

The Development Of Mercury Ion Selective Electrode With Ionophore 7,16-Di-(2-Methylquinoly1)-1,4,10,13-Tetraoxa-7,16-Diazacyclooctadecane (DQDC)

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Abstract

The development of mercury ion selective electrode (ISE-Hg) by using ionophore 7,16-Di-(2-methylquinoly1)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DQDC) in an electrode membrane sensing is explained. The study is aimed to construct an ion selective electrode for mercury by immobilization of ionophore DQDC in a polymeric PVC membrane electrode. Membrane electrode was constructed by casting and spin coated methods from the mixture of DQDC and plasticizer in a polymeric PVC matrix dissolved in a tetrahydrofuran solvent. The membrane has been characterized and used as a sensing material in an ISE-Hg. The developed ISE-Hg give sensitive and selective response to mercury, working range linearity lies between 0.005 mM – 1.0 mM Hg^{2+} , slope 25.82 mV per decade concentration of Hg^{2+} ($r^2 = 0.998$).

Keywords: potentiometric; membrane electrode, ionophore, ion selective electrode, ISE-Hg, mercury

1. Introduction

The development of potentiometric method with using ion selective electrode (ISE) for mercury is a great challenge to obtain an alternative analytical tool for low cost, simple instrumentation, fast response, high selectivity, and wide linear detection system. Potentiometric method has been considered as an attractive detection method because of the cheap and simple instrumentation required, commonly a pH-meter (Situmorang, et al., 2008). Tungsten metal electrode due to its responsive to potential changes has been used as sensing device, and its compatible for sensing component has been demonstrated in the construction of potentiometric sensor (Situmorang, 2001). Tungsten electrode has also been used as transducer for potentiometric biosensors with immobilization of enzyme in polytyramine for malic acid (Situmorang, et al., 2001). It was demonstrated that electrodeposited polytyramine (Situmorang, et al., 1999) could act as a substrate electrode and retain its ability to determine potential change (Situmorang, et al., 2002).

Various analytical methods have been developed for determination of mercury, they are using spectrophotometric methods with adsorbing agent of 1,5-diphenylthiocarbazone (Khan, et al., 2005) or with o-carboxy phenyl diazoamino p-azobenzene (Chatterjee et al., 2002). Spectrofluorometry with 2-hydroxy-1-naphthaldehyde-8-aminoquinoline fluorescent reagent has also introduced (Lietal, 2006). Chromatographic method has also been reported for the determination of mercury (Mondal & Das, 2003; Hu, 2002). Amperometric method for the determination of mercury have been reported (Majid, et al., 2002; Lu, et al., 2003). Inductively coupled plasma mass spectrometry (ICP-MS) has also been introduced for mercury determination (Zhang, et al., 2004). Another method by using capillary electrophoresis (Páger & Gáspár, 2002),

and capillary electrophoresis inductively coupled plasma mass spectrometry with microconcentric nebulization has also been reported (Lee & Jiang, 2000). The determination of mercury are still dominated by atomic absorption spectroscopy (AAS), those are with graphite furnace atomic absorption spectrometry (Da-Silva, et al., 2002; Izgi, et al., 2000), electrothermal atomic absorption spectrometry (Moreno, et al., 2002), and cold vapor generation-electrothermal atomic absorption spectrometry (Moreda-Piñeiro, et al., 2002). In practice, cold vapor atomic absorption spectrophotometry (CV-AAS) is a good choice because it has superiority in accuracy and sensitivity (Silva, et al., 2006, Rizea, et al., 2007). However, those are with relatively high cost instruments.

Potentiometric determination of mercury by using diazacrownionophore membrane electrode has been reported (Yang, et al., 1997; Yang, et al., 1998). Potentiometric device with ISE by incorporation of ionophore in membrane electrode is a robust analytical method for the determination of mercury. It was believed the key aspects on the success for the construction of ISE is based on its design with the integration of ionophore onto the membrane electrode. The development of ISE-Hg reported in this study is based upon successfully in the construction of ISE by using ionophore sensing device for the determination of lead (Situmorang, 2005) and mercury (Purba, et al., 2013). The construction of PVC membrane electrodes with incorporating ionophore is very important in the development of ion selective electrode for mercury (ISE-Hg). The purpose of this paper is to develop a potentiometric sensor for mercury with incorporation of ionophore 7,16-Di-(2-methylquinolyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DQDC) that is immobilized in a polymeric PVC membrane electrode. Synthesis of sensing agents of ionophore DQDC, the strategy to incorporate ionophore on to the PVC membrane electrode, the construction of ISE-Hg, and the characterization of the electrode for its performance to mercury are demonstrated in this study. The application of the electrode to ion-sensing components for mercury ion in batch analysis is also described.

2. Experimental

2.1 Reagents and Materials

All chemicals are laboratory reagent grade and used as received except where indicated. Starting material of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DC), Poly(vinyl chloride) (PVC: low molecular weight type) as membrane matrix material, 2-nitrophenyl octyl ether (NPOE) as membrane plasticizer, potassium tetrakis (p-chlorophenyl) borate (KTPCIPB) as anionic additive, 2-chloromethylquinoline, mercury nitrate, solvent of acetonitrile, tetrahydrofuran (THF), dichloromethane, and tungsten wire (99.9 %, Ø 0.5 mm) were all purchased from Aldrich Chemical Company.

2.2 Instrumentation

Potentiometric measurements were made with a Keithley 177-Microvolt Digital Multi Meter (Keithley Instrument, USA) connecting with MacLab/8 Analog Digital Instrument, Sydney, Australia, for data acquisition. The ion selective electrodes assembled with a tungsten wire electrode was constructed followed the procedures explained in previous report (Purba, et al., 2014). Commercial Ag/AgCl electrode containing 3 M KCl internal solution from Bioanalytical System (BAS) USA was used as reference electrode in all electrochemical experiments. High-resolution scanning electron microscope, SEM (Zeiss Neon) is used for membrane morphology studies.

2.3 Synthesis of Ionophore DQDC

Synthesis of ionophore as a sensing agent for mercury was very important part of the work because diazacrown ethers bearing a cation ligating pendant group on the nitrogen atom have successfully been used in cation membrane transport. Ionophore 7,16-Di-(2-methylquinolyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane is synthesized by the alkylation of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane with 2-chloromethylquinoline in acetonitrile containing sodium carbonate followed the modification of the procedures explained by Yang, et al., (1998). Another reaction was carried out in the dried analytical grade THF and dichloromethane solvents and done under an atmosphere of nitrogen as explained previously (Situmorang, et al., 2014).

2.4 Preparation of Membrane Electrodes

Preparation of membrane electrode is carried out by casting method and spin coated procedures to obtain sheet of PVC membrane from the mixture composition of matrix polymer PVC, plasticizer NPOE, ionophore DQDC, with added the anionic additive for polymeric membrane KTPCIPB in THF solution. The casting method procedure to prepare membrane electrode containing of ionophore was conducted followed the procedures explained previously (Purba, et al., 2014; Purba, et al., 2013), it was the modification from the procedure explained by Yang, et al., (1998). The membrane composition (in weight %) was 3% ionophore DQDC, 30% PVC, 67% NPOE and 50 mol% KTPCIPB were dissolved in 5 mL of dry tetrahydrofuran (THF) at constant

stirring, and poured onto casting apparatus (petridis) followed by evaporation of the solvent to form a thin, flat, and clear membrane sheet. Spin coating procedure in the preparation of the electrode membrane was also carried out. The same quantity of the mixture of ionophore DQDC, PVC and plasticizer are dissolved in 5 mL THF as explained above, and the liquid was put on sputtering apparatus, followed by two steps spinning, at 600 rpm for 10 second and at 800 rpm for 30 second, then let the solvent to evaporate to form a thin, flat, and clear membrane sheet. The use of spin-coated techniques in the preparation of membrane electrode has advantage in the good reproducibility of membrane thickness, and the membrane sheet is compatibel for the construction of ion selective electrode.

2.5 Preparation of ISE-Hg

The strategy by using membrane type system is a considered choice to construct ISE-Hg due to the simple fabrication of the electrode. Preparation of ISE-Hg is carried out followed the procedures explained in previous study (Situmorang, et al., 2005) with modification to obtain a better sensing for mercury. The ISE-Hg with membrane electrode was fabricated by attaching a disc of $\text{\O} 5$ mm diameter PVC membrane, which is cut from the PVC membrane sheet prepared above, to PVC body (approximate $\text{\O} 5.0$ mm internal diameter and 60 mm length) at one edge is glued by using a light paste of PVC in THF solution. The electrode is then filled with internal solution of 10 mM $\text{Hg}(\text{NO}_3)_2$ and 10 mM KCl solution. Pure tungsten (W) wire was firstly cleaned with 1 M nitric acid for 1 minute, followed by sonication, and finally rinsed with distilled water. The W-wire is then inserted into the electrode body that is immersed in an internal solution, and sealed the top with rubberseptum to construct an ISE-Hg. The Ag/AgCl (BAS) was used for external reference electrode. The construction of PVC membrane liquid-contact electrodes is selected in the construction of electrode body design because the electrode assembly is simple in the incorporation of ionophore in to the electrode. The design of ISE-Hg is illustrated in Figure 1.

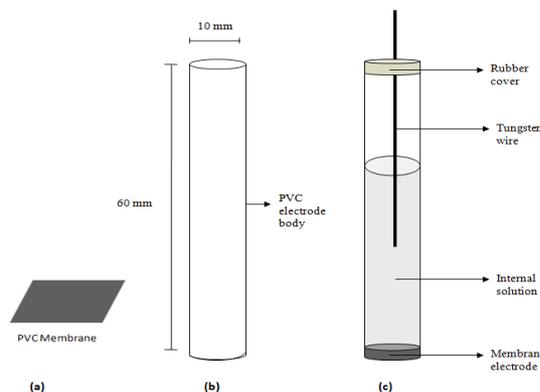


Figure 1. The design of ISE-Hg electrode containing of ionophore with PVC membrane liquid-contact electrode: (a) membrane electrode containing of ionophore DQDC, (b) a PVC electrode body, and (c) the ISE-Hg

2.6 Potentiometric Measurements

An ISE-Hg and Ag/AgCl reference electrode were immersed in a stirred bulk background solution of 10 mL nitric acid solution, pH 4.0, containing 10 mM KNO_3 . Standard solution of $\text{Hg}(\text{NO}_3)_2$ at different concentration (accurately measured) was introduced to the electrochemical cell from a syringe followed by stirring after each addition, successively starting from low concentration to higher concentrations of mercury standard solutions. Potential change was monitored on a digital mV meter interfaced with PowerLab, and the data were collected in personal computer. All measurements were carried out at 25 ± 0.5 °C. The calibration curve was done in the absence of interfering cations.

3. Result and Discussion

3.1 Optimization of Membrane Composition

Polymeric membrane of poly(vinyl chloride) (PVC) is popular to be used in the construction of ion selective electrode. The PVC is chosen as membrane matrix in this study with respect to the mechanical stability, chemical stability, chemical inertness (there is no competition with solution), the resulting membrane has no pores, and has low electrical resistance. The composition of ion-selective membranes have been optimized for mechanical properties to be suited for the construction of ISE-Hg. Membrane electrode at different ingredients consisted of

matrix polymer PVC, plasticizer NPOE and KTpCIPB and ionophore DQDC has been fabricated by using casting and spin coated procedures. The mechanical properties of the membrane and the performance of the ISE-Hg electrodes prepared with these compositions are listed in Table 1.

Table 1. The composition of membrane ingredients, consisted of ionophore DQDC, matrix polymer PVC, and plasticizer NPOE, and anionic additive KTpCIPB toward the membrane properties and electrode performances. The values given are to nearest weight percentage

No	Composition in 5 mL THF				Mechanical Properties of Membrane		ISE-Hg Performance	
	PVC (wt %)	NPOE (wt %)	DQDC (wt %)	KTp-CIPB (mol %)	Casting	Spin coating	Response	Slope (mV)
1	20	77	3	50	Clear, very elastic, thin	Clear, very elastic, very thin	very fast	25.42
2	30	67	3	50	Clear, very elastic	Clear, very elastic, thin	very fast	25.26
3	40	57	3	50	Clear, elastic	Clear, elastic	Fast	25.81
4	50	47	3	50	Clear, elastic, thick	Clear, elastic, thick	Slow	22.11
5	60	37	3	50	White, rigid, thick	White, rigid, thick	Slow	18.26
6	70	27	3	50	White, rigid, very thick	White, rigid, very thick	Very slow	13.38

The mechanical properties of membrane electrode are influenced by the composition of polymeric PVC and the plasticizer. It is observed that the thickness and hardness of the electrode membrane depended upon the amount of PVC used. When using higher amount of PVC the membrane became rigid, too dense, and resistive that results in longer response time needed in the potential measurement. However, a lower PVC content made the membrane too thin, results in poor mechanical strength, it is swelled up in the solution very fast, and broken easily. The membrane electrode prepared from low concentration of PVC (20 wt%) with high composition of plasticizer (77 wt%) produce very thin membrane sheet with clear in color, where membrane texture is very elastic. This condition is adequate for the preparation of membrane electrode for ISE-Hg, but with short life time. Increasing the amount of PVC will increase the thickness of the membrane electrode but sacrifice in the elasticity of the membrane sheet. The membrane electrode prepared from high amount of PVC (70 wt%) with low concentration of plasticizer (27 wt%) produce very thick membrane sheet with white in color, accompanied with rigid texture. The compositions of the membranes listed in Table 1 are compatible with the construction of ISE-Hg. The membrane prepared from very low amount of PVC (less than 20 wt%) could not be used for electrode materials because it was swelling very fast in the solution and broken easily. Therefore, compromise in the composition of polymer and plasticizer has to be considered in the preparation of the electrode membrane to obtain the membrane with good mechanical properties for ISE-Hg. The membrane electrode made from 30% PVC and 67% plasticizer NPOE give good quality membrane. The membrane is then to be used to produce an ISE with good electrode performance based on its response sensitivity to mercury, and enhance the life time of the electrode for continuous uses.

The performance of ISE-Hg for mercury is influenced by the membrane composition in an electrode. Variation in the composition of polymer and plasticizer (PVC and NPOE a fixed amount of 3% DQDC and 50 mol% KTpCIPB in the ingredient) on the electrode performance is observed from the speed of sensing response to target analyte and the signal recovery to get constant baseline. The sensitivity of the electrode, it is based on the slope from the calibration curve of standard solution for the electrodes containing different ratios of plasticizer to PVC were summarized in Table 1. It is observed that the thickness of the membrane influenced the sensitivity of the electrode. The sensitivity of the electrode increased slightly with a decrease in the PVC content. The ISE-Hg made from the membrane electrode consisted of 30% PVC and 67% plasticizer NPOE is the most sensitive electrode for mercury. The higher the amount of plasticizer in the membrane improved the speed response of the electrode, but the mechanical properties of the electrode became much worse. The membrane was too soft, more permeable to water, easily swelling, internal solution is leaching, and results in a steady degradation of electrode performance.

The effect of the amount of KTpCIPB (anionic additive) on the ion-selectivity of the membrane was examined in the PVC membrane electrode. The presence of the anionic additive aided the efficiency of the electrodes towards

the target cation by facilitating of the cation through the membrane. The addition of the anionic additive caused an increase in the response, a reduction of membrane resistance, an improvement of the speed of response, and a decrease in the effects of anions at high sample ionic strength. The best electrode response accompany with high selectivity was obtained when using 50 mol% KTpCIPB of the ionophore content of DQDC in the electrode membrane. Increase the amount of KTpCIPB in the membrane formula caused an increase in the sensitivity, but the selectivity towards primary ion reduced, because the selectivity was strongly governed by the ion selective feature of the KTpCIPB⁻ anions. The membrane electrodes prepared with 30% PVC, 67% plasticizer NPOE, 3% DQDC, and 50 mol% KTpCIPB relative to the ionophore content provided good response to mercury. The membrane prepared at optimum condition has been observed by using SEM to obtain its surface at different amplification as shown in Figure 2. The SEM microscopy results showed that the contour of the membrane electrode containing ionophore DQDC is not very smooth but it has no pore.

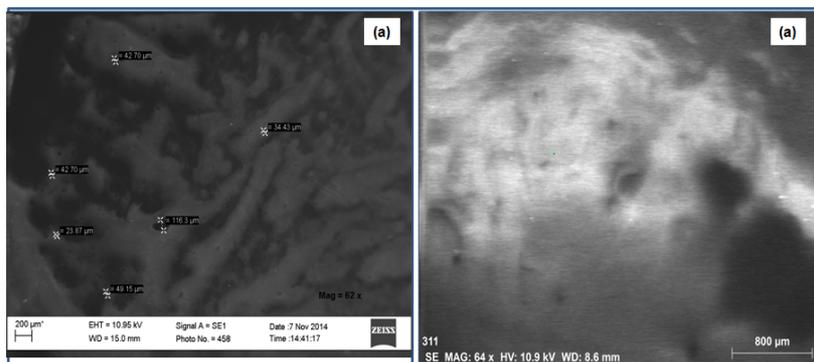


Figure 2. SEM images of PVC membrane electrode containing ionophore DQDC at different amplifications: (a) 200 μm , and (b) 800 μm

3.2 Determination of Hg^{2+} by Using ISE-Hg Electrodes

The electrode has been used for the determination of mercury in static system, and the potential was measured *versus* Ag/AgCl in solution containing of 10 mM potassium nitrate in nitric acid (pH 4.0). Typical signal output for the determination of series concentrations of mercury standard solutions and their calibration curves are presented in Figure 3. Potential responses given by the ISE-Hg electrode to mercury ion increases when increasing the concentration of Hg^{2+} in the solution (Figure 3A). The ISE-Hg has good performance in nitric acid solution (pH 4.0) where the response signal gives positive values, and constant base line was achieved at 30 seconds after the addition of mercury. There was no drifting signal in this condition, and the electrode sensitivity shows nearly Nernstian response. The calibration profile of ISE-Hg for mercury standard solution is presented in Figure 3C. The electrode gave linear response for 0.005 mM – 1.0 mM Hg^{2+} . A typical 95% confidence limit on the slope of ISE-Hg electrode is 25.82 mV per decade concentration of Hg^{2+} . The detection limit of an ISE-Hg electrode is 0.001 mM Hg^{2+} , where signal to noise ratio is two ($S/N = 2$). For comparison purposes, an ion selective electrode in the absence of ionophore in the membrane electrode (ISE-without DQDC) is also prepared. The electrode is used to determine mercury the same procedures as for ISE-Hg, and the signal profile for an ISE is shown in Figure 3B. There was no signal observed for mercury when the concentration of Hg^{2+} increased in the solution. The results have proved that the electrode responses to mercury are mainly generated by the presence of ionophore DQDC in the membrane electrode.

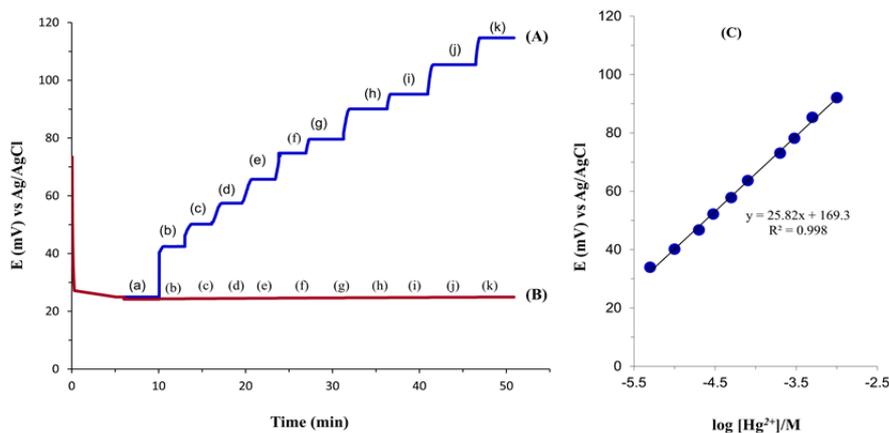


Figure 3. Typical response of ISE-Hg corresponding to successive addition of mercury in to nitric acid solution (pH 4.0) containing 10 mM KNO₃: (a) 0 μ M, (b) 5 μ M, (c) 10 μ M, (d) 20 μ M, (e) 30 μ M, (f) 50 μ M, (g) 0.1 mM, (h) 0.2 mM, (i) 0.3 mM, (j) 0.5 mM, and (k) 1.0 mM Hg²⁺. (A) ISE-Hg containing ionophore DQDC, (B) ISE without ionophore DQDC, (C) The calibration curve for mercury standard solution

3.3 Effect of DQDC on Electrode Performance

The effect of the quantity of ionophore in the membrane electrode was also investigated for electrode's sensitivity for mercury ion. The electrodes containing 1.5%, 2%, 3% and 4% DQDC respectively exhibited almost similar profiles with different in detection sensitivity (Figure 4). The electrode prepared with 3% ionophore DQDC in the electrode membrane gave good performance to mercury ion and good sensitivity was achieved, the slope is 25.82 mV per decade concentration of Hg²⁺. Response speed of the ISE-Hg at this condition is very fast, is only need 30 second to reach baseline for determination of mercury. An electrode constructed with 1.5% DQDC in the membrane electrode give low sensitivity (slope of 24.13 mV). The lifetime of the electrode with low concentration of ionophore was reduced due to slow leaching of entrapped DQDC from membrane when the electrode was washed during repeated uses. The electrode give good response to mercury when the amount of ionophore in the membrane electrode is 2% DQDC (slope of 25.26 mV). However, the response sensitivity is obtained lower than the sensitivity given by the ISE-Hg electrode containing 3% DQDC in the membrane (slope is 25.82 mV). Furthermore, the crystals were observed in the electrode membrane when the content of ionophore is increased to 4% DQDC. The electrode sensitivity at this condition was greatly reduced (slope of 22.74 mV). Therefore, the best condition on the preparation of ISE-Hg is chosen by immobilisation of ionophore 3% DQDC in the membrane electrode.

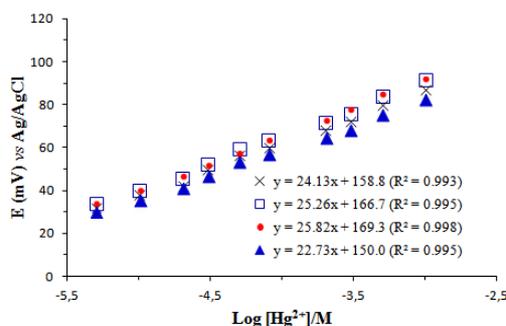


Figure 4. Calibration graphs for ISE-Hg for mercury when using different concentration of ionophore DQDC in electrode membrane: (x) ionophore 1.5%, (□) ionophore 2.0 mg, (●) ionophore 3.0 mg, and (▲) ionophore 4.0%

3.4 Selectivity of ISE-Hg

Selectivity of ISE-Hg has been tested for various types of cations, which are predicted to be interfering agents for mercury determination in real samples of polluted water samples. The response of ISE-Hg for 0.5 mM Hg²⁺ and the mixture of 0.5 mM Hg²⁺ with 0.1 mM each of these cations are listed Table 2. Those cations are

successively Mg^{2+} , Ca^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , Al^{3+} , Fe^{3+} , and Sn^{3+} . It was found that all cations added into mercury standard solution gave small change in the potential compare to a standard 0.5 mM Hg^{2+} . Potential changes are vary between 1 - 5%, where copper ion was the highest(5%) response. However, at moderate concentration (0.1 mM) of all those cations added into mercury standard solution were not interfere the measurement of the ISE-Hg. The results reveal that the developed ISE-Hg electrode is selective for mercury. The presence of ionophore DQDC in the membrane electrode has proven to give sensitive and selective response to mercury ion.

Table 2. The potential value of an ISE-Hg to 0.5 mM Hg^{2+} standard solution and the mixture of 0.5 mM interfering cations and 0.5 mM Hg^{2+}

Mixture of Mercury and Interfering Cations	Electrode responses (E, mV)		
	Mean	Change in E*	% Change*
Hg^{2+}	85.83	-	-
Mg^{2+}	87.93	2.10	2
Ca^{2+}	88.75	2.92	3
Zn^{2+}	87.60	1.77	2
Cu^{2+}	90.40	4.57	5
Cd^{2+}	88.44	2.61	3
Ni^{2+}	88.44	1.90	2
Al^{3+}	88.50	2.67	3
Fe^{3+}	87.97	2.14	2
Sn^{3+}	86.51	0.68	1

*The electrode response for the mixture of 0.5 mM Hg^{2+} + 0.5 mM interfering agents is compared with 0.5 mM Hg^{2+} .

3.5 Stability of ISE-Hg

An ISE-Hg has been tested for its stability and the lifetime of the membrane electrode when the electrode is used to determine mercury at long period of time. Repeat determination of 0.5 mM Hg^{2+} (one measurement per day) was carried out for 30 days, and the relative responses (%) of the electrode is presented in Figure 5. The electrode exhibited good stability at normal uses for one month. The electrode signal is steady reduce to become 94% after 30 days. This results is promising where the PVC is compatible to be used as polymeric matrix in the immobilisation of ionophore in the membrane electrode. The study is still now still under investigation to see if any response decreased due to the ionophore leaching out from the membrane for longer time of uses.

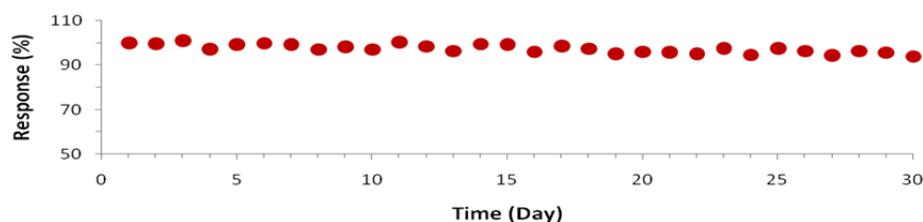


Figure 5. The response stability (%) of an ISE-Hg for repeated measurements of 0.5 mM Hg^{2+} for 30 days

4. Conclusion

The preliminary work on the construction of ISE-Hg by using ionophore DQDC in a membrane electrode has successfully done. This work demonstrated the compatibility of polymeric PVC membrane electrodes with ionophore DQDC as sensing agent in an ion selective electrode. The ISE-Hg give sensitive response to mercury ion, the working linearity range lies between 0.005 mM-1.0 mM Hg^{2+} , slope 25.82 mV per decade concentration of Hg^{2+} , and the detection limit 0.001 mM Hg^{2+} . This work is now still under investigation to obtain optimum conditions of the sensor for mercury.

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