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A new Hg (II) electrode for the analysis of mercury in sea food

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Abstract

A Hg (II) solid state electrode (ISE) was fabricated using HgS and sparingly soluble Cu and Ag sulfur salts, and the highest sensitivity of the ISE was obtained at the 10% HgS (w/w) composition. The ISE was found to have a slope of about 29 mV towards the Hg (II) ion (pHg 1,0-7,0 M). Hg-SE was found to have a response time of 20 s and it offers an operating range of pH 1,0 to 5,0. Their lifespan was measured as 1 year. It was determined that ISE was not sensitive to other ions. The LOD value of the electrode was measured as 5×10^{-8} M. In addition, after the electrode validation, it was used in Hg measurements in seafood.

1. INTRODUCTION

The most important effect of intensive industrialization on the environment and food is heavy metal pollution. Mercury (Hg) is an element that is among the heavy metals and has a high toxic effect. Low amounts of mercury inhibit the function of many vital functions with its strong toxic effect. For the determination of mercury ion AAS [1], ICP-OES [2-3], UV-vis spectrophotometry [4-5] and electroanalytical methods [6-7]. These methods are time consuming for complex samples and expensive.

Recently, it is more preferred in the analysis of trace elements due to the short test time, fast and cheap. Many electrodes sensitive to Hg (II) have been developed. They are solid membrane electrodes, usually based on different ionospheres. Ionophore such as tri dodecyl methyl ammonium iodide [8], thiosemicarbazone [9], poly (4-vinily pyridine) [10], dithiadiazacyclotetradecine [11], Calix [2] thieno [2] pyrrole [12], poly-o-toluidine Zr (IV) tungstate [13] and 2-(N-pipyridino methyl)-1-cyano cyclohexano [14]. The slope of these electrodes to the mercury ion is 25-28 mV between $1x10^{-1}$ and $1x10^{-6}$ M. The lifetime of the electrodes is maximum 6 months, the response times are long and the number of interfering ions is high.

In this study, Hg-SE was prepared from HgS, Cu_2S and Ag_2S salts prepared in the laboratory. Characterization of ISE was done. Component effect, response time, working pH range, and interference effect were examined. The validation of the method was performed according to the synthetic sample. Using ISE, the amount of mercury in fish, mussels and shrimp was measured as the 95% confidence level and the average of 10 values.

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2.MATERIALS AND METHODS

2.1. Reagents

HgS, Cu_2S and Ag_2S [15-16] less soluble salts used in the preparation of ISE were prepared under laboratory conditions. $Hg(NO_3)_2$ and metal salts (Merck) whose interferences are investigated have high analytical purity. The deionized water was used in the preparation of solutions. HNO_3 and $HClO_4$ (Merck) are acids used in the dissolving process of seafood.

2.2. Instruments

For potential measurements, Metrohm 781 ion meter, Ag/AgCl electrode as reference electrode and MTOPS MS 300 magnetic stirrer mixer were used.

2.3. Electrode Fabrication

Slightly soluble sulphurous salts of Hg, Cu and Ag were mixed in a certain ratio and amount of mortar and turned into a homogeneous mixture. It was pressed with a pressure of 10000 $kgcm^{-2}$ using a hydraulic press. The resulting thin tablet was adhered to an approximately 15 cm long glass tube with both ends open. An Ag wire to contact the tablet and the inside of the electrode were filled with epoxy resin. The resin dried in one day [17]. The life of the electrode, which is used 5-6 times a day, is about 2 years.

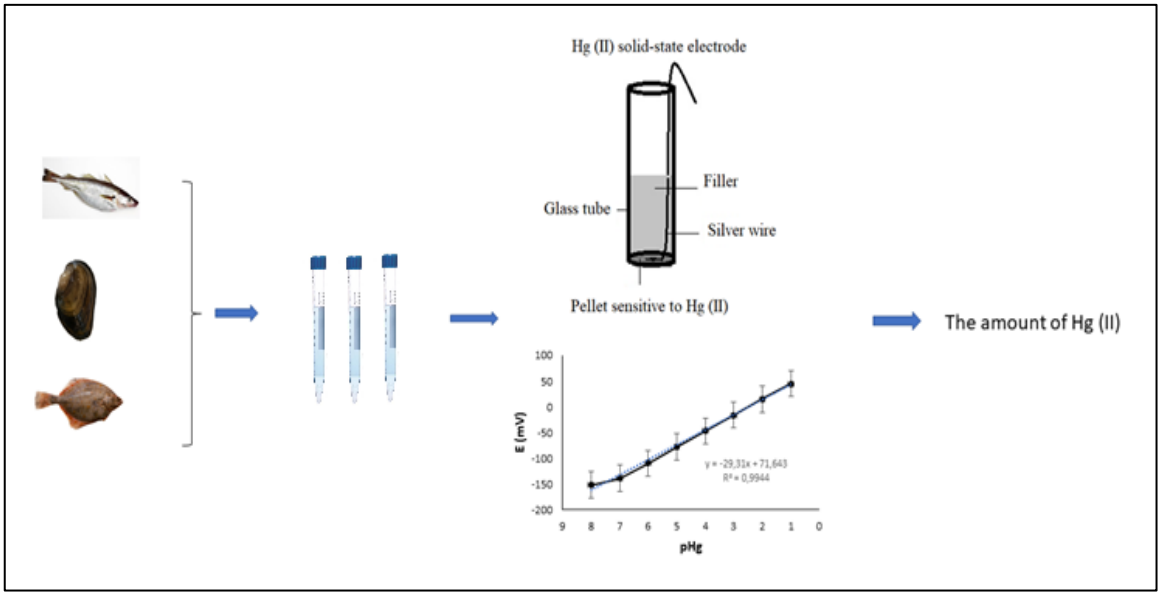
2.4. Potential Values

The cell diagram in Equation (1) was used in the working process. Potentials were carried out at 25 degrees and in 0,1 M KNO_3. Hg-SE sensitivity, it was determined that the potential change was in accordance with the Nernst equation by increasing the mercury concentration in the cell 10 times.

Ag-AgCl, KCl (sat.) | Hg solid-state membrane | sample solution | Ag-AgCl, KCl (satd.). (1)

2.5. Preparation of Seafood

Sea products to be used in the determination of mercury were brought from the Gulf of Izmit. The same procedure was used for thawing seafood. A certain amount of sample was dried in the oven for a certain time. A total of 8,0 mL of HNO_3 and $HClO_4$ mixture was added to this sample in a 4 to 1 ratio and disintegrated by heating in a long neck balloon (30 cm). After repeating this process 4 times, it was evaporated to approximately 1,0 mL. The volume of the sample was made up to 10,0 ml. The analysis procedure is given in diagram 1.



Scheme 1. *Analysis procedure*

3. RESULT AND DISCUSSION

3.1. Electrode Composition

The most of electrode performance is the electrode composition. Here, the electrode composition with high slope and selectivity was investigated. Electrodes in 6 different compositions were made as shown in Table 1 and values were recorded. When we look at the values in Table 1, the highest sensitivity for mercury ions is 10% HgS, 30% Cu_2S and 60% Ag_2S. The slope of ISE was calculated as 29,3 ± 0,2 and the sensitivity of the electrode was found to be compatible with the Nernst equation. In addition, the detection limit of ISE was obtained as 5×10^{-8} M (S/N=3) by using the calibration plot.

Table 1. *Sensitivity of electrodes with different composition ($1.0x10^{-1}$-$1.0x10^{-7}$ mol L^{-1})*

ISE	HgS, %	Cu_2S, %	Ag_2S, %	Slope, mV	R^2
1	5	30	65	19,5 ± 0,6	0,8573
2	10	30	60	29,3 ± 0,2	0,9999
3	10	40	50	23,7 ± 0,3	0,9248
4	15	30	55	25,2 ± 0,4	0,9455
5	20	30	50	26,1 ± 0,4	0,9681
6	5	20	75	14,8 ± 0,9	0,6213

3.2. Response Time

For the response time with a composition of 10% HgS, 30% Cu_2S and 60% Ag_2S, when ISE was added 10 times more than $1,0 \times 10^{-7}$ M Hg (II) concentration in the cell, the times during which the potential value was constant were recorded (Figure 1). Refrigerator responds to concentration changes in as little as 20 s.

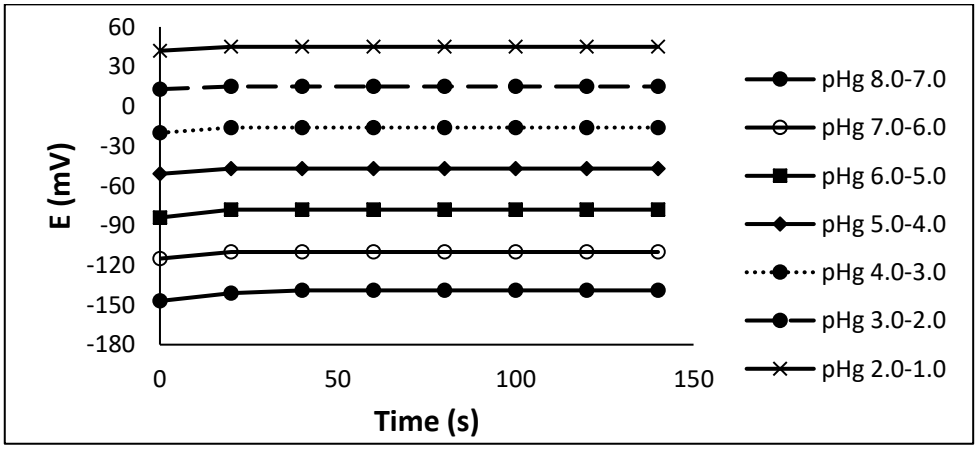


Figure 1. *Dynamic response time of ISE from 1×10^{-8} M to 1×10^{-1} M mercury concentration changes*

3.3. Effect of pH

While there was 1×10^{-3} M mercury in the cell, the pH values of the solution were changed by dropwise additions of nitric acid and ammonia. The changes in potential values were measured (Figure 2). Accordingly, it was observed that the electrode could work between pH 1,0 and 5,0. and the potential changed after pH 5,0. This is because mercury hydroxide forms after pH 5,0. This reduces the mercury ion and causes the potential to change.

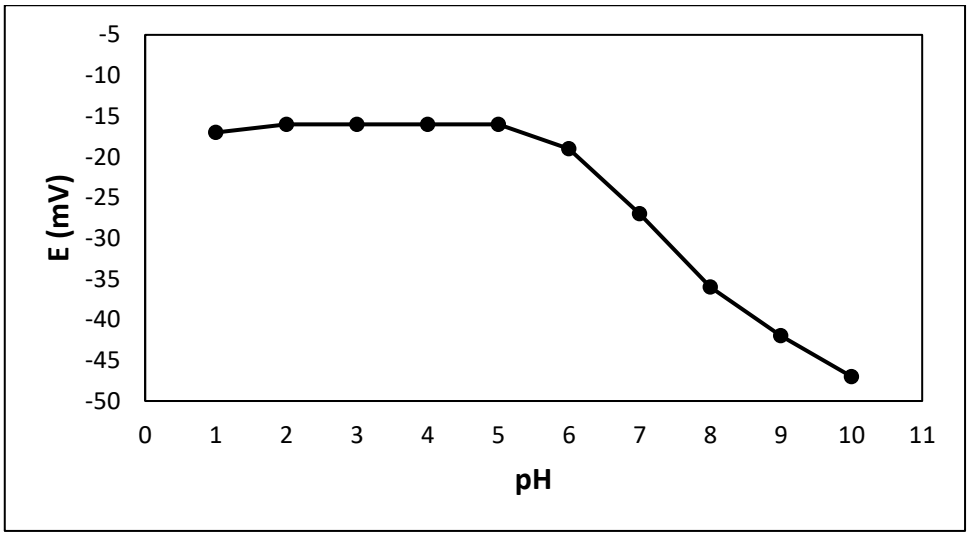


Figure 2. *Change of ISE sensitivity with pH*

3.4. Selectivity Study (K^{pot})

The K^{pot} of the proposed ISE is obtained by using (Eq. 2) [18]. The potential was measured when there was 1×10^{-3} M Hg (II) in the cell. Then, the potential values While there was a certain concentration of mercury in the cell, other ions were added and their effects on electrode sensitivity were examined (Figure 3). K^{pot} are shown in Table 2. In addition to the amount of mercury in food analysis, it does not have sufficient interference effect.

$$K^{pot} = \{a_{Hg} [\exp^{(\Delta E\ z\ Hg\ F/RT)} -1]\} / (a_M)^{zHg/zM} \quad (2)$$

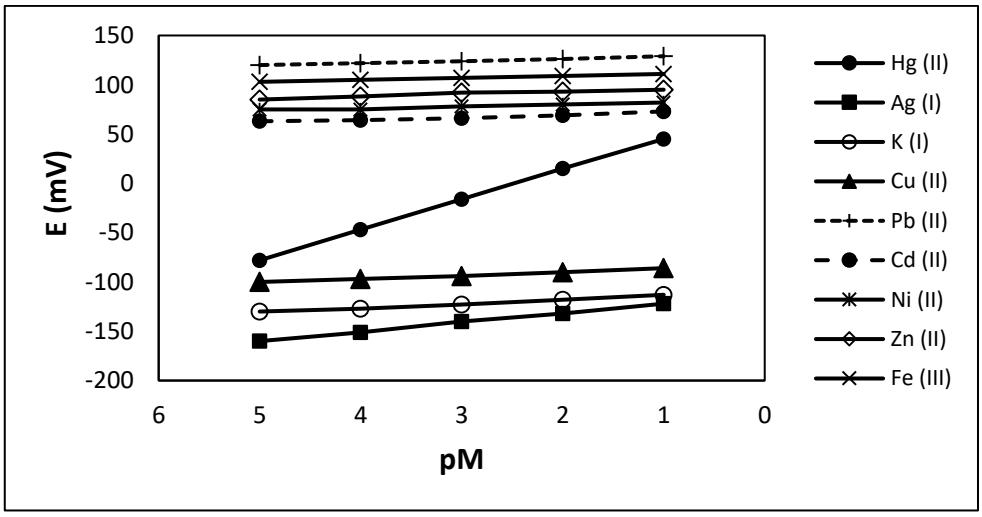


Figure 3. *Sensitivity of ISE to other ions*

Table 2. *K^{pot} of the interfering ions*

Interfering ion	K^{pot}	Interfering ion	K^{pot}
Ag^{+}	$2{,}15\times10^{-2}$	Cd^{2+}	$2{,}46\times10^{-3}$
K^{+}	$3{,}42\times10^{-3}$	Ni^{2+}	$2{,}18\times10^{-3}$
Cu^{2+}	$5{,}36\times10^{-3}$	Zn^{2+}	$3{,}11\times10^{-3}$
Pb^{2+}	$1{,}57\times10^{-3}$	Fe^{3+}	$4{,}83\times10^{-4}$

The analytical values of ISE were compared with other mercury electrodes and are given in Table 3. It appears to have superior properties to many mercury electrodes.

Table 3. *Comparison of some ISE*

Electrode	Slope, mV	LOD (M)	Lifetime (Months)	Reference
TDMAI	30	$5{,}0\times10^{-6}$	6	[8]
Thiosemicarbazone	29	$1{,}0\times10^{-6}$	2	[9]
Poly (4-vinily pyridine)	30	$5{,}0\times10^{-6}$	3	[10]
Dithiadiazacyclotetra decine	28	$8{,}0\times10^{-7}$	4	[11]
Calix [2] thieno pyrole	28	$1{,}0\times10^{-6}$	6	[12]
Poly-o-toluidine Zr (IV) tungstate	28	$1{,}0\times10^{-7}$	3	[13]
2-(N-pipyridino methyl)-1-cyano cyclohexano	29	$2{,}5\times10^{-7}$	2	[14]
HgS	29	$5{,}0\times10^{-8}$	12	This work

3.5. Analytical Application

In order to prove the usability of the prepared electrode, first, the amount of mercury at a certain concentration was measured with our electrode. The % recovery was determined and given in Table 4. According to these data, it was determined that the performance of our electrode in measurements was good.

Table 4. *Mercury ($\mu g g^{-1}$) and % recovery measured in synthetic samples with known concentration. (95% Confidence level and N=5)*

Sample	Concentration added ($\mu g g^{-1}$)	Concentration recovered ($\mu g\ g^{-1}$)	% Recovery
1	0,01	0,0098	98,0
2	0,05	0,0495	99,0
3	0,10	0,0995	99,5
4	0,15	0,1497	99,8

This method was applied to haddock, sole and mussel samples brought from Izmit Bay. The amounts of Hg (II) in the thawed seafood were measured as the 95% confidence level and the average of 5 measurements and are given in Table 5. The results were determined to be compatible with the mercury amounts previously measured in seafood [19].

Table 5. *The amount of mercury in haddock (Cod), sole (Solea volgaris) and mussel (Bivalvia) samples brought from the Gulf of Izmit. (95% Confidence level and N=5)*

Sample	$[Hg^{2+}]$: $\mu g\ g^{-1}$
Haddock	0,19 ± 0,01
Sole	0,28 ± 0,02
Mussel	0,032 ± 0,005

4. CONCLUSSION

In this study, a solid-state electrode based on HgS was prepared. ISE has a linear slope with respect to the first equation. This electrode shows a great advantage over other electrodes in the literature, with its characteristics such as being easy to prepare, responding quickly to mercury (II) ion, being insensitive to other ions, having a low detection limit, high selectivity and sensitivity [20-21]. The validation values of this electrode were good. In addition, it is seen to have a high performance in determining trace mercury amounts in seafood, food, environment and many real samples.

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CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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