

Measurements of contaminant elements of wines by inductively coupled plasma-mass spectrometry: A comparison of two calibration approaches

Sofia Catarino^{a,b,*}, A.S. Curvelo-Garcia^a, R. Bruno de Sousa^b

^a INIAP, Estação Vitivinícola Nacional, 2565-191 Dois Portos, Portugal

^b Instituto Superior de Agronomia, Departamento de Química Agrícola e Ambiental, Tapada da Ajuda, 1349-017 Lisboa, Portugal

Received 3 October 2005; received in revised form 28 December 2005; accepted 7 February 2006

Available online 15 March 2006

Abstract

The aim of the present work was to develop and validate an accurate method by ICP-MS focalized to the measurement of contaminant elements in wines, in special those with legal importance. In addition, we intended to evaluate the suitability of ICP-MS semi-quantitative methodology in order to reduce the time and cost of analysis. Twenty-six contaminant elements of wine (Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi and U) were measured using quantitative and semi-quantitative calibration approaches, in diluted white and red wines. In an early step potential interferences caused by Cl and Ca species were evaluated, in order to establish suitable mathematical corrections. For validation of ICP-MS procedures a few elements were determined by flame and electrothermal AAS. Reference wines from 1992 year, with provisional values, were analyzed and the results showed satisfactory agreement. The semi-quantitative calibration provided slightly higher limits of detection than those obtained by the quantitative calibration, and always lower than $0.1 \mu\text{g l}^{-1}$, except for Fe and Zn. For most elements the recovery percentages (between 90 and 100%) and precision of the results (R.S.D. (%) < 4) were similar for both modes. Differences lower than 20% of concentration was obtained for most elements. Both methodologies offer valuable alternatives to wine characterization and comparison purposes. For legal requirements control purposes, with reference to the importance of accurate results, quantitative approach is the most suitable alternative.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Wine; Contaminant elements; ICP-MS; Quantitative and semi-quantitative calibration

1. Introduction

Mineral content of wines depend on several factors, including soil, variety of grape, environmental conditions and viticultural and enological practices. The determination of some elements is of interest due to their toxicological or physiological properties, while others can lead to wine spoilage [1–5]. It should be noted that the levels of certain contaminant elements, such as Cu, Zn, As, Cd and Pb, at different stages of the winemaking process are of great concern because of legal requirements [6].

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique applied to a wide range of applications in analytical chemistry, with high selectivity and sensitivity and low analytical limits, so that it is an excellent tool for isotopic

analysis [7–15] and for detailed characterization of elemental composition of wine [16–27].

The application field of ICP-MS technique to wine is large. Different methodologies have been used in preliminary studies to classify wines according to their geographic origin or grape variety, from its trace composition, as a fingerprint [17,18,24,27,28]. A number of papers have been published reporting the use of ICP-MS methods for determine trace metals and rare earth elements in wine fingerprints [16,18,21–23,25,27,29]. In the last years this technique has been a very important tool to evaluate the changes in the contents of trace elements through the winemaking process. Nicolini et al. [25] have applied the ICP-MS technique to evaluate the changes in the contents of micro and trace elements in wine due to winemaking treatments. The changes of the metal composition in German white wines through the winemaking process were evaluated by Gómez et al. [26].

ICP-MS offers different quantification procedures depending on the accuracy and precision required. Isotope dilution mode

* Corresponding author. Tel.: +351 261 712106; fax: +351 261 712426.
E-mail address: sofia.catarino@clix.pt (S. Catarino).

of analysis presents the highest quality of results. However, when a high quality of results is needed quantitative approach may be a suitable strategy as well. This procedure requires external calibration with standards of each element to be determined. This strategy is time consuming and it is not easy to have a complete set of the multi-element standards required for the calibration. The application of this mode of quantification in wines has already been reported [12,16–19,22,23,25,27,30].

The semi-quantitative approach is a versatile application of ICP-MS, which is claimed to allow the determination of 81 elements with accuracy errors lower than 20% for most elements. The semi-quantitative analysis software available for ICP-MS instrumentation (Total Quant III from Perkin-Elmer – ELAN software, for instance) automatically corrects for isotopic interferences and interfering molecular species and produces a comprehensive report, listing each element present in the sample along with its concentration. Unlike quantitative analysis methods, calibration is achieved using just a few elements distributed throughout the mass range of interest. The calibration process is used to update internal response data that correlates measured ion intensities to the concentrations of elements in a solution. During calibration, the response data is adjusted to account for changes in the instrument's sensitivity due to variations in the sample matrix. This methodology has already been applied to wine [15,18,20,21,25,29,30]. Pérez-Jordán et al. [19] and Sagrado et al. [30] have compared two ICP-MS methods for analyzing wine samples (quantitative and semi-quantitative methodologies). For the majority of elements determined by both methodologies, comparable results were found. The advantages and limitations of the semi-quantitative calibration of an inductively coupled plasma-mass spectrometer for multi-element characterization of fortified and table wines were tested by Almeida and Vasconcelos [22]. The wine samples were submitted to an UV-irradiation treatment prior to analysis. Pruszkowski [31] have applied a semi-quantitative methodology of ICP-MS technique to wine, supporting its suitability for final sample characterization, such as total metal content and fingerprint.

Although the concentrations for only few elements in wines are currently under regulation, the increasing concern for health effects and environmental exposure will probably result in a longer list of potentially toxic elements, the concentrations of which have to be monitored in a near future. As far as we know, ICP-MS methodologies are not yet used in routine wine analysis by control laboratories. Nevertheless, the establishment of an ICP-MS methodology for contaminant elements of wine will carry great advantages to these control laboratories.

The purpose of the present study was to develop and validate an accurate method by ICP-MS focalized to the determination of contaminant elements in wines, in particular those which concentration is, or could be in a near future legally controlled. In addition, we intended to evaluate the suitability of ICP-MS semi-quantitative calibration, by comparison of the results obtained by both calibration approaches, in order to reduce the time and cost of analysis relatively to those of quantitative calibration.

2. Experimental

2.1. Apparatus

The analytical measurements were carried out with a Perkin-Elmer SCIEX Elan 9000 ICP-MS (Perkin-Elmer SCIEX, Norwalk, CT, USA) apparatus, equipped with a crossflow nebulizer, a Scott-type spray chamber made of Ryton and nickel cones. A peristaltic sample delivery pump with four channels, model Gilson, was used. Autosampler Perkin-Elmer AS-93 Plus was protected by a laminar-flow-chamber clean room class 100 (Reinraumtechnik Max Petek). Application software Elan – 6100 Windows NT (Version 2.4), was used.

For validation of the ICP-MS results, some elements were also determined by flame atomic absorption spectrometry (FAAS) (AAnalyst 100, Perkin-Elmer, Norwalk, CT, USA) and electrothermal atomic absorption spectrometry (ETAAS) (4110 ZL, Perkin-Elmer, Norwalk, CT, USA).

2.2. Material and reagents

Monoelement standard solutions of Be, Co and In (1000 mg l^{-1}), from Merck, and a solution with Mg, Cu, Rh, Cd, In, Ba, Ce, Pb and U ($10 \mu\text{g l}^{-1}$), from Perkin-Elmer were used for ICP-MS optimization procedures. Ultrapure concentrated HNO_3 (J.T. Baker), $\text{C}_2\text{H}_5\text{OH}$ (Lichrosolv, Merck) and Au (Merck, 1000 mg l^{-1}) for wash, blank and standard solutions were used. ICP-MS calibration was established with a multielement standard solution with 30 elements: Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, U (Perkin-Elmer, 10 mg l^{-1}). For ICP-MS internal standardisation standard solutions of Rh and Re (Merck, 1000 mg l^{-1}), were used. For the determination of Cl and Ca interference free ranges and interference ratios, a monoelement standard solution of Ca (1000 mg l^{-1}) and Suprapur HCl (30%), both from Merck, were used.

For AAS analysis, monoelement standard solutions of Al, Pb, Cd (Merck, 1000 mg l^{-1}) and Cu and Fe (Perkin-Elmer, 1000 mg l^{-1}), $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ as matrix modifiers, both from Merck (10 g l^{-1}), were used.

Purified water was produced using a Seralpur Pro 90CN apparatus (Seral, Ransbach-Baumbach, Germany). For solution preparation plastic material was only used. All the material was soaked in 20% HNO_3 (v/v) for at least 24 h and rinsed several times with purified water, before use.

2.3. Samples

White and red table wines were used for the study and comparison of quantitative and semi-quantitative approaches. A Portuguese red wine was used for AAS analysis comparison.

Three provisionally certified wines from a BCR intercomparison trial (BCR C white, BCR D liquor and BCR E red) were analyzed for method validation. These wines are from 1992 year and showed some precipitation material. Our attempt to get

younger reference wine materials had no success, so we decided to work with these wines, in spite of their state. To the best of our knowledge, no recent reference wine materials can be found for contaminant elements analysis in wines.

A 10-fold final dilution of wine samples, without any further sample preparation, was used for ICP-MS analysis.

HNO₃, a solution of Rh and Re (1 mg l⁻¹) and a solution of Au (1 mg l⁻¹) were added to samples in order to provide a final concentration of 1% (v/v), 10 and 200 μg l⁻¹, respectively. Blank solution and standards contained 1% HNO₃ (v/v), 1% C₂H₅OH (v/v), 10 μg l⁻¹ of Rh and Re, and 200 μg l⁻¹ of Au. The Au was used to eliminate the Hg and U memory effect at nebulizer chamber. The wine samples, blank and standard solutions were prepared daily, in polyethylene tubes.

2.4. ICP-MS determinations

The operating conditions were optimized daily, by using an aqueous solution containing 10 μg l⁻¹ of Mg, Ba, Ce, Cu, Cd, Rh, In and Pb, and monitoring the intensities of the isotopes ²⁴Mg, ¹⁰³Rh, ¹¹⁴In, ²⁰⁸Pb, ¹³⁸Ba and ¹⁴⁰Ce as well as the intensities at mass 69, 156 and 220 (corresponding to species ¹³⁸Ba²⁺, ¹⁴⁰Ce¹⁶O⁺ and background, respectively).

The chosen conditions were a compromise between the highest ¹⁰³Rh ion signal and the lowest percentage of doubly charge ions (obtained by the intensities ratio Ba²⁺/Ba⁺; always ≤3%) and of oxide ions (obtained by the intensities ratio CeO⁺/Ce⁺, always ≤3%), precision better than 2% and background <30 cps. The *Autolens* system was optimised with a 10 μg l⁻¹ Be, Co and In solution, and dual detector calibration with a 200 μg l⁻¹ solution with 29 elements.

Operating conditions used were as follows: r.f. power of 1200 W; sample uptake rate of 0.85 ml min⁻¹; nebulizer argon flow between 0.85 and 0.95 l min⁻¹.

For both modes of analysis, in order to get signal stabilization, a sample read delay of 75 s was chosen. Between samples or standards, the sampling system was rinsed with a 2% HNO₃ (v/v), 1% C₂H₅OH (v/v) and 200 μg l⁻¹ of Au solution for 75 s.

Rh and Re were used as internal standards for elements in the mass range (*m/z*) 7–138 and 205–238, respectively.

2.5. Determination of Cl and Ca species interference ratios—an approach to improve accuracy

In an early step, potential polyatomic interferences caused by Cl and Ca, two main elements in wine, their interference free ranges and interference ratios were evaluated, using ⁴³Ca and ³⁵Cl as references. The effects of several concentrations of Cl (20–1000 mg l⁻¹) and Ca (10–250 mg l⁻¹) on ⁴⁰Ar³⁵Cl, ³⁵Cl¹⁶O, ³⁵Cl¹⁸O, ⁴³Ca¹⁶O and ⁴⁴Ca¹⁶O species signal were studied. The stability of interference ratios over time was monitored, at 20 and 10 mg l⁻¹ Cl and Ca concentrations, respectively. These concentrations have been used taking into account both the usual levels of Cl and Ca in wines and the sample dilution factor.

Table 1

Isotopes monitored and concentration range for external calibration in the quantitative approach of analysis

Isotopes monitored	Concentration range (μg l ⁻¹) for external calibration
²⁰¹ Hg; ²⁰² Hg	0.1; 0.2; 0.5
⁹ Be; ⁵⁹ Co; ⁷¹ Ga; ⁷⁵ As; ⁸² Se; ¹⁰⁷ Ag; ¹¹¹ Cd; ¹¹⁵ In; ¹³³ Cs; ²⁰⁵ Tl; ²⁰⁹ Bi; ²³⁸ U	0.05; 0.25; 0.5; 2.5
⁷ Li; ⁵¹ V; ⁵³ Cr; ⁶⁰ Ni	0.25; 0.5; 2.5; 10
⁶⁵ Cu; ¹³⁸ Ba; ²⁰⁶ Pb; ²⁰⁷ Pb; ²⁰⁸ Pb	0.5; 2.5; 10; 50
²⁷ Al; ⁵⁵ Mn; ⁵⁷ Fe; ⁶⁶ Zn; ⁸⁵ Rb; ⁸⁸ Sr	2.5; 10; 50; 200

2.6. Quantitative approach

External calibration was used and the appropriate interpolation was carried out for each element to determine its concentration in the corresponding calibration line (Table 1).

A selection of isotopes of the elements to be determined was performed, except for monoisotopic elements. The selected isotopes were those free from isobaric or important matrix-induced interferences, when possible. Otherwise, suitable elemental equations, established after preliminary tests, which are presented in Section 3, were applied to correct isobaric and matrix-induced interferences. Since Pb isotope ratios may change from sample to sample, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb isotopes were measured. The ²⁰¹Hg and ²⁰²Hg isotopes were added in order to increase the signal intensity.

The experimental conditions used for the measurements were: dwell time = 50.0 ms; sweeps/reading = 30; reading/replicates = 1; replicates = 4; time per run = 235 s.

2.7. Semi-quantitative approach

A full mass spectrum (*m/z* = 6–240, omitting the mass ranges 16–18; 40, 41, 211–229) was obtained by full mass range scanning. A reference response table (Perkin-Elmer Total Quant III) was updated with the multielement standard solution at 10 μg l⁻¹. The software of the instrument performs automatic corrections of isobaric interferences.

The experimental conditions used for the measurements were: dwell time = 50.0 ms; sweeps/reading = 6; reading/replicates = 1; replicates = 1; time per run = 67 s.

2.8. Validation of ICP-MS procedures

The limits of detection (LOD) of the elements of interest were determined, for both calibration approaches. The LODs were calculated as being the concentrations corresponding to signals equal to three-fold the standard deviation of a blank solution signal (three replicates).

Recovery tests were carried out for a white and a red wine samples spiked with 0.2–500 μg l⁻¹ standard solution (depending of the element). Three different spikes of each element were performed and the solutions obtained were analyzed. The mean and the respective standard deviation were calculated from the three recovery values obtained for the three spikes.

The contents of Al, Cu, Cd and Pb, were determined by ETAAS [3–5], and those of Fe and Zn by FAAS. A Portuguese red wine was used in this study.

For validation of the ICP-MS results, three provisionally certified wines from a BCR intercomparison trial (BCR C white, BCR D liquor and BCR E red), for Al, Fe, Cu, Zn, Cd and Pb, were analyzed by quantitative analysis.

3. Results and discussion

As with all other atomic spectrometric analytical techniques, interferences of various types can occur during ICP-MS determinations. The most commonly observed result of matrix interference is the ion intensity if an analyte element becomes dependent upon the total composition of the sample. Several methods can be used to compensate for matrix-induced signal suppression such as matrix dilution and standard sample matrix simulation. Wine is a complex matrix that contains many inorganic and organic substances, which can affect signal intensity in ICP-MS. So, in order to reduce the matrix effect, initial studies of the method development included the establishment of the sample minimal preparation procedure. In an early step a five-fold dilution of samples was tested. Problems with signal suppression and signal instability were encountered probably due to progressive blocking of the sampling and skimmer cones. Thus a 10-fold dilution of samples was undertaken. This procedure enabled to reduce matrix effect and still yet allowed the trace elements quantification.

3.1. Cl and Ca species interference ratios and mathematical corrections

Spectral interferences are the result of other chemical species, which are present at the same atomic mass as the analyte of interest. A careful selection of isotopes was made in order to overcome isobaric overlaps. Sample constituents, usually in combination with oxygen, may generate polyatomic ions. In most cases, these interferences can be compensated by knowledge of the intensities of the oxide and the parent ion. A prior knowledge of polyatomic interferences cited in literature for a particular analyte may be helpful to the analyst for selecting reagents and conditions that would preclude or reduce [the possibility of] their formation. A good perspective of know polyatomic interferences was given by May and Wiedmeyer [32]. The fact that a spectral interference occurs at the isotope mass of an analyte does not necessarily mean that all determinations of this particular element are interfered. Whether interference occurs or not depends on the abundance of interfering species, intensities of parent ions of the interference, and on the ratio at which the interference occurs [33].

Fig. 1 shows the stability of Cl and Ca species interference ratios. $^{40}\text{Ar}^{35}\text{Cl}$ interference ratio seems to be stable all over the concentration range in study, and it was always lower than 0.0005, while $^{35}\text{Cl}^{16}\text{O}$ and $^{35}\text{Cl}^{18}\text{O}$ interference ratios increase with Cl concentration. $^{43}\text{Ca}^{16}\text{O}$ and $^{44}\text{Ca}^{16}\text{O}$ species interference ratios seem stable in the 10–1000 mg l^{-1} range of concentration. Cl level in wines is usually lower than 50 mg l^{-1}

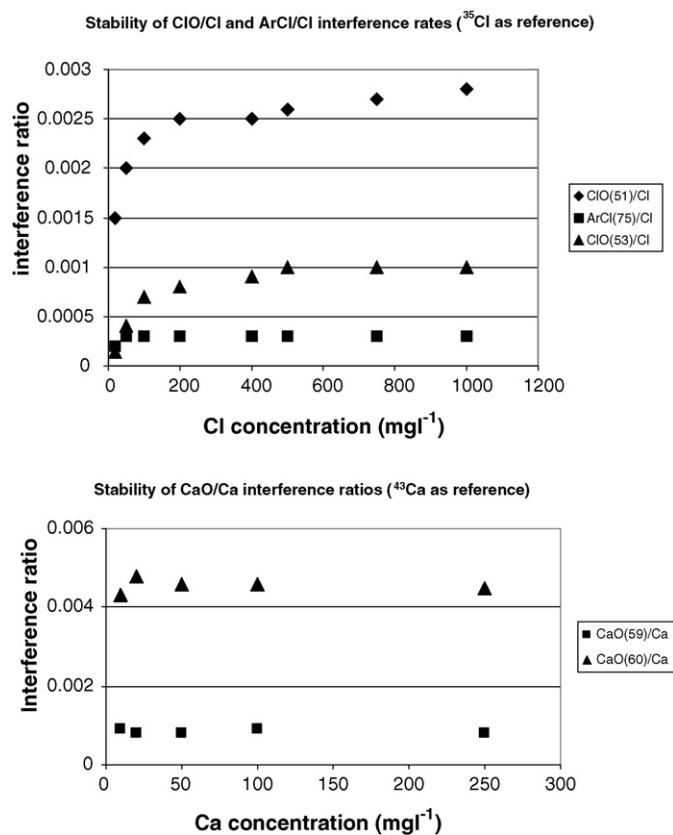


Fig. 1. Stability of Cl and Ca species interference ratios with Cl and Ca concentrations.

nerveless in some typified and rare situations it can achieve 1 g l^{-1} . Ca level in wines is usually lower than 150 mg l^{-1} . The stability of calculated interference ratios over time were evaluated, in order to investigate their suitability to be used as interference correction factor. The interference correction factors were monitored during 3 months, showing to be fairly stable over time (20 and 10 mg l^{-1} concentrations of Cl and Ca, respectively, were used in these studies).

The interference ratios were used in elemental equations to correct for the effect of polyatomic Cl and Ca species on ^{51}V , ^{53}Cr , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{75}As and ^{107}Ag isotopes. The software of the instrument performed an automatic correction for isobaric interferences. The correction equations for both types of interferences are shown in Table 2.

3.2. ICP-MS quantitative and semi-quantitative approaches figures of merit

Table 3 shows the detection limits (LODs) for both calibration approaches. The values are 10–100-fold lower than those reported by Baxter et al. [18], Pérez-Jordan et al. [19], Almeida and Vasconcelos [22], Taylor et al. [24] and Gómez et al. [26], all of them obtained using ICP-Quadropole MS apparatus. In general, major and minor elements in wine, such as Al, Cr and Fe, presents the highest LODs, nevertheless always lower than $0.1 \mu\text{g l}^{-1}$. The values are low enough to enable quality and

Table 2
Elemental equations applied for compensation of isobaric and matrix-induced polyatomic interferences in ICP-MS measurements

Analyte/isotope	Interfering species	Correction equations
^{51}V	$^{35}\text{Cl}^{16}\text{O}$	$\text{V} = I(^{51}\text{V}) - 0.0015 \times I(^{35}\text{Cl})$
^{53}Cr	$^{40}\text{Ar}^{13}\text{C}$, $^{35}\text{Cl}^{18}\text{O}$	$\text{Cr} = I(^{53}\text{Cr}) - 0.002 \times I(^{13}\text{C}) - 0.0015 \times I(^{35}\text{Cl})$
^{57}Fe	$^{40}\text{Ca}^{16}\text{O}^{1}\text{H}$	$\text{Fe} = I(^{57}\text{Fe}) - [0.0001 \times A(^{40}\text{Ca})/A(^{43}\text{Ca}) \times I(^{43}\text{Ca})]$
^{59}Co	$^{43}\text{Ca}^{16}\text{O}$	$\text{Co} = I(^{59}\text{Co}) - 0.0009 \times I(^{43}\text{Ca})$
^{60}Ni	$^{44}\text{Ca}^{16}\text{O}$	$\text{Ni} = I(^{60}\text{Ni}) - [0.0002 \times A(^{44}\text{Ca})/A(^{43}\text{Ca}) \times I(^{43}\text{Ca})]$
^{75}As	$^{40}\text{Ar}^{35}\text{Cl}$	$\text{As} = I(^{75}\text{As}) - 0.0002 \times I(^{35}\text{Cl})$
^{82}Se	^{82}Kr	$\text{Se} = I(^{82}\text{Se}) - [A(^{82}\text{Kr})/A(^{83}\text{Kr}) \times I(^{83}\text{Kr})]$
^{107}Ag	$^{91}\text{Zr}^{16}\text{O}$	$\text{Ag} = I(^{107}\text{Ag}) - 0.025 \times I(^{91}\text{Zr})$
^{115}In	^{115}Sn	$\text{In} = I(^{115}\text{In}) - [A(^{115}\text{Sn})/A(^{118}\text{Sn}) \times I(^{118}\text{Sn})]$
^{138}Ba	^{138}Ce , ^{138}La	$\text{Ba} = I(^{138}\text{Ba}) - [A(^{138}\text{La})/A(^{139}\text{La}) \times I(^{139}\text{La})] - [A(^{138}\text{Ce})/A(^{140}\text{Ce}) \times I(^{140}\text{Ce})]$
^{187}Re	^{187}Os	$\text{Re} = I(^{187}\text{Re}) - [A(^{187}\text{Os})/A(^{189}\text{Os}) \times I(^{189}\text{Os})]$

legal control of the contamination elements in wine. It should be referred that the International Organisation of Vine and Wine (OIV) defines maximum acceptable values for the concentration of the elements Cu, Zn, As, Cd and Pb in wine, of 1, 5, 0.2, 0.01 and 0.20 mg l⁻¹, respectively [6]. The semi-quantitative approach presents LODs, for most of the studied elements, similar or slightly higher than those obtained by the quantitative approach.

Results concerning the recovery tests are also present in Table 3. It can be seen that if Cr is excluded, recoveries between 80 and 120% were obtained for white and red wines. These recovery percentages are similar to those obtained by several authors [18,19,22] for table wines, using sample pre-preparation other than dilution or sample nebulizers other than crossflow. For Cr, an average recovery higher than 120% was obtained. This indicates that the correction of the matrix-induced polyatomic of $^{40}\text{Ar}^{13}\text{C}$ and $^{35}\text{Cl}^{18}\text{O}$ species was not effective for this element. Therefore, it was concluded that Cr could not be measured in the wine samples with the present methodology. The mathematical corrections used for V, Fe, Co, Ni and As interferences seem to be

appropriate. Some elements of medium mass (Ag, Cd, In) show recoveries close to 80%, despite the use of an internal standard with a similar mass (Rh). Re seems to be an appropriate internal standard for the elements with higher mass. It should be referred that in an initial step of our study, an attempt was made to use Sc as internal standard for elements of low mass, such as Li, Be and Al. However, the results were not satisfactory probably due to interferences affecting Sc. Once sample pre-treatment consists in a dilution, without destruction of the organic material, the results obtained are satisfactory. Preliminary tests in order to determine internal calibration recoveries showed similar values to those obtained by external calibration.

3.3. Comparison of analytical results obtained by ICP-MS quantitative and semi-quantitative approaches

In order to compare the results of quantitative and semi-quantitative approaches, white and red table wines were analysed, in parallel, by both modes of analysis (Cr was excluded). For each wine sample three independent replicates (external cal-

Table 3
Limits of detection (LODs)^a for both quantitative (Q) and semi-quantitative (SQ) approaches of analysis (μg l⁻¹). Recoveries percentages^b obtained using the quantitative (Q) approach

Element	LOD (Q)	LOD (SQ)	Recovery (Q)		Element	LOD (Q)	LOD (SQ)	Recovery (Q)	
			White wine	Red wine				White wine	Red wine
Li	0.003	0.003	97 ± 1	88 ± 1	Se	0.01	0.02	97.7 ± 0.9	88.9 ± 2
Be	0.001	0.003	98 ± 2	89 ± 1	Rb	0.001	0.001	96 ± 2	103 ± 3
Al	0.1	0.08	90 ± 2	99 ± 5	Sr	0.002	0.004	98 ± 18	98 ± 2
V	0.001	0.003	102 ± 1	101 ± 2	Ag	0.001	0.006	79 ± 3	81 ± 2
Cr	0.2	0.3	124 ± 4	136 ± 14	Cd	0.001	0.001	82 ± 1	83.0 ± 0.1
Mn	0.001	0.003	104 ± 4	105 ± 8	In	0.0002	0.0005	84 ± 2	83.0 ± 0.3
Fe	0.2	0.2	96 ± 4	110 ± 2	Cs	0.0003	0.0004	89 ± 1	98 ± 1
Co	0.0004	0.001	93 ± 2	90.8 ± 0.5	Ba	0.002	0.010	109 ± 2	81 ± 3
Ni	0.006	0.02	99 ± 3	102 ± 4	Hg	0.01	0.008	99 ± 3	100 ± 3
Cu	0.01	0.03	97 ± 3	91 ± 2	Tl	0.0003	0.0006	91 ± 3	93.7 ± 0.9
Zn	0.02	0.2	95 ± 3	97 ± 3	Pb	0.001	0.006	99 ± 1	92 ± 1
Ga	0.002	0.004	87.6 ± 0.6	84.8 ± 0.6	Bi	0.001	0.02	88 ± 6	93 ± 6
As	0.002	0.005	98 ± 3	95.0 ± 0.8	U	0.003	0.5	104 ± 5	106 ± 2

^a LODs were calculated as being the concentrations corresponding to signals equal to three-fold the standard deviation of a blank solution signal (three replicates).

^b Mean of recovery values of three different spikes ± S.D.

Table 4
Concentrations^a of the contaminant elements obtained ($\mu\text{g l}^{-1}$), using both the quantitative (Q) and semi-quantitative methods (SQ), for wine samples

Element	White wine		Red wine	
	Quantitative mode	Semi-quantitative mode	Quantitative mode	Semi-quantitative mode
Li	4.4 (0.2)	4.3 (0.2)	7.8 (0.1)	7.55 (0.06)
Be	1.09 (0.04)	0.96 (0.06)	0.127 (0.006)	0.15 (0.07)
Al	1437 (32)	1364 (9)	671 (3)	528 (5)
V	59 (2)	58.0 (0.8)	24.2 (0.2)	23.17 (0.07)
Mn	1036 (28)	1009 (3)	879 (24)	828 (2)
Fe	2147 (21)	1168 (5)	4490 (12)	2587 (14)
Co	4.3 (0.1)	4.47 (0.09)	2.87 (0.02)	2.76 (0.03)
Ni	24.5 (0.9)	27.5 (0.8)	18.2 (0.4)	19.2 (0.5)
Cu	49 (2)	44.2 (0.7)	237 (3)	226 (4)
Zn	661 (10)	819 (6)	642 (19)	758 (6)
Ga	1.7 (0.2)	1.6 (0.1)	2.1 (0.2)	1.83 (0.07)
As	10.6 (0.6)	11.2 (0.3)	3.73 (0.09)	3.76 (0.09)
Se	0.9 (0.1)	ND ^b	0.6 (0.2)	ND ^b
Rb	453 (10)	429.9 (0.8)	674 (18)	627 (3)
Sr	243 (6)	239 (3)	326 (10)	303 (11)
Ag	ND ^b	ND ^b	ND ^b	ND ^b
Cd	0.48 (0.02)	0.28 (0.04)	0.30 (0.02)	0.21 (0.01)
In	0.12 (0.01)	0.02 (0.01)	0.005 (0.003)	ND ^b
Cs	3.6 (0.01)	3.80 (0.01)	3.59 (0.03)	3.80 (0.1)
Ba	89 (2)	89.1 (0.3)	79 (1)	77.3 (0.03)
Hg	ND ^b	ND ^b	ND ^b	ND ^b
Tl	0.24 (0.01)	0.15 (0.03)	0.147 (0.006)	0.145 (0.002)
Pb	14.43 (0.02)	14.0 (0.3)	19.2 (0.3)	19.0 (0.1)
Bi	1.3 (0.1)	1.3 (0.7)	1.2 (0.6)	1.7 (0.1)
U	0.69 (0.01)	2.04 (0.08)	0.47 (0.02)	1.67 (0.04)

^a Concentration values correspond to the mean of three independent replicates (quantitative mode) and three dependent replicates (semi-quantitative mode) corresponding standard deviation (in brackets).

^b ND – not detected.

ibration) were carried out and the mean and the respective R.S.D. (%) calculated for each element.

The values of R.S.D. (%) changed between 0.2 and 4% for most elements (Table 4), both for quantitative and semi-quantitative approach. For Ga, Se, In and Bi R.S.D. (%) values were observed in white and red wine as follows: 12 and 10; 11 and 33, 8 and 60; 8 and 50%, respectively. These results could probably be explained by their relatively low concentration in wines. Nevertheless, these precisions are slightly better than those obtained by Pérez-Jordán et al. [19] and similar to those reported by Almeida and Vasconcelos [22].

As shown in Table 4, comparable results (differences lower than 20%) were obtained for all of the elements with exception of Fe, Zn, Se, Cd, In, Tl and U (white wine) and Al, Fe, Se, Cd, In, Bi and U (red wine). In most cases the differences were lower than 6% (white wine) and 10% (red wine). For Be and Ga the differences were between 10 and 20% in both wines. Se was not detected by semi-quantitative mode of analysis, neither in white nor red wine. For In and Tl the main reason for the differences in white wine, 80 and 60%, respectively, may be the fact that the respective concentrations are near the analytical limits of both modes of analysis, which precluded their accurate determination. For Cd, differences of 42 and 30% in

white and red wine were observed, probably due to their low concentration.

The differences observed for U, near to 200%, may be explained by the unsuitability of the semi-quantitative mode of analysis for such a high mass element. Differences between 42 and 45% were observed for Fe results. The results of quantitative mode were confirmed by AAS analysis, leading to the conclusion that either the automatic corrections made by the software for semi-quantitative mode were not successful or the calibration was not fit. As like for Fe, the differences observed for Al (21% in red wine) and Zn (23% in white wine and 18% in red wine) may be related to the unsuitability of the calibration used in semi-quantitative mode of analysis for major elements. In fact, it was used a standard solution with $10 \mu\text{g l}^{-1}$ of major, minor, trace and ultra-trace elements. As previously referred in Section 1, since sensitivity depends on experimental factors, it is important to update the set of response factors for each element in order to achieve accurate results. With reference to the importance of accurate results, such update should be performed with a multielement standard solution containing, for each element, the approximate concentration of those observed in wine.

In reference to the elements under legal control, it should be noted that for Zn and Cd, the comparison study revealed

large differences between the results obtained by the two calibration approaches (higher than 10%) and, hence, demonstrate the unsuitability of semi-quantitative approach in the analysis of these elements in wine. A linear least-squares adjustment of the results obtained by both modes of analysis was performed in order to evaluate the potential risk of error (the 95% confidence limits of the linear regression parameters are given). Non-comparable results (differences >20%) were not considered in the adjustment. A deviation of the slope from unity indicates proportional discrepancies between the two methods. A non-zero intercept is diagnosed as a constant discrepancy. The regression line for white wine yielded the equation: $y = (0.957 \pm 0.008)x + (1 \pm 4)$, $R = 0.9999$ ($n = 16$) (95% confidence level). For red wine the equation was $y = (0.937 \pm 0.005)x + (1 \pm 2)$, $R = 0.9999$ ($n = 15$) (95% confidence level). The regression line of the global results (including white and red wine samples) yielded the equation $y = (0.952 \pm 0.006)x \pm 2$, $R = 0.9999$ ($n = 31$) (95% confidence level). In both cases, white and red sample wines, high correlations were found, being very close to unity. However, the semi-quantitative mode analytical results are slightly lower than quantitative mode results, suggesting the existence of a slight bias. These observations are similar to those registered by Almeida and Vasconcelos [22], obtained either with table and fortified wines.

3.4. Validation of ICP-MS procedures

As referred, for validation of ICP-MS quantitative approach, six elements of a Portuguese red table wine were measured both by ICP-MS and AAS (Fig. 2). The differences between the results obtained by the two techniques were lower than 5% for all elements, with exception of Al (18%), demonstrating the accuracy of ICP-MS method. Linear least squares adjustment was applied to the six elements determined by AAS (x -axis) and ICP-MS (y -axis). The regression line of the global results yielded the equation: $y = (1.01 \pm 0.04)x + (3 \pm 40)$ (95% confidence level), with a correlation coefficient of $R = 0.9995$ ($n = 6$). Evidence of relative or fixed bias was not observed.

The results concerning the analysis of provisionally certified wines by quantitative ICP-MS approach are shown in Fig. 3.

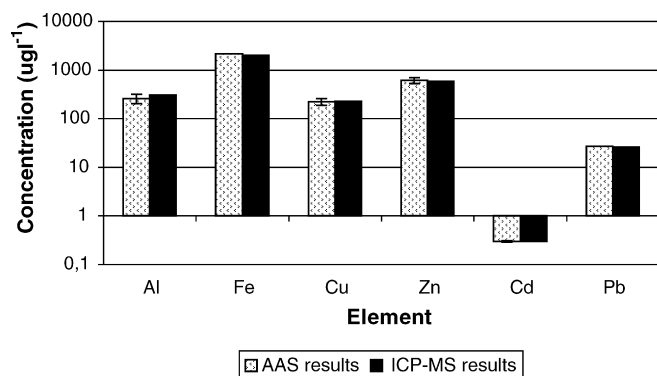


Fig. 2. Comparison between AAS and ICP-MS results ($\mu\text{g l}^{-1}$) obtained for the elements Al, Fe, Cu, Zn, Cd and Pb measured in a Portuguese red wine. The y -axis represents the logarithm of concentrations.

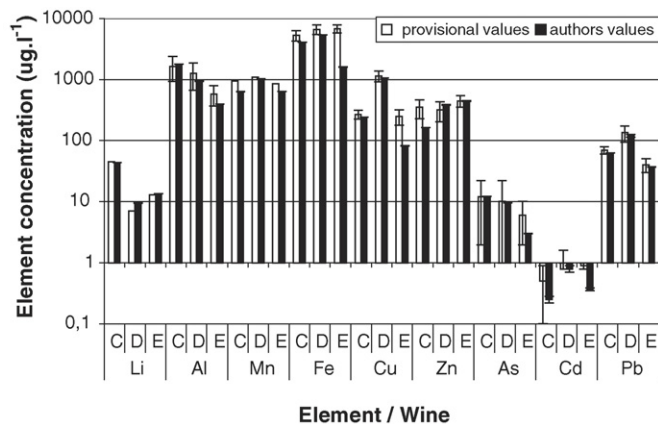


Fig. 3. Data for reference wines (BCR C, BCR D and BCR E, in the graph referred as C, D and E, respectively), showing values obtained by the authors and provisional values. The y -axis represents the logarithm of concentrations ($\mu\text{g l}^{-1}$) in order to obtain a better scatter of the data. Information about Li and Mn (provisional) concentration standard deviation of the three wines was not available.

Acceptable agreement was obtained within the tolerances supplied for all samples and analytes with the exceptions of Fe (BCR D and BCR E wines), Cd and Cu (BCR E wine). A linear least squares adjustment was applied to all elements determined, provisional data (x -axis) and our data (y -axis). For BCR C wine the equation $y = (0.79 \pm 0.09)x + (14 \pm 55)$ (95% confidence level), with a correlation coefficient of $R = 0.99$ ($n = 9$), was obtained. For BCR D wine the equation $y = (0.80 \pm 0.03)x + (40 \pm 75)$ (95% confidence level), with a correlation coefficient of $R = 0.999$ ($n = 9$), was obtained. If we exclude Fe data, for BCR E wine the equation $y = (0.8 \pm 0.2)x - (7 \pm 75)$ (95% confidence level), with a correlation coefficient of $R = 0.97$ ($n = 8$) was observed. The regression line of the global results (including the three wines), yielded the equation: $y = (0.80 \pm 0.03)x + (14 \pm 55)$ (95% confidence level), with a correlation coefficient of $R = 0.99$ ($n = 26$). The differences between our data and the provisional values indicate a systematic bias (our results were lower than the provisional values, that is, a slope significantly <1). The reason for this may be related to the precipitation phenomena observed in all the wines, but more intense in red wine (BCR E wine). As previously mentioned the wines are from 1992 year and showed some precipitation material. It is known that metals interact with polyphenols and pectic polysaccharides species, which, in part, precipitate during the ageing of wines.

4. Conclusions

In the present work it was demonstrated that ICP-MS quantitative and semi-quantitative approaches offer valuable alternatives to table wine characterization and comparison purposes. However, as a tool for legal control, quantitative approach is the most suitable alternative. For some elements with legal importance, namely for Fe, Zn and Cd, the comparison study reveals large differences between the results obtained using quantitative and semi-quantitative calibration. In spite of that, analytical

results of both methods are comparable in terms of precision and accuracy (relative differences <20%) for most of the elements. In contrast with quantitative methodology, semi-quantitative methodology is faster, 67 s per sample, which allows high sample throughput. Another advantage is the lower reagent consumption.

Acknowledgements

To “Programa de Apoio à Reforma dos Laboratórios do Estado” a research scholarship and to “Fundação para a Ciência e Tecnologia”, Lisbon, Portugal, a PhD scholarship (POCI2010, medida IV.3, SFRH/BD/17237/2004). To Doctor C. Marisa Almeida, from LAQUIPAI (Porto), for providing the reference wines.

References

- [1] A.S. Curvelo-Garcia, Controlo de Qualidade dos Vinhos, Química Enológica Métodos Analíticos, Instituto da Vinha e do Vinho, Lisboa, 1988 (Chapter VI).
- [2] A.S. Curvelo-Garcia, S. Catarino, *Ciência Téc. Vitiv.* 13 (1) (1998) 49.
- [3] S. Catarino, Ocorrência de chumbo e cádmio em vinhos, M.Sc. Thesis, University of Porto, Porto, 2000.
- [4] S. Catarino, A.S. Curvelo-Garcia, R. Bruno de Sousa, *At. Spectrosc.* 23 (6) (2002) 196.
- [5] S. Catarino, I. Pimentel, A.S. Curvelo-Garcia, *At. Spectrosc.* 26 (2) (2005) 73.
- [6] OIV, Recueil des Methods Internationales d’analyse des vins et des Mouts, Organisation Internationale de la Vigne et du Vin, Paris, 2005.
- [7] J.R. Dean, L. Ebdon, C. Massey, *Food Addit. Contam.* 7 (1) (1990) 109.
- [8] B.L. Gulson, T.H. Lee, K.J. Mizon, M.J. Korsch, H.R. Eschnauer, *Am. J. Enol. Vitic.* 43 (2) (1992) 180.
- [9] S. Augagneur, B. Medina, F. Grousset, *Fresenius J. Anal. Chem.* 357 (1997) 1149.
- [10] K.J.R. Rosman, W. Chisholm, S. Jimi, J.-P. Candelone, C.F. Boutron, P.-L. Teissedre, F.C. Adams, *Environ. Res.* 78 (1998) 161.
- [11] C.M.R. Almeida, M.T.S.D. Vasconcelos, *J. Anal. At. Spectrom.* 14 (1999) 1815.
- [12] I. Rodushkin, F. Odman, P.K. Appelblad, *J. Food Comp. Anal.* 12 (1999) 243.
- [13] B. Médina, S. Augagneur, M. Barbaste, F.E. Grousset, P. Buat-Ménard, *Food Addit. Contam.* 17 (6) (2000) 435.
- [14] M. Barbaste, L. Halicz, A. Galy, B. Medina, H. Emteborg, F.C. Adams, R. Lobinski, *Talanta* 54 (2001) 307.
- [15] C.M. Almeida, M.T.S.D. Vasconcelos, *J. Anal. At. Spectrom.* 16 (2001) 607.
- [16] A. Stroh, P. Bruckner, U. Vollkopf, *At. Spectrosc.* 2 (1994) 100.
- [17] J.D. Greenough, H.P. Longerich, S.E. Jackson, *Aust. J. Grape Wine Res.* 3 (1997) 75.
- [18] M.J. Baxter, H.C. Crews, M.J. Dennis, I. Goodall, D. Anderson, *Food Chem.* 60 (3) (1997) 443.
- [19] M.-Y. Pérez-Jordán, J. Soldevila, A. Salvador, A. Pastor, M. de la Guardia, *J. Anal. At. Spectrom.* 13 (1998) 33.
- [20] N. Jakubowski, R. Brandt, D. Stuewer, H.R. Eschnauer, Gortges, *Fresenius J. Anal. Chem.* 364 (1999) 424.
- [21] M.M. Castiñeira, R. Brandt, A. Von Bohlen, N. Jakubowski, *Fresenius J. Anal. Chem.* 370 (2001) 553.
- [22] C.M. Almeida, M.T.S.D. Vasconcelos, *Anal. Chim. Acta* 463 (2002) 165.
- [23] C.M.R. Almeida, M.T.S.D. Vasconcelos, M. Barbaste, B. Medina, *Anal. Bioanal. Chem.* 374 (2002) 314.
- [24] V.F. Taylor, H.P. Longerich, J.D. Greenough, *J. Agric. Food Chem.* 51 (2003) 856.
- [25] G. Nicolini, R. Larcher, P. Pangrazzi, L. Bontempo, *Vitis* 43 (1) (2004) 41.
- [26] M.D.M.C. Gómez, R. Brandt, N. Jakubowski, J.T. Andersson, *J. Agric. Food Chem.* 52 (2004) 2953.
- [27] G. Thiel, G. Geisler, I. Blechschmidt, K. Danzer, *Anal. Bioanal. Chem.* 378 (2004) 1630.
- [28] G.J. Martin, M. Mazure, C. Joutiteau, Y.L. Martin, L. Aguilé, P. Allain, *Am. J. Enol. Vitic.* 50 (4) (1999) 409.
- [29] M. Barbaste, Recherches sur l’origine géographique et le millesime des vins, Ph.D. Thesis, Université de Pau et Des Pays de l’Adour, 2001.
- [30] S. Sagrado, M.Y. Pérez-Jordan, A. Pastor, A. Salvador, M. De la Guardia, *J. Chemometrics* 16 (2002) 305.
- [31] E. Pruszkowski, Field Application Report, Perkin-Elmer, 2004.
- [32] T.W. May, R.H. Wiedmeyer, *At. Spectrosc.* 19 (5) (1998) 150.
- [33] Software Guide, Elan Version 2.4, Perkin-Elmer Scienc, Canada, 2001.