Analytical Methods

Arsenic speciation analysis in mono-varietal wines by on-line ionic liquid-based dispersive liquid–liquid microextraction

Leticia B. Escudero [a,b,d], Estefanía M. Martinis [a,c,d], Roberto A. Olsina [a,b], Rodolfo G. Wuilloud [a,c,d,*]

[a] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
[b] Instituto de Química de San Luis, Universidad Nacional de San Luis (INQUISAL-UNSL), San Luis, Argentina
[c] Laboratory of Analytical Chemistry for Research and Development (QUIANID), Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Padre J. Contreras 1300, Parque Gral. San Martín, M5502JMA Mendoza, Argentina
[d] Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Mendoza, Argentina

ABSTRACT

A highly efficient separation and pre-concentration method for arsenic species determination, based on ionic liquid (IL) dispersive microextraction technique implemented in a flow analysis system, is proposed. Highly selective separation of arsenite species [As(III)] was achieved by chelation with sodium diethyldithiocarbamate (DDTC) followed by dispersion with 40 mg of 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8mim][PF_6]) IL. Analyte extraction, retention and separation of IL phase were achieved with a packed microcolumn and As(III) was determined in eluent solution by electrothermal atomic absorption spectrometry (ETAAS). Concentration of As(V) was deduced by the difference between total inorganic arsenic and As(III). Thus, determination of total arsenic was performed by previous degradation of organo-arsenic species, followed by a reduction. Under optimal conditions, As(III) extraction efficiency was 100% and a sensitivity enhancement factor of 46 was obtained with only 4.0 ml of sample The method was successfully applied for arsenic speciation studies in mono-varietal wines.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Arsenic is a highly toxic metalloid that can be present in food, soil, water, air and living organisms (Cornelis, Caruso, Crews, & Heumann, 2003, 2005). It has been demonstrated in wine-related studies that arsenic is usually found in wines as a consequence of herbicides and insecticides used for grape production (Moreno, Cámara, Corns, Bryce, & Stockwell, 2000). International Office of Vine and Wine (OIV) has established the maximum contaminant level of arsenic in wines as 0.2 mg/l (2007). Despite marked differences in arsenic toxicology, there is no legislation for the maximum allowable concentration of specific arsenic species in wine. In order to obtain information about the bioavailability and toxicological effects of arsenic, it is necessary to obtain both qualitative and quantitative data regarding speciation.

Since arsenic concentrations in wine samples are usually very low, sensitive analytical techniques are required. Most of the works related to total arsenic determination in wines are based on hydride generation atomic absorption spectrometry (HG AAS) (Segura, Madrid, & Cámara, 1999; Tašev, Karadjova, & Stafilov,

2005) and inductively coupled plasma-mass spectrometry (ICP-MS) (Almeida, Vasconcelos, Barbaste, & Medina, 2002; Baxter, Crews, Dennis, Goodall, & Anderson, 1997). However, interference has been reported with ICP-MS in direct arsenic determination in wines because of the high ethanol content (Wangkarn & Pergantis, 1999). Different techniques have been used for arsenic speciation including gas chromatography (GC) (Campillo, Peñalver, Viñas, López-García, & Hernández-Córdoba, 2008) and high performance liquid chromatography (HPLC) (Šlejkovec, Van Elteren, & Byrne, 1997) because they offer advantages such as high sample number throughput and the potential for determining organo-arsenic species. These separation techniques are complex, and their instrumental and operation costs high for several routine analytical laboratories. For this reason, simple, sensitive and low cost nonchromatographic methods are needed for arsenic speciation studies in wine.

Generally, conventional microextraction techniques use volatile and toxic solvents for extraction (Munoz, Velez, & Montoro, 1999; Sounderajan, Udas, & Venkataramani, 2007). Ionic liquids (ILs) possess a number of unique properties such as negligible vapour pressure, thermal stability at high temperatures, and favourable viscosity and miscibility with water and organic solvents as well as specificity towards desirable ions (Liu, Jiang, & Jönsson, 2005). These properties make them attractive alternatives to replace

those using environmentally unfriendly solvents that produce volatile organic compounds. The use of ILs in LLME has been implemented in different techniques such as single-drop microextraction (SDME) (Martinis, Berton, Altamirano, Hakala, & Wuilloud, 2010; Martinis & Wuilloud, 2010) and dispersive liquid–liquid microextraction (DLLME) (Berton & Wuilloud, 2010; Gharehbaghi, Shemirani, & Baghdadi, 2009). DLLME has been shown to be an efficient approach because of its simplicity, extraction efficiency and low consumption of solvents (Martinis, Berton, Monasterio, & Wuilloud, 2010). However, this technique has been used mostly in a batch mode, which is time consuming and associated with a high risk of contamination. For these reasons, ILs have been combined with flow injection (FI) techniques for automation and miniaturisation handling during sample preparation (Berton & Wuilloud, 2011) improving precision and enrichment whilst decreasing limits of detection (LODs).

Up to date, there are not analytical methods reported in the literature for pre-concentration and determination of arsenic species in wine samples. Therefore, the aim of this work was to develop a sensitive and selective on-line DLLME method for arsenic speciation studies in wine samples based on benign solvents. The proposed method was coupled to electrothermal atomic absorption spectrometry (ETAAS) for arsenic speciation in different monovarietal wines produced in the Mendoza province, Argentina. Moreover, this work is one of first focusing on this important matter.

2. Materials and methods

2.1. Instrumentation

The measurements were performed with a Perkin Elmer (Uberlingen, Germany) Model 5100ZL atomic absorption spectrometry equipped with a transversely heated graphite atomizer, an arsenic Electrodeless Discharge Lamp (EDL) and a Zeeman-effect background correction system. Instrumental conditions used for arsenic determination in IL-enriched phase are shown in Table 1. A centrifuge (Luguimac, Buenos Aires, Argentina) model LC-15 was used to accelerate the phase separation process. A vortex model Bio Vortex B1 (Boeco, Hamburg, Germany) was used for mixing the reagents. A Horiba F-51 pH metre (Kyoto, Japan) was used for pH determinations.

The flow injection system has been employed previously by our group (Berton, Martinis, & Wuilloud, 2010; Berton & Wuilloud, 2011). Gilson (Villiers Le-Bell, France) Minipuls 3 peristaltic pumps equipped with Tygon-type pump tubes (Gilson) were employed to propel the sample, reagent and eluent. The sample injection was achieved using six-way rotary valves from Upchurch Scientific (Oak Harbour, WA, USA). A microbore glass column (10 mm effective bed length; 2 mm internal diameter), filled with Florisil® and fitted with porous 25 μm glass frits was used for on-line retention of the dispersed IL phase.

2.2. Reagents

Stock standard solutions of inorganic As(V) and As(III) species [1000 mg/l as sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) (99.998%) (Sigma–Aldrich, Milwaukee, WI, USA) and sodium (meta)arsenite ($AsNaO_2$) (99%) (Fluka, Buchs, Switzerland), respectively] were prepared with a final HNO_3 concentration of 0.05 mol/l. Disodium methylarsonate ($CH_3AsNa_2O_3 \cdot 6H_2O$) (MMA, 98%) (Fluka) and dimethylarsinic ($C_2H_7AsO_2$) (DMA, 98.6%) (Fluka) stock standard solutions (1000 mg arsenic/l) were prepared with ultrapure water and stored at 4 °C in amber-coloured HDPE bottles. Working solutions were prepared by diluting these stock solutions.

Table 1
Instrumental and experimental conditions for arsenic species determination.

Instrumental conditions	
Wavelength	193.7 nm
Spectral band width	0.7 nm
EDL lamp current	300 mA
Matrix modifier	5 μg Pd [Pd(NO$_3$)$_2$]
	3 μg Mg [Mg(NO$_3$)$_2$]

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (ml/min)
Graphite furnace temperature program				
Drying 1	110	1	30	250
Drying 2	130	15	30	250
Pyrolysis	600	10	10	250
Pyrolysis	800	5	10	250
Atomization	2300	0	3	–
Cleaning	2400	1	2	250

Extraction conditions	
Sample volume	4 ml
DDTC concentration	7.5×10^{-4} mol/l
Working pH	4
Buffer concentration	2.5×10^{-2} mol/l
Triton X-114 concentration	0.05% (w/v)
NaClO$_4$ concentration	1.5% (w/v)
[C$_8$mim][PF$_6$] IL amount	40 mg
Disperser solvent	Methanol (100 μl)
Shaking time with [C$_8$mim][PF$_6$] IL	4 s
Eluent	Methanol (10% (v/v) HNO$_3$)
Eluent volume	100 μl
Loading flow rate	0.5 ml/min
Elution flow rate	0.25 ml/min

A 1000 mg/l palladium nitrate solution [Pd(NO$_3$)$_2$·2H$_2$O (Fluka)] and 150 mg/l magnesium nitrate solution [Mg(NO$_3$)$_2$ (Merck, Darmstadt, Germany)] were prepared and used as chemical modifiers. These solutions were prepared in 0.1% (v/v) HNO$_3$ (Ultrex® II Mallinckrodt Baker, Phillipsburg, NJ, USA). A 4% (w/v) sodium diethyldithiocarbamate trihydrate (DDTC) > 99% (Fluka) solution was prepared in ultrapure water. A 2.0 mol/l acetic acid–acetate solution (Merck) adjusted to pH 4.0 by dissolution of sodium hydroxide (Merck) was employed as buffer solution. [C$_8$mim][PF$_6$] IL was synthesized according to a method proposed by Huddleston et al. (2001). Methanol (Merck) was used as a dispersant. Solutions of potassium iodide (99.9%) (Ultrex® II Mallinckrodt Baker) and sodium thiosulfate (99%) (Sigma–Aldrich) were prepared for reducing As(V). Hydrochloric acid (37%) from Merck was used. A NaClO$_4$·H$_2$O (Merck) solution 24% (w/v) was employed in order to adjust ionic strength. A surfactant solution containing 5% (w/v) Triton X-114 (Merck) was used to prevent the IL phase sticking to the Tygon tube walls. Synthetic magnesium silicate, Florisil® (100 Å pore size, 70–230 mesh particle size, Aldrich) was selected as filling material for the microcolumn. Ultrapure water (18 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Paris, France). All bottles destined for storing samples and standard solutions and the glassware were washed in 10% (v/v) nitric acid for 24 h and later rinsed with ultrapure water.

2.3. Sample collection and conditioning

Bottled wine samples were purchased at several local wine shops of Mendoza city (Argentina). Two typical varieties of wine in local consumption were studied. Malbec was chosen as the red variety and Sauvignon Blanc was selected as the white variety. All commercial products were 2009 vintage wine, with 6 months of ageing in oak barrels according to specifications given by manufacturers. Vintage year for wines was selected in order to analyse young wines, which are more accessible to common consumers. The wines were sampled by removing the cork, discarding approximately the first