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Ultratrace determination of Pb, Se and As in wine samples by electrothermal vaporization inductively coupled plasma mass spectrometry

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ABSTRACT

The determination of Pb, Se and As in wine has a great interest due to health risks and legal requirements. To perform the analysis of wine, two considerations must be taken into account: (i) the low concentration level of the analytes; and (ii) the risk of interferences due to wine matrix components. The goal of this work is to evaluate electrothermal vaporization (ETV) sample introduction for ultratrace determination of Pb, Se and As in wine samples by inductively coupled plasma mass spectrometry (ICP-MS). The results obtained with ETV-ICP-MS were compared to those obtained with conventional liquid sample introduction in ICP-MS and electrothermal atomic absorption spectrometry (ETAAS). Analytical figures of merit of ETV sample introduction strongly depend on the amount of wine sample, on the modifier nature (i.e. Pd, ascorbic acid or citric acid) and concentration and on the temperature program. Wine matrix components exert a great influence on analyte transport efficiency. Due to this fact, the analysis of wine cannot be performed by means of external calibration but the standard addition methodology should be used. The determination of Pb and Se in wine by ETV-ICP-MS provides similar results as conventional liquid sample introduction ICP-MS. For As, the concentration values obtained with ETV sample introduction were between two and four times lower than with the conventional system. These differences are related to the lower intensity of polyatomic interferences (i.e. $^{40}Ar^{35}Cl^{+}$ vs. $^{75}As^{+}$) obtained for ETV sample introduction when compared to the conventional system. Finally, no differences for Pb determination were observed between ETV sample introduction and ETAAS. Unfortunately, the limits of detection for As and Se in ETAAS were not low enough to quantify these elements in the wine samples tested.

1. Introduction

Elemental analysis of wine is of great interest from a nutritional, toxicological and origin point of view [1–5]. Moderate wine consumption provides significant amounts of several essential elements for the human organism (i.e. Se, Mo, Mn, etc.). On the other hand, special attention must be paid to the levels of certain toxic metals such as Pb or As at different stages of the winemaking process due to health risks and legal requirements [4]. Several authors have pointed out that trace element composition allows the determination of wine origin since the mineral composition of wine is related to sample provenance [3,5]. As a consequence, elemental pattern composition of wine can be used as a tool to prevent adulteration and fraud.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) are employed for trace and ultratrace elemental analysis of wine samples because of their multi-elemental capabilities and low limits of detection (LOD) [1–10]. In spite of the good performance of ICP-based techniques, direct wine analysis is very troublesome due to the high organic (i.e. ethanol 10–14%, organic acids, polysaccharides, etc.) and salt (e.g. K, Ca) content of wine samples [11–13]. High levels of ethanol and/or salts in the plasma cause severe spectral and non-spectral interferences [14,15]. Several strategies have been employed to mitigate/eliminate matrix effects when dealing with these samples. Wine samples could undergo a pre-treatment step such as dilution [1,3,5,6,16], acid digestion [4,7,8,10,12,13,16], or extraction [17], although these methodologies show several drawbacks. Among them are (i) a reduction in the analysis throughput; (ii) the impossibility to determine elements at very low concentrations; and (iii) an increase in the sample contamination risk during sample handling. On the other hand, different calibration strategies can be employed. The analysis of wine samples is usually performed by means of matrix matched standards but, when matrix effects are strong, alternative approaches such as standard addition [3,10,18] and internal standardization [3,18] give rise to more accurate results. Finally, the elemental analysis of wine samples can

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also be successfully accomplished by the appropriate selection of the sample introduction system. Thus, for instance, when employing microconcentric nebulizers [11,19], flow injection [20,21] or, more recently, a microwave desolvation system [22] spectral and non-spectral interferences due to wine matrix components were mitigated. Nonetheless, this approach does not completely avoid the need for sample treatment and/or careful selection of the calibration methodology.

Electrothermal vaporization (ETV) is considered as an alternative approach in ICP-MS elemental analysis of wine samples because appropriate selection of the temperature program and the modifier allow selective vaporization of the analyte from the matrix, decreasing both spectroscopic and non-spectroscopic matrix effects [23]. In addition, ETV sample introduction allows direct handling of wine samples without complex and time consuming treatments, thus minimizing the risk of contamination, the use of corrosive or hazardous reagents and analyte losses. Despite these attractive features of ETV sample introduction, to the best of our knowledge, this approach has not been applied for the elemental analysis of wine samples.

The goal of this work is the evaluation of ETV-ICP-MS for ultratrace determination of Pb, Se and As in wine samples. The influence of the sample volume, modifier nature and concentration and temperature program (i.e. pyrolysis temperature, T_{pyr}, and vaporization temperature, T_{vap}) on the signal has been studied. In addition, several calibration strategies (i.e. external calibration, standard addition and internal standardization) have been evaluated. Finally, ETV sample introduction has been applied to the analysis of different wine samples. In order to evaluate the results obtained, wine samples have also been analyzed by means of ICP-MS using a conventional liquid sample introduction system and by electrothermal atomic absorption spectrometry (ETAAS).

2. Experimental

2.1. Instrumentation and sample introduction systems

An Elan 5000 ICP-MS instrument (Perkin-Elmer SCIEX Instruments, Concord, Ontario, Canada) was used. The operating conditions are listed in Table 1. The analyte isotopes measured were ^{208}Pb, ^{82}Se and ^{75}As. In addition, ^{13}C and ^{37}Cl isotopes were selected to monitor wine matrix compounds. For ^{13}C and ^{37}Cl the OmniRange option for signal attenuation was selected to avoid detector damage. Two sample introduction systems were employed for ICP measurements: (i) an HGA-600 MS electrothermal vaporizer unit (Perkin-Elmer SCIEX, Concord, Ontario, Canada); and (ii) a cross-flow nebulizer coupled to a Ryton Scott-type spray chamber (i.e. the standard device provided with the instrument). The ETV system was coupled to the ICP torch by means a 140-cm PTFE tubing of 6 mm inner diameter. Samples were introduced into the furnace by an auto-sampler (model AS-60). Pyrolytically coated graphite tubes (PerkinElmer B009-1504) with platform were used. The temperature program for the ETV unit is summarized in Table 2. Instrumental conditions for ICP-MS were optimized according to the manufacturer instructions. A test solution containing 10 μg L^{-1} of Fe, Cr, Pb, Mn and Cu was measured daily in order to check the sensitivity of the ETV-ICP-MS instrument. A peristaltic pump (Perimax 12 Spetec GmbH, Erding, Germany) was employed to control the sample uptake rate of the nebulizer.

For comparison, wine samples were also analyzed by ETAAS, using a Perkin-Elmer Zeeman 5100 (PerkinElmer, Norwalk, CT, USA) atomic absorption spectrometer with Zeeman-effect background correction, equipped with HGA graphite furnace and AS-60 auto sampler. Furnace experimental conditions are shown in Table 3. Pyrolytically coated graphite tubes with platform (PerkinElmer B009-1504) were also used.

Table 1
ICP-MS operating conditions.

Plasma forward power (W)	1000
Argon flow rate (L min^{-1})	
Plasma	15
Auxiliary	0.4
Carrier	0.9[a]/1.5[b]
Data acquisition parameters	
Scanning mode	~~Peak hope transient~~
Signal measurement	Signal profile integrated
Dwell time (s)	100[a]/20[b]
Reading per replicate	5[a]/70[b]
Points per spectral peak	1
Sweeps per reading	100[a]/1[b]
Isotopes measured:	
Analyte	^{208}Pb, ^{82}Se, ^{75}As
Matrix	^{12}C, ^{37}Cl
Internal standard	^{103}Rh, ^{197}Au
Electrothermal vaporization	
Sample volume (μL)	Variable
Modifier volume (μL)	10
Conventional nebulization:	
Sample uptake rate (Q_l) (mL min^{-1})	1.0

[a] Conventional nebulization.
[b] Electrothermal vaporization.

Table 2
ETV temperature program.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Internal gas flow (mL min^{-1})
1	90	10	10	300
2	Variable	10	15	300
3[a]	Variable	0.7	10	300
4	2600	1.0	5	300
5	20	1.0	20	300

[a] Reading switched on during this step.

2.2. Reagents

High purity water (i.e. with conductivity lower than 18 MΩ cm^{-1}) obtained from a Milli-Q water system (Millipore Inc., Paris, France), nitric acid (Suprapur, Merck, Darmstadt, Germany), ethanol (LiChrosolv™, Merck, Darmstadt, Germany) and potassium nitrate (Sigma–Aldrich, Steinheim, Germany) were used throughout the work. Pb, Se and As standard mono-elemental solutions (Merck, Darmstadt, Germany) were employed to prepare calibration standards and to spike wine samples. In addition, Rh and Au mono-elemental solutions (Merck, Darmstadt, Germany) were employed for internal standardization purposes. Finally, palladium, citric acid and ascorbic acid (Sigma–Aldrich, Steinheim, Germany) were used as modifiers.

Table 3
ETAAS temperature program.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Internal gas flow (mL min^{-1})
1	90	10	10	300
2	Variable	10	15	300
3[a]	T_a	0.7	10	300
4	2600	1.0	5	300
5	20	1.0	20	300

T_a: atomization temperature 2100 °C for As and Se; 1800 °C for Pb.
[a] Reading switched on during this step.

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2.3. Wine samples

Four different Spanish wine samples were analyzed: two white (A: Rueda Ovación, Zamora; B: Bujovis, Penedés) and two red (C: Castillo de la Fuente, Valencia; D: Fontal Crianza, Cuenca). These samples were chosen to cover different matrix characteristics and origins. Sample D was selected for optimizing experimental conditions in ICP-MS and ETAAS.

2.4. Sample preparation

Wine samples were analyzed directly by means of ETV-ICP-MS and ETAAS. For comparison purposes, wine samples were digested using a microwave-assisted treatment in a closed vessel. To this end, 5 g of the selected wine were weighed into a PTFA digestion vessel and 5 mL of concentrated nitric acid were added. The mixture was allowed to react and after clearance of fumes (20 min) the vessel was closed. Afterwards the samples were digested in a CEM MDS-2000 microwave digestor (Matthews, NC, USA) using the program recommended by the manufacturer (six vessels, microwave power 350 W; four stages of 15 min at a pressure of 1.4×10^5, 2.8×10^5, 5.9×10^5 and 1.0×10^6 psi, respectively). Finally, the digested sample was made up to 15 g using de-ionized water. Digested samples were analyzed by means of ICP-MS using the conventional liquid sample introduction system and by ETAAS.

2.5. Calibration strategy

Several calibration strategies were applied to analyze wine samples by means of ICP-MS and ETAAS (see Table 4). Un-treated wine samples were analyzed directly by ETV-ICP-MS using ethanol 10% (w/w) matched standards. Additionally, 10% (w/w) alcohol matched standards with different amounts of potassium nitrate (i.e. 500–2000 mg L^{-1}) and nitric acid (0.1–0.5%, w/w) were evaluated and un-treated wine samples were also analyzed using the standard addition methodology. The analysis of digested wine samples by means of conventional liquid sample introduction ICP-MS was performed using acid matched standards (i.e. nitric acid ~~7~~M) and internal standardization. ^{103}Rh and ^{197}Au istopes were selected as internal standards to reduce matrix effects and improve precision. Finally, the standard addition methodology was employed for the analysis of both un-treated and digested wine samples in ETAAS.

3. Results and discussion

3.1. Influence of the sample volume

Fig. 1 shows the influence of the volume of wine introduced in the ETV device on the net ion intensity defined as the difference between the integrated intensity measured for a certain sample volume spiked with a selected amount of analyte and the corresponding non-spiked sample. Fig. 1 shows that the ionic intensity is increased when the volume of wine increases from 1 up to 4 μL. For wine volumes higher than 4 μL the intensity decreases again. To explain this behaviour it must be considered that when the sample volume is increased, the amount of concomitants is also increased [24–27]. Concomitants act as nuclei where the analyte condenses, avoiding losses on the cold parts of the sample introduction system. As a consequence, analyte transport to the plasma is improved. However, when the amount of concomitants (matrix) becomes too high, analyte losses arise due to changes in aerosol generation and transport to the plasma [25,26]. The cross-over point between both effects depends on the wine matrix composition, i.e. the optimum sample volume will be lower for wines with a heavier matrix. Nevertheless, no differences in the optimum sample volume were found for the different wine samples tested and therefore 4 μL of wine was selected for further studies.

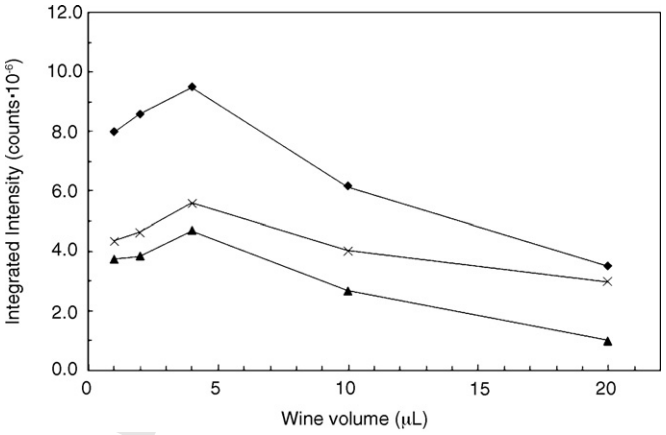

Fig. 1. Influence of the wine volume on the integrated intensity corresponding to ~~a~~ 1 ng of analyte ~~spike~~ in different wine sample volumes. (♦) $^{208}Pb^+$; (▲) $^{82}Se^+$; (×) $^{75}As^+$. T_{pyr} 120 °C; T_{vap}, 2300 °C. Modifier: ascorbic acid 10 μg. Se intensity has been multiplied by a factor of 10.

3.2. Influence of the modifier

Chemical modifiers are widely employed in ETAAS and ETV-ICP-MS to improve matrix-analyte separation and reduce matrix effects. When using ETV-ICP-MS, modifiers also play a significant role in analyte transport efficiency and, hence, they influence the ionic signal. Palladium, ascorbic acid and citric acid were tested as modifiers since they have been successfully employed for the determination of Pb, Se or As in complex matrices [27–30].

To check the influence of the modifier on the ionic signal intensities, analyte-spiked wine samples were measured with and without modifier. Fig. 2 shows the influence of the presence of different amounts of palladium and ascorbic acid on the integrated signal intensity relative to the corresponding value obtained without modifier. The results for citric acid were similar to those obtained with ascorbic acid. It is clear that the use of a modifier improves the ionic signal intensities (i.e. relative intensity values obtained are higher than one). The signal enhancement factor for each analyte depends on the modifier concentration and type. The results presented in Fig. 2 show that, for all the modifiers tested, the relative intensity increases when the amount of modifier is increased, and then decreases again. These results can be explained by the previously mentioned effect of concomitants on the analyte transport efficiency [24–27]. From the results obtained with the different modifiers at their optimum concentrations, it is concluded that the highest signals are obtained using 10 μg of ascorbic acid. Thus, for instance, relative intensity values for Pb and As using 10 μg of ascorbic acid as modifier were 1.5 and 4.4, respectively. However, for Se, 1 μg of palladium showed a higher relative intensity than 10 μg of ascorbic acid (2.1 vs. 1.7). Among the three modifiers tested, ascorbic acid (10 μg) was selected for further studies since it provides

Table 4
Sample preparation and calibration strategies with the different arrangements tested.

Technique	Wine	
	Un-treated	Digested
ETV-ICP-MS	Matrix matching or standard addition	–
Nebulizer-ICP-MS	–	Matrix matching + internal standardization
ETAAS	Standard addition	Standard addition

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the best results for simultaneous determination of Pb, Se and As in wine.

It is also important to point out that significant amounts of organic acids and polysaccharides are present in wine [31,32]. Thus, for instance, the citric acid concentration in wine ranges between 0.2 and 2.0 g L^{-1}. Ascorbic acid is not present in natural form in wine in significant amounts but it is usually added for wine stabilization purposes [33]. This means that the amount of ascorbic acid and citric acid present as modifier is the sum of the amount provided by the wine itself and the added amount of modifier. The contribution of ascorbic and citric acid from the wine (i.e. 0.8–8.0 μg) is similar to the amount added (i.e. 5–50 μg) and, as a consequence, optimum modifier concentration may depend on the wine sample tested. Nevertheless, no differences were observed in the optimum amount of ascorbic acid for the different wine samples tested in the present work.

3.3. Optimization of the ETV temperature program

Fig. 3A shows the influence of the pyrolysis temperature (T_{pyr}) on the ionic intensity of the different isotopes tested using 10 μg of ascorbic acid as modifier. Integrated intensity values shown in this figure correspond to the difference between spiked (i.e. 1 ng) and non-spiked wine samples. When increasing T_{pyr} the integrated ionic intensity for all the analytes was reduced. Thus, for instance, when T_{pyr} is increased from 100 to 450 °C, ionic signals decreased with 23 and 86% for Pb and As, respectively. Signal reduction can be related to: (i) analyte losses due to early analyte volatilization in the furnace; (ii) changes in the analyte transport efficiency to the ICP-MS; and/or (iii) changes in the plasma itself. In order to get more information about the processes inside the furnace, the corresponding pyrolysis curves in ETAAS were studied. In ETAAS, vaporization and atomization take place in the electrothermal atomizer, i.e. there is no need for analyte transport. Consequently, ETAAS experiments provide useful information about analyte stability in the furnace. Fig. 3B shows the influence of the T_{pyr} on the integrated absorbance in ETAAS using 10 μg of ascorbic acid as modifier. The absorbance was constant up to higher T_{pyr} than the ionic signal in ETV-ICP-MS, i.e. analyte losses due to early analyte volatilization in the furnace for ETV-ICP-MS are not significant for T_{pyr} below 450 °C. Therefore, it can be concluded that signal reduction in Fig. 3A is related to changes in the analyte transport efficiency or changes in the plasma behaviour. In fact, this has been previously reported by Silva et al. [27] analyzing carbon-containing matrices. These authors observed that Pb, Se and As signals in ETV-ICP-MS were increased at low

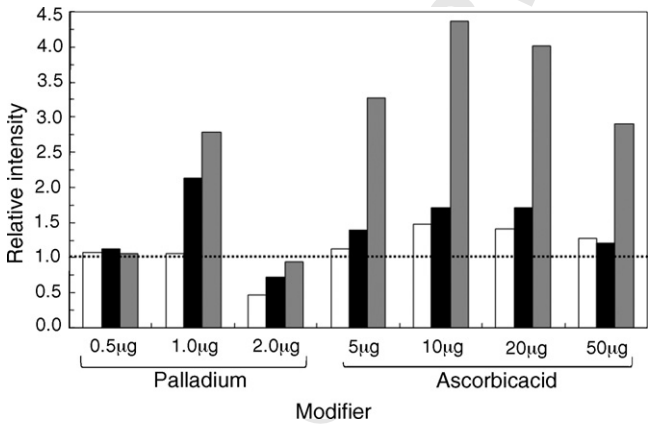

Fig. 2. Influence of the modifier on the integrated intensity relative to the value obtained without modifier for 1 ng analyte spiked wine samples. (□) $^{208}Pb^+$;(■) $^{82}Se^+$; (■) $^{75}As^+$. Wine volume 4 μL. T_{pyr}, 120 °C; T_{vap}, 2300 °C. ~~Analyte concentration: 1 ng.~~

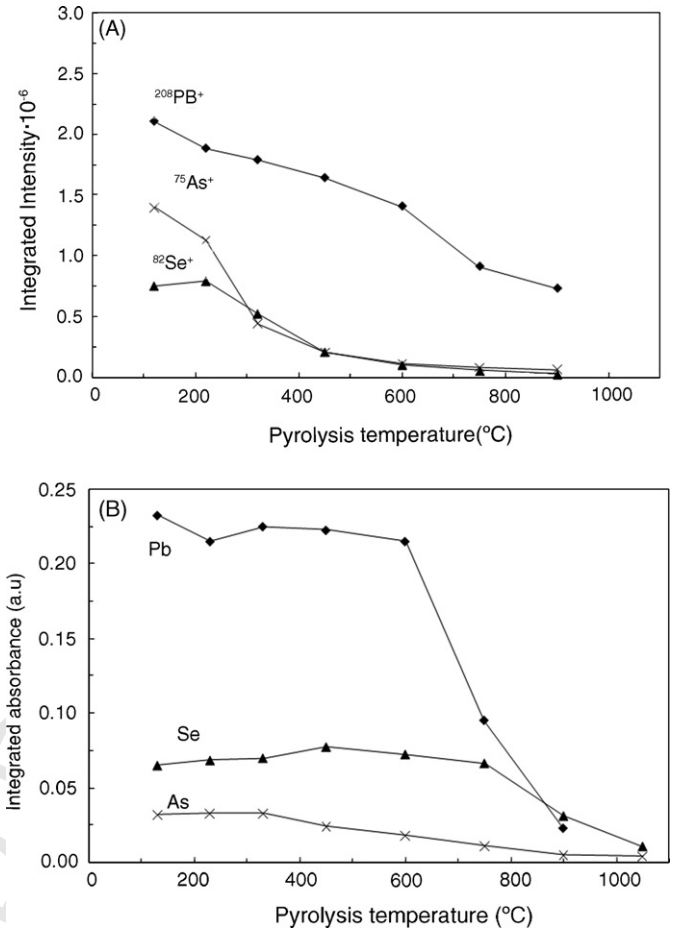

Fig. 3. Influence of the pyrolysis temperature on the signal in ETV-ICP-MS (A) and ETAAS (B) using 10 μg of ascorbic acid as modifier. Wine volume 4 μL. ETV T_{vap}, 2300 °C. Analyte amount spiked: 1 ng. Se intensity in ICP-MS has been multiplied by a factor of 10.

pyrolysis temperatures due to the beneficial effect of carbon on analyte transport efficiency. In addition, carbon-based non-spectral interferences in the plasma must be taken into account to explain Se and As signal enhancements [15,34]. In order to assess the validity of these assumptions for the wine matrix, the $^{13}C^+$ signal has been measured. The results obtained show indeed that carbon signals are enhanced when the pyrolysis temperature is reduced. Thus, for instance, the carbon signal for a T_{pyr} of 120 °C is six times higher than for 450 °C.

Finally, no influence of the vaporization temperature on the ionic signals has been observed in the range studied (i.e. 1800–2500 °C) regardless of the modifier employed. Therefore, in order to extend graphite tube lifetime, 2300 °C was selected for further studies.

3.4. Calibration strategy

First of all, external calibration was evaluated for elemental analysis of wine since this methodology is easy to apply and the analysis throughput is high. To this end, different matrix matched standards were prepared to simulate the wine matrix. Fig. 4 shows the ratio of the response in integrated intensity due to 1 ng of analyte added to a wine sample and the same amount of analyte in different matrix matched standard solutions using ascorbic acid as modifier. Considering the precision (5%, three replicates), relative intensity values between 0.9 and 1.1 (see dotted lines in Fig. 4) indicate where external calibration can be expected to be successful. However, the signals obtained in wine samples were up to 40% higher than those

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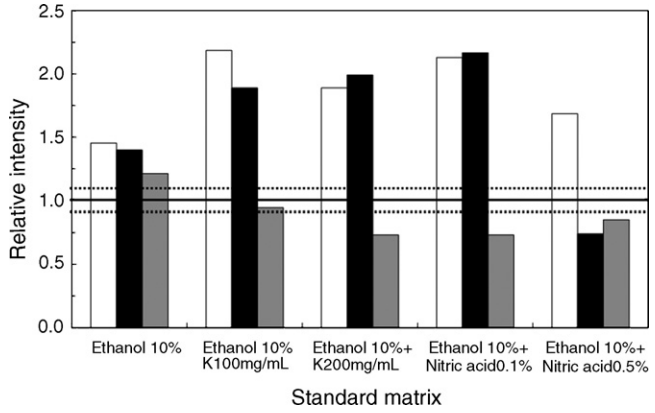

Fig. 4. Ratio of the response, due to 1 ng of analyte added to wine samples and the same amount of analyte added to different matrix solutions. (□) $^{208}Pb^+$; (■) $^{82}Se^+$; (▩) $^{75}As^+$. The intensities measured for the wine samples plus analyte addition have been corrected for the intensities measured for the wine samples without analyte additions. Wine and standard volume 4 μL. Modifier: ascorbic acid 10 μg. T_{pyr}, 120 °C; T_{vap}, 2300 °C. Analyte concentration: 1 ng.

in 10%-ethanol (w/w) standards due to wine matrix effects. In order to improve the analyte transport efficiency for the standards and to better match the wine matrix composition, new ethanol standards containing potassium were prepared. Potassium is the most abundant element in wine (in the g L^{-1} range) and can therefore exert great influence on the transport efficiency. Fig. 4 shows that 10%-ethanol (w/w) standards containing potassium are not useful for calibration purposes either since they provide different signal intensities in comparison to the signal intensities observed for wine samples. Thus, for instance, when using 10%-ethanol (w/w) plus 1000 mg L^{-1} potassium matched standards, the relative intensities for Pb and Se were 2.2 and 1.8, respectively. An alternative approach to modify the analyte transport efficiency for the standards is the use of acids [35] since their presence in the furnace leads to release of carbon particles from the graphite (i.e. carriers). However, standards prepared with nitric acid do not provide any improvement when compared to the 10%-ethanol (w/w) standards with or without potassium. Finally, it is also worth to mention that palladium and citric acid were also evaluated as modifier to see if their presence helps to reduce the differences in the signal between the sample and the aqueous standard but the results were similar to those obtained with ascorbic acid. It is clear that external calibration in ETV-ICP-MS cannot be used for the analysis of wine. Standard addition was therefore employed.

3.5. Wine analysis

Four wine samples have been analyzed by ETV-ICP-MS to determine Pb, Se and As levels using the standard addition methodology. The experimental conditions selected for ETV-ICP-MS measurements were those that provide the maximum sensitivity (i.e. 4 μL of sample, 10 μg of ascorbic acid as modifier and T_{pyr} and T_{vap} temperatures of 120 and 2300 °C, respectively).

Up to now, there is no certified wine reference sample available for elemental analysis. Therefore, to evaluate the accuracy of the results, alternative arrangements and methodologies were employed. On one hand, the conventional liquid sample introduction system (i.e. pneumatic nebulizer/double pass spray chamber) coupled to the ICP-MS was employed to analyze digested wine samples. Wine digestion destroys matrix components mitigating matrix effects due to organic compounds. External calibration with nitric acid matched standards and internal standardization were applied. Nitric acid standards were prepared to match the acid concentration in the digested samples (i.e. 4 M). Internal standardization was also employed to mitigate matrix effects and improve precision. According to Thompson and Houk [36], an internal standard should have an atomic mass and first ionization potential (IP) as close as possible to those of the analyte. $^{103}Rh^+$ (IP 7.46 eV) and $^{197}Au^+$ (IP 9.23 eV) were selected as internal standards for Pb (IP 7.42 eV) and As (IP 9.81 eV) and Se (IP 9.75 eV) determination, respectively. The analysis of un-treated and digested wine samples was also carried out by means of ETAAS, since this technique is based on a different principle and therefore does not suffer from the same interferences as ICP-MS. Several authors have reported that aqueous standards can be successfully employed for elemental wine analysis by ETAAS using un-treated or 1:1 diluted samples [37,38]. However, in our case, strong signal suppression was observed for un-treated and 1:1 diluted wine samples when compared to the standards. No temperature program and modifier tested could mitigate wine matrix effects and, hence, the standard addition methodology was also employed in ETAAS. Furnace experimental conditions and modifier employed for ETAAS measurements (Table 3) were the same as those employed for ETV-ICP-MS (Table 2).

3.5.1. Lead

Table 5 shows the results of Pb determination in the wine samples. No differences in the Pb concentration were found in ICP-MS for ETV sample introduction and conventional nebulization within a confidence level of 95% (three replicates). It is important to point out that Rh was used as internal standard in ICP-MS with conventional nebulization. When Au was employed as internal standard, Pb concentration values were between 20 and 30% lower than those obtained with Rh. These differences can be expected and explained from the different IP of Pb and Au. In addition, it must be taken into account that the Au ionization is significantly influenced by the presence of carbon in the plasma [34]. The results obtained in ICP-MS for both sample introduction systems were in agreement with those obtained in ETAAS regardless of the sample treatment employed (un-treated and digested wine samples). From these results, it can be concluded that ETV-ICP-MS can be successfully employed for Pb determination in wine samples. The limit of quantification (LOQ) for Pb, defined as 10 times the standard deviation of the blank [39], is 0.5 μg L^{-1}.

3.5.2. Selenium

Table 5 shows that similar Se concentration values were found with ICP-MS for both ETV sample introduction and conventional nebulization. The internal standard selected for Se determination was Au since both elements have similar IP and they are also affected by the same non-spectral interference due to carbon presence in the plasma [34]. When internal standardization is not employed or using Rh as internal standard, Se values for the conventional system were up to 37% higher than those for ETV. The Se ~~LODs, defined as three times the standard deviation of the blank [39],~~ in ETAAS were not low enough to quantify this element in the wine samples analyzed (LOQ <5.0 μg L^{-1}).

3.5.3. Arsenic

Table 5 also shows the results obtained for As determination in ICP-MS. As it can be observed, As concentration values strongly depend on the sample introduction system used. Thus, results for As obtained using conventional nebulization were about 3–4 times higher than those obtained with the ETV device. In order to understand these differences, several error sources can be considered. Firstly, acids employed in the digestion procedure may contain some As impurities. However, the contribution from As in the acids to the As concentration in the digested wine samples (i.e. 0.3 μg L^{-1}) was taken into account by the measurement of the blank, and therefore, this effect can be neglected. Another possible source of error may be the carbon-related non-spectroscopic matrix effects.

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Table 5
Analyte concentration values in wine samples using different methodologies of analysis. ETV-ICP-MS/ETAAS: wine amount, 4 μL. Modifier: ascorbic acid, 10 μg. T_{vap}, 2300 °C; T_{pyr}, 120 °C.

Analyte	Wine sample	Analyte concentration (μg L^{-1})[a]			
		Digestion/nebulizer-ICP-MS[b]	Un-treated/ETV-ICP-MS	Digestion/ETAAS	Un-treated/ETAAS
Pb	A	10.0 ± 0.4	8.5 ± 0.8	9.4 ± 0.7	11 ± 3
	B	7.9 ± 0.4	7.4 ± 0.7	9.0 ± 0.6	9 ± 3
	C	15.1 ± 0.7	13 ± 2	14 ± 2	16 ± 2
	D	8.9 ± 0.6	7.7 ± 0.6	9.5 ± 0.7	10 ± 3
Se	A	2.8 ± 0.4	1.9 ± 0.3	<5.0	<5.0
	B	2.3 ± 0.3	1.7 ± 0.4	<5.0	<5.0
	C	2.9 ± 0.5	2.7 ± 0.5	<5.0	<5.0
	D	3.5 ± 0.3	2.5 ± 0.5	<5.0	<5.0
As	A	8.7 ± 0.2	3.4 ± 0.5	<7.0	<7.0
	B	7.5 ± 0.5	2.5 ± 0.3	<7.0	<7.0
	C	9.5 ± 0.4	2.6 ± 0.6	<7.0	<7.0
	D	6.3 ± 0.3	3.8 ± 0.4	<7.0	<7.0

[a] ~~Uncertainties are presented in form of confidence ranges obtained as $t \times s$ where t is the Student's t (4.3 for a 95 % confidence level) and s is the standard deviation of three replicates of the analysis.~~
[b] Internal standardization employed: Pb (Rh), Se and As (Au).

Similar to what was discussed for Se, the presence of carbon also enhances $^{75}As^+$ signals [34]. In order to mitigate this interference for the conventional system, Au was employed as internal standard since preliminary studies have shown that Au behaves like As when carbon is present in the plasma [34]. Finally, the differences can also be related to the spectral interference caused by $^{40}Ar^{35}Cl^+$ on the $^{75}As^+$ signal. Chloride is present in wine samples in concentration levels between 100 and 200 mg L^{-1} [7]. In order to evaluate the influence of $^{40}Ar^{35}Cl^+$ interference on the $^{75}As^+$ signal obtained in ETV-ICP-MS, the signal of the $^{37}Cl^+$ was monitored. The higher the $^{37}Cl^+$ signal the more pronounced $^{40}Ar^{35}Cl^+$ interference is expected. Fig. 5 shows the normalized signal profiles for $^{75}As^+$ and $^{37}Cl^+$ isotopes. In addition, $^{208}Pb^+$ and $^{82}Se^+$ signal profiles have been included for comparison purposes. As it can be observed, ~~As, Pb Se and As~~ do not reach the plasma simultaneously. The As signal increases 2 s before Pb signal starts to increase. Fig. 5 also shows that $^{75}As^+$ and $^{37}Cl^+$ signal profiles are partially time resolved. The $^{75}As^+$ signal appears about 1.4 s before the $^{37}Cl^+$ signal and, therefore, the possible $^{40}Ar^{35}Cl^+$ interference on the $^{75}As^+$ is partially mitigated. When using conventional nebulization, As and Cl are introduced simultaneously into the plasma and consequently it is not possible to correct for this spectral interference in a quadruple MS without reaction/collision cell [40]. The LOQ for As in ETAAS (~~i.e. <~~7 μg L^{-1}) was not low enough to provide a reference value to check the magnitude of the $^{40}Ar^{35}Cl^+$ interference in ETV-ICP-MS. Nonetheless, the results obtained for atomic absorption spectrometry suggest that As values for the conventional system suffer from this interference since the As concentration for almost all the wine samples tested were higher than the LOQ obtained in ETAAS.

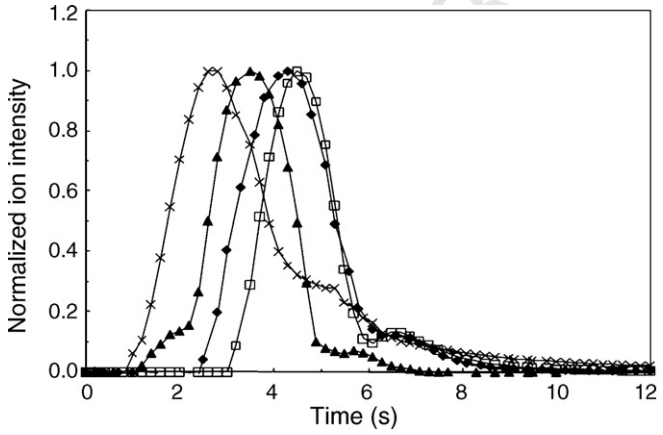

Fig. 5. ETV vaporization curves of several analytes and matrix components. (♦) $^{208}Pb^+$; (▲) $^{82}Se^+$; (×) $^{75}As^+$; (□) $^{35}Cl^+$. Wine volume 4 μL. Modifier: ascorbic acid 10 μg. T_{pyr}, 120 °C; T_{vap}, 2300 °C. Analyte concentration: 1 ng.

4. Conclusions

ETV-ICP-MS is a useful technique for ultratrace determination of Pb, Se and As in wine samples. Analytical figures of merit using ETV sample introduction strongly depend on the sample volume, modifier and temperature program selected. Special attention must be paid to wine matrix components since they influence the analyte transport efficiency. As a consequence, the standard addition methodology is mandatory. The results of Pb analysis by ETV-ICP-MS were in agreement with those observed for the conventional nebulizer sample introduction system in ICP-MS and results obtained with ETAAS. For Se and As determination by conventional nebulization ICP-MS, special attention must be paid to the carbon-based non-spectral and, thus, the appropriate selection of the internal standard is critical. Finally, ETV sample introduction in ICP-MS allows mitigating the intensity of polyatomic interferences (i.e. $^{40}Ar^{35}Cl^+$) on As determination when compared to the conventional nebulizer sample introduction system.

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