



Highly sensitive potentiometric sensor for detection of mercury in Cl^- -rich samples



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ABSTRACT

Potentiometric sensors have been exploited for the determination of Hg^{2+} ions. However, applications of such sensors are limited to mercury detection in the absence of a Cl^- -rich background since Hg^{2+} can readily form coordination complexes with Cl^- . This paper describes a potentiometric sensor for the determination of anionic mercury species using tert-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) as anion-selective ionophore and tridodecylmethylammonium chloride as ion exchanger. An asymmetric membrane rotating ion-selective electrode configuration is used to improve the detection sensitivity. By using HgCl_3^- as a model of anionic mercury species, the proposed method allows potentiometric detection of mercury down to nanomolar levels in samples containing 0.05 M NaCl background electrolyte. The practical application of the proposed sensor has been performed for the determination of total mercury concentrations in diluted seawater samples.

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1. Introduction

Mercury pollution is increasingly becoming a serious environmental problem throughout the world since mercury tends to accumulate in food chains and can cause cell death, brain damage and birth defects [1]. Therefore, routine detection of mercury is vital for environmental monitoring and assessment. Currently available detection methods for mercury include cold vapor atomic absorption spectrometry [2,3], atomic fluorescence spectrometry [4,5], and inductively coupled plasma mass spectrometry [6]. Although these approaches are well established, they require expensive apparatus and complicated sample pretreatment [7,8].

As generic and highly successful electrochemical sensors, ion-selective electrodes (ISEs) have shown to be promising for environmental trace analysis and potentiometric biosensing [9–11]. Today ISEs routinely offer detection limits in the nanomolar or lower concentration range without any accumulation step [12–18].

A few ISEs have been reported for the determination of trace-level mercury ions, specially divalent mercury ions (i.e., Hg^{2+}) [19–22]. Unfortunately, the present Hg^{2+} -ISEs are not practically useful in Cl^- -rich media such as seawater samples where mercury mainly exists in the forms of anionic species such as HgCl_4^{2-} and HgCl_3^- owing to the favorable complexation of Hg^{2+} with Cl^- [23]. Very few ISEs have been reported for the determination of anionic mercury ions. Kim et al. reported a novel ISE based on neutral carrier for potentiometric detection of mercury anions in Cl^- -rich media [24]. However, the detection limit of the method for detection of mercury anionic species in 0.05 M NaCl is around the micromolar range. This poses serious limit to its use at trace levels as required for determining mercury in environmental samples. Thus, the development of a highly sensitive potentiometric sensor for mercury in Cl^- -rich environmental samples still remains a challenge.

Herein, we present a novel and highly sensitive potentiometric sensor for detection of mercury species in Cl^- -rich samples. The proposed anion-selective membrane electrode is fabricated by using the neutral carrier tert-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) (lead ionophore IV) as the chloro-mercury anion-selective ionophore and tridodecylmethylammonium chloride (TDMACl) as the anion exchanger. Potentiometric detection of mercury is performed in the presence of 0.05 M NaCl background which ensures the anionic forms of mercury species. To improve the detection sensitivity of the potentiometric sensor,

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the asymmetric membrane rotating ISE configuration based on the nonequilibrium steady-state diffusion process of primary ions at the sample–membrane interface is used [25,26]. By choosing HgCl_3^- as a model, the proposed method shows a low detection limit of 4.5×10^{-10} mol/L in the presence of 0.05 M NaCl. This sensing strategy can offer promising potential for potentiometric detection of mercury species at trace levels in Cl^- -rich media such as seawater and biological samples.

2. Experimental

2.1. Reagents and materials

High molecular weight poly (vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), TDMACl, the lipophilic salt tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), lead ionophore IV and the H^+ ionophore 5-(octadecanoyloxy)-2-(4-nitrophenylazo) phenol (ETH 2412) were purchased from Fluka AG (Buchs, Switzerland). NaCl was Suprapure from Sigma–Aldrich. The certified reference material of seawater sample (GBW(E) 080042) was provided by the Second Institute of Oceanology, China. Aqueous solutions were prepared with freshly deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system. A stock solution was prepared by dissolving HgCl_2 in 0.05 M NaCl and then diluted to various concentrations of working solutions with 0.05 M NaCl. Tetrahydrofuran (THF) was freshly distilled prior to use. All other reagents were analytical grade and used without any further purification.

2.2. Preparation of ISE membranes and electrodes

The traditional homogeneous HgCl_3^- -ISE membranes contained (in wt%) lead ionophore IV (1), TDMACl (1), *o*-NPOE (65), and PVC (33). The components of each membrane (totaling 360 mg) were dissolved in THF (2.5 mL) and poured into a glass ring (i.d. 36 mm) fixed on a glass support to obtain a transparent membrane of ~ 200 - μm thickness. After overnight evaporation of the solvent, 8-mm diameter disks were punched from the mother membranes and glued to a plasticized PVC tubing with THF/PVC slurry. The asymmetric membranes were prepared by evenly spreading 5 μL of a TDMACl solution (0.7 mg/mL in THF) on the surface (8-mm diameter) of the membrane matrix containing (in wt%) lead ionophore IV (1), ETH 2412 (0.5), ETH 500 (1), *o*-NPOE (27.5), and PVC (70) and letting the active layer dry for 1 h. For mercury detection, 0.05 M NaCl and 0.05 M NaCl solution added with 4.4 μM HgCl_2 were used as the inner filling solutions for the asymmetric and conventional homogeneous membrane based ISEs, respectively. For evaluation of the selectivity coefficients, 0.01 M NaCl was used as the inner filling solution for both electrodes. All the electrodes were conditioned in a solution identical to the inner filling solution for 1 day.

2.3. EMF measurements

A rotating silver disk electrode (ATA-1B, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd., China) with a diameter of 3 mm was used as internal reference electrode as described before [25]. The plasticized PVC tubing with the asymmetric ISE membrane glued at the distal end was filled with the internal filling solution of 0.05 M NaCl and then screwed onto the silver disk electrode. All experiments were performed with a rotating (at 3000 rpm) or stirring mode configuration (using a stir bar operating at 200 rpm). Electromotive force (EMF) values were measured at 20–21 $^\circ\text{C}$ using a PXSJ-216 pH meter (Shanghai, China) in the

galvanic cell: saturated calomel electrode (SCE) 0.1 M LiOAc/sample solution/ISE membrane/inner filling solution/AgCl/Ag.

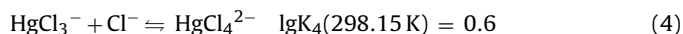
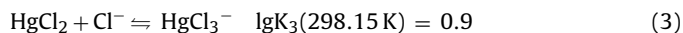
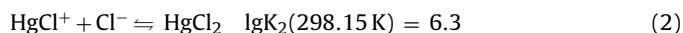
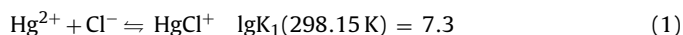
Potentiometric selectivity coefficients were determined by the separate solution method (see the Supporting information for details) [27]. The EMF values were corrected for the liquid-junction potentials with the Henderson equation. The ion activity coefficients were calculated according to the Debye–Hückel equation [28].

2.4. Reproducibility procedure

After each measurement, the asymmetric membrane based HgCl_3^- -selective electrode was washed with deionized water for 30 s and then with 50 mM $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffer solution of pH 10.0 for 10 min to strip HgCl_3^- out of the sensing membrane. The electrode was reconditioned in 20 mM citric acid/ Na_2HPO_4 buffer solution of pH 7.4 containing 0.05 M NaCl for 10 min to restore the membrane.

3. Results and discussion

It has been well established that Hg(II) ions can complex with chloride ions and form HgCl^+ , HgCl_2 , HgCl_3^- and HgCl_4^{2-} as described below [23,24,29]:



According to the above equations, it can be calculated that in Cl^- -rich samples such as seawater samples with a typical chloride ion concentration of about 0.5 M, the dominant species is the negatively charged mercury chloride complex HgCl_4^{2-} which constitutes about 78.7% of the total mercury species. The anionic and neutral chloro-mercury complexes HgCl_3^- and HgCl_2 constitute 17.9 and 3.0%, respectively. However, it should be noted that almost all of the previously developed ISEs used for mercury are limited to the detection of positively charged Hg^{2+} ions. There is only one potentiometric sensor reported by Kim et al. for the determination of anionic chloro-mercury complexes. However, the sensor cannot be utilized in practical mercury detection owing to its limited sensitivity [24]. In this work, we explored a highly sensitive potentiometric sensor for the determination of chloro-mercury anions. Lead ionophore IV was used as the ionophore for selective recognition of chloro-mercury complexes. By employing the asymmetric membrane based ISE configuration previously reported by our group [25,26], potentiometric detection of trace-level mercury in Cl^- -rich samples can be achieved.

3.1. Feasibility of the proposed approach

Selective interaction between a given analyte anion and a lipophilic carrier within the membrane is essential for the development of anion-sensitive polymeric membranes that exhibit non-Hofmeister potentiometric selectivity patterns [30]. In order to achieve selective and sensitive potentiometric detection of anionic mercury chloride complexes, ion carriers that selectively recognize these complexes are required. It has been well known that ionophores containing sulfur and nitrogen donor atoms coordinate selectively with heavy metal ions such as Hg^{2+} , Ag^+ and Pb^{2+} . Nevertheless, it is still unknown that whether or not these ionophores can form strong complexes with metal chloride complexes such as HgCl_3^- and AgCl_2^- . In this work, lead ionophore IV which was usually employed as the Pb^{2+} -selective ionophore was used as the

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