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Determination of total mercury in seafood by ion-selective electrodes based on a thiol functionalized ionic liquid

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ABSTRACT

A mercury(II) ion-selective electrode with an ionic liquid (IL), 1-methyl-2-butylthioimidazolium bis(trifluoromethanesulphonyl)imide ($[C_1C_4Sim]NTf_2$) as active material was constructed. Parameters affecting the performance of the electrodes such as the dosages of the IL and carbon nanotubes and the aqueous pH values were investigated. Experimental results indicated that the optimal composition of the electrode filling material was 47.6% $[C_1C_4Sim]NTf_2$, 47.6% tetrabutylphosphonium bis(trifluoromethanesulphonyl)imide (TBPNTf₂) and 4.8% carboxylic multi-walled carbon nanotubes (MWCNTs-COOH). Under the selected conditions, the proposed electrodes showed a good linear response in the concentration range of 10^{-10} – 10^{-5} mol L⁻¹ and had a detection limit of 4.1×10^{-11} mol L⁻¹. No great interference from common metal ions was found. The proposed electrodes were applied to determine Hg²⁺ in seafood samples; the results were comparable to those of the direct mercury analyzer.

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1. Introduction

Mercury (Hg) is one of the most toxic elements impacting on human and ecosystem health and all mercury species are toxic [1–3]. Fish and other seafood products concentrate mercury in

their bodies and thus contain high concentrations of mercury [1,3]. Multiple analytical techniques such as cold vapor atomic absorption spectrometry (CV-AAS) [3], graphite furnace atomic absorption spectrometry (GF-AAS) [4], direct mercury analyzer [5], cold vapor atomic fluorescence spectrometry (CV-AFS) [6] and inductively coupled plasma mass spectrometry (ICP-MS)

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[7] were usually used to determine total mercury in environmental, food and biological samples. These techniques are undoubtedly highly sensitive and stable. However, they require expensive and complex instruments, training special skills and complicated analysis procedures. Ion-selective electrode (ISE) is a favorable alternative because of its high selectivity, high sensitivity, low cost, ability for portability and time saving [8–13]. Han et al. developed a mercury ion-selective electrode based on 2-mercaptobenzimidazol ionophore as the sulfur containing sensing material. This electrode suffered from a low interference from Sr^{2+} and was almost no interference from alkali, alkaline earth, transition and heavy metal ions. The electrode exhibited a linear response within the concentration range of 1×10^{-2} – 1×10^{-7} mol L⁻¹. This electrode was applied for the determination of Hg(II) content in real samples and the results show good correlation with the data obtained by AAS [8]. Mai et al. fabricated a solid-contact mercury ion-selective electrode by covering a thin layer of conductive polymer membrane (polypyrrole-PPy) on paste carbon electrode. The electrode showed excellent potentiometric response over a wide concentration range (10^{-9} to 10^{-2} mol L⁻¹) with a detection limit of 6×10^{-10} mol L⁻¹. Furthermore, this electrode also exhibited good selectivity towards Hg²⁺ in comparison with other common ions [9]. Despite the progress made in this field, there is a continuous demand for the development of mercury ion-selective electrodes with high sensitivity to determine trace mercury in real samples.

Ionic liquids (ILs) have excellent electrical conductivity because they are composed entirely of ions [14]. Carbon nanotubes (CNTs) also have high charge transfer capacity. The combination of the two compounds could generate new electrode materials with excellent electrochemical properties. Wardak fabricated a new cadmium selective electrode by using 1-butyl-3-methylimidazolium hexafluorophosphate (an IL) as a lipophilic ionic additive and multi-walled carbon nanotubes (MWCNTs) as the ion-to-electron transducer; the resultant electrode exhibited high potential stability, low detection limit (2.3×10^{-9} mol L⁻¹), short response time and excellent selectivity [15].

In this work, an ion-selective electrode for mercury using a thiol functionalized ionic liquid and MWCNTs as ionophores was fabricated. Parameters affecting the performance of the proposed mercury ion-selective electrode were optimized. Finally, the proposed ion-selective electrode was applied to determine total mercury in seafood.

2. Experimental

2.1. Materials

Mercury nitrate monohydrate ($\text{HgNO}_3 \cdot \text{H}_2\text{O}$, $\geq 99\%$) was purchased from Xiya Chemical Reagent Co., Ltd. (Chengdu, China). Hydrogen peroxide (H_2O_2 , 30%, GR), chitosan (CS, with $>95\%$ deacetylation), nano graphite powder (99%, 40 nm), 2-mercapto-1-methylimidazole (98%), *n*-butyl bromide ($>99\%$) and nitric acid (HNO_3 , 70%, electronic grade) were obtained from Aladdin Reagent Co. (Shanghai, China). Carboxylic multi-walled carbon nanotubes (MWCNTs-COOH, $>95\%$, diameter 10–20 nm,

length 10–30 nm, carboxyl content 2.0%) was purchased from Beijing Dk Nano Technology Co., Ltd. (Beijing, China). Lithium bis(trifluoromethanesulphonyl)imide (LiNTf_2 , 98%) were obtained from Energy Chemical Co., (Shanghai, China). Tetrabutylphosphonium bis(trifluoromethanesulphonyl)imide (TBPNTf₂, 99%) was obtained from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). All the other reagents were of analytical grade unless stated otherwise. Ultrapure water (18.2 MΩ cm) produced by an Aquapro purification system (Aquapro International Co., Ltd., Dover, DE) was used throughout the experiments.

Seafood samples including sea lettuce, prawn, pomfret, ribbonfish, scallop and octopus were purchased from local supermarket. For the prawn, pomfret, ribbonfish and scallop samples, the inedible bones, scales, head, viscera, shells and skins were removed and only muscles were retained.

All the samples were dried at 40 °C in an oven to a constant weight and crushed by a disintegrator (model: 08A1, Xulang Co., Guangzhou, China) to minus 100 mesh.

2.2. Synthesis of the thiol functionalized IL

The thiol functionalized IL, 1-methyl-2-butylthioimidazolium bis(trifluoromethanesulphonyl)imide ($[\text{C}_1\text{C}_4\text{Sim}]\text{NTf}_2$), was synthesized by referring to the reported literature [16]. Typically, 0.2 mol of 2-mercapto-1-methylimidazole were dissolved into 30 mL of anhydrous ethanol and then an equimolar amount of *n*-butyl bromide was added; after refluxing for 12 h at 70 °C, ethanol was removed by vacuum-rotary evaporation. The resulting sticky liquid was dissolved into 30 mL of water. Then, 0.2 mol of LiNTf_2 were added and two immiscible phases were formed under stirring for 10 min. After removal of the upper water phase, the bottom phase was washed several times, each time with 10 mL of water until Br^- free, as indicated by the AgNO_3 test of the water washings. After vacuum drying 24 h at 70 °C, $[\text{C}_1\text{C}_4\text{Sim}]\text{NTf}_2$ was obtained as a light yellow liquid (91% yield). The chemical structure of $[\text{C}_1\text{C}_4\text{Sim}]\text{NTf}_2$ was characterized by the proton nuclear magnetic resonance (¹HNMR) spectroscopy (500 MHz, solvent: DMSO-*d*₆): δ (chemical shift, ppm), 0.867–0.896 (t, 3H), 1.342–1.416 (m, 2H), 1.500–1.559 (m, 2H), 3.140–3.169 (t, 2H), 3.818 (s, 3H), 7.756–7.761 (d, 1H), 7.802–7.806 (d, 1H).

2.3. Preparation of the mercury(II) ion-selective electrode

For preparation of the electrode filling material, 47.6% (wt%, similarly hereinafter) of $[\text{C}_1\text{C}_4\text{Sim}]\text{NTf}_2$, 47.6% of TBPNTf₂ and 4.8% of MWCNTs-COOH were mixed at 70 °C and subsequently sonicated for 20 min to obtain a homogenous mixture.

The working electrode was fabricated by packing the electrode filling material (17.2 mg) into the end of a glass tube (openings at both ends, 2 mm inner diameter, 5 cm length). Electrical contact was achieved via inserting a copper wire (8 cm length, 0.4 mm diameter) into the glass tube. This copper wire can move up and down to press the electrode filling material down when renewal of the electrode surface is needed. The electrode surface was smoothed and polished on a weighing paper. The electrode was activated by immersing into 1.0×10^{-5} mol L⁻¹ of Hg²⁺ solution for 2 h before use.

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