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Original Article

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

Juan Miao [a], *Xin Wang* [b], *Yunchang Fan* [b,c,*], *Jing Li* [d], *Lina Zhang* [b,c,**], *Guitao Hu* [b], *Can He* [e], *Can Jin* [b]

[a] *Medical College, Henan Polytechnic University, Jiaozuo 454003, China*
[b] *College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, China*
[c] *Key Laboratory of Green Coal Conversion of Henan Province, Henan Polytechnic University, Jiaozuo 454003, China*
[d] *Yunnan Academy of Tobacco Science, Kunming 650106, China*
[e] *School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454003, China*

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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 ($TBPNTf_2$) 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 Hg^{2+} in seafood samples; the results were comparable to those of the direct mercury analyzer.

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)

* *Corresponding author*. College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, China. Fax: +863913987815.
** *Corresponding author*. College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, China.
E-mail addresses: yunchangfan2009@163.com (Y. Fan), zhln@hpu.edu.cn (L. Zhang).
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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 Hg^{2+} 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 ($HgNO_3 \cdot H_2O$, ≥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 (TBPN Tf_2, 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 ($[C_1C_4Sim]NTf_2$), 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, $[C_1C_4Sim]NTf_2$ was obtained as a light yellow liquid (91% yield). The chemical structure of $[C_1C_4Sim]NTf_2$ was characterized by the proton nuclear magnetic resonance (^{1}HNMR) 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 $[C_1C_4Sim]NTf_2$, 47.6% of $TBPNTf_2$ 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 Hg^{2+} solution for 2 h before use.

2.4. Sample preparation

All the seafood samples were treated with microwave digestion method [17,18]: 0.3000 g of a specific sample and 4.0 mL of concentrated HNO_3 were added into a polytetrafluoroethylene microwave digestion vessel and then 1.0 mL of H_2O_2 (30%) was added dropwisely. After eliminating the bubbles, the digestion vessel was sealed by a cap and putted into a microwave digestion system (model: MD6H, Aopule Co., Chengdu, China). The digestion program is as follows: microwave power, 800 W; the temperature increases from room temperature to 120 °C within 5 min and maintains at 120 °C for 5 min; subsequently, the temperature increases to 155 °C over 5 min and then keeps constant for 15 min. After digestion and cooling, the digestion solution was diluted to 25 mL with water. Before measurements, the digestion solutions were pretreated according to the reported works [11–13]: 5.0 mL of a specific digestion solution was taken and its pH was adjusted to 3.0 with NaOH solution (1.0 mol L^{-1}); finally, this solution was diluted to 50 mL with HNO_3 solution of pH 3.0. Blank experiments were carried out in a similar way.

2.5. Determination of Hg^{2+} by the direct mercury analyzer

The measurements of total mercury were conducted on a direct mercury analyzer (model DMA-80, Milestone GmbH, Leutkirch im Allgau, Germany). Exactly 0.070 g of a specific sample was placed in the sample boat and was subsequently allowed to dry and decompose in a furnace to liberate mercury. The detection wavelength was set at 253.65 nm. The running program of the direct mercury analyzer is listed in Table 1.

2.6. Determination of Hg^{2+} by the proposed electrodes

A pHS-3B digital pH/mV meter (Shanghai Leici Instrument Factory, Shanghai, China) was used to measure the potential of Hg^{2+}. A saturated Hg/Hg_2Cl_2 was used as the reference electrode. The Hg^{2+}-selective electrode and the reference electrode were immersed into 10 mL of the Hg^{2+} solution until the potential reading was constant. For the measurements of the real samples, the same electrode was used.

3. Results and discussion

3.1. Optimization of the proposed electrodes

In this work, ILs and nanomaterials were used to construct a set of the Hg^{2+}-selective electrodes with a variety of compositions. The slopes of the calibration curves (electromotive force versus $\log C_{mercury(II)}$) were used as the criteria for optimization. All the experiments were conducted in triplicate and the data are presented as average values.

3.2. The choice of additives

Generally, multi-walled carbon nanotubes and nano graphite powders have better conductivity; chitosan (CS) can coordinate with metal ions because it contains glucosamine groups [19]. These three compounds are usually used as additives of the ion-selective electrodes to improve the sensitivity [20–22]. A comparison of their performance is shown in Fig. 1. As can be seen, the addition of MWCNTs-COOH and nano graphite powders enhances the sensitivity of the electrodes. However, a slight decrease in sensitivity is observed when CS is added due to its poor conductivity [22]. Since MWCNTs-COOH have best sensitivity, it was adopted for the following experiments.

3.3. Selection of the component ratio of the electrode filling materials

The electrode filling materials were composed of MWCNTs-COOH, $[C_1C_4Sim]NTf_2$ and $TBPNTf_2$. Thereinto, $[C_1C_4Sim]NTf_2$ acts as the active material; the solid-state IL, $TBPNTf_2$ which has good intermiscibility with $[C_1C_4Sim]NTf_2$, is used as the binder. To investigate the influence of the ratio (w/w, similarly hereinafter) of $TBPNTf_2$ to $[C_4NH_2C_2im]NTf_2$ on the electrode performance, additional experiments were conducted by fixing the ratio of the mixture of $TBPNTf_2$ and $[C_4NH_2C_2im]NTf_2$ to MWCNTs-COOH at 20:1, meanwhile changing the ratio of $TBPNTf_2$ to $[C_4NH_2C_2im]NTf_2$. The results illustrated in Fig. 2 panel A indicate that the sensitivity of the

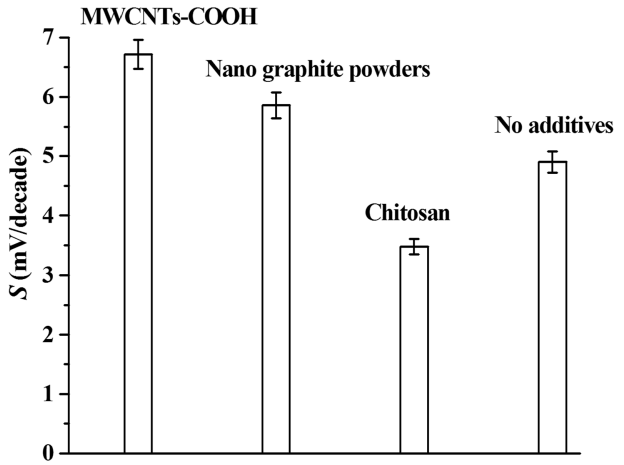

Fig. 1 – A comparison of the performance of different additives; pH 3.0, $[C_1C_4Sim]NTf_2$:$TBPNTf_2$:additive = 10: 10:1 (w/w).

Table 1 – Operation conditions of the direct mercury analyzer.

Drying temperature/°C	Drying time/s	Decomposition temperature/°C	Decomposition time/s	Amalgamation temperature/°C	Amalgamation time/s	Signal recording time/s	Rinsing time/s
200	60	800	120	650	12	30	60

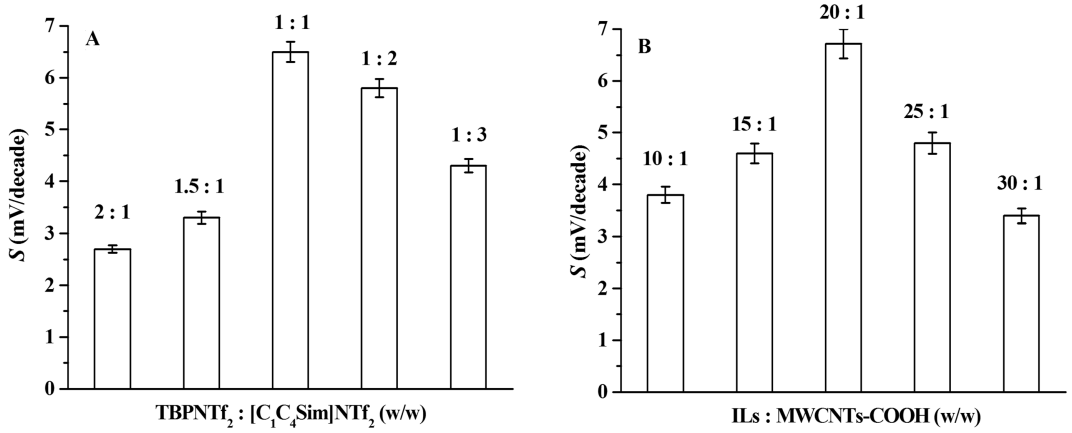

Fig. 2 – The influence of the composition of the electrode filling materials; pH 3.0.

electrode increases with the ratio of $TBPNTf_2$ to $[C_1C_4Sim]NTf_2$ up to 1:1 and then decreases with further increase in the ratio of $TBPNTf_2$ to $[C_1C_4Sim]NTf_2$. This phenomenon can be interpreted by the facts that $[C_1C_4Sim]NTf_2$ is the active material, higher levels of $[C_1C_4Sim]NTf_2$ result in higher sensitivity ($TBPNTf_2$:$[C_1C_4Sim]NTf_2$ = 2:1 to 1:1); further increase in the content of $[C_1C_4Sim]NTf_2$ make the filling materials a bit mobile and unstable, reducing the sensitivity accordingly. Based on these results, 1:1 was selected as the optimal ratio of $TBPNTf_2$ to $[C_1C_4Sim]NTf_2$ for the subsequent experiments.

For the optimization of the ratio of the mixture of $[C_1C_4Sim]NTf_2$ and $TBPNTf_2$ to MWCNTs-COOH, extra experiments were carried out by fixing the ratio of $[C_1C_4Sim]NTf_2$ to $TBPNTf_2$ at 1:1 with changing the dosage of MWCNTs-COOH. As shown in Fig. 2 panel B, the sensitivity of the proposed electrodes increases within the range of 30:1–20:1 (ILs: MWCNTs-COOH). The possible reasons lie in that MWCNTs-COOH have better conductivity; the increase in the content of MWCNTs-COOH improves the conductivity of the electrodes, increases the transduction of the chemical signal to electrical signal and therefore increases the sensitivity of the electrodes [23]. However, further increase in the dosage of MWCNTs-COOH (e.g., 15:1 and 10:1) decreases the sensitivity of the electrodes (Fig. 2 panel B). The possible reasons mainly lie in two aspects: (I) the increase in the dosage of MWCNTs-COOH obviously decreases the content of $[C_1C_4Sim]NTf_2$ (the active material); (II) because MWCNTs-COOH have a large ratio of surface area to mass, the increase of the dosage of MWCNTs-COOH results in the high surface area formed on the electrode surface that may offer special opportunities for the capturing mercury ions on the surface of the electrodes [23]. Based on these results, 20:1 was selected as the optimal ratio of the mixture of $[C_1C_4Sim]NTf_2$ and $TBPNTf_2$ to MWCNTs-COOH.

3.4. *Influence of pH*

The influence of pH on the sensitivity of the proposed electrodes was conducted by determining the slopes of the calibration curves (the pH values of the cell were adjusted by the addition of very small volumes of HNO_3 (1.0 mol L^{-1}) or NaOH (1.0 mol L^{-1})) at different pH values. The results shown in Fig. 3 indicate that the sensitivity of the proposed electrodes increases within the pH range of 1.0–2.0, keeps constant within pH 2.0–3.0 and then decreases with further increasing pH values. The possible reasons lie in that when pH < 2.0, the ligands (sulfur atoms of the $[C_1C_4Sim]NTf_2$) on the electrode surface may be protonated, thereby losing their capacity to complex with the mercury ions. When pH is above 3.0, the decrease in the sensitivity is attributed to the formation of mercury(II) hydroxide [24]. Based on these results, pH 3.0 was selected for the following studies.

3.5. *Influence of the conditioning time*

In general, a new electrode should be conditioned before use [25,26]. As can be seen from Fig. 4, the electrode sensitivity keeps constant when the conditioning time is above 2 h. The conditioning time of the reported Hg^{2+}-selective electrodes is 24 h [11]. That is to say, short conditioning time is one of the advantages of the proposed sensors. The fast kinetics of the complexation of Hg^{2+} with $[C_1C_4Sim]NTf_2$ may be responsible for this short conditioning time. Based on this result, 2 h was regarded as the optima.

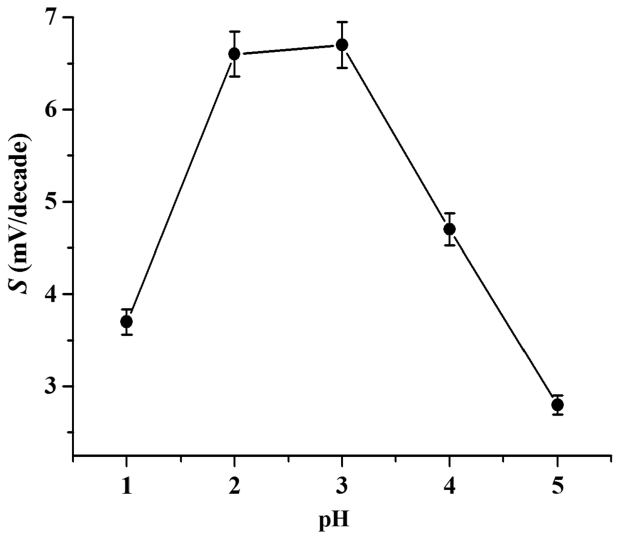

Fig. 3 – Influence of pH on the response of the proposed electrode.

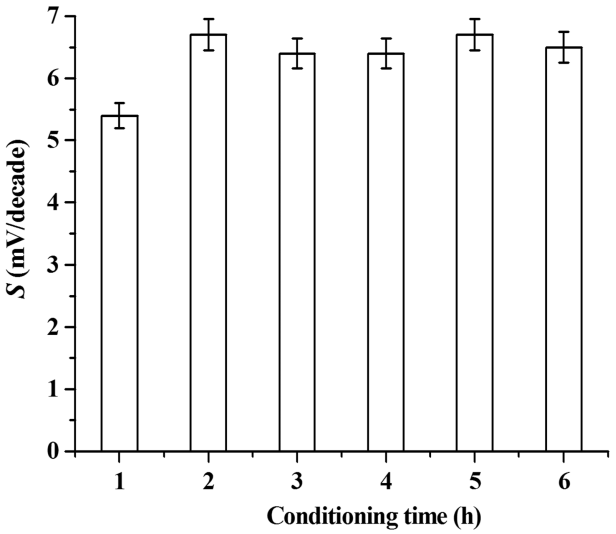

Fig. 4 – Influence of the conditioning time on the response of the proposed electrode.

3.6. Response time

Response time of the proposed Hg^{2+}-selective electrode was measured via determining the average time required to achieve potential values within ±1 mV of the steady state potential of the electrode after its immersion in a series of solutions of Hg^{2+} (10^{-10}–10^{-5} mol L^{-1}) [27]. The experimental results shown in Fig. 5 indicate that over the concentration range studied, the proposed electrode exhibits rapid responses (about 5 s).

3.7. Reproducibility

Two methods were used to evaluate the reproducibility of the proposed electrodes: (I) the same proposed electrode was used to measure consecutively Hg^{2+} solution (1.0×10^{-7} mol L^{-1}) at 3-min interval for 2 h (40 times). The experimental results indicated that the relative standard deviation (RSD) of the potential values of the forty successive determinations was 0.84%; (II) ten independent electrodes were prepared and used to measure Hg^{2+} solutions. The experimental results showed that the RSD values of the slopes (potential versus log$C_{mercury(II)}$) was 2.1%. These results indicated that the proposed electrodes also had better reproducibility as compared to the reported electrodes [11,13,24].

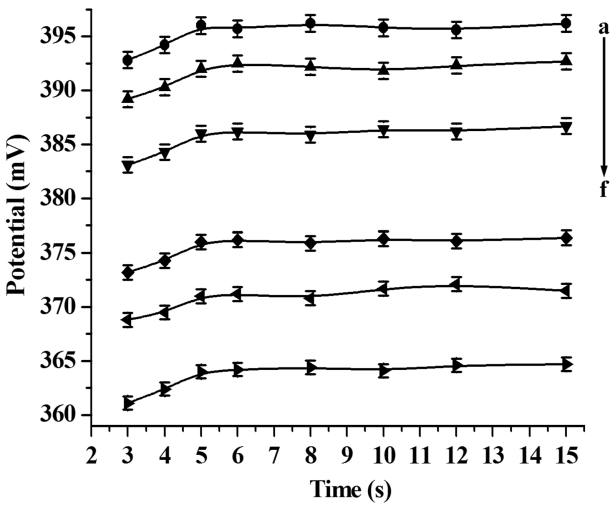

Fig. 5 – Response time of the proposed electrode for Hg^{2+}; from a to f: 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9} and 10^{-10} mol L^{-1}, respectively.

3.8. Selectivity

Selectivity which is one of the most important characteristics of the ion-selective electrodes is measured in terms of the selectivity coefficients. It measures the response of the ion-selective electrodes towards the primary ion in the presence of other ions present in the sample solutions. In this work, the selectivity coefficients were determined by the fixed interference method (FIM), in which the selectivity coefficients are evaluated graphically by fixing the activity of an interfering ion at 1.0×10^{-4} mol L^{-1}, and varying the activity of Hg^{2+} [20,28,29]. The intersection of the extrapolated linear portions of this plot indicates the value of a_i that is to be used to calculate the selectivity coefficient from the following equation [20,28,29]:

$$K^{FIM}_{Hg^{2+},j} = \frac{\alpha_i}{\alpha_j^{\frac{Z_i}{Z_j}}} \quad (1)$$

where $K^{FIM}_{Hg^{2+},j}$ is the selectivity coefficient; i, j, α and Z denote the target ion (Hg^{2+}), an interfering ion, ion activity and charge number of an ion, respectively. The resulting values are listed in Table 2. For all tested ions, the selectivity coefficients ($\log K^{FIM}_{Hg^{2+},j}$) are in the range of −3.80 to −8.60, indicating that these cations give no significant interference in the performance of the proposed electrodes [8,12,13,24].

3.9. The lifetime and the reuse of the proposed electrodes

To investigate the lifetime, the proposed electrodes were used to determine successively the Hg^{2+} solution for two weeks (one time per day). There were no remarkable changes in the slopes of the calibration curves and the RSD value of the slopes was only 1.6%. However, after one month of use, the slope decreased to 81.4% of its initial value. To reuse the proposed electrodes, two methods were adopted: (I) the

Table 2 – Selectivity coefficients of the proposed electrode for different interfering ions.

Interfering ion	$\log K^{FIM}_{Hg^{2+},j}$
Ca^{2+}	−3.80
Mg^{2+}	−4.44
Na^{+}	−4.66
Cu^{2+}	−4.68
Pb^{2+}	−5.14
Ba^{2+}	−5.22
Cd^{2+}	−5.95
Al^{3+}	−6.41
NH_4^{+}	−6.78
K^{+}	−8.60

electrode surface was polished to expose a new fresh layer and the electrode could be used to measure Hg^{2+} without loss of its sensitivity (the slope of the proposed electrode was 103.1% of its initial value). (II) The used electrodes were treated by constant potential reduction in NaCl aqueous solution (0.2 mol L^{-1}) at −0.5 V for 30 min. After this treatment, the slope of the proposed electrode reached 98.0% of its initial value.

3.10. Working concentration range and detection limit

Under the selected conditions, the potentiometric response of the proposed electrodes to Hg^{2+} was studied in the concentration range of 10^{-12}–10^{-5} mol L^{-1}. The experimental results shown in Fig. 6 indicate that the linear response is obtained in the range of 10^{-10}–10^{-5} mol L^{-1} with a correlation coefficient (r) of 0.9941. The detection limit (LOD) of the proposed electrode was calculated according to the IUPAC recommendations [25,29–31] from the intersection of two extrapolated linear portions of the calibration curve (Fig. 6); it was found to be 4.1×10^{-11} mol L^{-1}. The slope of the calibration curve is 6.7 mV/decade, which is lower than the value predicted by the Nernstian equation (29.5 mV/decade for bivalent cations), showing sub-Nernstian behavior. Similar phenomena have also been reported by Bryce and coworkers [32]. They developed new silver ion-selective electrodes with thiones as active compounds; these electrodes exhibited sub-Nernstian behavior due to the irreversible binding between silver ions and the sulfur atoms of the thione groups. Therefore, it can be expected that the sub-Nernstian response of the proposed electrodes is also caused by the irreversible binding between the mercury ions and the sulfur atoms of $[C_1C_4Sim]NTf_2$. Additionally, there several papers have reported the use of ion-selective electrodes to determine mercury ions [9,11,13,24,33,34]. The performance of the proposed electrode was then compared with the reported ones; the results are listed in Table 3. As can be seen, the proposed electrode exhibits high sensitivity and rapid response.

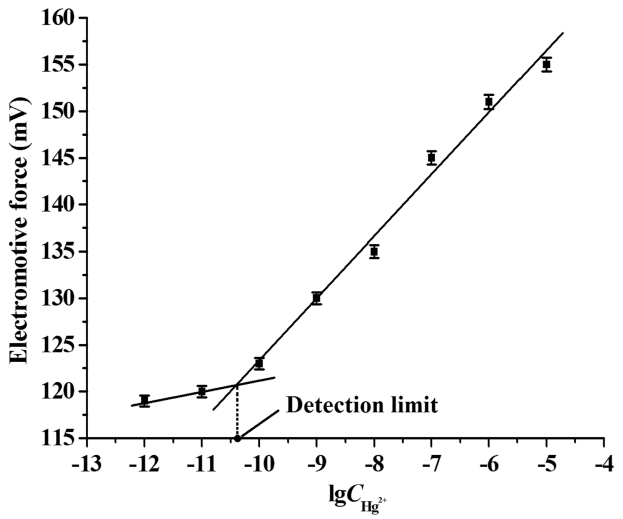

Fig. 6 – Calibration curve of the proposed mercury(II) ion-selective electrode.

Table 4 – Analytical results of mercury in the seafood samples (average values, $n = 3$).

Sample	Found by the proposed electrode (mg kg^{-1})	Found by the direct mercury analyzer (mg kg^{-1})
Sea lettuce	43.4	47.3
Prawn	194.3	197.7
Pomfret	190.9	189.2
Ribbonfish	358.7	395.4
Scallop	211.9	208.7
Octopus	135.3	137.7

3.11. Determination of Hg^{2+} in seafood samples

The proposed electrode was applied to determine mercury contents in seafood samples. Besides, a reference method based on the direct mercury analyzer was used for evaluation of the accuracy of the obtained results. The results shown in Table 4 indicate that the results obtained by the proposed electrode are in good agreement with those obtained by the direct mercury analyzer. Furthermore, recovery experiments were also conducted and higher recoveries were obtained (97.7%–103.3%). These results suggest that the proposed electrodes can be used for the rapid and low cost measurement of Hg^{2+} in complicated samples.

4. Conclusions

A mercury(II) ion-selective electrode based on an IL, $[C_1C_4Sim]NTf_2$, as active material with simple preparation was developed for the determination of total mercury in seafood. The proposed electrode is characterized by fast response, reasonable stability and higher sensitivity (LOD, 4.1×10^{-11} mol L^{-1})

Table 3 – Comparison of the proposed mercury(II) ion-selective electrode with the reported ones.

Reference	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Response time (s)	Conditioning time
[11]	1.0×10^{-9}–1.0×10^{-1}	9.1×10^{-10}	30	Not mentioned
[34]	1.8×10^{-6}–1.0×10^{-1}	1.0×10^{-6}	<30	3 days
[9]	1.0×10^{-9}–1.0×10^{-2}	6.0×10^{-10}	60	Not mentioned
[13]	1.0×10^{-9}–1.0×10^{-2}	1.0×10^{-10}	5	Not mentioned
[33]	7.5×10^{-6}–5.0×10^{-2} (pH 6.5) 5.0×10^{-6}–1.0×10^{-2} (pH 4.0)	8.0×10^{-7} (pH 6.5) 4.5×10^{-7} (pH 4.0)	<20	1 day
[24]	1.0×10^{-8}–1.0×10^{-2}	2.0×10^{-9}	<7	48 h
This work	1.0×10^{-10}–1.0×10^{-5}	4.1×10^{-11}	5	2 h

as compared to the reported electrodes (Table 3). The presence of common metal ions does not affect the determination of mercury(II) ions. The proposed electrode was applied to determine total mercury in seafood samples; the results obtained are in good agreement with those of the direct mercury analyzer. A comparison of the response characteristics between the proposed electrode and the reported mercury(II) ion-selective electrodes indicates that the proposed electrode is superior.

Conflicts of interest

All authors have no conflicts of interest to declare.

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