

THE METHOD DEVELOPMENT OF ANALYSIS Cd, Cu, Pb AND Zn IN SEA WATER BY ADSORPTIVE STRIPPING VOLTAMMETRY (ASV) IN THE PRESENCE OF CALCON AS COMPLEXING AGENT

Deswati*, Hamzar Suyani, and Safni

Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Andalas University, Kampus Unand Limau Manis Padang, 25163

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ABSTRACT

A sensitive and selective adsorptive stripping voltammetric (AdSV) method to determine Cd(II), Cu(II), Pb(II) and Zn(II) in sea water is proposed. The aim of this study was to get optimum condition for the determination of Cd(II), Cu(II), Pb(II) and Zn(II). Adsorptive stripping voltammetry has been used for ultra trace determination of Cd(II), Cu(II), Pb(II) and Zn(II) using calcon as a complexing agent (ligand). In this case, the optimum conditions were reached at 0.1 M KCl supporting electrolyte, concentration of 0.5 mM calcon for Cd(II), Cu(II) 0.3 mM while 0.7 mM for Pb(II) and Zn(II), pH 6 for Cu(II) and pH 7 for Cd(II), Pb(II) and Zn(II), accumulation potential -0.5 V for Cu(II) and Pb(II) and -0.6 V for Cd(II) and Zn(II) and accumulation time 70 sec for Cd(II), 90 sec for Cu(II) and Pb (II) while 50 s for Zn(II). At the optimum condition the relative standard deviations were 7.80%, 4.25%, 8.70% and 0.86% for Cd(II), Cu(II), Pb(II) and Zn(II) respectively for eight replicates ($n = 8$) measurements of 10 $\mu\text{g/L}$ Cd(II), Cu(II), Pb(II) and Zn(II). The method was applied for the direct determination of Cd(II), Cu(II), Pb(II) and Zn(II) in sea water around Bungus, Padang City. Concentration Cd(II), Cu(II), Pb(II) and Zn(II) in sample were 13.200 $\mu\text{g/L}$ for Cd(II), 17.200 $\mu\text{g/L}$ for Cu(II), 0.089 $\mu\text{g/L}$ for Pb(II) and 62.000 $\mu\text{g/L}$ for Zn(II) with recovery of 98.68%, 97.99%, 96.17% and 99.96% for Cd(II), Cu(II), Pb(II) and Zn(II), respectively.

Keywords: trace metal analysis; calcon; sea water; adsorptive stripping voltammetry

ABSTRAK

Metoda selektif dan sensitif penentuan Cd(II), Cu(II), Pb(II) dan Zn(II) dalam air laut secara voltammetri stripping adsorptif telah dilakukan. Tujuan dari penelitian ini adalah untuk mendapatkan kondisi optimum Cd(II), Cu(II), Pb(II) dan Zn(II). Voltammetri stripping adsorptif telah digunakan untuk penentuan ultra runtu Cd(II), Cu(II), Pb(II) and Zn(II) dengan menggunakan kalkon sebagai pengompleks (ligand). Dari hasil penelitian ini, didapatkan kondisi optimum yaitu KCl 0,1 M sebagai elektrolit pendukung, konsentrasi kalkon untuk Cd(II) 0,5 mM, Cu(II) 0,3 mM sedangkan untuk Pb(II) dan Zn(II) 0,7 mM, pH 6 untuk Cu(II) dan pH 7 untuk Cd(II), Pb(II) dan Zn(II), potensial akumulasi $-0,5$ Volt untuk Cu(II) dan Pb(II) dan $-0,6$ Volt untuk Cd(II) dan Zn(II) dan waktu akumulasi untuk Cd(II) 70 detik, untuk Cu(II) dan Pb(II) 90 detik sedangkan untuk Zn(II) 50 detik, Pada kondisi optimum tersebut diperoleh standar deviasi relatif dengan delapan kali pengulangan ($n = 8$), pada pengukuran masing-masing larutan standar Cd(II), Cu(II), Pb(II) dan Zn(II) 10 $\mu\text{g/L}$ adalah : 7,8%, 4,25%, 8,70% dan 0,86%. Metoda ini diaplikasikan untuk penentuan Cd(II), Cu(II), Pb(II) dan Zn(II) secara langsung dalam air laut sekitar Bungus, Kota Padang. Konsentrasi sampel yang diperoleh adalah : 13,200 $\mu\text{g/L}$ untuk Cd(II), 17,200 $\mu\text{g/L}$ untuk Cu(II), 0,089 $\mu\text{g/L}$ untuk Pb(II) dan 62,000 $\mu\text{g/L}$ untuk Zn(II), dengan nilai perolehan kembali (recovery) untuk masing-masing Cd(II), Cu(II), Pb(II) and Zn(II) adalah : 98,68%, 97,99%, 96,17% dan 99,96%.

Kata Kunci: analisis logam runtu; logam berat; air laut; voltammetri stripping adsorptif

INTRODUCTION

The development of industrial sector in a variety of coastal and marine areas is increasing, so more and more environment pollution caused problems. Pollution occurs in coastal areas and marine waters due to a decrease in its support because of variety of human

activities so that living organisms in the waters are affected. One form of pollution that occurs in marine waters is in the form of heavy metals such as Hg, Cu, Cd, Cr, Pb, Fe, Zn and Ni [1]. At certain concentration, the presence of heavy metals in water may cause pollution to the waters.

* Corresponding author. Tel/Fax : +62-751-462193
Email address : deswati_ua@yahoo.co.id

Heavy metal that naturally found in sea water is very low, that ranges between 10^{-5} – 10^{-2} mg/L, while the matrix samples (salinity) is quite high [2]. Various analytical methods have been widely used for the determination of metals such as: potentiometry using ion selective electrodes, atomic absorption spectrophotometry, polarography but, these methods are not able to measure the metal ions at very small concentration, although they have previously been done pre-concentration by solvent extraction [3]. Thus it needs an alternative method that can overcome the above problems. Adsorptive stripping voltammetry was selected as an alternative method of analysis due to its high sensitivity, low detection limit in $\mu\text{g/L}$ level, simple and easy sample preparation. In adsorptive stripping voltammetry pre-concentration time is short, generally less than 1 min [4-6].

Adsorptive stripping voltammetry is one of the stripping voltammetry method that is widely used in the determination of heavy metals because it has a good sensitivity, metals with very small concentrations can be determined [6-7]. The method consists of several steps, namely: 1) formation of metal complexes with ligand; 2) absorption of complexes on the electrode surface, and 3) measurement of currents with potential scan the anode or cathode. The total accumulated metal is proportional to the time given [6,8].

The purpose of this technique is to create a more selective analysis and lower detection limit. Selectivity can be improved by selecting a suitable complexing agent (ligand) and supporting electrolyte [8]. Ligand is a substance that contains one or more free electron pairs that can act as an electron donor in the formation of complex compounds with metal ions. Ligand has a variety of functional groups that can interact with metal ions. Various types of ligands have been used in this research, among others: ammonium pyrrolidine dithiocarbamate (APDC), dimethyl glyoxime (DMG), oxine (8-hydroxy quinolin) and calcon. From the results of variations of ligand (complexing agent) studied, calcon showed a better complexing agent because it provides the highest peak current [9].

Calcon has $\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}_5\text{S}$ molecular formula with IUPAC name of 2-hydroxy-1-(2-hydroxy-1-naphthylazo)-naphthalen-4-sulfonic acid sodium salt, with a relative mass of 416.39 g/mol. This compound is a product of condensation reactions between benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) and acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$). Calcon can also be considered as ketones, a group of benzalacetophenone derivative from natural $\text{ArCOCH}=\text{CHAr}$ with orange color, such as curcumin, erydictyol, hesperitin and maringinin. Utilization of calcon is associated with the group of (2-hydroxy-1 naphthylazo) in the structure. Calcon role as a complexing is supported by the free electron pair (lone

pair electrons) from dihydroxyl group that can bind metal ions to form the metal-calcon complex [10].

Supporting electrolytes used in this research are KCl and NH_4Cl , which are required to suppress migration current, to control potential by reducing the resistance of the solution, to eliminate electromigration effects, and to maintain a constant ionic strength. Detection limit is lowered by increasing analyte concentration absorbed on electrode surface [8,11].

In previous research, adsorptive stripping voltammetric technique was used for the determination Ni(II) by using calcon [12]. The results obtained that optimum conditions for Ni(II) was at pH 11 and calcon concentration of 15 μM . The method of adsorptive stripping voltammetry is highly sensitive and selective so that it can be used to determine the species in solution at very small concentration [14], where Cr(VI) complexed with 2,2-bipyridine at 10 μM concentration, detection limit was 0.1692 $\mu\text{g/L}$ at pH 5 [15]. The advantages of this method are: high salinity of sea water samples did not interfere in the determination, selective, fast, simple, low running costs and can for the simultaneous determination of copper, bismuth and lead in the presence of thymolphthalexone [16] and simultaneous determination of Traces of cadmium and zinc by using 5-phenyl-1,2,4-triazol-3-tion (PTT) as complexes agent [17].

The problem of the research is that the presence of heavy metal ions (Cd, Cu, Pb and Zn) in sea waters is very dangerous, because it is toxic that damage the environment and biotic life, if the presence exceeded the minimum threshold is prescribed. Known concentration of the metal ions in waters is very small, while the matrix concentration (salinity) is large enough.

Existing methods for determination of metal ions is Flame Atomic Absorption Spectrophotometry (AAS), but these methods is not able to measure metal ions at very small concentration. Although pre-concentration was conducted to reduce or eliminate the high concentration salt from sea water using solvent extraction methods, the high salt concentration in the sample still interferes with the process of atomization in flame atomic absorption spectrophotometer [3]. Methods for the determination of metal ions in sea water by adsorptive stripping voltammetry still did not obtain suitable conditions.

To overcome the problem mentioned above a better condition of adsorptive stripping voltammetry is needed to get a selective and sensitive method. The parameter studied were variations of supporting electrolyte (KCl and NH_4Cl), selection of suitable complexing agent for each metal ion (calcon, APDC, DMG and oxine), variations of complexing agent concentration (calcon), variation of pH solution,

accumulation potential and accumulation time. To determine the precision, accuracy and sensitivity of method, relative standard deviation (SDR), recovery and detection limit were determined. The method at optimum condition was applied for the determination of Cd(II), Cu(II) Pb(II) and Zn(II) in seawater around Bungus, Padang City.

EXPERIMENTAL SECTION

Materials

The materials used for this study were Cd(NO₃)₂, Cu(NO₃)₂, Pb(NO₃)₂, Zn(NO₃)₂, KCl, NH₄Cl, concentrated HCl, concentrated HNO₃, acetate buffer, calcon, methanol, APDC, DMG, oxine, NH₄OH, sea water, Whatman filter paper, doubly distilled water and nitrogen gas.

Instrumentation

The instrument used in this study were 797 Computrace with Metrohm HMDE working electrode, a reference electrode Ag/AgCl/KCl 3 M, and the Pt electrode as a counter electrode; pH meter model 80 Griffin (Griffin & George Loughborough, UK), analytical balance Mettler AE 200, Toledo, OH, USA; and glassware commonly used in laboratory.

Procedure

Variations in supporting electrolyte (KCl and NH₄Cl)

A total of 10 mL of standard solution of Cd(II) 10 µg/L, 0.5 mL of 0.1 M KCl and 0.3 mL of 1 mM calcon was put into the voltammetric vessel. Potential was adjusted to -0.7 V, accumulation time of 60 sec at pH 7. Measurement performed to obtain the value of the peak current (Ip), the same was also done against 0.1 M NH₄Cl. The curve between peak current and concentration of supporting electrolyte (KCl and NH₄Cl) was constructed to determine the optimum supporting electrolyte. The same experiments was performed on Cu(II), Pb(II), Zn(II). From the results of these studies it was found that the optimum supporting electrolyte was KCl.

Variations of Complexing agent

Into the vessel of voltammetric, it was put 10 mL of standard solution of 10 µg/L Cd(II), 0.5 mL of 0.1 M KCl was added, pH was adjusted to 7, then added a variety of complexes, among others: calcon, APDC, DMG and oxine at a certain concentration into the solution of a total volume of 20 mL. Measurements were taken at the accumulation time of 60 sec. After measurement completed, the data in the form of the peak current value

(Ip) were generated. A curve between peak current and complexing agent was constructed to determine a suitable complexing agent for Cd(II). The same procedure were carried out for Cu(II), Pb(II) and Zn(II). From the results of this study the optimum complexing agent obtained for each metal ion was calcon. For subsequent studies, calcon was used as complex optimum.

Variation of calcon concentration

A total of 20 mL standard solution of 10 µg/L Cd(II) and 0.5 mL of 0.1 M KCl were put into the voltammetric vessel. Adjust accumulation potential to -0.7 V, accumulation time of 60 sec and pH 7 by the addition of NH₄OH. Calcon was added as a complexing agent at a concentration of 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.5 mM, 0.6 mM, 0.7 mM, 0.8 mM and 0.9 mM. Measurements performed to obtain the value of the peak current (Ip). A curve between the calcon concentration and the peak current (Ip) was constructed to determine the optimum concentration of calcon. The same thing was also done to Cu(II), Pb(II) and Zn(II).

Variation of pH

A total of 20 mL standard solution of 10 µg/L Cd(II) and 0.5 mL of 0.1 M KCl put into the voltammetric vessel was adjusted to the pH at the range of 3 – 9 by adding acetate buffer, then 0.3 mL calcon added at optimum concentration for each metal that has been obtained. It was adjusted the accumulation potential to -0.7 V for Cd(II) and Cu(II) whereas the -0.6 V for Pb(II) and Zn(II) and accumulation time of 60 sec. Measurements were performed to obtain the value of the peak current (Ip). A curve between pH variation and the peak current (Ip) was constructed to determine the optimum pH measurements.

Variation of potential accumulation

A total of 20 mL of standard solution of 10 µg/L Cd(II) and 0.5 mL of 0.1 M KCl were put into the voltammetric vessel. Then add 0.3 mL calcon the optimum concentration (the highest peak currents), pH optimum and the accumulation time 60 sec. After that the solution was measured by the variation of accumulation potential -0.3 to -0.8 V. Furthermore a curve between the peak current and accumulation potential (Ip) was constructed to determine the optimum accumulation potential. The same thing was also done to the Cu(II), Pb(II) and Zn(II).

Variation of accumulation time

A total of 20 mL standard solution of 10 µg/L Cd(II) and 0.5 mL of 0.1 M KCl were put into the

voltammetric vessel, then added 0.3 mL calcon to the optimum concentration. Accumulation potential is set in accordance with the obtained optimum accumulation potential, the pH optimum. Measurements were performed to obtain the value of the peak current (I_p). A curve between variation times of accumulation with peak current (I_p) was constructed to determine the accumulation time. The same things were done to Cu(II), Pb(II) and Zn(II).

Determination of the Relative Standard Deviation

10 mL standard solution of 10 $\mu\text{g/L}$ Cd(II) and 10 mL of 0.1 M KCl were put into voltammetric vessel, pH was adjusted to 7.0 by addition of NH_4OH , then was added 0.3 mL of 0.5 mM calcon, deposition potential -0.7 V and the accumulation time 70 sec. Performed measurements with repetition as much as 8 times. The same things were done for Cu(II), Pb(II) and Zn(II) [18-19].

Application Method

The sample used in this study taken in the form of sea water around Bungus, Padang City. Samples taken were preserved with 65% HNO_3 with a ratio of 1:1000.

RESULT AND DISCUSSION

In this study the determination of Cd(II), Cu(II), Pb(II) and Zn(II) by adsorptive stripping voltammetry (ASV) was conducted. The optimum measurement conditions were required for measurement. Therefore several parameters namely; variation supporting electrolyte (NH_4Cl and KCl), complexing agent variations include: APDC, DMG, and oxine calcon, variations in the concentration of complex optimum (calcon), pH of solution, accumulation potential and accumulation time variations were studied.

Variations supporting electrolyte

The influence of supporting electrolyte 0.1 M NH_4Cl and 0.1 M KCl against the peak current (I_p) for the metals Cd(II), Cu(II), Pb(II) and Zn(II) with the potential accumulation of -0.7 V, deposition time 60 sec, 0.3 mL of 1 mM calcon were shown in Table 1.

The addition of supporting electrolyte serves as to conduct electrical current in the solution so that the analyte is not affected by a given difference of potential changes rapidly. In addition, to suppress the flow of migration, controlling the potential for reduced solution resistance as well as keeping the total ionic strength constant [8,11]. At the table, it is showed that the addition of supporting electrolyte 0.1 M NH_4Cl and 0.1 M KCl against the flow generated peak for Cd(II) there is a little difference of 0.003 μA , while for the metal ions Cu(II),

Table 1. The relationship between the variation of supporting electrolyte on the peak current (I_p)

0.1 M Supporting Electrolyte	Peak Current (I_p)			
	Cd(II) (μA)	Cu(II) (μA)	Pb(II) (μA)	Zn(II) (μA)
NH_4Cl	0.075	11.550	0.013	15.510
KCl	0.078	33.790	0.021	48.320

Table 2. Effect of variation the complexing agent on peak current (I_p)

Variation of the complex	Peak current (I_p)			
	Cd(II) (μA)	Cu(II) (μA)	Pb(II) (μA)	Zn(II) (μA)
APDC	0.004	Nd	Nd	36.470
DMG	0.062	29.520	1.580	29.690
Calcon	0.078	33.800	1.740	48.460
Oxine	0.040	0.022	0.020	Nd

Nd = Not detected

Pb(II) and Zn(II) with the addition of supporting electrolyte 0.1 M NH_4Cl and 0.1 M KCl there were significant differences. The resulting peak flow for the third highest on the metal ions is to use a 0.3 M KCl. This is because K^+ ions are smaller than the ion NH_4^+ , so its speed to overcome the movement of ions in solution (electro migration) is much greater than NH_4^+ ion. As a result, the peak current generated using KCl as the supporting electrolyte is much greater than using NH_4Cl . For subsequent studies 0.1 M KCl was used as supporting electrolyte.

Variations complexing agent

Ammonium pyrrolydine dithiocarbamate (APDC), dimethyl glyoxime (DMG), oxine and calcon serves as a complexing agents, giving effect to the voltammogram of Cd(II), Cu(II), Pb(II) and Zn(II). Effects may be studied by comparing the peak current generated from metal complexes with the complexing agents mentioned above. The measurement results can be seen in Table 2. Measurements were made with the same complex concentration of 1 mM, 60 sec accumulation time, accumulation potential -0.7 volts in 0.5 mL of 0.1 M KCl at pH: 7.0: 6.0: 4.0 and pH 3.6 for Cd(II), Cu(II), Pb(II) and Zn(II).

Table 2 shows that the metal ions Cd(II), Cu(II), Pb(II) and Zn(II) can be detected with the use calcon as complex, which giving the highest peak current, its value in a row 77.590 μA , 33.800 μA , 1.740 μA and 48.460 μA . Cd(II), Cu(II), Pb(II) and Zn(II) can form complexes with dimethyl glyoxime (DMG), the resulting peak current 0.062 μA , 29.520 μA , 1.580 μA and 29.690 μA , the current generated were smaller than calcon used as complexing agent. The use of APDC as a complexes agent did not provide the peak current (not detectable) especially for Cu(II) and Pb(II), this is

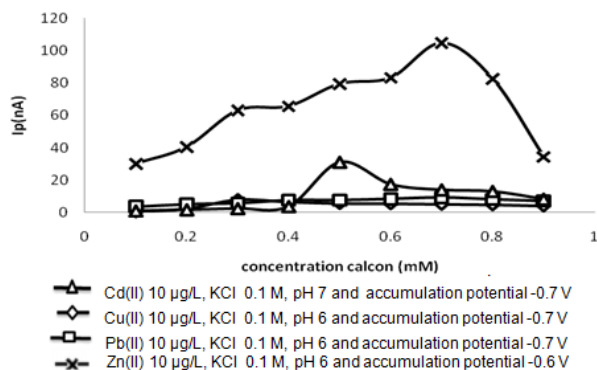


Fig 1. The effect of calcon concentration on peak current

due to APDC does not form complexes with Cu(II) and Pb(II). However, Zn(II) forming complexes with APDC which produced a peak current of 36.47 μ A can be seen in Table 2. The use of oxine as complexing agent results in peak current 0.040 μ A, 0.220 μ A, 0.020 μ A and undetectable, respectively for the metal ions Cd(II), Cu(II), Pb(II) and Zn(II). Metal ions Pb(II) and Zn(II) produced very small currents, even though ions Zn(II) peak current produced is not detected. It means here that oxine did not form complexes with Pb(II) or with Zn(II). From the results shown in Table 2, calcon was chosen as the optimum complexing agent. For subsequent studies calcon was used as a complexing agent,

Variation of calcon concentration

In this study the relationship between the concentration calcon with peak current of a standard solution of Cd(II), Cu(II), Pb(II) and Zn(II) each 10 μ g/L with a potential accumulation -0.7 V to Cd(II), Cu(II), Pb(II) and -0.6 V for Zn(II), accumulation time 60 sec, pH 7 for Cd(II) and pH 6 for Cu(II), Pb(II) and Zn(II) was determined. The concentration variation calcon in 20 mL of test solution were 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.5 mM, 0.6 mM, 0.7 mM, 0.8 mM and 0.9 mM. The result can be seen in Fig. 1.

Fig. 1 shows that the peak current increased with increasing concentration below 0.4 mM calcon for Cu(II) and 0.5 mM for Cd(II). This happened because there were still Cd(II) and Cu(II) that did not yet form complex with calcon. At concentrations above 0.5 mM calcon a decline in peak current existed. This is due to the occurrence of competition between the ligand absorbed on the electrode surface at deposition step (pre-concentration) and forming complexes with metal ions. Peak currents generated as a result of reduction of metal-ligand complexes absorbed on the surface of the working electrode at stripping step. The peak current generated depended upon calcon concentration used. At higher calcon concentration, it was difficult the metal-

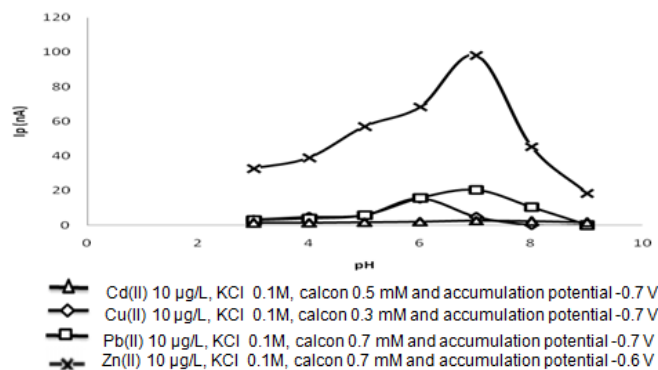


Fig 2. The effect of pH on peak current

ligand complex to be reduced so that the resulting peak current getting smaller. As for Pb(II) and Zn(II) an increase in the peak current at calcon concentration 0.1 mM – 0.7 mM, indicated the formation of complexes of Pb(II) with calcon or Zn(II) with increasing calcon. At concentrations above 0.7 mM calcon, a decline in peak current made possible the competition between complexing agent as a ligand in binding to metal ions so that the current decreased. For that reason, calcon at 0.5 mM concentration was chosen as the optimum conditions for Cd(II), 0.3 mM for Cu(II), while 0.7 mM for Pb(II) and Zn(II). At the optimum concentration, metal ions and complexing agent (calcon) formed a complete complex so as to provide optimum current.

Variation of pH

The complex formation between the Cd(II), Cu(II), Pb(II) ions and Zn(II) ions with calcon at deposition (pre-concentration) step were affected by pH. At the proper pH it was expected more and more Cd-calcon, Cu-calcon, Pb-calcon and Zn-calcon complexes formed at the electrode surface so that they would produce high peak current at the time of measurement. Effect of pH on peak current (I_p) was studied for a standard solution of Cd(II), Cu(II), Pb(II) and Zn(II) at a concentration of 10 μ g/L each, by varying the pH of 5 – 9. Fig. 2 shows that the peak currents are influenced by pH for each metal ion. At pH 3 to pH 6, Cu(II) produced increasing peak currents, while ions Cd(II), Pb(II) and Zn(II) increased to pH 7. This was because with increasing pH of the solution, there were more Cd(II), Cu(II), Pb(II) and Zn(II) in the form of free ions. As a result, the ions were trapped on the surface of the working electrode forming metal-calcon complex, so that the resulting peak currents increased. The pH also affects the stability of the complex formed, and also affected the concentration of analyte deposited on the working electrode, increasing peak current generated. High peak current occurs at pH 6 optimum

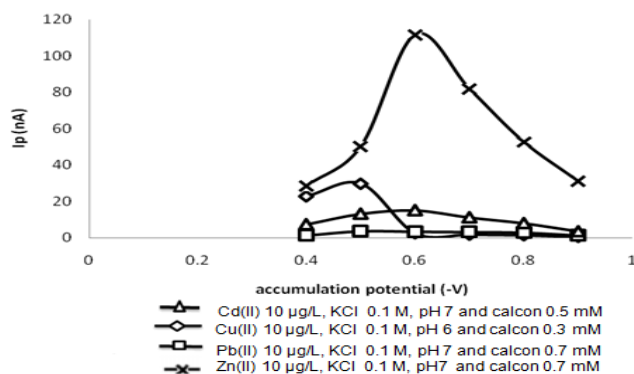


Fig 3. The effect of accumulation potential on peak current

for ion Cu(II) and pH 7 for Cd(II), Pb(II) and Zn(II), because at these pH, there were many metal ions in the form of free ions, so that many Cd(II), Cu(II), Pb(II) and Zn(II) got trapped on the electrode surface thus forming complexes with calcon.

At pH 7 to pH 9 with a peak current decreased, this was due to complex formation between the ions Cd(II), Cu(II), Pb(II) and Zn(II) with calcon disturbed by OH⁻ ions becoming more and more in solution with increasing pH. At high pH the metal ions would be more dominant OH⁻ ions reacting to form metal hydroxide, which reacted with calcons reduced. At a certain pH the metal ions formed precipitated as its hydroxides and, consequently resulting smaller current.

Variation of accumulation potential

In this study the determination of the relationship between the accumulation potential with peak current of Cd(II), Cu(II), Pb(II) and Zn(II) was examined in the range -0.4 V to -0.9 V. Accumulation potential is the potential at the time of analyte deposited on the working electrode. The result can be seen in Fig. 3.

Curve shows that in every variation of accumulation potential tested, it gave a different value of peak current. For Cd(II) and Zn(II) at a potential of -0.4 V to -0.6 V peak current produced was increasing, while for the ions Cu(II) and Pb(II) in the range of potential -0.4 V to -0.5 V. In the potential range -0.6 to -0.9 V curve dropped down significantly, especially for Cu(II). This suggests a process of deposition (accumulation) of the analyte complex on the surface of the working electrode which reaches a maximum at -0.5 V to Cu(II) and Pb(II) and -0.6 V to Cd(II) and Zn(II). For Cd(II) and Zn(II) can be seen from Fig. 3, at a potential of -0.4 V to -0.6 V the curve rose with a relatively small increase for the ions Cd(II), whereas for Zn(II) the increase curve (peak current) was large enough. At -0.5 V potential was optimum accumulation potential for Cu(II) and Pb(II), while for Cd(II) and Zn(II) -0.6 V, because the peak

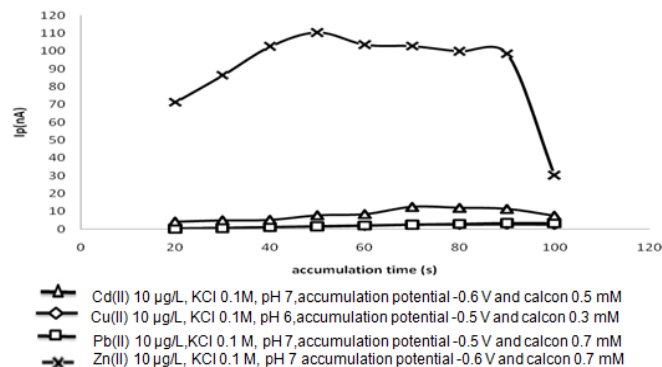


Fig 4. The relationship between the accumulation time on peak current

currents was generated at the maximum. At potential -0.7 V current reduced, this was caused by reduction of analyte complex during deposition process [8].

Variation of accumulation time

Accumulation time is the time when the analyte accumulated or deposited on the surface of the working electrode in the form of Hanging Mercury Drop Electrode (HMDE). Effect on the deposition time during the accumulation step (pre-concentration). At the accumulation time pre-concentration was useful to improve sensitivity and lower detection limits [8,11]. The time of accumulation of Cd(II), Cu(II), Pb(II) and Zn(II) affected the stability of the complex formed on the electrode surface. The study carried out the determination of the relationship between accumulation times with peak currents that were tested, by varying the accumulation time as follows: 20, 30, 40, 50, 60, 70, 80, 90 and 100 sec. The result can be seen in Fig.4.

Fig. 4, shows that the accumulation time affected peak currents of Cd(II), Cu(II), Pb(II) and Zn(II). The increase in accumulation time increased the peak current, since Cd(II), Cu(II), Pb(II) and Zn(II) ions bonded to calcon accumulated on the working electrode increased until they finally saturated.

At the time of accumulation, measurements with 20 sec to 60 sec increasing the peak current was not so great, especially for the peak current Cd(II), Cu(II) and Pb(II) because the ions Cd(II), Cu(II) and Pb(II) that accumulated at the working electrode was still small. The peak current on accumulation time of 70 to 90 sec increased slightly. At accumulation time of 90 sec, the peak current increased significantly, especially for the Cu(II) and Pb(II) ions. Time of 90 sec was chosen as the optimum accumulation time for the next determination of ion Cu(II) and Pb(II), while for Cd(II) it was 70 sec. Accumulation time of more than 90 sec did not increase the peak current, whereas, it, otherwise,

even decreased. Longer accumulation time would cause saturation of electrode [8,11].

In Fig. 4, it can also be seen that the accumulation of 20 to 50 sec the peak current produced by Zn(II) was quite high when compared with the other three metal ions. It meant that quite large Zn(II) accumulated at the working electrode so that the current increased. At the accumulation time of more than 50 sec did not increase in peak current, even it tended to decrease. This happened because of the working electrode where the process of accumulation has been saturated so that the resulting current also decreased. Accumulation time of 50 sec was used as the optimum accumulation time for the determination of Zn(II) hereinafter.

Relative standard deviation (RSD)

The relative standard deviation shows the precision of the method at the same operating conditions. The determination of the relative standard deviation performed at optimum conditions have been defined above. At the optimum conditions with 8 times replicates ($n = 8$) measurements of 10 $\mu\text{g/L}$ standard solution Cd(II), Cu(II), Pb(II) and Zn(II) were 7.80%, 4.25%, 8.70% and 0.86%. The result can be seen in Table 3.

According to the AOAC method, the value of relative standard deviation was smaller than 8% at concentration of 10 $\mu\text{g/L}$. That means this method has a high degree of precision because the RSD obtained for each metals was smaller than 8%, except for Pb(II) that was greater than 8%.

Recovery

To determine the level of accuracy of this method, it was necessary to determine the value of recovery. Samples of known concentration were added the number of standard solution, and then compared with the concentrations of samples and standards added. In this study the recovery of sea water samples studied was taken from Bungus, Padang City. The results of recovery of Cd(II), Cu(II), Pb(II) and Zn(II) by adsorptive stripping voltammetry at the optimum conditions, its value obtained were 98.68%, 97.99%, 96.17% and 99.96%, respectively.

According to the AOAC method, the percent recovery for the solution with the concentration of 50 $\mu\text{g/L}$ was in the range of 70% – 110%. That is, this method has high accuracy [18].

This method were applied to the determination of Cd(II), Cu(II), Pb(II) and Zn(II) in seawater around the waters of Bungus, Padang City, using the optimum conditions for measurement that had been obtained for each metal ion them. Measurements were conducted by standard addition method. The concentration obtained for

Table 3. Measurement results of 10 $\mu\text{g/L}$ Cd(II), Cu(II), Pb(II) and Zn(II)

Replicates	Peak current (μA)			
	Cd(II)	Cu(II)	Pb(II)	Zn(II)
1	4.260	46.360	4.710	73.340
2	4.750	47.310	5.170	73.370
3	4.740	46.150	4.220	72.810
4	4.020	41.700	3.990	71.410
5	4.360	44.290	4.130	73.200
6	5.140	45.500	4.490	73.090
7	4.830	45.020	4.460	72.960
8	4.500	47.880	4.150	72.790
Average	4.575	45.526	4.415	72.871
SD	0.3588	1.9358	0.3844	0.6299
RSD	7.80%	4.25%	8.70%	0.86%

Cd(II), Cu(II), Pb(II) and Zn(II) in seawater samples Bungus, Padang City were 13.200 $\mu\text{g/L}$; 0.089 $\mu\text{g/L}$; 17.163 $\mu\text{g/L}$ and 62.000 $\mu\text{g/L}$, respectively.

CONCLUSION

It can be concluded that the optimum conditions for measurement of Cd(II), Cu(II), Pb(II) and Zn(II) by adsorptive stripping voltammetry were: 0.1 M KCl as optimum supporting electrolyte, calcon as the optimum complexing agent. Calcon optimum concentration obtained for Cd(II) 0.5 mM, Cu(II) 0.3 mM while 0.7 mM for Pb(II) and Zn(II), at pH 7 for Cd(II), Pb(II) and Zn(II), whereas for Cu(II) at pH 6, the accumulation potential - 0.5 V for Cu(II) and Pb(II), while -0.6 V for Cd (II) and Zn(II) and the accumulation time of Cd(II) 70 s, Cu(II) and Pb(II) 90 sec while the Zn(II) 50 sec. At the optimum conditions, the relative standard deviation was obtained with 8 replicates ($n = 8$) measurements standard solution Cd(II), Cu(II), Pb(II) and Zn(II) 10 $\mu\text{g/L}$ were: 7.80%, 4.25%, 8.70% and 0.86%, respectively. This method was applied to the determination of Cd(II), Cu(II) and Pb(II) directly in seawater waters of Bungus, Padang City. The concentration obtained were: 13.200 $\mu\text{g/L}$ for Cd(II), 17.100 $\mu\text{g/L}$ for Cu(II), 0.089 $\mu\text{g/L}$ for Pb(II), while for Zn(II) 62.000 $\mu\text{g/L}$ with a recovery value (Recovery) for each Cd(II), Cu(II), Pb(II) and Zn(II) were 98.68%, 97.99%, 96.17% and 99.96%, respectively.

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