Elemental profiling of Malbec Wines for geographical origin using an Agilent 4200 MP-AES

Application note

Food testing

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Introduction

Red wine produced from the Malbec grape is increasing in popularity in the United States. However, the US is a relatively small producer of the wine compared to Argentina, where it is the most extensively planted grape variety in the country. With rising imports into the US from Argentina there are growing concerns relating to the validation of the geographical origin of this wine.

Typically ICP-MS is used to distinguish between wines originating from different regions by comparing the relative concentrations of mineral elements, which are characteristic of the soil composition of the region of production. In this study, a cost-effective approach has been taken using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) to measure 6 elements (Sr, Rb, Ca, K, Na and Mg). Agilent's Mass Profiler Professional (MPP) integrated chemometrics software and another data analysis package were used to model the MP-AES results to distinguish the geographical origin of 41 Malbec wine samples produced in Argentina and the USA.

Experimental

Samples

Malbec grapes from the 2011 vintage were sourced from 41 different geographical sites; 26 from the Mendoza region of Argentina and 15 from California, USA. In order to reduce the impact of the wine making process on the elemental composition of each wine, and to preserve any elemental differences arising from the geographical origin, two central winemaking facilities only were used to produce the wine. Table 1 lists all the samples, with their detailed geographical origin. Details of the winemaking procedure can be found in the original study [1].

Calibration standards and reagents

Single-element calibration standards (Ca, K, Mg, Na at 10,000 mg/L, and Sr at 1,000 mg/L) were purchased from VHG Labs (Manchester, NH, USA), Rb 1,000 mg/L was from SPEX CertiPrep (Metuchen, NJ, USA), and concentrated nitric acid was obtained from JT Baker (Instra-Analyzed grade, Center Valley, PA, USA). The ionization buffer solution (100,000 mg/L Cs; Agilent, Santa Clara, CA, USA) was diluted to 2,000 mg/L in 1% HNO_3 prior to use. Ultrapure water (18 MΩcm, EMD Millipore Bellerica, MA, USA) and Uvasol spectroscopy grade ethanol from Merck (Whitehouse Station, NJ, USA) were used for the calibration solutions and dilutions.

Instrumentation

An Agilent 4200 MP-AES fitted with a MicroMist concentric nebulizer and baffled cyclonic spray chamber was used throughput the study. An External Gas Control Module (EGCM) was used to inject air into the nitrogen plasma to prevent carbon present in the wine samples from building up on the torch. This ensures stable results over the course of the analysis and reduces the background emissions generated by the organic species present in the sample. A 2,000 mg/L cesium (Cs) Ionization Buffer solution was constantly mixed with the sample stream immediately before entering the spray chamber, using a simple mixing tee.

Each element (Sr, Rb, Ca, K, Na and Mg) was monitored at a specific wavelength to ensure interference-free detection. EGCM and read time settings were optimized for each element. The instrument was calibrated and tuned daily using an Agilent wave calibration solution.

All wine samples were analyzed in triplicate after a 1:50 dilution in 5% HNO_3. A 6-point calibration between 0 and 500 mg/L was carried out for each element in matrix-matched calibration solutions (5% HNO_3 and 0.2% ethanol) to account for matrix interferences of the ethanolic wine solutions.

The sample introduction and calibration parameters used are given in Table 2 and 3 respectively.

Statistical data analysis

Data analysis of the concentrations of the 6 monitored elements monitored in each of the Malbec wines was carried out in RStudio (version 0.98.501, Boston, MA) and Agilent's Mass Profiler Professional (MPP; version 12.61). Multivariate analysis of variance (MANOVA) and individual univariate analysis of variance (ANOVA) for each element were run in RStudio. Elements that differed significantly among the wines were further used in an untargeted Principal Component Analysis (PCA) within the MPP software to visualize the sample differences. As a final analysis, Partial Least Squares – Discriminate Analysis (PLS-DA) was used for the geographical classification of the wines, according to country and to region within a country.

Table 1. Samples included in the study. For each wine sample, the district, department, and altitude is shown. *Denotes samples from the Yolo region - the only US region outside a recognized American Viticultural Area (AVA). *Source: Nelson et al [1].*

Sample code	District	Department / AVA or County	Altitude (meters above sea level)	Sample code	District	Department /AVA or County	Altitude (meters above sea level)
M1	La Consulta	San Carlos	999	M22	El Peral	Tupungato	1235
M2	Perdriel	Luján	964	M23	El Peral	Tupungato	1235
M3	La Consulta	San Carlos	999	M24	El Peral	Tupungato	1241
M4	La Consulta	San Carlos	999	M25	Gualtallary	Tupungato	1354
M5	La Consulta	San Carlos	999	M26	Gualtallary	Tupungato	1353
M6	Las Compuertas	Luján	1022	C1	Yountville	Napa	Not available
M7	Las Compuertas	Luján	1022	C2	Mount Veeder	Napa	315
M8	Las Compuertas	Luján	1022	C3	Mount Veeder	Napa	510
M9	Altamira	San Carlos	1024	C4	Mount Veeder	Napa	497
M10	Altamira	San Carlos	1043	C5	Oak Knoll District	Napa	25
M11	Altamira	San Carlos	1096	C6	Alexander Valley	Sonoma	58
M12	Altamira	San Carlos	1047	C7	Alexander Valley	Sonoma	68
M13	Altamira	San Carlos	1043	C8	Alexander Valley	Sonoma	53
M14	Altamira	San Carlos	1024	C9	Hames Valley	Monterey	214
M15	Gualtallary	Tupungato	1342	C10	Monterey County	Monterey	154
M16	Altamira	San Carlos	1052	C11	Lodi	San Joaquin	61
M17	El Peral	Tupungato	1235	C12	Winters*	Yolo	88
M18	Lunlunta	Maipú	931	C13	Winters*	Yolo	77
M19	Lunlunta	Maipu	930	C14	Winters*	Yolo	70
M20	El Peral	Tupungato	1235	C17	Red Hills	Lake	648
M21	El Peral	Tupungato	1235				

Table 2. 4200 MP-AES operating conditions. *Source: Nelson et al [1]*

Parameter	Value					
Element	Sr	Rb	Mg	Ca	Na	K
Monitored wavelength (nm)	407.771	780.027	279.553	396.847	589.592	769.897
EGCM setting	Low	Low	Med	High		
Pump rate (rpm)	10					
Sample tubing	Org-Grn					
Ionization buffer tubing	Org-Grn					
Waste tubing	Blue-Blue					
Read time (s)	5		2			
Number of replicates	3					
Sample uptake delay (s)	50					
Stabilization delay (s)	20					
Fast pump during uptake	Yes					
Background correction	Auto					

Table 3. Calibration parameters used for wine sample analysis. *Source: Nelson et al [1]*

Element	λ (nm)	Calibration Range (mg/L)	Background Correction	Calibration fit	Correlation Coefficient
Sr	407.771	0-5	auto	linear	0.9999
Rb	780.027	0-5	auto	linear	0.9997
Mg	279.553	0-5	auto	linear	0.9998
Ca	396.847	0-5	auto	linear	0.9999
Na	589.592	0-5	auto	linear	0.9999
K	769.897	0-20	auto	linear	0.99999

Results and discussion

Three sigma detection limits were determined by analyzing 10 sample blanks. All 6 of the elements monitored were detected in the 41 different wine samples at concentrations above their limits of detection (LODs), as shown in Table 4. All elements also differed significantly among the wine samples in a multi- and univariate analysis of variance at an α level of 5%. Thus, all 6 elements were included in the subsequent PCA and PLS-DA analyses.

Figure 1a shows a clear separation of the wines by country of origin, with only a slight overlap of two US wines. The component loadings plot (Figure 1a) shows that the elemental differences in Na and Sr primarily account for the separation by country of origin.

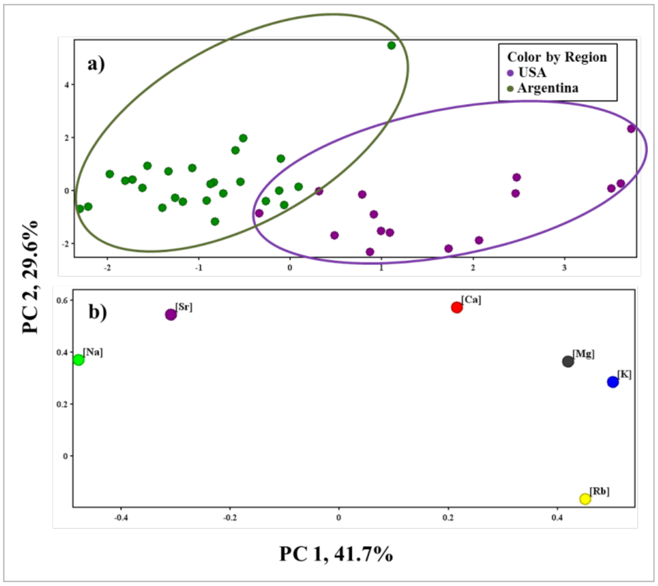

Figure 1. 2D PCA bi-plots using the 6 elements which differed significantly among the wine samples. (a) Product plot showing the wine samples color coded by geographical origin, (b) Loadings plot with 6 elements (Sr, Rb, Ca, K, Ca, Na and Mg). *Source: Nelson et al. [1].*

However, an almost 100% correct classification of the wines according to their country of origin was obtained using PLS-DA (Figure 2). Using cross-validation, the prediction accuracy for the USA wines was 93.3% and 96.2% for the Argentina wines, leading to an overall accuracy of 95.1% for the PLS-DA model (Table 5). The incorrectly classified wines (M1 for the Argentina wines and C12 for the USA wines), were most likely due to their higher/lower levels in Na, Mg, and K (M1 was low in Na, Mg, and K; C12 was high in Mg) compared to the other wines in the same class. Excellent classification was achieved. If a larger set of samples had been available, we would have tested to see how the model performs with complete unknown samples.

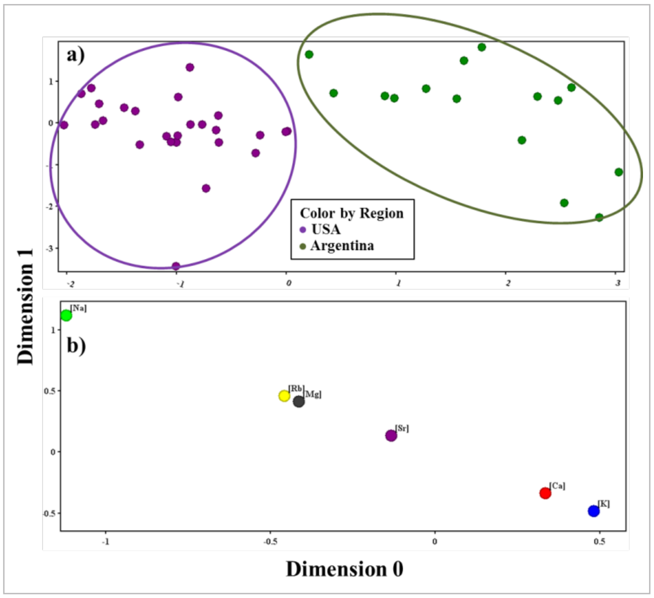

Figure 2. 2D PLS plots using the 6 elements which differed significantly among the wine samples. (a) Sample plot showing the separation of the wines according to geographical origin, with no overlap. (b) Element loadings plot. *Source: Nelson et al [1]*

Table 4. Detection limits (DL) and elemental concentrations for the wines from Argentina and the USA. Shown are mean $\bar{x}$, standard error of the mean $\sigma_{\bar{x}}$, and the minimal (min) and maximal (max) concentrations. Concentrations (mg/L) are given for the elements that differed significantly among the five wineries ($P \leq 0.05$). *Source: Nelson et al [1]*

		Wines from California, USA		**Wines from Mendoza, Argentina**	
	DL	$\bar{x} \pm \sigma_{\bar{x}}$	min – max	$\bar{x} \pm \sigma_{\bar{x}}$	min – max
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sr	0.0018	0.45 ± 0.02	0.24 - 0.83	0.77 ± 0.04	0.23 - 1.59
Rb	0.0004	3.37 ± 0.03	0.57 - 7.83	0.99 ± 0.02	0.55 - 2.19
Mg	0.0012	80.87 ± 0.42	61.75 - 144.86	72.87 ± 0.54	53.55 - 116.29
Ca	0.0016	51.78 ± 0.19	43.26 - 74.01	50.46 ± 0.25	33.22 - 95.08
Na	0.0007	4.90 ± 0.09	3.38 - 8.46	37.48 ± 0.48	13.71 - 121.87
K	0.0020	1444.42 ± 10.53	1120.94-2219.84	1181.22 ± 15.45	976.85-1989.12

Table 5. Result of the cross validation (leave one out algorithm) for the PLS-DA run on the 2 countries. *Source: Nelson et al [1]*

	USA (predicted)	Argentina (predicted)	Accuracy
Argentina (true)	1 (= M1)	25	96.2%
USA (true)	14	1 (= C12)	93.3 %
Overall accuracy			95.1 %

Conclusions

The Agilent 4200 MP-AES is an easy-to-use, low cost instrument suitable for geographical origin analysis of wine samples when combined with a data analysis package such as Agilent's Mass Profiler Professional (MPP). Six elements, Sr, Rb, Mg, Ca, Na, and K, were useful for broad classification of geographic origin of Malbec wines from Argentina and the US, with 14 out of 15 US samples correctly classified and only 1 out of 26 of the Argentinian wines wrongly classified.

Reference

1. Jenny Nelson, Helene Hopfer, Greg Gilleland, Daniel Cuthbertson, Roger Boulton, Susan E Ebeler. Elemental Profiling of Malbec Wines Made Under Controlled Conditions by Microwave Plasma Atomic Emission Spectroscopy. Am. J. Enol. Vitic. Published ahead of print April 2015

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