Food Chemistry 212 (2016) 65–71

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

Electromembrane extraction and spectrophotometric determination of As(V) in water samples

Mohammad Ali Kamyabi *, Ali Aghaei

Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791 Zanjan, Iran

ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form 17 May 2016
Accepted 23 May 2016
Available online 24 May 2016

Keywords:
As(V)
Electromembrane extraction
Molybdenum blue complex
Water samples

ABSTRACT

In this study, for the first time electromembrane extraction (EME) was used as a highly efficient sample pre-treatment method for the UV–VIS spectrophotometric determination of As(V) in water samples. The influences of experimental parameters during EME were investigated and optimized using one-variable-at-a-time methodology as follows: organic solvent: 1-octanol + 2.5% (V/V) di-(2-ethylhexyl) phosphate, applied voltage: 70 V, extraction time: 15 min, pH of acceptor: 13, stirring rate: 750 rpm. The method allowed the determination of As(V) in the range of 5–300 ng mL^{-1}. The relative standard deviation was found to be within the range of 3.4–7.6%. The limit of detection, corresponding to a signal to noise ratio of three, was 1.5 ng mL^{-1}. The proposed method was finally applied to the determination of As(V) in water samples and relative recoveries ranging from 95 to 102% were obtained.

1. Introduction

Arsenic is an important environmental element because of its high toxicity at the level of parts per billion. It enters drinking water supplies from natural deposits in the earth or from agricultural and industrial practices. Industrial arsenic is mainly used as a wood preservative, but arsenic is also used in dyes, paints, drugs, soaps, and semi-conductors. Agricultural applications, mining, and smelting are other sources which may release arsenic in the environment. The contamination of drinking water and groundwater with arsenic has been reported in various regions of the world especially in developing countries (Meharg, 2005). Arsenic can occur in the environment in several oxidation states (−3, 0, +3 and +5) but in natural waters is mostly found as inorganic forms of trivalent arsenite (As(III)) and pentavalent arsenate (As(V)) which the first form, As(III), is more toxic (Jain & Ali, 2000). On the other hand inorganic arsenic forms are more toxic than organic forms which may however occur where waters are significantly impacted by industrial pollution (Hughes, 2002; Jain & Ali, 2000). Redox potential and pH are the most important factors controlling arsenic speciation. Under oxidising conditions, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3 will predominate. As a result, As(V) is the predominant form of inorganic arsenic especially in surface water (Smedley & Kinniburgh, 2001). It was previously proved that in excessive amounts, arsenic causes gastrointestinal damage and cardiac damage. There are some evidences that arsenic is also carcinogenic (Abernathy, Thomas, & Calderon, 2003; Zackheim, 1968). According to World Health Organization (WHO) guideline on drinking water quality, the maximum permitted concentration of arsenic in drinking water is 10 μg L^{-1}(WHO, 2011) Therefore, simple, rapid, highly sensitive, and accurate methods required for the determination of trace amounts of arsenic especially in environmental samples. Various analytical methods have been used for arsenic determination, including titrimetry (Rao, Sarojini, & Gandikota, 1972), chemiluminescence (Li & Lee, 2005), atomic absorption spectrometry (Welz & Melcher, 1985), inductively coupled plasma atomic emission spectrometry (ICP-OES) (De Oliveira, McLaren, & Berman, 1983), inductively coupled plasma mass spectrometry (ICP-MS) (Feng, Chen, Tian, & Narasaki, 1998), and spectrophotometry (Hu, Lu, & Jing, 2012; Lenoble, Deluchat, Serpaud, & Bollinger, 2003; Morita & Kaneko, 2006; Revanasiddappa, Dayananda, & Kumar, 2007). Recently, Ma et al. reviewed the papers published since 2005 on techniques for the measurement of arsenic in water samples (Ma, Sengupta, Yuan, & Dasgupta, 2014).

Except spectrophotometry, most of the other methods used in determination of arsenic require trained staff, expensive experimental setup and running cost. Therefore, many spectrophotometric methods have been developed as an alternative for the

---

* Corresponding author.
E-mail address: makamyabi@gmail.com (M.A. Kamyabi).

http://dx.doi.org/10.1016/j.foodchem.2016.05.139
0308-8146/© 2016 Elsevier Ltd. All rights reserved.

determination of arsenic instead of conventional techniques. Method of Molybdenum blue is one of the most popular spectrophotometry methods in determination of arsenic (DeSasa & Rogers, 1954). It is based on the reduction of the yellow molybdeoarsenic acid to intensely absorbing blue color which subsequently can be measured spectrophotometrically at 840 nm. It should be noted that among different forms of arsenic, only As (V) can form molybdenum blue. Hence, any other forms of arsenic such as As(III) must be first converted to As(V) in order to determine using molybdenum blue method. Although the method of molybdenum blue is poorer than that of atomic absorption in sensitivity and rapidity, it is characterized by a higher accuracy and precision. On the other hand it suffers from poor selectivity because of strong interference of Phosphate ion and different metal ions, such as copper, nickel, cobalt and zinc.

Electromembrane extraction (EME) is a new microextraction method in which an electrical voltage is applied to enhance the transport of charged species across a hollow fiber membrane (Pedersen-Bjergaard & Rasmussen, 2006). Although electromembrane extraction has been mainly used for charged organic samples such as basic drugs, it was generalized to metal ions for the first time in 2008 (Basheer, Tan, & Lee, 2008). Some other successful applications of this method have been reported for determination of inorganic anions and heavy metals, so far (Chanthasakda, Nitiyanontakit, & Varanusupakul, 2016; Davarani, Moazami, Keshtkar, Banitaba, & Nojavan, 2013; Khajeh, Pedersen-Bjergaard, Barkhordar, & Bohlooli, 2015; Kubáň, Strieglerová, Gebauer, & Boček, 2011; Safari, Nojavan, Davarani, & Morteza-Najarian, 2013; Tan, Basheer, Ng, & Lee, 2012). According to our knowledge, to date, no electromembrane extraction has been reported for determination of arsenic. In this study, we aim to improve the selectivity of the conventional Molybdenum blue method by using Electromembrane extraction as a very efficient sample clean up and pre-concentration method and also to lower the limit of detection of the method down to a level that covers the WHO recommended value of 10 µg L^{-1} arsenic in drinking water. We successfully applied the proposed method for determination of As(V) in different environmental samples.

2. Experimental

2.1. Chemicals

Analytical grade standard solution of 1000 mg L^{-1} H_3AsO_4, 1-octanol ($C_8H_{18}O$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), sodium metabisulfite ($Na_2S_2O_5$), potassium iodide (KI), iodine (I_2), hydrazine sulphate ($H_6N_2O_4S$) and sulfuric acid (H_2SO_4) were purchased from Merck (Darmstadt, Germany). Di-(2-ethylhexyl) phosphate (DEHP) was purchased from Fluka (Buchs, Switzerland). weak base anion-exchange resin, Indion GS 3000 (type 1), was purchased from ion exchange India ltd (Delhi, India) with an effective particle size of 0.5–0.65 mm.

All chemicals were analytical grade and were used as supplied without further purification. HPLC-grade water was purchased from Merck and was used to prepare all solutions.

2.2. Working solutions and reagents

Working solutions of As(V) were daily prepared by diluting appropriate volumes of the standard solution of arsenic. Iodine reagent was prepared by dissolving 0.25 g of iodine in 100 mL water containing 0.4 g potassium iodide. Sodium metabisulfite solution was freshly prepared by dissolving 0.5 g of the solid reagent in 10 mL water. Sodium hydrogen carbonate solution was prepared by dissolving 4.2 g of the solid in 100 mL water. Ammonium molybdate solution was prepared by dissolving 1.0 g of the solid in 10 mL water and 90 mL of 3.0 M sulphuric acid. Hydrazinium sulphate solution was prepared by dissolving 0.15 g hydrazinium sulphate in 100 mL water. Molybdenum reagent was prepared by mixing same volumes of ammonium molybdate solution and hydrazinium sulphate solution just before running the experiment.

2.3. Apparatus

A UV–VIS spectrophotometer,(HACH-LANGE, model DR-2800, Germany), with a micro-volume glass cell (500 µL) and a macro-volume glass cell (3500 µL) both with a path length of 1.0 cm was used for absorbance measurements at 840 nm. The pH measurements were made with bench top pH meter, (WTW, model Inolab 730, Germany).

2.3.1. Equipments for EME

The equipment used for the EME of As(V) is presented by Fig. 1. A 10 mL glass vial with an internal diameter of 2.0 cm and a height of 4.5 cm was used as the extraction vessel. A PP Q3/2 polypropylene hollow fiber (Membrana, Wuppertal, Germany) with an internal diameter of 0.60 mm, 200 µm wall thickness, and 0.2 µm pores was used to immobilize the supported liquid membrane (SLM) and holding the acceptor phase. The platinum electrodes with diameters of 0.25 mm, obtained from Pars Pelatine (Tehran,Iran), coupled to a power supply model Hy-30002E with a programmable voltage in the range of 0–300 V and with a current output in the range of 0–2 A from Hyelec (Zhejiang, China). During the extraction, the vessel was stirred by a magnetic hot plate stirrer from VELP Scientifica (Milan, Italy).

2.4. EME procedure

To a 50 mL sample solution, 1 mL of 0.1 mol L^{-1} Bis-Tris buffer solution (pH 7.3) was added and the mixture was passed through an ion exchange resin column at a flow rate of 2 mL min^{-1} in order to remove the phosphate ion which may be present in sample solution. (Indion GS 3000 (type 1)). Five milliliters of the sample solution pretreated as described above was transferred into the sample vial. A short piece of polypropylene hollow fiber (3.5 cm) dipped in 1-octanol with 2.5% (v/v) DEHP for 10 s and then the excess amount of solvent was removed with a medical wipe. 10 µL of a 100 mM sodium hydroxide solution, as acceptor solution, was injected into the lumen of the hollow fiber using a microsyringe.

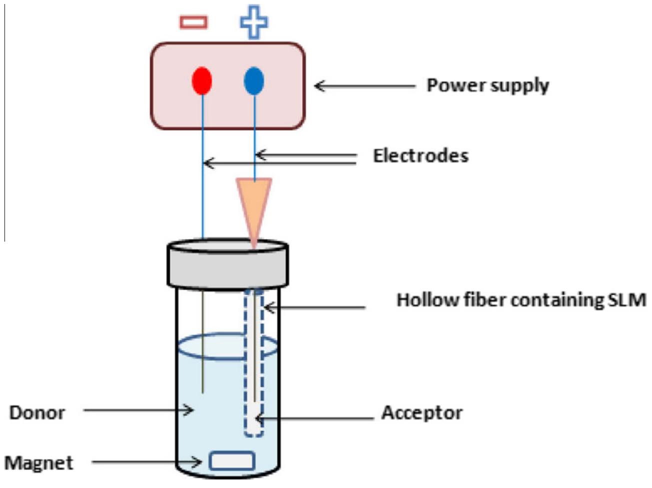

Fig. 1. Equipments used for electromembrane extraction of As(V).