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Solid phase microextraction method using a novel polystyrene oleic acid imidazole polymer in micropipette tip of syringe system for speciation and determination of antimony in environmental and food samples

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ABSTRACT

A simple, rapid and sensitive solid phase microextraction method was used for the speciation of inorganic antimony (Sb) by using a novel synthesized polymeric material in micropipette tip of syringe system. In present methodology, the specie of Sb (III) made hydrophobic complex with diethyl dithiocarbamate (DDTC) at pH 5.5 and subsequently adsorbed on polystyrene oleic acid imidazole polymer (POIP), whereas Sb(V) did not made complex and adsorbed on the polymer, remained in aqueous solutions. The strategy of multivariate was carried out to screen out the different variables and assessed the optimum values of their experimental values for the extraction efficiency of analyte. Then the analyte was sorbed on the polymer in micropipette tip of syringe system was quantitatively eluted by different types of acids at different levels for 2–6 aspirating/dispensing cycles. The extracted Sb(III) ions with modifiers were directed into the graphite furnace atomic absorption spectrometry for analysis. The limit of detection (LOD), limit of quantification (LOQ) and preconcentration factor (PF) for Sb(III) was found to be 6 ng L^{-1}, 20 ng L^{-1} and 100. The RSD value was found to be 4.2%. The standard addition method and certified reference materials were checked for accuracy and validity of method. The developed method was effectively applied for the determination of total and inorganic species of Sb(III) and Sb(V) in different types of water samples, whereas only total Sb was determined in acid digested soil, Tuna fish, rice, spinach, black tea, mixed fruit juice and ice tea samples.

1. Introduction

Antimony has been widely used in alloys, pharmaceutical samples, ceramics, glass and dyestuffs. Its concentration in various environmental samples is very low [1,2]. On other side antimony (Sb) was one of the most poisonous elements and has severe effects on human health and other living organisms [3,4]. It was reported that, Sb is a toxic element and it has toxicological and chemical properties resembles to those of arsenic [5]. Antimony occurs in two oxidation states in the environment and may also forms numerous organic and inorganic species having dissimilar toxic and physicochemical properties [6]. Inorganic antimony compounds are greater in toxicity than its organic compounds [7–9]. The Sb(III) ions toxicity is 10 folds greater than Sb (V) ions [8,10]. Deposition of Sb can take place in living things and apply significant-toxic effect on humans and other living organisms throughout a period of life and its toxicity might cause cancer of lung [11,12].

The concentration of Sb in consumable water must be less than 5 mg L^{-1} [13,14]. Since concentrations of antimony in biological and environmental samples are very small, for the purpose of determination of trace quantities of inorganic species of Sb in biological and environmental samples, influential techniques are necessary and merely some of them show sufficient sensitivity [14–17]. Numerous analytical techniques such as inductively coupled plasma optical emission spectrometry, inductively coupled plasma mass spectrometry, hydride generation, electrothermal atomic absorption spectrometry (ETAAS), neutron activation analysis, atomic fluorescence spectrometry have been carried out for measurement of Sb concentrations in the environmental samples [6,18–22]. To achieve consistent outcomes, an effective extraction and preconcentration step is required before analysis for species of Sb by ETAAS, because of low detection limit of Sb and matrix effects. Numerous enrichment-separation methods counting

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membrane filtration, cloud point extraction, coprecipitation, solid phase microextraction, liquid–liquid extraction and others methods have been carried out for analysis of Sb species [6,18–22].

Macroperoxide initiators have been successfully used in free radical polymerization of vinyl monomers in order to obtain block copolymers [23]. Eco-friendly autoxidation of unsaturated plant oils [24,25] and fatty acids [26] results in their peroxidized polymers which are called macro peroxide initiators. In this manner, the fatty acid macroperoxide initiators used in the olefin polymerization leading to fatty acid-poly olefin conjugate biopolymers [26]. Because of their additional –COOH functional groups in the fatty acid macroperoxide initiators, one pot polymerizations were applied [27,28]. In this work, first time styrene polymerization and imidazol amidation reaction in one pot synthesis were carried out to obtain poly styrene-*co*-oleic acid-*co*-imidazol co-polymer. According to our literature survey polystyrene oleic acid imidazole polymer (POIP) was not used as adsorbent in solid phase microextraction (SPME) method by using micropipette tip of syringe system. The present method has some advantages such as simple, rapid, low cost, sensitive and selective for separation, preconcentration and speciation of inorganic Sb.

In this work, polystyrene oleic acid imidazole polymer (POIP) was selected as adsorbent for solid phase microextraction of Sb(III) and Sb (V) speciation in mineral water, tap water and spring water samples. The present method was also applied to determined total Sb in soil and different food samples after microwave acid digestion method.

2. Experimental

2.1. Instrument

A Perkin Elmer Analyst 700 model (Norwalk, CT, USA) AAS equipped with deuterium background corrector and with HGA graphite furnace have been used for measurement of Sb(III). The Sb operating conditions of ETAAS were observed to be drying 1 (temperature 100 °C, ramp time 5 s, hold time 20 s), drying 2 (temperature 140 °C, ramp time 15 s, hold time 15 s), pyrolysis (temperature 1150 °C, ramp time 10 s and hold time 20 s), atomization (temperature 2250 °C, ramp 0 and hold time 5 s) cleaning (temperature 2600 °C, ramp time 1 s and hold time 3 s).

2.2. Solutions and reagents

Analytical reagent-grades were carried out throughout the work. Polystyrene oleic acid imidazole polymer (POIP) polymer has been synthesized and used as adsorbent as shown in Fig. 1 [25,29]. A 1000 mg L^{-1} Sb (III) stock solution was prepared by $SbCl_3$ (Sigma-Aldrich). Preparation of stock solution of 1000 mg L^{-1} Sb(V) was done by dissolution of $SbCl_5$ (Sigma-Aldrich). The standards pH was maintained to pH 2–8 with phosphate, acetate, borate and ammonia buffer solutions. Deionised water was used for all dilutions. Diethyl dithiocarbamate (DDTC) was taken from Sigma (St. Louis, MO, USA). Magnesium nitrate and palladium was used as matrix modifier.

2.3. Preconcentration procedure

About 3.5 mg of polystyrene oleic acid imidazole polymer (POIP) polymer was placed into a micropipette tip assembled with syringe system. The syringe system was washed with 1 mol L^{-1} HCl, 1 mol L^{-1} NaOH, methanol, acetone and ethanol for removing the impurities. The buffer solutions have been used to condition the syringe system before applying solid phase microextraction method. Replicate six standard solutions containing 0.2 μg L^{-1} of Sb(III) was arranged and pH 5.5 was maintained by using acetate buffer solution. 300 μL of diethyl dithiocarbamate 0.1% (w/v) was mixed to the solution and kept for 2–5 min to achieved the metal-DDTC complex. The solution was allowable to run through the micropipette type of syringe system containing

Polystyrene oleic acid imidazole polymer

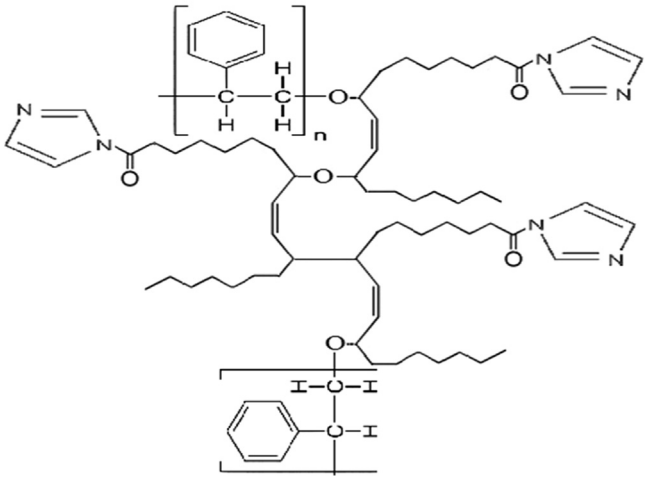

Fig. 1. The structure of the Polystyrene oleic acid imidazole polymer (POIP).

polymer by pulling and pushing of syringe. Metal-DDTC complex retained on the adsorbent then it was eluted with 0.5 mL of 2 mol L^{-1} HNO_3 by 3 times pulling and pushing cycles of syringe system. 20 μL sample solution containing Sb(III) ions plus 10 μL of mixture of 0.015 mg Pd and 0.010 mg $Mg(NO_3)_2$ as matrix modifier were injected into ETAAS.

2.4. Reduction of Sb(V) to Sb(III) and measurement of total antimony

For total Sb measurement, L-cysteine of 0.5% (m/v) was added at pH 5.5 to 50 mL of standard solution containing 0.2 μg L^{-1} of Sb (III) and 0.2 μg L^{-1} of Sb(V) and heated for 20 min in water bath [30,31]. Afterwards the reduction, the solutions were flow through the syringe system containing adsorbent in micropipette tip. Adsorbed Sb ions on the polymer were eluted with 0.5 mL of 2 mol L^{-1} HNO_3. Concentration Sb(III) was measured by ETAAS. The concentration of Sb(V) ion was measured by subtracting the concentration of Sb (III) from total Sb contents.

2.5. Factorial design test

The Plackett–Burman design (PBD) was carried out as a selection method with the purpose of introduction the important factors that affect the SPME of Sb(III) in standard, environmental and food samples using polymeric material in syringe system [32]. The experimental design applications decrease the time of method development in addition delivered less uncertain conditions of extraction, therefore easing interpretation of data. For the estimation of five variables at two concentration levels, a PBD with simply 16 experiments is defined instead of the $2^5 = 32$, necessary for a design of full factorial. The smaller (-) and greater (+) concentrations of five variables were stated in Table 1. Matrix of PBD is given in Table 2, whereas effects of significant factors were tested by variance analysis (ANOVA) using p-value. The relations

Table 1
Variables and their level for low (-) and high (+).

Variables	Symbol	Low (-)	High(+)
Amount of Adsorbent(mg)	A	1	6
pH	P	2	8
Ligand concentration(0.1%)	L	200 μL	600 μL
Pulling and pushing of syringe for adsorption (cycles)	PA	2	10
Pulling and pushing of syringe for desorption (cycles)	PD	2	6