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## Highly sensitive potentiometric sensor for detection of mercury in Cl<sup>-</sup>-rich samples

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**Abstract**

Potentiometric sensors have been exploited for the determination of  $\text{Hg}^{2+}$  ions. However, applications of such sensors are limited to mercury detection in the absence of a  $\text{Cl}^-$ -rich background since  $\text{Hg}^{2+}$  can readily form coordination complexes with  $\text{Cl}^-$ . 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  $\text{HgCl}_3^-$  as a model of anionic mercury species, the proposed method allows potentiometric detection of mercury down to subnanomolar 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.

**Keywords:** Potentiometry; Ion-selective electrodes; Asymmetric membranes; Anionic mercury species;  $\text{Cl}^-$ -rich samples

## 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.<sup>1</sup> Therefore, routine detection of mercury is vital for environmental monitoring and assessment. Currently available detection methods for mercury include cold vapor atomic absorption spectrometry,<sup>2,3</sup> atomic fluorescence spectrometry,<sup>4,5</sup> and inductively coupled plasma mass spectrometry.<sup>6</sup> Although these approaches are well-established, they require expensive apparatus and complicated sample pretreatment.

As generic and highly successful electrochemical sensors,<sup>7,8</sup> ion-selective electrodes (ISEs) have shown to be promising for environmental trace analysis and potentiometric biosensing.<sup>9-11</sup> Today ISEs routinely offer detection limits in the nanomolar or lower concentration range without any accumulation step.<sup>12-18</sup> A few ISEs have been reported for the determination of trace-level mercury ions, specially divalent mercury ions (i.e.,  $\text{Hg}^{2+}$ ).<sup>19-22</sup> Unfortunately, the present  $\text{Hg}^{2+}$ -ISEs are not practically useful in  $\text{Cl}^-$ -rich media such as seawater samples where mercury mainly exists in the forms of anionic species such as  $\text{HgCl}_4^{2-}$  and  $\text{HgCl}_3^-$  owing to the favorable complexation of  $\text{Hg}^{2+}$  with  $\text{Cl}^-$ .<sup>23</sup> 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  $\text{Cl}^-$ -rich media.<sup>24</sup> 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<sup>-</sup>-rich environmental samples still remains a challenge.

Herein, we present a novel and highly sensitive potentiometric sensor for detection of mercury species in Cl<sup>-</sup>-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, the asymmetric membrane rotating ISE configuration based on the nonequilibrium steady-state diffusion process of primary ions at the sample-membrane interface is used.<sup>25,26</sup> By choosing HgCl<sub>3</sub><sup>-</sup> as a model, the proposed method shows a low detection limit of  $4.5 \times 10^{-10}$  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<sup>-</sup>-rich media such as seawater and biological samples.

## 2. Experimental section

### *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<sup>+</sup> 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 $\Omega$  cm specific resistance) obtained with a Pall Cascada laboratory water system. A stock solution was prepared by dissolving HgCl<sub>2</sub> 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.

#### *Preparation of ISE membranes and electrodes*

The traditional homogeneous HgCl<sub>3</sub><sup>-</sup>-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- $\mu$ m 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  $\mu$ L 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  $\mu$ M HgCl<sub>2</sub> 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.

#### *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.<sup>25</sup> 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 using a PXSJ-216 pH meter (Shanghai, China) in the galvanic cell: saturated calomel electrode (SCE) 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).<sup>27</sup> 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.<sup>28</sup>

#### *Reproducibility procedure*

After each measurement, the asymmetric membrane based  $\text{HgCl}_3^-$ -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  $\text{HgCl}_3^-$  out of the sensing membrane. The electrode was reconditioned in 20 mM citric acid/ $\text{Na}_2\text{HPO}_4$  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  $\text{HgCl}^+$ ,  $\text{HgCl}_2$ ,  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{2-}$  as described below:<sup>23,24,29</sup>



According to the above equations, it can be calculated that in Cl<sup>-</sup>-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  $\text{HgCl}_4^{2-}$  which constitutes about 78.7% of the total mercury species. The anionic and neutral

chloro-mercury complexes  $\text{HgCl}_3^-$  and  $\text{HgCl}_2$  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  $\text{Hg}^{2+}$  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.<sup>24</sup> 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,<sup>25,26</sup> potentiometric detection of trace-level mercury in  $\text{Cl}^-$ -rich samples can be achieved.

#### *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.<sup>30</sup> 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  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ . Nevertheless, it is still unknown that whether or not these ionophores can form strong complexes with metal chloride complexes such as  $\text{HgCl}_3^-$  and  $\text{AgCl}_2^-$ . In this work,

lead ionophore IV which was usually employed as the  $\text{Pb}^{2+}$ -selective ionophore was used as the ion carrier for chloro-mercury anionic complexes for the first time. The chemical structure of lead ionophore IV is shown in Scheme 1. Since lead ionophore IV contains four sulfur, four nitrogen and four oxygen atoms which are good coordinating sites for mercury atom, it can be expected that the ligand will form strong coordination interactions with the mercury atom center in the chloro-mercury anionic complexes.<sup>31,32</sup> Additionally, it should be noted that the chloride concentration influences the Hg speciation. In 0.05 M NaCl, the dominant species are  $\text{HgCl}_2$ ,  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{2-}$  with a distribution of 66.7%, 27.7% and 5.6%, respectively.<sup>24</sup> In this case, we assume that  $\text{HgCl}_3^-$  is dominantly responsible for the observed anionic response of the proposed sensor. Consequently,  $\text{HgCl}_3^-$  is used as the representative anion for the chloro-mercury anionic complexes in all further experiments. The sensing mechanism of the proposed ionophore and the schematic representation of the coordination between the ionophore and  $\text{HgCl}_3^-$  were shown in Scheme S1 in the Supporting Information. In order to decrease the membrane resistance, reduce cation interference and improve selectivity of the proposed sensor, the anion exchanger TDMAC was incorporated into the sensing membrane.

#### *Influence of the ion carrier*

To illustrate whether conventional neutral ionophores for metal cations can bind strongly and selectively to anionic metal chloride complexes, potentiometric anion selectivity coefficients of the ionophore-free and neutral ionophore incorporated

membranes were compared. The selectivity coefficients of the proposed membranes were evaluated by using Bakker' method to eliminate the influence of the inherent sensitivity limit on the ISE response toward interfering ions.<sup>27</sup> The logarithmic Nikolskii coefficients for  $\text{HgCl}_3^-$  ( $\log K_{\text{HgCl}_3^-, Y}^{\text{pot}}$ ) over other anions are summarized in Table 1. It is clear that the anion-selective membrane using lead ionophore IV as an anion carrier and TDMACl as ion exchanger shows excellent selectivity to  $\text{HgCl}_3^-$  over other anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$  and  $\text{MoO}_4^{2-}$ . The high discrimination against these anions allows  $\text{HgCl}_3^-$  ISE to be used in the presence of a high interfering background. Notably, the obtained selectivity coefficients of the ionophore-based membrane electrode over all potential interfering anions are superior to those of the ionophore-free anion-exchanger-based electrode. Of particular significance is the fact that selectivity over chloride is enhanced nearly 1000-fold. The marked enhancement in chloride selectivity can allow trace-level potentiometric analysis of mercury in  $\text{Cl}^-$ -rich background such as marine and biological environments. These results indicate that  $\text{HgCl}_3^-$  can preferentially interact with lead ionophore IV within the polymeric membrane phase of the electrode. Also, this observation suggests the possibility that lead ionophore IV serves as an ionophore for the anionic mercury species.

#### *Potentiometric responses of the homogeneous membrane to $\text{HgCl}_3^-$*

The homogeneous membrane containing 1wt% lead ionophore IV and 1wt% TDMACl was used for detection of  $\text{HgCl}_3^-$ . Figure 1 shows the potential response of

the homogeneous membrane based on lead ionophore IV to  $\text{HgCl}_3^-$  in 0.05 M NaCl. As expected, the ISE formulation appears to be effective for the measurement of  $\text{HgCl}_3^-$ . The proposed electrode based on the ionophore-doped membrane conditioned by the primary ions (i.e.,  $\text{HgCl}_3^-$ ) shows a sub-Nernstian response of 48.7 mV / decade over the concentration range of  $5.0 \times 10^{-7}$  to  $5.0 \times 10^{-5}$  mol L<sup>-1</sup>, which is more than 1 order of magnitude lower than that reported by Kim et al.<sup>24</sup> It should be noted that the response behavior of the electrode with a slope of 48.7 mV / decade slightly deviates from the Nernstian response. This deviation can be ascribed to the contribution of the divalent  $\text{HgCl}_4^{2-}$  ions in the test solution.

As shown above, the proposed anion-selective electrode based on the homogeneous membrane can be effectively used for the determination of  $\text{HgCl}_3^-$ . However, according to the US Environmental Protection Agency (EPA) standard, the MAL (maximum allowable level) of  $\text{Hg}^{2+}$  ions in drinking water is 10 nM.<sup>33</sup> Thus, the obtained detection limit cannot satisfy the requirement for trace-level analysis of mercury in aqueous environmental samples. Based on the selectivity for  $\text{HgCl}_3^-$  over  $\text{Cl}^-$ , the expected lower detection limit may be  $\sim 10^{-10}$  M  $\text{HgCl}_3^-$  in the presence of 0.05 M NaCl. This is much lower than the value obtained with the homogeneous membrane based electrode. The poor detection limit is probably due to the leaching of  $\text{HgCl}_3^-$  from the ISE membrane into the measuring solution.<sup>34-38</sup>

#### *Asymmetric membrane rotating ISE configuration for sensitive detection of $\text{HgCl}_3^-$*

In our previous reports, it has been well established that an asymmetric membrane

rotating ISE configuration can be utilized to significantly improve the detection sensitivity of potentiometric measurements with a high-interfering background.<sup>25,26</sup>

The response mechanism of the proposed ISE sensing mode is based on the nonequilibrium steady-state diffusion process of primary ions at the sample-membrane interface. Such nonequilibrium mechanism has been successfully applied to sensitive detection of polyions and lipophilic anions such as perchlorate and periodate.<sup>39,40</sup> By promoting the accumulation of primary ions in the boundary layer of the ISE membrane phase by using the asymmetric membrane with high PVC content and rotating the membrane electrode, the nonequilibrium potential response can be largely enhanced and thus the detection sensitivity is improved.

In this work, we extend the application of the asymmetric membrane rotating ISE configuration to the detection of anionic mercury chloride complexes. The asymmetric membrane was formed by evenly spreading the TDMACl solution onto the surface of PVC membrane matrix as described before.<sup>25</sup> In order to eliminate the ion exchange of primary ions in the membrane phase by interfering ions in the sample solution, the proposed electrode is conditioned only with interfering ions (e.g., 0.05 M NaCl) before measurements. The lipophilic salt ETH 500 was added to lower the resistance of the PVC membrane matrix. The illustration of asymmetric ISE membrane for the determination of  $\text{HgCl}_3^-$  is shown in Scheme 2. As established in our previous work, the detection limit can be improved by suppressing the transmembrane ion fluxes of  $\text{HgCl}_3^-$  that have a decisive influence on the potential response. The potential response with the asymmetric membrane is shown in Figure 2.

As expected, the  $\text{HgCl}_3^-$ -selective electrode based on the asymmetric membrane exhibits a significantly improved performance. Detailed analysis of the experimental results reveals that there is a linear dependence of the EMF change on the concentration of  $\text{HgCl}_3^-$  in the range of 1.0-40 nM ( $\gamma = 0.999$ ) with a lower detection of  $4.5 \times 10^{-10}$  mol/L ( $3\sigma$ ). This detection limit is more than two orders of magnitude lower than that reported by other researchers.<sup>24</sup> Above all, the proposed approach yields a detection limit much below the EPA defined limit (i.e., 10 nM) in drinking water.

#### *Interference study*

The selectivity of the proposed asymmetric membrane was also characterized by using Bakker's method. The selectivity coefficients for  $\text{HgCl}_3^-$  over a series of relevant interfering anions are shown in Table 2. As can be seen, the proposed electrode based on asymmetric membrane shows an excellent selectivity to  $\text{HgCl}_3^-$  over other anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , which is also consistent with that obtained by the homogeneous membrane with lead ionophore IV (Table 1). The high sensitivity and excellent selectivity of the proposed asymmetric membrane configuration offer great potential for trace-level potentiometric detection of  $\text{HgCl}_3^-$  in the presence of a high electrolyte background, especially for seawater and biological fluid samples.

#### *Reversibility*

The regeneration process of the proposed electrode is similar to that of the heparin

sensor described earlier.<sup>41</sup> The schematic representation of the regeneration process is shown in Scheme 3. The electrically charged  $H^+$  ionophore ETH 2412 is incorporated as an additional ionophore into the  $HgCl_3^-$ -sensing membrane. This membrane will respond to pH only at low  $H^+$  concentrations (e.g., pH 10.0), while  $HgCl_3^-$  anions are coextracted with  $H^+$  ions into the membrane at pH 7.4. The membrane renewal was accomplished by stripping  $HgCl_3^-$  out of the membrane with a base solution of pH 10.0. Effective stripping of  $HgCl_3^-$  from the pH cross-sensitive potentiometric sensor is demonstrated in Figure 3. As illustrated, the potential response is fully reversible with a good reproducibility of a 0.5 mV standard deviation (30 nM, n = 5).

#### *Application*

The asymmetric membrane based  $HgCl_3^-$ -selective electrode exhibits a high sensitivity and excellent selectivity for the detection of mercury under optimum experimental conditions. The feasibility of the proposed electrode for mercury determination was evaluated by assessing total mercury potentiometrically in the certified reference material of the seawater sample (GBW(E) 080042). Since the concentration of  $Cl^-$  in the seawater samples is 0.5 M, all samples were diluted 1:10 with deionized water before measurement. After dilution, the mercury contents in spiked seawater samples were potentiometrically determined with the proposed membrane electrode. The results are given in Table 3. It can be seen that the recoveries of seawater samples vary from 98% to 109%, indicating that the proposed sensor has promising potential for the determination of total mercury contents in

marine samples.

#### 4. Conclusions

A highly sensitive and selective potentiometric sensor for the determination of mercury anions using lead ionophore IV as anion-selective ionophore and TDMACl as ion exchanger has been described. Combined with the asymmetric membrane rotating ISE configuration, the sensor offers a low detection limit of  $4.5 \times 10^{-10}$  mol/L for  $\text{HgCl}_3^-$  in 0.05 M NaCl. It is expected that various metal-chloride complexes at trace levels in  $\text{Cl}^-$ -rich media such as marine and biological environments can be determined by using different anion-selective ionophores.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

#### Author Contributions

‡Equal contribution.

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**Table 1**

Selectivity coefficients of traditional homogeneous membranes with and without lead ionophore IV

Y	$\log K_{\text{HgCl}_3^-, Y}^{\text{pot}}$ <sup>a</sup>		Y	$\log K_{\text{HgCl}_3^-, Y}^{\text{pot}}$ <sup>a</sup>	
	Without ionophore <sup>b</sup>	With Ionophore <sup>b</sup>		Without ionophore <sup>b</sup>	With ionophore <sup>b</sup>
Cl <sup>-</sup>	-5.8	-8.6	SeO <sub>4</sub> <sup>2-</sup>	-9.3	-11.4
SO <sub>4</sub> <sup>2-</sup>	-8.9	-11.1	CrO <sub>4</sub> <sup>2-</sup>	-6.9	-9.5
NO <sub>3</sub> <sup>-</sup>	-2.8	-5.1	WO <sub>4</sub> <sup>2-</sup>	-8.5	-9.6
OH <sup>-</sup>	-6.1	-8.2	MoO <sub>4</sub> <sup>2-</sup>	-9.5	-11.2
SCN <sup>-</sup>	-2.5	-4.3	MnO <sub>4</sub> <sup>-</sup>	0.9	-1.3
ClO <sub>4</sub> <sup>-</sup>	-1.7	-3.1	AgCl <sub>2</sub> <sup>-</sup>	0.6	-1.8

<sup>a</sup> Mean value obtained from three corresponding pairs of concentrations of HgCl<sub>3</sub><sup>-</sup> and the respective interfering anion in the Nernstian response range  $\pm$  standard deviation.

<sup>b</sup> Membrane with 1 wt% TDMACl.

**Table 2**

Potentiometric selectivity coefficients,  $\log K_{\text{HgCl}_3^-, Y}^{\text{pot}}$ , obtained with the separate solution method for the proposed asymmetric membrane based ISE.

Y	$\log K_{\text{HgCl}_3^-, Y}^{\text{pot}}$ <sup>a</sup>	Y	$\log K_{\text{HgCl}_3^-, Y}^{\text{pot}}$ <sup>a</sup>
Cl <sup>-</sup>	-8.7	SeO <sub>4</sub> <sup>2-</sup>	-10.8
SO <sub>4</sub> <sup>2-</sup>	-10.9	CrO <sub>4</sub> <sup>2-</sup>	-10.1
NO <sub>3</sub> <sup>-</sup>	-4.7	WO <sub>4</sub> <sup>2-</sup>	-10.1
OH <sup>-</sup>	-8.1	MoO <sub>4</sub> <sup>-</sup>	-10.5
SCN <sup>-</sup>	-3.8	MnO <sub>4</sub> <sup>2-</sup>	-1.7
ClO <sub>4</sub> <sup>-</sup>	-2.6	AgCl <sub>2</sub> <sup>-</sup>	-1.4

<sup>a</sup> Mean value obtained from three corresponding pairs of concentrations of HgCl<sub>3</sub><sup>-</sup> and the respective interfering anion in the Nernstian response range  $\pm$  standard deviation.

**Table 3**

Total mercury concentrations determined by the proposed approach in spiked seawater samples.<sup>a</sup>

	Total mercury ( $\mu\text{g/L}$ )	Amount found ( $\mu\text{g/L}$ )	Recovery (%)
GBW(E) 080042	1.0	<sup>b</sup>	<sup>b</sup>
+ 20 $\mu\text{g/L}$ HgCl <sub>2</sub>	21.0	21.8 $\pm$ 0.1	109
+ 40 $\mu\text{g/L}$ HgCl <sub>2</sub>	41.0	39.4 $\pm$ 0.3	98
+ 50 $\mu\text{g/L}$ HgCl <sub>2</sub>	51.0	52.8 $\pm$ 0.3	106

<sup>a</sup> Average value of three determinations  $\pm$  standard deviation.

<sup>b</sup> Undetectable.

**Figure Captions**

**Scheme 1.** Chemical structure of lead ionophore IV.

**Scheme 2.** Representation of the asymmetric ISE membrane for the determination of  $\text{HgCl}_3^-$ .

**Scheme 3.** Illustration of the membrane renewal process.

**Fig. 1.** Time-dependent EMF response traces of the traditional homogeneous membrane based ISE conditioned with the primary ions for measuring  $\text{HgCl}_3^-$  in 0.05 M NaCl under constant stirring. The inset shows the corresponding calibration curve. Homogeneous membrane ingredients: 1 wt% lead ionophore IV, 1 wt% TDMACl, 65 wt% *o*-NPOE and 33 wt% PVC. The inner filling solution of the proposed electrode was 0.05 M NaCl solution added with 4.4  $\mu\text{M}$   $\text{HgCl}_2$ .

**Fig. 2.** Potential traces for the asymmetric membrane rotating ISE for measuring  $\text{HgCl}_3^-$  in 0.05 M NaCl. The inset shows the calibration curve for  $\text{HgCl}_3^-$  detection. The asymmetric membranes were prepared by evenly spreading 5  $\mu\text{L}$  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). 0.05 M NaCl was used as the internal filling solution. The rotation speed was 3000 rpm.

**Fig. 3.** Reversibility of the proposed asymmetric membrane based ISE for detection of  $\text{HgCl}_3^-$  in 0.05 M NaCl. The concentration of  $\text{HgCl}_3^-$  was  $3 \times 10^{-8}$  M. After each

measurement, a 10 min stripping with 50 mM  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  buffer solution of pH 10.0 was employed. The other conditions are as given in Fig. 2.

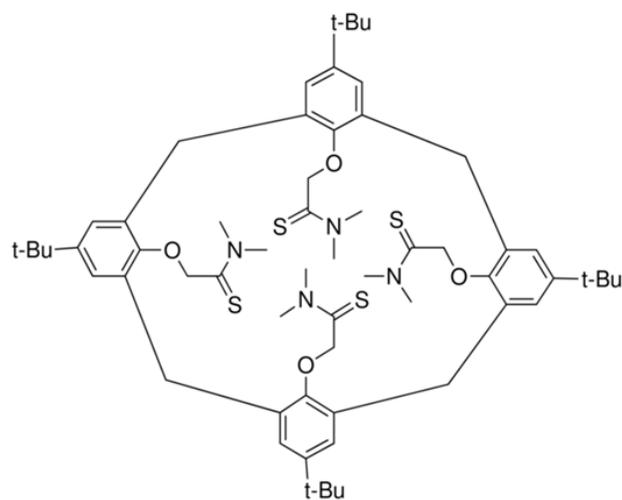
### **Highlights**

A sensitive potentiometric sensor for detection of  $\text{HgCl}_3^-$  is reported.

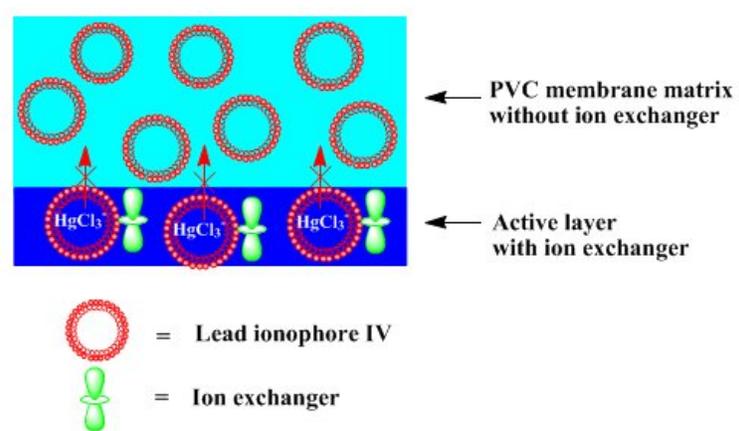
Lead ionophore IV is used as the ion carrier for the anionic chloro-mercury complex.

Asymmetric membrane configuration is employed to improve the sensor sensitivity.

The proposed method allows for potentiometric detection of mercury in  $\text{Cl}^-$ -rich media.



Scheme 1



Scheme 2



Scheme 3

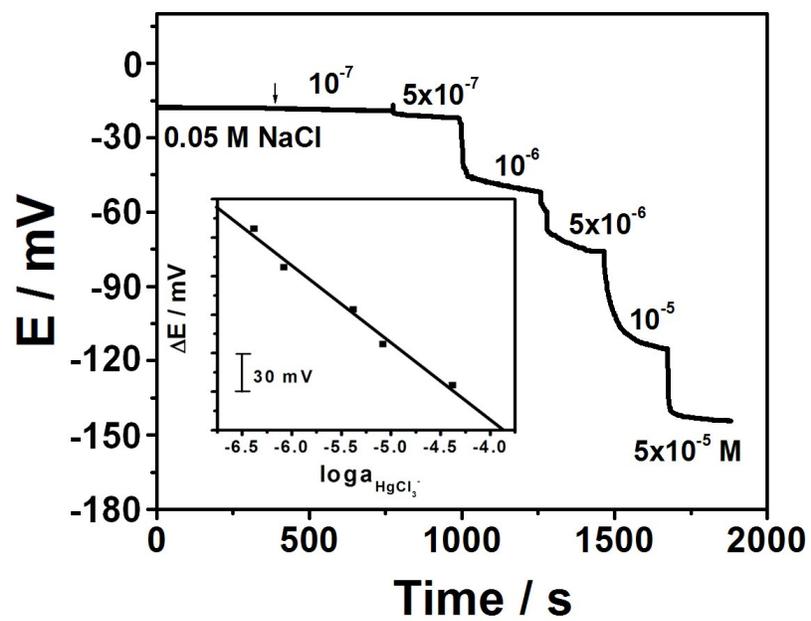


Fig. 1

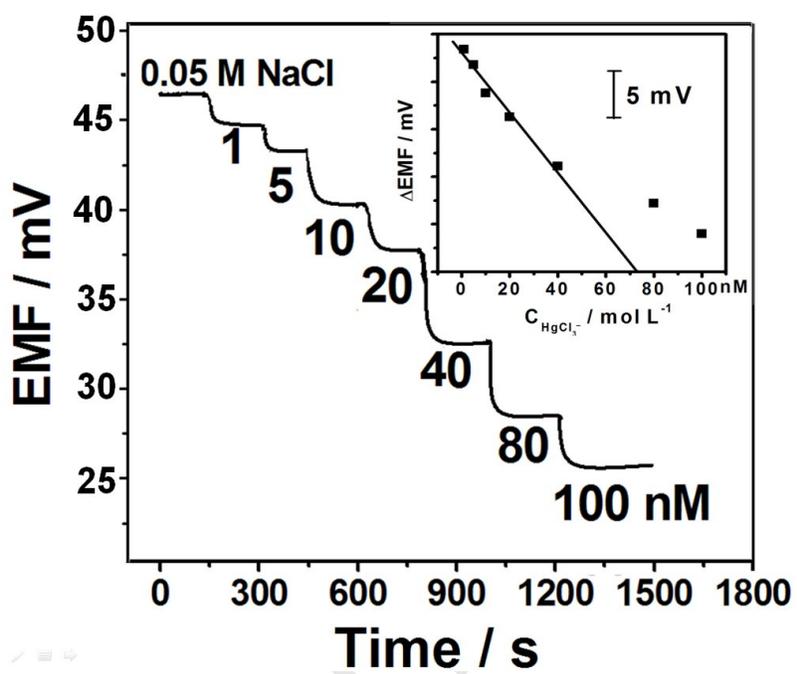


Fig. 2

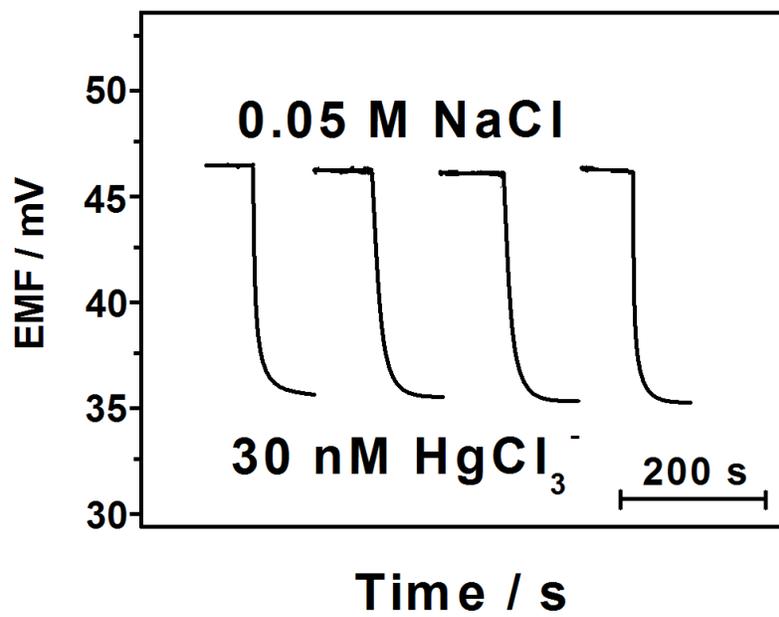


Fig. 3

## Biographies

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