



Direct determination of Cd, Cu and Pb in wines and grape juices by thermospray flame furnace atomic absorption spectrometry

Daniela Schiavo^a, José Y. Neira^b, Joaquim A. Nóbrega^{a,*}

^a Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, P.O. Box 676, 13560-970 São Carlos, SP, Brazil

^b Departamento de Análisis Instrumental, Facultad de Farmacia, Universidad de Concepción, Casilla 237, Concepción, Chile

ARTICLE INFO

Article history:

Received 5 February 2008

Received in revised form 10 May 2008

Accepted 12 May 2008

Available online 18 May 2008

Keywords:

Thermospray

FAAS

Copper

Cadmium

Lead

Wine

Grape juice

ABSTRACT

The applicability of thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) was evaluated for direct determination of Cu, Cd and Pb in wines and grape juices. The developed procedure does not require preliminary acid digestion of the samples. The optimum conditions for determination of Cu, Cd and Pb in wines were studied and the performance was compared to those typically obtained by flame atomic absorption spectrometry (FAAS). A sample volume of 150 μL was introduced into a heated nickel tube at a flow rate of 0.54 mL min^{-1} and 0.14 mol L^{-1} HNO_3 was used as sample carrier flowing at 2.5 mL min^{-1} for determining all analytes. The effect of ethanol concentrations on Cu, Cd and Pb absorbance signals were studied. All determinations were carried out by adopting optimized conditions and quantification was based on the standard additions method. Limits of detection (LOD) of 12.9, 1.8 and 5.3 $\mu\text{g L}^{-1}$ ($n = 14$) for Cu, Cd and Pb, respectively, were obtained for wine samples ($3\sigma_{\text{blank}}/\text{slope}$, $n = 14$). Relative standard deviations (R.S.D., %) of 2.7, 2.1 and 2.6 for Cu, Cd and Pb, were obtained ($n = 6$) for wine samples. The values determined for grape juice samples were similar to these ones. The analytical throughput was 45 determinations h^{-1} and accuracy was checked by addition-recovery experiments.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Trace metals play an important effect in the quality of wine. They promote specific redox processes during maturing that give a good appearance to the wines. However, high concentrations of Cu, Fe, Mn and Zn may cause instability and turbidity [1]. Other metals, such as As, Cd and Pb, are toxic [2].

The current legislation in Brazil demands a strict control of the levels of contamination for metals in beverages [3]. Wine and grape juices are widely consumed beverages and they can contain metals added to remove sulfur oxides and from other sources. The control of Cu concentration is important because high amounts can cause oxidative spoilage of the wine leading to lightening of red wine and darkening of white wine [4,5]. The total copper concentration in red and white wines must be 0.3 and 0.5 mg L^{-1} . In wines, the main sources of copper are equipments used in the wine production, additions of copper salts (CuSO_4) and pesticides employed during growth. The maximum allowed level of copper in wine is 1.0 mg L^{-1} [3,6].

A significant amount of Cd may be present in wines due to residues of agrochemical products used such as insecticides and

fungicides and also by contact with equipments employed for wine production. The consumption of large quantities of wine can imply in accumulation of Cd in the organism [5]. The maximum allowed concentration of Cd in wine is 10 $\mu\text{g L}^{-1}$ [6–8]. On the other hand, the maximum allowed amount of Pb in wine established by the Office International de la Vigne et du Vin (OIV) is 200 $\mu\text{g L}^{-1}$ [6] and according to the Brazilian legislation is 300 $\mu\text{g L}^{-1}$ [3]. The source of Pb contamination in alcoholic beverages may be either raw material or technological processes, for instance, corks are covered by a film made of plastic, by a foil made of Pb or by an alloy containing Al [9]. The intoxication caused by intake of foods containing Pb can cause severe damages to health such as encephalic alterations, headache, cardiovascular and hepatic problems [10].

Several techniques have been described to determine metals in wines such as atomic spectrometry (FAAS, electrothermal atomization AAS, inductively coupled plasma optical emission spectrometry) [11,12] and electroanalytical techniques [4,13,14]. An official method for trace metal determination in wine is provided by AOAC (Official Methods of Analysis of AOAC International) which does not consider previous acid digestion and recommend sample dilution [15]. The typical sensitivity reached by FAAS does not allow the adoption of this strategy when Cu, Cd and Pb concentrations are at $\mu\text{g L}^{-1}$ levels.

A recent work has shown the advantage of thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) for direct

* Corresponding author. Tel.: +55 16 3351 8088; fax: +55 16 3351 8350.
E-mail address: djan@ufscar.br (J.A. Nóbrega).

determination of Cu, Mn, Pb and Zn in commercial beer at $\mu\text{g L}^{-1}$ [16]. The TS-FF-AAS technique is relatively recent and few applications for determination of metals in beverages were described in the literature. A previous work has demonstrated its applicability for determining Cu and Zn in fruit juices and bovine milk [17]. The main advantage of TS-FF-AAS is the significant increment of sensitivity by adapting a simple and low cost Ni tube to the flame. This simple device associated to a ceramic capillary allows the total introduction of the sample and increases the residence time of the atomic cloud in the atomizer. Both effects help to improve the formation of analyte atoms and, consequently, the sensitivity.

The aim of this work was to develop a procedure for direct determination of Cu, Cd and Pb in wines and grape juices by TS-FF-AAS. Since these elements are usually present at low levels in wine and grape juices, sensitive analytical techniques are required. TS-FF-AAS was employed due to its simplicity, suitable sensitivity, low cost and rapidity when compared to electrothermal atomization in a graphite furnace AAS. The effective dilution factor was chosen based on ethanol effects on sensitivity. The system was optimized and the standard additions method (SAM) was employed for Cu, Cd and Pb determination in wine and grape juice samples.

2. Experimental

2.1. Instruments and accessories

All experiments were carried out in a Varian SpectraAA-640 flame atomic absorption spectrometer (Varian, Mulgrave, Australia) equipped with a deuterium lamp background corrector. The instrument parameters for determination of Cu, Cd and Pb by TS-FF-AAS are shown in Table 1. Hollow cathode lamps of Cu, Cd and Pb (Varian) were employed. All data acquisition was carried out in peak area mode.

2.2. Arrangement of the TS-FF-AAS

The TS-FF-AAS system consists of a peristaltic pump with 8 channels (Ismatec, Labortechnik Analytik, Glatbrugg-Zürich, Switzerland) furnished with Tygon® propulsion tube (i.d. = 0.89 mm), Teflon® extension tube (i.d. = 0.8 mm), a lab-made acrylic commutator injector was utilized for sample introduction, a lab-made thermospray flame furnace unit, including a ceramic capillary (Friatec, Mannheim, Germany, i.d./o.d. 0.5 mm/2.0 mm, and 100 mm of length) and nickel tubes. The tube employed contains 99.7% of Ni and it has the following specifications: 10 cm of length, 1 cm of i.d and 1.2 cm of o.d. One of the tubes employed has six holes of 2 mm in its bottom for increasing the temperature inside of the tube. The second tube does not have any hole in its bottom. Both Ni tubes have a central hole with 2 mm of diameter. This central hole is perpendicular to the bottom holes and it is used for introduction of the ceramic capillary tube. The Ni

tube was positioned on a lab-made stainless steel support with four ceramic pins on the flame burner. The thermospray was generated by contact between the nickel tube on the flame and the heated ceramic capillary. Samples were introduced inside of the heated tube without the need of a nebulizer and losses of sensitivity caused by the poor nebulization efficiency were totally circumvented.

2.3. Reagents

All solutions were prepared using analytical-grade reagents. Water was distilled and deionized (Milli-Q, Millipore Corp., Bedford, MA, USA). All glassware and polypropylene flasks were washed with soap, soaked in 10% (v/v) nitric acid and rinsed with deionized water prior use.

Standard stock solutions of Cu, Cd and Pb containing 1000 mg L^{-1} (Tec-Lab, Hexis, São Paulo, Brazil) were used for application of the SAM and reference solutions of Cu, Cd and Pb were prepared by diluting the stock solution. Solutions containing 2–30% (v/v) of ethanol were prepared by diluting ethanol absolute anhydrous 99.7% (v/v) (Mallinckrodt-Baker, Xalostoc, Mexico).

A 0.14 mol L^{-1} HNO_3 solution was prepared by diluting concentrated HNO_3 (Merck, Darmstadt, Germany).

2.4. Influence of solution medium on Cu, Cd and Pb absorbance signals

Solutions containing 1.0 mg L^{-1} of Cu in 2.0, 5.0, 8.0, 11, 15, 20, 30% (v/v) ethanol medium were evaluated by FAAS and TS-FF-AAS with both Ni tubes. This same study was carried out for solutions containing 25 and $500 \mu\text{g L}^{-1}$ of Cd and Pb, respectively, in the same media. In this case, measurements were only performed using the Ni tube with six holes.

The influence of each medium, i.e. water, nitric acid and ethanol, on the transport and atomization processes of the sample was also evaluated. Solutions containing 1.0 mg L^{-1} of Cu, 25 and $500 \mu\text{g L}^{-1}$ of Cd and Pb, respectively, were prepared in different media: (a) water; (b) 0.14 mol L^{-1} HNO_3 ; (c) 2% (v/v) ethanol; (d) 0.14 mol L^{-1} HNO_3 plus 2% (v/v) ethanol.

2.5. Optimization of sample flow rate, sample volume, and measurement time

The experiments here described were carried out using a solution containing 1.0 mg L^{-1} of Cu in 2% (v/v) ethanol. All measurements were performed using the Ni tube with six holes.

The effect of the carrier flow rate on Cu absorbance signals was evaluated for 0.46, 0.54, 0.57 and 0.85 mL min^{-1} . The volume of the sample loop was kept in $150 \mu\text{L}$.

The carrier flow rate was kept in 0.54 mL min^{-1} and the effect of the sample volume on the absorbance signals was studied for 150, 300 and $450 \mu\text{L}$ sampling loops.

Afterwards, the acquisition of the transient signals was made in 80 s because this period of time was sufficient to measure transient signals when injecting a sample volume of $150 \mu\text{L}$ without compromising the analytical throughput.

2.6. Sample preparation

Wine samples were analyzed without any step of sample digestion. A simple 1:6 v/v dilution with 0.14 mol L^{-1} HNO_3 was performed to reach an ethanol concentration around 2% (v/v). This ethanol concentration provided maximum sensitivity.

For determination of the metals in grape juices, samples were analyzed directly. The obstruction of the ceramic capillary tube

Table 1
Instrument parameters for determination of Cu, Cd and Pb by TS-FF-AAS

Variables	Cu	Cd	Pb
Flow rate (mL min^{-1})	0.54	0.54	0.54
Sample volume (μL)	150	150	150
Air flow rate (L min^{-1})	13.5	13.5	13.5
Acetylene flow rate (L min^{-1})	2.0	2.0	2.0
Measurement time (s)	80	80	80
Spectral resolution (nm)	0.5	0.5	0.5
Lamp current (mA)	4.0	4.0	10.0
Wavelength (nm)	327.4	228.8	283.3
Height of the Ni tube (cm)	1.5	0.3	0.3
Carrier	HNO_3 1% (v/v)	HNO_3 1% (v/v)	HNO_3 1% (v/v)

Download English Version:

<https://daneshyari.com/en/article/1245445>

Download Persian Version:

<https://daneshyari.com/article/1245445>

[Daneshyari.com](https://daneshyari.com)