The use of ICP-MS & ICP-MS-MS techniques for food geographic traceability

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Workshop A.I.S.E.T.O.V. 2019 Piacenza 21 Giugno 2019

Introduction

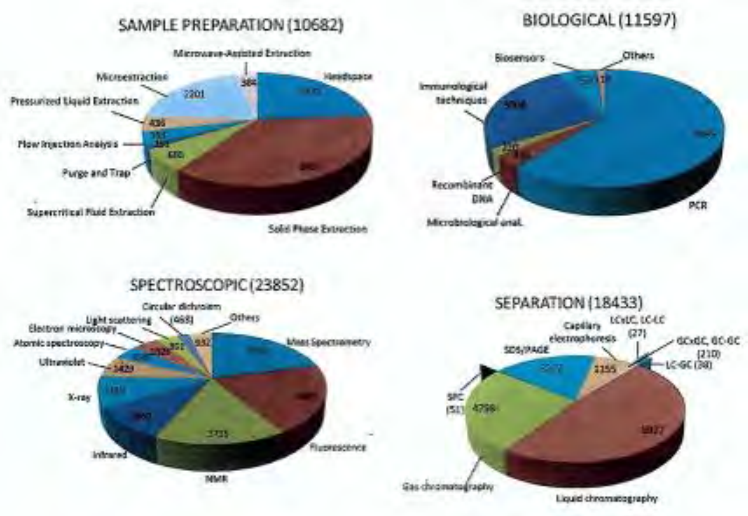
Wet chemistry was the most used technique in the past for food analysis; thereafter there appeared analytical techniques based on NIR and MIR spectroscopy, mass spectrometry (MS), isotope ratio mass spectrometry (IRMS), multielementar analysis (ICP-MS; ICP-MS/MS) and nuclear magnetic resonance (NMR). In general the choice of a suitable technique is not an easy task to do and it often happens that one technique is not sufficient and two or more ones are required to reach the final goal.

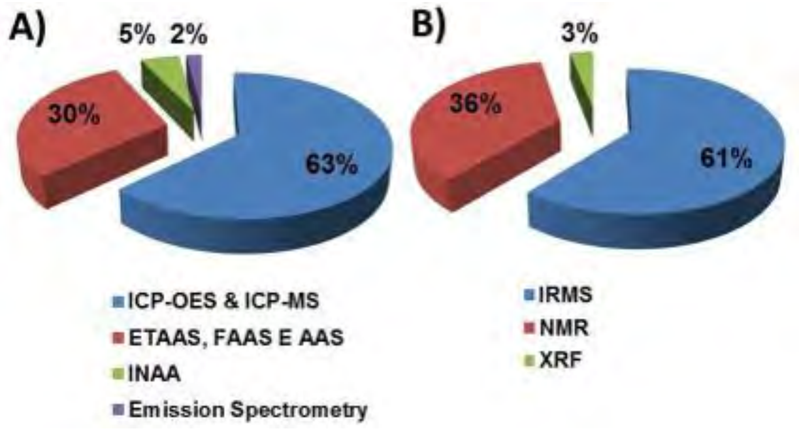
Principal techniques		Core techniques
Mass spectrometry techniques	**IRMS**	Isotope Ratio Mass spectrometry
	ICP-MS	Inductively Coupled Plasma Mass Spectrometry
	PTR-MS	Proton Transfer Reaction Mass Spectrometry
	GC-MS	Gas Chromatography Mass Spectrometry
Spectroscopic Techniques	**NMR**	Nuclear Magnetic Resonance Spectroscopy
	IR, FTIR	Infrared Spectroscopy
		Fluorescence Spectroscopy
	AAS, AES	Atomic Spectroscopy
Separation Techniques	**HPLC**	High Performance Liquid Chromatography
	GC	Gas Chromatography Mass Spectrometry
	CE	Capillary Electrophoreris
Other Techniques		Sensor Technology
	PCR	DNA Technology

Source: Luykx & van Ruth, 2008

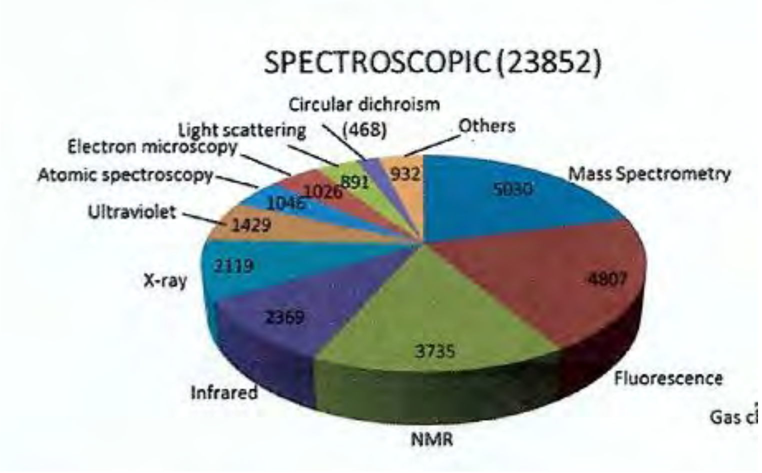
Spectroscopic techniques for food geographical traceability

In recent years it was observed an increase of the use of spectroscopic techniques vs other techniques (e.g. biological , genetical etc.) for food tracebility. As far as elemental analysis is concerned the use of ICP-OES and ICP-MS are the dominant techniques (63%), followed by ETAAS, FAAS and AAS (30%), INAA (5%) and Emission Spectrometry (2%).





Source : Gonzalves et al., 2009

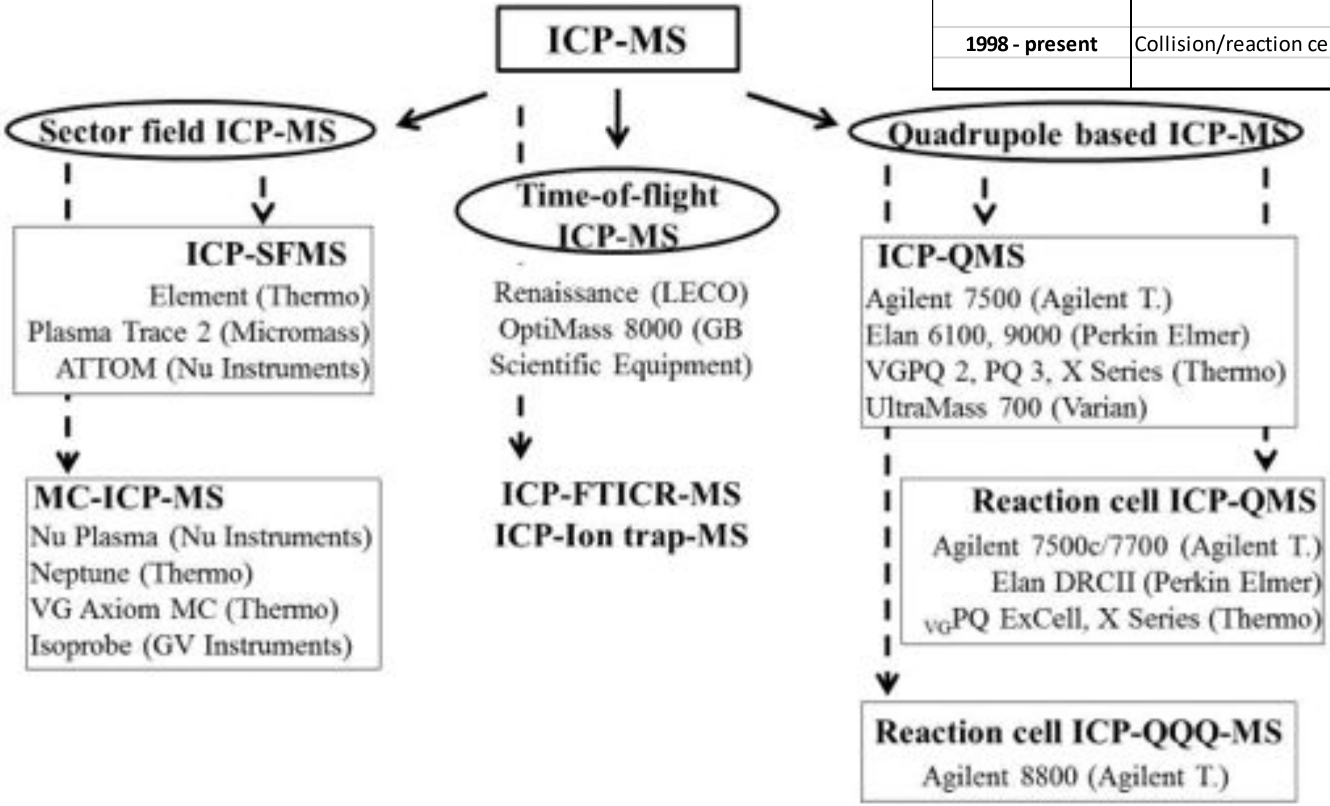


Source : FSTA database in the 2001- 2010 time

Elemental analysis:
story and types of instruments

Period	Development
1878 - 1983	Initial ICP-MS evolution, quadrupoles, demonstration, adoption
1983 - 1988	Quadrupole ICP-MS reigns
1988 - 1993	Sector-field, high resolution ICP-MS arrives
1993 - 1998	Miscellaneous analyzers in vogue (ion trap, TOF, ICR,MC)
1998 - present	Collision/reaction cells rage

Summary of ICP-MS instrumentations
from different companies
Source : C. Andreozzi 2017 doctorate thesis



ICP-MS

Sector field ICP-MS

ICP-SFMS
Element (Thermo)
Plasma Trace 2 (Micromass)
ATTOM (Nu Instruments)

MC-ICP-MS
Nu Plasma (Nu Instruments)
Neptune (Thermo)
VG Axiom MC (Thermo)
Isoprobe (GV Instruments)

Time-of-flight ICP-MS
Renaissance (LECO)
OptiMass 8000 (GB Scientific Equipment)

ICP-FTICR-MS
ICP-Ion trap-MS

Quadrupole based ICP-MS

ICP-QMS
Agilent 7500 (Agilent T.)
Elan 6100, 9000 (Perkin Elmer)
VGPQ 2, PQ 3, X Series (Thermo)
UltraMass 700 (Varian)

Reaction cell ICP-QMS
Agilent 7500c/7700 (Agilent T.)
Elan DRCII (Perkin Elmer)
$_{VG}$PQ ExCell, X Series (Thermo)

Reaction cell ICP-QQQ-MS
Agilent 8800 (Agilent T.)

Source :
Eiden & Barinaga , 2004

Which foods ?

Triticum Aestivum L.

wine

milk

cheese

potato

ICP-MS

Beef

Saffron

Onion

Lycopersicum esculentum L.

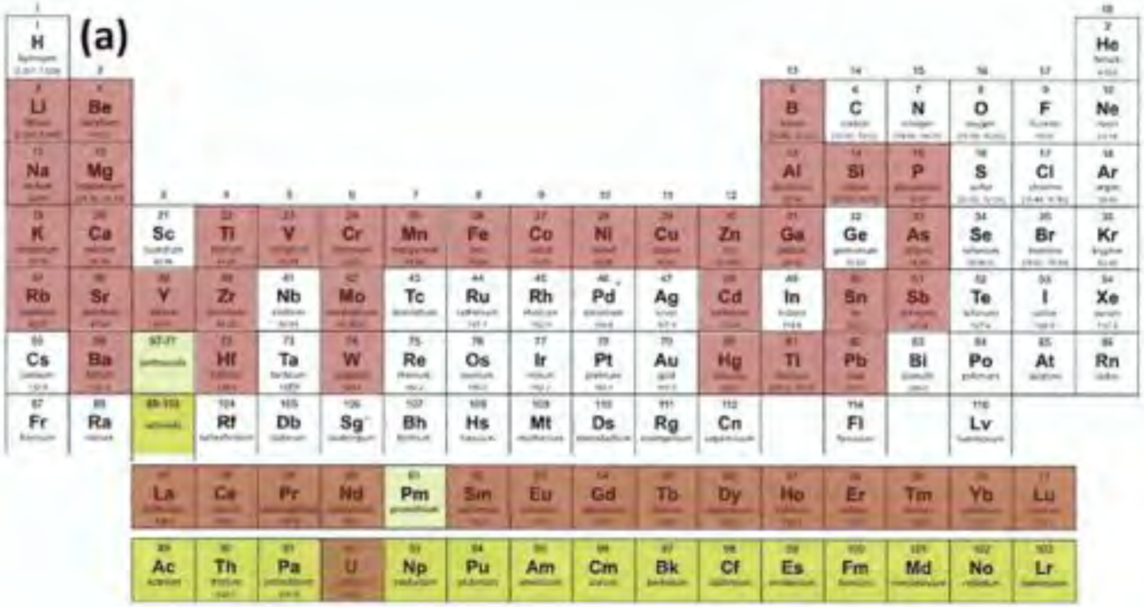
The application of ICP-MS to wine traceability

The assessment of wine traceability and authenticity is a critical issue that has gained a lot of interest internationally.

In wines the combination of instrumental analysis with multivariate statistics, have allowed the successfull classification of various products according to varieties, ***geographical origin***, and certain aspects of the winemaking process.

Which elements ?

year	Authors	Country
1988	Pereira	Spain
1989	Eschnauer et al.	Germany
1999	Kristl et al.	Slovenia
2003	Aceto	Italy
2003a	Almeida &Vasconcelos	Portugal
2003b	Almeida &Vasconcelos	Portugal
2004	Castinera Gomez Brandt et al	Germany
2004	Nicolini et al.	Italy
2007	Rossano et al.	Hungary
2009	Volpe et al.	Italy
2011	Tariba	Croatia
2012	Cheng & Liang	China



Elements that can be changed by grapegrowing and /or winemaking practices.We can have:

1) ***«Natural» elements*** *which are the result of their presence in the vineyard soil and their uptake by wine plant (Al, B, Ba, Li, Mg, Mo, Si, Sr, Ti, REEs);*
2) ***«Artificial» elements*** *which result from human interventation, environmental pollution (Pb, Co, Cr, Ni, V, Cd e Hg);*
3) ***Elements that are both «natural» and «artificial»*** *e.g. Ca, Mg, Co, Zn, Fe, P, Na, e K.*

Which elements ?

year	Authors	Country
1997	Greenhough et al.	Canada
1997	Baxter et al.	Great Britain
1997	Baxter et al.	Spain
2003	Taylor et al.	Canada
2003	Marengo & Aceto	Italy
2004	Cartinera Gomez et al.	Germany
2004	Thiel et al.	Germany
2005	Sperkova & Suchanek	Czech Republic
2005	Coetzee et al.	South Africa
2006	Angus et al.	New Zealand
2007	Iglesias et al.	Spain
2011	Perez Trujillo et al.	Spain
2012	Martin et al.	Australia
2013	Sen & Tokatli	Turkey

Several studies have evaluated the use of multi-element fingerprints for the determination of geographical origin of wines.The elements that were found to discriminate among different wine regions are summarized in figure. The most discriminating elements in these studies include: ***Sr, Mn, Li, Co, Rb, B, Cs, Zn, Al, Ba, Si, Pb and Ca.***

13 elements

Studies of wine traceability made by ICP-MS

2005
SOUTH AFRICA

40 wines

ICP-MS
Perkin Elmer Sciex Elan 5000 quadrupole

2011
ARGENTINA

51 wines

Q-ICPMS
Thermo Ensemble X7 series

2015
ARGENTINA

57 wines

ICPMS
Perkin Elmer SCIEX, ELAN DRC-e

2018
PORTUGAL

47 wines

ICP-MS
Agilent 8800 triple quadrupole

Studies of wine traceability made by ICP-MS

2018
JAPAN

214 wines

ICP-MS
Agilent 7700x

2019
SPAIN

34 wines

ICP-MS
Agilent 8800 triple quadrupole

2019
ITALY/USA

46 wines

Sangiovese

ICP-MS
Agilent 8800 triple quadrupole

2019
USA

133 wines

ICP-MS
Agilent 8900 triple quadrupole with CRC

2005 - Study of ICP-MS use for the geographic origin of South African wines

5060 J. Agric. Food Chem. 2005, 53, 5060–5066

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Multi-element Analysis of South African Wines by ICP–MS and Their Classification According to Geographical Origin

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40
wines

Robertson
Swartland
Stellenbosch

Aims of the work: the specific aims of this study were the determination of the elemental composition of wines from ***Robertson, Stellenbosh, and Swartland,*** tree main wine producing areas in the Western Cape province of South Africa, and the use of these data to uniquely classify wines from these areas according to a multivariate statistical procedure. A set of indicator elements suitable for discriminant analysis and specific for South African wines was to be determined. The feasibility of including red and white wines in the same data set for provenance determination was evaluated.

On ***40 total wines 40 elements*** were determined by ***ICP-MS (Perkin Elmer Sciex Elan 5000 quadrupole based)*** following:

1) Suitable sample preparation (dilution 1:1 with use of 0.14M HNO_3 to lower ethanol concentration till to 5-6%, which reduces the matrix effect, so stabilizing plasma;
2) Digestion in microwave oven with use of HNO_3): ***Li, B, Na, Mg, Al, Si, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Nd, W, Tl Pb e U.***

40

20

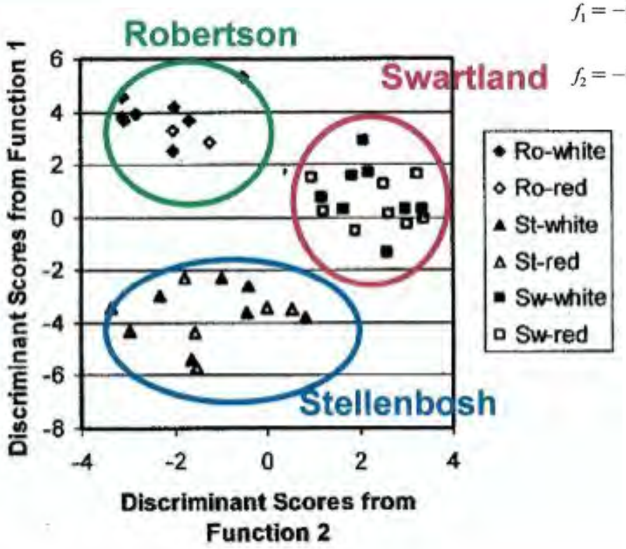
Because of the low numbers of samples (number of wines) respect to the number of variables (elemental concentrations) the Authors preceeded as follows:

1) ***A reduction of numbers of variables was done (from 40 to 20) in order to perform suitable statistical analysis;***
2) ***Variable reduction was done after an ANOVA approach; the new 20 variables were: Li, B, Mg, Al, Si, Cl, Sc, Mn, Ni, Ga, Se, Rb, Sr, Nb, Cs, Ba, La, W, Tl e U*** **; some of these elements (Mg, Cl, Si, Nb, La e U) were removed when big analytical polyatomic background uncertaines were observed.**

2005 - Study of ICP-MS use for the geographic origin of South African wines

The multivariate analysis consisted of the application of discriminant analysis (DA), where the discriminant functions are linear combinations of the independent variables (elemental concentrations), following a suitable data treatment: (were $\log_e$ – transformed) in order to reduce outlier effects).

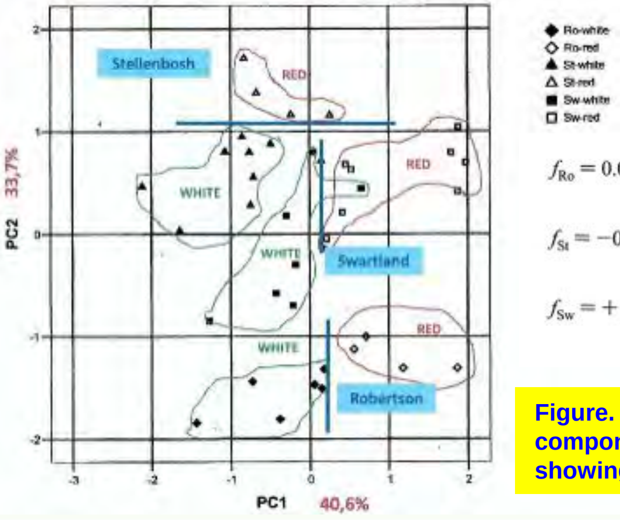
The adoption of this procedure allowed the Authors to improve model's robustness. ***These functions permitted a classification of wines, correct at 100%.*** The figure shows the distribution of white and red wines (completely mixed) among three distinct clusters. The Authors believed interesting to go on with the classification with the aim of improving separation of white from red wines.



$$f_1 = -0.416 \ln(\mathrm{Al}) + 1.034 \ln(\mathrm{Mn}) - 1.144 \ln(\mathrm{Rb}) + 0.659 \ln(\mathrm{Ba}) + 0.541 \ln(\mathrm{W}) - 0.301 \ln(\mathrm{Tl}) \quad (1)$$

$$f_2 = -0.678 \ln(\mathrm{Al}) + 0.326 \ln(\mathrm{Mn}) - 0.597 \ln(\mathrm{Rb}) + 0.509 \ln(\mathrm{Ba}) - 0.012 \ln(\mathrm{W}) + 0.996 \ln(\mathrm{Tl}) \quad (2)$$

Moreover, with the aim of discriminating white wines from red ones, also inside the same area, a PAIRWISE DISCRIMINAT ANALYSIS was carried out, following a PCA carried out on **12 elements** (Al, Sc, Mn, Ni, Ga, Se, Ru, Sr, Cs, Ba, W e Tl) which gave, through new linear combinations, some base parameters with results similar to the previous one used.



$$f_{\mathrm{Ro}} = 0.001 \ln(\mathrm{Se}) + 0.067 \ln(\mathrm{Rb}) - 0.013 \ln(\mathrm{Cs}) + 0.969 \ln(\mathrm{Tl}) \quad (3)$$

$$f_{\mathrm{St}} = -0.777 \ln(\mathrm{Al}) + 0.903 \ln(\mathrm{Mn}) - 1.246 \ln(\mathrm{Rb}) + 0.927 \ln(\mathrm{Ba}) + 0.431 \ln(\mathrm{W}) \quad (4)$$

$$f_{\mathrm{Sw}} = +0.882 \ln(\mathrm{Al}) - 0.623 \ln(\mathrm{Mn}) + 1.096 \ln(\mathrm{Rb}) + 0.494 \ln(\mathrm{Sr}) - 0.881 \ln(\mathrm{Ba}) - 1.776 \ln(\mathrm{Tl}) \quad (5)$$

Figure. Scatterplot of the PC1 and PC2 component scores of red and white wines showing differentiation according to region.

2005 - Study of ICP-MS use for the geographic origin of South African wines: Conclusions

This study has highlight the skill of the techniques of multivariate statistical analysis based on data of trace elements in order to discriminate different geographical provenances.

Here pairwise discriminant analysis (PDA) was successfully used for the first time together with to a semi-quantitative use of ICP-MS.

2011 - Study of ICP-MS use for the geographic origin of Argentinian wines

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Fingerprints for Main Varieties of Argentinean Wines: Terroir Differentiation by Inorganic, Organic, and Stable Isotopic Analyses Coupled to Chemometrics

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51 wines

Aim of the work: Our main goal was to obtain a reliable fingerprint from typical Argentinean red wines on the basis of organic, inorganic, and isotopic patterns, considering the influence of provenance soil. Thus, we measured **33 elements**, $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ isotopic ratios, and 10 phenolic compounds, of threee selected wine varieties and soils from three different geographical regions and applied chemometrics for data analysis. Until 2011 there were not published papers which deal together the elemental composition, the isotopic profile and polyphenolic profiles or the association between stable isotopes and elements from soils where grapes were grown for wine production.

Sampling: Wine and soil samples were collected from the three major wine production regions of Argentina: Mendoza, San Juan, and Córdoba, areas with different geological settings.

Wines

Were obtained directly from producers having both GMP (Good Manufacturing Practices) and traceability systems for two vitages (2007 and 2008)

Cabernet Sauvignon, Malbec, Syrah

Córdoba 9

Mendoza 21

San Juan 21

Soils

Were sampled in depths 10-20 cm to avoid surface-soil pollution arising from the surrounding environment and to reduce the effects of fertilizers and variable organic matter content and 50 cm from the side of the plot to reduce the effects of fertilizers and the organic matter.

2011 - Study of ICP-MS use for the geographic origin of Argentinian wines

Preparation of wine samples for elemental analysis

5 mL in quartz vessel
+ addition of 6 mL HNO_3 conc.
↓
Digestion in a microwave closed system
↓
Quantitative transfer of samples to 25 mL volumetric flasks, completing the volume with ultrapure water
↓
Filtration using 0.45 µm filters
Use of spikes
↓
All recoveries ranged between 86 and 114%

Preparation of soil samples for analysis of bioavailable elements

Drying of samples at 40°C during 2 days
↓
Homogenization and sieving samples with a 2 mm acrylic sieve
↓
Drying at 40°C for 1 night
↓
Contact of 20 g of sieved soil with 50 mL of NH_4NO_3 1M
↓
Stirring for 2h
↓
Settle for 1h
↓
Filter at 0.45 µm
↓
Acidify with 0.5 mL HNO_3 conc

33 elements

Q-ICPMS
Thermo Ensemble X7 series

Quadrupole inductively plasma mass spectrometry for elements except Na. Instrument equipped with ASX-100 autosampler model (CETAC, NE). Sample introduction made by a microflow concentric nebulizer, Peltier cooled spray camera.

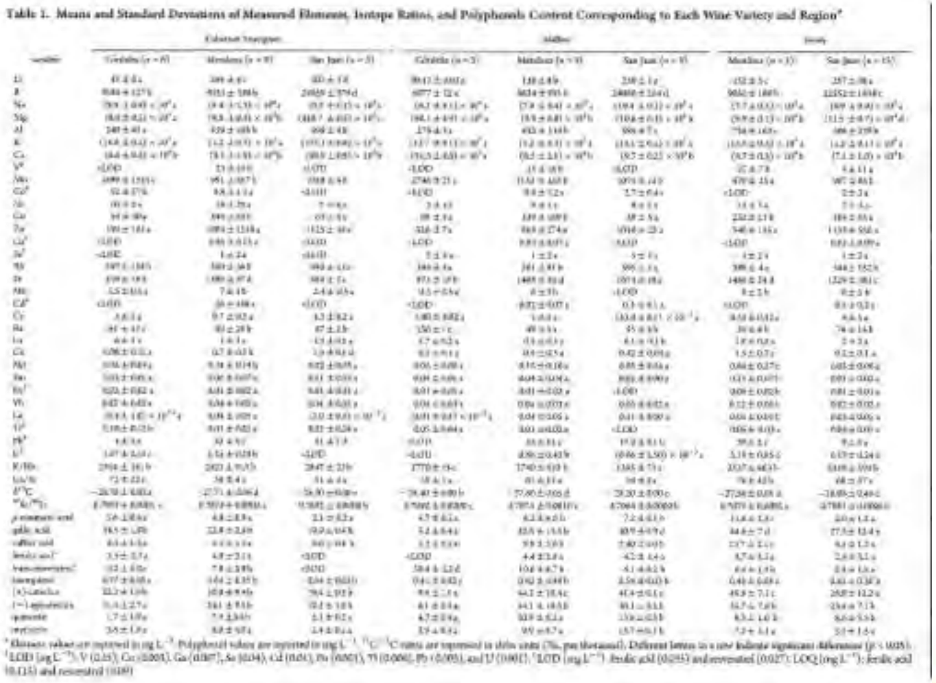


Table 1. Means and Standard Deviations of Measured Elements, Isotope Ratios, and Polyphenols Content Corresponding to Each Wine Variety and Region

In addition isotopic analysis ($\delta^{13}C$, $\delta^{87}Sr$) and determination of some phenolic constituents have been carried out.

2011 - Study of ICP-MS use for the geographic origin of Argentinian wines : Results

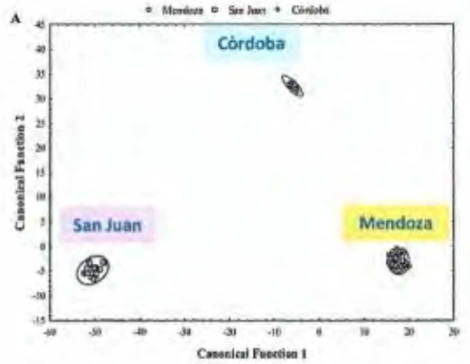
Geographical origin Classification

The application of backward stepwise ***DA (Discriminant Analysis)*** allowed 100% discrimination between wines from the 3 studied regions selecting 19 significant variables of 45. It is noteworthy that the discrimination was possible including variables of the three groups analysed :

-- ***organic*** (*trans*- resveratrol, kaempferol, and (+) -catechin);

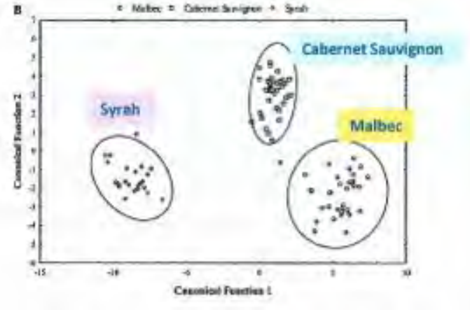
-- ***inorganic components*** (B, Na, Mg, Ca, Mn, Co, Ni, Cu, Rb, Sr, Ba, la, Pb and Ca/Sr);

-- ***isotopic ratios*** ($\delta^{13}C$; $^{87}Sr/^{86}Sr$);



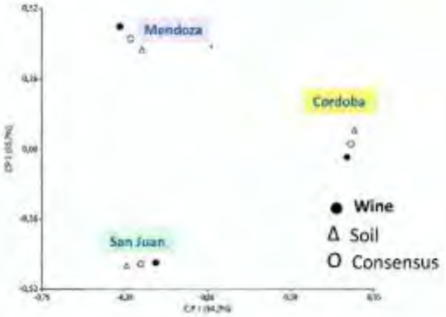
Wine variety Classification

Backward stepwise ***DA (Discriminant Analysis)*** allows us to classify 100% of the analysed wines from the 3 varieties, pointing out 21 significant variables to obtain such discrimination: ferulic acid, kaempferol,(+) -catechin, Li,Mg,Al,K,Ca,Co,Cu,Zn,Rb,Cd,La,Ce,Lu,Pb,U,Ca/Sr,$\delta^{13}C$ and$^{87}Sr/^{86}Sr$. It is worth mentioning that parameters belonging to three studied groups were included by DA. These results were in accordance with what found by Fabani et al (2009) for Mg, Zn, K and Ca.



Correlation between soil and wine composition

Elemental composition and isotopic analysis were performed on the bioavailable fraction of solis, because the composition of this fraction has been considered more directly correlated with thye multielement composition of the wine leaves and grapes.Some elements (Ba, K, La, B, V, and Cd) exhibit a good corrispondence between its content in both soil and wine for the three provinces; others (Ca) less. GPA (Generalized Procustes Analysis) produces a configuration of the different geographical regions that reflects the consensus among the wines and soils. Data obtained from wine have a significant consensus (98.8%) with those corresponding to soil. CCA (Canonica Correlation Analysis) was applied to assess the corrispondence between soil and wine composition. The CCA shows a **significant correlation ($r = 0.99$; $p <0.001$)** between soil and wine. This last result indicates that 99% of variability observed between wines could be attributed to the vineyard soil with consideration for its environment «*terroir*».



2011 - Study of ICP-MS use for the geographic origin of Argentinian wines : Conclusions

The Authors conclude that both elemental and isotopic compositions, including geochemical ratios, such as K/Rb and Ca/Sr allow a good differentiation among wine-producing regions.

Mg concentrations and $^{87}Sr/^{86}Sr$ values were the best discriminators of wine provenance in the studied regions. Moreover the inclusion of the phenolic profile allows a better differentiation between wine varieties from the same region, resveratrol being one of the most significant organic components for this purpose.

It is worth remarking that, in this case study, DA gives satisfactory results for the wine differentiation, proving an important data reduction, selecting the most important variables for discrimination.

Therefore, the use of combined analytical sources (organic, inorganic and isotopic components) presents a powerful strategy to obtain a reliable fingerprint for the evaluation of wine provenance in association with the characteristics of its terroir. Furthermore, GPA and CCA allow matching the wine profile with the soil composition.

2015 - ICP-MS use for classification of monovarietal Argentinean white wines by their elemental profile

Food Control 57 (2015) 268–274

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Classification of monovarietal Argentinean white wines by their elemental profile

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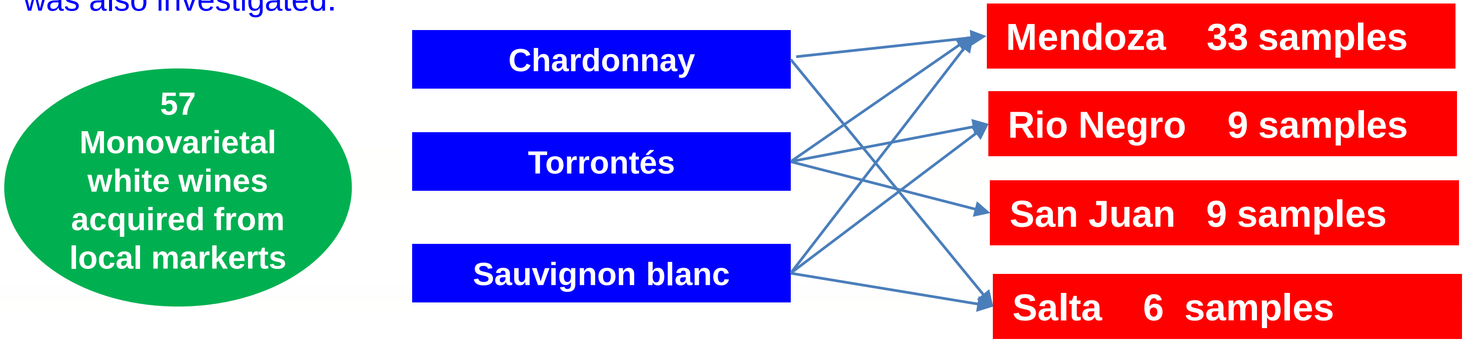
Purpose of the work: was to develope and validate a chemometric model with the principal aim of finding out relationships between element concentrations and geographical origin of Argentinean white wines which would enable assesing their genuineness. Three white wine varieties of greatest exportation in Argentina, namely: Chardonnay, Torrontés and Sauvignon blanc, from four different wine growing regions: Mendoza, Rio Negro, San Juan and Salta were evaluated throughout trace element determination by ICPMS. The effect of factors such as variety and vintage on the multielement composition of white wines was also investigated.



57 Monovarietal white wines acquired from local markerts

Chardonnay

Torrontés

Sauvignon blanc

Mendoza 33 samples

Rio Negro 9 samples

San Juan 9 samples

Salta 6 samples

UNIVERSITÀ CATTOLICA del Sacro Cuore

2015 - ICP-MS use for the classification of monovarietal Argentinean white wines by their elemental profile

Analytical procedure

1 mL of wine was placed into 15 mL polypropilene flask and then, the volume was completed to 10 mL with HNO_3 (1%), and the mixture was shaken vigorously. Rhodium ($^{103}Rh^{+}$) was added as internal standard.
In order to optimize ICPMS operating conditions wine samples prepared as indicate above, were spiked with multielement Perkin-Elmer 3, and Hg monoelement standard solution, to a final concentration of 40 μL^{-1} .A blank solution was always measured and taken into consideration. The solutions were introduced into the plasma at 0.8 mL min^{-1} applying 1000 W RF power and 0.85 L min^{-1} nebulizer gas flow rate before their optimization. The isotopes measured were:

^{7}Li, ^{9}Be, ^{51}V, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{74}Ge, ^{75}As, ^{85}Rb, ^{88}Sr, ^{98}Mo, ^{111}Cd, ^{138}Ba, ^{202}Hg, ^{205}Tl, ^{208}Pb and ^{209}Bi

18 elements

Samples microwave digestion was performed for comparative purposes. In this case, 500 µL of wine samples were added with 7.0 mL of HNO_3 and 1.0 mL of H_2O_2 in PTFE flasks, then they were submitted to a microwave temperature program (10-min ramp to 200 ° C and a step of 10 min at 200 ° C, up to 1000 W), and, after that, diluted to 50 mL with ultrapure water. Before digest, samples were spiked to reach a final concentration of 40 μL^{-1} of the analytes. The digested samples were analysed by ICPMS using the conventional cross-flow nebulizer and a Scott-type spray chamber and external calibration with $^{103}Rh^{+}$ as internal standard.

MULTIVARIATE STATISTICS:
-- PCA as a descriptive tool to visualize data in 2D;
-- LDA to evaluate classification models

Statistical software package: Unscrambler X 10.3 (CAMO-ASA, Norway).

ICPMS
Perkin Elmer SCIEX, ELAN DRC-e

2015 - ICP-MS use for the classification of monovarietal Argentinean white wines by their elemental profile

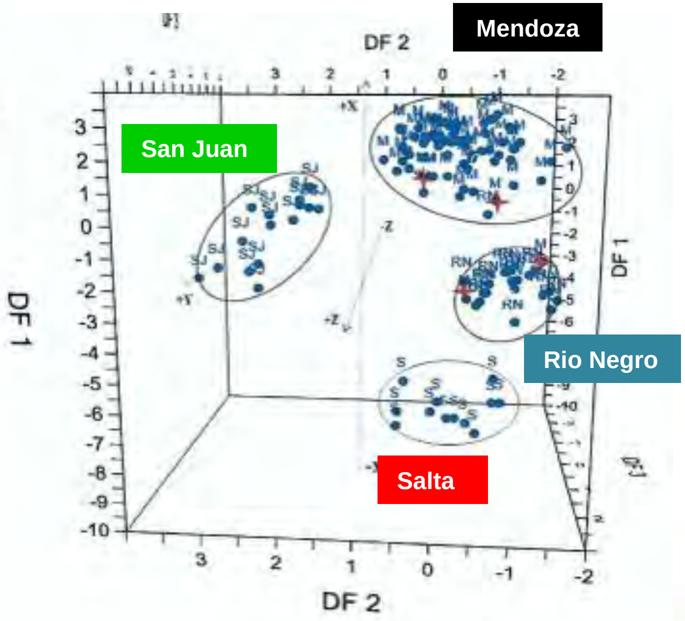
***PCA** was used like exploratory analysis for visualizing groups in Argentinean white wines, element concentration data were used as response matrix. Elements that presented concentration values below the limit of quantification were not statistically evaluated. A matrix with 114 samples and 17 variables was constructed. Two first principal components were extracted, explaining 95.95% of the accumulated variance; in figure PC1 and PC2 score plots in the plane are shown.*

***LDA (Linear Discriminant Analysis)** was performed for further evaluation of elemental concentrations to classify wine samples according to the geographical origin. Thus, metal contents in wine were taken as chemical descriptors.*

$$DF_1 = -3.48\ 10^{-1}{*}As + 1.13{*}Ba - 1.06448\ 10^{-1}{*}Co + 3.62\ 10^{-1}{*}Mo - 2.75\ 10^{-1}{*}Pb$$

$$DF_2 = -1.04{*}As - 1.18\ 10^{-2}{*}Ba - 1.75\ 10^{-2}{*}Co + 1.09\ 10^{-1}{*}Mo - 1.39\ 10^{-1}{*}Pb$$

$$DF_3 = 8.56\ 10^{-2}{*}As - 3.30\ 10^{-1}{*}Ba - 6.50\ 10^{-1}{*}Co + 5.42\ 10^{-1}{*}Mo + 7.69\ 10^{-1}{*}Pb$$



In this study, discriminant functions (DF) were obtained from the training set, to classify samples into four groups; thus, three DF were needed to fully partition the data.

A complementary graphical representation of the studied wines was achieved. As a result, figure depicted the space defined by the first three discriminant functions, that explained 93.2% of the total variance; in this graph it could be clearly seen the separation among wine from Mendoza, Rio Negro, San Juan and Salta provinces. The same studies were performed to assess grape variety and vintage discrimination in white wines; multielemental composition has shown to have little influence on the grape variety and vintage in white wines.

2015 - ICP-MS use for the classification of monovarietal Argentinean white wines : Conclusions

The outcomes suggest that the largest contributing factor to the geographical origin discrimination seems to be the *element profile of the Argentinean white wines*.
The easy and rapid method for sample preparation consisting in a simple dilution 1:10, makes the proposed method a striking option for routine analysis, taking into account mainly the multielement determination ability of ICPMS.

This, along with multivariate statistical analysis based on a combination of principal component analysis (PCA) and discriminant analysis (DA), allowed differentiation of the most famous four Argentinean wine-growing regions. ***Of overall elements determined, only Ba, As, Pb, Mo and Co were identified as suitable indicators for the discrimination.***
The developed model indicates a potential application for provenance genuineness purposes, authenticity and quality control of wines. Nevertheless, it would be necessary to perform an assessment of non-correctly classified samples and the possible reasons that contribute to the differences observed. Besides, it might be appropriated to condect studies involving soil multielement determination to correlate the soil with respective wine, and thus corroborate and strenghten the research.

4

2018 - Multielement composition of amphora wines from Alentejo by ICPMS

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Food Control

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Multi-element composition of red, white and palhete amphora wines from Alentejo by ICPMS

Maria João Cabrita [a], [*], Nuno Martins [c], Pedro Barrulas [b], Raquel Garcia [c], [d], Cristina Barrocas Dias [b], Eva P. Pérez-Álvarez [e], Ana Maria Costa Freitas [a], Teresa Garde-Cerdán [e]

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47 wines

16 Red wines

16 White wines

15 Palhete wines

Objective of the work: was to characterize the elemental composition of Vinhos de Talha, to assess their mineral composition and to evaluate the levels of some trace elements that have legal limits imposed by legislation, ultimately aiming to ensure consumer food safety. Another objective was exploring the possibility of using mineral composition to establish the geographic origin of the wines. This work also contribute to protect these wines against falsifications and fraudolent use of denomination labels and is the first scientific work dealing with mineral characterization of amphora wines.

Map of wine samples distribution

*Wines were sampled from freshly opened bottles and transferred to 50 mL plypropilene flasks. Oenological parameters such as alcoholic content, total acidity, volatile acidity and pH were measured according to OIV methods***.**

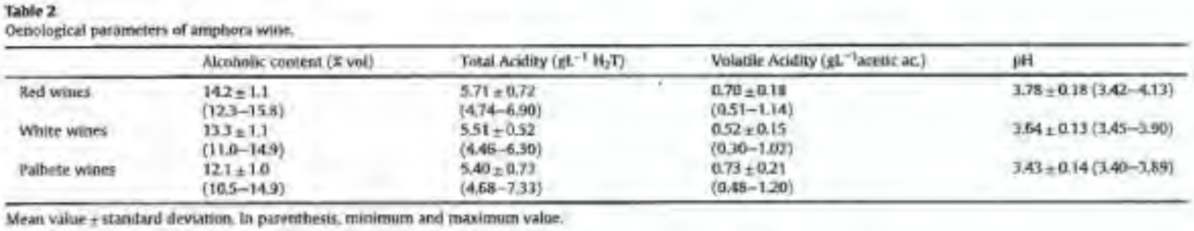


Table 2
Oenological parameters of amphora wine.

	Alcoholic content (% vol)	Total Acidity (gL^{-1} H_2T)	Volatile Acidity (gL^{-1}acetic ac.)	pH
Red wines	14.2 ± 1.1 (12.3–15.8)	5.71 ± 0.72 (4.74–6.90)	0.70 ± 0.18 (0.51–1.14)	3.78 ± 0.18 (3.42–4.13)
White wines	13.3 ± 1.1 (11.0–14.9)	5.51 ± 0.52 (4.46–6.30)	0.52 ± 0.15 (0.30–1.02)	3.64 ± 0.13 (3.45–3.90)
Palhete wines	12.1 ± 1.0 (10.5–14.9)	5.40 ± 0.73 (4.68–7.33)	0.73 ± 0.21 (0.48–1.20)	3.43 ± 0.14 (3.40–3.89)

Mean value ± standard deviation. In parenthesis, minimum and maximum value.

2018 - Multielement composition of wines from Alentejo (Portugal) by ICPMS

For ICPMS analysis, samples were diluted with an acid solution of 2% nitric acid in order to improve the stability of the analytes in the wine matrix and signal suppression effects.

Samples were diluted as follows:

- **-- 1000 fold for major elements;**
- **-- 100 fold for Al, Fe, Co,Ni,Cu,Zn, Sr and Cs;**
- **-- 10 fold fo the other elements.**

30 elements

ICP-MS-68-A; ICP-MS-68-B; ICP-MS-68-C

the three calibration standards, that contain the internal standard (Ir). Stock solutions were prepared using a synthetic wine containing ethanol (12% v/v) and tartaric acid (pH=3.2) to mimic the wine matrix and dilutions were done with the 2% nitric acid solution.

Calibration curves were built from a wide range of concentrations (0,0.25,0.5,1,2.5,5,10,20,50,100,200,500,1000,2000,3000µL^{-1})

For elements calibration curves had R^2 >0.999.

All measures were carried out with an Agilent 8800 triple quadrupole, equipped with a MicroMist nebulizer and a quartz spray chamber (ICP-QQQ). Nickel sampling and skimmer cones were used. Shield plate was used to avoid secondary charges which could generate interferences for the analysis.

ICP-MS
Agilent 8800 triple quadrupole

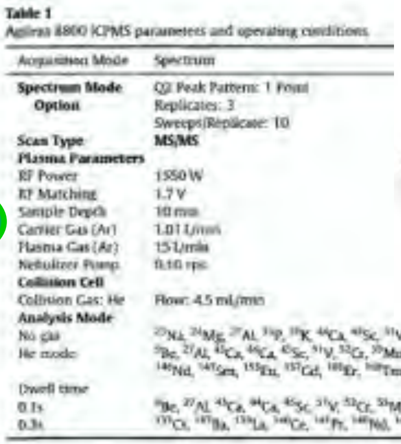


Table 1
Agilent 8800 ICPMS parameters and operating conditions

Acquisition Mode	Spectrum
Spectrum Mode Option	Q2 Peak Pattern: 1 Point Replicates: 3 Sweeps/Replicate: 10
Scan Type	**MS/MS**
Plasma Parameters	
RF Power	1550 W
RF Matching	1.7 V
Sample Depth	10 mm
Carrier Gas (Ar)	1.01 L/min
Plasma Gas (Ar)	15 L/min
Nebulizer Pump	0.10 rps
Collision Cell	
Collision Gas: He	Flow: 4.5 mL/min
Analysis Mode	
No gas	^{23}Na, ^{24}Mg, ^{27}Al, ^{31}P, ^{39}K, ^{44}Ca, ^{45}Sc, ^{51}V and ^{55}Mn
He mode	^{9}Be, ^{27}Al, ^{43}Ca, ^{44}Ca, ^{45}Sc, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{61}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{78}Se, ^{88}Sr, ^{111}Cd, ^{115}In, ^{193}Ir, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{208}Pb and ^{209}Bi
Dwell time	
0.1s	^{9}Be, ^{27}Al, ^{43}Ca, ^{44}Ca, ^{45}Sc, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{61}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{78}Se, ^{88}Sr, ^{111}Cd, ^{115}In and ^{193}Ir
0.3s	^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{208}Pb and ^{209}Bi

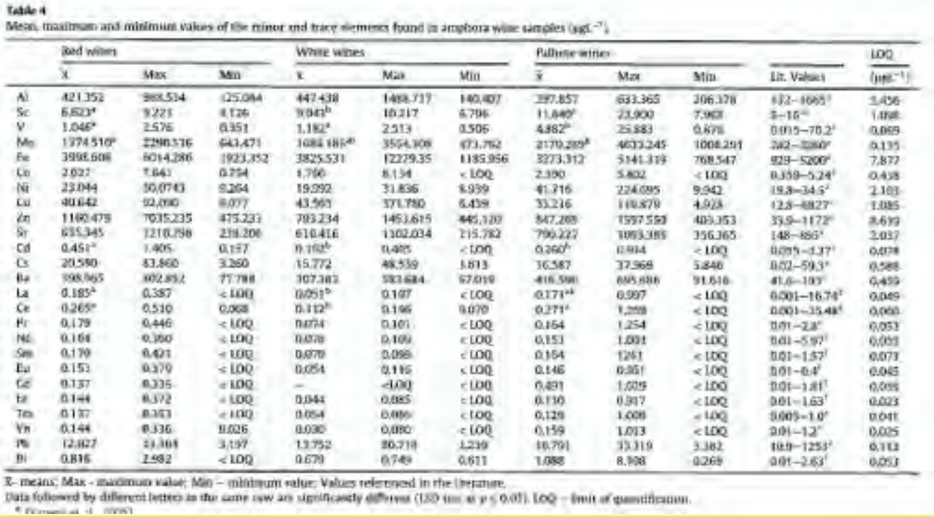


Table 4
Mean, maximum and minimum values of the minor and trace elements found in amphora wine samples (µgL^{-1}).

	Red wines			White wines			Palhete wines				LOQ
	$\bar{x}$	Max	Min	$\bar{x}$	Max	Min	$\bar{x}$	Max	Min	Lit. Values	(µgL^{-1})
Al	421.352	988.534	125.084	447.438	1488.717	140.407	397.857	633.365	206.378	132–1665	3.456
Sc	6.623^{a}	9.221	4.126	9.043^{b}	10.217	6.796	11.840^{c}	23.900	7.968	3–16	1.898
V	1.046^{a}	2.576	0.351	1.182^{a}	2.513	0.506	4.882^{b}	25.883	0.676	0.015–70.2	0.069
Mn	1374.516^{a}	2298.536	643.471	1684.185^{ab}	3554.308	473.762	2170.289^{b}	4633.245	1008.291	242–3260	0.135
Fe	3998.606	6014.286	1923.352	3825.531	12279.35	1185.956	3273.312	5141.319	768.547	929–5200	7.877
Co	2.027	7.643	0.754	1.796	8.134	< LOQ	2.390	5.802	< LOQ	0.359–5.24	0.438
Ni	23.044	50.0743	9.264	19.592	31.836	6.939	41.716	224.095	9.942	19.8–34.5	2.103
Cu	40.642	92.090	8.077	43.565	371.780	6.439	33.216	119.879	4.923	12.8–4827	1.085
Zn	1160.479	7035.235	475.233	793.234	1453.615	445.320	847.288	1597.550	403.353	33.9–1172	8.699
Sr	635.345	1210.798	239.206	610.416	1302.034	215.782	790.227	1063.385	356.365	148–865	2.037
Cd	0.451^{a}	1.405	0.157	0.102^{b}	0.485	< LOQ	0.260^{b}	0.914	< LOQ	0.035–3.37	0.078
Cs	20.590	83.860	3.260	15.772	48.539	3.813	36.587	37.968	5.848	0.02–59.3	0.588
Ba	398.965	802.852	77.788	307.383	583.684	67.019	416.598	695.686	91.616	41.6–193	0.459
La	0.185^{a}	0.387	< LOQ	0.051^{b}	0.107	< LOQ	0.171^{ab}	0.997	< LOQ	0.001–16.74	0.049
Ce	0.265^{a}	0.510	0.068	0.112^{b}	0.196	0.070	0.271^{a}	1.258	< LOQ	0.001–35.48	0.060
Pr	0.179	0.446	< LOQ	0.074	0.101	< LOQ	0.164	1.254	< LOQ	0.01–2.8	0.053
Nd	0.164	0.360	< LOQ	0.078	0.109	< LOQ	0.153	1.001	< LOQ	0.01–5.97	0.055
Sm	0.170	0.421	< LOQ	0.070	0.098	< LOQ	0.164	1.261	< LOQ	0.01–1.57	0.073
Eu	0.153	0.379	< LOQ	0.054	0.116	< LOQ	0.146	0.851	< LOQ	0.01–0.4	0.045
Gd	0.137	0.335	< LOQ	–	<LOQ	< LOQ	0.491	1.029	< LOQ	0.01–1.81	0.055
Er	0.144	0.372	< LOQ	0.044	0.085	< LOQ	0.130	0.917	< LOQ	0.01–1.63	0.023
Tm	0.137	0.353	< LOQ	0.054	0.086	< LOQ	0.129	1.008	< LOQ	0.005–1.0	0.041
Yb	0.144	0.336	0.026	0.030	0.080	< LOQ	0.159	1.013	< LOQ	0.01–1.2	0.025
Pb	12.827	33.384	3.197	13.752	80.718	1.239	10.791	33.319	3.382	10.9–1253	0.113
Bi	0.816	2.982	< LOQ	0.678	0.749	0.611	1.088	8.308	0.269	0.01–2.63	0.053

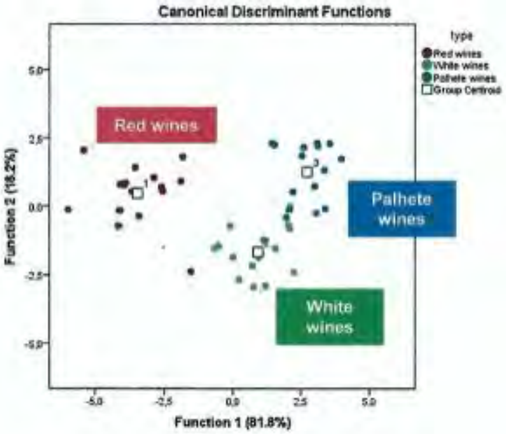
$\bar{x}$– means; Max - maximum value; Min – minimum value; Values referenced in the literature.
Data followed by different letters in the same row are significantly different (LSD test at p ≤ 0.05). LOQ – limit of quantification.

2018 - Multielement composition of wines from Alentejo (Portugal) by ICPMS: Results

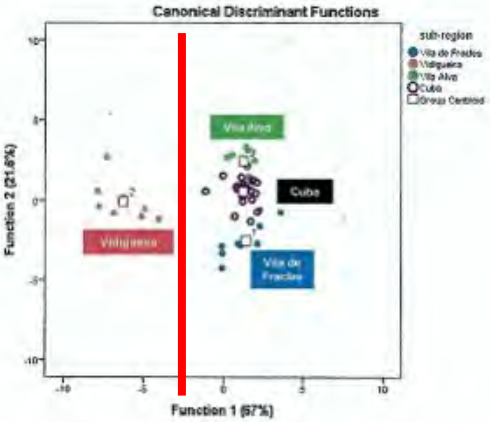
Statistics

Canonical Discriminant Analysis (CDA) , a supervised technique tha assigns groups of variables to the data set, using IBM SPSS Statistics vers. 20 was performed on data expressing major and minor elements in wines (independent variables), tio classify different types of wines (grouping variables): first goup variable according to wine type, red, white or palhete wines; second group variable according to wine geographic origin.

Discrimination of the types of wines: *a linear discriminant analysis was performed to verify if mineral content allows us a classification of wines according to the type of wines. The location of wine samples within the plane defined by the two canonical functions is shown in figura where the first discriminant function explains 81.8% of the variance, while the second function explains the 12.2%: this reflects the discriminating ability of the LDA model with quite good separation among wine samples according to the type of wine.*



Discrimination of the origin of wines: *a linear discriminant analysis was performed to verify if mineral content allows us a classification of wines according to the sub-region of origin. The first discriminant function explains 67.0% of the variance, whereas the second function explains 21.6%. The first function is able to discriminate wine from* ***Vidigueira*** *region from other regions which need the second function to be discriminated even if at lower lever, probably due to a geological similarity of soils of* ***Vila de Fracles, Vila Alva and Cuba****. Probably the complementary use of an isotopic technique which could improve the analytical information about the origin.*



2018 - Multielement composition of wines from Alentejo (Portugal) by ICPMS: Conclusions

In this work, the first one dealing with Alentejo's amphora wines, an ICPMS procedure enabled the quantification of 30 mineral elements from 47 samples of different types of amphora wines.

The statistical analysis of data obtained by ICPMS have shown some differences between red, white and palhete wines concerning their multi-element composition.

Regarding the mineral content of the amphora wines, they are in accordance with those found in literature.

Results obtained within this study seems to indicate that mineral content of amphora wines are not affected by the clay vessels, since the impermeabilization with pine pitch, or even in some cases with epoxy resins, does not allow a lixiviation of minerals from the clay into the wine.

By applying linear discriminant analysis, we were able to separate the wines according to type of wine, and even a fairly separation of wines was achieved when considering their origin.

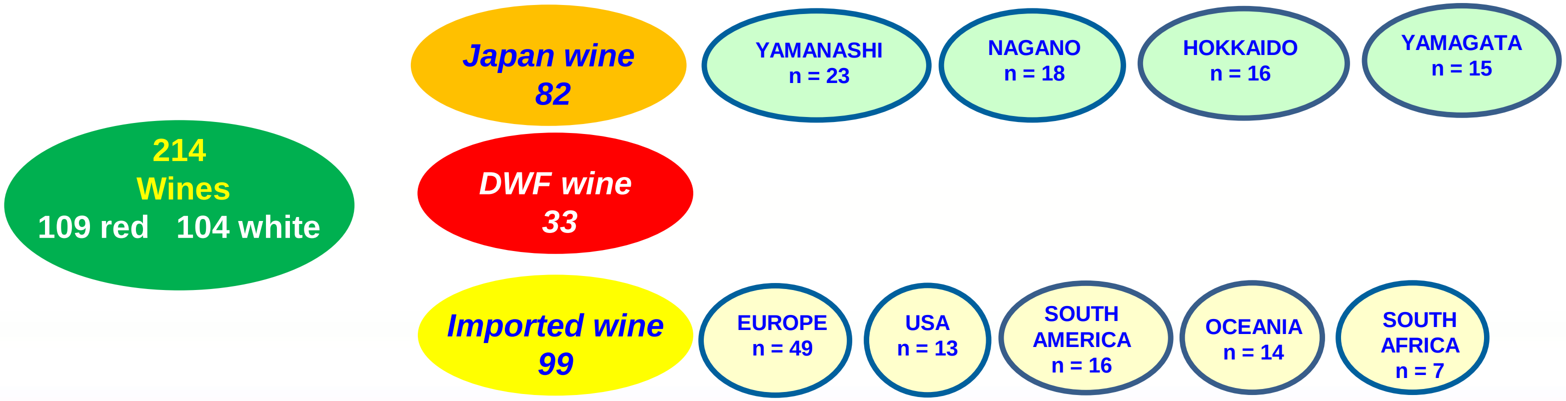
2018 - Discrimination of wine from grape cultivated in Japan, imported wine and others by ICPMS multielemental analysis


ELSEVIER

Discrimination of wine from grape cultivated in Japan, imported wine, and others by multi-elemental analysis

Hideaki Shimizu,* Fumikazu Akamatsu, Aya Kamada, Kazuya Koyama, Masaki Okuda, Hisashi Fukuda, Kazuhiro Iwashita, and Nami Goto-Yamamoto

Objective of the work: to our knowledge, however, there are no reports of the discrimination of Japan wine from DWF (Domestically produced Wine mainly from Foreign ingredients) or the discrimination of geographic origin within Japan. Here, therefore, we have analyzed the mineral composition of ***214 wine samples*** by ICP-MS and ICP-AES, and carried out LDA analysis both for the *discrimination of three wine groups (Japan wine, imported wine and DWF)* and for the *discrimination of four main domestic wine-producing regions: Yamanashi, Nagano, Hokkaido and Yamagata Prefectures.*


214
Wines
109 red 104 white

Japan wine
82

YAMANASHI
n = 23

NAGANO
n = 18

HOKKAIDO
n = 16

YAMAGATA
n = 15

DWF wine
33

Imported wine
99

EUROPE
n = 49

USA
n = 13

SOUTH AMERICA
n = 16

OCEANIA
n = 14

SOUTH AFRICA
n = 7

2018 - Discrimination of wine from grape cultivated in Japan, imported wine and others by ICPMS multielemental analysis

In Japan market place it is difficult for consumers to distinguish between:

?

Japan wine: *domestically made from grapes cultivated in Japan only.*
National Tax Agency: National Tax Agency report 2016.
http://www.nta.go.jp/foreign_language/Report_pdf/2016.htm
National Tax Agency Tokio (2016).

DWF : *Domestically produced Wine mainly from foreign ingredients including imported concentrated grape juice.*

Sample preparation: *2 mL of wine was mixed with 5 mL of 61% nitric acid in a digestion vessel. The sample was left at room temperature for 60 min and then diluted by adding ultra-pure water, obtained by a MilliQ system to a total volume of 50 mL (final concentration of HNO_3 = 6%).*

ICP-MS 7700x
Agilent (USA)

40 elements

Why 22 elements out?
Their concentrations were below LOD in many samples or the relative standard deviation of their measurements was > 10%.

18 elements

Li, B, Na, Mg, Si, P, S, K, Ca, Mn, Co, Ni, Ga, Rb, Sr, Mo, Ba, and Pb

Recovery rates of the 18 mineral elements were determined by spiking a wine sample with known amounts of each element according to Okuda. **Recovery rates from spike recovery tests ranged from 81% (Ni) to 103% (Sr) for ICP-MS and 93% (S) to 108% (Na) for ICP-AES**.

ICP-AES 9000
Shimadzu (Japan)

Statistical analysis (DA)

2018 - Discrimination of wine from grape cultivated in Japan, imported wine and others by ICPMS multielemental analysis

Statistics

All statistical tests were performed by using JMP 12.2 SAS (USA). ANOVA was used to test differences among the three wine groups and among the four main domestic wine-producing regions. Tukey's honestly significant difference (HSD) test was performed at $p < 0.05$ of significance. LDA (Linear Discriminant Analysis) was carried out to discriminate the wine samples according to geographical origin.

Three wine groups

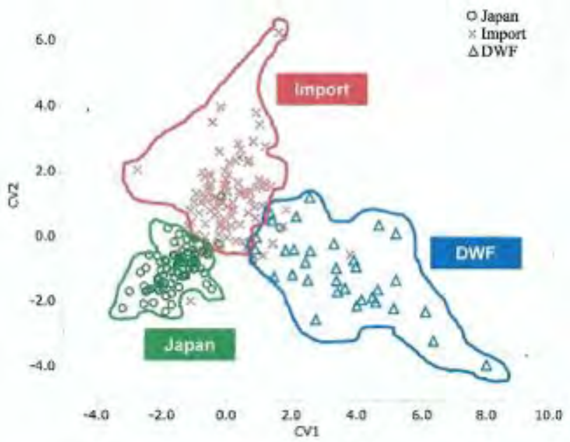
An LDA model was created to discriminate the three wine groups using 18 elements. In the model every group was well separated.

Elements Canonical variate function 1(CV1) = ***Ga, Ba, Na, K, Li, Mo, Pb***

Elements Canonical variate function 2 (CV2) = ***Ga, Ba, B, Li, Co, Mg, Pb, K, Ca, Sr***

Accuracy of LDA model *= 91.1% (195 of the 214 correctly classified)*

Prediction of LDA model *= 87.9% (188 of the 214 correctly predicted)*



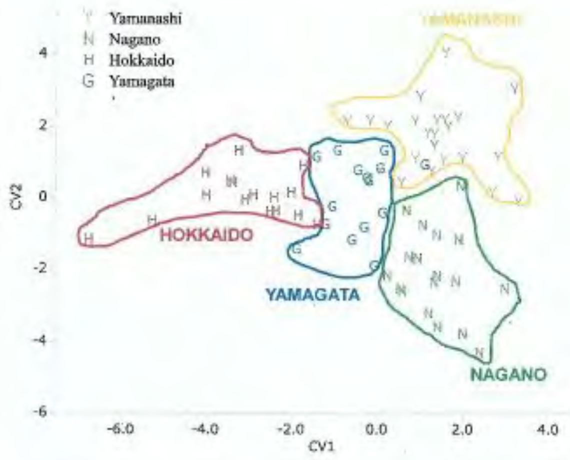
Four wine making regions

The discriminant scatterplot of 72 samples subjected to the LDA model showed that every category was defined to a certain extent.

The classification score *of these 72 samples was 93.1%; that is 67 of the 72 samples were correctly classified*

The prediction score was not high : *76.4% ; that is 55 of the 72 samples correctly predicted*

Comment: *The mineral composition of wines from the four Japanese regions was very similar; the SD was large, and the differences were smaller than those observed among the three wine groups; this close mineral composition probably contributed to the low percentage of cross-validation. The LDA models might increase in discriminating accuracy if combined with another analytical technique such as stable isotope analysis.*



2018 - Discrimination of wine from grape cultivated in Japan, imported wine and others by ICPMS multielemental analysis: Conclusions

In summary, our LDA model based on 18 mineral concentrations was shown to be useful for the discrimination of Japan wine, imported wine and DWF, and it is promising as an underlying method to support Japan wine and the new Japan wine legislation.

To our knowledge, this is also the first study to investigate the possibility of classifying wines from Japanes domestic regions by mineral composition.

2019- Classification of Spanish wines by ICP-MS multielement analysis

Food Chemistry 270 (2019) 273–280

Contents lists available at ScienceDirect

Food Chemistry

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Classification of wines according to several factors by ICP-MS multi-element analysis

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34 wines

26 Red wines

8 White wines

Aim of the work: In this study, major, minor and trace elements of 34 AOC Rioja wines (red and white) were determined by ICP-MS. Different calibration methodologies (standard addition and external calibration) and two different approaches for the pre-treatment of samples (direct acidic dilution of the wines and digestion procedures) were compared. Moreover, the element content was used in order to classify the wines according to different grape varieties, geographical zones, soil types, foliar nitrogen application, with or without SO_2 addition and oak ageing.

8 White wines
Viura Tempranillo

Different edaphoclimatic conditions

26 Red wines
Tempranillo, Garnacha, Maturana, Graciano

Different soils:
Fluventic Haploxerepts, Typic Calcixerepts, petrocalcic Palexeroll)

Sample preparation

Two different procedures:
1) *Acid wine dilution;*
2) *Acidic digestion.*

Digestion. *Wine digestion was carried out in the PFA beackers adding 5 mL of each wine and 2 mL of 65% HNO_3 ; then the beackers were put on a hotplate between 50 and 70° C until the samples became colorless because of the digestion of the acid. Once the digestion step had been completed, the solutions were cooled to room temperature. The tepered samples were transferred to PFA volumetric flasks and fulfilled with Milli-Q water up to 50 mL.*

2019 - Classification of Spanish wines by ICP-MS multielement analysis

ICP-MS analysis

*Multi-element determination was performed on an Agilent 8800 Triple Quadrupole ICP-MS, equipped with a Micromist nebulizer. In accordance with the analytes of interest, the collision/reaction cell was in : **no-gas mode, He-mode, O_2 mode** and , **NH_3 mode.***

In no-gas mode *22 masses were determined:*
Na, Mg, K, Ru, Rh, Cd, In, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb, Ir, Pb and Bi.

In He-mode *24 masses were determined:*
Na, Mg, Al, K, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Sr, Ru, Rh, Cd, In, Cs, Ba, Ir, Pb and Bi.

In O_2 mode *5 masses were determined:*
P, As, Ru, Rh and Ir.

In NH_3 mode *4 masses were determined:*
Ca, Ru, Rh and Ir.

ICP-MS
Agilent 8800 triple quadrupole

STATISTICAL ANALYSIS

One-way ANOVA statistical analysis was performed using SPSS vers. 21.0; differences between averages were compared using Duncan test at 0.05 probability level. Discriminant Analysis was carried out on data for classification according to different grape varieties, geographical zones, soil types, foliar N applications, with or without SO_2 addition, and oak ageing.

Two calibration modes were carried out:

external calibration: *prepared from high purity standards (ICP-MS-68B-A) diluted in synthetic wine (12% ethanol & 4g/L tartaric acid) and 2% HNO_3 in order to obtain 10 conc solut: 0,1,10,50,100,200,500,1000,1500,3000 mg/L.*

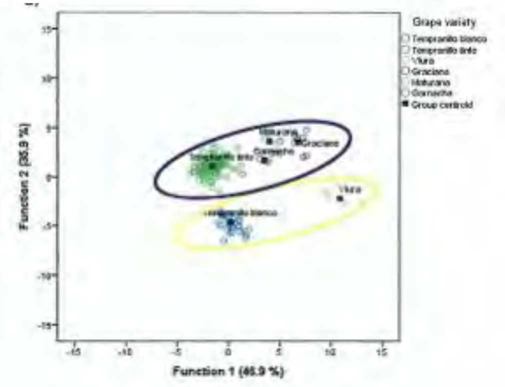
standard addition calibration: *was different for minor, trace and major elements; for minor elements 3 mL of one of the wine samples were mixed with 2% HNO_3 and the necessary amount of the high purity standards (ICP-MS-68B-A) up to 5 mL in order to obtain 6 different conc solutions: 0, 50, 100, 200, 400 and 800 µg/L; for major elements also 3 mL of one of the wine samples were mixed with 2% HNO_3 and the necessary amount of the high purity standards (ICP-MS-68B-A) up to 5 mL in order to obtain 5 different conc solutions: 0, 500, 1000, 2000 and 4000 mg/L.*

Both calibration models, were employed for dilution and digestion sample procedures.

2019 - Classification of Spanish wines by ICP-MS multielement analysis: Results

ICP-MS classification of wines was done done according to: grape variety, aging, geographic iscrimination, types of soil and different type of N foliar treatment.

Grape variety

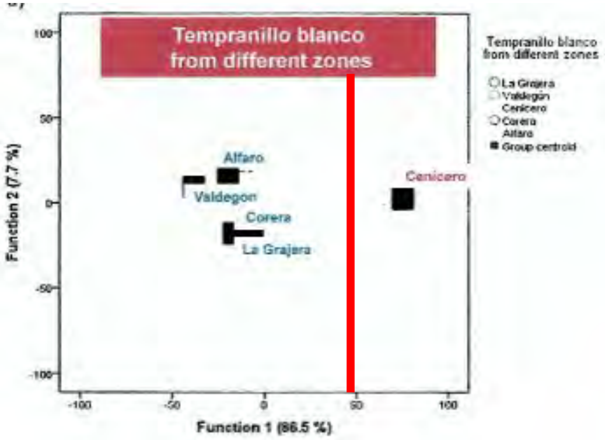


The results of DA applied for classifying the different grape varieties (Tempranillo blanco, Tempranillo, Viura, Graciano, Maturana and Garnacha) show that the two discriminant functions showed a good separation (82.8% of the variance) between wines form white to red varieties.

***Function 1** (with Sr, Ca and Co (+) and Zn and Ba (-) explained 46.9% ;*

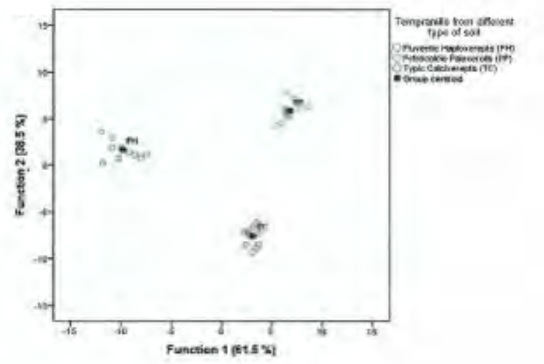
***Function 2** (with Mn, K, Ba and Cs (+) and Mg (-) explained 35.9% of the variance.*

Geographical areas



*Terminillo blanco variety was studied with a DA to differentiate 5 production areas; the total variance explained was 94.2%, so subsivided: 86.5% for **Function 1** (Sr and Ba (+) ; Ni and Pb (-); 7.7% for **function 2** (Ni, Pb and Ba (+); Cu (-)). Function 1 showed a good separation among wines from **Cenicero** zone and samples from other areas*

Type of soil



The elements composition was used to distinguish between wines from vineyards with different types of soils. Total variance explaind was 100% so subdivided: 61.5% for function 1 (Cs and Pb (+)); 38.5% for function 2 (Cs and Pb (+); As (-)). These discriminant functions allowed us to correctly classify 100% of the studied samples. Despite the complexity of the soil type distribution in Rioja region, successfull classificvation from this small geographical vineyard area was achieved by means of the ICP-MS procedures as observed by other authors (Coetzee et al 2014) which stated that the variability of trace element composition of the soils, depends on the distribution of soil types in the area.

2019 - Classification of Spanish wines by ICP-MS multielement analysis: Conclusions

In order to analyze major, minor and trace elements in red and white wines using ICP-MS the best method was digestion with internal standard calibration for major elements; whilst the most of the minor and trace elements did not present significant differences between the four methods exhamined.

The content of these elements in the wines allowed their differentiation according to several factors.

The wines form different geographical zones were differentiated according to Sr, Ba, Ni, and Cu.

ICP-MS analytical methodology could be a useful tool to fingerprint wines according to viticultural and oenological parameters.

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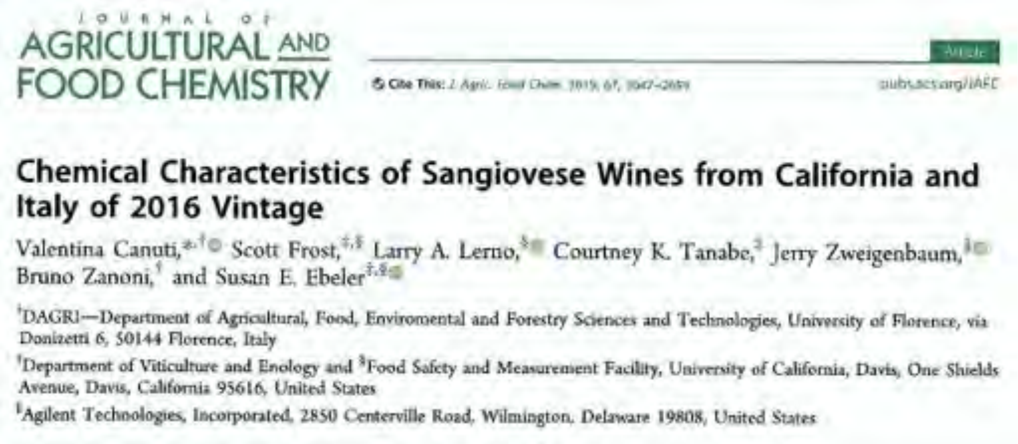
2019 - Chemical characteristics of Sangiovese wine. Cfr Italy/USA vintage 2016



JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

Cite This: J. Agric. Food Chem.

pubs.acs.org/JAFC

Chemical Characteristics of Sangiovese Wines from California and Italy of 2016 Vintage

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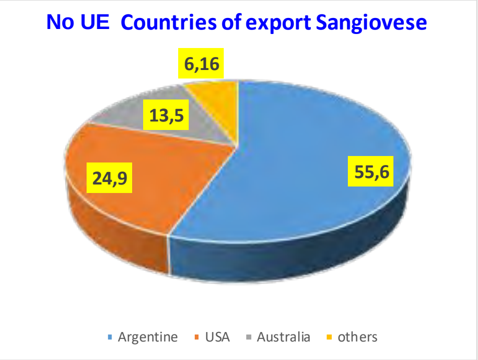
Objective of the work: This study sought to define and compare the regional chemical characteristics of Californian and Italian Sangiovese wines from the 2016 vintage. Two aspects were considered:

a) Chemical characterization and differentiation of Sangiovese wines from California and Italy;

b) *Expression of Sangiovese varietal character in two different regions by creating predictive models based on compositional profiles.*

*To our knowledge, **this is the first extensive regionality study** attempted for Sangiovese wines.*



No UE Countries of export Sangiovese

California, with 727 ha, represents about the 91% of the total USA area for wine production; on 4653 wineries present there, about 3% produce Sangiovese wine.

2019 - Chemical characteristics of Sangiovese wine. Cfr Italy/USA vintage 2016

harvest 2016

46 Commercial wines

20 Italy

26 California

54 Elements

54 elements were quantified in each wine using a similar dilute-and-shoot method previously established at UC Davis (USA).

The samples were diluted 5-fold with a solution of 3% nitric acid and 1% hydrochloric acid in plastic (metal free) centrifuge tubes; all samples were stored at 4 ° C until analysis took place. All wine were analysed in triplicate. Elements were monitored in «no gas», «helium» and/or «high energy helium gas mode».

Calibration functions were made using multielement calibration standards 1, 2A, 3 and 4 from SPEX, and Calibration Mix majors from Agilent. Single element standards was also used for some elements. NIST 1643e Trace Metals in Water (USA) was analyzed. All calibration standards, blanks and CRMs were made with a matrix-matched solution of 3% nitric acid, 1% hydrochloric acid and 3% ethanol when analyzing the 5-fold diluted wine samples.
A 6-point calibration between 0 and 500 µg/L was carried out for 24 elements in matrix-matched calibration solutions (5% NHO_3 and 4% ethanol) to account for matrix interferences of the ethanolic wine solutions. Elements were detected using a 3-point peak pattern in triplicate with 100 sweeps per replicate. Previous studies have shown that a reduction of the ethanol content to around 5% is a good compromise between a stable plasma and sufficient sensitivity.

ICP-MS
Agilent 8800 triple quadrupole

2019 - Chemical characteristics of Sangiovese wine. Cfr Italy/USA vintage 2016: Results

***Statistics**. ANOVA (Analysis of Variance) was employed, considering country/growing region and replications as factors, and frequency distribution, analyzed by the Chi-square test using Statgraphics Centurion. Principal component Analysis (PCA) and the Soft Independent Modeling of Class Analogy (SIMCA) were performed using Unscrambler.*

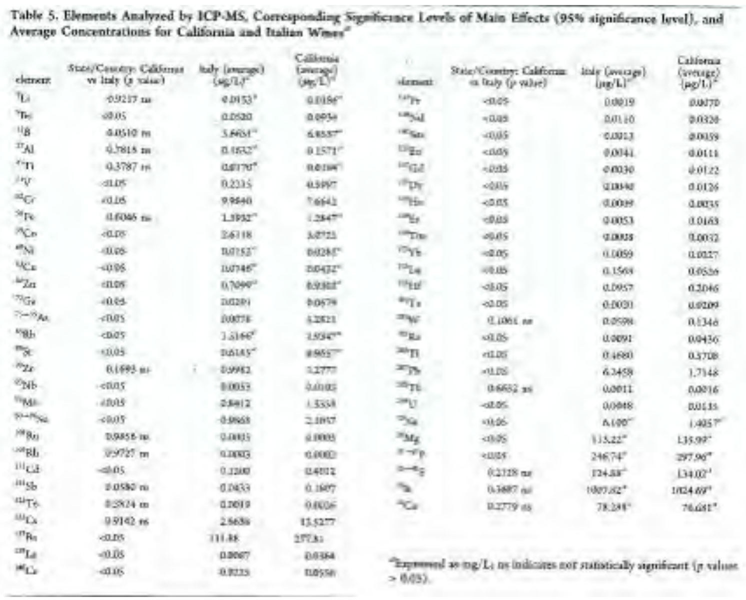


Table 5. Elements Analyzed by ICP-MS, Corresponding Significance Levels of Main Effects (95% significance level), and Average Concentrations for California and Italian Wines[a]

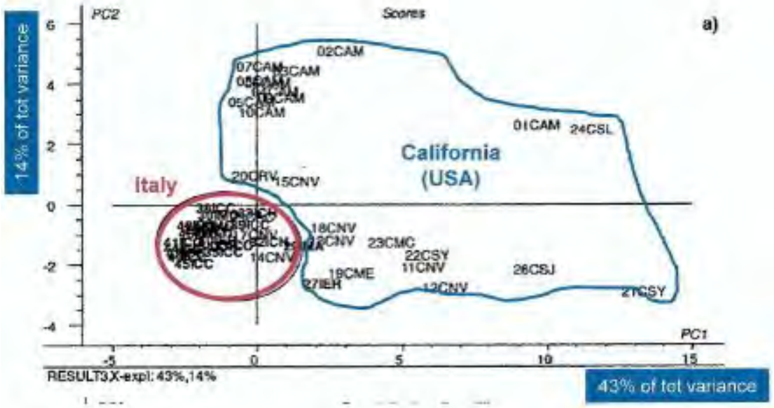
element	State/Country: California vs Italy (p value)	Italy (average) (µg/L)[a]	California (average) (µg/L)[a]
^{7}Li	0.9217 ns	0.0153[a]	0.0186[a]
^{9}Be	<0.05	0.0520	0.0934
^{11}B	0.0510 ns	3.6651[a]	6.8537[a]
^{27}Al	0.7818 ns	0.1632[a]	0.1571[a]
^{47}Ti	0.3787 ns	0.0170[a]	0.0186[a]
^{51}V	<0.05	0.2335	0.5997
^{52}Cr	<0.05	9.9840	7.6642
^{54}Fe	0.6046 ns	1.3932[a]	1.2847[a]
^{59}Co	<0.05	2.6118	3.0725
^{60}Ni	<0.05	0.0152[a]	0.0285[a]
^{65}Cu	<0.05	0.0746[a]	0.0432[a]
^{66}Zn	<0.05	0.7090[a]	0.9303[a]
^{71}Ga	<0.05	0.0201	0.0679
^{75}As	<0.05	0.0078	4.2821
^{85}Rb	<0.05	1.5166[a]	1.9347[a]
^{88}Sr	<0.05	0.6185[a]	0.9655[a]
^{90}Zr	0.1693 ns	0.9982	1.2777
^{93}Nb	<0.05	0.0053	0.0103
^{95}Mo	<0.05	2.8412	1.5558
Sn	<0.05	0.8668	2.1057
^{101}Ru	0.9858 ns	0.0015	0.0005
^{103}Rh	0.9727 ns	0.0003	0.0002
^{111}Cd	<0.05	0.1200	0.4512
^{121}Sb	0.0580 ns	0.0433	0.1607
^{125}Te	0.5824 ns	0.0019	0.0026
^{133}Cs	0.9142 ns	2.5636	13.5277
^{137}Ba	<0.05	111.88	277.81
^{139}La	<0.05	0.0067	0.0364
^{140}Ce	<0.05	0.0225	0.0550
^{141}Pr	<0.05	0.0019	0.0070
^{146}Nd	<0.05	0.0110	0.0328
^{147}Sm	<0.05	0.0013	0.0059
^{153}Eu	<0.05	0.0041	0.0111
^{157}Gd	<0.05	0.0030	0.0122
^{163}Dy	<0.05	0.0040	0.0126
^{165}Ho	<0.05	0.0009	0.0035
^{166}Er	<0.05	0.0053	0.0163
^{169}Tm	<0.05	0.0008	0.0032
^{172}Yb	<0.05	0.0059	0.0027
^{175}Lu	<0.05	0.1569	0.0526
^{178}Hf	<0.05	0.0957	0.2046
^{181}Ta	<0.05	0.0030	0.0209
^{182}W	0.1061 ns	0.0598	0.1346
^{185}Re	<0.05	0.0091	0.0436
^{205}Tl	<0.05	0.4680	0.3708
^{208}Pb	<0.05	6.2458	1.7148
^{232}Th	0.6652 ns	0.0011	0.0016
^{238}U	<0.05	0.0048	0.0135
^{23}Na	<0.05	6.100[a]	1.4057[a]
^{24}Mg	<0.05	115.22[a]	135.99[a]
P	<0.05	246.74[a]	297.96[a]
S	0.2328 ns	124.88[a]	134.02[a]
K	0.3687 ns	1007.82[a]	1024.69[a]
^{44}Ca	0.2779 ns	78.248[a]	76.681[a]

[a] Expressed as mg/L; ns indicates not statistically significant (p values > 0.05).

46 wines

54 elements determined
6 – 238 m/z

38 Elements
Significantly different
Good for ANOVA



***Along PC1** wines were separated based on their concentration of the elements :Yb, Tm, Er, Mo, Nb, La, Re, ce, Ho, Ce, Ga and U; Italian wines were principally characterized by higher levels of Lu, Cu and Pb.*
***Along PC2** wines were separated based on their levels of Na and Sr; the Na content depends on the distance from the sea or from soil composition.*

***Elemental profiling**. ANOVA (Analysis of Variance) was employed, considering country/growing region and replications as factors, and frequency distribution, analyzed by the Chi-square test using Statgraphics Centurion. Principal component Analysis (PCA) and the Soft Independent Modeling of Class Analogy (SIMCA) were performed using Unscrambler.*

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2019 - Chemical characteristics of Sangiovese wine. Cfr Italy/USA vintage 2016: Conclusions

This study sought to define and compare the regional chemical characteristics of Sangiovese wines from two regions, California and Italy, by combining multiple chemical analysis.

By combining multiple chemical analyses, volatile profile, color indices, phenol composition and elemental profiles, it was possible to describe the differences and similarities between the two regions.

Volatile and elemental profiles were most effective at characterizing the wine from the two regions.

This is the first time that an extensive regionality study has been attempted for Sangiovese wines made in California and Italy. The results of this study expand our current knowledge of Sangiovese wines and the contribution of regional characteristics to the composition of wine.

Future studies to characterize the sensory profiles and relate the chemical properties to sensory characteristics are also needed.

2019 - Geographic classification of U.S. Washington State wines by elemental analysis with ICP-MS

Food Chemistry: X 1 (2019) 100007

Contents lists available at ScienceDirect

Food Chemistry: X

journal homepage: www.journals.elsevier.com/food-chemistry-x

Geographic classification of U.S. Washington State wines using elemental and water isotope composition

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Objective of the work: In the present study, elemental and water isotope analyses were performed to characterize Washington State (WA) wines with the goal of differentiating them chemically from those produced in California (CA) , Europe (EU) and South America (SA). Using state-of-the-art analytical instrumentation, specific signatures are sought that are based on characteristic soil and climate features of eastern WA. Through this effort, a database and statistical model are built that can help detect wine wine fraud of WA wines.

133 wines

70 Washington State

17 California State

33 Central Europe

13 South America

116 Red

17 white

Procedure *Wine samples were collected in 20-mL amber glass vials with Teflon lined caps that had been acid cleaned in 5% nitric acid and stored in ultrapure water until use. Before analysis, a 2.0 mL aliquot of wine was filtered through a 0.2 µm pore-sized syringe filter, into a new acid cleaned amber glass vial. To achieve a tested adequate dilution of 1:20, 1.0 mL of the filtered wine was diluted to 20 mL with nanopurewater containing 1.0% ultrapure HNO_3 and 0.5% ultrapure HCl directly into an acid cleaned 15-mL HDPE test tube for analysis on the ICP-MS. All acid cleaning and sample/standard preparation took place in a class 1000 clean laboratory.*

2019 - Geographic classification of U.S. Washington State wines by elemental analysis with ICP-MS: results

62
elements

37
elements

PCA

ICP-MS
Agilent 8900 triple quadrupole with CRC
(Cavity Ring-Down Spectroscopy)

Collision/Reaction Cell (CRC) is suitable to resolve spectral interferences. This technique provides unsurpassed sensitivity and selectivity for (ultra) trace elements . Collision and reaction gases were He, H_2, and O_2 and provided affective removal of interferences, including Ar interferences of $^{75}As^+$, $^{40}Ca^+$, $^{56}Fe^+$ and $^{80}Se^+$.

B, Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Pb, Th

The higher concentration elements, Mg, Si, Mn, Rb and Sr are considered to be soil derived, entering the grape through root uptake. The figure shows Mn, Cu and Rb concentrations in wines of the 4 regions; WA always shows, for these parameters, the lower values, significantly different from other three regions.

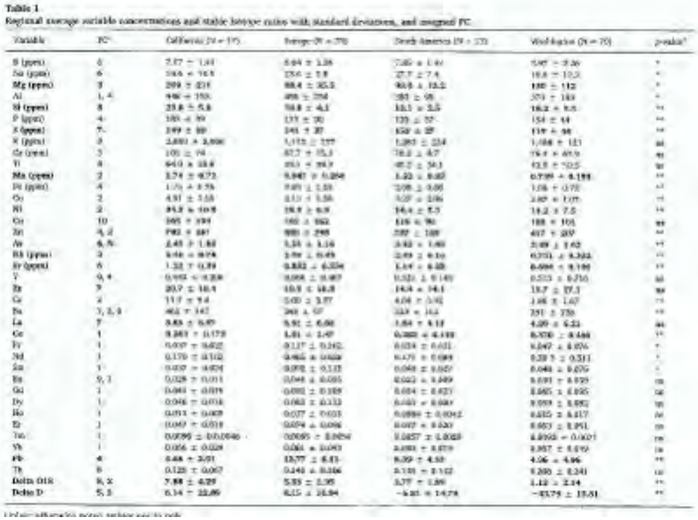
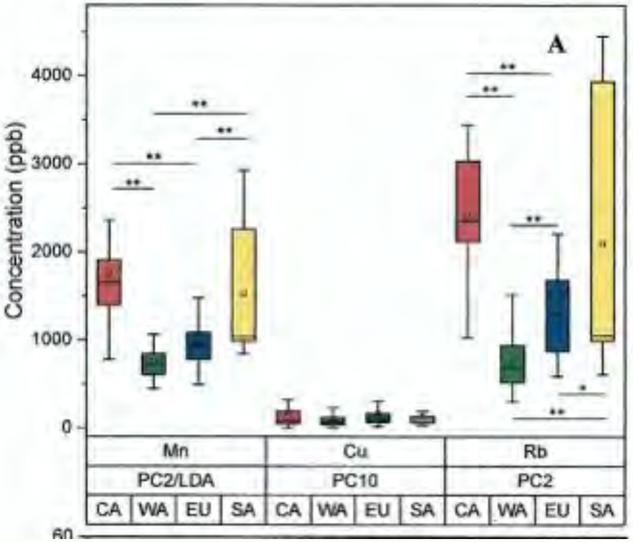


Table 1



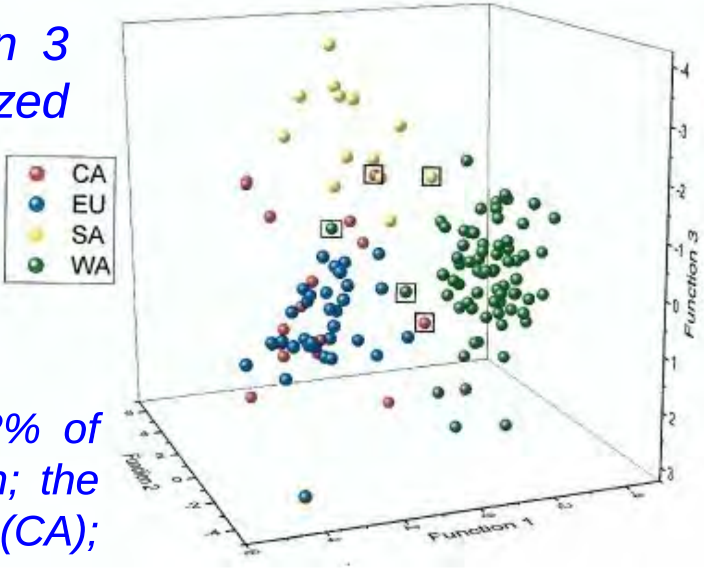
2019 - Geographic classification of U.S. Washington State wines by elemental analysis with ICP-MS: results and Conclusions

LDA

11 elements

Mn, Zn, Pb, Ni, As, δD, La, Ce, Si, Zr & Sr

LDA combined the 11 components in 3 linear functions with standardized coefficients for each component listed.



F(1) = predominant in δD;
F(2) = predominat in Pb and Ni;
F(3) = predominant in Mn, As and Si.

Classification results of the model show that overall 96.2% of samples were correctly assigned to their respective region; the percentage of assignment within each region was: 88.2 (CA); 100% (EU); 92.3% (SA); 97.1% (WA) wines

The linear combination of Pb and Ni seems to be important in discriminating CA wines, while the linear combination of Mn, As and Si provided significant discrimination power for SA wines. δD proved particularly important in discriminating WA wines from all others.

This is the first study** of this kind to chemically characterize and geographically assign WA wines compared to those produced in other parts of the world. **These results provide a preliminary tool that can be used to effectively authenticate WA wines.

Thanks for your listening