Heavy Metals, Rare Earth Elements, and Isotopic Fingerprint of Venetian Protected Designation Origin Sparkling Wines

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Abstract

Purpose: World imports of Italian sparkling wines fell by 9% in value and 5% in quantities. In view of this, the quality characterisation these products is desirable to increase their market value and restore their global visibility.

Methodology: For this purpose, in this paper, heavy metals (Cd, Co, Cr, Cu, Fe, Ga, Hf, Hg, Mn, Mo, Nb, Ni, Pb, Re, Sb, Sn, Ta, Th, Tl, U, W, V, Zn, Zr), rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) and isotopes ratio ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$, $^{87}Sr/^{86}Sr$) were analysed in Italian sparkling wines with PDO certification by HR-ICP-MS and MC-ICP-MS. The samples were produced in the Veneto region, and they were compared to white and red wines from the same area.

Findings: Sparkling wines present a characteristic elemental pattern compared to white and red ones, with lower content of heavy metals and higher content in REEs.

$^{87}Sr/^{86}Sr$ resulted in a powerful micro-scale geographical origins marker while Pb ratios as winemaking process one, both useful to prevent possible frauds.

Multivariate data analyses, such as PCA and PLS-DA, were used to develop a model of recognition of Venetian sparkling wines.

Originality: The good classification of sparkling wines was achieved (95%), proving the suitable use of these analytes as markers for recognising sparkling wines and their geographical origin verification. To the best of our knowledge, this is the first study investigating heavy metals, rare earth elements and isotopes in Venetian sparkling wine for their recognition.

Keywords: sparkling wine; elemental analysis; chemometric; heavy metals; rare earth elements; isotopes ratio.

1. Introduction

In recent years the worldwide production of sparkling wines has marked a constant growth. In 2021 the sparkling wine market amounted to 41 billion dollars versus 36 billion dollars in 2020. According to forecasts, the sparkling wine market will grow by 55 billion dollars in 2025.

With 86% of world production, Europe countries are the leaders. Italy holds the first position (22%), followed by France (19%), Germany (15%), Spain (12%), Russia (10%) and the United States (6%).

Although, more and more sparkling wines come from the American continent, with a volume increase of 30% in the last seven years (Thome and Paiva, 2020).

83% of sparkling wines are white, 15% rosé and 2% red. The proportion of rosé has slightly increased in recent years (Rossetto and Galletto, 2019). The sparkling red wines come only from Italy. In addition, the brut version accounts for 81% of world production, in contrast to the demi-sec 14% and extra brut 5%.

Italy has had a growing production since 2009 and is the leading exporter of sparkling wines with 41% of total exports, followed by France with 24% and Spain with 22%. Nevertheless, France covers the first position in terms of value due to the higher average price of an exported bottle (Bassi *et al.*, 2020).

In Italy, in 2020, 750.6 million bottles of sparkling wine were produced, equal to 5.6 million hectoliters (Bassi *et al.*, 2021). The production comprises more than 90% of white sparkling wines, while rosés represent only 4% of the total, with even lower percentages for red ones. Of these 750.6 million bottles, 82% are products with Protected Designation of Origin (PDO) certification, 1% of Protected Geographical Indication (PGI) certification, while the rest (107 million bottles) are non-certified sparkling wines, varietal and common ones (Galletto *et al.*, 2021).

From the point of view of the markets, in 2020, due to the pandemic, world imports of Italian sparkling wines fell by 9% in value and 5% in quantities compared to 2019.

The United States is the most important and solid market by value, with 20% of the share of import absorption, followed by the United Kingdom (12%), Japan (8%) and Germany (7%).

In quantity, Great Britain slightly surpasses the USA (18% against 17%), followed by Germany (7%). For Italy, foreign markets represent a fundamental channel. 70% of the production made in Italy is destined for export (Rossetto and Gastaldello, 2018).

In this context, the quality characterisation of Italian sparkling wines is desirable to increase their market value. Recently, the analysis of elemental and isotopic contents in wine has been widespread to assess these products' origin and quality.

The analysis of elements' content was investigated to be involved as descriptors of different winemaking steps (Granell *et al.*, 2022; Mir-cerdà *et al.*, 2022). Granell et al. have pointed out that Cu and K were abundant in musts while Na, Ca Fe, and Mg increased during the fermentation. Indeed, Mir-Cerdà et al. have found that Zn, Al, Mn, Fe, Ni and V can be used as indicators of oenological treatments.

The mineral content was also used to differentiate sparkling wines from champagne (Jos *et al.*, 2004). Jos et al. highlighted that the K concentration was similar in sparkling wine and champagne while P was higher in champagne samples, probably due to a difference between raw materials.

An interesting study by Debastiani et al. has examined the migration of the elements from sparkling wine to cork stoppers. They have found that Mg, S, K, Ca, Cu, and Sr concentrations increased in the stoppers during storage time while P and Fe decreased (Debastiani *et al.*, 2021).

Yamashita et al. in 2019 and Rodrigues et al. in 2021 have proposed a sparkling wines classification from the origin country based on multi-elemental content and multivariate analysis (Rodrigues *et al.*, 2020; Yamashita *et al.*, 2019). The authors successfully discriminated among sparkling wines coming from Brazil, Argentina, Spain and France.

Besides, the isotopes' ratio determination was also found in the literature recognising the geographical origin of sparkling wines (Cellier, Berail, *et al.*, 2021; Cellier, Bérail, *et al.*, 2021). A study by Cellier et al. showed discrimination of French sparkling wines from other European and Non-Europeans ones based on $^{87}Sr/^{86}Sr$ and $^{208}Pb/^{206}Pb$ signatures (Cellier, Berail, *et al.*, 2021; Cellier, Bérail, *et al.*, 2021). Therefore, in this study, the isotopic ratio measurements have also been conducted with the aim of pointing out specific markers of Venetian sparkling wines.

Studies performing a multi-elemental and isotopes characterisation of Italian sparkling wines are very scarce.

Thus, in this study, heavy metals (Cd, Co, Cr, Cu, Fe, Ga, Hf, Hg, Mn, Mo, Nb, Ni, Pb, Re, Sb, Sn, Ta, Th, Tl, U, W, V, Zn, Zr), rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) and isotopes ratio ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$, $^{87}Sr/^{86}Sr$) were analysed in Italian sparkling wines with PDO certification by HR-ICP-MS and MC-ICP-MS.

The vast majority (82%) of sparkling wines with a PDO in Italy in 2020 were produced in the Veneto region, with 528 million bottles and a quantity of 3.9 million hectolitres (Basso, 2019). For this reason, 20 sparkling wine samples from the Veneto region were collected and analysed. The results were compared to Venetian non-sparkling wine samples (14 white and 8 red ones). Tukey HSD test was applied to point out significant differences for analytes investigated.

Going beyond, chemometrics tools, such as Principal Component Analysis (PCA), variable stepwise and Partial Least-Squares Discriminant Analysis (PLS-DA) were employed to highlight particular trends and to individuate specific markers for sparkling wines.

2. Materials and Methods

2.1 Sample collection and preparation

The wine samples used in this study were purchased in selected wineries in the Italian market. All samples reported the PDO statement on the label. The samples were produced in the Verona and Vicenza provinces of the Veneto region. Forty-two samples (produced in 2015-2022) were collected,

including 20 sparkling wines, 14 white wines, and 8 red wines. The production sites of samples collected were reported in Figure 1.

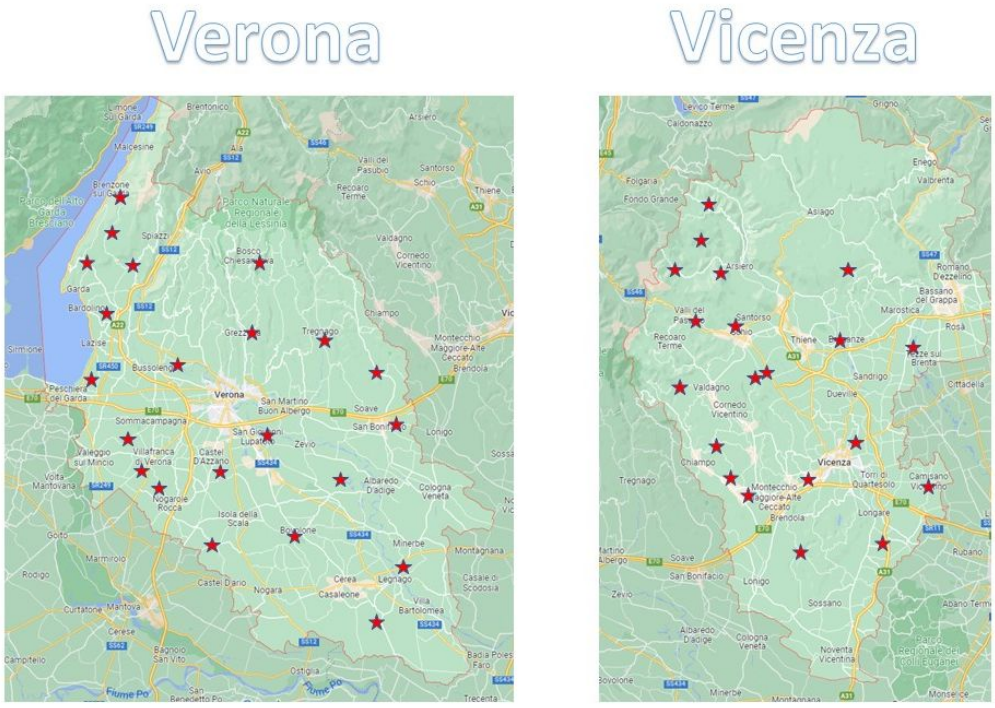

Figure 1. Production sites of collected samples in Verona and Vicenza provinces of the Veneto region.

2.2 Chemicals and reagents

Nitric acid (HNO_3, Sigma-Aldrich Chemie Gmbh, Munich, Germany) used in this work were of analytical grade. Water used was de-ionised Milli-Q water (Millipore, Bedford, MA, USA) purified by reverse osmosis followed by ion-exchange cartridges. For dilution of wine samples and samples digests, water was further purified by sub-boiling distillation in Teflon stills. Pre-packed 2 ml columns with Sr-Spec resin (Eichrom Technologies LLC 1955 University Lane Lisle, IL, USA) were used as supplied. For instrumental mass-bias correction NIST SRM 987 - Strontium Carbonate, NIST SRM 951a – Boric Acid and NIST SRM 981 – Common Lead Isotopic Standard (all from National Institute of Standards and Technology, Gaithersburg, MD, USA) was used. For controlling the method accuracy, a set of certified reference materials (CRM) have been included and processed throughout the entire procedure (digestion, separation and analysis): SLRS-5 River Water CRM for Trace Metals and NASS-6 Seawater CRM for Trace Metals (both from the National Research Council, Canada), NIST SRM 1547 Peach Leaves (National Institute of Standards and Technology, Gaithersburg, MD, USA) and GBW 07410 soil (National Re-search Centre of Geoanalysis, Beijing, China).

2.3 Instrumentation

All measurements of element concentrations were performed by double-focusing sector field ICP-MS ELEMENT XR (Thermo Scientific, Bremen, Germany) equipped with introduction system consisting of demountable quartz torch with 1.5 mm i.d. sapphire injector, platinum capacitive de-coupling shield, nickel sampler cone, high sensitivity 'X-type' skimmer cone and PFA spray chamber with two gas inlet ports (Cetac Technologies, Omaha, NE, USA), micro-concentric PolyPro nebuliser and FAST SD2 au-to-sampler (ESI, Perkin-Elmer, Santa Clara, USA) equipped with a six-port valve and a 1.5-ml sample loop filled and rinsed by vacuum suction. Methane addition to the plasma was used to decrease formation of oxide-based spectral interferences, improve sensitivity for elements with high first ionisation potentials, and to minimise matrix effects (Rodushkin *et al.*, 2005). Operating conditions and measurement parameters for concentration measurements were reported in Table 1. (Engström *et al.*, 2004).

Table 1. ICP-SFMS operating conditions and measurement parameters

Rf power/W	1450
Sample uptake rate/ml min^{-1}	0.3
Argon gas flow rates/l min^{-1}	
Coolant	16
Auxiliary	1.0
Nebulizer	0.95-0.98
Introduction system	Fassel torch, 1.5 mm i.d., capacitive de-coupling system, MicroMist AR40-1-F02 nebulizer, Scott type (double-pass) PFA spray chamber, nickel cones (X-skimmer cone)
Ion lens settings	Adjusted to obtain maximum signal intensity
Isotopes	
Low resolution mode (LRM)	^{7}Li, ^{9}Be, ^{11}B, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{109}Ag, ^{111,114}Cd, ^{115}In, ^{118,120}Sn, ^{121,123}Sb, ^{125,126}Te, ^{127}I, ^{133}Cs, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147,149}Sm, ^{151,153}Eu, ^{157,160}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{171,173}Yb, ^{175}Lu, ^{178,180}Hf, ^{181}Ta, ^{184}W, ^{185,187}Re, ^{190,192}Os, ^{191,193}Ir, ^{194,195}Pt, ^{197}Au, ^{201,202}Hg , ^{205}Tl, $^{206,207.208}$Pb, ^{209}Bi, ^{232}Th, ^{238}U

Medium resolution mode (MRM)	^{23}Na, ^{27}Al, ^{28}Si^{35}Cl, ^{44}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{69}Ga, ^{79}Br, ^{115}In
High resolution mode (HRM)	^{24}Mg, ^{31}P, ^{32}S, ^{39}K, ^{72,74}Ge, ^{75}As, ^{78}Se, ^{101,102}Ru, ^{103}Rh, ^{105,106,108}Pd, ^{115}In
Acquisition mode	E-scan
No. of scans	6 for each resolution
Acquisition window/%[a]	10 in LRM; 100 in MRM and HRM
Search window/%[a]	10 in LRM; 80 in MRM and HRM
Integration window/%[a]	10 in LRM; 60 in MRM and HRM
Dwell time per sample/ms	10 in LRM; 20 in MRM, 50 in HRM
No. of samples per nuclide	100 in LRM, 25 in MRM and HRM

[a] Percent of peak width

Strontium and lead isotope ratio measurements were performed by NEPTUNE PLUS (Thermo Scientific, Bremen, Germany) MC-ICP-MS. Cup configurations used and operating conditions and measuring parameters are given in Table 2 (Rodushkin *et al.*, 2016). A laboratory UltraWave single reaction chamber microwave digestion system (Milestone, Sovisole, Italy) was used for sample digestions.

Table 2. MC-ICP-MS operating parameters and measurement conditions for isotope ratio measurements [b]. Table modified from Rodushkin et al. (2016).

Elements	Configuration of introduction system	Resolution mode	Integration time (s)	Sample uptake rate (m	Dynamic mode configuration	Cup configuration								
						L4	**L3**	**L2**	**L1**	**C**	**H1**	**H2**	**H3**	**H4**

				L mi n^{-1})										
B	Pumped Micromist nebuli zer, mini cyclonic spray chamber, X-type skimmer cone	Low	0.52 4	0.4 0- 0.5 0	-	-	^{10}B	-	-	-	^{11}B	-	-
Pb/ Tl	Aridus/Apex desolvating systems, self-aspirating microconcentric PFA nebulizer, X-type skimmer cone	Low	0.52 4	0.0 4- 0.0 6	-	^{202}H g	^{203}Tl	^{204}Pb (^{204}Hg)	^{205}Tl	^{206}Pb	^{20} ^{7}P b	^{20} ^{8}P b	-
Sr	Pumped Micromist nebuli zer, double spray chamber, H-type skimmer cone	Low	0.26 2	0.2 0- 0.2 5	^{82}K r	^{83}Kr	^{84}Sr (^{84}Kr)	^{85}Rb	^{86}Sr (^{86}Kr)	^{87}Sr (^{87}Rb)	^{88}Sr	-	-

[b] RF power: 1400– 1450 W. Coolant gas flow: 15 L min^{-1}. Auxiliary gas flow: 1.4 L min^{-1}. Sample gas flow: 0.9–1.25 L min^{-1}. Additional gas flow (N_2, Aridus and Apex) 0.01–0.02 L min^{-1}. Ion lens settings: adjusted daily to obtain maximum sensitivity and signal stability. Zoom optic settings: adjusted daily to obtain maximum resolution. Number of blocks: 9. Number of cycles per block: 5. Number of integrations: 3–5. Amplifier rotation: left.

2.4 Sample preparation and analysis

Sample preparation was performed in Class 10 000 clean laboratory areas by personnel wearing clean room attire. General precautions detailed by (Rodushkin *et al.*, 2010) were taken to minimise contamination. Laboratory materials used during sample preparation were soaked in 0.7 M HNO_3 for 24 h at room temperature and rinsed with de-ionised Milli-Q water prior to use. For multi-elemental analyses wine samples were diluted 40-fold with 1.4 M HNO_3. Set of method blanks and CRMs was prepared with each batch of samples and concentrations of the 39 elements were determined by ICP-SFMS. Matrix effect correction was accomplished by internal standardisation (Indium added to all measurement solutions at 2.5 µg/l concentration) and quantification was done by external calibration with synthetic, concentration-matched standards. The rest of the original sample digests was evaporated to dryness in 25 ml Teflon beaker at 95°C on a ceramic-top hot plate, followed by dissolution in 3 ml of 3M HNO_3 and Sr/Pb separation on Sr-specific columns using Sr elution with 0.05M HNO_3 following by Pb elution with 0.002% EDTA. A 0.1 ml aliquot of separates was diluted

50-fold with 1.4 M HNO_3 and analysed by ICP-SFMS (same approach as for sample digests). This provides (I) information on analyte concentration needed to prepare concentration- and acid strength-matched solutions for isotope ratio measurements, (II) direct assessment of analyte recovery, (III) control over separation efficiency from matrix elements, (IV) test for presence of potentially spectrally interfering elements either from sample matrix or from handling contamination. Separated fractions were diluted to the same concentrations and a set of bracketing standards matching samples in analyte and internal standard concentrations (Tl added to solutions for Pb isotope ratios) and acid strength was prepared. Instrumental mass bias correction has been performed using a combination of standard-sample bracketing and internal normalisation (based on tabulated $^{88}Sr/^{86}Sr$ or $^{205}Tl/^{203}Tl$ ratios).

2.5 Analytical Validation

Summary of figures of merit of analytical methods used for multi-elemental analysis are provided in Table 3.

Table 3. Figures of merit of analytical method

	LOD[a]/LOQ[b] (µg/L)	Reproducibility[c] (%)	Mean recovery[d] %
Cd	0.003/0.01	5	98
Ce	0.01/0.04	3	93
Co	0.02/0.05	2	96
Cr	0.1/0.3	4	90
Cu	0.2/0.6	3	102
Dy	0.001/0.003	20	94
Er	0.001/0.003	12	93
Eu	0.001/0.002	14	92
Fe	5/17	4	97
Ga	0.01/0.04	8	94
Gd	0.003/0.009	8	94
Hf	0.001/0.004	24	96
Hg	0.03/0.1	8	92
Ho	0.0003/0.001	7	94
La	0.006/0.02	6	92
Lu	0.0001/0.0003	8	95
Mn	0.3/0.8	3	97
Mo	0.01/0.03	5	96
Nb	0.0001/0.0003	9	92
Nd	0.006/0.02	10	94
Ni	0.03/0.1	3	100
Pb	0.04/0.12	4	103
Pr	0.001/0.003	4	94
Re	0.0001/0.0003	16	88
Sb	0.01/0.03	4	94

Sm	0.0001/0.0003	14	92
Sn	0.07/0.2	3	90
Ta	0.0001/0.0003	NA[e]	91
Tb	0.0002/0.0006	17	94
Th	0.002/0.006	5	93
Tl	0.001/0.003	3	96
Tm	0.0005/0.002	16	94
U	0.007/0.02	2	95
W	0.02/0.06	12	91
V	0.0001/0.0003	8	101
Yb	0.001/0.003	16	93
Zn	4/14	4	102
Zr	0.004/0.01	4	90

[a] Limit of detection calculated as 3 times the standard deviation of preparation blanks analysed in several instrumental sequences.

[b] Limit of quantification calculated as 10 times the standard deviation of preparation blanks analysed in several instrumental sequences.

[c] Calculated as the relative standard deviation for concentration obtained in 18 samples/CRMs prepared and analysed as duplicates (results below respective LOD are omitted).

[d] Calculated as mean ratio of measured concentrations to target/information concentration of analyte for CRMs used.

[e] Precision estimate is unavailable because of analyte concentrations below respective LOD in all duplicates.

[f] Recovery estimate is unavailable because of analyte concentrations below respective LOD or target/information concentrations are absent.

The limits of detection (LOD) and limits of quantification (LOQ) were calculated as three respective ten times the standard deviation for element's concentrations detected in preparation blanks (n>10). The accuracy of the data was assessed by analyses of the CRMs and presented as mean recoveries calculated as ratio of ICP-SFMS results to certified, indicative or information values, where such were available. Method reproducibility was evaluated from replicate preparation/analysis of samples and CRMs, and as a rule was better than 10% RSD for elements presented in tested matrixes at concentrations 10 times above respective LODs (Table 4). Isotope ratios obtained in CRMs provided in Table 4. Reproducibility of isotope ratio measurements was as a rule better than 0.005% RSD for Sr and Pb.

Table 4. Isotope ratios obtained for CRMs

CRMs	$^{87}Sr/^{86}Sr$ measured (SD, n=3)	$^{87}Sr/^{86}Sr$ published (SD, n=3)	$^{206}Pb/^{207}Pb$ measured (SD, n=3)	$^{206}Pb/^{207}Pb$ published (SD, n=3)	$^{208}Pb/^{207}Pb$ measured (SD, n=3)	$^{208}Pb/^{207}Pb$ published (SD, n=3)
SLRS-5	0.711086(36)	0.7111	NA	NA	NA	NA
NASS-6	0.709211(29)	0.70918	NA	NA	NA	NA
NIST SRM 1547	0.713382(25)	0.71339	1.21281(6)	1.213	2.48227(13)	2.482

2.6 Statistical analysis

Analysis of variance (ANOVA) and mean comparison by Tukey's honest significant difference (HSD) for the unequal number of samples at 5% level were performed using JMP 15 Pro (SAS Institute). Principal Component Analysis (PCA) and Partial Least-Squares Discriminant Analysis (PLS-DA) were performed with JMP 15 Pro. Before the chemometric assessment, an autoscaling pre-treatment was carried out on the data matrix (Conti et al., 2007).

3. Results and discussion

3.1 Heavy metals

As reported by the International Union of Pure and Applied Chemistry (IUPAC) it is possible to define as a heavy metal each chemical element with a density greater than 5 g/cm3. In this study, heavy metals, such as Cd, Co, Cr, Cu, Fe, Ga, Hf, Hg, Mn, Mo, Nb, Ni, Pb, Re, Sb, Sn, Ta, Th, Tl, U, W, V, Zn and Zr, were analysed by HR-ICP-MS in wines.

Some heavy metals are essential elements for life as they are involved in important metabolic processes (Co, Co, Cr, Cu, Fe, Mn, Mo, Ni, Sn, V and Zn) while others, i.e., Cd, Hg, Cr and Pb, are recognised as toxic for living organisms even at low concentrations.

The total heavy metal content (∑H.M.) and the single heavy metal content were reported in Table 5. It should be noted that:

(i) sparkling wines showed the lowest ∑H.M. mean content (2348.881 µg/L), close to white wines, but a concentration almost halved compared to red wines (4207.096 µg/L);

(ii) the most abundant heavy metals in all samples were Zn, Mn and Fe. They were found in the highest concentration in red wines and lowest in sparkling wines. The differences were also confirmed by HSD Tukey which pointed out statistical differences for Mn and Fe;

(iii) Cu, Ga, Th, W and V have an opposite trend, and these metals have the highest content in the sparkling wines compared to the others (Ga and Th differences statistically significant by HSD Tukey);

(iv) regarding the toxic metals, sparkling wines showed the lowest concentration of Cd and Hg, while Cr and Pb were lower than red and white wines, respectively. Nevertheless, none of these four elements reported differences statistically significant).

It is worth noting literature investigating these analytes in sparkling wines, including Italian ones, is very scarce.

However, we can infer some comparisons:

(i) Fe and Mn were the most studied elements;

(ii) Fe was found at 360-920 µg/L concentration by (Debastiani *et al.*, 2021), 1070-1850 µg/L by (Rodrigues *et al.*, 2020) and 520-2770 µg/L by (Jos *et al.*, 2004);

(iii) the same authors have investigated Mn, reporting 1300-1900 µg/L (Debastiani *et al.*, 2021), 510 – 1590 µg/L (Rodrigues *et al.*, 2020) and 451-940 µg/L (Jos *et al.*, 2004) concentrations. The levels found in the literature have a good overlap with the ranges of our study (Fe: 460 – 1000 µg/L; Mn: 370 – 990 µg/L);

(iv) Zn concentration was investigated by (Debastiani *et al.*, 2021) (620 – 900 µg/L) and (Jos *et al.*, 2004) (208-575 µg/L). Also, in this case, the literature data are in good agreement whit our results (500 – 1400 µg/L);

(v) Cd, Ni and Pb have been investigated only by Jon et al. Their results were in good accord with this study, even if they have used some specific techniques (graphite furnace atomic absorption and hydride generation atomic absorption) to detect those elements (Jos *et al.*, 2004).

Table 5. Heavy metals concentration in sparkling wine samples by HR-ICP-MS, reported as µg/L. Rows not linked by the same letter are statistically different by HSD Tukey.

Elements	Statistics	Sparkling	White	Red
Cd	Mean	0.19 [a]	0.21 [a]	0.24 [a]
	S.D.	0.058	0.069	0.11
	Min	0.1	0.17	0.14
	Max	0.28	0.36	0.37
Co	Mean	2.4[ab]	2[b]	2.9[a]
	S.D.	0.44	0.3	0.5
	Min	1.5	1.6	2.3
	Max	3.1	2.4	3.5
Cr	Mean	11 [a]	10 [a]	17 [a]

	S.D.	6.3	0.87	3.7
	Min	3.2	8.7	13
	Max	27	11	21
Cu	Mean	190 [a]	100 [a]	140 [a]
	S.D.	210	93	170
	Min	17	11	11
	Max	670	260	360
Fe	Mean	690[b]	780[b]	1800[a]
	S.D.	210	360	170
	Min	460	490	1600
	Max	1000	1500	2000
Ga	Mean	0.13[a]	0.12[ab]	0.045[b]
	S.D.	0.063	0.046	0.018
	Min	0.046	0.038	0.029
	Max	0.26	0.18	0.071
Hf	Mean	0.065 [a]	0.075 [a]	0.068 [a]
	S.D.	0.061	0.043	0.048
	Min	0.0042	0.014	0.042
	Max	0.19	0.14	0.14
Hg	Mean	0.016 [a]	0.026 [a]	0.033 [a]
	S.D.	0.012	0.014	0.012
	Min	0.00017	0.0023	0.023
	Max	0.038	0.04	0.048
Mn	Mean	660[b]	700[b]	1100[a]
	S.D.	180	160	220
	Min	370	490	790
	Max	990	870	1300
Mo	Mean	2.6 [a]	1.7 [a]	1.5 [a]
	S.D.	3.5	0.59	0.95
	Min	0.65	0.82	0.75
	Max	12	2.5	2.9
Nb	Mean	0.23 [a]	0.15 [a]	0.058 [a]
	S.D.	0.25	0.14	0.019
	Min	0.061	0.022	0.032
	Max	0.92	0.36	0.078
Ni	Mean	30 [a]	34 [a]	26 [a]
	S.D.	9.9	38	6.7
	Min	14	11	18
	Max	46	120	34
Pb	Mean	12 [a]	17 [a]	11 [a]
	S.D.	11	12	5.2
	Min	2.8	4.9	7.2
	Max	40	33	18
Re	Mean	0.0018[b]	0.0025[b]	0.021[a]
	S.D.	0.0016	0.0013	0.026
	Min	0.00019	0.00081	0.0057
	Max	0.0046	0.0042	0.06
Sb	Mean	0.41 [a]	0.37 [a]	0.41 [a]
	S.D.	0.16	0.085	0.4

	Min	0.21	0.23	0.17
	Max	0.65	0.47	1
Sn	Mean	2.2 [a]	2.6 [a]	2.5 [a]
	S.D.	1.5	2.4	1.2
	Min	0.32	0.63	1.3
	Max	4.6	7.4	3.9
Ta	Mean	0.0027[b]	0.0043[a]	0.0036[ab]
	S.D.	0.00072	0.0017	0.00066
	Min	0.0015	0.0026	0.0028
	Max	0.0036	0.0075	0.0043
Th	Mean	0.0056[b]	0.0052[b]	0.017[a]
	S.D.	0.0042	0.011	0.0044
	Min	0.00046	0.000014	0.01
	Max	0.012	0.029	0.019
Tl	Mean	0.28 [a]	0.29 [a]	0.3 [a]
	S.D.	0.082	0.14	0.11
	Min	0.15	0.16	0.17
	Max	0.41	0.56	0.4
U	Mean	0.24 [a]	0.26 [a]	0.4 [a]
	S.D.	0.36	0.28	0.54
	Min	0.012	0.048	0.073
	Max	1.2	0.86	1.2
W	Mean	0.41 [a]	0.33 [a]	0.2 [a]
	S.D.	0.45	0.14	0.13
	Min	0.086	0.15	0.081
	Max	1.5	0.54	0.36
V	Mean	23 [a]	2.5 [a]	1.9 [a]
	S.D.	39	0.73	1.9
	Min	1.2	2	0.82
	Max	120	4.1	4.8
Zn	Mean	720 [a]	750 [a]	1100 [a]
	S.D.	250	210	320
	Min	500	510	660
	Max	1400	990	1400
Zr	Mean	3.7 [a]	3.9 [a]	2.5 [a]
	S.D.	3	2.2	1.2
	Min	0.26	1.1	1.5
	Max	9.8	8.2	4.2
∑H.M.	-	**2348.881**	**2405.543**	**4207.096**

3.2 Rare earth elements

The concentration of lanthanide elements, also known as Rare Earth Elements (REEs), has shown an increase in the environment due to their extensive use in electronic industry and agriculture practices (Conti *et al.*, 2020; Gonzalez *et al.*, 2014). REEs are constituents of some fertilisers widely used in

agriculture for their property to increase the production yield of crops. Moreover, the REE's direct application to crops has been demonstrated to influence plant growth and germination (Thomas *et al.*, 2014). In addition, it was also demonstrated that the REE concentration could be maintained from soil to plants, and it can variate according to species and soil type (Censi *et al.*, 2014).

Aiming to assess the relationship between production sites and wine samples, we have measured the concentration of 14 REEs (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) in Venetian sparkling wines by HR-ICP-MS. The results of REEs determination in sparkling, white and red wines were reported in Table 6, as well as the HSD Tukey results.

From this study, we can infer some results:

(i) the sparkling wines showed the highest REEs concentration 0.9473 µg/L, followed by white wines (0.8683 µg/L) and red ones (0.7812 µg/L);

(ii) the REEs concentration in sparkling wines has an opposite trend compared to heavy metals. Thus, sparkling wines present a characteristic elemental pattern compared to white and red ones, with lower content of heavy metals and higher content in REEs;

(iii) the highest REEs concentration in sparkling wines was led by Ce (the most abundant lanthanide), La and Nd. Together with Pr and Sm, these REEs have been found in the highest concentration in sparkling wines, followed by red wines and in the lowest concentrations in white ones;

(iv) Dy, Er, Ho, Lu, Tm and Yb concentrations showed a different trend, in sparkling wines, the concentrations of these REEs were similar to the red ones, while the highest concentration was found in the white wine samples.

To the best of our knowledge, literature data on REEs in sparkling wines are scarce, thus, no comparison was possible.

Two papers were found investigating REEs in soil and grape berries (Pepi *et al.*, 2016) and in soil and leaf (Pepi *et al.*, 2018). The REEs profile in wine differs significantly from other matrices (i.e., grapes) due to the winemaking processes (fermentation, bleaching, etc.) that alter the elemental composition.

Table 6. Rare Earth Elements concentration in sparkling wine samples by HR-ICP-MS, reported as µg/L. Rows not linked by the same letter are statistically different by HSD Tukey.

Elements	Statistics	Sparkling	White	Red
Ce	Mean	0.32 [a]	0.11 [a]	0.23 [a]
	S.D.	0.59	0.13	0.11

	Min	0.024	0.027	0.079
	Max	2	0.4	0.32
Dy	Mean	0.039 [a]	0.089 [a]	0.051 [a]
	S.D.	0.058	0.2	0.04
	Min	0.004	0.0065	0.02
	Max	0.2	0.54	0.11
Er	Mean	0.042 [a]	0.15 [a]	0.044 [a]
	S.D.	0.051	0.32	0.035
	Min	0.0093	0.013	0.025
	Max	0.18	0.86	0.097
Eu	Mean	0.0075 [a]	0.0052 [a]	0.013 [a]
	S.D.	0.0066	0.0018	0.0022
	Min	0.0043	0.0031	0.0097
	Max	0.026	0.0079	0.015
Gd	Mean	0.03 [a]	0.026 [a]	0.038 [a]
	S.D.	0.044	0.05	0.032
	Min	0.0056	0.0019	0.0095
	Max	0.15	0.14	0.082
Ho	Mean	0.0099 [a]	0.03 [a]	0.01 [a]
	S.D.	0.015	0.066	0.0093
	Min	0.0014	0.0019	0.0034
	Max	0.051	0.18	0.024
La	Mean	0.16 [a]	0.034 [a]	0.11 [a]
	S.D.	0.33	0.044	0.09
	Min	0.0089	0.0049	0.037
	Max	1.1	0.13	0.24
Lu	Mean	0.014 [a]	0.047 [a]	0.0092 [a]
	S.D.	0.012	0.085	0.0054
	Min	0.0025	0.0063	0.0048
	Max	0.045	0.24	0.017
Nd	Mean	0.17 [a]	0.058 [a]	0.14 [a]
	S.D.	0.33	0.062	0.085
	Min	0.012	0.021	0.045
	Max	1.1	0.19	0.24
Pr	Mean	0.038 [a]	0.011 [a]	0.03 [a]
	S.D.	0.075	0.011	0.018
	Min	0.0033	0.0016	0.0085
	Max	0.25	0.033	0.049
Sm	Mean	0.035 [a]	0.014 [a]	0.038 [a]
	S.D.	0.069	0.014	0.023
	Min	0.0031	0.0044	0.013
	Max	0.23	0.044	0.066
Tb	Mean	0.0059 [a]	0.0081 [a]	0.0068 [a]
	S.D.	0.0074	0.015	0.0062
	Min	0.00075	0.00082	0.0024
	Max	0.026	0.043	0.016
Tm	Mean	0.007 [a]	0.026 [a]	0.0072 [a]
	S.D.	0.0088	0.055	0.0066
	Min	0.0012	0.0017	0.0037

	Max	0.031	0.15	0.017
Yb	Mean	0.069 [a]	0.26 [a]	0.054 [a]
	S.D.	0.081	0.51	0.031
	Min	0.015	0.022	0.033
	Max	0.29	1.4	0.099
∑REEs	-	**0.9472**	**0.8683**	**0.7812**

3.3 Isotopes ratio

To verify the origin of food were usually involved the study of Carbon and Oxygen isotopes. The use of non-conventional isotopes is recently spreading, such as Strontium and Lead (Irrgeher and Prohaska, 2016).

Sr occurs in four isotopes, including ^{87}Sr and ^{86}Sr used to calculate the age of the rocks. Sr easily replaces Ca, being their atomic radius similar, and it is found in sufficiently high concentrations in minerals. Although Sr is not an essential element to plants, the transfer factor soil-to-crop is high, so it can be found in plant and plant-derived food (O'Sullivan *et al.*, 2022).

Also, Pb has four stable isotopes, and it comes from the soil, but its natural concentration in plants is low. The Pb accumulation in plants was strictly related to a contaminated environment due to anthropogenic activity, such as mining, industry, coal-burning and gasoline (Nasr *et al.*, 2022).

All these factors enable Sr and Pb isotopes as suitable markers of specific geographical situations. In this study a MC-ICP-MS was used to determinate $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$, $^{87}Sr/^{86}Sr$ ratios in sparkling wines. Isotopes ratio results, as well as the HSD Tukey ones, are reported in Table 7.

Table 7. Strontium and lead isotopes ratio in sparkling wine samples analysed by MC-ICP-MS. Rows not linked by the same letter are statistically different by HSD Tukey.

Elements	Statistics	Sparkling	White	Red
208Pb/206Pb	Mean	2.0949[a]	2.0754[b]	2.0934[a]
	S.D.	0.006462	0.012974	0.013539
	Min	2.0814	2.0516	2.074
	Max	2.1034	2.0912	2.1037
207Pb/206Pb	Mean	0.85579[a]	0.84286[b]	0.8566[a]
	S.D.	0.005182	0.005539	0.00651
	Min	0.84535	0.83658	0.84757
	Max	0.86284	0.84941	0.86198
206Pb/204Pb	Mean	18.572[a]	18.754[a]	18.564[a]
	S.D.	0.29233	0.25315	0.105
	Min	18.142	18.299	18.476

	Max	19.096	19.082	18.715
208Pb/207Pb	Mean	2.448[a]	2.4624[b]	2.4438[a]
	S.D.	0.007517	0.00737	0.004083
	Min	2.4377	2.4524	2.4379
	Max	2.4621	2.4719	2.447
87Sr/86Sr	Mean	0.70621[b]	0.70754[a]	0.70848[a]
	S.D.	0.001181	0.001008	0.000579
	Min	0.7054	0.70636	0.70779
	Max	0.70862	0.709	0.70899

From Table 7 we can draw some relevant findings:

(i) significative differences in the 87Sr/86Sr ratio in sparkling wine (0.70621) compared to white (0.70754) and red (0.70848) ones;

(ii) significant differences for 208Pb/206Pb, 207Pb/206Pb, and 208Pb/207Pb between sparkling wine and white one.

The point (i) deserves attention. Strontium ratio difference was usually related to different geographical origins (Hiraoka *et al.*, 2016).

Indeed, in a recent study, Cellier et al. have found different ratios for French and Spain samples (0.70800 – 0.70900) and for Italian ones (0.70700) (Cellier, Berail, *et al.*, 2021).

Due to the unknown origin of the samples, it is difficult to make a comparison. Nevertheless, our results differ from those reported for Italian samples by Cellier et al.

This finding should confirm the use of $^{87}Sr/^{86}Sr$ as a powerful micro-scale geographical origins marker, strictly related to "terroir" characteristics.

This agrees with the fact that all the samples analysed in our paper arose from two bordering provinces (Verona and Vicenza) of the Veneto region.

About point (ii), lead isotopes content in wines may differ in different winemaking processes, being widely used in machinery. As well known, in Italy, during the sparkling wines winemaking process is used the refermentation in the autoclave. On the other hand, the refermentation step is usually not employed in the other types of winemaking processes (Prusova *et al.*, 2022). So, the differences found in lead isotopes should be used to recognise the sparkling wine winemaking process and prevent fraud associated with blending.

Indeed, due to the significant economic losses related to fraud in the wine sector, the valorisation of typical products and their possible recognition is required. In this regard, the use of isotope analysis to prevent fraud in the wine sector was also indicated by art. n° 39 of regulation EU 2018/2732, aiming to build an analytical database of isotopic data (Temple, 2018).

3.4 Chemometric assessment

A model of recognition of Venetian sparkling wines was developed by using multivariate data analysis, including heavy metals, rare earth elements, and isotopes ratio results.

Thus, explorative data analysis was performed by Principal Component Analysis (PCA), reported in Figure 1. It is possible to note that all samples are grouped in the centre of the diagram of the first two components, with 47.6% of explained variance.

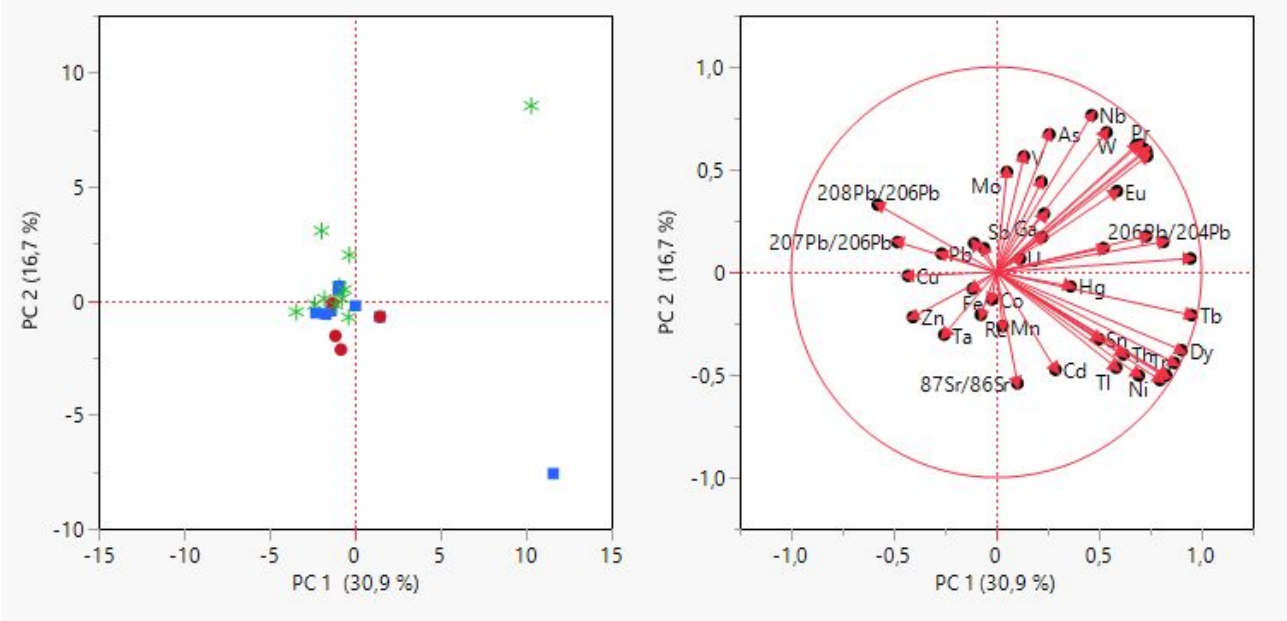

Figure 1. Unsupervised PCA of heavy metals, rare earth elements and isotopes ratio results. Green star : sparkling wine; Blue square: white wine; Red circle: red wine.

To enhance the visualisation of samples in the PCA graph, the outliers were detected by the T^2 (Mahalanobis distance), quantiles range and Cauchy's distribution methods.

The same six outliers were found (four sparkling wine samples and two white) in all the methodologies involved. These samples presented deviations from the behavior of samples in the same class. Indeed, the six outliers deviated more than 80% of variables and their inclusion would affect the subsequent treatment. Therefore, the six outliers were deleted from the data set, and PCA was then reperformed (Figure 2). This handling consented us to enhance the grouping of samples. Red wine samples were all located on the right side of the graph, while a slight overlap of sparkling and white wine is still visible.

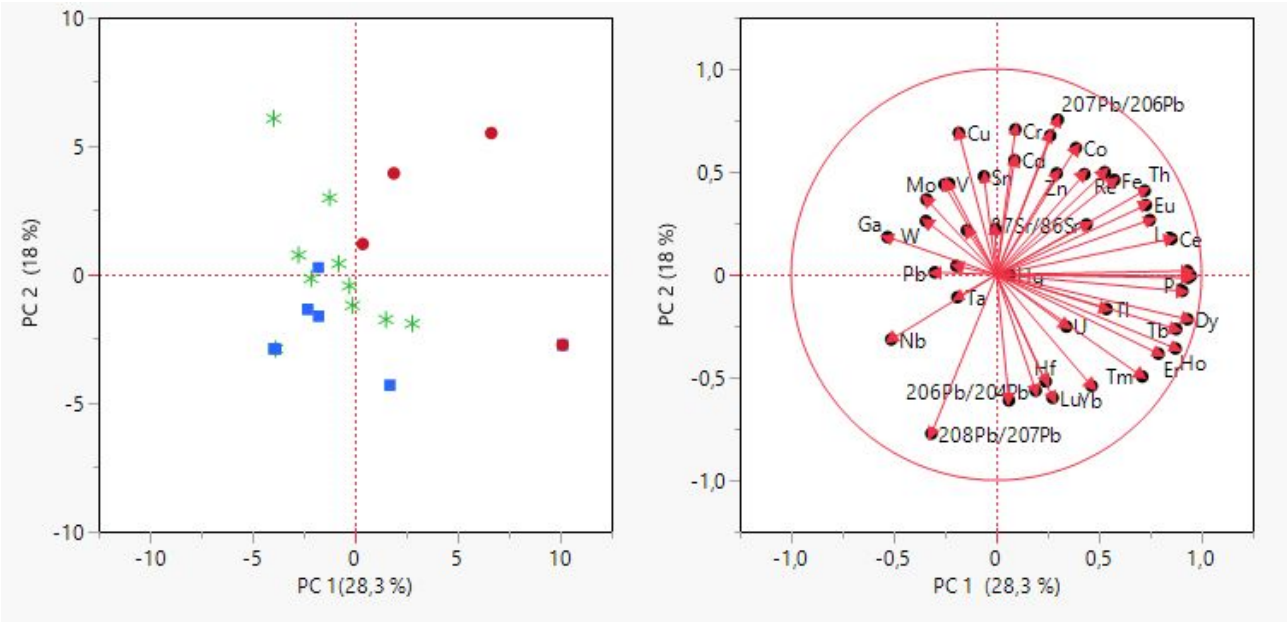

Figure 2. PCA of heavy metals, rare earth elements and isotopes ratio results without outliers. Green star : sparkling wine; Blue square: white wine; Red circle: red wine.

Subsequently, a variable selection was performed to point out the most informative analytes to differentiate sparkling wine samples from white and red ones (Table 8) F-test and p-value for the categorization in the three types of samples (red, white and sparkling wines) were reported in Table 8. The thresholds used to select the most informative variables were F-test > 3.5 and p-value < 0.05 (Ciano *et al.*, 2022). According to this process, the most suitable variables were Fe, $^{87}Sr/^{86}Sr$, Eu, Cr, Mn, Hg, Th, Re, Ga, Sm, Zn and Dy.

Table 8. Results of ~~stepwise~~ variables selection expressed as F-test and p-value.

Variables	F-test	p-value	Selection
Fe	64.879	$2.17E^{-09}$	*
$^{87}Sr/^{86}Sr$	33.569	$1.60E^{-06}$	*
Eu	32.069	$2.36E^{-06}$	*
Cr	29.195	$5.14E^{-06}$	*
Mn	21.708	$4.73E^{-05}$	*
Hg	17.259	0.00021	*
Th	15.013	0.00046	*
Re	11.67	0.00166	*
Ga	9.348	0.00433	*
Sm	9.192	0.00463	*
Zn	6.807	0.0134	*
Dy	5.102	0.03043	*
Gd	3.886	0.05686	ns

Pr	3.589	0.06671	ns
Nd	3.554	0.06798	ns
Nb	3.446	0.0721	ns
Cd	3.291	0.07851	ns
Ta	3.249	0.08032	ns
Ho	2.889	0.09832	ns
Mo	2.825	0.10199	ns
V	2.22	0.14542	ns
Er	2.183	0.14877	ns
La	2.165	0.15039	ns
Ce	2.023	0.164	ns
Tm	2.008	0.16553	ns
Tb	1.914	0.17556	ns
$\delta^{11}B$ ‰	1.86	0.18161	ns
Ni	1.732	0.19696	ns
$^{208}Pb/^{206}Pb$	1.7	0.20101	ns
Co	1.515	0.2269	ns
Zr	1.431	0.23991	ns
Cu	0.768	0.38712	ns
U	0.766	0.38767	ns
Sn	0.731	0.39853	ns
$^{207}Pb/^{206}Pb$	0.68	0.41523	ns
Yb	0.589	0.44817	ns
Hf	0.493	0.48724	ns
$^{206}Pb/^{204}Pb$	0.482	0.49222	ns
W	0.11	0.74224	ns
Lu	0.033	0.85672	ns
$^{208}Pb/^{207}Pb$	0.027	0.87123	ns
Pb	0.02	0.88742	ns
Sb	0.018	0.89323	ns
Tl	0.002	0.96402	ns

*variable selected; ns: variable not significant

A relevant finding to point out was that the significant variables belongs to all three categories of analytes investigated. For heavy metals the variables selected were Fe, Cr, Mn, Hg, Th, Re, Ga and Zn; for rare rare earth elements were Eu, Sm and Dy while for isotope ratios only $^{87}Sr/^{86}Sr$ was selected. Therefore, the integrated approach that considers heavy metals, rare earth elements and isotope ratios selected in this study resulted in a suitable tool to investigate the geographical origin of Venetian sparkling wines.

PCA was then reperformed (Figure 3) only with selected variables with a gain of 18.2% of explained variance (46.3% vs 64.5%). An improvement in grouping was also reached. The samples appeared more separated but to develop an efficient tool, a discrimination model was necessary.

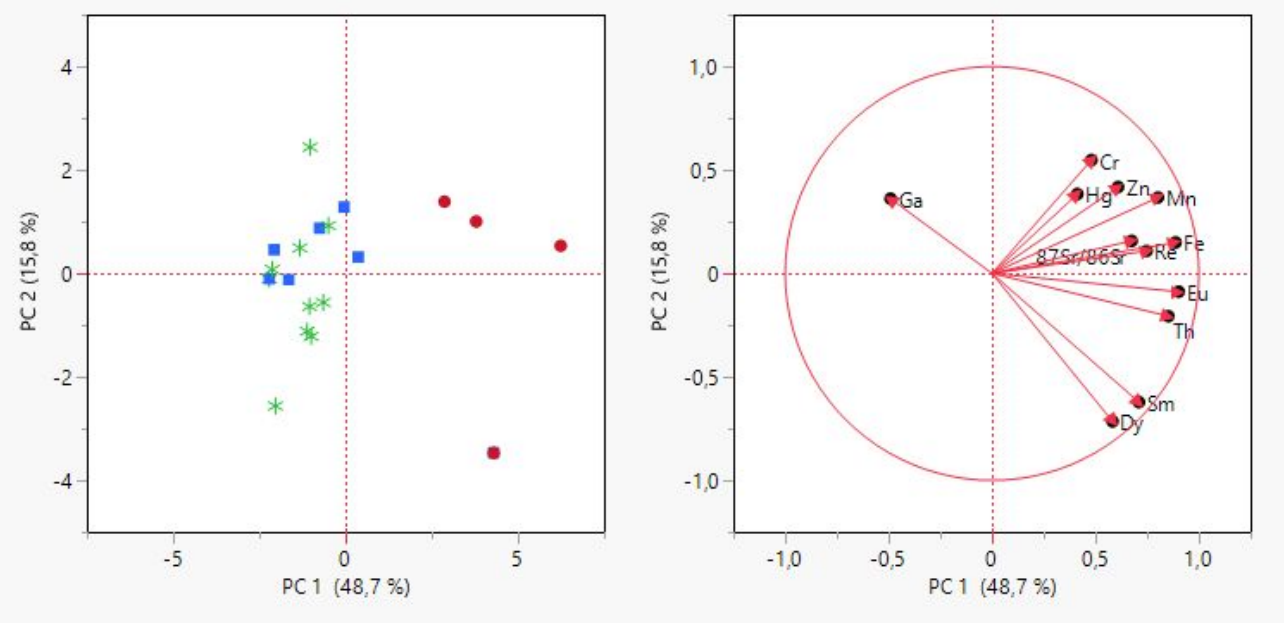

Figure 3. PCA of heavy metals, rare earth elements and isotopes ratio using selected variables. Green star : sparkling wine; Blue square: white wine; Red circle: red wine.

In this regard, Partial Least Square Discriminant Analysis (PLS-DA) was performed to classify sparkling wine samples. NIPLAS alghoritm was involved to estimate the model and a 10-fold ~~leave-more-out~~ cross validation was performed (Wold, 1974). The data-set was randomly divided into test and training a sets. The model estimation was built by using training set and four samples were randomly used to test the model. The process was repeated until each different test set was used to validate the model.

Finally, a prediction model was built as the average of all the models built during cross-validation.

The prevision formula to recognise sparkling wines calculated was the following:

$$\textbf{(1)} \quad \boldsymbol{Sparkling\ wines} = \mathbf{0.1277\ Cr + 0.2648\ Dy + 0.2672\ Eu - 1.1189\ Fe + 0.4647\ Ga - 0.2360\ Hg - 0.3304\ Mn + 0.0466\ Re - 0.3729\ Sm - 0.4021}$$
$$\mathbf{^{87}Sr/^{86}Sr + 1.0643\ Th + 0.6339\ Zn}$$

The variable that highly influenced the prevision formula were Fe and Th (coefficient > 1). A medium effect was reported by Zn while the other variables had a minimal effect, especially Re.

This results were corroborated by the HSD Tukey test previously conducted among variables mean of the different categories. Indeed, the sparkling wine samples have reported a significant difference in Fe, Ga, Mn, $^{87}Sr/^{86}Sr$, and Th content from white and red ones.

Thereofore, this formula was used to predict the belonging of sparkling wines in their own category. Similar formulas were also calculated for white and red wines. The confusion matrix of categories (sparkling, white and red wines) is reported in Table 9.

Table 9. Confusion matrix for sparkling, red and white wine samples by PLS-DA

Observed	**Predicted**		
	White	*Red*	*Sparkling*
White	13	0	1
Red	0	8	0
Sparkling	1	0	19

Just one sparkling wine samples was wrongly attribuited to the white wine class. So, a correct classification of 95 % was achived for sparkling wines.

These outstanding findings prove the use of heavy metals, rare earth elements and isotope ratios as suitable markers for the classification of sparkling wines and their geographical origin verification.

Conclusions

In Italy, in 2020, 5.6 million hectolitres of sparkling wine were produced, of whom 82% are products with PDO certification. The Italian market of sparkling wines fell by 9% in value and 5% in quantities compared to previous years. The quality characterisation of Italian sparkling wines is desirable to increase their market value. For this purpose, in this paper, heavy metals (Cd, Co, Cr, Cu, Fe, Ga, Hf, Hg, Mn, Mo, Nb, Ni, Pb, Re, Sb, Sn, Ta, Th, Tl, U, W, V, Zn, Zr), rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) and isotopes ratio ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$, $^{87}Sr/^{86}Sr$) were analysed in Italian sparkling wines (n = 42) with PDO certification by HR-ICP-MS and MC-ICP-MS.

It was found that sparkling wines had the lowest heavy metals content (∑H.M. = 2348.881 µg/L), of which the most abundant were Zn, Mn and Fe. Regarding the toxic metals, sparkling wines showed the lowest concentration of Cd and Hg, while Cr and Pb were lower than red and white wines, respectively. REEs concentration has an opposite trend compared to the heavy metals being their content higher in sparkling wines (∑REEs = 0.9473 µg/L).

The isotope ratio analysis showed significant differences in the $^{87}Sr/^{86}Sr$, $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, and $^{208}Pb/^{207}Pb$ ratios in sparkling wine compared to white and red ones. Strontium ratio should be used as a powerful micro-scale geographical origins marker while lead as winemaking process one, both useful to prevent possible frauds.

A recognition model of Venetian sparkling wines was developed using multivariate data analysis, such as PCA and PLS-DA. The good classification of sparkling wines achieved (95%) proved the use of heavy metals, rare earth elements and isotope ratios as suitable markers for recognising sparkling wines and their geographical origin verification.

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