



## Sub-nanomolar detection of zinc on the ion-imprinted polymer modified glassy carbon electrode



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### ABSTRACT

A glassy carbon electrode (GCE) modified with zinc ion-imprinted polymers (GC/IIP) was used for the determination of sub-nanomolar amounts of zinc in the tap water samples by means of anodic stripping voltammetry (ASV). The GC/IIP modified electrode revealed a significant improvement for zinc detection compared with the bare GCE. Zinc ion-imprinted polymers were synthesized by thermal polymerization and zinc ions were removed by leaching the IIP by HCl and after drying in the oven, utilized for the electrode modification. The potential was scanned from  $-0.3\text{ V}$  to  $+0.4\text{ V}$  versus Ag/AgCl and variable affecting parameters such as pH, deposition duration time, deposition potential and stirring speed were optimized for ASV detection. The resulting calibration curve exhibited a linear response within a concentration range of  $5 \times 10^{-10}$  to  $1 \times 10^{-8}\text{ M}$  with a low detection limit of  $0.5\text{ nM}$ . Finally, the method was successfully applied to the determination of water samples.

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### Introduction

Zinc is an essential trace element for humans, animals and plants. It is vital for many biological functions and plays a crucial role in more than 300 enzymes in the human body. Zinc plays a vital role in fertility, treatment of anorexia, growth, taste, smell, skin, hair and immune system. The tolerable upper limit for zinc was set at  $40\text{ mg day}^{-1}$  for adults over 19. Higher dose may cause gastrointestinal reactions including nauseous, vomiting, cramps and discomfort, so determination of this metal in serum blood, hair, water, and soil and food samples is very important. Various methods can be used for determination of metal ion, including liquid–liquid extraction, solid–liquid extraction (or solid-phase extraction, SPE) [1,2], flame atomic absorption spectrometry (FAAS) [3] and electrochemistry [4–7], but analytical chemists searches for easier and faster methods with high selectivity and sensitivity. Voltammetric techniques have several advantages such as their low cost, short analysis time and sensitivity.

Numerous studies have been done to the determination of Zn ions by voltammetry methods including carbon paste electrode [8], zinc electrodeposition on the surface of the working electrode [9], carbon nano-tube on glassy carbon electrode [10], organic chelating groups [11], mercury film electrode [12], and hanging

mercury drop electrode [13–15]. For metal ion sensors, the selectivity is usually evaluated by the relative capacities for binding competing metals, but most of the procedures with determination of low levels of zinc do not provide an appropriate selectivity, so we solved this problem with modified glassy carbon electrode by ion imprinted polymers of zinc. The polymers was prepared against some interferes such as Co(II), Cd(II), Ni(II) which, were found to be lower adsorption by synthesized IIPs.

Ion-imprinted polymers are as molecular imprinted polymers, but ion imprinting is a method for making binding sites to match the charge, size, and coordination number of the ion [16]. Metal ion-imprinted polymers can be applied to the pre-concentration and the sample clean-up stages for metal ion determination. The binding strength of recognition in polymer depends on the type and number of interaction sites, the template shape and rigidity of monomer-template [17,18], so in ion imprinting the choice of a complexing ligand is very important because it directly influences selectivity of the sorbent. The ligand was embedded inside the polymer matrix through some trapping process. Ion imprinting polymers are ideally propitious to construct, the main advantages of imprinted polymers are their robustness, easy preparation and low cost and they demonstrate high chemical and physical stability that can be used in aggressive media and harsh environmental conditions. The general procedure for producing an ion-sensing polymer includes the following steps: (1) selection of a suitable ligand and preparation of a ligand–metal complex and (2) synthesis of copolymers of ion complexes with monomers and cross-linkers

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in order to create selective cavities inside the polymer network. Moreover, template ions can be easily extracted from the polymeric particles by leaching with a mineral acid after leaching the cavities are complementary in shape and size of the imprint metal ion.

In the present work for obtaining an improved voltammetric technique we report an electrochemical sensor for Zn based on an ion imprinted polymers on the glassy carbon electrode studied by anodic stripping voltammetry by which stripping analysis has been widely recognized as a powerful tool for trace analysis. Stripping voltammetry is an electro-analytical technique with an extremely low detection limit. IIP was synthesized using 8-hydroxyquinoline and styrene and casted on a glassy carbon electrode utilizing Nafion. The GCE/IIP was then applied to the determination of sub-nanomolar concentrations of zinc using square-wave anodic stripping voltammetry (SW-ASV) in tap water samples.

## Experimental

### Apparatus

All voltammetric measurements were carried out by means of an Autolab potentiostat/galvanostat (model 30(2)) under pure Argon atmosphere. Experiments were done in a conventional electrochemical cell holding 50 mL and three-electrode system, consisting of saturated Ag/AgCl electrode as the reference electrode, modified glassy carbon electrode as the working electrode, and a platinum wire as the auxiliary electrode. The temperature was maintained at  $25.0 \pm 0.5^\circ\text{C}$ , using a water thermostatic bath.

FT-IR spectra were recorded in the region of  $400\text{--}4000\text{ cm}^{-1}$  was recorded in KBr pellets utilizing a BRUCKER vector 22 FT-IR spectrophotometer. The spectrum obtained after multiple scans was a plot of transmittance percent against wave number. Scanning electron microscopy (SEM) images were captured employing XL-30 SEM. A personal computer was used for data storage and processing.

### Reagents

A stock solution of  $1.0 \times 10^{-3}\text{ M}$  zinc was prepared by dissolving appropriate amount of  $\text{ZnCl}_2$  in  $1.0 \times 10^{-3}\text{ M}$  hydrochloric acid. Hydrochloric acid (30% for trace analysis), 2-methoxyethanol, 2,2'-azobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EGDMA), styrene,  $\text{ZnCl}_2$ , and 8-hydroxyquinoline were of analytical grade were obtained from Merck and Co. Double distilled deionized water was used for preparation of solutions.

### Preparation of Zn(II)-ion imprinted and non-imprinted polymers

The Zn(II) imprinted polymers were prepared by thermal polymerization. The oxine was used as a non-vinylated ligand. Zn-IIPs were synthesized in two steps: (1) preparation and isolation of binary complexes of Zn-oxine with 1 mmol of Zn and 2 mmol of oxine with 10 mL of 2-methoxyethanol, as porogen, they were mixed and stirred for 15 min and (2) copolymerization of the formed binary complex with 8 mmol of styrene, as a monomer, and 32 mmol of ethylene glycol dimethacrylate (EGDMA), as a cross-linker, and AIBN, as a chemical initiator. The obtained solutions were purged using nitrogen gas for 10 min to remove molecular oxygen from it, then sealed. The reaction temperature was maintained at  $60^\circ\text{C}$  for 24 h in an oil bath. The resulting light yellow solid polymers were washed with deionized water, dried and then ground. For leaching of zinc(II), the obtained IIP and non-imprinted polymer particles were stirred with  $6\text{ mol L}^{-1}$  HCl

for 12 h. Then, the precipitated particles were washed using deionized water until a neutral pH value is set. Finally, because of leaching the Zn(II) ions the color of IIPs powder were changed from light yellow to white. The resulting white powder was dried at  $60^\circ\text{C}$ . The non-imprinted polymer (NIP) was synthesized similar to Zn(II) imprinted polymers, however, the synthesis was done in the absence of Zn(II) ions. The prepared IIP and NIP were used for modified glassy carbon electron fabrication.

### Preparation of the GC/IIP modified electrode

For the preparation of GCE/IIP, the GCE surface was first mechanically polished with  $0.05\text{ }\mu\text{m}$   $\alpha$ -alumina powder and rinsed thoroughly with acetone and doubly distilled water. For construction of the GC/IIP modified electrode, 0.20 g of powdered IIP or NIP was dispersed in deionized water and  $40\text{ }\mu\text{L}$  Nafion 0.5% was added to the suspension. Upon ultrasonication agitation for 15 min, a homogeneous stable IIP-Nafion suspension was obtained. A  $10\text{ }\mu\text{L}$  aliquot of IIP-Nafion suspension was casted on the GC electrode surface, and dried in oven at  $35^\circ\text{C}$ .

### Determination procedure

The general procedure for obtaining square-wave anodic stripping voltammetry was followed in a 50 mL solution containing  $1.0 \times 10^{-3}\text{ M}$  HCl (pH 3.0). The solution was transferred into a dry voltammetric cell and was purged by high purity Argon gas for 10 min before ASV measurements. A short time pre-concentration carried out with a stirring speed of 260 rpm. The potential was scanned between  $-0.3$  and  $0.8\text{ V}$  using square-wave modulation with  $0.0015\text{ V}$  step amplitude,  $0.02\text{ V}$  pulse amplitude, and frequency of 8 Hz. The calibration curve was drawn and linear regression and detection limits were calculated.

## Results and discussion

### Characterization of Zn-imprinted polymeric particles

#### FT-IR spectra were recorded for prepared Zn-IIP particles

Fig. 1 shows the IR spectra of un-leached (Fig. 1a) and leached zinc imprinted polymers (Fig. 1b). As is expected, the characteristic bonds of polymeric matrix (styrene-ethylene glycol dimethacrylate) are observed in all materials. The bonds observed at  $2957.30\text{ cm}^{-1}$  correspond to the C–H stretching vibrations of the aromatic and aliphatic system,  $3601.41\text{ cm}^{-1}$  for OH,  $1727\text{ cm}^{-1}$  for carbonyl group in EGDMA. The aromatic ring bending vibrations of the 1458 and  $1635, 1159\text{ cm}^{-1}$  for C–O can be observed. The weak O–H stretching band in un-leached IIP is due to the presence of Zn ions and interaction of Zn(II) with deprotonated –OH group of oxine. In the leached polymer, there is a broad band around  $3601\text{ cm}^{-1}$ . So, it is clear that in leaching process, only zinc is removed from the polymeric networks. The leached zinc imprinted polymers were analyzed utilizing XRF experiment. The results of analysis indicated that there was not any Zn in the leached zinc imprinted polymers.

#### Microanalysis

The SEM images in Fig. 2 show the three-dimensionally microporous structure of IIP films on the GCE surface, and an array of closely packed polymer particles embedded in Nafion is observed on the surface, which is kept in contact with the sample solution. The microporous surface of Zn(II)-IIP films provides high specific surface area and more interaction sites, and can also offer increased mass transport and easier accessibility to the active sites through the electrode. This suggests that the IIP particles are

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