



Differentiation Between Argentine and Austrian Red and White Wines Based on Isotopic and Multi-Elemental Composition

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In this work, the characterization of white and red wines from Austria and Argentina was carried out based on the isotopic and multi-elemental profile data. They were determined using vanguard techniques such as isotope ratio mass spectrometry and inductively coupled plasma mass spectrometry. In particular, Al, As, B, Ca, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, V, Zn, δ^{18} O, and δ^{13} C were determined. The results show that the samples of wines from Argentina generally present higher concentrations of the elements analyzed compared to Austrian wines. δ^{18} O values from wine water were characteristic of each country, while δ^{13} C values from ethanol did not present any geographical distinction. Linear discriminant analysis using isotopes and elements allowed us to classify 100% of the wines according to the origin and additionally, 98.4% when separately investigating red and white wines. The elements Sr, Li, V, Pb, B, Mn, Co, Rb, As, Na, Mg, Zn, and δ^{18} O were identified as sensitive indicators capable of differentiate wines according to their production origin. Furthermore, Sr, Li, Na, 8¹³C, 8¹⁸O, Ca, B, Fe, Mn, V, Mg, Co, and Zn contributed to the differentiation of wines according to origin and color. To our knowledge, it is the first work that involves the measurement of a wide range of elements and stable isotopes in white and red wines in Argentina, as well as in Austria. This research highlights the power of the application of stable isotopes and multi-element data in multivariate statistical analysis, in order to obtain an accurate differentiation of wines origin.

Keywords: chemical fingerprint, multi-elemental analysis, stable isotopes, discriminant analysis, geographical origin

INTRODUCTION

Wine is a unique and widely-consumed alcoholic beverage worldwide since early civilization (Vystavna et al., 2014). Wine production is a major economic agricultural activity and its commercial value is derived significantly by the geographic area, year of grape production, cultivation and quality (Raco et al., 2015). It is viewed as a luxury product, which makes it highly susceptible to fraud and adulteration (Ranaweera et al., 2021). Wine counterfeiting or adulteration refers to the illegal techniques that have the goal to substitute one valuable component with a cheaper one to increase profit, thus deceiving the consumer (Geana et al., 2016). Manipulations can be ascribed to both its intrinsic (e.g., dilution of wines with water, addition

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Julieta Griboff, Magdalena V. Monferrán, Centro de Investigaciones en Bioquímica Clínica e Inmunología (CIBICI) - Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Nacional de Córdoba, Facultad de Ciencias Químicas, Depto. Bioquímica Clínica, Cdad. Universitaria, Córdoba, Argentina

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Griboff J, Horacek M, Wunderlin DA and Monferrán MV (2021) Differentiation Between Argentine and Austrian Red and White Wines Based on Isotopic and Multi-Elemental Composition. Front. Sustain. Food Syst. 5:657412. doi: 10.3389/fsufs.2021.657412 of alcohol, sugar, coloring, or flavoring substances) and its extrinsic properties (e.g., fraudulent misrepresentation of the cultivar, producer, and geographic origin) (Villano et al., 2017).

Special emphasis is placed on certifying the origin of wine since the geographic origin (terroir) has a fundamental impact on the wine profile and quality (Bejjani et al., 2014). In recent times, stable isotope analysis has been applied in numerous studies to determine the geographical origin of wines (Magdas et al., 2012; Camin et al., 2015; Durante et al., 2016, Horacek et al., 2019a,b; Horacek et al., 2021). Isotopic fractionation is related to the type of plant and area of growth, which are in correlation with climatic factors (humidity, temperature, amount of precipitation, etc.), as well as geographical factors (distance from the sea or other evaporation source, elevation, altitude, latitude) (Dordevic, 2015). The stable isotopes of oxygen (δ^{18} O) values of water of the grape are modified during ripening and harvest with the processes of evaporation and condensation of the water cycle (Dutra et al., 2013). The specific climatic conditions of a location, which already influence the isotopic composition of the precipitation, additionally modify the transpiration of leaves and fruit, resulting in the δ^{18} O of water of wines reflect the location where the product comes from Roßmann et al. (1999) and Raco et al. (2015). The stable isotopes of carbon (δ^{13} C) value of wine ethanol are closely related to the origin of fermented sugar and can also be affected by climatic factors, especially drought stress (Roßmann et al., 1996, Horacek et al., 2015).

Furthermore, the fingerprinting of the content of metals in wines is a valuable method to authenticate their geographical origin (da Costa et al., 2020). The mineral composition of wine is influenced by endogenous sources, such as elements naturally present in the soil where grapes are grown, or climatic conditions; and exogenous sources, associated with external impurities that reach wine, such as the use of pesticides/fertilizer, machinery in the winery, or use of fining agents (Preti, 2019, Viviers et al., 2013). In particular, white and red wines are produced by different winemaking procedures and consequently, a differential metal uptake may result (Haseeb et al., 2019; Dumitriu et al., 2021). Moreover, knowledge of the elemental composition of wine is also very important due to their toxic effect on the human body in case of excessive intake and the impact on the quality (Płotka-Wasylka et al., 2018). Metals play an important role in the stability, color and clarity of wines that affect their organoleptic characteristics (Bimpilas et al., 2015).

In order to enhance the ability to assure wine authenticity, the outputs derived from analytical techniques have been combined with multivariate statistical analysis to differentiate samples according to the country/region they come from, variety, or other properties (Fan et al., 2018; Yamashita et al., 2019). The main goal of this work was to study whether the wines from Argentina (South America) and Austria (Europe) could be characterized and differentiated according to the isotopic and multi-elemental profile. Therefore, the analysis of 18 elements, δ^{18} O and δ^{13} C was carried out in 62 wine samples, 37 from Argentina, and 25 from Austria. Subsequently, chemometric analysis (linear discriminant analysis) was used to find the most discriminative variables to distinguish among countries and color of wine.



FIGURE 1 | World map in which the countries under study are highlighted; Argentina (South America) and Austria (Europe).

MATERIALS AND METHODS

Wine Samples

A set of 62 wines purchased from the major wine-producing regions of Argentina (32 red and 5 white samples) and Austria (6 red and 19 white samples) were subject of this study (Figure 1). However, it is noteworthy that in statistical terms, some categories are smaller than the other and for more accurate results it will be necessary to analyses a large number of samples. The wine samples were collected from the vintage years of 2008, 2009, 2012, 2013, 2014, and 2015. Different wine varieties were collected, which included the main grape varieties in the different countries. The grape varieties under study were Cabernet Sauvignon, Malbec, Merlot, Pinot Noir, and Syrah for red wines and Chardonnay, Torrontés, and Viognier for white wines from Argentina and Chardonnay, gruener Veltliner, Rhine Riesling, Welschriesling, Pinot blanc (Weissburgunder), Müller Thurgau, and Sauvignon blanc for white and Zweigelt, Blaufränkisch, and blue Wildbacher (Blauer Wildbacher) for red wines from Austria. Wines were sampled from freshly opened bottles and transferred to polypropylene flasks for isotopic and multi-element analysis. The plastic containers used to place the wine samples for element analysis were previously cleaned by washing with 10 % HNO₃ (Merck, ultrapure grade) for at least 24 h, and then rinsed copiously with ultra-pure water (Vrček et al., 2011).

Multi-Element Analysis

Al, As, B, Ca, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, V, and Zn were measured using an Agilent 7500cx Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent Technologies, CA-USA), equipped with an ASX-100 autosampler (CETAC Technologies, Omaha, NE-USA). Wine samples were digested using Teflon tubes. First, \sim 2.5 mL of wine sample was digested using 3 mL of HNO₃ (sub-boiling) in closed Teflon tubes on heating plates set to 220°C, during 6 h. Digested samples were quantitatively transferred to 10 mL volumetric flasks, completing the volume with HNO₃ 2%, followed by filtration using 0.45 μ m filters. This process was done in triplicate. All samples were stored at 4°C until analysis. Moreover, three samples were spiked to verify recovery percentages of elements. Variable amounts of mixed standard solutions, containing all elements analyzed were added to the wine sample prior to sample digestion, to double the starting concentration for each element. The rest of the procedure was the same as used for non-spiked samples. The average recovery was 98 \pm 7%. In addition, the accuracy of measurements of the ICP-MS was checked through the analysis of a standard reference material (NIST 1643e, Freshwater). The recoveries of the reference and spiked samples for tested elements are shown in **Supplementary Table 1**.

Isotopic Analysis

The determination of ¹⁸O/¹⁶O isotopic ratio from the water extracted from wine and of ¹³C/¹²C isotopic ratio in the ethanol extracted from wine was performed. Prior to analysis, the wine samples were distilled using an automated distillation control system (Eurofins/Nantes, France) in order to extract the ethanol and water. The samples were measured at the BLT Wieselburg stable isotope facility. Carbon isotopes were measured by injecting the alcohol in a Flash HT elemental analyzer (ThermoFisher, Bremen, Germany). The produced CO₂ gas is flushed by continuous helium flow into a Delta V IRMS (ThermoFisher, Bremen, Germany) and analyzed for their stable isotope ratio. Oxygen isotopes were measured by equilibration method in a gas bench (ThermoFisher, Bremen, Germany) and the equilibrated gas (mixture 0.36% CO₂ in Helium 5.0) is flushed by continuous gas flow into a Delta V IRMS (ThermoFisher, Bremen, Germany) for stable isotope ratio determination.

The results are expressed in the conventional δ -notation in % with respect to the V-SMOW (Vienna-Standard Mean Ocean Water) and to the V-PDB (Vienna-PeeDee Belemnite) standards for oxygen and carbon, respectively. The enlarged reproducibility of measurements of δ^{13} C and δ^{18} O were better than \pm 0.1 and \pm 0.2‰, respectively. For quality control certified standards and reference materials were analyzed together with the wine samples. Among the measured standards are V-SMOW, SLAP (both provided by the International Atomic Energy Agency (IAEA) Vienna), BCR 660, BCR 656 [both produced by the Institute of Reference Materials and Measurements (IRMM) from Geel, Belgium].

Statistical Analysis

The results were expressed as maximum, minimum, mean values and standard deviations and were processed according to four wine categories. The groups were defined as follows: Arg- white and Arg-red (white and red wines from Argentina, respectively) and Aut-white and Aut-red (white and red wines from Austria, respectively). Shapiro–Wilks and Levene tests were used to assess normality and homogeneity of variances, respectively. The data obtained satisfy these assumptions and were processed statistically by analysis of variance (ANOVA), to examine the difference between groups of wines, using DGC at p < 0.05 to compare means (Balzarini et al., 2015). Linear discriminant analysis (LDA, stepwise mode) was executed in

order to differentiate countries and wine types by multivariate models. All the statistical analyses were performed using InfoStat (V1.1) and Statistica 7.0 Software.

RESULTS AND DISCUSSION

Elemental Profiling of Four Wine Groups

Table 1 summarizes the results obtained for the set of Argentine and Austrian samples, according to red and white wines. Regarding the mean concentrations, the elements were divided into "macro elements" (concentration $\geq 1 \text{ mg L}^{-1}$) and "trace elements" (concentration $<1 \text{ mg L}^{-1}$). Among the results, the variability of element concentration in each group of samples is considerable, showing a wide range of values for each element even in wines from the same geographical area and type. It should be noted that the results presented correspond to average values of samples of wines from different varietals, producers and years. Elemental wine composition is influenced by many factors, including the mineral composition of soil, viticultural practices, environmental factors, fermentation process, and the procedure of storage condition (Gutiérrez et al., 2017).

Despite this, the wines from Argentina showed higher concentrations for most of the elements, except for of Al, Ni, Rb, and Zn, which showed no significant differences between the countries under study and the wine color. Considering that some elements exhibit a good correspondence between its content in both soil and wine, the results obtained would indicate that the geochemical or soil composition is very different between countries, and presumably, the Argentine soil has higher levels of metals than the Austrian soil. The values adopted by these elements are within the range reported in the literature for wines from different countries (Kment et al., 2005; Galgano et al., 2008; Jurado et al., 2012; Espinoza Cruz et al., 2020). A few elements were statistically differentiated in the four groups; Sr and Li (the latter not detected in Aut-red). Strontium is considered a very interesting parameter in the study on the geographical origin of wines because it is an element less prone to being altered by anthropogenic influences (Gremaud et al., 2004).

Considering the Argentine samples, Ca, B, K, Mg, As, Co, and V did not show statistically significant differences between white and red wines. However, Cu, Mn, and Sr were found in higher concentration in red wines and Fe, Na, Li, and Pb in white wines. The results received for Argentinean wines were comparable with those reported in the literature available about this country. It should be noted that to our knowledge, it is the first work that involves the measurement of a wide range of elements in white and red wines in Argentina, as well as in Austria. Azcarate et al. (2015) analyzed the elemental composition of 57 Argentine white wines, those results were similar on As, Cu, Li, Rb, and Sr concentrations found in Arg-white. Instead, in the present study Co, Mn, Ni, and V were found in lower concentration and Pb in higher concentration. Pb may come from fungicidal treatments, sealed or corroded containers, or from pollution (Potortí et al., 2017). On the other hand, Di Paola-Naranjo et al. (2011) analyzed several elements in typical Argentinean red

	Arg-white		Arg-red		Aut-white		Aut-red		
	Minimum– maximum	$\text{Mean} \pm \text{SD}$	Minimum– maximum	$\text{Mean} \pm \text{SD}$	Minimum– maximum	$\text{Mean} \pm \text{SD}$	Minimum– maximum	$\text{Mean} \pm \text{SD}$	
Macro elem	ents (mg L ⁻¹)								
В	4-10	$7\pm2^{\rm A}$	3–18	$8\pm4^{\rm A}$	1–12	$3\pm2^{\mathrm{B}}$	3–8	$5\pm2^{\mathrm{B}}$	
Ca	53-114	$79\pm23^{\rm A}$	43–96	$69\pm13^{\rm A}$	40-86	$54\pm11^{\mathrm{B}}$	45-62	$54\pm7^{\mathrm{B}}$	
Fe	1–6	4 ± 2^{A}	1–41	$2\pm1^{\text{B}}$	0.2-1.7	$1.0\pm0.4^{\rm C}$	0.3–1.6	$1.1\pm0.5^{\rm C}$	
К	687-1,584	$1,\!243\pm337^{\rm A}$	790–1,606	$1,182 \pm 191^{\rm A}$	384-1,780	$644\pm354^{\mathrm{C}}$	658–1,349	$925\pm236^{\rm B}$	
Mg	66–131	$91\pm28^{\rm A}$	77–118	$100\pm9^{\rm A}$	58-105	$78\pm10^{\mathrm{B}}$	56-103	$81\pm16^{\rm B}$	
Na	52-200	$120\pm68^{\rm A}$	17-200	$51\pm40^{\mathrm{B}}$	5–16	$8\pm3^{\rm C}$	4–15	$7\pm4^{\rm C}$	
Trace eleme	ents (μg L ^{−1})								
AI	275-1,388	$947\pm444^{\rm A}$	n.d12,260	$729 \pm 2,135^{A}$	n.d169	50 ± 57 $^{\rm A}$	n.d156	$99\pm57^{\rm A}$	
As	n.d19	$11\pm9^{\rm A}$	n.d32	$11\pm7^{\text{A}}$	<l< td=""><td colspan="2"><lod< td=""><td colspan="2"><lod< td=""></lod<></td></lod<></td></l<>	<lod< td=""><td colspan="2"><lod< td=""></lod<></td></lod<>		<lod< td=""></lod<>	
Со	0.7–3.4	$2.5\pm1.1^{\rm A}$	0.3–9.8	$2.1\pm1.6^{\rm A}$	0.3-1.8	$1.0\pm0.4^{\rm B}$	0.7-1.7	$1.1\pm0.4^{\rm B}$	
Cu	34–137	$95\pm42^{\mathrm{B}}$	18-869	$191\pm208^{\rm A}$	5–198	$57\pm50^{\mathrm{B}}$	52-82	$67\pm11^{\mathrm{B}}$	
Li	115–267	$187\pm67^{\rm A}$	n.q250	$100\pm54^{\rm B}$	n.q13	$6 \pm 5^{\rm C}$	< LOD		
Mn	584–981	$830\pm149^{\rm B}$	599-1,291	$996\pm174^{\rm A}$	267–953	$485\pm187^{\rm C}$	467–938	$729\pm198^{\rm B}$	
Ni	3–22	$12\pm7^{\rm A}$	1–262	$17\pm46^{\rm A}$	3–16	8 ± 4^{A}	7–22	$13\pm6^{\mathrm{A}}$	
Pb	4–33	$20\pm11^{\text{A}}$	n.q30	$11\pm7^{\text{B}}$	2–6	4 ± 1^{C}	2–4	$3 \pm 1^{\rm C}$	
Rb	423-1,316	$810\pm381^{\rm A}$	585-1,669	$970\pm286^{\rm A}$	260-1,564	$706\pm395^{\rm A}$	154–1,878	$894\pm605^{\rm A}$	
Sr	742-1,178	$911\pm162^{\rm B}$	684–1,613	$1,215 \pm 245^{\rm A}$	93–195	$142\pm31^{ m D}$	233–446	$364\pm86^{\rm C}$	
V	1–56	$29\pm21^{\text{A}}$	1–131	$40\pm34^{\rm A}$	0.3–5.3	$1.3\pm1.1^{\rm B}$	0.3–2.9	$0.8\pm1.0^{\rm B}$	
Zn	161–655	$367\pm221^{\rm A}$	1-2,161	$495\pm355^{\rm A}$	75–642	$318\pm140^{\rm A}$	242-441	$352\pm73^{\rm A}$	
Stable isoto	pes								
δ ¹³ C	-27.30 to -25.7	$1-26.21\pm0.70^{A}$	-29.7 to -26.5	$-27.56 \pm 0.63^{\rm A}$	-29.08 to -25.61	-27.64 ± 1.02^{A}	-28.72 to -25.45	$-26.91 \pm 1.23^{\rm A}$	
δ ¹⁸ Ο	2.20-2.80	$2.50\pm0.42^{\text{A}}$	0.08-6.47	$2.60\pm1.68^{\text{A}}$	0.03–3.13	$1.12\pm0.85^{\text{B}}$	0.48–1.82	$1.43\pm0.64^{\text{B}}$	

TABLE 1 | Means and standard deviations of measured elements and stable isotopes corresponding to Arg-white, Arg-red, Aut-white, and Aut-red samples.

n.d., not determined; <LOD, below limit of detection. LODs: Al 1.02 μ g L⁻¹; As 0.09 μ g L⁻¹. n.q., not quantified; <LOQ, below limit of quantification. LOQs: Li 0.06 μ g L⁻¹; Pb 0.05 μ g L⁻¹. Different letters in the same row indicate significant differences among the four categories P < 0.05.

wines and the concentrations were compatible with those found in this study.

Regarding Austrian samples, for the majority of elements, there are no significant differences between the red and white wines, except for K, Mn, and Sr, which are present in higher concentrations in red wines and Li in white wines. A study conducted by Gruber et al. (2006) determined the concentration of Ca, Fe, K, Mn, Rb, and Sr in Austrian red and white wine. The informed values are similar to those obtained in this study, generally with the minimum concentration reported. It is noteworthy that a harmful element such as As was not detected in any wine sample from Austria, while in the Argentine ones it was. Arsenic is one of the most toxic pollutants abundantly present in the earth's crust (Litter et al., 2019). Argentina is one of the most affected countries by the natural presence of high concentrations of this element in soil and groundwater (Bardach et al., 2015).

Knowledge of the mineral content in wine is of considerable interest because of their repercussions in organoleptic, hygienic, and nutritional characteristics as well as their toxicological implications (Gutiérrez et al., 2017). In moderate quantities, the consumption of wine contributes to obtain elements that are essential to the human organism (such as Ca, Co, Cu, K, Fe, Mg, Mn, Ni, and Zn), while others must be controlled due to their potential toxicity (such as As, Cd, Cr, Hg, and Pb) (Rocha et al., 2019). In accordance with the maximum acceptable limits of B, As, Cu, Pb, and Zn, defined by the International Organization of Vine and Wine—OIV (International Code of Oenological Practices., 2020), none of the element concentrations analyzed in this work exceeds the risk levels reported by this intergovernmental organization, of which Argentina and Austria are member countries.

Values of δ^{18} O of Wine Water and δ^{13} C of Ethanol

The studied samples were characterized by δ^{18} O of water in the range of 2.20–2.80, 0.08–6.47, 0.03–3.13, and 0.48–1.82‰ for Arg-white, Arg-red, Aut-white, and Aut-red, respectively (**Table 1** and **Figure 2A**). Among the studied countries, significant differences were observed in the results of δ^{18} O of water, with lower oxygen isotope values for the Austrian wines. Wines from each country did not differ between white and red. The value of this parameter has a strong relationship with location and the origin of the water the vines accessed, and climatic conditions (Fan et al., 2018). Differences in the isotopic ratio of precipitation are present in hot and dry areas compared



to wet and cold areas (Dutra et al., 2013). Usually, more positive values of δ^{18} O indicate lower altitude, higher temperature and/or lower rainfall and/or coastal environment (Magdas et al., 2012; Wu et al., 2019; Horacek et al., 2021; Leder et al., 2021). Based on this, and the specific characteristics of each country, the more enriched values of the Argentine wines can be dominantly explained by the warmer climate they are produced in with respect to the Austrian wines. However, this difference in δ^{18} O between Austrian and Argentine is reduced (lower than to be assumed), as in Argentine most wine regions widely irrigate their vineyards using water coming from high-altitude mountainous areas. The origin of this irrigation water, possessing a low δ^{18} O value, which in turn is transferred into the vines, thus resulting in depleted δ^{18} O-values of wines from these regions (Horacek et al., 2021).

 $\label{eq:table_table_table} \textbf{TABLE 2} \mid \textbf{Result of classification using linear discriminant analysis in the four group of samples.}$

	Percent correct	Aut-white	Aut-red	Arg-white	Arg-red
Aut-white	100.00	19	0	0	0
Aut-red	83.33	1	5	0	0
Arg-white	100.00	0	0	5	0
Arg-red	100.00	0	0	0	32
Total	98.39	20	5	5	32

The range of values of δ^{18} O found in the Austrian samples was similar to the range found in Austrian wines previously (Philipp et al., 2018) and in wines from Germany (Monakhova et al., 2014), but showing less variation with respect to those



found in studies conducted in other neighboring countries like Switzerland (Gremaud et al., 2004) and Italy (Raco et al., 2015). Conversely, the range of isotopic values of Argentine wines is wider than those found in the neighboring country Brazil (Adami et al., 2010; Dutra et al., 2013).

The δ^{13} C ethanol values of the studied wines range from -27.3 to -25.7%, -29.7 to -26.0%, -29.1 to -25.6% and -28.7 to -25.5% for Arg-white, Arg-red, Aut-white, and Autred, respectively (**Figure 2B**). No significant differences were observed between the analyzed samples from Argentina and Austria in terms of δ^{13} C. Considering that grape vines are C3 plants and assume typical values between -29 and -24%, all the samples show expected δ^{13} C ethanol values (Wu et al., 2019). This would indicate that the oenological practices carried out are similar for wine production in both countries, according to the non-addition of C4 sugar (cane or maize sugars) (Geana et al., 2016) and the absence of clear drought stress, as the latter results in an increase of the δ^{13} C-value (Ballantyne et al., 2011; Horacek et al., 2015).

The values reported in the present study are similar to the range found in Austrian wines (Philipp et al., 2018) and in different European countries; for example, Italy where the range was -28.9 to -25.7% (Bonello et al., 2018), France where it was from -29.5 to -24.1% (Wu et al., 2021), and Romania where it was from -29.2 to -25.2% (Geana et al., 2016).

Verification of Wine Origin

Linear discriminant analysis (LDA) is one of the most widely used statistical methods for classification purposes

in the field of food analysis (Magdas et al., 2021). The wine samples from Argentina and Austria were subjected to Forward stepwise LDA, providing a mathematical model to classify and identify the particular fingerprints, regarding to the isotopic and multi-elemental profile, according to their origins. The analysis of the data set allows distinguishing between the countries with 100% certainty on the basis of 13 variables out of 20: Sr, Li, δ¹⁸O, V, Pb, B, Mn, Co, Rb, As, Na, Mg, and Zn. In similar studies, some of these selected variables have been reported for statistical analysis in LDA models as contributing to the differentiation of milk in Argentina (Griboff et al., 2019) and carrots in Austria (Jandric et al., 2020), demonstrating the usefulness of multivariate statistical approaches, that apply chemical data, for the characterization, and differentiation of food from different countries.

Another LDA was executed to discriminate the four wine groups (Arg-white, Arg-red, Aut-white, and Aut-red) using elements and stable isotopes. **Table 2** present the classification results of the Forward stepwise LDA performed. Classification of the wine samples by the LDA model showed 98.4% accuracy (**Figure 3**). In other words, 61 of the 62 samples were correctly predicted and only one sample belonging to the Aut-red group, could not be classified correctly. As can be seen from **Figure 3**, white and red wines originating in Argentina clearly differ according to their multi-element and isotopic profile. However, for white and red wines from Austria a complete differentiation is not achieved. Thirteen elements and both stable isotopes contributed to the differentiation of the four groups: Sr, Li, Na, δ^{13} C, δ^{18} O, Ca, B, Fe, Mn, V, Mg, Co, and Zn. Similar variables that made the strongest contribution to the differentiation of wine were reported by Di Paola-Naranjo et al. (2011) in Argentina, Horacek et al. (2019b) in Central Europe, Wu et al. (2021) in France and Shimizu et al. (2018) in Japan.

CONCLUSIONS

To our knowledge, this is the first report for a wide variety of elements and stable isotopes, from both Argentinean and Austrian origins, in white and red wines. Furthermore, the execution of the multivariate statistical analysis using elemental concentrations and stable isotopes proved to be a powerful strategy to differentiate the origin of wine on a global scale. On the one hand, the metal content was remarkably different between Austrian and Argentine wines, where the latter has generally higher concentrations. On the other hand, δ^{18} O values from wine water were shown to be efficient in differentiating wines according to the country of origin. However, the δ^{13} C values from ethanol did not allow the differentiation of wines according to their origin or color. Moreover, LDA models using isotopes and minerals have shown that good wine origin/color classification can be reached. In this work, the proposed LDAs showed a great potential ability for wine discrimination, with the accuracy rate of 100 and 98.4% classifying wines from Argentina and Austria, and the four groups, respectively. Therefore, we estimate that using the merged data from these techniques in combination with multivariate analysis is worthwhile and effective in wine traceability.

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DATA AVAILABILITY STATEMENT

The original contributions generated for the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author/s.

AUTHOR CONTRIBUTIONS

JG: methodology, investigation, and writing—original draft. MH: conceptualization, methodology, writing—review and editing, and funding acquisition. DW: conceptualization, writing—review and editing, and funding acquisition. MM: conceptualization, methodology, and writing—review and editing. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

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