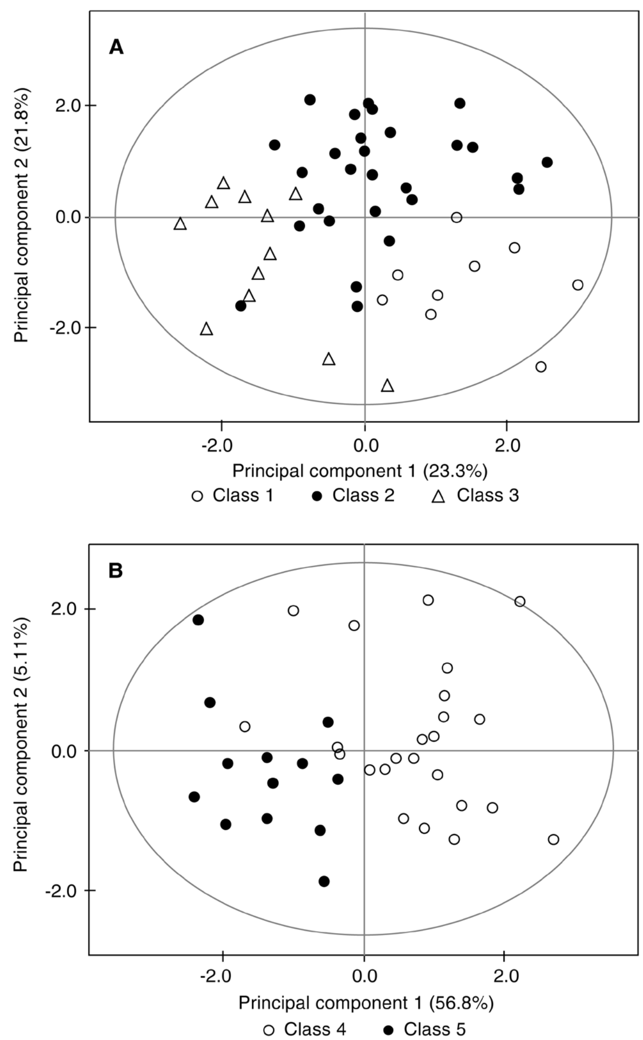

Figure 2 The PLS-DA score plots of red-rosé (**A**) and white (**B**) wines based on mineral content discriminated according to geographical region: (**A**) Class 1: Elazığ-Diyarbakır, Class 2: Denizli, Class 3: Thrace-Bozcaada-Izmir-Manisa; (**B**) Class 4: Thrace-Izmir-Manisa-Denizli, Class 5: Cappadocia-Tokat. The explained variation by each component is given in parenthesis on the axes.

defined with respect to grape variety. For the red wines, a two-component PLS-DA model was developed with Mn, Cu, B, Ca, Al, Ba, Li, K, and Zn ($R^2_Y = 0.191$, $Q^2 = 0.116$). The elements were defined by the VIP feature of Simca software as the significant variables in the discrimination. Results indicated that the wines of two native varieties, Boğazkere and Öküzgözü, could be discriminated from the other varieties based on their higher Ca and lower B and Cu levels (Figure 3A). The majority of these native wines were from the eastern regions (Diyarbakır and Elazığ). There were also five wine samples of Boğazkere and Öküzgözü from central Anatolia (Cappadocia and Tokat). These wines were also clustered among other Boğazkere and Öküzgözü samples, despite the regional differences. For the white wines, a two-component PLS-DA model was developed with Co, Cu, Li, K, Pb, Sr, Mg, Mn, and Na ($R^2_Y = 0.293$, $Q^2 = 0.191$). The discrimination between Emir and Muscat white wines was considered to be based on the higher Li and Sr and lower Cu levels of Emir wines and higher Pb, Co, and Mn levels of Muscat wines (Figure 3B). Emir is a native grape variety in central Anatolia, whereas Muscat is grown mostly in western Anatolia. Western Turkey is a highly industrialized area, which may help to explain the relatively higher Pb content of Muscat wines from Izmir, Manisa, Denizli, and Thrace. Details of PLS-DA models for red and white wines and the membership probabilities of samples in the validation sets are given in Supplemental Tables 1 and 2.

Hierarchical cluster analysis was successful in showing differences between some red and white wines. For red wines, native Öküzgözü wines were discriminated from the wines of Syrah and Cabernet Sauvignon varieties (Figure 4). The Euclidean technique and ward linkage method was preferred. The models were established using the variables used in the

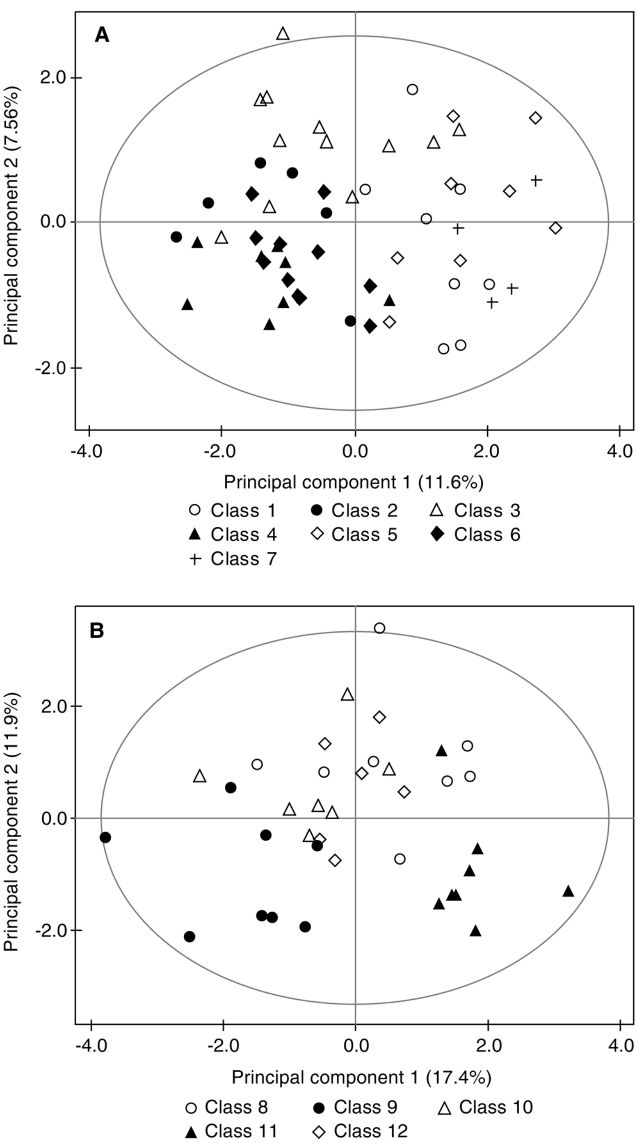

Figure 3 The PLS-DA score plots of red-rosé wines (**A**) and white wines (**B**) based on mineral content discriminated according to grape variety: (**A**) Class 1: Boğazkere, Class 2: Cabernet Sauvignon, Class 3: Kalecik Karası, Class 4: Merlot, Class 5: Öküzgözü, Class 6: Syrah, Class 7: Çalkarası; (**B**) Class 8: Chardonnay, Class 9: Emir, Class 10: Narince, Class 11: Muscat, Class 12: Sultaniye. The explained variation by each component is given in parenthesis on the axes.

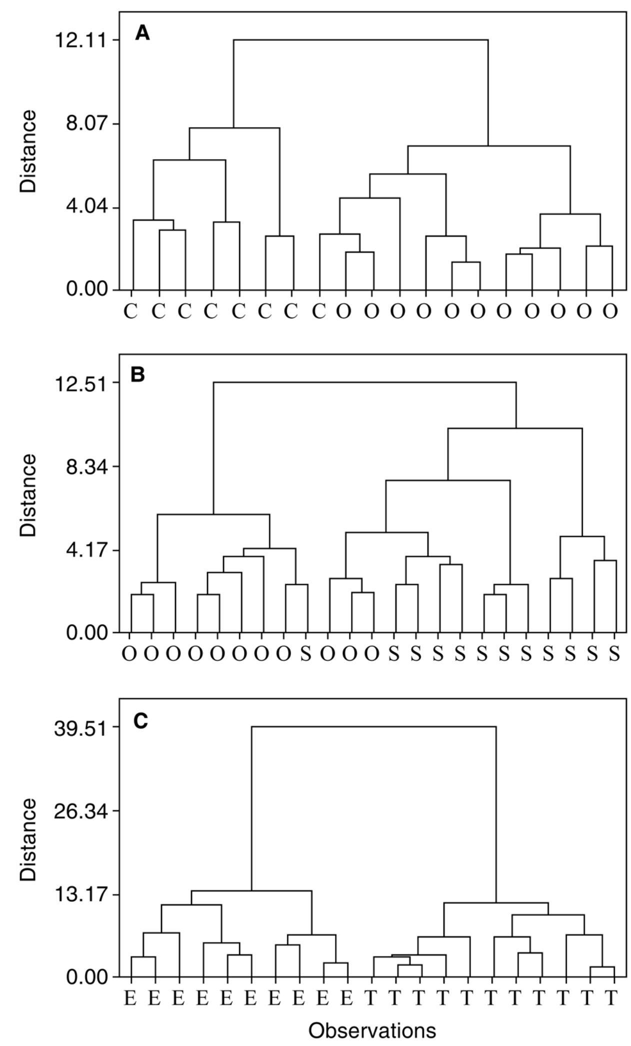

Figure 4 Dendrograms of some red and white wines based on mineral contents: **A**: Öküzgözü (O) and Cabernet Sauvignon (C) wines; **B**: Öküzgözü (O) and Syrah (S) wines; **C**: Emir (E) and Muscat (T) wines.

PLS-DA model for varietal discrimination of red wines. One Cabernet Sauvignon wine from the 2008 harvest year was clustered with the Öküzgözü variety (Figure 4A), and three Öküzgözü wines from 2009 harvest year were clustered within the Syrah group (Figure 4B). There was also one Syrah wine from 2006 harvest year located in the Öküzgözü cluster. For white wines, Muscat and Emir could be discriminated using the same variables used in the PLS-DA model of white wines. All the samples belonging to the two varieties were clustered in their own groups (Figure 4C).

Discussion

The elemental profiles of red and white wines differed from each other with higher levels of K and Ba and lower levels of Li in red wines. The slightly higher levels of minerals in red wines can be explained by the prolonged leaching of minerals from the grape during maceration (Coetzee et al. 2005, Martin et al. 2012). Statistical analyses were performed separately on the red–rosé wines and white wines.

The information for the wine samples in this study was based on the data given on the wine bottles. It should be emphasized that these commercial samples were produced under different conditions. The expected variability in their chemical composition due to the different vineyards, harvest year, or grape varieties might also be affected by the different production practices. Despite these various sources of variations, the wines of some varieties and some geographical origins separated themselves from others.

A limited number of samples made it difficult to fully evaluate the effect of variety and vineyard location. This was especially the case for the wines belonging to certain grape varieties, which were grown in one particular region only, such as Emir wines produced from Emir grapes of Cappadocia. Therefore, a confounding conclusion from the interpretation of data for regional and varietal classes could occur. In other words, it is not possible to be certain whether the differences of this wine are due to geographical origin or grape variety, with the available samples.

The performance of mineral content was also investigated for the discrimination of wine samples according to harvest years. The results of PCA indicated that the mineral profile of wine samples were independent of their vintage. Similar results have been reported (Martin et al. 2012).

Conclusion

The monovarietal wines produced from the native and nonnative grape varieties grown in Turkey were characterized in terms of elemental composition. The wine samples were classified with multivariate statistical techniques to show that the geography—where the grape was grown–determines the presence of certain minerals in wines. Regional discrimination was possible between the western and eastern wine-producing areas with the discriminating power of minerals such as Sr, Li, Ni, Ba, B, Pb, Ca, and Al. The wines of vineyards in western Turkey, where industrialization is high, discriminated themselves with relatively higher amounts of Pb, but still less than the allowable maximum level. Wines of some native Turkish grape varieties, such as Öküzgözü and Emir, had distinctive characteristics compared with the other wine samples.

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