Analytica Chimica Acta 689 (2011) 52–59

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Application of an Hg^{2+} selective imprinted polymer as a new modifying agent for the preparation of a novel highly selective and sensitive electrochemical sensor for the determination of ultratrace mercury ions

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ARTICLE INFO

Article history:
Received 3 October 2010
Received in revised form 1 January 2011
Accepted 18 January 2011
Available online 25 January 2011

Keywords:
Hg^{2+} imprinted polymer
Electrochemical sensor
Carbon paste electrode
Ultratrace level

ABSTRACT

A simple and very selective electrode, based on a mercury ion imprinted polymer (IIP), and its application for the determination of Hg^{2+} ions in the real samples is introduced. Mercury ion selective cavities were created in the vinyl pyridine based cross-linked polymer. In order to fabricate the sensor carbon particles and polymer powder were mixed with melted n-eicosane. An explicit difference was observed between the responses of the electrodes modified with IIP and non imprinted polymer (NIP), indicating proper performance of the recognition sites of the IIP. Various factors, known to affect the response behavior of selective electrode, were investigated and optimized. The interference of different ionic species with the response of the electrode was also studied. The results revealed that, compared to previously developed mercury selective sensors, the proposed sensor was more selective, regarding the common potential interferer. This sensor showed a linear response range of 2.5×10^{-9}–5.0×10^{-7} M and lower detection limit of 5.2×10^{-10} M (*S*/*N*). The sensor was successfully applied to the determination of mercury in real samples.

1. Introduction

Mercury is one of the most toxic elements in the environment, because of its high reactivity, its extreme volatility and its relative solubility in water and living tissues [1]. Contamination of the environment with mercury has unfortunately remained a serious problem, despite noticeable efforts in recent years [2–4]. The element is also famous for the fact that ionic mercury and its derivatives tend to bioaccumulate in the human body which leads to the gathering of high concentrations of the element, which can in turn cause symptoms such as weakness, sleeplessness, paranoia, excessive salivation, skin itching and swelling, fever, memory loss, elevated blood pressure, tremors, gingivitis, excitability etc. Mercury poisoning can result from inhaling its vapor, its ingestion, injection or absorption through the skin and does most of the damage to the neurologic, gastrointestinal, and renal systems [5–8].

Determination of trace levels of mercury is of great urgency and hence great efforts have been made to analyze the element in trace levels by means of a wide range of spectrometric methods such as atomic fluorescence spectrometry, atomic absorption spectrometry and UV spectrophotometry [9–12]. These techniques are cost intensive, time consuming, hard to use and more importantly not suitable for the task of in situ testing and monitoring. On the other hand, electrochemical methods are the most favorable techniques for the determination of metal ions because of their high sensitivity in addition to low costs, ease of operation and portability. Stripping analyses of mercury have been reported by using different electrodes such as gold electrodes [13], iridium electrodes [14] and gold coated carbon electrodes [15].

In order to enhance the sensitivity and selectivity of the electrochemical determination of mercury, chemical modification of electrodes has received increasing attentions in the past decades. Numerous studies have been directed to the determination of mercury(II) ion by modified electrodes. The modifiers used have included organic chelating groups [16–23], polymers [24–29], silica and sol–gel [30–34], clays [35–40] and clays grafted with organic chelating groups [41]. Most of the procedures, however, have faced difficulties achieving the sensitivity required for the determination of low levels of mercury(II) ion in some real samples. Moreover, these materials do not provide a proper selectivity towards Hg^{2+} in the presence of some potential interferers like Cd^{2+}, Pb^{2+}, and Cu^{2+}. Therefore, there is still an urgent demand for a highly selective modifier in this field.

Molecular imprinted polymers (MIP) are new high selective synthetic receptors with molecular recognition sites designed for a particular analyte. MIP technology has been developed as a method

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0003-2670/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.aca.2011.01.036

for the preparation of synthetic receptors by polymerization of self assembled complexes, formed by functional monomers and a template in the pre-polymerization mixture [42–48]. This technology can also be used for the preparation of polymers containing inorganic cation selective sites as the so-called ion imprinted polymers (IIP) [49–52]. Different kinds of imprinted polymers have so far been reported for the recognition of mercury ions [53–56].

Recently, we have reported several papers describing the application of MIP particles as a recognition element of the electrochemical sensors such as voltammetric and potentiometric sensors for different kinds of molecular analytes [57–60]. Due to the high selectivity of these materials, the electrode containing imprinted materials tends to show selective behaviors. Besides, this modifying agent can pre-concentrate the analyte in the electrode due to the high adsorption capacity of these materials. The obtained interesting results from the previous works provoked us to design a novel Hg^{2+} electrochemical sensor, using ion imprinted polymers. As mentioned before, each of the described modifying agents, previously used in Hg^{2+} electrodes, possessed some advantages and suffered from some shortcommings. For example, organic chelating agents provide a moderate selectivity, but suffer from instability in the response. Zeolite and sol–gels provide high stability and adsorption capacity, while suffering from an inherently low selectivity. Although, polymeric materials like perfluorinated polymers provide considerably lower detection limit [28], they function based on the ion exchanging mechanism and their selectivity is thus not considerable. On the other hand, it seems that the electrodes modified with Hg^{2+} IIP possesses approximately the advantages of most of the previously stated modifying agents. IIP has a high selectivity even more than organic chelating agents. It provides high adsorption capacities comparable with that of clays and zeolite, providing high sensitivity and lower detection limit. Also, IIP materials usually show a high stability and durability against harsh chemical environments. In other words, electrodes modified with ion imprinted polymers bring together the advantages of different kinds of modifying agents in a single modified electrode. Moreover, both IIP and carbon paste are cheap materials and thus a carbon paste electrode modified with IIP can provide an efficient and cheap sensor for Hg^{2+} determination.

In this work, the Hg^{2+} selective imprinted polymer was synthesized based on a new formulation. The obtained Hg^{2+} imprinted polymer was used as a modifying agent and mixed with carbon powder in the presence of melted n-eicosane in order to prepare a Hg^{2+} selective voltammetric sensor. The prepared electrode showed very interesting analytical characteristics.

2. Experimental

2.1. Instrument and reagents

Electrochemical data were obtained with a three-electrode system using a PGSTAT302 Metrohm potentioastat/galvanostat. The carbon paste electrodes modified with IIP or non imprinted polymer (NIP) were used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

Vinyl pyridine (Merck, Germany) was purified by distillation under reduced pressure. Ethylene glycol dimethacrylate (EDMA) (Sigma–Aldrich, USA), was distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4 °C until use. 2,2′-(2-Methyl propionitrile) was obtained from Acros Organic, Geel, Belgium. Dimethyl sulfoxide (DMSO) and $Hg(NO_3)_2{\cdot}4H_2O$ were from Merck, Germany. Other chemicals were of analytical grade and were purchased from Merck, Germany.

2.2. Preparation of Hg(II) imprinted polymer and modified electrode

In order to prepare IIP, 1 mmol $Hg(NO_3)_2$ and 4 mmol 4-vinyl pyridine were dissolved in 20 mL of DMSO. Then, 0.15 g of the initiator (2,2′-azobisisobutyronitrile) and cross-linker (EDMA), dissolved in 3 mL DMSO, was mixed with the previous solution and purged with N_2 gas for 10 min. The polymerization was carried out in a water bath at 70 °C for 24 h. The obtained polymer particles were firstly washed with ethanol and then washed with a 0.1 M HCl solution. Finally, the particles were washed with distilled water and dried at 60 °C. The NIP was prepared, using the same protocol in the absence of Hg(II). The prepared IIP and NIP were used for carbon paste electrode fabrication.

2.3. Preparation of the sensors

For construction of the sensor (IIP-CP), 0.02 g graphite was homogenized in a mortar with 0.005 g of powdered IIP for 10 min. Subsequently, n-eicosane, 0.007 g was melted in a dish in a water bath, and heated at 45–50 °C. The graphite/IIP blend was then added to the melted n-eicosane and mixed with a stainless steel spatula. The final paste was used to fill a hole (2.00 mm in diameter and 3 mm in depth) at the end of an electrode body, previously heated at 45 °C. After cooling at room temperature, the excess of solidified material was removed with the aid of a sheet of paper sheet. The electrode can be reused after each experiment by moving the electrode surface on a paper sheet in order to rub out a thin layer of the electrode surface.

2.4. Determination procedure

The prepared electrode was inserted into the solutions containing the Hg^{2+} (pH = 2.5) while being stirred. Then, the electrode was inserted into the washing solution (water-neutral pH), remaining in this solution for 15 s. The electrode was finally placed in the electrochemical cell containing 10 mL of HCl (0.12 M). At first, a negative pre-potential of −1.2 V was applied to the electrode for 30 s and then a differential pulse voltammetry was performed from −0.10 to 0.3 V.

3. Results and discussion

3.1. Mercury ion imprinted polymer

Several formulations have already been reported for preparation of mercury ion imprinted polymers. Liu et al. [56] have prepared IIP for mercury by copolymerizing mercury chloride, diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycoldimethacrylate (EGDMA) as a cross-linker. Another work in this field is from Denizli and his coworkers [53] who applied N-Methacryloyl-(L)-cysteine as both a functional monomer and complexing agent. Copolymerization of the methacrylic acid as the monomer, and trimethylolpropane trimethacrylate as the cross-linking agent, in the presence of Hg(II)-1-(2-thiazolylazo)-2-naphtholcomplex is another method reported by Dakova et al. [55]. Recently, Singh and Mishra [54] have described a new formulation for Hg(II)-ion-imprinted polymer (IIP) by the formation of a binary complex of mercury with 4-(2-thiazolylazo) resorcinol and its thermal copolymerization with methacrylic acid (monomer) and ethylene glycol dimethadrylate (crosslinker), and in cyclohexanol as a porogen.

In all of the described procedures an additional ligand has been applied for preparing IIPs, which increases the complexity of the preparation method. In the present work, however, we applied a