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A new cloud point extraction procedure for determination of inorganic antimony species in beverages and biological samples by flame atomic absorption spectrometry

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ABSTRACT

A new cloud-point extraction (CPE) for the determination of antimony species in biological and beverages samples has been established with flame atomic absorption spectrometry (FAAS). The method is based on the fact that formation of the competitive ion-pairing complex of Sb(III) and Sb(V) with Victoria Pure Blue BO (VPB^+) at pH 10. The antimony species were individually detected by FAAS. Under the optimized conditions, the calibration range for Sb(V) is 1–250 μg L^{-1} with a detection limit of 0.25 μg L^{-1} and sensitive enhancement factor of 76.3 while the calibration range for Sb(III) is 10–400 μg L^{-1} with a detection limit of 5.15 μg L^{-1} and sensitive enhancement factor of 48.3. The precision as a relative standard deviation is in range of 0.24–2.35%. The method was successfully applied to the speciative determination of antimony species in the samples. The validation was verified by analysis of certified reference materials (CRMs).

1. Introduction

Antimony can be found in the environment as a result of human activities. Inorganic compounds of antimony are more toxic when compared with organic compound of many other elements (Madrakian & Bozorgzadeh, 2009). Its toxicity may change according to oxidation state of antimony. For instance, trivalent antimony Sb(III) is ten times more toxic than pentavalent antimony Sb(V). It is reason for this that Sb(III) shows high interest to red blood cells, and sulfhydryl groups of cell components (Cornelis, 2005). According to researches made in literature (Bach, Dauchy, Chagnon, & Etienne, 2012), Sb_2O_3 and Sb_2S_3 cause to lung tumors in rats. These chemical compounds are carcinogenic for humans. Therefore, they are listed as precursor pollutants by United States Environmental Protection Agency (USEPA) and the European Commission (Hansen et al., 2010). In spite of its toxicity, antimony is used as therapeutic agents against several tropical diseases. Systemic antimony therapy is preferred for multiple lesions that leishmaniasis disease causes (Sundar & Chakravarty, 2010). Antimony-containing compounds are used in glass, ceramic production, the polyethylene terephthalate (PET) bottles and fire retardants (Welle & Franz, 2011). Plastic bottles, which is made using PET, are widely used in worldwide for packetizing of alcoholic and nonalcoholic beverages. As a result of this use, antimony and its derivatives can penetrate into beverages depending on storage time of bottles, temperature, and concentration in the polymer of the dissolved chemical species, nature, type and solubility of the sample of dissolved chemical species (Sánchez-Martínez, Pérez-Corona, Cámara, & Madrid, 2013; Westerhoff, Prapaipong, Shock, & Hillaireau, 2008). The maximum amount of antimony for beverages packaged in PET bottles has been reported for some counties as follows: 40.0 μg kg^{-1} in Europe, 6.0 μg kg^{-1} by United States Food and Drug Administration (FDA), 50.0 μg kg^{-1} in Japan and 20.0 μg kg^{-1} by World Health Organization (WHO) (Shotyk & Rachler, 2007; Westerhoff et al., 2008; WHO, 2011). Daily intake of antimony can be 6.0 μg kg^{-1}. Namely, intake of 420 mg of antimony for a 70 kg adult human can be tolerated (Sergio et al., 2014). The excess of this value can cause toxic properties. Thus, determination of the antimony in beverages and foods is an extremely important topic.

Several analytical techniques such as hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) (Feng, Narasaki, Chen, & Tian, 1999), microwave induced plasma atomic emission spectrometry (MIP-AES) (Zhang, Zhang, Zhao, Quan, & Jia, 2012), anodic stripping voltammetry (ASV) (Zong, Long, & Nagaosa, 2011), flame atomic absorption spectrometry (FAAS) (Dessuya et al., 2013), electrothermal vaporization inductively coupled plasma atomic emission spectrometry

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(ETV-ICP-AES) (Li, Hu, & Jiang, 2006), atomic fluorescence spectrometry (AFS) (Cava-Montesinos, Cervera, Pastor, & Guardia, 2003), inductively coupled plasma mass spectrometry (ICP-MS) (Maher et al., 2012), ion chromatography (IC) coupled with hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) (Depoi & Pozebon, 2012), X-ray fluorescence spectrometry (XRF) (Margui, Sague, Queralt, & Hidalgo, 2013), cathodic striping voltammetry (CSV) (El-Shahawi, Bashammakh, Al-Sibaai, Bahaffi, & Al-Gohani, 2011), electrothermal atomic-absorption spectrometry (ET-AAS) (Ojeda, Rojas, Pavıon, & Martıın, 2005) kinetic-spectrophotometric determination (Afkhami, Madrakian, & Abdolmaleki, 2005) and spectrophotometry (Madrakian & Bozorgzadeh, 2009) were used for determination of antimony and antimony species in beverages and biological samples until now. Among these techniques, atomic absorption spectrometry is still widely used in analytical chemistry. Moreover, the device has advantages such as convenience, selectivity, speed, precision and accuracy than others. The amounts of Sb species in beverages and biological samples are very low. Separation and preconcentration methods such as solid phase extraction (SPE) (Calvo-Fornieles, Torres, Alonso, Cordero, & Pavon, 2011), liquid–liquid extraction (LLE) (Serafimovska, Arpadjan, & Stafilov, 2011), liquid membrane extraction (LME) (Zeng, Yang, & Zhou, 2011), single-drop extraction (SDE) (Fan, 2007), dispersive liquid–liquid microextraction (DLLME) (Yousefi, Shemirani, & Jamali, 2010) and cloud point extraction (CPE) (Samadi-Maybodi & Rezaei, 2012) have been applied prior to analysis.

The first CPE are described by Miura, Ishii, and Watanabe (1976), and Watanabe and Tanaka (1978). After this date, CPE based on separation/preconcentration method has started to attract intense attention. The reason for this interest have "green chemistry" properties such as low toxicity of surfactants, the use of dilute solutions in experiments, inexpensive compared to organic solvents, and not volatile. Also, the CPE enables higher recovery efficiency and a large pre-concentration factor (Liang & Yang, 2010). Micelles-assisted extraction method is a wide range of applications in several different matrixes such as water, blood, urine, food samples, mineral waters, wastewaters, and wine in analytical chemistry (Jiang, Wen, & Xiang, 2010). Cloud point temperature is defined as the temperature that micelles are formed and became turbid of surfactants in aqueous solution (Pytlakowska, Kozik, & Dabioch, 2013). Above the temperature, the micellar solution is separated into two phases that a surfactant-rich phase of a small volume and a dilute aqueous phase. For elementary analysis, after a hydrophobic complex formation with a suitable chelating agent, analyte is extracted to the surfactant-rich phase (Filella, Belzile, & Chen, 2002). Also, the optimization of the experimental parameters such as ligand concentration, surfactant type and concentration, pH, ionic strength and solvent type and volume should be conducted.

The main aim of the existing study is to optimize a new CPE procedure for determining low levels of inorganic antimony species, Sb(III), Sb(V) and total Sb by FAAS, to develop a low cost and accessible analytical methodology for most laboratories which are involve in routine analysis, to apply the developed method into the wide range of matrices such as beverages, plasma and serum samples, and consequently to validate the method by using the CRMS.

2. Materials and methods

2.1. Instrumentation

AAS-6300 atomic absorption spectrometer (Shimadzu, Kyoto, Japan) equipped with D_2-background correction, an antimony hollow cathode lamp and an air-acetylene flame atomiser was used for the speciative determination of antimony in the biological and beverages samples. The wavelength, lamp current, spectral bandwidth, burner height, acetylene and air flow rates were 217.6 nm, 10 mA, 0.5 nm, 7 mm, 2.0 L min^{-1} and 10.0 L min^{-1}, respectively. 50 mL calibrated centrifuge tubes in the centrifuge (Universal-320, England) was used to accelerate the phase separation. A thermostatic water bath (EPC 4420, Termal, Turkey) was used to maintain the temperature in CPE experiments. The pH measurements were carried out using a pH-2005 digital pH meter equipped with a glass-calomel electrode (pH-2005, JP Selecta, Barcelona, Spain). Eppendorf vary-pipettes (10–100 and 200–1000 μL) were used to deliver accurate volumes. A refrigerator was used to keep the biological and beverages samples fresh and cool till the analysis.

2.2. Reagents and standards

Ultra-pure water with a resistivity of 18.2 MΩ cm was prepared using a Labconco (USA) water purification system. All solutions were prepared using this ultra-pure water. Before starting of experiment, all glassware and polyethylene (PE) bottles used in the experiment were treated firstly with 10% (w/v) HNO_3 solution and then with diluted HCl solution. Lastly, all experimental materials were washed with ultra-pure water. A stock Sb(III) and Sb(V) solution of 1000 μg mL^{-1} were prepared by dissolving appropriate amounts of potassium hexahydroxyantimonate and antimony trichloride (Sigma, St. Loius, MO, USA) in ultra-pure water. Stock solutions of 1.0×10^{-3} mol L^{-1} Victoria Pure Blue BO (VPB^+) (Sigma, St. Louis, MO, USA) were prepared fresh daily by dissolving an appropriate amount of the reagent in ultra-pure water. Then, working solutions were prepared by stepwise dilution of the stock solution just before use. The prepared all stock solutions were stored in PE bottles in a refrigerator at 4 °C. Triton X-114 solution of 5.0% (v/v) (Sigma, USA) was prepared by dissolving 5 mL of surfactant in 100 mL of ultra-pure water. A 0.04 mol L^{-1} of Britton–Robinson (BR) buffer solution of pH 10 was used to keep pH of the solutions. The BR buffer at pH 10 was prepared by dissolving appropriate amounts of mixing 0.4 mol L^{-1} H_3PO_4, 0.4 mol L^{-1} CH_3-COOH and 0.4 mol L^{-1} H_3BO_3 with the apropriated amount of 0.4 mol L^{-1} sodium hydroxide solution.

2.3. General CPE procedure

For the CPE, aliquots of 3.0 mL of sample or standard solution of Sb(III) in the range of 10–400 μg L^{-1} and Sb(V) in the range of 1–250 μg L^{-1}, 0.7 mL of BR buffer solution that have pH 10, 0.6 mL of 1.0×10^{-3} mol L^{-1} VPB^+, 0.9 mL of 20.0% (w/v) NaCl and 0.7 mL of 5.0% (v/v) Triton X-114, respectively were added into a 50 mL centrifuge tube and volume was completed to 50 mL with ultra-pure water. The solution was kept in a thermostatic water bath at 45 °C for 8 min to ensure turbidity. Then, centrifugation was made 8 min at 3500 rpm in order to separate the surfactant-rich phase. After cooling in an ice-bath, the surfactant-rich phase was separated from aqueous phase inverting the tubes. In order to decrease viscosity of obtained surfactant-rich phase, micellar phase was diluted to 1.5 mL with THF. Then, the resultant solution was directly introduced into FAAS for determination of Sb species. Finally, the Sb contents of beverages and biological samples were determined by using either calibration curve or standard addition calibration curve in order to control the matrix effect in which the Sb concentration is around the detection limit.

2.4. Analysis of biological, beverage and CRMs samples

For the present study, six canned beverages without alcohol, four different brands of beverages with alcohol, and four of the