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Application of a microwave-based desolvation system for multi-elemental analysis of wine by inductively coupled plasma based techniques

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ABSTRACT

Elemental wine analysis is often required from a nutritional, toxicological, origin and authenticity point of view. Inductively coupled plasma based techniques are usually employed for this analysis because of their multi-elemental capabilities and good limits of detection. However, the accurate analysis of wine samples strongly depends on their matrix composition (i.e. salts, ethanol, organic acids) since they lead to both spectral and non-spectral interferences. To mitigate ethanol (up to 10% w/w) related matrix effects in inductively coupled plasma atomic emission spectrometry (ICP-AES), a microwave-based desolvation system (MWDS) can be successfully employed. This finding suggests that the MWDS could be employed for elemental wine analysis. The goal of this work is to evaluate the applicability of the MWDS for elemental wine analysis in ICP-AES and inductively coupled plasma mass spectrometry (ICP-MS). For the sake of comparison a conventional sample introduction system (i.e. pneumatic nebulizer attached to a spray chamber) was employed. Matrix effects, precision, accuracy and analysis throughput have been selected as comparison criteria. For ICP-AES measurements, wine samples can be directly analyzed without any sample treatment (i.e. sample dilution or digestion) using pure aqueous standards although internal standardization (IS) (i.e. Sc) is required. The behaviour of the MWDS operating with organic solutions in ICP-MS has been characterized for the first time. In this technique the MWDS has shown its efficiency to mitigate ethanol related matrix effects up to concentrations of 1% (w/w). Therefore, wine samples must be diluted to reduce the ethanol concentration up to this value. The results obtained have shown that the MWDS is a powerful device for the elemental analysis of wine samples in both ICP-AES and ICP-MS. In general, the MWDS has some attractive advantages for elemental wine analysis when compared to a conventional sample introduction system such as: (i) higher detection capabilities; (ii) lower ethanol matrix effects; and (iii) lower spectral interferences (i.e. ArC^+) in ICP-MS.

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1. Introduction

Determination of the elemental composition of wines is a very interesting and useful issue for different reasons. From a toxicological point of view, wine is an important dietary source of some elements that can be harmful for humans if dosed at sufficiently high levels (i.e. Pb, As or Cd) [1]. When dealing with the wine manufacturing processes some elements have determinant effects on the final organoleptical properties and, therefore, their concentration must be monitored (i.e. Cu, Fe) [2]. Finally, the elemental composition can be used as a fingerprint of a particular wine so its origin and authenticity can be traced back [3]. It is important to note that the elemental content of wine depends on several variables (i.e. grapes type, soil characteristics and environmental conditions) and can be altered due to contamination from several sources during the manufacturing process [4,5]. The determination of elemental composition of wines has been addressed using a wide spectrum of different techniques such as chromatography [6], electrochemical methods [7–9] or atomic spectrometry [10–12]. In the last group, inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) are the most employed because of their good analytical performance (i.e. low limits of detection, multi-elemental capabilities and wide dynamic range). However, direct analysis of wine samples using ICP techniques is very troublesome due to severe interferences caused by the matrix components. Wines have a complex composition that includes different inorganic and organic dissolved substances. In the former group potassium, sulphates and phosphates are the most concentrated ones (i.e. present in the g L^{-1} range) [13,14] whereas, among the organic compounds, ethanol is the main component (found typically in the 10–15% range) but compounds such as monosaccharides and polysaccharides, polyalcohols and organic acids can also be found at concentrations of several g L^{-1} [14]. Interferences due to wine matrix components in ICP techniques can be divided in two groups: spectral and non-spectral. The former are related to the limited resolution capability of the spectrometer. Thus, for instance, the analysis of Se in carbon-rich matrices using ICP-AES is interfered by the CO molecular band [15]. In ICP-MS, the analysis of Cr and Cu using the most abundant isotopes (i.e. $^{52}\text{Cr}^+$ and $^{63}\text{Cu}^+$, respectively) in matrices with high levels of carbon and/or sodium could be hindered due to the $^{52}\text{ArC}^+$ and $^{63}\text{ArNa}^+$ polyatomic interferences. Non-spectral interferences are defined as any signal variation induced by the matrix components. Thus, the signal in both ICP-AES and ICP-MS could be enhanced or depressed when carbon [16,17] or easily ionisable elements (EIE) [18] are present in the matrix. Augagneur et al. [19] reported a 5 fold signal suppression when an undiluted wine samples was introduced in the ICP-MS compared with aqueous standards. These interferences are usually generated in the sample introduction system and/or in the processes of excitation of the atoms in ICP-AES and the transport of the ions in ICP-MS. In addition, wine matrix components could produce the clogging of the nebulizer and/or the injection tube and the deposition of material on the torch and on the ion lenses system [20]. The magnitude of these interferences varies with the amount of the matrix components loading the

plasma and its energetic capability to handle them. These, in turn, depend on the concentration of the sample matrix components, the instrumental conditions, the sample introduction system and the sample treatment used [21].

Different sample treatments methodologies have been employed to mitigate matrix effects for elemental wine analysis in ICP techniques. Thus, wine dilution (ratios ranging from 1:1 to 1:10) [11,22–26], sample evaporation to dryness and subsequent dissolution of the residue [27] and UV [28] or MW-radiation aided sample digestion [4,5] have been employed. In general terms, all the proposed sample treatments give rise to a significant reduction in the analysis throughput, increase the limit of detection of the method and enhance the sample contamination risk during sample handling. An alternative approach used to minimize matrix effects is the use of different calibration strategies. In general terms, the analysis of wine samples has been usually performed by means of matrix matched standards according to the sample preparation step procedure. Nonetheless, standard addition [22,23,4] and internal standardization (IS) [22,4] have also been tested.

In addition, in order to avoid complex sample treatments, as well as matrix effects, several authors have also evaluated the use of different sample introduction systems alternative to the conventional one (i.e. a pneumatic nebulizer attached to a spray chamber). Elemental wine analysis has been successfully performed by means of flow injection systems [29,30] or micro-concentric nebulizers [19]. When using these devices, the amount of matrix transported to the plasma is reduced and, hence, the magnitude of matrix effects. A membrane-based desolvation system has also been evaluated for elemental wine analysis [31]. However, the recoveries obtained with this device have been very poor since its behaviour strongly depends on the wine matrix composition.

Recently, a new design of a microwave-based desolvation system (MWDS) has been reported in the literature [32,33]. In this system the aerosol generated by a concentric pneumatic nebulizer is introduced into a single pass spray chamber vertically placed at the centre of a MW cavity where it is irradiated. Afterwards, before the aerosol reaches the plasma, part of the solvent vapour is eliminated by means of two condensers placed in series. The MWDS has afforded higher sensitivities and up to 10 times lower limits of detection than a conventional sample introduction system (i.e. pneumatic concentric nebulizer coupled to a double pass spray chamber) [32]. This fact makes the system very suitable for the analysis of elements in very low concentrations. The microwave-based desolvation system has been evaluated in both ICP-AES and ICP-MS using different solutions of inorganic acids, organic acids and alcohols [32–35]. Results obtained show that analytical figures of merit of the MWDS are strongly affected by matrix characteristics since MW heating is related to the sample dielectric properties [34,35]. Nevertheless, the MWDS has been employed successfully to mitigate non-spectral matrix effects in ICP-AES due to the presence of alcohol solutions or organic acids [33]. Thus, the emission intensity obtained for an ethanol 10% w/w solution is the same to that obtained when using water standards. These results suggest that the MWDS could be a useful sample introduction system when dealing with alcohol containing solutions. This fact is the key

for elemental wine analysis since pure aqueous standards (i.e. without ethanol) could be used to perform the analysis.

The aim of the present work is to evaluate the behaviour of the MWDS for the multi-elemental analysis of wine samples in ICP-AES and ICP-MS. To this end, the behaviour of the MWDS operating with organic solutions has been firstly evaluated in ICP-MS. After that, different sample treatments and calibration strategies have been evaluated in terms of matrix effects, precision, accuracy and analysis throughput. For the sake of comparison, a conventional sample introduction system (i.e. pneumatic nebulizer attached to a spray chamber) has also been tested. Finally, the MWDS was employed to analyze different wine samples.

2. Experimental

2.1. Reagents

High purity water (i.e. with conductivity lower than $18\text{ M}\Omega\text{ cm}^{-1}$) obtained from a Milli-Q water system (Millipore Inc., Paris, France), nitric acid (Trace select™, Fluka Chemie GmbH, Switzerland), ethanol (LiChrosolv™, Merck, Darmstadt, Germany), Merck IV and Merck XII multi-elemental solutions (Merck, Darmstadt, Germany) and Sc, Be, Ti, Ce and U single-element standard solutions (J.T. Baker, Deventer, Netherlands) were used throughout the work.

2.2. Samples

Four different Spanish wine samples were analyzed: a white one (Enrique Mendoza, 2004), two red (Dominio de la peseta, 2003 and Marques de Alicante, 2002) and one brandy (Puertoluz, 2001). These samples were chosen for covering a wide range of matrix characteristics and origins. Samples were acquired at local supermarkets. The ethanol content for the white and red wines was ranged between 10 and 11% w/w whereas for the brandy was 28% w/w.

2.3. ICP instrumentation

ICP-AES measurements were performed by means of an Optima 3000 ICP-AES system (Perkin-Elmer, Shelton, CT, USA). A VG PQ Excell CCT instrument (ThermoElemental, Winsford, Cheshire, UK) was employed for ICP-MS measurements. Table 1 shows the operating conditions employed with both instruments. In all cases, experimental conditions were optimized in order to obtain the lowest ethanol matrix effects and the highest sensitivity. Emission lines of elements used in ICP-AES together with their E_{sum} , defined as the sum of excitation and ionization energies, are shown in Table 2. In addition, the m/z values of the isotopes measured by ICP-MS are gathered in Table 2.

2.4. Strategies of analysis

Different sample introduction systems, sample treatments and calibration methodologies have been evaluated through this work for elemental wine analysis in both ICP-AES and

Table 1 – Operating conditions employed in ICP-AES and ICP-MS

Perkin-Elmer Optima 3000 ICP-AES	
Plasma forward power (W)	1450
Argon flow rate (L min^{-1})	
Plasma	15
Auxiliary	0.5
Nebulizer	$0.6^{\#}-0.7^{\$}$
Sample uptake rate ($\mu\text{L min}^{-1}$)	100
Observation height (mm ALC)	$5^{\#}-10^{\$}$
Injector inner tube diameter (mm)	0.8
Integration time (s)	0.1
Read time (s)	1
Replicates	3
VG PQ-Excell CCT ICP-MS	
Plasma forward power (W)	1450
Argon flow rate (L min^{-1})	
Plasma	13
Auxiliary	1.0
Nebulizer	Variable
Sample uptake rate ($\mu\text{L min}^{-1}$)	Variable
Scanning mode	Peak Hopping
Points per peak	3
Dwell time (μs)	500
Number of sweeps	30
Replicates	3
[#] Conventional sample introduction system (CS).	
^{\$} MWDS.	

ICP-MS. Fig. 1 shows a detailed scheme of the different experimental procedures evaluated in the present work.

2.4.1. Sample introduction systems

For each ICP technique the MWDS and the conventional sample introduction system supplied with the instrument for routine analysis were employed. When dealing with ICP-AES experiments, the conventional system (CS) consisted of a pneumatic concentric nebulizer (TR-30-A3, Meinhard, Santa Ana, CA, USA) coupled to a Rytan double pass spray chamber. For ICP-MS measurements the conventional system (TCS) consisted of a Conikal nebulizer (AR-30-1F3E, Glass Expansion, Melbourne, Australia) and a thermostated (-5°C) single pass spray chamber provided with an impact bead. The detailed description of the MWDS system can be found elsewhere [32].

Sample uptake rate was controlled in all cases by means of a peristaltic pump (Perimax 12 Spetec GmbH, Erding, Germany). The nebulizer gas was supplied at a controlled flow rate by means of a calibrated flowmeter (Cole-Palmer Ins. Co., Chicago, IL, USA) in all the experiments, irrespective of the sample introduction system employed.

2.4.2. Sample treatments

For ICP-AES measurements, wine samples were analyzed directly or after dilution 1:5 using both the CS and the MWDS. When using ICP-MS, only dilution 1:10 was employed. As it has been pointed out previously, wine matrix components are a source of interferences (i.e. spectral and non-spectral). In

Table 2 – Analytical lines of the elements with their excitation and ionization energies, as well as m/z values of isotopes analyzed using ICP-AES and ICP-MS, respectively

Elements	ICP-AES		ICP-MS	
	Wavelength (nm) (line type)	E_{sum} (eV) ^{&}	m/z	E_{ion} (eV)
Li	670.781 (I)	1.85	7	5.39
Be	234.861 (I)	5.28	9	9.32
	313.042 (II)	13.28		
Mg	285.213 (I)	4.35	–	–
	280.270 (II)	12.07		
Na	589.592 (I)	2.10	–	–
Al	396.152 (I)	3.14	27	5.96
Ar	420.068 (I)	3.95	–	–
Ca	396.847 (II)	9.26	–	–
Sc	357.253 (II)	10.03	45	6.54
	361.384 (II)	9.99		
Ti	334.941 (II)	10.57	47	6.82
	336.121 (II)	10.54		
V	–	–	51	6.74
Cr	267.710 (II)	12.92	52	6.77
Mn	257.610 (II)	12.29	55	7.43
Fe	238.204 (II)	13.07	–	–
Co	228.616 (II)	13.70	59	7.86
Ni	221.647 (II)	14.03	60	7.64
Cu	324.754 (II)	3.82	65	7.72
Zn	213.856 (I)	5.80	66	9.40
Ga	294.364 (I)	4.31	69	5.99
Sr	460.733 (I)	2.69	88	5.70
Zr	–	–	90	6.84
Mo	–	–	95	7.10
Ag	–	–	107	7.58
Cd	214.438 (II)	14.77	111	8.99
In	–	–	115	5.79
Ba	455.403 (I)	7.93	138	5.21
Ce	–	–	140	5.47
W	–	–	182	7.98
Tl	–	–	205	5.11
Pb	220.353 (II)	14.79	208	7.42
U	–	–	238	6.08

[&] $E_{\text{sum}} = E_{\text{exc}} + E_{\text{ion}}$.

order to evaluate the magnitude matrix effects for the different sample treatments, a recovery test was performed. To this end, wine samples were spiked with a small volume of the multi-elemental solution Merck IV and XII (i.e. 10 mg L^{-1} and $100 \mu\text{g L}^{-1}$ for ICP-AES and ICP-MS, respectively).

As a reference value, wine samples were analyzed by ICP-AES and ICP-MS using the respective conventional system (i.e. CS or TCS) after a microwave (MW) aided acid digestion in a closed vessel. Sample digestion destroys organic wine components (i.e. ethanol, organic acids, polysaccharides, etc.) reducing their influence on analyte transport efficiency and plasma thermal conditions. Wine samples were digested in a CEM 100 MSP MW oven (Matthews, NC, USA) using the method recommended by the manufacturer for this kind of samples. Thus, 5 g of the selected wine were weighted into a PTFE 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 the MW oven. Finally, the digested sample was made up to 15 g using de-ionized water.

2.4.3. Calibration strategy

Several calibration strategies have been employed for elemental wine analysis in ICP-based techniques [22,4]. Among them, external calibration using aqueous and matrix matched standards and internal standardization were evaluated in the present work since both methodologies are the most convenient for multi-elemental analysis: they are easy to apply, consume a low sample volume and the analysis throughput is high.

The analysis of undiluted and diluted wine samples was performed using pure aqueous and ethanol standards for both the MWDS and the CS (or the TCS). For the digested wine samples, acid matched standards were prepared in order to minimize the matrix effects on the signal related to the acid employed in the digestion procedure [36].

Internal standardization methodology was employed for the analysis of undiluted, diluted and digested wine samples. Be, Sc, Ti and Ar were evaluated as internal standards for ICP-AES measurements whereas Be, Sc, Ce and U were tested for ICP-MS. The concentration of internal standard added to the

wine samples was 10 mg L^{-1} and $100 \mu\text{g L}^{-1}$ for ICP-AES and ICP-MS, respectively.

3. Results and discussion

3.1. Application of the MWDS in ICP-AES

3.1.1. Direct wine analysis

As it has been reported in previous works, no differences on the sensitivity and LODs are observed for the MWDS when working with pure aqueous and ethanol solutions up to 10% w/w [33]. These findings suggest that ethanol-containing samples (such as wine samples) can be directly analyzed using pure aqueous standards. At the present, there is not available any wine sample for which the elemental composition is certified. Therefore, a recovery test was performed to evaluate the possibility of direct wine analysis using the sample introduction systems tested.

Fig. 2 shows the recovery values obtained for several elements with the MWDS using two sets of standards prepared in different matrices (pure aqueous and ethanol 10% w/w). The results shown in this figure were obtained for the Dominio de la Peseta red wine, but similar results were obtained for the three remaining samples. Taking into account the recovery precision (i.e. 5% on average), values between 95 and 105% (i.e. dotted lines in Fig. 2) indicate a total recovery. As it can be observed in Fig. 2, the direct analysis of wine samples always provided recovery values lower than 100%. Nevertheless, the magnitude of the effects depends on the sample introduction system employed. Thus, when using the CS, higher sensitivity

Fig. 2 – Recoveries obtained for a spiked wine sample analyzed by ICP-AES using different sample introduction systems and standard solutions: (■) MWDS/ethanol 10% w/w standards; (□) MWDS/pure aqueous standards; (■) CS/ethanol 10% w/w standards.

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ties (i.e. 30% in average) for ethanol 10% w/w standards than for the pure aqueous ones were observed due to the highest aerosol transport efficiencies afforded by the former [37,38]. These results indicate that pure aqueous standards should be discarded for wine analysis using the CS. The recovery yield using the CS with ethanol 10% w/w standards was in the 70–80% range for most of the elements analyzed. The recovery values for the MWDS were between 50 and 60% for a confidence level of 95% (three replicates), irrespective of the set of standards used for calibration (pure aqueous and ethanol 10% w/w) [33]. No difference on the precision of the recovery yields for the MWDS and CS was observed. R.S.D. values ranged from 2 to 7% depending on the element considered (i.e. on average 4%).

The poor recovery values obtained for the direct wine analysis using both sample introduction systems (Fig. 2) can be attributed to the non-volatile wine matrix components since the volatile ones have been minimized for the CS using ethanol standards. In fact, it must be taken into account that wine contains a significant amount of easy ionisable elements (i.e. K^+ , Ca^{2+} , Mg^{2+}) [13,14], which are a well-known source of matrix effects in the plasma [18]. Nonetheless, matrix effects due to organic species (i.e. sugars, organic acids) should not be underestimated [17]. The MWDS affords higher analyte transport efficiencies than the CS. As a consequence, also the amount of interferences reaching the plasma increases thus giving rise to higher amounts of non-volatile matrix components in the plasma. Therefore, it must be taken into account that the magnitude of matrix effects due to these species is higher for the MWDS than for the CS [39]. In addition, non-volatile matrix components affect the evaporation and condensation process through the aerosol pathway modifying the analyte transport efficiency when comparing to pure aqueous or ethanol 10% w/w standards [40–42]. These phenomena may be important since the standards were not matrix matched for non-volatile compounds.

From the results shown in Fig. 2, it can be concluded that the direct wine analysis is strongly affected by the wine non-volatile matrix components, irrespective of the sample introduction system employed. Nonetheless, volatile related

Fig. 1 – Scheme of the different arrangements and methodologies evaluated to analyze wine samples in ICP-AES and ICP-MS.

matrix effects (i.e. ethanol) for the CS should also be taken into consideration and the standards must be prepared with the same ethanol content than the sample. The absence of ethanol matrix effects on the recoveries for the MWDS indicates that just one set of standards (pure aqueous standards) are required to analyze wine samples of different ethanol content and, as a consequence, the analysis throughput can be increased.

In order to mitigate matrix effects caused by non-volatile components, alternative analysis approaches have been evaluated: sample dilution and internal standardization.

3.1.2. Sample dilution

Fig. 3 shows the recovery results for different elements with the MWDS and the CS for a 1:5 wine diluted sample. According to the dilution factor employed, ethanol 2% w/w standards were prepared for the analysis using the CS. When operating with the MWDS, pure aqueous standards were employed according with the results shown in Fig. 2. From a practical point of view it is important to note that the analysis of the diluted samples must be performed in the same day since after some few hours, a precipitate could appear due to the modification of the sample pH. As it can be observed in Fig. 3, the dilution of the wine improves the recovery results found when the sample was analyzed directly (Fig. 2). Thus, the average recovery values for the MWDS and the CS were $90 \pm 3\%$ and $86 \pm 3\%$, respectively.

The dilution step reduces the amount of salts and organic components introduced to the plasma and, hence, the magnitude of matrix effects. Nonetheless, it is important to keep in mind that a compromise between matrix effects and sensitivity is mandatory to select the most appropriate dilution factor. Thus, sample dilution factors higher to 1:5 are difficult to apply in routine analysis due to the impossibility to analyze the lowest concentrated elements. This fact is more significant for the CS than for the MWDS. It must be taken into account that the former shows lower analyte transport efficiency than the desolvation system and, as a consequence, poorer sensitivities and detection limits [32,33]. In addition, it must be taken into account that the sample dilution methodology is

Fig. 3 – Recoveries obtained for a spiked diluted 1:5 wine sample analyzed by ICP-AES using different sample introduction system and standard solutions: (□) MWDS/pure aqueous standards; (■) CS/ethanol 2% w/w standards.

time consuming and prone to errors. Finally, it is also worth to mention that, despite the differences on the magnitude of matrix effects, precision values were similar for both dilution and direct analysis regardless the sample introduction system employed.

3.1.3. Internal standardization

IS has been widely employed to mitigate matrix effects and the instrumental noise, leading to the improvement on both accuracy and repeatability. Several authors have pointed out that the efficiency of IS depends on the fulfilling of three requirements [43–45]: (i) true simultaneous measurements of the analytical and reference signals; (ii) selection of the optimal operating conditions in order to minimize the plasma-related matrix effects (i.e. plasma robustness); and (iii) optimal selection of the reference line, since both the internal standard and the analyte emission lines must behave similarly in terms of signal variations to be effective for compensating matrix effects. In order to accomplish the above mentioned requirements, all the signals registered were measured simultaneously using the appropriate sample and integration time settings, whereas plasma robust conditions were assured by using high plasma power values (i.e. 1450 W) and long residence times (i.e. $Q_g \leq 0.7 \text{ L min}^{-1}$). When multi-elemental analysis has to be carried out, the appropriate selection of the internal standard candidate is not an easy task since several investigations have pointed out that a single internal standard is inadequate to cover the wide range of different responses of the analytical spectral lines due to matrix components [46–48]. According to Harmse and McCrindle [49], the analytical spectral line and the internal standard spectral line should have similar wavelengths and first ionization potentials. In the present study Sc, Be and Ti were investigated for IS purposes since these elements are not found in the wine samples analyzed in significant amounts (i.e. $<2 \mu\text{g L}^{-1}$). Several atomic and ionic lines of these elements were selected to cover a wide range of E_{sum} energies (Table 2). These elements were added to the sample before the recovery test was carried out using the appropriate volume of single-element standards solutions. In addition, the Ar I 396.152 nm emission line was also evaluated as an internal standard since its emission is affected by wine matrix components. This element is always present in the plasma itself and its use as internal standard could reduce the time consumed for the sample preparation step [50].

Fig. 4 shows the influence of the analyte line E_{sum} values on the recovery for undiluted wine samples for the MWDS and the CS using the IS methodology. As it can be observed in this figure, the recovery yields depend on the internal standard, the sample introduction system and the standard considered. In general terms, no trends of the analyte line E_{sum} on the recovery was observed for the different internal standards evaluated. Among the different internal standards, the best recovery values (i.e. 90–100%) were obtained for Sc and Ti. Nonetheless, especial attention should be paid on the characteristics of the line employed. Thus, for instance, when using the MWDS and ethanol 10% w/w standards (Fig. 4A), the results obtained for the Sc II 357.253 and the Sc II 361.384 were quite different in spite of the fact that both ionic lines have close E_{sum} values (i.e. 9.99 and 10.03 eV). Thus, the Sc II

Fig. 4 – Influence of the analyte line E_{sum} values on the recovery for undiluted wine samples with the using different sample introduction systems, standard solutions and internal standards. (A) MWDS/ethanol 10% w/w standards; (B) MWDS/pure aqueous standards; (C) CS/ethanol 10% w/w standards; (D) CS/pure aqueous standards: (●) Ar I 420.068; (■) Be I 234.861; (▲) Sc II 361.384; (×) Sc II 357.253; (○) Ti II 336.121; (□) Ti II 334.941; (Δ) Be II 313.042.

357.253 line affords an average recovery yield of $99 \pm 3\%$. In contrast, when the Sc II 361.384 line is employed, the average recoveries dropped to $72 \pm 3\%$. This situation is not unusual, since discrepancies in the extent of matrix effects between two or more different lines of the same element have been reported previously [49,50]. It is interesting to note that the recovery values depend on the composition of the standards as it can be observed in Fig. 4. Thus, when using ethanol 10% w/w standards with the CS (Fig. 4C), recoveries for the different internal standards ranged between 72 and 126% whereas for pure aqueous standards (Fig. 4D), the values were between 44 and 314%. Similar results were observed for the MWDS (Fig. 4A and B). For the CS, as it has been quoted above previously, when IS is not employed, the emission intensity for pure aqueous standards was 30% lower than for ethanol 10% w/w standards due to the lower aerosol transport efficiency of the former. The use of an IS compensates these differences since the analyte and the internal standard transport rates ratios into the plasma are similar, irrespective of the amount of aerosol reaching the plasma. Finally, it has been observed that the precision of the measurements was improved when using the IS methodology compared with the direct analysis (i.e. 2–3% vs 2–7%). These results are the expected since matrix induced signal variations, as well as the flicker noise and drift, are compensated using this methodology [46,47].

The results shown above highlight the complexity of the matrix effects in the plasma and the importance of the selection of the appropriate internal standard. Among the lines tested, the Sc II 357.253 line seems the best choice to perform a multi-elemental analysis of wine for all the arrangements studied.

3.1.4. Analysis of wine samples

Since no certified wine sample is commercially available, the wine samples were analyzed by ICP-AES using the CS after a sample digestion treatment. These results have been employed as a reference. In order to evaluate the accuracy of the results obtained using this methodology, a recovery test was firstly performed. To this end, spiked wine samples were digested and analyzed using acid matched standards, so that potential matrix effects due to the nitric acid presence are reduced [53]. In general terms, recoveries were slightly higher than 100% (i.e. $110 \pm 4\%$), thus indicating the presence of some matrix effects. The use of the IS methodology further improves the accuracy of the analysis. Thus, when using the Sc II 357.253 line as IS, total recoveries were obtained (i.e. $104 \pm 3\%$). Similar results were observed for the Ti lines and the Sc II 361.384 line. The higher recoveries obtained using the digestion treatment when compared to the direct analysis (Fig. 2), are explained taken into account that this sample treatment efficiently destroys organic wine matrix components reducing its influence on analyte transport efficiency and plasma thermal conditions. In addition, it also worth to mention that the original samples becomes diluted (i.e. 5 g in 15 mL) and, therefore, the matrix load into the plasma (i.e. mainly salts) is additionally reduced.

Table 3 shows the results obtained for the wines analysis directly or after a digestion treatment. The direct wine analysis was performed using the MWDS with pure aqueous standards and the CS with ethanol 10% w/w standards. In all cases, IS

Table 3 – Results of the analysis of four wine samples in ICP-AES using different sample introduction systems and sample treatments[#]

Element [†]	Enrique Mendoza			Puertoluz			Dominio de la Peseta			Marques de Alicante		
	Digestion	Ethanol standards	MWDS	Digestion	Ethanol standards	MWDS	Digestion	CS	Ethanol standards	Digestion	CS	Ethanol standards
Mn	0.72 ± 0.03	0.81 ± 0.03	0.73 ± 0.02	0.15 ± 0.01	0.12 ± 0.01	0.13 ± 0.02	0.74 ± 0.04	0.81 ± 0.04	0.77 ± 0.04	1.21 ± 0.08	1.35 ± 0.03	1.12 ± 0.04
Fe	1.15 ± 0.09	1.3 ± 0.1	1.20 ± 0.04	0.64 ± 0.05	1.0 ± 0.1	0.56 ± 0.04	1.56 ± 0.07	1.6 ± 0.1	1.53 ± 0.06	2.6 ± 0.1	2.5 ± 0.1	2.20 ± 0.03
Na	34.0 ± 0.8	35.8 ± 0.7	32.6 ± 0.5	22.8 ± 0.7	24 ± 1	20.7 ± 0.3	9.0 ± 0.2	9.1 ± 0.4	8.2 ± 0.4	17.2 ± 0.1	19.7 ± 0.5	15.8 ± 0.3
Ca	51.8 ± 0.7	49.7 ± 0.7	52.9 ± 0.4	7.5 ± 0.2	7.6 ± 0.6	8.6 ± 0.3	65 ± 2	64 ± 2	68 ± 2	80.2 ± 0.4	76 ± 1	79 ± 1
Mg	100 ± 5	109 ± 2	97 ± 5	17.0 ± 0.5	24 ± 2	15 ± 1	112 ± 2	120 ± 4	121 ± 4	104 ± 3	111 ± 3	105 ± 4
Sr	0.76 ± 0.01	0.83 ± 0.04	0.85 ± 0.06	0.10 ± 0.01	0.18 ± 0.02	0.19 ± 0.01	1.29 ± 0.05	1.3 ± 0.1	1.43 ± 0.08	1.24 ± 0.04	1.23 ± 0.02	1.30 ± 0.07
Cu	ND	ND	0.10 ± 0.02	1.34 ± 0.09	1.8 ± 0.1	1.35 ± 0.07	ND	ND	0.11 ± 0.02	0.58 ± 0.04	0.64 ± 0.07	0.64 ± 0.04
Li	ND	ND	0.09 ± 0.01	ND	ND	0.040 ± 0.002	ND	ND	0.090 ± 0.008	ND	ND	0.080 ± 0.009
Al	ND	0.40 ± 0.07	0.68 ± 0.06	ND	0.31 ± 0.05	0.54 ± 0.08	ND	0.34 ± 0.06	0.65 ± 0.03	ND	0.4 ± 0.08	0.65 ± 0.03
Zn	0.97 ± 0.08	1.2 ± 0.3	0.99 ± 0.08	0.52 ± 0.06	ND	0.57 ± 0.05	0.78 ± 0.07	1.4 ± 0.3	0.81 ± 0.05	0.65 ± 0.06	0.7 ± 0.05	0.72 ± 0.04
Ba	0.040 ± 0.005	0.07 ± 0.01	0.10 ± 0.01	ND	ND	0.022 ± 0.003	0.080 ± 0.005	0.12 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.18 ± 0.02	0.16 ± 0.01

Sc II 357.253 was employed as internal standard in all cases.

[†] Values in mg L⁻¹.[#] Errors are presented in form of confidence intervals obtained as t 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.

methodology was employed. When the IS was not employed, the concentration values obtained for undiluted wine samples were 20–30% lower than the values shown in Table 3 due to wine matrix effects. For digested wine samples, as it has been previously discussed, less influence of the internal standard on the reported concentration value was observed (i.e. 5%). Due to the higher ethanol content of the brandy, this sample was 2.5 fold diluted with water before the analysis was carried out in order to avoid the plasma extinction. Results in Table 3 indicate a good agreement between the data obtained with the MW digestion treatment and the direct analysis, irrespective of the sample introduction system employed. It is interesting to point out that the number of elements successfully determined for the MWDS was higher than those for the CS due to the better analytical performance of the former device [32].

From the results shown above, it is clear that the direct analysis of wine samples in ICP-AES using the MWDS affords several attractive features when comparing to the CS. In one hand, complex sample treatments are not required with the MWDS and therefore, the analysis throughput is improved (the complete MW acid digestion treatment for just one sample requires at least 2 h). On the other hand, the MWDS shows better sensitivity, as well as, lower LODs than the CS system [32,33]. As a consequence, the use of the MWDS permits to determine elements in lower concentrations and/or use higher sample dilution factors than the CS. Finally, the MWDS does not require ethanol matched standards to perform an accurate analysis, increasing the analysis throughput when wine samples of different ethanol content are analyzed. Nonetheless, this advantage is partially counterbalanced by the use of IS.

3.2. Application of the MWDS in ICP-MS

In spite of the good limits of detection achieved by the MWDS in ICP-AES, the determination of the elements present at the lowest level of concentration is sometimes difficult. ICP-MS affords higher sensitivity and lower LODs than ICP-AES, allowing the analysis of elements in the ng L⁻¹ range. Nevertheless, it is important to note that ICP-MS is more susceptible to matrix effects than ICP-AES, since interference effects can also arise during extraction, focusing and transport of ions from the plasma to the spectrometer.

The MWDS has not ever been employed for the analysis of organic samples in ICP-MS. Due to this reason, and prior to its application to the direct wine analysis, it is necessary to evaluate the behaviour of this device when operating with ethanol solutions in ICP-MS. For the sake of comparison, the performance of a thermostated conventional system (TCS) was also evaluated.

3.2.1. Characterization of the MWDS operating with ethanol solutions

In order to characterize this system, the influence of the nebulizer gas flow (Q_g) and the sample uptake rate (Q_l) on the ionic intensity have been evaluated.

Fig. 5 shows the influence of Q_g on the ¹¹⁵In⁺ ionic intensity for different ethanol solutions using the MWDS (Fig. 5A) and the TCS (Fig. 5B). As it can be observed in this figure, the ¹¹⁵In⁺ ionic intensity peaks when Q_g is increased for both the

Fig. 5 – Influence of the nebulizer gas flow rate (Q_g) and matrix composition on the ionic intensity of the $^{115}\text{In}^+$ using (A) the MWDS and (B) the TCS: (●) Water; (■) ethanol 1% w/w; (▲) ethanol 5% w/w; (×) ethanol 10% w/w. Q_i 100 $\mu\text{L min}^{-1}$.

MWDS and the TCS. The position of the maximum depends on the matrix and the sample introduction system. Thus, an increase in the ethanol concentration reduces the optimum Q_g for both the MWDS and the TCS. When using the TCS, the optimum Q_g was always 0.1 L min^{-1} higher than for the MWDS, regardless the matrix of the solution. These results are explained attending to the so-called “zone model” [54]. According to this model, there is a zone in the plasma where a maximum density of single charged ion occurs. Increasing Q_g leads to a spatial shift of the ion zone in the direction of the sampling cone, whereas a decrease in the flow rate results in a spatial shift to the opposite direction. The maximum signal intensity is obtained when the zone of maximum ion density is sampled. The position of this ion zone depends on the amount of solvent introduced in the plasma [16]. Hence, when alcohol solutions are employed, solvent transport rate to the plasma is increased due to the high ethanol volatility and, consequently, more energy is required to atomize solvent molecules. This means that the atomization-ionization processes are delayed and a decrease in the Q_g is required to move the zone of maximum ion density downstream. The differences in the optimum Q_g obtained for the MWDS and the TCS are also explained taken into account the solvent load to the plasma [32]. Thus, the lower optimum Q_g for the MWDS when comparing to the TCS is related to the higher solvent load of the former.

As it can be observed in Fig. 5, when the ethanol content in the sample increases, the ionic intensity obtained for both the MWDS and the TCS is reduced. Thus, for instance, the $^{115}\text{In}^+$ ionic intensity for pure aqueous and ethanol 5% w/w solution using the MWDS was 3.88×10^6 and 1.96×10^6 counts. These results are explained taken into account that, despite ethanol solutions shows a higher analyte transport rate, the higher alcohol load into the plasma cools the plasma central channel reducing the atomization-ionization efficiency [37]. In addition, the presence of a significant amount of carbon can modify the ion extraction process [16]. It is interesting to point out that ionic signals for $^{75}\text{As}^+$ and $^{82}\text{Se}^+$ did not behave as it is shown in Fig. 5 for $^{115}\text{In}^+$. In fact, it was observed that ionic signals for those elements were enhanced when increasing the ethanol concentration. Thus, $^{75}\text{As}^+$ signal for a 1% w/w ethanol solution was 2.5 times higher than for a pure aqueous one. Similar results were observed for the TCS. The origin of this behaviour is related to a charge transfer reaction mechanism from carbon charged species to analyte atoms in the plasma that enhance analyte ionization efficiency and, hence, ionic signals [16]. Nevertheless the scope of the present work was not to study this kind of specific interferences but the general trend.

Finally, a carefully inspection of Fig. 5 reveals that the maximum ionic intensities for the MWDS were up to 10 times higher than for the TCS, regardless the solution tested. These results can be attributed to the higher aerosol transport efficiency of the MWDS when comparing to the TCS.

Fig. 6 shows the influence of Q_i on the $^{115}\text{In}^+$ ionic intensity for the ethanol solutions using the MWDS (Fig. 6A) and the TCS (Fig. 6B). As it can be observed in Fig. 6A for the MWDS and all the solutions tested, a maximum in the ion intensity is reached at 100 $\mu\text{L min}^{-1}$ when Q_i is increased. However for the TCS (Fig. 6B), the higher the Q_i , the higher the ionic signal is obtained. In order to explain these results, it must be considered that when Q_i is increased, higher amount of analyte is introduced in the plasma per unit of time and, as a consequence, the sensitivity should raises up. However, this also means an increase in the amount of solvent loading the plasma that could affect plasma excitation/ionization conditions. To evaluate the solvent load for both the MWDS and the TCS, the oxide level (i.e. CeO^+/Ce^+) has been monitored [32]. Thus, when increasing Q_i from 100 to 400 $\mu\text{L min}^{-1}$, the oxide level for the pure aqueous solution using the MWDS and the TCS was enhanced 3.4 and 1.9 times, respectively. Similar behaviour was observed for the ethanol solutions. According to these results, a higher deterioration of the plasma excitation/ionization conditions (i.e. lower excitation and ionization capabilities) is expected for the MWDS than for the TCS.

Here in after, Q_g of 1.0 L min^{-1} and Q_i of 100 $\mu\text{L min}^{-1}$ were selected for further experiments with the MWDS since these conditions afford the best sensitivity conditions and the lowest oxides levels for a multi-elemental analysis. For the TCS, Q_g of 1.1 L min^{-1} and Q_i of 100 $\mu\text{L min}^{-1}$ were employed as compromise conditions. The RF power for both devices was kept at 1350 W to assure maximum analyte and matrix atomization/ionization in the plasma.

3.2.2. Direct analysis

From the results shown in Figs. 5 and 6 it can be concluded that direct analysis of wines using ICP-MS is not advisable due to the high influence of the sample ethanol composition on the ionic signal. In addition, it must be kept in mind that the presence of salts in wine could also modify the ionic intensity. In fact, preliminary experiments showed that the $^{115}\text{In}^+$ ionic signal for ethanol 10% w/w solutions containing 1500 mg L^{-1} potassium (i.e. a typical amount found in the literature for wine samples) was 10 times lower than that obtained in absence of this element. On the other hand, carbon and salts deposits appears in the spectrometer interface deteriorating the long-term instrument performance. Therefore, alternative methodologies are required to carry out the elemental analysis of wine samples in ICP-MS.

3.2.3. Sample dilution

A carefully inspection of Figs. 5 and 6 reveals that operating with the MWDS, solutions containing ethanol 1% w/w does not produce significant signal suppression. According to these results, a 1:10 sample dilution ratio could be used to mitigate ethanol related matrix effects. The dilution approach can also be used for the TCS although, for this arrangement, the ionic intensity for the ethanol 1% w/w solution is still 33% lower than for a pure aqueous one and, hence, a higher dilution factor should be employed to eliminate matrix effects. However, detection capabilities for this device are deteriorated.

Fig. 6 – Influence of the sample uptake rate (Q_1) and matrix composition on the ionic intensity of the $^{115}\text{In}^+$ using (A) the MWDS and (B) the TCS: (●) Water; (■) ethanol 1% w/w; (▲) ethanol 5% w/w; (x) ethanol 10% w/w. MWDS: Q_g 1.0 L min^{-1} ; TCS: Q_g 1.1 L min^{-1} .

In order to evaluate the magnitude of matrix effects for the dilution approach, a recovery test was performed. To this end, wine samples were diluted according to their labelled alcohol content to reduce ethanol concentration up to 1% (i.e. 1:10 dilution for the white and red wines and 1:28 for the brandy). Ethanol 1% w/w standards were employed for the TCS whereas for the MWDS, only aqueous standards were selected since alcohol concentrations up to 1% does not influence the ionic signal obtained with this device (Figs. 5 and 6).

The recovery values for the 1:10 diluted Dominio de la Peseta wine sample using the MWDS and the TCS were always lower than 100% irrespective of the sample introduction system used, thus indicating that matrix effects are still significant for both the MWDS and the TCS. It is important to recall that the 1:10 dilution factor was selected to minimize ethanol matrix effects but interferences due to non-volatile species (i.e. salts, organic acids, etc.) are still present. The magnitude of the non-spectral matrix effects is expected to be minimized by further diluting the wine samples. However, a compromise dilution factor must be selected to analyze those elements in low concentration (i.e. Cd). Results evidence that the actual recovery values obtained depended on the sample introduction system employed. Thus, recoveries for the TCS using ethanol 1% w/w standards were on average $80 \pm 4\%$ whereas for the MWDS were substantially lower reaching recovery values of $55 \pm 5\%$ on average. As it was pointed out previously in ICP-AES, the aerosol transport efficiency for the MWDS is higher than for the TCS and, as a consequence, higher amount of wine is transported into the plasma increasing matrix effects. Similar behaviour has been observed previously using a membrane-based desolvation system [42]. Using this device, recoveries for a diluted 1:1 wine sample were not higher than 10% due to the presence of salts in the sample.

It is interesting to point out that, when using the TCS, spectral interferences might occur due to the presence of carbon in the plasma. Thus, for instance, the Cr recovery for this device was $120 \pm 5\%$ due to the fact that the ionic signal of the $^{52}\text{Cr}^+$ isotope is enhanced by the $^{52}\text{ArC}^+$. When using the MWDS, this interference is reduced since the Cr recovery for pure aqueous and ethanol 1% w/w was similar. These results indicate that the MWDS reduces the amount of carbon transported into the plasma and, therefore, the carbon related spectral interferences.

3.2.4. Internal standardization

In order to reduce the extent of the matrix effects, the use of IS was also evaluated in ICP-MS. Thompson and Houk [55] suggested that the internal standard should have an atomic mass and first ionization potential as close as possible to those of the analyte. However, other authors have claimed that the appropriate selection of the IS depends on the sample concomitant elements [56], and even only one single IS can be used for multi-elemental analysis [57]. In the present work, $^9\text{Be}^+$, $^{45}\text{Sc}^+$, $^{140}\text{Ce}^+$ and $^{238}\text{U}^+$ were evaluated as potential internal standards candidates for multi-elemental wine analysis by ICP-MS. These isotopes were selected since their concentration in the wine samples analyzed was not significant (i.e. lower than 2 µg L^{-1}) and to cover a wide range of ionization potentials and masses (i.e. 9.32–5.47 eV and 9–238 m/z).

Fig. 7 shows the recoveries obtained for the diluted Dominio de la Peseta wine sample using the MWDS and the TCS after internal standardization. Ethanol 1% w/w and pure aqueous standards were employed for both the MWDS (Fig. 7A and B) and the TDS (Fig. 7C and D). As it can be observed in Fig. 7, the recoveries registered depend on the sample introduction system, the standard solution, the internal standard and the analyte considered. In general terms, the use of an internal standard mitigates matrix effects. Thus, when using $^{45}\text{Sc}^+$ as internal standard, recoveries for the MWDS and the TCS were, on average, $99 \pm 3\%$ and $105 \pm 3\%$, respectively. Nonetheless, special attention should be paid to the composition of the standards. For the TCS system, the recoveries using $^9\text{Be}^+$ as internal standard using aqueous standards ranged between 300 and 20% whereas for ethanol 1% w/w standard recoveries were between 100 and 140%. The influence of the matrix on the recovery was less significant for the MWDS since recoveries for $^9\text{Be}^+$ using both pure aqueous and ethanol 1% w/w standards were between 75 and 145%.

Among the different IS selected, the best behaviour in terms of mean recovery for the different standard and sample introduction systems was obtained with $^{45}\text{Sc}^+$. Hence, this isotope was selected as the best candidate for multi-elemental analysis using the IS methodology.

3.2.5. Analysis of wine samples

Sample digestion treatment and the use of a TSC has been employed as a reference methodology for elemental wine analysis in ICP-MS. A recovery test was performed to evaluate the accuracy of this approach. Digested wine samples were analyzed using acid matched standards and the TCS. The averaged recoveries obtained for the different analytes were $98 \pm 5\%$. Similar results were obtained using $^{45}\text{Sc}^+$ as IS (i.e. $103 \pm 3\%$). From this experiment, it can be concluded that microwave digestion treatment efficiently destroys wine matrix components. In addition, the wine sample becomes diluted reducing the matrix load into the plasma and, hence, the matrix effects.

Table 4 shows the results of the analysis performed. Wine samples were analyzed after 1:10 dilution (1:28 dilution factor for brandy) or a MW aided digestion treatment. The analysis of diluted wine samples for both the MWDS and the TCS was performed using ethanol 1% w/w and pure aqueous standards, respectively. Digested samples were analyzed using acid matched standards. In all cases, $^{45}\text{Sc}^+$ was employed as internal standard to mitigate matrix effects and to improve signal precision. As it can be seen in Table 4, there is a general agreement between the data obtained using the different methodologies tested. Nonetheless, significant differences arise for the Cr determination. Thus, the lowest Cr concentration values were obtained for the digestion treatment followed by diluted samples analyzed by the MWDS and the TCS. As it was previously pointed out, when carbon is introduced into the plasma, $^{52}\text{Cr}^+$ is significantly interfered by $^{52}\text{ArC}^+$. From the results shown in Table 4, it is clear that $^{52}\text{ArC}^+$ overlapping seems less significant for digested wine samples than for the diluted ones. Sample digestion destroys wine organic components (i.e. ethanol, organic acids, etc.) reducing the amount of carbon present in the sample. For the diluted wine samples, the MWDS reduces the amount

Fig. 7 – Recoveries obtained in ICP-MS using different sample introduction systems, standard solutions and internal standards: (A) MWDS/ethanol 1% w/w standards; (B) MWDS/pure aqueous standards; (C) CS/ethanol 1% w/w standards; (D) CS/pure aqueous standards: (●) $^9\text{Be}^+$; (■) $^{45}\text{Sc}^+$; (▲) $^{140}\text{Ce}^+$; (x) $^{238}\text{U}^+$.

Table 4 – Results of the analysis of four wine samples in ICP-MS using different sample introduction systems and sample treatments[#]

Element [‡]	Enrique Mendoza			Puertoluz			Dominio de la Peseta			Marques de Alicante		
	CS		MWDS	CS		MWDS	CS		MWDS	CS		MWDS
	Digestion	Ethanol standards	Water standards	Digestion	Ethanol standards	Water standards	Digestion	Ethanol standards	Water standards	Digestion	Ethanol standards	Water standards
Pb	10 ± 1	11 ± 1	9.0 ± 0.4	38 ± 3	38 ± 3	31 ± 3	11 ± 1	13 ± 1	13 ± 1	47 ± 1	52 ± 2	44 ± 3
Bi	1.7 ± 0.1	2.6 ± 0.1	1.9 ± 0.1	1.5 ± 0.1	1.2 ± 0.1	1.91 ± 0.04	1.39 ± 0.02	1.62 ± 0.04	1.59 ± 0.08	1.43 ± 0.09	1.66 ± 0.04	1.31 ± 0.09
Ni	29 ± 2	29 ± 5	32 ± 3	21 ± 2	23 ± 4	24 ± 4	26 ± 2	16 ± 2	25 ± 4	36 ± 1	28 ± 3	38 ± 5
Co	7.2 ± 0.7	10 ± 1	8.2 ± 0.6	2.4 ± 0.1	2.0 ± 0.3	2.1 ± 0.4	4.5 ± 0.3	6.0 ± 0.7	4.3 ± 0.1	4.1 ± 0.1	5.0 ± 0.5	5.1 ± 0.6
Cd	0.35 ± 0.02	0.37 ± 0.09	0.43 ± 0.06	0.38 ± 0.06	0.26 ± 0.07	0.42 ± 0.06	0.15 ± 0.02	0.15 ± 0.04	0.25 ± 0.04	0.50 ± 0.06	0.65 ± 0.09	0.65 ± 0.03
Ga	5.8 ± 0.7	7.0 ± 0.6	6.3 ± 0.4	3.9 ± 0.4	5.0 ± 0.4	2.1 ± 0.4	7.4 ± 0.3	6.0 ± 0.6	8.0 ± 0.6	9.0 ± 0.6	10 ± 0.2	10.9 ± 0.6
Cr	70 ± 7	600 ± 80	120 ± 30	28 ± 7	740 ± 80	260 ± 60	71 ± 8	620 ± 70	110 ± 20	60 ± 3	480 ± 60	150 ± 40
Mo	11.6 ± 0.9	7.6 ± 0.7	10.2 ± 0.9	9.4 ± 0.7	5.7 ± 0.6	8.7 ± 0.6	12.0 ± 0.1	10.01 ± 0.9	10.7 ± 0.8	10.6 ± 0.7	9.95 ± 0.07	10.8 ± 0.6
Zr	6.0 ± 0.3	6.9 ± 0.5	6.8 ± 0.7	2.6 ± 0.3	2.0 ± 0.4	3.1 ± 0.4	1.15 ± 0.04	1.2 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	1.7 ± 0.2	2.5 ± 0.1
W	1.7 ± 0.1	1.8 ± 0.2	1.7 ± 0.2	2.0 ± 0.2	2.5 ± 0.2	2.0 ± 0.3	2.3 ± 0.2	2.4 ± 0.2	2.0 ± 0.2	1.5 ± 0.1	1.2 ± 0.2	1.12 ± 0.04
V	6.5 ± 0.6	6.4 ± 0.3	7.6 ± 0.4	4.4 ± 0.5	6.7 ± 0.7	5.6 ± 0.4	44 ± 2	52 ± 2	40 ± 3	6.6 ± 0.3	6.9 ± 0.4	7.8 ± 0.4
Ti	150 ± 10	170 ± 10	190 ± 40	45 ± 4	65 ± 6	70 ± 10	280 ± 40	320 ± 20	280 ± 20	211 ± 8	240 ± 20	220 ± 20
Ag	4.3 ± 0.4	3.9 ± 0.3	4.4 ± 0.2	2.1 ± 0.3	2.8 ± 0.3	1.7 ± 0.2	1.4 ± 0.1	1.0 ± 0.1	0.9 ± 0.1	2.2 ± 0.2	1.62 ± 0.06	1.9 ± 0.2
Tl	0.11 ± 0.01	0.26 ± 0.03	0.38 ± 0.02	0.090 ± 0.007	0.11 ± 0.02	0.26 ± 0.03	0.14 ± 0.01	0.29 ± 0.02	0.26 ± 0.02	0.17 ± 0.02	0.19 ± 0.01	0.31 ± 0.02
In	0.11 ± 0.03	0.23 ± 0.03	0.16 ± 0.01	0.08 ± 0.02	0.39 ± 0.01	0.17 ± 0.02	0.08 ± 0.02	0.22 ± 0.02	0.12 ± 0.01	0.09 ± 0.01	0.22 ± 0.03	0.11 ± 0.01

⁴⁵Sc⁺ isotope was employed as internal standard in all cases.[‡] Values in µg L⁻¹.[#] Precision is presented in form of confidence intervals obtained as ts 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.

Table 5 – Summary of the different arrangements tested in this work in terms of LODs and matrix effects

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ICP technique		ICP-AES				ICP-MS							
Sample introduction system	Calibration Strategy	CS				MWDS				CS			
		MWDS		IS		External calibration		IS		External calibration		IS	
		Water		EtOH		Water		EtOH		Water		EtOH	
Sample treatment	Direct analysis	4	4	5	1	2	4	1	1	1	1	1	
	Dilution	4	4	5	2	3	4	4	4	5	2	3	
Score: 1 (not recommended)–5 (highly recommended).													

of volatile components reaching the plasma and, therefore, $^{52}\text{ArC}^+$ spectral interference when compared to the TCS. In fact, the chromium background for the MWDS was one order of magnitude lower than that for the TCS, irrespective of the standard employed (i.e. pure aqueous and ethanol 1% w/w). Finally, it is also worth to mention that the signal R.S.D. for all the elements were in the 5–10% range. The higher R.S.D. values were obtained for those elements present below the $10\text{ }\mu\text{g L}^{-1}$ level.

From the results shown above, it can be concluded that the most useful methodology to analyze wine samples by ICP-MS is sample dilution and internal standardization using the MWDS. This methodology minimizes the magnitude of matrix effects and spectral interferences. In addition, when compared to the sample digestion treatment, it is less time consuming and the risk of sample contamination is avoided. Finally, the MWDS affords better LODs than the TCS and, as a consequence, elements in lowest concentration can be determined. Nonetheless, both systems allowed the determination of all the analytes studied in the present work.

4. Conclusions

Desolvation has been successfully applied for elemental wine analysis in inductively coupled plasma based techniques for the first time. The microwave-based desolvation system allows the accurate analysis of wine samples. Nonetheless, special attention must be paid to the sample preparation step and the calibration methodology in order to mitigate matrix effects due to non-volatile matrix components. Table 5 shows a summary of the results obtained in this work. In that table, the different arrangements were evaluated in terms of LODs and matrix effects where score values closed to 5 indicates the lowest LODs and matrix effects (i.e. highly recommended option for wine analysis.). The best option to analyze wine samples in ICP-AES is by means the MWDS, without any sample treatment, using pure aqueous standards and Sc as internal standards. The dilution approach can also be employed though LODs are deteriorated. In ICP-MS, wine samples must be diluted to reduce ethanol concentration up to 1% w/w otherwise the sensitivity is strongly depressed. The analysis of wine samples in ICP-MS can be successfully performed by means the MWDS and internal standardization (i.e. Sc). This arrangement reduces interferences due to wine matrix non-volatile components. In general terms, the MWDS affords some attractive features for elemental wine analysis when comparing to a conventional sample introduction system. Among them: (i) higher sensitivities that allow the analysis of those elements in low concentration; (ii) lower ethanol matrix effects and; (iii) lower spectral interferences in ICP-MS (i.e. ArC^+).

Uncited references

[51,52].

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