

Isotope Ratios of Lead in Italian Wines by Inductively Coupled Plasma Mass Spectrometry

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Lead and its isotope ratios (IRs) in 83 Italian wines from 42 different administrative provinces produced on laboratory scale in 2000 were measured by inductively coupled plasma mass spectrometry. Lead had a median of 19.0 $\mu\text{g/L}$, ranging from 10.0 up to 149 $\mu\text{g/L}$ and was higher in the samples from northwestern Italy. The values of the IRs were (mean \pm standard deviation) 1.171 ± 0.011 for $^{206}\text{Pb}/^{207}\text{Pb}$, 2.071 ± 0.017 for $^{208}\text{Pb}/^{206}\text{Pb}$, 2.425 ± 0.014 for $^{208}\text{Pb}/^{207}\text{Pb}$, 17.84 ± 0.32 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.24 ± 0.31 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 37.31 ± 0.52 for $^{208}\text{Pb}/^{204}\text{Pb}$. These ratios agree with those in the literature for several European regions. $^{206}\text{Pb}/^{207}\text{Pb}$ distinguished the northwestern from the northeastern and southern Italian wines, and the southern samples were distinguishable only from the northwestern ones. $^{208}\text{Pb}/^{206}\text{Pb}$ distinguished the northwestern from the southern Italian samples. Nevertheless, the lead IRs do not seem to be a very effective tool for the origin authentication of wines from different Italian regions.

KEYWORDS: Wine; lead isotope ratios; inductively coupled plasma mass spectrometry

INTRODUCTION

Because of its toxicity, the content of lead in wine was investigated frequently and factors influencing its concentration were reviewed by several authors during the past decades (1–7). Lead content was discussed in relation to the location in grape berry (8–11), complexation with polysaccharides (12, 13), uptake of arbuscular mycorrhizae (14), mulching vine with municipal waste compost (15), winemaking technique, winery equipment and materials (6, 16–22), pesticides (23, 24), and soil and air pollution (9, 10, 25–28).

Lead has four stable isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb , the last three with radiogenic origins from ^{238}U , ^{235}U , and ^{232}Th , respectively. Lead added to gasoline and lead measured in urban air, vegetation, and topsoils near to the roads showed identical isotope compositions (29–32). Research in Missouri and California showed the possibility to distinguish among sources of lead contamination on the basis of the isotope ratios (IR) of lead, as the isotopic composition in the above-mentioned matrixes was different from that in the local lead ores, refined metal, and topsoils and dust near smelters (33). Although gasoline combustion and industrial fumes are usually considered among the main sources of lead pollution, Dean et al. (34) suggested that the naturally occurring lead in vineyard soil may be the principal source of lead for wines from rural areas, confirming previous findings (35). Rosman et al. (36) suggested that the gasoline was not a significant lead source for French wines of the vintages from 1950 to 1991. This is because of the poor correlations observed between the trimethyl lead concentration associated with automobile emissions and the total

Table 1. ICP-MS Operating Conditions and Mass Spectrometer Settings for the Measurement of the Total Pb Content and the Determination of the IRs

	instrument operating parameters	
	concentration measurements	isotope ratios
RF power	1300	1300
sampling depth	6.3	6.3
plasma gas (L/min)	16	16
auxiliary gas (L/min)	1	1
carrier gas (L/min)	1.39	1.39
ion lens setting	adjusted to obtain maximum signal intensity	adjusted to obtain maximum signal intensity
sample uptake rate (mL/min)	0.4	0.4
points/mass	3	3
no. of sweeps	100	1000
dwel time/159 (ms)	45	
dwel time/200 (ms)		9
dwel time/203 (ms)		4.5
dwel time/204 (ms)		9
dwel time/205 (ms)		4.5
dwel time/206 (ms)		4.5
dwel time/207 (ms)		4.5
dwel time/208 (ms)	45	4.5
no. of replicates	3	3

lead in the wines and between the data of the IRs of petrol and aerosol. However, more recently, Médina et al. (28) deemed that the content of lead in wine could be due to gasoline-derived atmospheric input and not to contamination during the wine-making process. Besides, reflecting the airborne pollution, the IRs of lead can be useful traceability parameters of the continental origin of wines.

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Table 2. Geographic and Variety Distribution of the Wine Samples^a

macroregion (samples)	administrative province (no. of samples)	cultivar
C (<i>n</i> = 27)	Ancona (1), Ascoli (1), Cagliari (2), Campobasso (2), Chieti (1), Firenze (3), Livorno (1), Latina (2), Oristano (2), Perugia (3), Pisa (1), Pescara (1), Rieti (1), Roma (1), Siena (2), Sassari (2), Viterbo (1)	Aglianico, Carignano, Malvasia, Merlot, Montepulciano, Moscato, Nuragus, Sangiovese, Trebbiano, Vernaccia, Verdicchio, Vermentino
N-E (<i>n</i> = 18)	Bolzano (1), Padova (1), Trento (1), Treviso (6), Udine (5), Venezia (2), Vicenza (2)	Cabernet sauvignon, Chardonnay, Pinot blanc, Pinot gris, Prosecco, Sauvignon, Raboso, Traminer
N-W (<i>n</i> = 23)	Alessandria (2), Asti (3), Aosta (1), Brescia (2), Cuneo (2), Imperia (1), Mantova (2), Modena (3), Reggio Emilia (3), La Spezia (2), Pavia (2)	Bonarda, Cabernet sauv., Chardonnay, Erbaluce, Freisa, Blanc de Morgeux, Marani, Salamino, Sorbara, Moscato, Nebbiolo, Pinot blanc, Vermentino
S (<i>n</i> = 15)	Bari (5), Benevento (1), Cosenza (1), Crotone (1), Napoli (2), Reggio Calabria (1), Trapani (4)	Bianco di Alessano, Falanghina, Greco, Inzolia, Nero d'Avola, Piediroso, Sangiovese, Zibibbo

^a C, central Italy; N-E, northeastern Italy; N-W, northwestern Italy; and S, south Italy.

Thermal ionization mass spectrometry (TIMS) is a well-established method to measure IRs with high accuracy (37, 38). Inductively coupled plasma mass spectrometry (ICP-MS) does not achieve the precision of TIMS but is considered as sufficient to differentiate the continental origin of wine (34, 38–40). More recent instruments further increased the sensitivity of the ICP techniques (41). The relatively short sample preparation and analysis time of ICP-MS (38) make this technique useful for routine measurements of the isotopic composition of lead with adequate precision (28). Several authors analyzed wine by ICP-MS after simple dilution or addition of nitric acid to the sample (28, 34, 38–40), but wines very rich in alcohol and polymeric organic compounds, particularly sugars, need a more drastic sample preparation with UV irradiation or HPMW digestion to reduce matrix interferences (42, 43). Because ICP-MS does not have the same sensitivity for different masses due to differences in ion transmission and detection (37, 44), it is necessary to correct the instrumental data for mass discrimination phenomena to improve accuracy in IRs measurements. Two different procedures for mass bias correction are reported: external correction with Pb isotope certified materials and internal correction with Tl as internal standard (IS); Tl was chosen for its constant IR in nature and the mass proximity of its isotopes to Pb isotopes. Both methods were considered suitable for accurate IRs determinations (42, 43).

According to Rosman et al. (36), the chemical processes during winemaking do not significantly alter the isotopic composition. Médina et al. (28) observed that the values of the IRs between wines produced in a winery and laboratory were equivalent. To guarantee the geographical origin, we analyzed wines produced on a laboratory scale from officially sampled monovariety grapes in several Italian growing areas. This paper describes the lead content and the isotope characteristics of the wines and fills the gap of knowledge about Italian products.

MATERIALS AND METHODS

ICP-MS. A HP 4500 equipped with a Fassel torch, Babington nebulizer, Scott type spray chamber (Hewlett-Packard Co., Corvallis, U.S.A.), and autosampler ASX 500 (CETAC Technologies Inc., Omaha, NE) was used. Operating conditions and mass spectrometer settings are summarized in **Table 1**.

Materials. Eighty-three wines of 47 different grape varieties from 42 Italian administrative provinces (**Table 2**) of the vintage 2000 were analyzed. According to their different industrial and economical history,

Table 3. Content of Lead Measured in Certified Material (Mean ± 2 × SD)

	Pb (μg/L)	
	certified values	measured values (<i>n</i> = 3)
IMEP-16	27.18 ± 0.33	27.00 ± 0.20

the provinces were grouped in the four traditional Italian macrozones: south (S; number of samples (*n*) = 15), central (C; *n* = 27), northeast (N-E; *n* = 18), and northwest (N-W; *n* = 23).

Grape sampling from traditional growing areas and wine processing were carried out and guaranteed by the official laboratories of the Italian Ministry of Agriculture according to the EC Commission Regulation No. 2729/2000 and previous regulations (EEC Commission Regulations No. 2347/91 and No. 2348/91; EC Commission Regulations Nos. 1754/97 and 1932/97) in which there are defined rules for establishing databanks for the analysis of stable light bioisotopes. Wines were stored at 5 °C in rinsed PE bottles until the analysis. Bottles were opened after cleaning of the neck and closure areas to remove dust and dirt. A 0.1 mL amount of HNO₃ was added, in a rinsed polypropylene vial, to 5 mL of wine sampled directly from the bottle with a rinsed pipet and diluted to a final volume of 10 mL with water.

Reagents. Milli-Q water was used for rinsing, sample dilution, and preparation of blanks and standards. Suprapure HNO₃, used to acidify samples and standards, was from Carlo Erba Reagenti (Milano, Italy). A monoelement standard solution of 1 g/L of Pb was from Merck (catalog no. 1.19776; Merck KGaA, Darmstadt, Germany). Solutions of 1 g/L of Tb (catalog no. 456142R) and Tl (catalog no. 456162V) supplied by BDH (BDH Laboratory Supplies, Lutterworth, Leicestershire, England) were used as IS for quantitative analysis and determination of IRs, respectively.

External Calibration (EC). Standard solutions of 0.1, 1, 10, and 100 μg/L of lead in 1% v/v HNO₃ were used as EC.

IS-1. A 250 μg/L Tb solution (final concentration in sample 10 μg/L) was added automatically on line as IS to correct matrix interferences in the quantitation of lead.

IS-2. A 80 μg/L Tl solution (final concentration in sample 3 μg/L) was added on line to correct mass discrimination phenomena in the IRs determination.

Certified Materials. IMEP-16 wine by the International Measurement Evaluation Program (45) was used to assess accuracy in the quantitative analysis (**Table 3**). NIST SRM 981 and SRM 982, dissolved in 1% v/v HNO₃ in order to have a final concentration of 100 μg/L, and IMEP-16 wine were used to check accuracy in the isotope analysis (**Table 4**).

Table 4. Lead IRs Measured in Three Certified Samples (* Mean $\pm 2 \times$ SD; ** Mean $\pm 1.96 \times$ SD)

IMEP-16*					
$^{204}\text{Pb}/^{208}\text{Pb}$		$^{206}\text{Pb}/^{208}\text{Pb}$		$^{207}\text{Pb}/^{208}\text{Pb}$	
certified values	measured ($n = 3$)	certified values	measured ($n = 3$)	certified values	measured ($n = 3$)
0.02661 \pm 0.00044	0.02638 \pm 0.00023	0.4778 \pm 0.0044	0.4774 \pm 0.0118	0.4101 \pm 0.0026	0.4102 \pm 0.0034
SRM 981**					
$^{204}\text{Pb}/^{206}\text{Pb}$		$^{207}\text{Pb}/^{206}\text{Pb}$		$^{208}\text{Pb}/^{206}\text{Pb}$	
certified values	measured ($n = 3$)	certified values	measured ($n = 3$)	certified values	measured ($n = 3$)
0.059042 \pm 0.000037	0.058454 \pm 0.000717	0.91464 \pm 0.00033	0.912615 \pm 0.005996	2.1681 \pm 0.0008	2.161 \pm 0.019
SRM 982**					
$^{204}\text{Pb}/^{206}\text{Pb}$		$^{207}\text{Pb}/^{206}\text{Pb}$		$^{208}\text{Pb}/^{206}\text{Pb}$	
certified values	measured ($n = 3$)	certified values	measured ($n = 3$)	certified values	measured ($n = 3$)
0.027219 \pm 0.000027	0.027417 \pm 0.000361	0.46707 \pm 0.00020	0.467219 \pm 0.008293	1.00016 \pm 0.00036	1.002 \pm 0.020

Lead Content and IR Analysis. Each sample was analyzed for 70 s, and the sampling system was rinsed with 5% HNO_3 for 160 s. Pb was quantified on the basis of ^{208}Pb using the EC and IS-1 solutions. Mathematical correction of ^{204}Hg interference on ^{204}Pb signal was applied for the IR determination: the signal at m/z 200 ($^{200}\text{Hg}^+$) was multiplied by 0.297 (the natural IR $^{204}\text{Hg}/^{200}\text{Hg}$) and then subtracted from the signal at 204 ($^{204}\text{Hg}^+$ plus $^{204}\text{Pb}^+$). Because of the low content of ^{204}Pb and ^{200}Hg in wine, their signals were measured for 9 s, and the other isotopes were measured for 4.5 s. Mass discrimination was corrected using the IS-2 solution. Pb ratios were corrected in comparison with the Tl IR ($^{205}\text{Tl}/^{203}\text{Tl} = 2.3871$) measured simultaneously. The corrected values were obtained by the power laws (46):

$$^{206}\text{Pb}/^{204}\text{Pb} = ([^{206}]/^{204}\text{Pb})(2.3871/([^{205}]/[^{203}]])$$

$$^{207}\text{Pb}/^{204}\text{Pb} = ([^{207}]/^{204}\text{Pb})(2.3871/([^{205}]/[^{203}]))^{1.5}$$

$$^{208}\text{Pb}/^{204}\text{Pb} = ([^{208}]/^{204}\text{Pb})(2.3871/([^{205}]/[^{203}]))^2$$

$$^{207}\text{Pb}/^{206}\text{Pb} = ([^{207}]/[^{206}]) (2.3871/([^{205}]/[^{203}]))^{0.5}$$

$$^{208}\text{Pb}/^{206}\text{Pb} = ([^{208}]/[^{206}]) (2.3871/([^{205}]/[^{203}]))$$

$$^{208}\text{Pb}/^{207}\text{Pb} = ([^{208}]/[^{207}]) (2.3871/([^{205}]/[^{203}]))^{0.5}$$

IMEP-16 wine was analyzed as the first and final sample of each series of measurements as a quality control. Data were statistically evaluated and plotted with STATISTICA for Windows v. 5.1, 1997 (StatSoft Italia S.r.l., Padova, Italy).

RESULTS AND DISCUSSION

The amount of lead in the 83 wine samples ranges from 10.0 up to 149 $\mu\text{g}/\text{L}$. The median is 19.0 $\mu\text{g}/\text{L}$, and the 25th and 75th percentiles are 13.1 and 35.8 $\mu\text{g}/\text{L}$, respectively. **Figure 1** shows the lead content distribution in wine samples from the different macrozones. Southern, central, northeastern, and northwestern Italy wines have medians of 16.7, 14.9, 18.7, and 31.0 $\mu\text{g}/\text{L}$, respectively. All samples have a Pb content far below the present legal limit of 200 $\mu\text{g}/\text{L}$ defined by the European Commission (Regulation Ce 466/2001). Because of the distribution and the low number of the samples per macrozone, nonparametric tests—i.e., Kolmogorov–Smirnov, Kruskal–Wallis, and Median tests (47)—are used to check differences among zones. The samples from northwest Italy differ from those from northeast and central Italy according to all of the used tests. Kolmogorov–Smirnov and Kruskal–Wallis tests discriminate south from northwest samples. No other differences are observed. Probably, these differences relate with the higher

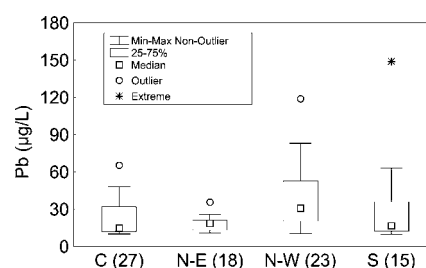


Figure 1. Box plots of the lead content in wine samples from different macroregions of Italy. Legend: south (S), central (C), northeast (N-E), and northwest (N-W). Number of samples between brackets. Respectively, outliers and extremes are higher than the 75th percentile of 1.5 and 3 times the interval between the 25th and 75th percentile.

Table 5. *R* Values and Significance of the Linear Correlations between the Content of Lead ($\mu\text{g}/\text{L}$) and IRs in Italian Wines^a

	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
Pb	-0.5073***	0.3330**	-0.3682**
	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Pb	0.2340*	0.4489***	0.0136 ns

^a Key: $n = 83$; ns, not significant; *, **, ***, significantly different with $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively.

presence of the metallurgic industry in northwestern Italy, also named the “industrial triangle”, and with the high human population and car density of that area.

Computed on the basis of the 83 available samples, the various IRs average (\pm standard deviation (SD)) as follows: $^{206}\text{Pb}/^{207}\text{Pb}$, 1.171 \pm 0.011; $^{208}\text{Pb}/^{206}\text{Pb}$, 2.071 \pm 0.017; $^{208}\text{Pb}/^{207}\text{Pb}$, 2.425 \pm 0.014; $^{206}\text{Pb}/^{204}\text{Pb}$, 17.84 \pm 0.32; $^{207}\text{Pb}/^{204}\text{Pb}$, 15.24 \pm 0.31; and $^{208}\text{Pb}/^{204}\text{Pb}$, 37.31 \pm 0.52. Significant correlations are observed between lead content and each IR, except with $^{208}\text{Pb}/^{204}\text{Pb}$ (**Table 5**). Similar correlations were previously observed by Augagneur et al. (40) for $^{206}\text{Pb}/^{207}\text{Pb}$ and by Marisa et al. (42) for $^{208}\text{Pb}/^{206}\text{Pb}$.

Comparing four different IRs to the bibliographic data (**Figure 2a,b**), the Italian samples cover the central part of the range of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and overlap perfectly the values of different European areas, Italy included (34, 41). They were also inside the larger range of the samples from the U.S.A. and Australia. Few bibliographic references report on the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio. The values observed for the Italian samples tend to be

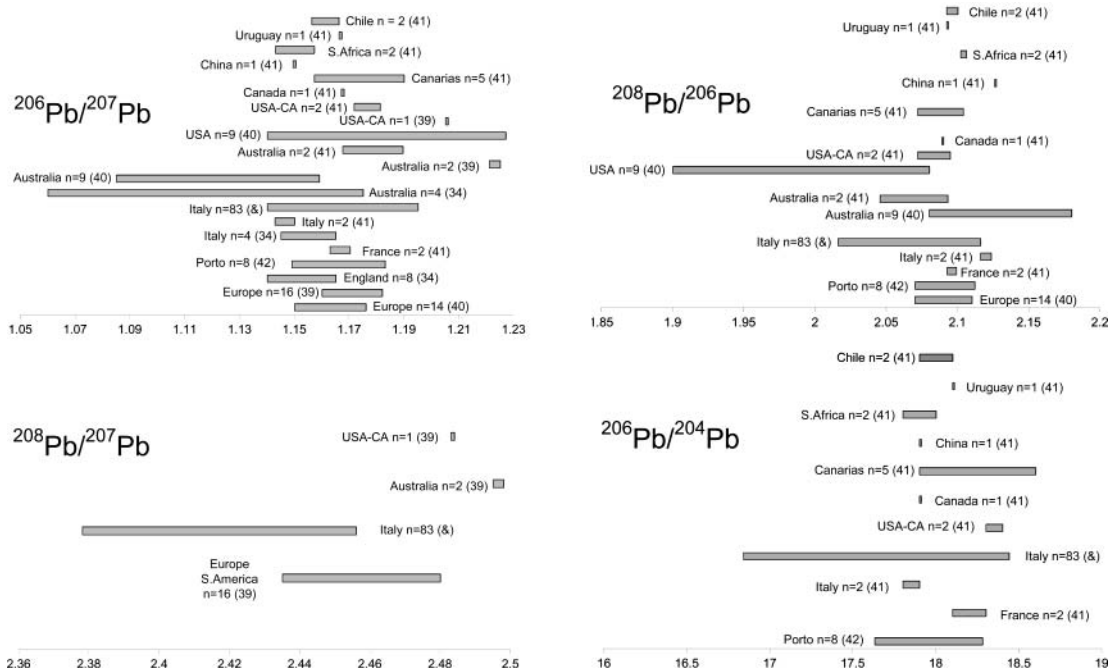


Figure 2. (a) Ranges of the values of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ for wines from different geographical areas, as reported in the literature. Legend: n , number of samples; references between brackets; and &, data of the present paper. (b) Ranges of the values of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ for wines from different geographical areas, as reported in the literature. Legend: see a.

Table 6. Values of the IRs of Wines from Different Italian Macroregions^a

IRs	significance	C ($n = 27$)		N-E ($n = 18$)		N-W ($n = 23$)		S ($n = 15$)	
		mean \pm SD	Tuckey	mean \pm SD	Tuckey	mean \pm SD	Tuckey	mean \pm SD	Tuckey
$^{206}\text{Pb}/^{207}\text{Pb}$	**	1.170 \pm 0.010	abc	1.175 \pm 0.005	ab	1.163 \pm 0.011	c	1.177 \pm 0.012	a
$^{208}\text{Pb}/^{206}\text{Pb}$	**	2.073 \pm 0.017	ab	2.067 \pm 0.008	ab	2.078 \pm 0.019	a	2.060 \pm 0.013	b
$^{208}\text{Pb}/^{207}\text{Pb}$	ns	2.427 \pm 0.016		2.429 \pm 0.010		2.417 \pm 0.013		2.426 \pm 0.015	
$^{206}\text{Pb}/^{204}\text{Pb}$	ns	17.77 \pm 0.41		17.92 \pm 0.22		17.87 \pm 0.28		17.78 \pm 0.30	
$^{207}\text{Pb}/^{204}\text{Pb}$	ns	15.19 \pm 0.36		15.25 \pm 0.21		15.37 \pm 0.30		15.10 \pm 0.24	
$^{208}\text{Pb}/^{204}\text{Pb}$	ns	37.33 \pm 0.51		37.27 \pm 0.66		37.32 \pm 0.49		37.33 \pm 0.47	

^a Legend: C, central Italy; N-E, northeastern Italy; N-W, northwestern Italy; S, south Italy. Mean values with the same letter do not differ significantly at the Tuckey's test, $p < 0.05$.

lower than for the samples reported in the literature (39) for wines from Europe, North and South America, and Australia. The values of the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio are comparable to those reported for other European areas (40) and for Porto wines (42) and intermediate between those from the U.S.A. and Australia. Italian wines cover a larger range than that reported for Porto wines by Marisa et al. (42). The observed $^{206}\text{Pb}/^{204}\text{Pb}$ ratio was definitely wide. The large number of samples analyzed and the low sensitivity and accuracy of the applied analytical technique for ^{204}Pb may be the reason.

Differences among the wines from the Italian macroregions are observed only for the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Table 6). In particular, $^{206}\text{Pb}/^{207}\text{Pb}$ distinguishes the northwestern from the northeastern and southern Italian wines, while the southern samples were distinguishable only from the northwestern ones. The $^{208}\text{Pb}/^{206}\text{Pb}$ ratio distinguishes only the northwestern from southern Italian samples. High $^{208}\text{Pb}/^{206}\text{Pb}$ and low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values seem to characterize the wines from the northwestern Italy area with the highest density of inhabitants and industries.

To conclude, the paper presents a wide survey of the content of lead and its isotopic composition in wines produced on a laboratory scale from 42 Italian administrative provinces. Some significant differences among Italian macroregions are established. The IRs of lead by ICP-MS do not seem to be a very

effective tool for origin authentication of wines from different Italian regions. This, probably, is also as a consequence of the complexity of viticultural orography and population distribution in Italy, as well as of the pollution sources and the origin of Pb, with different isotope compositions, used by the petroleum companies.

LITERATURE CITED

- (1) Castelli, A.; Cavallaro, A.; Cerutti, G.; Fittipaldi, M. Pb, Cr, Cd, Zn, Mn, Cu, Fe di vini nazionali: analisi mediante spettrofotometria di assorbimento atomico. *Riv. Vitic. Enol.* **1974**, *27*, 247–257.
- (2) Stefani, R. Il contenuto in piombo dei vini del Trentino-Alto Adige. *Vini d'Italia* **1978**, *36*, 343–345.
- (3) Eschnauer, H. Trace elements in must and wine: primary and secondary contents. *Am. J. Enol. Vitic.* **1982**, *33*, 226–230.
- (4) Scherlock, J. C.; Pickford, C. J.; White, G. F. Lead in alcoholic beverages. *Food Addit. Contam.* **1986**, *3*, 347–354.
- (5) Smart, G. A.; Pickford, C. J.; Sherlock, J. C. Lead in alcoholic beverages: a second survey. *Food Addit. Contam.* **1990**, *7*, 93–99.
- (6) Ough, C. S. Lead in Wines—A Review of Recent Reports. *Am. J. Enol. Vitic.* **1993**, *44*, 464–467.
- (7) Teissedre, P. L.; Cabanis, J. C. Origine et réduction des teneurs en plomb dans les vins. *Rev. Fr. Oenol., Cahiers Techniques* **1993**, *142*, 41–44.

- (8) Gabrielli Favretto, L.; Maraspin, M.; Vojnovic, D. Indagine sull'inquinamento da cadmio e piombo dei chicchi d'uva e del vino. *Riv. Soc. Ital. Sci. Aliment.* **1986**, *15* (1–2), 63–68.
- (9) Teissedre, P. L.; Cabanis, M. T.; Champagnol, F.; Cabanis, J. C. Lead Distribution in Grape Berries. *Am. J. Enol. Vitic.* **1994**, *45*, 220–228.
- (10) Angelova, V. R.; Ivanov, A. S.; Braikov, D. M. Heavy metals (Pb, Cu, Zn and Cd) in the system soil–grapevine–grape. *J. Sci. Food Agric.* **1999**, *79*, 713–721.
- (11) Nicolini, G.; Larcher, R.; Mattivi, F. ICP-OES and ICP-MS measurement of mineral elements in grapes and wines: Analytical, compositional and enological aspects. *Proceedings of the VIII Congreso Latinoamericano de Viticultura y Enologia*, 12–16 November 2001, Montevideo, Uruguay.
- (12) Pellerin, P.; O'Neill, M. A.; Pierre, C.; Cabanis, M. T.; Darvill, A. G.; Albersheim, P.; Moutounet, M. Complexation of plumb dans les vins par les dimères de rhamnogalacturonane II, un polysaccharide pectique du raisin. *J. Int. Sci. Vigne Vin* **1997**, *31*, 33–41.
- (13) Green, A. M.; Scollary, G. R. Influence of metal ions on lead complexation in wine. *Aust. J. Grape Wine Res.* **2000**, *6*, 197–202.
- (14) Karagiannidis, N.; Nikolaou, N. Influence of Arbuscular Mycorrhizae on Heavy Metal (Pb and Cd) Uptake, Growth, and Chemical Composition of *Vitis vinifera* L. (cv. Razaki). *Am. J. Enol. Vitic.* **2000**, *51*, 269–275.
- (15) Pinamonti, F.; Nicolini, G.; Dalpiaz, A.; Stringari, G.; Zorzi, G. Compost Use in Viticulture: Effect on Heavy Metal Levels in Soil and Plants. *Commun. Soil Sci. Plant Anal.* **1999**, *30*, 1531–1549.
- (16) Médina, B.; Guimberteau, G.; Sudraud, P. Dosage du plomb dans les vins; une cause d'enrichissement: les capsules de surbouchage. *Conn. Vigne Vin* **1977**, *11*, 183–193.
- (17) Seppi, A.; Sperandio, A. I metalli dei vini. Teoria e verifica sperimentale della corrosione delle attrezzature metalliche di cantina. *Vini d'Italia* **1978**, *112*, 35–42.
- (18) Gulson, B. L.; Lee, T. H.; Mizon, K. J.; Korsch, M. J.; Eschnauer, H. R. The Application of Lead Isotope Ratios to the Determine the Contribution of the Tin–Lead to the Lead Content of Wine. *Am. J. Enol. Vitic.* **1992**, *43*, 180–190.
- (19) Teissedre, P. L.; Cabanis, M. T.; Daumas, F.; Cabanis, J. C. Evolution de la teneur en plomb au cours de l'elaboration des vins des Côtes du Rhône et de la Vallée du Rhône. *Rev. Fr. Oenol., Cahiers Scientifiques* **1993**, *140*, 249–254.
- (20) Mínguez, S.; Hernandez, P.; Gonzalo, M. Selective extraction of lead from wine with ionic exchange resins. In *Oenologie '95. Proceedings of the 5e Symposium International d'Oenologie*; Lonvaud-Funel, A., Ed.; TEC&DOC: Paris, France, 1996; pp 632–636.
- (21) Mínguez, S.; Hernandez, P.; García, J.; Médina, B.; Bartra, E.; Vilavella, M.; Espinás, E. Presence du plomb dans les vins et efficacité des techniques soustractives. Comm. Groupe d'Experts "Technologie du vin"; 8–9 September 1997; OIV: Paris, 1997.
- (22) Larcher, R.; Nicolini, G. Survey of 22 mineral elements in wines from Trentino (Italy) using ICP-OES. *Ital. J. Food Sci.* **2001**, *13*, 233–241.
- (23) Crecelius, E. A. Arsenite and arsenate levels in wine. *Bull. Environ. Contam. Toxicol.* **1977**, *18*, 227–230.
- (24) Handson, P. D. Lead and Arsenic Levels in Wines Produced from Vineyards where Lead Arsenate Sprays are Used for Caterpillar Control. *J. Sci. Food Agric.* **1984**, *35*, 215–218.
- (25) Basile, G.; Tarallo, V. Influenza del traffico automobilistico sul contenuto in piombo dei vini. *Boll. Lab. Chim. Prov.* **1974**, *25* (9), 185–188.
- (26) Prospero, S.; Piga, C. Contenuto in rame, zinco e piombo nei vini prodotti in Sardegna. *Riv. Vitic. Enol.* **1988**, *41*, 375–386.
- (27) Angelova, V.; Ivanov, A.; Braikov, D.; Ivanov, K. Heavy metal (Pb, Cu, Zn and Cd) content in wine produced from grape cultivar Mavrud, grown in an industrially polluted region. *J. Int. Sci. Vigne Vin* **1999**, *33*, 119–131.
- (28) Médina, B.; Augagneur, S.; Barbaste, M.; Grousset, F. E.; Buat-Ménard, P. Influence of atmospheric pollution on the lead content of wines. *Food Addit. Contam.* **2000**, *17*, 435–445.
- (29) Petterson, C. C.; Settle, D. M. Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a scale. *Mar. Chem.* **1987**, *22*, 137–162.
- (30) Berwick, I. D. G. The rise and fall of lead in petrol. *Phys. Technol.* **1987**, *18*, 158–164.
- (31) Chow, T. J.; Johnstone, M. S. Lead Isotopes in Gasoline and Aerosol of Los Angeles Basin, California. *Science* **1967**, *147*, 502–503.
- (32) Chow, T. Lead Accumulation in Roadside Soil and Grass. *W. Nature* **1970**, *225*, 295–296.
- (33) Rabinowitz, M. B.; Wetherill, G. W. Identifying Sources of Lead Contamination by Stable Isotope Techniques. *Environ. Sci. Technol.* **1972**, *6*, 705–709.
- (34) Dean, J. R.; Ebdon, L.; Massey, R. C. Isotope ratio and isotope dilution analysis of lead in wine by inductively coupled plasma-mass spectrometry. *Food Addit. Contam.* **1990**, *7*, 109–116.
- (35) Facchetti, S. Mass spectrometry applied to studies of lead in the atmosphere. *Mass Spectrom. Rev.* **1988**, *7*, 503–533.
- (36) Rosman, K. J. R.; Chisholm, W.; Jimi, S.; Candelone, J.-P.; Boutron, C. F.; Teissedre, P.-L.; Adams, F. C. Lead Concentrations and Isotopic Signatures in Vintages of French Wines between 1950 and 1991. *Environ. Res. A* **1998**, *78*, 161–167.
- (37) Longerich, H. P.; Freyer, B. J.; Strong, D. F. Determination of lead isotope ratios by inductively plasma-mass spectrometry (ICP-MS). *Spectrochim. Acta* **1987**, *42B*, 39–48.
- (38) Augagneur, S.; Medina, B.; Grousset, F. Measurement of lead isotope ratios in wine by ICP-MS and its applications to the determination of lead concentration by isotope dilution. *Fresenius J. Anal. Chem.* **1997**, *357*, 1149–1152.
- (39) Rodushkin, I.; Oedman, F.; Appelblad, P. K. Multielement Determination and Lead Isotope Ratio Measurement in Alcoholic Beverages by High-Resolution Inductively Coupled Plasma Mass Spectrometry. *J. Food Comput. Anal.* **1999**, *12*, 243–257.
- (40) Augagneur, S.; Medina, B.; Grousset, F. Lead isotope ratios in wine: contribution to wine authenticity. *Abstracts Book 1st Symposium In Vino Analytica Scientia 1997: Analytical Chemistry for Wine, Brandy and Spirit*; Soc. Fr. Chim. Anal., Ed.: Bordeaux, France, 1997; pp 204–207.
- (41) Barbaste, M.; Halicz, L.; Galy, A.; Medina, B.; Emteborg, H.; Adams, F. C.; Lobinski, R. Evaluation of the accuracy of the determination of lead isotope ratios in wine by ICP MS using quadrupole, multicollector magnetic sector and time-off-flight analyzers. *Talanta* **2001**, *54*, 307–317.
- (42) Marisa, C.; Almeida, R.; Tiresa, M.; Vasconcelos, S. D. Determination of lead isotope ratios in port wine by inductively coupled mass spectrometry after pretreatment by UV-irradiation. *Anal. Chim. Acta* **1999**, *396*, 45–53.
- (43) Marisa, C.; Almeida, R.; Teresa, M.; Vasconcelos, S. D. UV-irradiation and MW-digestion pretreatment of Port wine suitable for the determination of lead isotope ratios by inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **1999**, *14*, 1815–1821.
- (44) Ketterer, M. E.; Peters, M. J.; Tisdale, J. P. Verification of a Correction Procedure for Measurement of Lead Isotope Ratios by Inductively Coupled Plasma Mass Spectrometry. *J. Anal. At. Spectrom.* **1991**, *6*, 439–443.
- (45) Van Nevel, L.; Quérel, C. R.; Norgaard, J. V.; Smeyers, P.; De Smet, M.; Papadakis, I.; Taylor, P. D. P. *The International Measurement Evaluation Programme IMEP-16 Pb in Wine*. EUR19898EN, European Commission Joint Research Centre: Geel, Belgium, 2001.
- (46) Wasserburg, G. J.; Jacobsen, S. B.; De Paolo, D. J.; McCulloch, M. T.; Wen, T. Precise Determination of Samarium/Neodymium Ratios, Samarium and Neodymium Isotopic Abundances in Standard Solutions. *Geochim. Cosmochim. Acta* **1981**, *45*, 2311–2323.

- (47) Vitali, O. Test non parametrici per parametri di posizione e di scala. Test non parametrici di indipendenza e per la verifica di ipotesi funzionali. In *Statistica per le Scienze Applicate*, 1st ed.; Vitali, O., Ed.; Cacucci Editorie: Bari, Italy, 1993; Vol. II, pp 267–371.

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