Potentiometric Measurement Of Polymer-Membrane Electrodes Based On Lanthanum

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Abstract. Quantitative analysis of rare earth elements which are considered as the standard method that has a high accuracy, and detection limits achieved by the order of ppm is inductively coupled plasma atomic emission spectroscopy (ICPAES). But these tools are expensive and valuable analysis of the high cost of implementation. In this study be made and characterized selective electrode for the determination of rare earth ions is potentiometric. Membrane manufacturing techniques studied is based on immersion (liquid impregnated membrane) in PTFE 0.5 pore size. As ionophores to be used tri butyl phosphate (TBP) and bis(2-etylhexyl) hydrogen phosphate. There is no report previously that TBP used as ionophore in polymeric membrane based lanthanum. Some parameters that affect the performance of membrane electrode such as membrane composition, membrane thickness, and types of membrane materials studied in this research. Manufacturing of Ion Selective Electrodes (ISE) Lanthanum (La) by means of impregnation La membrane in TBP in kerosene solution has been done and showed performance for ISE-La. FTIR spectrum results for PTFE 0.5 pore size which impregnated in TBP and PTFE blank showed difference of spectra in the top 1257 cm^{-1}, 1031 cm^{-1} and 794.7 cm^{-1} for P=O stretching and stretching POC from group -OP =O. The result showed shift wave number for P =O stretching of the cluster (-OP=O) in PTFE-TBP mixture that is at the peak of 1230 cm^{-1} indicated that no interaction bond between hydroxyl group of molecules with molecular clusters fosforil of TBP or R_3P = O. The membrane had stable responses in pH range between 1 and 9. Good responses were obtained using 10^{-3} M La(III) internal solution, which produced relatively high potential. ISE-La showed relatively good performances. The electrode had a response time of 29±4.5 second and could be use for 50 days. The linear range was between 10^{-5} and 10^{-1} M.

Keywords: Lanthanide, Potentiometry, ESI-La, TBP, D2EHPA
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INTRODUCTION

Lanthanum is one of rare earth elements is known as an important element of their nature, especially having a strong magnetic properties. It's elements found in nature in the form of minerals such as monazite. Monazite is one mineral that contains lots of rare earth metal element (REE') of the lanthanide group. This mineral 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. REE' these elements, are now widely used for the manufacture of goods innovative high-tech, such as permanent magnets, catalysts, fiber optics, optoelectronics, ceramics pizoelectric, rechargeable batteries, microwave equipment, etc., so that now the element REE has regarded as one of the 21st century [1,2]. But the element of REE' mostly have physical and chemical properties are similar, making it hard splitting into each element. It is also the cause of rare earth metals such as lanthanides become expensive [3].

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. 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 [4]. For the purposes of monitoring the treatment process, quality control, and REE' presence in a given material, required analytical methods that have high accuracy and selectivity, low detection limits, and high reproducibility. The method is 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 solution include spectrophotometry, isotope dilutions mass spectrophotometry, neutron activation analysis, X-ray fluorescence spectrometry, etc [5]. However, many of these spectroscopic methods requires a lot of time involving multiple samples and also expensive for most analytical laboratories [6]. Meanwhile, if using chromatographic methods require a long sample preparation. Therefore, alternative methods are needed that meet the analytical criteria, simple in execution and relatively inexpensive. One method that has the potential of the electrode is the potentiometric method with membranous. 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 [7]. Membranous electrode has many types, and in this paper was chosen with reference to the type of tube and the solution in as well as sensor ionophores required. Therefore, it is feasible the development of methods to make sensors for lanthanide ions with high selectivity using the appropriate ionophores. Inspite of widespread activity in the field of ion selective electrodes during the last two decades, the efforts to make suitable based on potentiometric for rare earth elements no report previously. 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. Therefore, the use of microelectrode and an electrode in the potentiometric analysis REE' is growing. Meanwhile, the transport mechanism in the impregnated liquid membrane (ILM) and the bulk membrane (BM) is based on the price coefficient of distribution of the species are transported in membrane and solution interfaces (external and internal). With reference to the extraction solvent has managed quite well for the extraction of REE' with supported liquid membrane (SLM) using organophosphate compounds such as TBP, TOPO, and EHEHP D_2EHPA. Hence, in this paper the compound will be studied or used as ionophores 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 and D_2EHPA lanthanides have been performed and shown to occur transport from the aqueous phase to organic phase by using TBP and D_2EHPA. In addition, both compounds have not been used as ionophores in potentiometric systems.

Method for making membranes as sensors developed at this time both have advantages and disadvantages. The advantages in terms of preparation ILM is easier, faster transport, and from the aspect of mobility at the ILM ionophores higher while the lack of ILM is the leakage rate during the experiments ionophores higher. Meanwhile, the excess solvent and BM is the arrangement of ionophores fused with the membrane material, so that the evaporation time strongly retained ions in the membrane structure, but the mobility of ionophores on the BM is slower because more meetings/densed and shorter trajectory measurements. 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 La^{3+}, Gd^{3+}, and Yb^{3+} by using D_2EHPA and TBP as ionophore and its applications for measurement of monazite and bentonite ore from Bangka Belitung island and compare with standard method of ICP-AES.

MATERIAL AND METHOD

MATERIAL

Di-(2-etylhexyl) phosphoric acid and try butyl phosphate were obtained from Sigma Aldrich. High molecular weight poly(vinyl chloride), potassium tetrakis (4-chlorophenyl) borate (KTCPB), o-nitro phenyl octyl ether (NPOE), PTFE (Advantec, Japan) with pore size 0,45 µm pore and 0,2 µm pore. All other reagents used were of analytical grade and the solutions were prepared in doubly distilled water.

Potential Measurement

The potential measurements of the solutions, prepared in the concentration range 1.0×10^{-1} - 1.0×10^{-6} M La^{3+} ions, were carried out at 25±1 °C with a Keithly 6 ½ instrument pH/Ion meter. Leak less Ag/AgCl electrode (EDAQ) were employed as reference electrodes and potential were measured by setting up the following assembly:

Internal Reference electrode| internal | solutions Membrane | Test Solutions | External reference electrode

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Membrane and Electrode Preparation

The method reported by [8,9,10] was adopted for the fabrication of membranes. Membrane prepared in two method, Impregnated Liquid membrane (ILM) and bulk membrane (BM). Impregnated Liquid membranes used for prepared ESI-La, with Teflon, length 10 cm, 1,5 diameter. PTFE (Advantec, Japan) with pore size 0,45 µm pore and 0,2 µm pore (impregnated in TBP and D_2EHPA), for 12 and 24 hours respectively. Bulk membranes was prepared by dissolving varying amounts (10 -100 mg), PVC, NPOE and KTCPB in THF. The solution was evaporated on a plane glass with an area of 1.5 x 4 cm^2. The electrode was prepared by gluing the electrode tube to the membrane. The inner reference electrode Ag/AgCl and the inner solution (a mixture of 10^{-3} M KCl and 10^{-3} 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} M LaO_3 solution for 24 hours. The homogeneous mixture was poured into glass rings placed on smooth glass plates and the solvent was allowed to evaporate overnight, yielding a membrane of about 0.5 mm thickness and 10 mm diameter. A number of membranes of different compositions were prepared and only those which gave reproducible and stable potentials were selected for further studies.

RESULT AND DISCUSSION

Working Concentration Range and Slope

In this study, there are three electrode was made and prepared. The potential response of all the three electrode using PTFE membrane 0,45 µm pore size with TBP in kerosene was investigated by varying the concentration of the test solution from 1.0×10^{-1} - 1.0×10^{-6} [10].

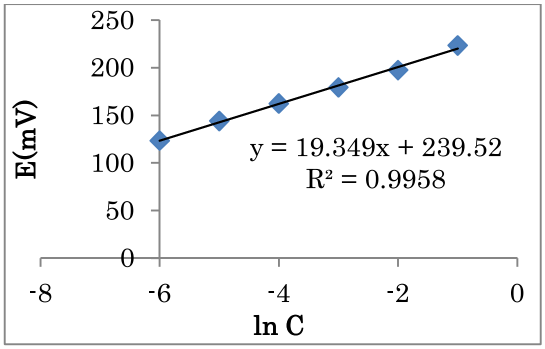

FIGURE 1. Curve calibration for Electrode 3

The result showed that electrodes 1 and electrodes 2 exhibit linear potential in the concentration range 2.5×10^{-1}-1.0×10^{-6} and 2×10^{-1}-1.0×10^{-6}. Hence, based on curve calibration (electrode 1 and 2, not shown) Nernstian slope for electrode 1 and 2 were 15.44 and 18.66 mV per decade activity, respectively. Meanwhile, to obtain better electrode properties, the effect of TBP concentration was studied. The electrodes 3 is impregnated in TBP 0.5 M exhibit more linear potential response in the concentration range 1.5×10^{-1}- 1.0×10^{-6} with a ideal-Nernstian slope of 19.34 mV per decade activity. These electrode showed better Nernstian slope than electrode 1 and 2. The bonds between lanthanum ion and TBP in PTFE membrane was strong enough to make complexes. The interpretation is connected with chemisorptions of the primary ion from solution onto the surface of the electrode [9].

The Effect of pH on the Potential Response

The effect of pH on the potential response of the electrode was studied at different concentration, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} M over the pH range 1-10. A series of solutions of La^{3+} with pH ranging from 1 to 10 were prepared by adding H_2SO_4 and NaOH solutions. Solution potentials were measured by the cell system. pH dependence of the membrane electrode was investigated at 1.0×10^{-3} M La^{3+} concentration in the pH range 1-10 by adjusting the pH solution with H_2SO_4 and NaOH. It was observed that the potential remains constant in the pH range relatively 4-9 and the same was taken as the working pH range of the electrodes. These results were relatively the same as those reported by other researchers, stating that pH was kept constant at 3-8 [6,7].

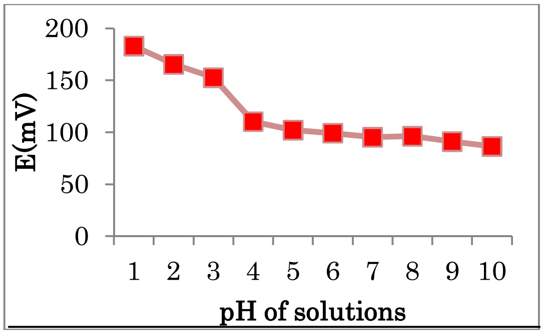

FIGURE 2. Effect of pH on Potential response

Response Time and Performance of Electrodes

TABLE 1. Performance of TBP-PTFE membrane sensor

Electrode Number	Slope mV/decade	Working concentration	R^2
Electrode 1	15.44	2.5×10^{-1}-1.0×10^{-6}	0.9960
Electrode 2	18.66	2×10^{-1}-1.0×10^{-6}	0.9990
Electrode 3	19.34	1.5×10^{-1}- 1.0×10^{-6}	0.9950

From the table 1 its seen the potential response of all the three electrodes using membranes of PTFE and TBP of different composition was investigated by varying the concentration of the test solution from 105×10^{-1}- 1.0×10^{-6}. The results obtained are given in Table 2 for the response time each electrode. It is seen that the electrodes nos. 1 and 2 having membranes of exhibits linear potential response in the concentration. Range but slope are closely to Nernstian-law. The table 2 shown response time of electrode 1, 2, and 3 respectively. It is seen that electrode 3 has the faster response comparing with electrode 1 and 2.

TABLE 2. Response time of electrodes

Electrode Number	Composition	Response time
Electrode 1	PTFE-TBP	30
Electrode 2	PTFE-TBP	31
Electrode 3	PTFE-TBP	29.45

The selectivity of the electrodes in the present of various cations was evaluated by the match fixed method at 1.0×10^{-2} M concentration of interfering ions. A perusal of selectivity coefficient data (not presented) indicates that the electrodes are sufficiently selective over a large number of cation electrode 3. This behavior may be due the selective uptake of Lanthanum by TBP and D2EHPA in comparison to other species. It is worth mentioning that the observed selectivity coefficient values for Gd^{3+} are due to characteristics of the membrane in the electrode caused by the difference in response properties of TBP and D_2EHPA. Hence, the electrode 3 is better than other electrodes and can be used for the sensor in the presence of equal concentration of La^{3+} ion.

IR Spectra

The spectrum results for PTFE 0.2 pore size which impregnated in TBP and PTFE blank showed difference of spectra in the top 1257 cm^{-1}, 1031 cm^{-1} and 794.7 cm^{-1} for P=O stretching and stretching POC from group -OP=O. The result showed shift wave number for P=O stretching of the cluster (-OP=O) in PTFE-TBP mixture that is at the peak of 1230 cm^{-1} indicates that no interaction bond between hydroxyl group of molecules with molecular clusters fosforil of TBP or $R_3P = O$.

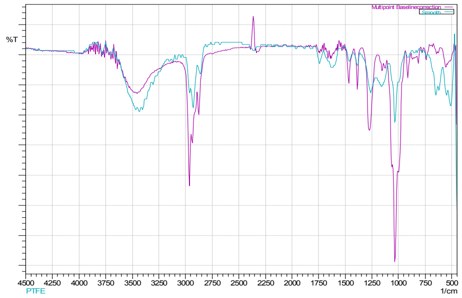

FIGURE 3. Spectrum FTIR for ESI-La impregnated membrane TBP

CONCLUSIONS

In summary, potentiometric selectivity of polymer-membrane electrodes based on lanthanum is one of method used as quantitative analysis of rare earth elements which are considered as the standard method that has a high accuracy, fast response time, and low detection limits. Hence, electrode was prepared by PTFE impregnated membrane in TBP and D_2EHPA. The results showed that among electrode 1, 2 and 3, the electrode 3 was having the best performance with regard to the working electrodes and shown ideal Nernstian slope 19.34 m V per decade activity.

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REFERENCES

1. Attas, A. Novel PVC membrane selective electrode for the determination of chlozapine in pharmaceutical preparation. *Int. J. Electrochem. Sci*.9-19. (2009).
2. Morais, CA and Ciminelli, V.S.T. Process development for the recovery of High-grade lanthanum by solvent extraction. *Hydrometallurgy,* **73**, 237- 244.(2004).
3. 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** 1427-1430. (2007).
4. Darviche, *et.al*. Lanthanide recognition: A Ho^{3+} Potentiometric membrane sensor. *Int. J. Electrochem*.Sci. **3** 1288-1298 (2008).
5. Mittal, S.K., Kumar S.K.,and Sharma,H.K PVC-Based dicyclohexano-18-crown-6 sensor for La(III) ions. Talanta **62** 801-805. (2004).

6. Faridbod, *et.al*. The fabrication of potentiometric membrane sensors and their application. *African Journal of Biotechnology.* **25** 2967-2987. (2008).
7. Ganjali M.R., *et al*. Ppt levels detection of samarium (III) with a coated graphite sensor based on an antibiotic, *Analytical Sciences*, **20** 1007-1011. (2007).
8. Suyanta, *et. al*. Lanthanum (III) selective Electrode Based on 1,10-Diaza-4,7 13, 16 tetraoxacycyclooctadecane-N,N'-Diacetic Acid (DACDA) as an ionophore. Ph.D thesis. 2006.
9. 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.
10. 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 Chemica Acta*. **443** 41-51 (2001).