Preparation and Characterization Lanthanum(III)-MBTH Carbon Paste Working Electrode by Differential Stripping Voltammetry

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Abstract:

Ultra trace determination of lanthanum(III) has been studied by preparation and characterization MHBT carbon paste working electrode by differential stripping voltammetry. The electrode was prepared by the mixture of 3-methyl-2-hydrazinobenzothiazole (MHBT), carbon powder and paraffin block. The mixture are melted and posted in a teflon tube that has 0.4 cm of diameter and 5 cm in long. The electrode is connected with copper wire and the surface is polished with paper polish. The surface of electrode are identified by Phenomworld SEM-based imaging and analysis. The voltammetry method consists of two steps. The first step is the formation and adsorptive accumulation of metal ion with chelating agent at the electrode surface. The second step is stripping the complex from the electrode surface into the solution. The stripping step generates current which is recorded as voltammogram. Characterization of working electrode is by differential stripping voltammetry technics. The characterization is done with the EDAQ-Voltammeter. The good condition for lanthanum analysis by differential stripping voltammetry was at 0,43 volt potential deposition (scan potential -1000 mV to 1000 mV), 50 nA of current, and scan rate: 50 mV/s. The electrode can response lanthanum ion that has concentration between 10^{-7} to 10^{-10} M. The linierity of this method is very good with correlation coefficient attaining 0.98. The limit detection obtained was 5.0×10^{-10} M.

Key words: lanthanum(III), MBTH, differential adsorptive stripping voltammetry, carbon paste electrode.

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1. Introduction

Rare earth elements are known as important inorganic compounds, because of their properties, especially their strong magnetic property. One of the important elements is lanthanum[1]. To analyze the lanthanum required analysis methods that have low limit of detection, high sensitivity and selectivity. Generally, determination of lanthanum using techniques of atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrophotometer (ICP-MS) and inductively coupled plasma-atomic emission spectrophotometer (ICP-AES)[2]. AAS techniques lack the ability to have a very high limit of detection so can not be used on samples of very small concentration. While ICP-MS and ICP-AES required a huge investment and high operational costs.

Ion selective electrode (ISE) in potentiometry is one method of analysis that is simpler and inexpensive but can used as a good method. Ion selective electrodes with neutral carriers were developed for some elements especially for alkali, earth alkali and transition elements. They are successful methods for analysis. For rare earth elements, a very little work on the system have been done by some researcher. Only a few reports are found in the literature on the preparation of ore rare earth ion selective electrodes [3]. My team was try to prepare an ion selective electrode for rare earth elements, especially for lanthanum. But the result is low sensitivity (in order of ppm).

Development of electroanalysis for the determination of the metal with low concentration was obtained by adsorptive stripping voltammetry method (AdSV)[3]. This method has also been conducted to determine the lanthanum. AdSV method can detect the metal in the level picomolar (pM), so it is very useful for the determination of metal with a very low concentration in the sample environment, industry, and analysis of clinical samples. Lanthanum has a very low reduction potential (-2.52V) so it is difficult to be reduced. Therefore, lanthanum can not be determined using voltammetry directly. In this research, determination of lanthanum with adsorptive stripping voltammetry using ligand as complexing agent. Choudury [4]and Ganjali [5] was learn about complexation MBTH compound with lanthanum and the apply to potentiometry analysis.

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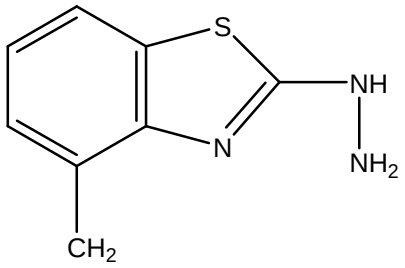
The 4-metil-hidrazino benzotiasol (MHBT) compound as a organic ligand that have S and N atom donor. This compound have molecular structure below [6-7].



Pigure 1: MHBT molecular stucture

MHBT dapat membentuk kompleks dengan ion lantanum dan beberapa ion logam lain. Besarnya yang nilainya dapat dilihat pada tabel 3.

Table 3: Complexes constant value of some metals ion with MHBT in acetonitryle solvent

No	Ion	Log K_f	No	Ion	Log K_f
1	La^{3+}	5,85 ± 0,20	7	Yb^{3+}	2,73 ± 0,05
2	Ce^{3+}	2,95 ± 0,12	8	Cu^{2+}	2,61 ± 0,04
3	Sm^{3+}	2,59 ± 0,07	9	Co^{2+}	2,43 ± 0,05
4	Eu^{3+}	2,57 ± 0,03	10	Mg^{2+}	2,50 ± 0,06
5	Gd^{3+}	2,93 ± 0,06	11	Be^{2+}	2,50 ± 0,08
6	Dy^{3+}	2,81 ± 0,04			

The value of K_f from complexes lanthanum-MHBT is 5,85±0,20. The value is big relatively than other ions. The value indicate that MHBT compound can make stable complexes molecule with lanthanum. So the phenomena can be use as basic of sensors models in electrochemistry of voltammetry. Beside the MHBT, there are another compound as derivate of MHBT that we call MBTH (methyl benzothyazole hydrochloride).

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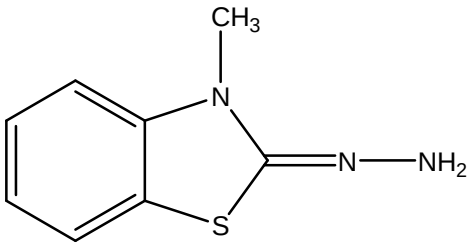


Pigure 2: MBTH molecular stucture

The structure of MHBT and MBTH is relative same, so the function as ligand will be same. For the reason, we will use the MBTH as active membrane in carbon active membrane for absorptive voltammetry. Coudury [7] and Muji Harsini, et all [8] was prepare carbon coated electrode with alizarin as active membrane can be sensor for lanthanum in picomolar (pM) order. Election of carbon paste electrode as working electrode because it is easily to be prepared, can adsorb organic compound, inert and therefore not easily to be oxidized and reduced. Thus, this method is expected to increase the sensitivity of analysis. Parameters which were learned include the accumulation potential, the accumulation time, solution pH, precision, limit of detection, linearity, sensitivity, and recovery.

2. Materials and Method

2.1 Chemicals and Materials

The chemicals used in this research were graphite powder, solid paraffin, lanthanum chloride heptahydrate ($LaCl_3.7H_2O$), 4-metil-hidrazino benzotiasol (MHBT), potassium chloride, nitric acid, and potassium nitrate. While the water used in this research is ultra high pure water.

2.2 Equipments

The instrument used in the research were voltammeter EDAQ Potenstiostat equipped three electrode, the carbon paste working electrode, a reference electrode of Ag/AgCl, and platinum as auxiliary electrode, the sample container/ electrochemical cells, magnetic mixer, and equipment used in the analytical chemistry laboratory. Surface electrode test is used PHENOM-Dekstop Scanning Electron Microscope (SEM).

2.3 Procedure

Preparation of Carbon Paste Electrode

The mixture of MBTH, graphite powder and solid paraffin (2 : 4 : 4 by weight) was prepared in a watch glass with heating using hotplate and mixing until a homogeneous paste was obtained. In warm condition, the mixture included in the teflon tube (ϕ 4 mm) with pressing. The electrode is connected with copper wire and the surface is polished with paper polish.

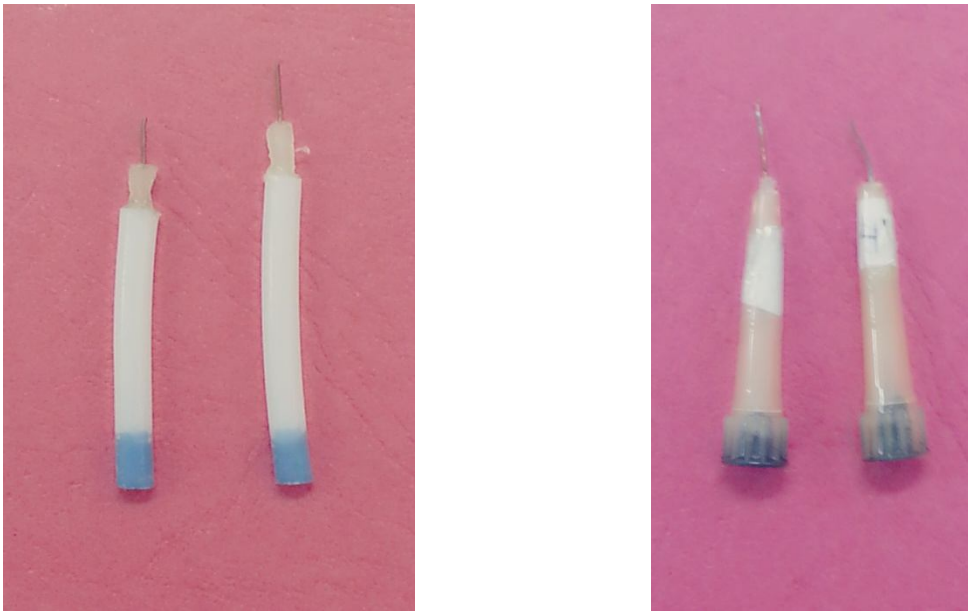
Characterization of Carbon Paste Electrode

Characterization of lanthanum carbon paste electrode are done by two step. Ste p I is characterization surface electrode by SEM test. The test is done by PHENOM-Dekstop Scanning Electron Microscope (SEM). Step II is characterization by EDAQ-VOLTAMMETRY. The technique type for characterization is by differential adsorption voltammetry. The characterization is used as base of analysis of lanthanum (III) with voltammetry system.

3. Results and Discussion

3.1 Preparation of Lanthanum Carbon Paste Electrode

We have two kind of electrode that are teflon tube and micro pipet tube. The shape of the electrode are in figure 3. The electrode is used as working electrode in voltammetry.



(a) (b)

Fig. 3 Show the shape of electrode.

3.2. Characterization by PNENOM-SEM

The characterization is used to look the surface of the electrode. With the Photo-SEM the surface can look in the figure 4. From the figure, the instrument can indicate 3 part lanthanum, as in number 1, 2 and 3 in + code.

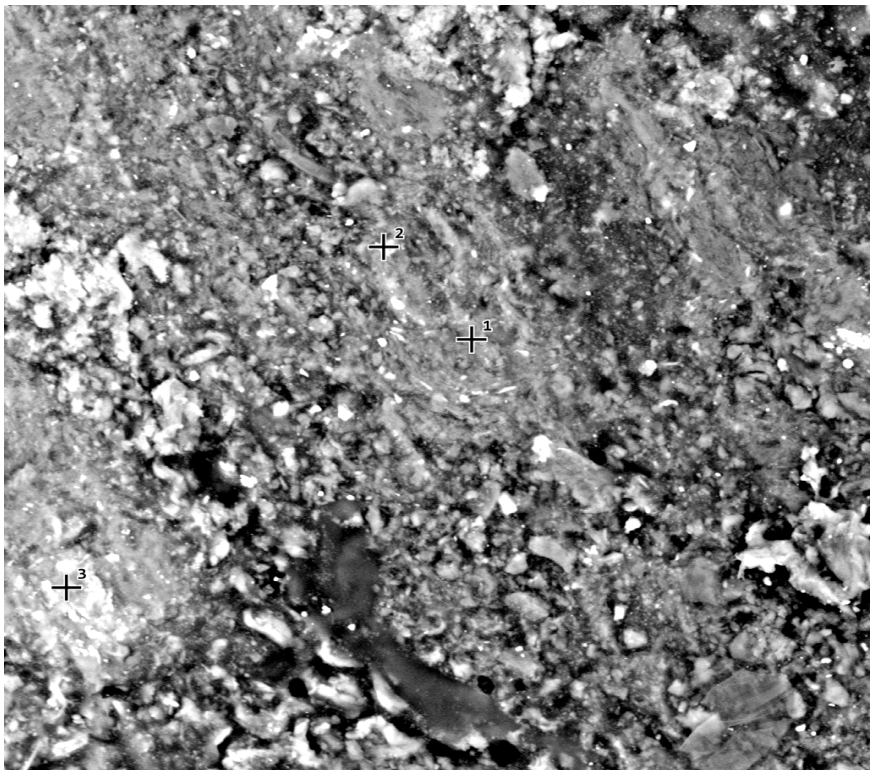


Figure 4 : Shape of surface electrode in SEM

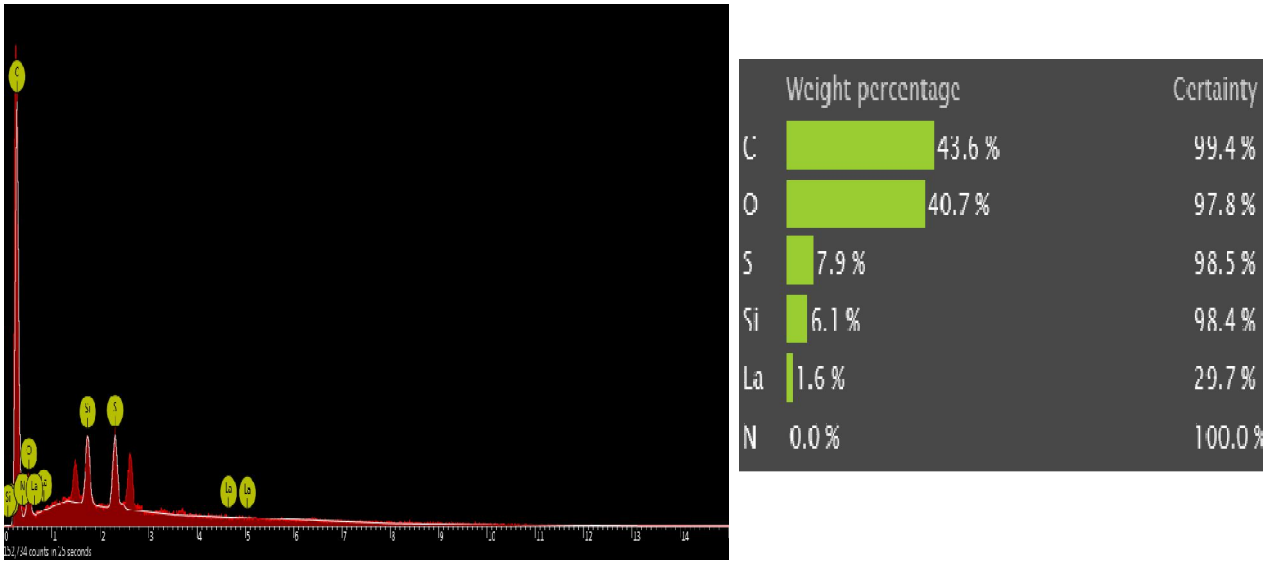


Figure 5; Result from identification of compound in electrode

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From the figrure 5 and then analysis by mathematics calculation from PNENOM-SEM programe, we result the composition compound that tabulated in figure 6(b). From the analysis indicate that lanthanum is contain 1.6 % in matrix membrane electrode. So we conclude that lanthanum is absorbed in surface area of electrode.

3.3 Characterization by EDAQ-Voltametry

For analysis, we must be find a good condition. Lanthanum carbon paste electrode was be characterization by differential stripping voltammetry. We scan potential from -1000 mV to 1000 V. Scan rate is 50 mV/minute and electricity range is 50 nA. The result of scanning potential in lanthanum solution can see in figure 6.

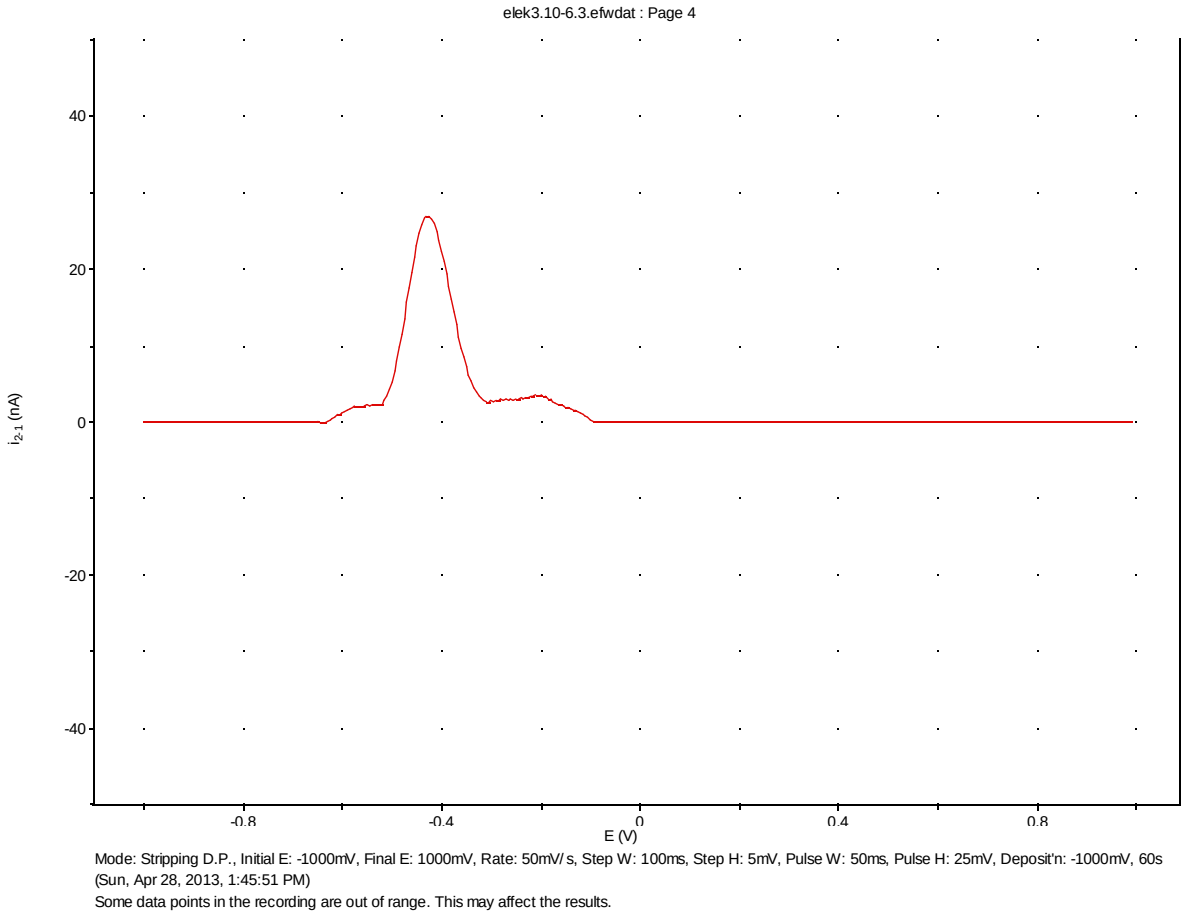

Figure 6. T result or peak current lanthanum carbon paste electrode

From the picture 6 we get a good peak from lanthanum 10^{-6} M, that have characteristic peak at -0,40 mV.

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3.2 Parameter Analysis of Lanthanum by Differential Stripping Voltammetry

From characterization with EDAQ-voltammetry by differential stripping voltammetry we used condition to analysis of lanthanum from simulation sample. With some standard solution we measure of current. The data is in the table 2.

No	Concentration of Lanthanum standard solution (M)	Current (nA)
1	10^{-6}	25.21
2	10^{-7}	11.56
3	10^{-8}	9.60
4	10^{-9}	7.32
5	10^{-10}	5.54
6	10^{-11}	4.56

From data in table 2, we calculate the correlation between lanthanum concentration and current by mathematic excel computer programme. The result is mathematic equation $Y = 1.82x10^{7} X + 7.26$ and coefficient correlation 0,96. So we assume that the situation is equal with basic concept voltammetry from Ilkovich[3]. In the end, we assume the limit detection is 10^{-11} M.

4. Conclusions

Preparation and characterization lanthanum carbon paste electrode was prepared. The membrane with MBTH active compound can adsorb lanthanum ion to surface electrode, that is indicated on SEM test. Peak current get specific area on potential -0,4 volt. The condition can be used to analysis of lanthanum in simulation sample and get limit detection 10^{-11} M.

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