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- Judul : The Influence of NaCl and Na₂SO₄ as Supporting Electrolyte on Analysis of Lead (II) in Seawater by Stripping Voltammetry using Hanging Mercury Drop Electrode
- Penulis : Miratul Khasanah*, Handoko Darmokusumo, Rochmawati
- Jurnal : Malaysian Journal of Fundamental and Applied Sciences, 2014,10(3), 115-118
(dari Seminar ICOWOBAS 2013)



Miratul Khasanah <miratulkhasanah@gmail.com>

[MJAS] Paper entitled "The Influence of NaCl and Na₂SO₄...."

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Kepada: miratulkhasanah@gmail.com

15 November 2013 pukul 06.12

Title: The Influence of NaCl and Na₂SO₄ as Supporting Electrolyte on Analysis of Lead (II) in Seawater by Stripping Voltammetry using Hanging Mercury Drop Electrode
Corresponding Author: Miratul Khasanah
Authors: Miratul Khasanah, Handoko Darmokusumo, Rochmawati

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This manuscript is written almost fully according to the format set, although the spacing format is sometimes wrong (double spacing when it isn't necessary). There should also be space between figures and the texts. The format for the references is also wrong. The English should be improved and revised, as many mistakes were done all over the manuscript, making it very hard to understand at times.

Date : 21/10/2013

The Influence of NaCl and Na₂SO₄ as Supporting Electrolyte on Analysis of Lead (II) in Seawater by Stripping Voltammetry using Hanging Mercury Drop Electrode

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ABSTRACT

The influence of NaCl and Na₂SO₄ as supporting electrolyte on lead (II) analysis in seawater by stripping voltammetry was studied. The instrumental parameters obtained in this recent study were deposition potential -1000 mV, deposition time 150 s, and stirring rate 2000 rpm. The concentration of supporting electrolyte that used was 300 µg/L NaCl and 1800 µg/L Na₂SO₄. The detection limit and sensitivity of the method using NaCl as supporting electrolyte were 0.1483 µg/L and 29.207 nA L/µg, respectively. The precision in the range of 1-5 µg/L of lead (II) was 1.01-6.37%. Lead (II) analysis voltammetrically using Na₂SO₄ as supporting electrolyte resulted the analytical performance as follow: detection limit 0.5498 µg/L, sensitivity 8.037 nA L/µg, precision 0.34-5.9%. Analysis of lead (II) by stripping voltammetry using NaCl and Na₂SO₄ as supporting electrolyte resulted recovery 99.90% (n=3) and 104.2% (n=3), respectively. The presence of both NaCl and Na₂SO₄ slightly amplified the lead (II) current signal.

Keywords : lead (II), supporting electrolyte, stripping voltammetry

1. INTRODUCTION

Lead is one of the most well-known toxic heavy metals for people and environment [1], thus its trace analysis is very important. In recent decades, a number of techniques have been developed for sensitive analysis for lead (II), including atomic absorption spectroscopy, inductively coupled plasma (ICP) atomic emission spectroscopy, X-ray fluorescence spectrophotometry, ICP-mass spectrometry and so on [2-6]. However, these methods generally require expensive instruments, complicated sample pretreatment, and have high detection limit.

The demand for detecting trace and ultratrace levels of inorganic substances of environmental, industrial or clinical significance is growing continuously. In order to enhance the sensitivity and reduce the detection limits of instrumental methods, particularly voltammetric method, extensive efforts are still made. The remarkable sensitivity of stripping voltammetry is attributed to the unique coupling of in situ preconcentration step with an advanced voltammetric measurement of the accumulated analyte. Both the electrolytic and adsorptive accumulation schemes offer convenient quantitation of nanomolar concentrations following short pre-concentration periods and detection limits as low as 10⁻¹⁰-10⁻¹¹ M. Another advantageous feature of stripping techniques is faster, smaller, cheaper, simpler and better analysis [7].

Analysis of lead (II) in sea water by using potentiometric stripping have been reported [8]. The result showed that the supporting ions in sea water can amplify the analytical signal, so it is necessary to conduct further research on the influence the ions in seawater may play a role as a supporting electrolyte in the analysis of lead (II) by voltammetry.

In this study, the effect of the addition of Na₂SO₄ and NaCl as the supporting electrolyte on the analysis of lead (II) by using stripping voltammetry has been conducted. The presence of Na⁺, Cl⁻, and SO₄²⁻ ions in sea water of each is 30.63%, 54.97%, and 7.69%, respectively [9].

2. EXPERIMENTAL

2.1. Materials and instruments

Chemicals used were lead (II) nitrate, mercury (II) nitrate, nitric acid 65%, sodium chloride, sodium sulphate (Merck, Darmstadt, Germany), and high purity N₂. The ultra high pure (UHP) water was used as solvent.

The instruments used in this study were 797 Computrace Voltammetry (MVA system-1) equipped with a sample container, stirrer, processor units, personal computer, hanging mercury drop electrode (HMDE), reference electrode Ag/AgCl (KCl 3M) and Pt auxiliary electrodes, micropipette and other supporting equipments.

2.2 Procedure

2.3.1 Optimization of the research conditions

The research conditions optimized were deposition potential, deposition time, and stirring rate of the solution. The optimization of research conditions used 25.0 mL lead (II) 3 µg/L contained 0.3% nitric acid. Then, the solution was analyzed with stripping voltammetry. Deposition potential was varied from -100 to -1100 mV, deposition time from 30 to 180 seconds, stirring rate from 0 to 2800 rpm. The size of mercury drop as working electrode was 0.4822 mm² [8].

2.3.2 Influence of sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) as supporting electrolyte

Influence of supporting electrolyte was studied by adding NaCl and Na₂SO₄ with various concentration of 300-1800 µg/L to lead (II) solution 3 µg/L contained nitric acid 0.3%. The solutions were analyzed by stripping voltammetry using HMDE. Deviation of current value of each supporting electrolyte addition toward current of 3 µg/L lead (II) standard solution without supporting electrolyte was determined.

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2.3.3 Calibration curve and method validity

Each of the lead (II) standard solution of 1, 2, 3, 4, and 5 µg/L in solution of the nitric acid 0.3% was added with supporting electrolyte and analyzed by stripping voltammetry using HMDE. The data was used to create calibration curve and to determine the method validity, including linearity, precision (relative standard deviation/RSD), sensitivity, and detection limit. Recovery was studied by adding the lead (II) standard solution to the artificial sea water.

3. RESULTS & DISCUSSION

3.1. Optimization of Research Parameters

Deposition potential is the potential that used to lead (II) to be deposited on the surface of the working electrode HMDE during the process of electrolysis. The lead (II) ion is reduced and forming amalgam on the surface of the electrode. Reaction that occur at the electrodes is

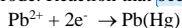


Fig. 1 shows that the optimum deposition potential is -1000 mV. The lower potential generated the higher current. However, the deposition potential -1100 mV resulting low current signal indicated a significant decrease in the peak on the graph. The selection of the best deposition potential is based on the potential that generates the highest peak current as much as possible and not give side reactions [7].

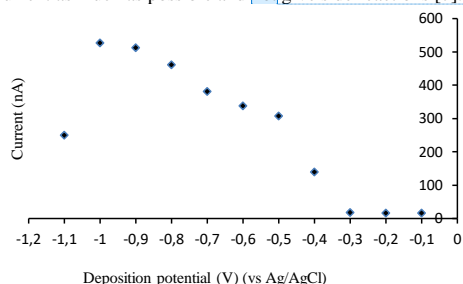


Fig. 1 Curve of deposition potential effect on the lead (II) current

Deposition time is the time used to accumulate the analyte on the electrode surface during the electrolysis step. This step involved the deposition and adsorption of the analyte on the electrode surface, or electron transfer mechanism on modified electrode surface, depending on the interaction between analyte and the electrode. The longer the deposition time, the greater number of analyte is deposited on the working electrode. The current is proportional to the analyte concentration. The relationship between accumulated analyte on the electrode surface versus accumulation time explained by Faraday's law [7,10]. Based on the Faraday's law it is shown that the longer deposition time is given, the more analyte will be deposited on the electrode. Election of deposition time done is to obtain an efficient time analysis and to prevent interferences that occur which is caused by saturation of electrode or formed the intermetallic compounds [11].

The results can be seen in Fig. 2 which shows that the peak current height of lead (II) increased in accordance with the longer deposition time. While at the deposition time 180 s, the peak current decreased. This is due to the saturation of the electrode surface by the analyte.

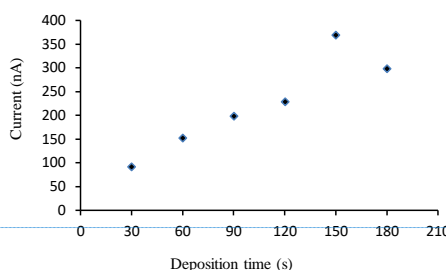


Fig. 2 Curve of the deposition time effect on the current of lead (II)

The Fig. 3 explains the more stirring rate speed up, the higher current obtained. It caused by stirring rate affect to the thickness of diffusion layer become thinner, so the current increased, according to equation below.

$$i = \frac{nFADC}{\delta}$$

$$\delta = \frac{K}{U^\alpha}$$

with i is current in ampere, n is amount of electron, F is Faraday's number, A is wide of electrode surface (cm^2), D is coefficient of diffusion (cm^2s^{-1}), C is concentration in mol cm^{-3} , δ is thickness of diffusion layer, K and α is a constant, and U is stirring rate [7,10].

Stirring of the solution generate an unexpected convection current in the process of accumulating of analyte onto electrode. If the solution had been unstirred, the longer time was taken to accumulate the analyte. Beside that, the current obtained was not reproducible because of the solution was not homogeneous [10]. Moreover, speed up of stirring rate causing a vibration that bothering of electrode stability which is pursuing accumulation process of lead (II) to the electrode surface. Election of stirring rate based on reproducibility current with high in precision and accuracy and a good peak voltammogram. In this study, 2000 rpm was chosen as optimum stirring rate.

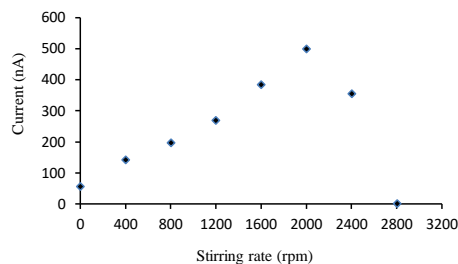


Fig. 3 Curve of the stirring rate effect on the current of lead (II)

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Fig. 3 shows that the faster the rate of stirring the increased peak current generated. However, the stirring rate 2400 rpm and 2800 rpm showed quite sharp of reducing peak currents. The faster the stirring rate given the concentration gradient became steeper and convection currents generated will also increase, resulting in thinning of the diffusion layer, this triggers the outbreak of mercury droplets.

3.2. Influence of supporting electrolyte

In this study, NaCl and Na₂SO₄ were selected as supporting electrolyte because both of compounds were greatest component in seawater. The addition of supporting electrolyte on the analysis by stripping voltammetry used to minimizing migration current caused by the presence of an electrical field [7,10]. If an electrical field is applied to an electrolyte solution, the ions would tend to move where cations move toward the cathode and anions move towards the anode. Ion migration is causing current flow in the cell. With the addition of the supporting electrolyte, mass transport caused by migration flows can be reduced so that the current can be generated solely from diffusion events.

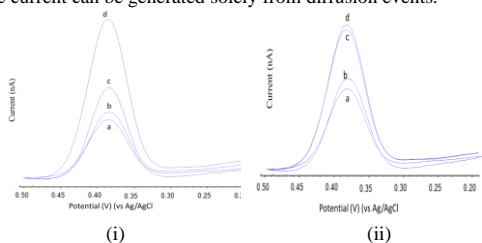


Fig. 4 Voltammogram of lead (II) in the (i) NaCl dan (ii) Na₂SO₄ matrices with concentration (a) 0 µg/L, (b) 300 µg/L, (c) 1500 µg/L and (d) 1800 µg/L.

Addition of NaCl 300 µg/L enhances the peak current of lead (II) (Fig. 4(i)). This is due to the formation of PbCl₂ with ionic bonds that can be terminated by the presence of a strong acid (HNO₃ 0.3%). K_{sp} PbCl₂ is 2.4 x 10⁻⁴ [12]. The addition of NaCl 1500 µg/L causes a significant increase in peak flow due to the concentration of complex compounds are not formed because the charge exceeds that easily ionized in water so that resulting a very high peak current.

Fig. 4 (ii) shows that the addition of Na₂SO₄ can increase peak currents of lead (II). This is due to SO₄²⁻ as weak ligand that do not form complexes with lead (II), so PbSO₄ easily ionized in water and cause an increase in the current signal. On this analysis does not form a precipitate PbSO₄ because the multiplication resulted by a standard solution of lead (II) 3 µg/L and 1800 µg/L Na₂SO₄ to produce PbSO₄ (Q) is 1.15 x 10⁻¹⁵, that is far less than K_{sp} of saturated PbSO₄ (1.7 x 10⁻⁵) [12].

3.3 Calibration curve and method validity

The calibration curve of lead (II) were made from lead (II) solution of 1-5 µg/L in the Na₂SO₄ and NaCl matrices, and generated regression equation of $y = 29.20x -$

4.159 and $y = 8.037x + 2.669$, respectively. The intercept of three calibration curves in Fig. 5 are not zero, which indicate an electrical background (non-faradaic current) during analysis. The current arise from the transfer of charge particles continuously in the electrically field (migration).

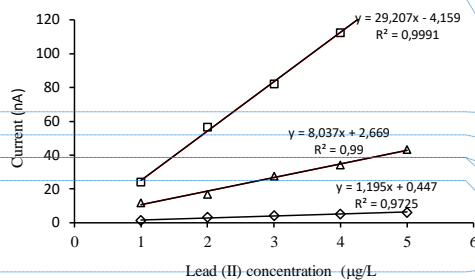


Fig. 5 Calibration curve of (◇) lead (II), lead (II) + (Δ) 1800 µg/L Na₂SO₄ and (□) 300 µg/L NaCl

The current that expected to be measured in the analysis voltammetrically is diffusion current, which flows arising from the existence of a concentration gradient of lead (II) on the bulk solution and the electrode surface. Migration current can be reduced with the addition high concentrations of supporting electrolyte (about 100 times the analyte concentration) [7, 10].

Table 1 Data of lead (II) analysis in sea water

Solution	Found lead (II) (µg/L)	Recovery (%)
Artificial seawater ^{a)}	0	99.9
Artificial seawater ^{b)} + 5 µg/L lead (II)	4.995	
Artificial seawater ^{b)}	0	104.2
Artificial seawater ^{b)} + 5 µg/L lead (II)	5.21	
Seawater A	3.84	103.4
Seawater A + 5 µg/L lead (II)	9.00	
Seawater B	5.17	103.4
Seawater B + 5 µg/L lead (II)	10.34	

a) containing 300 µg/L NaCl
b) containing 1800 µg/L Na₂SO₄

Data in Table 2 shows the precision of analytical method were smaller than 2/3RSD_{Horwitz} (30% for µg/L or 10⁻⁹ M level) [13-14] and statistically acceptable. The obtained recovery in the artificial sea water contained NaCl and Na₂SO₄ matrices were 96.9 (n=3) and 104.2% (n=3), respectively. The accuracy of the method is very good and statistically acceptable (accuracy for 1 µg/L concentration level is 40-120%) [13-14]. The superior method offer an alternative for lead (II) analysis in seawater.

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Table 2 Validity of the analytical method

Parameter	Pb(II)	Pb(II) + electrolyte of	
		NaCl	Na ₂ SO ₄
Linearity(r)	0.9991	0.9995	0.9949
Sensitivity (nA.L/μg)	1.195	29.207	8.037
RSD ^o (%)	10.47-18.41	1.01-6.37	0.34-5.90
LOD (μg/L)	0.0103	0.1483	0.5498
Recovery (%)	-	99.9	104.2

n = 3

[NaCl] = 300 μg/L

LOD = limit of detection

[Na₂SO₄] = 1800 μg/L

4. CONCLUSION

The NaCl and Na₂SO₄ amplify the current signal on the analysis of lead (II) by voltammetry. Analysis of lead (II) in artificial sea water in this study showed recovery of 99.90% and 104.16% with the use of NaCl and Na₂SO₄ as supporting electrolyte, respectively. This suggests that stripping voltammetry method can be used as the appropriate methods to analyze lead (II) in seawater.

ACKNOWLEDGEMENT

The authors thank the Department of Chemistry, Faculty of Sciences and Technology Universitas Airlangga for laboratory and instrumental facilities.

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[MJAS] Paper entitled "The Influence of NaCl and Na₂SO₄...."

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21 November 2013 pukul 12.15

Kepada: Hadi Nur <hadi@ibnusina.utm.my>

Dear **Prof. Hadi Nur**

We have already revised the paper and sent it (attachment) to you. We are delightful to hear that our manuscript would be published in the MJFAS. Thank you very much for opportunity and your attention.

Sincerely yours,

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Received xxx, Revised xxx, Accepted xxx, Available online xxx

ABSTRACT

The influence of NaCl and Na₂SO₄ as supporting electrolyte on lead (II) analysis in seawater by stripping voltammetry was studied. The instrumental parameters obtained in this recent study were deposition potential -1000 mV, deposition time 150 s, and stirring rate 2000 rpm. The concentration of supporting electrolyte used was 300 µg/L NaCl and 1800 µg/L Na₂SO₄. The detection limit and sensitivity of the method using NaCl as supporting electrolyte were 0.1483 µg/L and 29.207 nA L/µg, respectively. The precision in the range of 1-5 µg/L of lead (II) was 1.01-6.37%. Lead (II) analysis voltammetrically using Na₂SO₄ as supporting electrolyte resulted in the analytical performance as follow: detection limit of 0.5498 µg/L, sensitivity of 8.037 nA L/µg, precision of 0.34-5.9 %. Analysis of lead (II) by stripping voltammetry using NaCl and Na₂SO₄ as supporting electrolyte resulted in recovery of 99.90 % (n=3) and 104.2 % (n=3), respectively. The presence of both NaCl and Na₂SO₄ slightly amplified the lead (II) current signal.

| lead (II) | sea water | supporting electrolyte | hanging mercury drop | stripping voltammetry |

1. INTRODUCTION

Lead is one of the most well-known toxic heavy metals for people and environment [1], thus its trace analysis is very important. In recent decades, a number of techniques have been developed for sensitive analysis for lead (II), including atomic absorption spectroscopy, inductively coupled plasma (ICP) atomic emission spectroscopy, X-ray fluorescence spectrophotometry, ICP-mass spectrometry and so on [2-6]. However, these methods generally require expensive instruments, complicated sample pretreatment, and have high detection limit.

The demand for detecting trace and ultratrace levels of inorganic substances of environmental, industrial or clinical significance is growing continuously. In order to enhance the sensitivity and reduce the detection limits of instrumental methods, particularly voltammetric method, extensive efforts are still being done. The remarkable sensitivity of stripping voltammetry is attributed to the unique coupling of in situ preconcentration step with an advanced voltammetric measurement of the accumulated analyte. Both the electrolytic and adsorptive accumulation schemes offer convenient quantitation of nanomolar concentrations following short pre-concentration periods and detection limits as low as 10⁻¹⁰-10⁻¹¹ M. Another advantageous feature of stripping techniques is faster, smaller, cheaper, simpler and better analysis [7].

Analysis of lead (II) in sea water by using stripping potentiometry have been reported [8]. The result showed that the supporting ions in sea water can amplify the analytical signal, so it is necessary to conduct further research on the influence the ions in seawater that may play

a role as a supporting electrolyte in the analysis of lead (II) by voltammetry.

In this study, the effect of the addition of Na₂SO₄ and NaCl as the supporting electrolyte on the analysis of lead (II) by using stripping voltammetry has been conducted. The presence of Na⁺, Cl⁻, and SO₄²⁻ ions in sea water of each are 30.63%, 54.97%, and 7.69%, respectively [9].

2. EXPERIMENTAL

2.1. Materials and instruments

Chemicals used were lead (II) nitrate, mercury (II) nitrate, nitric acid 65%, sodium chloride, sodium sulphate (Merck, Darmstadt, Germany), and high purity N₂. The ultra high pure (UHP) water was used as solvent.

The instruments used in this study were 797 Computrace Voltammetry (MVA system-1) equipped with a sample container, stirrer, processor units, personal computer, hanging mercury drop electrode (HMDE), reference electrode Ag/AgCl (KCl 3M), Pt auxiliary electrodes, micropipette and other supporting equipments.

2.2 Procedure

2.2.1 Optimization of the research conditions

The research conditions optimized were deposition potential, deposition time, and stirring rate of the solution. The optimization of research conditions used 25.0 mL lead (II) 3 µg/L containing 0.3% nitric acid. Then, the solution was analyzed with stripping voltammetry. Deposition potential was varied from -100 to -1100 mV, deposition

time from 30 to 180 seconds, stirring rate from 0 to 2800 rpm. The size of mercury drop as working electrode was 0.4822 mm² [8].

2.3.2 Influence of sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) as supporting electrolyte

Influence of supporting electrolyte was studied by adding NaCl and Na₂SO₄ with various concentration of 300-1800 µg/L to lead (II) solution 3 µg/L containing nitric acid 0.3%. The solutions were analyzed by stripping voltammetry using HMDE. Deviation of current value of each supporting electrolyte addition toward current of 3 µg/L lead (II) standard solution without supporting electrolyte was determined.

2.3.3 Calibration curve and method validity

Each of the lead (II) standard solution of 1, 2, 3, 4, and 5 µg/L in solution of the nitric acid 0.3% was added with supporting electrolyte and analyzed by stripping voltammetry using HMDE. The data was used to create calibration curve and to determine the method validity including linearity, precision (relative standard deviation/RSD), sensitivity, and detection limit. Recovery was studied by adding the lead (II) standard solution to the artificial sea water.

3. RESULTS & DISCUSSION

3.1. Optimization of Research Parameters

Deposition potential is the potential that is used to deposit lead (II) on the surface of the working electrode HMDE during the process of electrolysis. The lead (II) ion is reduced and forms amalgam on the surface of the electrode. Reaction that occurs at the electrodes is

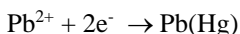


Fig. 1 shows that the optimum deposition potential is -1000 mV. The lower potential generated the higher current. However, the deposition potential of -1100 mV resulted in low current signal indicated a significant decrease in the peak on the graph. The selection of the best deposition potential is based on the potential that generates the highest peak current as much as possible and does not give side reactions [7].

Deposition time is the time used to accumulate the analyte on the electrode surface during the electrolysis step. This step involved the deposition and adsorption of the analyte on the electrode surface, or electron transfer mechanism on modified electrode surface, depending on the interaction between analyte and the electrode. The longer the deposition time, the greater number of analyte is deposited on the working electrode. The current is proportional to the analyte concentration. The relationship between accumulated analyte on the electrode surface versus accumulation time explained by Faraday's law [7,10].

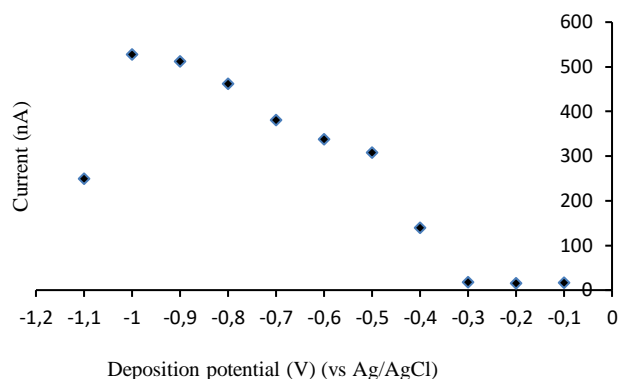


Fig. 1 Curve of deposition potential effect on the lead (II) current

Based on the Faraday's law it is shown that the longer deposition time is given, the more analyte will be deposited on the electrode. Election of deposition time done is to obtain an efficient time analysis and to prevent interferences that occur which is caused by saturation of electrode or formed the intermetallic compounds [11].

The results shown in Fig. 2 shows that the peak current height of lead (II) increased in accordance to longer deposition time. While at the deposition time of 180 s, the peak current decreased. This is due to the saturation of the electrode surface by the analyte.

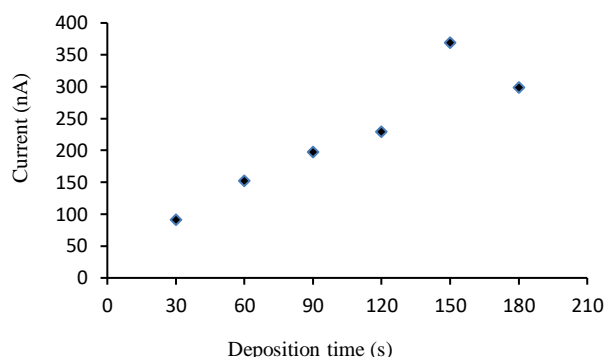


Fig. 2 Curve of the deposition time effect on the current of lead (II)

The Fig. 3 explains the higher the speed of stirring rate, the higher current obtained. It is because the stirring rate affected the thickness of diffusion layer which becomes thinner, so the current increased, according to equation below.

$$i = \frac{nFADC}{\delta} \tag{1}$$

$$\delta = \frac{K}{U^\alpha} \tag{2}$$

with *i* is current in ampere, *n* is amount of electron, *F* is Faraday's number, *A* is wide of electrode surface (cm²), *D* is coefficient of diffusion (cm²s⁻¹), *C* is concentration in mol

cm^{-1} , δ is thickness of diffusion layer, K and α is a constant, and U is stirring rate [7,10].

Stirring of the solution generated an unexpected convection current in the process of accumulating the analyte onto electrode. If the solution had been unstirred, longer time has to be taken to accumulate the analyte. Besides that, the current obtained was not reproducible because the solution was not homogeneous [10]. Moreover, speeding up the stirring rate caused a vibration that interrupted the stability of the electrode which is pursuing accumulation process of lead (II) to the electrode surface. Election of stirring rate is based on reproducibility current with high in precision and accuracy and a good peak voltammogram. In this study, 2000 rpm was chosen as the optimum stirring rate.

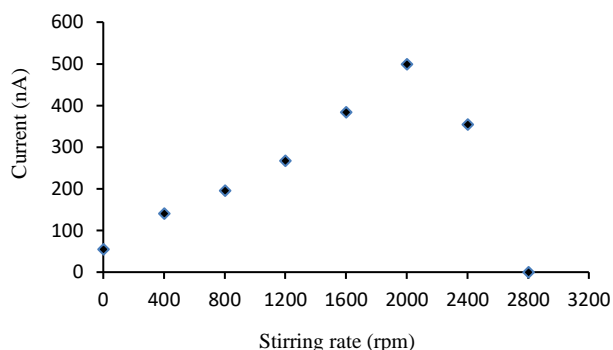


Fig. 3 Curve of the stirring rate effect on the current of lead (II)

Fig. 3 shows that the faster the rate of stirring, the higher the increase in peak current generated. However, the stirring rate of 2400 rpm and 2800 rpm showed quite sharp reduce in peak currents. The faster the stirring rate, the concentration gradient became steeper and convection currents generated will also increase, resulting in thinning of the diffusion layer. This triggers the outbreak of mercury droplets.

3.2. Influence of supporting electrolyte

In this study, NaCl and Na_2SO_4 were selected as supporting electrolyte because both of the compounds were the greatest component in seawater. The addition of supporting electrolyte in the analysis by stripping voltammetry was used to minimize migration current caused by the presence of an electrical field [7,10]. If an electrical field is applied to an electrolyte solution, the ions would tend to move where cations move toward the cathode and anions move towards the anode. Ion migration caused current flow in the cell. With the addition of the supporting electrolyte, mass transport caused by migration flows can be reduced so that the current can be generated solely from diffusion events.

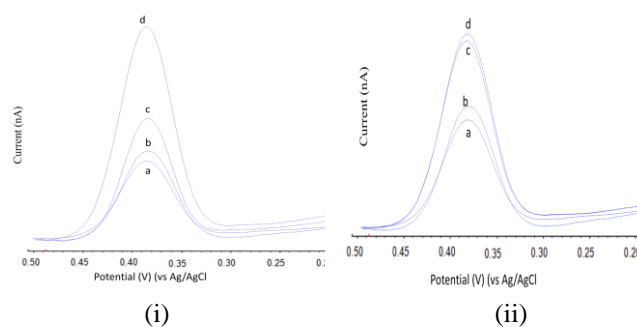


Fig. 4 Voltammogram of lead (II) in the (i) NaCl dan (ii) Na_2SO_4 matrices with concentration (a) 0 $\mu\text{g/L}$, (b) 300 $\mu\text{g/L}$, (c) 1500 $\mu\text{g/L}$ and (d) 1800 $\mu\text{g/L}$

Addition of NaCl 300 $\mu\text{g/L}$ enhances the peak current of lead (II) (Fig. 4(i)). This is due to the formation of PbCl_2 with ionic bonds that can be terminated by the presence of a strong acid (HNO_3 0.3%). K_{sp} of PbCl_2 is 1.7×10^{-5} [12], while the multiplication of the concentration of NaCl 300 $\mu\text{g/L}$ and lead (II) 3 $\mu\text{g/L}$ to produce PbCl_2 (Q) is 3.8×10^{-19} . Fig. 4 (ii) shows that the addition of Na_2SO_4 can increase peak currents of lead (II). This is due to SO_4^{2-} as weak ligand that does not form complexes with lead (II), so PbSO_4 can easily ionized in water and cause an increase in the current signal. In this analysis there is no formation of precipitate PbSO_4 , because the lead (II) concentration of 3 $\mu\text{g/L}$ and 1800 $\mu\text{g/L}$ Na_2SO_4 resulting Q of 1.8×10^{-13} , that is far less than the K_{sp} of saturated PbSO_4 (1.6×10^{-8}) [12].

3.3 Calibration curve and method validity

The calibration curve of lead (II) were made from lead (II) solution of 1-5 $\mu\text{g/L}$ in the Na_2SO_4 and NaCl matrices, and generated regression equation of $y = 29.20x - 4.159$ and $y = 8.037x + 2.669$, respectively. The intercept of the three calibration curves in Fig. 5 are not zero, which indicate an electrical background (non-Faradic current) during analysis.

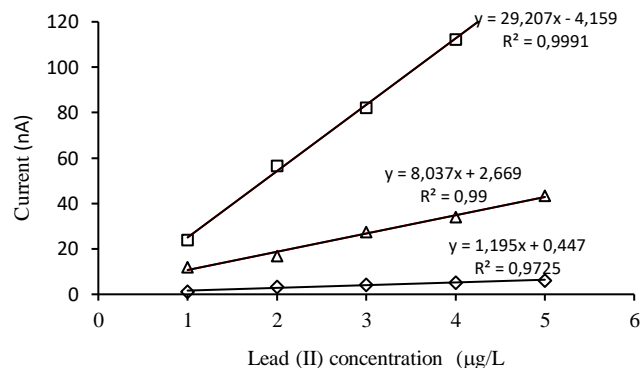


Fig. 5 Calibration curve of (◇) lead (II), (Δ) lead (II) + 1800 $\mu\text{g/L}$ Na_2SO_4 and (□) lead (II) + 300 $\mu\text{g/L}$ NaCl

The current arised from the transfer of charge particles continuously in the electrically field (migration). The current that is expected to be measured in the analysis

voltammetrically is diffusion current, which flows arising from the existence of a concentration gradient of lead (II) on the bulk solution and the electrode surface. Migration current can be reduced with the addition of high concentrations of supporting electrolyte (about 100 times the analyte concentration) [7, 10].

Table 1 Data of lead (II) analysis in sea water

Solution	Found lead (II) ($\mu\text{g/L}$)	Recovery (%)
Artificial seawater ^{a)}	0	99.9
Artificial seawater ^{a)} + 5 $\mu\text{g/L}$ lead (II)	4.995	
Artificial seawater ^{b)}	0	104.2
Artificial seawater ^{b)} + 5 $\mu\text{g/L}$ lead (II)	5.21	
Seawater A	3.84	103.4
Seawater A + 5 $\mu\text{g/L}$ lead (II)	9.00	
Seawater B	5.17	103.4
Seawater B + 5 $\mu\text{g/L}$ lead (II)	10.34	

a) containing 300 $\mu\text{g/L}$ NaCl

b) containing 1800 $\mu\text{g/L}$ Na₂SO₄

Data in Table 2 shows the precision of analytical method were smaller than 2/3RSD_{Horwitz} (30% for $\mu\text{g/L}$ or 10⁻⁹ M level) [13-14] and statistically acceptable. The obtained recovery in the artificial sea water contained NaCl and Na₂SO₄ matrices were 96.9 (n=3) and 104.2% (n=3), respectively. Meanwhile, the recovery in sea water sample was 103.4%. The accuracy of the method is very good and statistically acceptable (accuracy for 1 $\mu\text{g/L}$ concentration level is 40-120%) [13-14]. This superior method offer an alternative for lead (II) analysis in seawater.

Table 2 Validity of the analytical method

Parameter	Pb(II)	Pb (II) + electrolyte of	
		NaCl	Na ₂ SO ₄
Linearity(r)	0.9991	0.9995	0.9949
Sensitivity (nA.L/ μg)	1.195	29.207	8.037
RSD* (%)	10.47-18.41	1.01-6.37	0.34-5.90
LOD ($\mu\text{g/L}$)	0.0103	0.1483	0.5498
Recovery (%)	-	99.9	104.2

n = 3

[NaCl] = 300 $\mu\text{g/L}$

LOD = limit of detection

[Na₂SO₄] = 1800 $\mu\text{g/L}$

4. CONCLUSION

The NaCl and Na₂SO₄ amplified the current signal on the analysis of lead (II) by voltammetry. Analysis of lead (II) in artificial sea water in this study showed recovery of 99.90% and 104.16% with the use of NaCl and Na₂SO₄ as supporting electrolyte, respectively. This suggests that stripping voltammetry method can be used as the appropriate methods to analyze lead (II) in seawater.

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The influence of NaCl and Na₂SO₄ as supporting electrolyte on analysis of lead (II) in seawater by stripping voltammetry using hanging mercury drop electrode

Miratul Khasanah

Handoko Darmokusumo

. Rochmawati

DOI: <https://doi.org/10.11113/mjfas.v10n3.263>

Keywords: lead (II), sea water, supporting electrolyte, hanging mercury drop, stripping voltammetry

Abstract

The influence of NaCl and Na₂SO₄ as supporting electrolyte on lead (II) analysis in seawater by stripping voltammetry was studied. The instrumental parameters obtained in this recent study were deposition potential

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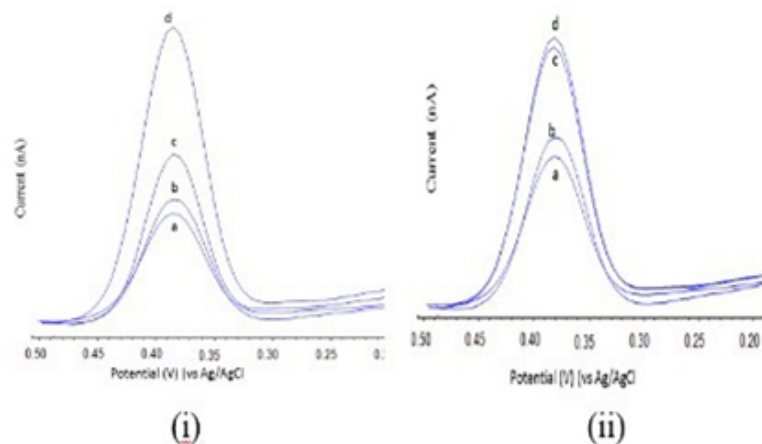
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GRAPHICAL ABSTRACT



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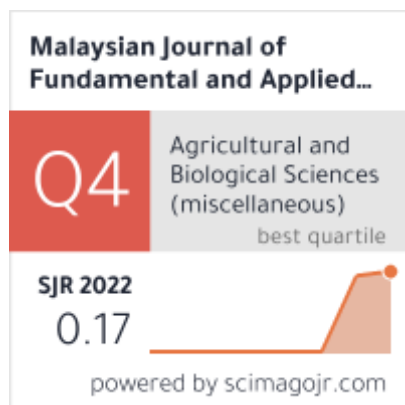
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The influence of NaCl and Na₂SO₄ as supporting electrolyte on analysis of Lead(II) in seawater by stripping voltammetry using hanging mercury drop electrode

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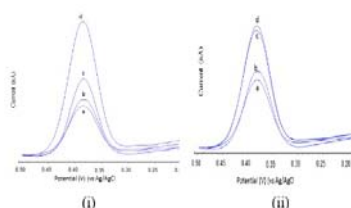
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Analysis of lead (II) in sea water by using stripping potentiometry have been reported [8]. The result showed that the supporting ions in sea water can amplify the analytical signal, so it is necessary to conduct further research on the influence the ions in seawater that may play a role as a supporting electrolyte in the analysis of lead (II) by voltammetry.

In this study, the effect of the addition of Na₂SO₄ and NaCl as the supporting electrolyte on the analysis of lead (II) by using stripping voltammetry has been conducted. The presence of Na⁺, Cl⁻, and SO₄²⁻ ions in sea water of each are 30.63%, 54.97%, and 7.69%, respectively [9].

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2.2 Procedure

2.3.1 Optimization of the research conditions

The research conditions optimized were deposition potential, deposition time, and stirring rate of the solution. The optimization of research conditions used 25.0 mL lead (II) 3 µg/L containing 0.3% nitric acid. Then, the solution was analyzed with stripping voltammetry. Deposition potential was varied from -100 to -1100 mV, deposition time from 30 to 180 seconds, stirring rate from 0 to 2800 rpm. The size of mercury drop as working electrode was 0.4822 mm² [8].

2.3.2 Influence of sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) as supporting electrolyte

Influence of supporting electrolyte was studied by adding NaCl and Na₂SO₄ with various concentration of 300-1800 µg/L to lead (II) solution 3 µg/L containing nitric acid 0.3%. The solutions were analyzed by stripping voltammetry using HMDE. Deviation of current value of each supporting electrolyte addition toward current of 3 µg/L lead (II) standard solution without supporting electrolyte was determined.

2.3.3 Calibration curve and method validity

Each of the lead (II) standard solution of 1, 2, 3, 4, and 5 µg/L in solution of the nitric acid 0.3% was added with supporting electrolyte and analyzed by stripping voltammetry using HMDE. The data was used to create calibration curve and to determine the method validity including linearity, precision (relative standard deviation/RSD), sensitivity, and detection limit. Recovery was studied by adding the lead (II) standard solution to the artificial sea water.

3. RESULTS & DISCUSSION

3.1. Optimization of Research Parameters

Deposition potential is the potential that is used to deposit lead (II) on the surface of the working electrode HMDE during the process of electrolysis. The lead (II) ion is reduced and forms amalgam on the surface of the electrode. Reaction that occurs at the electrodes is

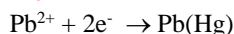


Fig. 1 shows that the optimum deposition potential is -1000 mV. The lower potential generated the higher current. However, the deposition potential of -1100 mV resulted in low current signal indicated a significant decrease in the peak on the graph. The selection of the best deposition potential is based on the potential that generates the highest peak current as much as possible and does not give side reactions [7].

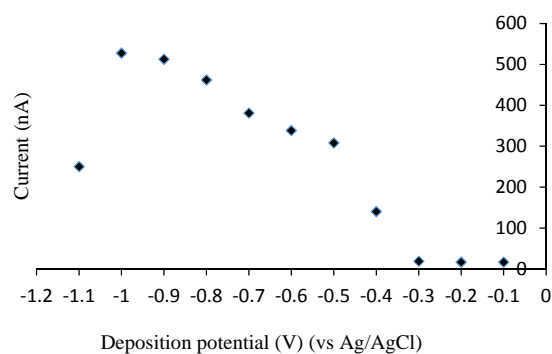


Fig. 1 Curve of deposition potential effect on the lead (II) current

Deposition time is the time used to accumulate the analyte on the electrode surface during the electrolysis step. This step involved the deposition and adsorption of the analyte on the electrode surface, or electron transfer mechanism on modified electrode surface, depending on the interaction between analyte and the electrode. The longer the deposition time, the greater number of analyte is deposited on the working electrode. The current is proportional to the analyte concentration. The relationship between accumulated analyte on the electrode surface versus accumulation time explained by Faraday's law [7,10].

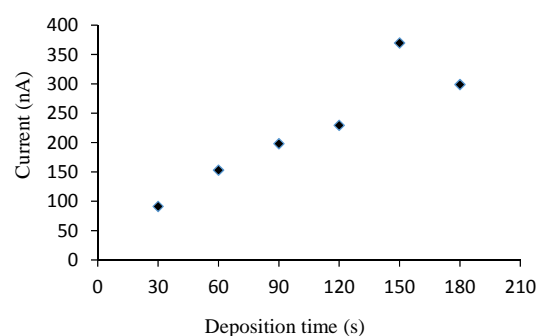


Fig. 2 Curve of the deposition time effect on the current of lead (II)

Based on the Faraday's law it is shown that the longer deposition time is given, the more analyte will be deposited on the electrode. Election of deposition time done is to obtain an efficient time analysis and to prevent interferences that occur which is caused by saturation of electrode or formed the intermetallic compounds [11].

The results shown in Fig. 2 shows that the peak current height of lead (II) increased in accordance to longer deposition time. While at the deposition time of 180 s, the peak current decreased. This is due to the saturation of the electrode surface by the analyte.

The Fig. 3 explains the higher the speed of stirring rate, the higher current obtained. It is because the stirring rate affected the thickness of diffusion layer which becomes

thinner, so the current increased, according to equation below.

$$i = \frac{nFADC}{\delta} \quad (1)$$

$$\delta = \frac{K}{U^\alpha} \quad (2)$$

with i is current in ampere, n is amount of electron, F is Faraday's number, A is wide of electrode surface (cm^2), D is coefficient of diffusion (cm^2s^{-1}), C is concentration in mol cm^{-3} , δ is thickness of diffusion layer, K and α is a constant, and U is stirring rate [7,10].

Stirring of the solution generated an unexpected convection current in the process of accumulating the analyte onto electrode. If the solution had been unstirred, longer time has to be taken to accumulate the analyte. Besides that, the current obtained was not reproducible because the solution was not homogeneous [10]. Moreover, speeding up the stirring rate caused a vibration that interrupted the stability of the electrode which is pursuing accumulation process of lead (II) to the electrode surface. Election of stirring rate is based on reproducibility current with high in precision and accuracy and a good peak voltammogram. In this study, 2000 rpm was chosen as the optimum stirring rate.

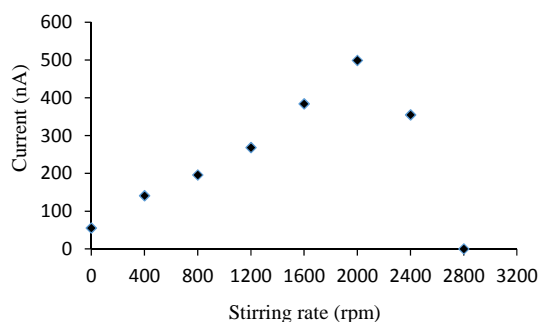


Fig. 3 Curve of the stirring rate effect on the current of lead (II)

Fig. 3 shows that the faster the rate of stirring, the higher the increase in peak current generated. However, the stirring rate of 2400 rpm and 2800 rpm showed quite sharp reduce in peak currents. The faster the stirring rate, the concentration gradient became steeper and convection currents generated will also increase, resulting in thinning of the diffusion layer. This triggers the outbreak of mercury droplets.

3.2. Influence of supporting electrolyte

In this study, NaCl and Na_2SO_4 were selected as supporting electrolyte because both of the compounds were the greatest component in seawater. The addition of supporting electrolyte in the analysis by stripping

voltammetry was used to minimize migration current caused by the presence of an electrical field [7,10]. If an electrical field is applied to an electrolyte solution, the ions would tend to move where cations move toward the cathode and anions move towards the anode. Ion migration caused current flow in the cell. With the addition of the supporting electrolyte, mass transport caused by migration flows can be reduced so that the current can be generated solely from diffusion events.

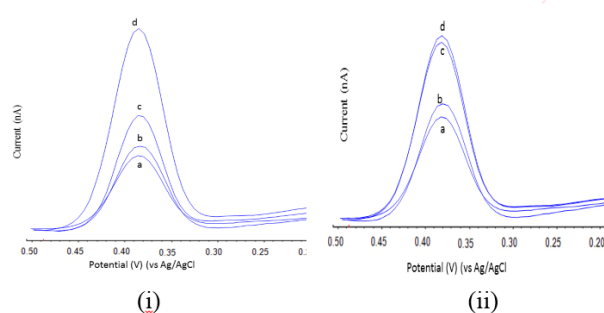


Fig. 4 Voltammogram of lead (II) in the (i) NaCl dan (ii) Na_2SO_4 matrices with concentration (a) 0 $\mu\text{g/L}$, (b) 300 $\mu\text{g/L}$, (c) 1500 $\mu\text{g/L}$ and (d) 1800 $\mu\text{g/L}$

Addition of NaCl 300 $\mu\text{g/L}$ enhances the peak current of lead (II) (Fig. 4(i)). This is due to the formation of PbCl_2 with ionic bonds that can be terminated by the presence of a strong acid (HNO_3 0.3%). K_{sp} of PbCl_2 is 1.7×10^{-5} [12], while the multiplication of the concentration of NaCl 300 $\mu\text{g/L}$ and lead (II) 3 $\mu\text{g/L}$ to produce PbCl_2 (Q) is 3.8×10^{-19} . Fig. 4 (ii) shows that the addition of Na_2SO_4 can increase peak currents of lead (II). This is due to SO_4^{2-} as weak ligand that does not form complexes with lead (II), so PbSO_4 can easily ionized in water and cause an increase in the current signal. In this analysis there is no formation of precipitate PbSO_4 , because the lead (II) concentration of 3 $\mu\text{g/L}$ and 1800 $\mu\text{g/L}$ Na_2SO_4 resulting Q of 1.8×10^{-13} , that is far less than the K_{sp} of saturated PbSO_4 (1.6×10^{-8}) [12].

3.3 Calibration curve and method validity

The calibration curve of lead (II) were made from lead (II) solution of 1-5 $\mu\text{g/L}$ in the Na_2SO_4 and NaCl matrices, and generated regression equation of $y = 29.20x - 4.159$ and $y = 8.037x + 2.669$, respectively. The intercept of the three calibration curves in Fig. 5 are not zero, which indicate an electrical background (non-Faradic current) during analysis.

The current arised from the transfer of charge particles continuously in the electrically field (migration). The current that is expected to be measured in the analysis voltammetrically is diffusion current, which flows arising from the existence of a concentration gradient of lead (II) on the bulk solution and the electrode surface. Migration current can be reduced with the addition of high concentrations of supporting electrolyte (about 100 times the analyte concentration) [7, 10].

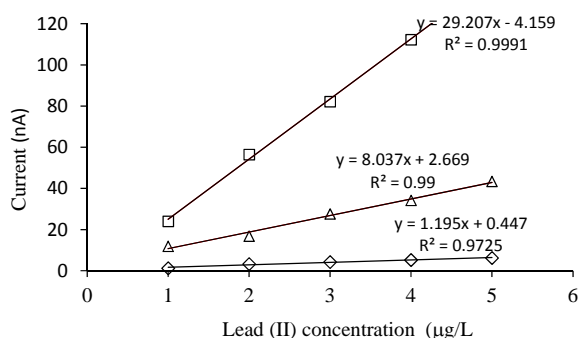


Fig. 5 Calibration curve of (◇) lead (II), (Δ) lead (II) + 1800 µg/L Na₂SO₄ and (□) lead (II) + 300 µg/L NaCl

Table 1 Data of lead (II) analysis in sea water

Solution	Found lead (II) (µg/L)	Recovery (%)
Artificial seawater ^{a)}	0	99.9
Artificial seawater ^{a)} + 5 µg/L lead (II)	4.995	
Artificial seawater ^{b)}	0	104.2
Artificial seawater ^{b)} + 5 µg/L lead (II)	5.21	
Seawater A	3.84	103.4
Seawater A + 5 µg/L lead (II)	9.00	
Seawater B	5.17	103.4
Seawater B + 5 µg/L lead (II)	10.34	

a) containing 300 µg/L NaCl
b) containing 1800 µg/L Na₂SO₄

Table 2 Validity of the analytical method

Parameter	Pb(II)	Pb (II) + electrolyte of NaCl Na ₂ SO ₄	
Linearity(r)	0.9991	0.9995	0.9949
Sensitivity (nA.L/µg)	1.195	29.207	8.037
RSD ^{a)} (%)	10.47-18.41	1.01-6.37	0.34-5.90
LOD (µg/L)	0.0103	0.1483	0.5498
Recovery (%)	-	99.9	104.2

n = 3
LOD = limit of detection
[NaCl] = 300 µg/L
[Na₂SO₄] = 1800 µg/L

Data in Table 2 shows the precision of analytical method were smaller than 2/3RSD_{Horwitz} (30% for µg/L or 10⁻⁹ M level) [13-14] and statistically acceptable. The obtained recovery in the artificial sea water contained NaCl and Na₂SO₄ matrices were 96.9 (n=3) and 104.2% (n=3), respectively. Meanwhile, the recovery in sea water sample was 103.4%. The accuracy of the method is very good and statistically acceptable (accuracy for 1 µg/L concentration level is 40-120%) [13-14]. This superior method offer an alternative for lead (II) analysis in seawater.

4. CONCLUSION

The NaCl and Na₂SO₄ amplified the current signal on the analysis of lead (II) by voltammetry. Analysis of lead (II) in artificial sea water in this study showed recovery of 99.90% and 104.16% with the use of NaCl and Na₂SO₄ as supporting electrolyte, respectively. This suggests that stripping voltammetry method can be used as the appropriate methods to analyze lead (II) in seawater.

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