analytica chimica acta 629 (2008) 24–37

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journal homepage: www.elsevier.com/locate/aca

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

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ARTICLE INFO

*Article history:*
Received 24 April 2008
Received in revised form
8 September 2008
Accepted 8 September 2008
Published on line 16 September 2008

*Keywords:*
Microwave
Desolvation system
Inductively coupled plasma
Atomic emission spectrometry
Mass spectrometry
Wine

## 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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0003-2670/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2008.09.023

## 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 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. $^{52}Cr^+$ and $^{63}Cu^+$, respectively) in matrices with high levels of carbon and/or sodium could be hindered due to the $^{52}ArC^+$ and $^{63}ArNa^+$ 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 sample 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 [4,22,23] and internal standardization (IS) [4,22] 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 [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