

## La(III) Ion Selective Electrode with PTFE Membrane Containing Tributyl Phosphate Ionophore

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**Keywords:** Lanthanum, electrode selective ion, ionophore, tributyl phosphate (TBP)

**Abstract.** Methods for the quantitative determination of lanthanum that have been developed are generally spectroscopic methods such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and X-ray fluorescence spectrometry, which has relatively high operational costs. The feasibility of the potentiometric method using ion selective electrode (ISE) as an alternative method for lanthanum (III) determination needs to be studied because it is simple, easy to use, and has high sensitivity and selectivity. In this study, we developed ion selective electrode using PTFE membrane impregnated with tributyl phosphate (TBP) as ionophore. TBP is commonly used as a complexing agent for rare-earth ions in supported liquid membrane (SLM) separation process. We found that the compound can be used as an ionophore for ISE. This study aims to make a lanthanum ion selective electrode (III) (La-ISE) which has a Nernstian response. The parameters studied in the construction of this electrode were the effects of PTFE membrane immersion ionophore solution, ionic strength adjuster (ISA), and the inner solution composition. The performance parameters studied for the La-ISE were linear range, response time, detection limit, selectivity, and the lifetime of the electrode. Construction of the electrode begins with the preparation of the PTFE membrane as the main component. PTFE membrane was impregnated for 12 hours in the TBP solution having a concentration of 0.25 M or 0.50 M in kerosene. After it was dried, the membrane was attached to the end of the electrode tube with adhesive. Then, the electrode was filled with an internal solution containing a mixture of KCl  $10^{-3}$  M with La (III)  $10^{-3}$  M. The internal reference electrode was Ag/AgCl electrode. Before it was used, the electrode was soaked in a solution of La (III)  $10^{-3}$  M for 12 hours. The effect of TBP concentration on the electrode performance was studied using two concentrations of TBP: 0.25 M and 0.50 M. The calibration curves obtained using both electrodes have good linearity. Nernst factor obtained from both electrodes is similar, although the Nernst factor obtained with an electrode having 0.50 M TBP closer to the theoretical value. ISA used in the measurement was  $\text{KNO}_3$ . The effect of ISA on the performance of the electrode was studied using electrodes containing TBP with the concentration of 0.25 M or 0.50 M. The concentration of  $\text{KNO}_3$  used in this study was 0.01 M and 0.10 M. The Nernst factors obtained with electrodes containing 0.25 M TBP, in general, higher than those obtained with electrodes containing 0.50 M TBP in the same ISA. Electrode containing 0.50 M TBP resulted in the Nernst factor close to theoretical value when a measurement was conducted in 0.10 M  $\text{KNO}_3$ .

### Introduction

Lanthanum is one of the rare earth elements known having strong magnetic properties. Lanthanum has received much attention electrochemically due to its applications in the hydrogen storage materials of batteries, ion selective electrode, chemical sensor, electrocatalytic hydrogenation, and ion gate effect [1]. Found in nature in the form of minerals such as monazite and xenotime. Monazite and xenotime are minerals that contain lots of rare earth metal element (REE's) of the lanthanide group. These monazite also found in Indonesia, but not yet processed and utilized optimally because of the mastery of monazite ore processing technology still needs to be improved and strengthened. Lanthanides are very important metals in the high technology industry because of

their unique electronic, optical, and magnetic properties, and therefore their demand has been increasing in recent years. But the element of REE's mostly have physical and have very fundamental chemical properties are similar, which makes it difficult hard splitting into each element. It is also the cause of rare earth metals such as lanthanides become expensive [2]. Currently, many researchers who give great attention to rare earth metals are widely applied in industry. Therefore, the required development of method for the determination and recovery of rare earth metals. Determination a method has been developed which includes conventional means such as chemical precipitation, reverse osmosis, adsorption, ion exchange, and solvent extraction, but many difficulties are found in a variety of methods [3].

To monitor the treatment process, quality control, and presence of REE's in given material, required analytical methods that have high accuracy and selectivity, low detection limits, and high reproducibility. The method that considered to meet these criteria, among others, spectroscopic techniques such as inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma atomic emission spectrometry (ICPAES), and X-ray fluorescence spectrometry. Hence, the available methods for low-level determination of rare-earth ions in the solution include spectrophotometry, isotope dilutions mass spectrophotometry, neutron activation analysis, X-ray fluorescence spectrometry, etc [4]. However, many of these spectroscopic methods require a lot of time involving multiple samples and also expensive for most analytical laboratories [5].

One method that has the potential of the electrode is the potentiometric method with the membrane. The Potentiometric method provides several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, very low detection limits, wide measurement range, an acceptable selectivity, and low cost. This will make the availability of micro-electrodes and electrodes for the determination of the required REE [6]. The quick determination of minute quantities of ionic species by simple methods has great importance in analytical chemistry. Potentiometric detection based on ion selective electrodes (ISEs) is the simplest of all and offers unique advantages [7]. The Membrane electrode has many types, and in this paper was chosen regarding the type of tube and the solution in as well as sensor ionophore required. Therefore, it is feasible for the development of methods to make sensors for lanthanide ions with high selectivity using the appropriate ionophore. Electrodes for the potentiometric determination can yield several benefits such as ease and speed of preparation and procedures, simple instrumentation, relatively fast response, wide measurement range, and low cost. Potentiometric detectors based-on ion selective electrode is suited for fast, accurate, reproducible, and selective determination of various metal ions. Such potentiometric detectors offer advantages such as selectivity, sensitivity, good precision, simplicity, and so on. These methods allow direct on-line monitoring of the concentration of selected species without pretreatment [8].

Carrier-based ion selective electrodes (ISEs) are used extensively for the direct selective detection of ionic species. For this type of electrode, the formation constant of the ion-ionophore complex within the membrane phase is a very important parameter that dictates the practical selectivity of the sensor. In the area of membrane-based ISEs, the emphasis has been focused on the development of new ionophore and the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs. Fabrication of a new, ion-specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility, and low cost, is always in need [9].

In this paper the compound organophosphates especially TBP will be studied or used as ionophore in membranes in selective electrodes ion. The principle of formation of the measured potential in both surface and transport based on this principle the same as that occurs in the extraction, while the TBP solvent extraction lanthanides have been performed and shown to occur transport from the aqueous phase to organic phase by using TBP. Besides, TBP has not been used as an ionophore in potentiometric systems. Hence, to study the character of the membrane on the electrode as a potentiometric sensor, needed characterization, membrane potential, response time, sensitivity, selectivity towards the primary ion and ion bullies are less than  $10^{-3}$ , age (lifetime) is relatively long and has a design size can be miniaturized.

The main objective of this work is to introduce a selective and sensitive electrode for lanthanum, for the potentiometric monitoring of trace amount of  $\text{La}^{3+}$ , by using TBP as ionophore. Despite of ion selective electrode based on ionophore, ligand is well established for many widespread activities in the field of ion selective electrodes during the last two decades, however, there is no report previously in the literature TBP as ionophore and its applications for measurement ion  $\text{La}^{3+}$ .

## Experimental

### 1.1 Equipment

All potentiometric measurements were made at  $25 \pm 1^\circ\text{C}$  with Ohmmeter instrument pH/mV meter. The glass cell, where the  $\text{La}^{3+}$  ion-selective electrode was placed, and a double junction saturated calomel electrode (SCE) was used as an internal reference electrode.

### 1.2 Chemicals and solutions

Tributyl phosphate was obtained from Sigma Aldrich. Kerosene from sigma Aldrich, PTFE (Advantec, Japan) with pore size  $0,45 \mu\text{m}$  and  $0,2 \mu\text{m}$ . All other reagents used were of analytical grade and the solutions were prepared in doubly distilled water.

### 1.3 Membrane and Electrode Preparation

The method reported by [8,9,10] was adopted for the fabrication of membranes. Membrane prepared in the Impregnated Liquid membrane (ILM). Impregnated Liquid membranes used for prepared ESI-La, with Teflon, length 10 cm, and 1,5 diameter. PTFE (Advantec, Japan) with pore size  $0,45 \mu\text{m}$  pore and  $0,2 \mu\text{m}$  pore (impregnated in TBP), immersed for 12 and 24 hours respectively. The saturated calomel electrode and the inner solution (a mixture of  $10^{-3} \text{ M KCl}$  and  $10^{-3} \text{ M La}^{3+}$ ) was set in the tube and connected to coaxial cable. The electrode was conditioned before potentiometric measurement by immersing it into  $10^{-3} \text{ M La (III)}$  solution for 12 and 24 hours. Several membranes of different compositions were prepared and only those which gave reproducible and stable potentials were selected for further studies.

Construction of the electrode begins with the preparation of PTFE membrane as the main component. PTFE membrane was impregnated for 12 hours in TBP solution having concentration of 0.25 M or 0.50 M in kerosene. After it was dried, the membrane was attached to the end of electrode tube with adhesive. Then, the electrode was filled with internal solution containing mixture of KCl  $10^{-3} \text{ M}$  with La (III)  $10^{-3} \text{ M}$ . The internal reference electrode was Ag/AgCl electrode. Before it was used, the electrode was soaked in a solution of La (III)  $10^{-3} \text{ M}$  for 12 hours.

In this study, the electrode was made and prepared in each different condition (Membrane thickness, the concentration of ionophore TBP, the concentration of ionic strength adjuster (ISA), Impregnation time, Influence of pH, Lifetime, limit detection).

### 1.4 Potential Measurement

The potential measurements of the solutions, prepared in the concentration range  $1.0 \times 10^{-1}$  -  $1.0 \times 10^{-6} \text{ M La}^{3+}$  ions, were carried out at  $25 \pm 1^\circ\text{C}$  with a Metrohm instrument pH/Ion meter. Saturated calomel electrode was employed as reference electrodes and potential were measured by setting up the following assembly:

$\text{Ag/AgCl/KCl, La}^{3+}$  (internal)/membrane/ $\text{La}^{3+}$  (eksternal)|| $\text{KCl/Hg}_2\text{Cl}_2/\text{Hg}$

## Result and Discussion

### 2.1 Working Concentration Range and Slope

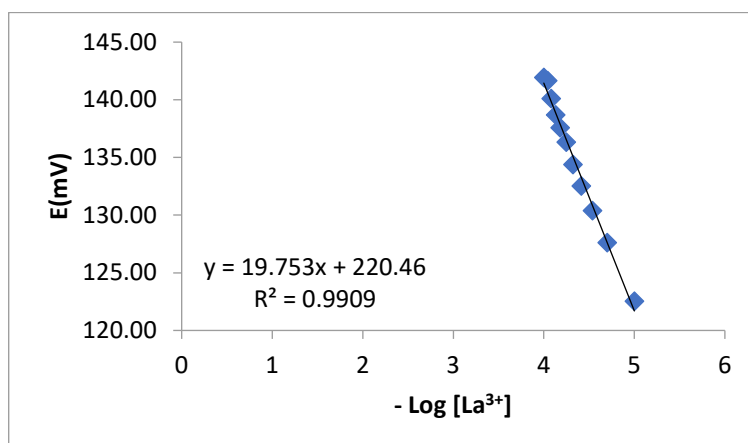


Figure 1. The Calibration curve of La (III) membrane electrode based on TBP

The equation obtained above is a linear function also seen that the value of the slope of the curve in the range of 19 mV/decade which means that even this sensitivity is Nernstian. Theoretically the value of the Nernst factor for La electrodes is 19.7 mV/decade. This fact proved that the presence of ionophores in the membrane is very helpful in the process of La ion transport from the liquid/membrane phase. Based on the above equation it can be concluded that the PTFE membrane responds to potential changes relatively quickly as evidenced by the constant sensitivity and intercept values. The intercept values and sensitivity of the four equations show a practical value that remains. Intercepts range from 220.0 mV, while sensitivity ranges from 19.0 mV/decade to 19.2 mV/decade. While from the correlation coefficient  $R = 0.9909$ . In addition, it appears that there is a correlation or relationship between the electrode potential as a function of significant La concentration.

### 2.2 The effect of TBP and ISA concentration

The ionophore concentrations in the membrane is one of the factors that influence the electrode sensitivity and selectivity [6,11]. To see the effect of PTFE membrane immersion in TBP ionophores in the kerosene solvent on the electrode potential response is done by impregnation in TBP at concentrations of 0.25 M and 0.50 M in the kerosene solvent. The linear regression equation for potential responses with a 0.50 M TBP concentration is as follows:

$$E = 253.8 \text{ mV} + 20.7 \text{ mV/decade} \log [\text{La}^{3+}] \quad R^2 = 0.9970 \quad (1)$$

The effect of TBP concentration on the electrode performance was studied using two concentrations of TBP: 0.25 M and 0.50 M. The calibration curves obtained using both electrodes has good linearity. Nernst factor obtained from both electrodes are similar, although the Nernst factor obtained with electrode having 0.50 M TBP closer to the theoretical value.

Furthermore, in this section the effect of ion strength buffer (ISA) on this study is studied response of selective membrane electrodes for La ions. The electrodes were also made using a membrane that was immersed in 0.25 M TBP ionophore solution and 0.50 M TBP in kerosene solvent. Meanwhile, as an ion strength buffer solution (ISA) used only  $\text{KNO}_3$  with concentrations varying 0.1 M and 0.01 M [10].

In general, from the study of the effect of ionophore concentration and the effect of ISA on the ESI-La electrode potential response it was concluded that the use of 0.50 M TBP in kerosene solvents produced electrode responses that approached Nernstian. In addition, these two influences practically do not provide significant changes to intercepts. It can be concluded that the electrodes made in this study have a uniform geometry based on relatively different values of sensitivity and intercept. Referring to the sensitivity and intercept electrode data, this also proved that the membrane used has a uniform structure and porosity of the membrane.

### 2.3 The Effect of pH on the Potential Response

The effect of pH on the potential response of the electrode was studied at different concentration, Standard of  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ M over the pH range 1-10. A series of solutions of  $\text{La}^{3+}$  with pH ranging from 1 to 10 were prepared by adding  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  solutions. Solution potentials were measured by the cell system. pH dependence of the membrane electrode was investigated at series of standard  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ M  $\text{La}^{3+}$  concentration in the pH range 1-10 by adjusting the pH solution with  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . It was observed that the potential remains constant in the pH range relatively 4-5 and the same was taken as the working pH range of the electrodes. These results indicating the applicability of this electrode in the specific pH range were relatively the same as those reported by other researchers, stating that pH was kept constant at 3-8 [6,7]. On the contrary, relatively noteworthy fluctuations in the potential regarding pH behaviour took place below and above the formerly stated pH limit. The fluctuation above the pH value of 6 might be justified by the formation of soluble and insoluble  $\text{La}^{3+}$  ion hydroxyl complexes in the solution. Hence, the fluctuations below the pH value of 3 were attributed to the partial protonation of the employed ionophore [11]. Considering that deprotonation of the complexes of chelating reagent is one of the key processes for the complex formation. The pH of a sample solutions seem to strongly affect the potentiometric responses. Therefore, influent of protonation and deprotonation complex formation was measured by investigated the pH dependence of the potentiometric responses to the lanthanoid ion.

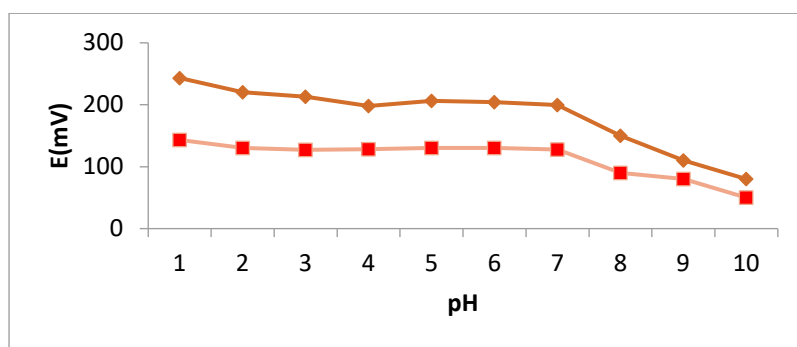


Figure 2. Effect of pH on Potential response of ISE-La (III)

Figure 2 above explained the correlation between potentiometric response and pH suggest that the potentiometric responses observed with the membrane to the metal ion are induced by the formation of complexes. A typical potential versus pH curve, increasing solution of pH, potential relatively stable and close to Nernstian slope is 19 mV per decade., was observed from  $\text{pH} \approx 7$  to 2 both  $10^{-2}$  or  $10^{-4}$  concentration. This pH response suggested that TBP impregnated membrane PTFE at the membrane interface successively protonate with increasing the  $\text{H}^+$  concentration of the solution.

### 2.4 The study of Sensor properties

The properties of an ion-selective electrode are characterized by parameters like these: measuring range and detection limit, response time, selectivity, life time.

#### 2.4.1 Detection limit and Measuring range

Range measurements, the linear range of the electrode is defined as part of the calibration curve by linear regression which indicates that the data points do not deviate from linearity by more than 2 mV. Range measurements on an ion selective electrode (ISE) including the linear part of the calibration curve. Detection limits and measurement ranges are determined from the graph of the relationship between potential and  $\text{La}^{3+}$  ion concentration. The potentiometric sensor is indicated by the magnitude/value of the membrane potential measured in the analyte. The smaller the concentration of the analyte that can be detected by following Nernst's law, the lower the electrode detection limit [9]. Therefore, the magnitude of detection can be determined through sloping straight line intersections that are still Nernstian and horizontally which are no longer Nernstian [3,5,9,13] as shown in Figure 3 below:

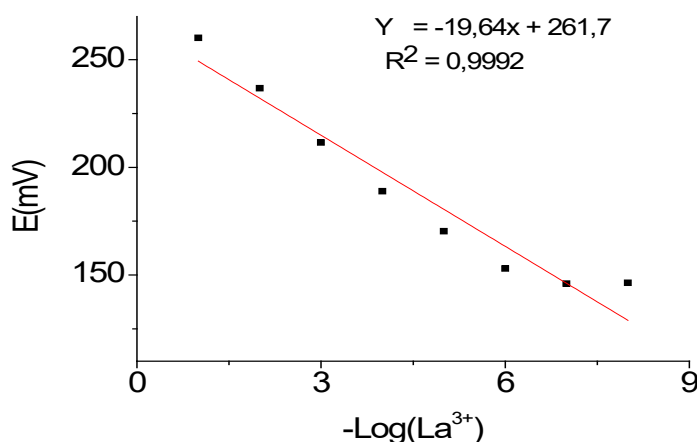


Figure 3. Graph for ESI-La detection limit

Limits of detection are determined from the graph of the relationship between the potential and the concentration of ions La. Based on the graph, it can be determined the limit of detection by the oblique intersection of straight lines and flat. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was  $3.98 \times 10^{-7}$  M.

#### 2.4.2 Response time

In this study, the practical response time was recorded by changing solution with different La(III) concentration from  $9.9 \times 10^{-6}$  -  $2.06 \times 10^{-4}$  M. The response time of an electrode is evaluated by measuring the average time required to achieve a potential within  $\pm 0.1$  mV of the final steady-state potential. The response time of the microelectrode was found to be about 27,7 seconds in the whole concentrations.

The ability of electrodes to respond to analytes is determined by the presence of ionophores or active ingredients present in the PTFE membrane. The more sensitive the active ingredient or ionophore to the analyte, the electrode will respond faster. The faster the electrode gives a constant potential response, the better the electrode. To study the ability of ESI-La to respond to  $\text{La}^{3+}$  ions, the response time of 4 ESI-La electrodes is measured at various concentrations. Furthermore, response time data can be seen in the following table:

Table 1.

La(III) [M]	Response time of electrode (seconds)				Average (seconds)
	1	2	3	4	
$10^{-5}$	24	29	28	20	25,3
$10^{-4}$	29	29	28	28	28,5
$10^{-3}$	28	28	29	28	28,3
$10^{-2}$	27	27	28	30	28,0
$10^{-1}$	29	30	27	27	28,3
Average (seconds)	26,8	28,6	28	26,6	27,7

The table above is based on the measurement of the potential of each electrode used to measure the potential of a  $\text{La}^{3+}$  solution at various concentrations. Potential was observed since the electrode was dipped in a solution for up to 300 seconds. The average electrode response time at various concentrations was 27.7 seconds.

#### 2.4.3 Selectivity of electrodes

Selectivity is an important factor for ESI-La electrodes. According to [5,6,13], the selectivity of ion selective electrodes is related to the complex stability between ions and ionophores. Therefore, ESI-La is expected to only respond to  $\text{La}^{3+}$  ions in solution and not respond to other ions. To see the

effect of other ions on ESI-La, the electrode potential is measured in the presence of other ions. The presence of other ions studied were alkaline earth ions ( $\text{Ca}^{2+}$ ), ion group transition elements ( $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ), lanthanide group ions ( $\text{Ce}^{3+}$  and  $\text{Nd}^{3+}$ ).

Table 2. The electrode selectivity constant for several other ions

$\text{M}^{n+}$	$K_{A,B}^{pot}$	Log $K$
$\text{Ca}^{2+}$	$1,17 \times 10^{-2}$	-2,6
$\text{Pb}^{2+}$	$4,57 \times 10^{-3}$	-1,93
$\text{Fe}^{3+}$	$1,65 \times 10^{-2}$	-2,34
$\text{Nd}^{3+}$	$1,2 \times 10^{-1}$	-1,78
$\text{Ce}^{3+}$	$4,3 \times 10^{-1}$	-0,92
$\text{La}^{3+}$	1	0

Based on the selectivity constant in the table above it appears that the presence of  $\text{Pb}^{2+}$  ions is relatively unobtrusive because the  $K_{A,B}^{pot}$  value is very small (reaching hundreds of times less than the response to  $\text{La}^{3+}$  ions). Hence, the presence of  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  ions gives relatively little interference so it is not significantly disturbing. Meanwhile, the ions in one group compared in this study were only  $\text{Ce}^{3+}$  ions and  $\text{Nd}^{3+}$  ions did not significantly interfere with the measurement of  $\text{La}^{3+}$  ions, although the selectivity of  $\text{Ce}^{3+}$  and  $\text{Nd}^{3+}$  ions was only around the unit times smaller than  $\text{La}^{3+}$  ions.

#### 2.4.4 Lifetime of electrodes

The lifetime of the electrodes is tested by measuring the potential of several standard solutions, to obtain the slope of a curve that follows Nernst's law. The slope of the curve that no longer follows Nernst's law shows that the electrode has changed its ability to respond to the analyte. Therefore, to see the ability of the electrodes, the use of electrodes at various ages is 1, 3, 5, 7, 14 to 105 days (15 weeks). In each measurement, the slope of the curve is calculated as stated in the relationship graph between the magnitude of the slope of the electrode curve as a function of time.

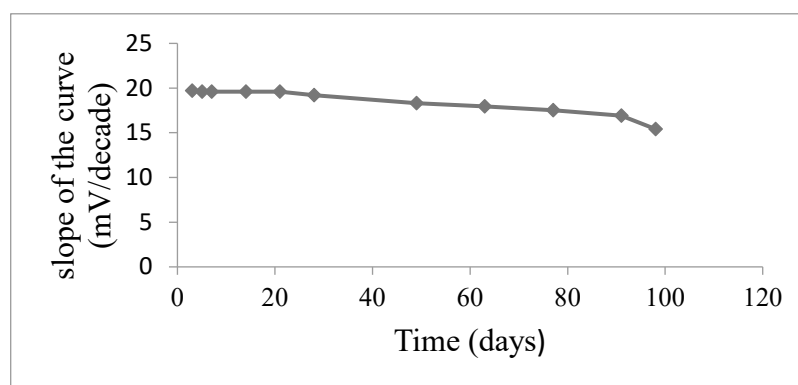


Figure 4. Changes to the slope of the age range 1 to 105 days

The figure above shows a relatively constant curve slope (about 19 mV/decade) until the measurement time for 60 days, after which the slope of the curve begins to decline and at the age of 3 months electrodes, the slope of the curve is relatively small (14 mV /decade). Furthermore, with the slope of this smaller curve, the electrodes have decreased capability, which means their sensitivity decreases.

#### Summary

In summary, potentiometric selectivity of polyimide-membrane electrodes based on lanthanum is one of methods used as quantitative analysis of rare earth elements which are considered as the standard method that has high accuracy, fast response time, and low detection limits. Hence, the electrode was prepared by PTFE impregnated membrane in TBP. The Selectivity of ISE-La showed

that electrode didn't respond to alkaline elements and transition elements but still respond to lanthanide elements such as  $Ce^{3+}$  and  $Nd^{3+}$ .

### Acknowledgments

The authors gratefully acknowledge research support from to Ministry of education and culture of Indonesia and I'MHERE Program, Faculty mathematic and natural sciences, Institute Technology of Bandung (ITB), and Faculty of Science, UIN Sultan Maulana Hasanuddin Banten.

### References

- [1] Shou-Qing Liu and Hong yuan Chen. Spectroscopic and voltammetric studies on a lanthanum hexacyanoferrate modified electrode. *Journal of Electroanalytical chemistry*, 528 (2002) 90-195.
- [2] Attas, A. Novel PVC membrane selective electrode for the determination of chlozapine in pharmaceutical preparation. *Int. J. Electrochem. Sci*, (2009) 9-19.
- [3] Morais, CA and Ciminelli, V.S.T. Process development for the recovery of High-grade lanthanum by solvent extraction. *Hydrometallurgy*, 73, (2004) 237- 244.
- [4] Shimojo, K, Naganawa, H, Noro, J and Kubota, F. Extraction Behavior and separation of lanthanides with a diglycol amic Acid Derivative and a Nitrogen-donor Ligand. *Analytical Sciences*, 23 (2007) 1427-1430.
- [5] Darviche, *et.al.* Lanthanide recognition: A  $Ho^{3+}$  Potentiometric membrane sensor. *Int. J. Electrochem.Sci.* 3 (2008)1288-1298.
- [6] Aghaie, *et.al.* Tin (II)-Selective membrane potentiometric sensor using a crown ether as neutral carrier. *Sensors and actuators B.* 107 (2004) 756-761.
- [7] Mittal, S.K., Kumar S.K., and Sharma,H.K PVC-Based dicyclohexano-18-crown-6 sensor for La (III) ions. *Talanta* 62 (2004) 801-805.
- [8] Attas, A. Novel PVC membrane selective Electrode for the Determination of Clozapine in Pharmaceutical Preparations. *Int. J.Electrochem. Sci.* 4 (2009) 9-19.
- [9] Mahajan, R.K, Inderpreet Kaur and Manoj Kumar. Silver ion-selective electrodes employing Schiff base p-tert-butyl calyx[4] arene derivatives as neutral carriers. *Sensor and Actuators B.* 91 (2003) 26-31.
- [10] Ganjali M.R., *et al.* Ppt levels detection of samarium (III) with a coated graphite sensor based on an antibiotic, *Analytical Sciences*, 20 (2007) 1007-1011.
- [11] Ganjali, Emami, and Rezapour. Novel gadolinium poly(vinyl chloride) membrane sensor based on a new S-N Sciff's base. *Analytica chimica acta*, 495 (2003) 51-59.
- [12] Ajay K. Jain, Vinod K. Gupta, Lok P. Singh, Upendra Khurana. Novel PVC-based membrane sensors selective for vanadyl ions. *Talanta* 46 (1998) 1453–1460.
- [13] Ito, K, Goto, C and Noguchi, K. Lanthanoid ion selective solvent polymeric membrane electrode based on 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone. *Analytica Chimica Acta.* 443 (2001) 41-51.