



Imprinted polymer-based extraction for speciation analysis of inorganic tin in food and water samples

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ABSTRACT

In this study, an ion imprinted polymer (IIP), tin (IV)–4-(2-pyridylazo) resorcinol (PAR) complex (Sn(IV)–PAR–IIP) has been synthesized for speciation and selective solid-phase extraction (SPE) of tin species from food and water samples. For this purpose, copolymerization of Sn(IV)–4-(2-pyridylazo) resorcinol (PAR) complex was performed using methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and 2,2'-Azobisisobutyronitrile (AIBN) as functional monomer, cross-linking agent, and initiator, respectively. The polymer particles were characterized by FT-IR, and thermogravimetric (TG) analyses. The effects of different variables such as solution pH, mass of the polymer, extraction and elution time, and type and volume of the eluent for elution of tin were evaluated by Box–Behnken design and response surface methodology. The significance of independent variables and their interactions were tested by the analysis of variance (ANOVA) with 95% confidence limits. The optimal conditions at extraction step were 8, 70 mg, and 25 min for solution pH, amount of polymer, and extraction time, respectively. Also, the optimal values for the elution step were 6.5 mL of HCl (4 M) as the eluent volume and type and elution time of 120 min. The detection limit of the proposed method was found to be $1.3 \mu\text{g L}^{-1}$ and a linear dynamic range (LDR) in the range of $5\text{--}200 \mu\text{g L}^{-1}$ was obtained. The influence of various cationic interferences on recovery percentage of Sn(IV) was studied. The method was applied to recovery and determination of tin species in different real samples.

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1. Introduction

Tin is one of the toxic metals, which could accumulate in animals' tissues and the human body [1]. Tin is not easily oxidized in air and is used to coat other metals to prevent corrosion. Tin is widely used in tin plating, tin chemicals, brass and bronze, and niche uses [2]. Tin-plated steel containers are widely used for food preservation and production of beverage cans. This application comprises a large portion of the market for metallic tin. According to the Food and Agriculture Organization (FAO) of the United Nations and the World Health Organization (WHO), the maximum limit for tin in canned foods is 250 mg kg^{-1} [3]. Also, Blunden and Wallace provided some evidence suggesting that consumption of beverages or food containing tin above 200 mg kg^{-1} is accompanied by some gastrointestinal effects [4]. There are mainly two chemical species of inorganic tin (Sn(II) and Sn(IV)) in environmental samples. Several methods have been reported in the literature for determination of tin, including atomic emission spectrometry [5–9], electrochemical methods [10–12], spectrophotometry [13–19], and atomic absorption spectrometry [20–26]. However, most

of the above-mentioned methods are non-specific, complicated, and affected by sample matrix. Trace analysis of inorganic tin species in an environmental sample requires a chemical separation and pre-concentration step to eliminate matrix effects. Therefore, developing a new, specific separation technique, which provides speciation of tin compounds, is interested. To perform speciation of inorganic tin, the separation methods reported in the literature are usually based on solvent extraction [20,21,27] and solid-phase extraction [28].

In order to improve the selectivity of sample preparation procedure, selective materials as imprinted polymer sorbents can be employed. These materials possess cavities designed for a target analyte; thus, providing a retention mechanism based on molecular recognition [29,30].

Imprinted polymers (IIPs) represent a new class of materials possessing high selectivity and affinity for the target molecule [31–34]. This technique was first introduced by Wulff in 1995 [35] and developed quickly. Imprinting of synthetic polymers is a process wherein functional and cross-linking monomers are copolymerized in the presence of the target analyte that acts as a template. Subsequent removal of the imprinted target reveals binding sites that are complementary in size and shape to the analyte. Therefore, an analyte memory is created into the polymer,

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which is capable of rebinding the analyte with a very high specificity. Finally, this gives a sorbent with high stability and selectivity, large capacity, easy preparation through binding of the analyte, low-cost synthesis, and increased stability towards pH, solvent, and temperature, which provides high sample clean-up for very complicated matrix [36–38].

The purpose of this study is to combine ion imprinted polymers (IIPs) with GFAAS for extraction and speciation analysis of inorganic tin in environmental water samples. Effects of several factors such as solution pH, type, volume and concentration of the eluent, and extraction and elution times of the analyte on the polymer were investigated and optimized with the aid of response surface methodology. Under optimal conditions, the analytical parameters were obtained and the method was examined with real sample analysis.

2. Experimental

2.1. Materials and reagents

All the chemicals used for synthesis of the polymer including methacrylic acid (MAA) as the functional monomer, ethylene glycol dimethacrylate (EGDMA) as the cross-linker, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as the template ion, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 4-(2-pyridylazo) resorcinol (PAR) as the ligand, and methanol as the solvent were prepared from Merck (Darmstadt, Germany). 2,2'-azobisisobutyronitrile (AIBN) as the initiator was purchased from Acros Organics (USA). Acetic acid, sodium hydroxide, perchloric acid, and HCl were of the highest purity available from Merck. Ultrapure water was prepared using a Milli-Q system from Millipore (Bedford, MA, USA).

The tap and sea water samples were obtained from Shahid Beheshti University (Tehran, Iran) and the Caspian Sea (Anzali, Iran) respectively. All the water samples were held in polyethylene bottles and stored in darkness at 4 °C and analyzed within 48 h of collection with no pre-treatment. Canned tuna samples were purchased at local markets. The tomato and can content were homogenized thoroughly in a food blender with stainless steel cutters. A sample was then taken and digested promptly as follows: 10 g of the homogenized sample was weighed into a beaker and 10 mL of conc. HNO_3 was added; after boiling until the volume was reduced to about 5 mL, conc. HCl was added and heated gently until the sample bumping (from evolution of Cl_2) stopped. Then, the solution was allowed to cool, transferred in a 25-mL volumetric flask, and diluted to the mark with distilled water.

2.2. Preparation of standard solutions

The stock solution of $3 \times 10^{-3} \text{ mol L}^{-1}$ of tin(IV) was prepared by dissolving appropriate amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 2 mol L^{-1} HCl and standardized by a known method [39]. A stock solution of tin(II) was also prepared by dissolving sufficient weight of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in concentrated HCl. Then it was diluted to the mark in 100-mL volumetric flask. Working standard solutions were prepared by appropriate dilution with ultrapure water on a daily basis. All the solutions were stored in the fridge (4 °C) and brought to the ambient temperature just prior to use. The PAR ligand stock solution was prepared in methanol.

2.3. Instrumentation

A Perkin–Elmer 503 atomic absorption spectrometer with a deuterium lamp background correction, equipped with a HGA-2100 furnace controller was used in the study. The instrumental parameters and temperature program used for graphite atomizer are listed in Table 1. All pH measurements were carried out by a

Table 1
Operating parameters for ET-AAS.

Spectrometer parameter				
Wavelength (nm)				286.3
Slit (mm)				1.3
Lamp current (mA)				5
Step	Temperature (°C)	Ramp time (sec)	Hold time (sec)	Gas flow (mL min ⁻¹)
Drying	100	0	20	300
Ashing	600	20	15	300
Atomization	2500	0	5	Stop
Cleaning	2750	0	2	300

digital WTW Metrohm 827 ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. A vacuum pump was obtained from Leybold (Germany). Also, adjustable vacuum gauge and controller were obtained from Analytichem International (Harbor City, CA, USA). Fourier transform infrared (FT-IR) spectra ($4000\text{--}200 \text{ cm}^{-1}$) in KBr were recorded using Bruker IFS66/S FT-IR spectrometer. Heidolph heater stirrer model MR 3001 (Germany) was employed for heating and stirring of the solutions. Thermal gravimetric and differential thermal analyses (TG/DTA) were carried out on a Bahr STA-503 instrument under air atmosphere.

2.4. Synthesis of IIP

The Sn(IV)-ion imprinted polymer beads were prepared by bulk polymerization [38,40]. Tin(IV) was prepared by heating 0.200 g of pure granulated tin with 20 mL of concentrated sulfuric acid. The mixture was then heated to dryness in order to expel sulfur dioxide. The residue was dissolved in about 25 mL of methanol at the ambient temperature and then 1 mmol of PAR (ligand) was dissolved into this solution and the resultant mixture was stirred for 1 h to form Sn–PAR complex. After preparation of the complex, 1 mmol MAA (functional monomer) and 10 mmol EGDMA (cross linker), and 0.1 mmol AIBN were added to the above-mentioned solution, which then purged with nitrogen for 10 min and the flask was sealed under nitrogen. Polymerization was performed in an oil bath at 65 °C for 24 h under atmosphere of nitrogen. Afterward, red color polymer was crushed, ground, and sieved to obtain particles with diameters in the range of 50–80 μm . Fine particles were removed by suspending polymer beads in acetone and by decantation of acetone for three times. After preparation of IIP, complete removal of the template was accomplished by a mixture of hydrochloric acid (5 M) and 10% acetic acid for several times to create free cavities complementary in size, shape, and functionality ready for the analyte recognition. The complete template removal was checked by GF-AAS. Finally, the particles were dried under vacuum in desiccators and used for the extraction studies. Synthesis of IIP is schematically shown in Fig. 1.

2.5. IIP extraction procedure

Batch experiments were used for extraction and elution studies. The dry imprinted polymer (70 mg) without template was immersed in 200 mL solution containing an unknown concentration of Sn(IV) ion. After stirring for 25 min, the solution was filtered and ultrapure water was used for elution of the adsorbed matrix. The solid polymer was dissolved in 6.5 mL hydrochloric acid (4 M) and stirred for 2 h. The yielded solution was subsequently filtered and the concentration of Sn(IV) ions was measured with GF-AAS. The concentration of Sn(II) was calculated by subtracting Sn(IV) from the total Sn.

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