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The Sensitive and Simple Determination of Trace Metals Fe, Co, Ni and Cr in Water Samples by Adsorptive Stripping Voltammetry (AdSV) in The Presence of Calcon

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ABSTRACT

Adsorptive stripping voltammetry has been used for trace determination of Fe(III), Co(II), Ni(II) and Cr(III) using calcon as a complexing agent. The aim of this study was to get optimum condition for the determination of Fe(III), Co(II), Ni(II) and Cr(III). In this case, the optimum conditions were reached concentration of 0.6 mmol/L calcon for Fe(III) and Ni(II), Co(II) 0.7 mmol/L while 0.4 mmol/L for Cr(III), pH 6 for Fe(III), pH 7 for Co(III) and Ni(II) and pH 5 for Cr(III), accumulation potential -0.8 Volt for Fe(III), -0.7 Volt for Ni(II), -0.4 Volt for Co(III) and -0.5 Volt for Cr(III) and the accumulation time 50 s for Fe(III), 70 s for Co(III), 60 s for Ni(II) and 90 s Cr(III). At the optimum conditions the relative standard deviation were 0.52%, 1.77%, 0.52% and 1.34% for Fe(III), Co(II), Ni(II) and Cr(III) for eight replicates ($n = 8$) measurements of 10 $\mu\text{g/L}$ Fe(III), Co(III), Ni(II) and Cr(III). The method was applied to the direct determination of Fe(III), Co(III), Ni(II) and Cr(III) in seawater around of Bungus district, water tap and water of Lubuk Minturun district of Padang city. Concentration of each metal ions of all three samples were aqual, ie.: 697.6 L, 1046.7, 14.7 $\mu\text{g/L}$ for Fe(III); 255.6, 139.5, 0.1 for Co(III), 509.66 $\mu\text{g/L}$, 112.57 $\mu\text{g/L}$, 19.59 $\mu\text{g/L}$ for Ni(II) and 232.1, 180.2, 15.2 $\mu\text{g/L}$ for Cr(III) with recovery of 100.5%, 102.6%, 97.4% and 99.5% for Fe(III), Co(II), Ni(II) and Cr(III), respectively.

Keywords: trace metal analysis, adsorptive stripping voltammetry

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INTRODUCTION

Heavy metal pollution is a threat to human health, animals and the ecosystem, mainly caused by rapid industrial and technology activities and their consequences and poses a serious environmental problem cause of high level of toxicity [1]. At certain concentration, the presence of heavy metals in water may cause pollution to the waters.

Toxic metal ion such as Fe, Co, Ni and Cr in water and the environment is very dangerous, because it is toxic that damages the environment and biotics life, if the presence exceeded the minimum threshold is prescribed. It is well known that concentration of the metal ions in waters and the environment, soil, rocks and biological materials is very small (trace) in the order of ng/kg to mg/kg, while the sample matrix, namely salt content in sea water is large enough and also bound in a complex matrix [2].

The existing methods for the analysis of metal ions such as method of Flame Atomic Absorption Spectrometry (FAAS) and inductively coupled plasma atomic method of emissions spectrophotometry (ICP-AES). However, both methods more over expensive and less practical and these methods are not able to measure the metal ions at trace level [3]. Although they have previously been done pre-concentration by solvent extraction to reduce the high salinity of a sample of sea water [4]. Therefore, is needed an alternative method that can overcome the limitations of the two methods.

Adsorptive stripping voltammetry was chosen as an alternative method of analysis because it has many advantages such as: high salt content of sea water does not interfere, high sensitivity, low detection limit in ug/L, simple and easy sample preparation, rapid analysis, less infra structure [5-7]. In addition, with this method it is possible to learn chemical species of heavy metals [8-9], which can not be done with other methods.

This method can be used for the simultaneous determination of Cu and Pb in seawater by using calcon as complexing agent [10]. Simultaneous determination of Cd, Cu, Pb and Zn in sea water by AdSV [11], Simultaneous determination of cadmium, copper and lead in sea water by AdSV [12], the simultaneous determination of copper, bismuth and lead in the presence of thymolphthalexone [13] and simultaneous determination of trace of cadmium and zinc by using 5-phenyl-1,2,4-triazol-3-tion (PTT) as complexes agent [14].

Almost all methods of determination of metals in very small amounts require considerable time on pre-concentration step prior to measurement. In adsorptive stripping voltammetry pre-concentration time is short, generally less than one minute [15]. The purpose of this technique is to make the analysis more selective and lower detection limit. Selectivity can be improved by selecting the ligand and the electrolyte solution, which is used the more selective ligand selectivity, the better. Detection limit lowered by increasing the concentration of the analyte adsorbed on the electrode surface [5,16].

The use of adsorptive stripping voltammetry technique has been reported for the determination of metals Cd, Cu, Pb and Zn in seawater using optimum calcon as complexing and 0.1 M KCl supporting electrolyte [5]. Furthermore, the results of testing being conducted optimum conditions that have been obtained are, for the analysis of metals Cd,

Cu, Pb and Zn in sea water simultaneously, using calcon as complexing and 0.1 M KCl as supporting electrolyte [11], the determination of Ni with dimethylglyoxime [17]. Santos-Echheandia [19] have reported direct determination of Co, Cu, Fe, Ni and V for simultaneous with adsorptive cathodic stripping voltammetry using a mixture of ligand (dimethyl glyoxime and chatecol). Furthermore, reported the direct determination of Ni and Co simultaneously in natural water and sediment to the cathode adsorptive stripping voltammetry, using dimethyl glyoxime as complexing agent. Saryati and Wardiyati [20] was used adsorptive stripping voltammetry for the determination of Fe and Al in environmental samples by using complexing solochrome violet RS (SVRS), supporting electrolyte acetate buffer pH 4.5. Furthermore, Kenji and Nakaya [21], have reported a method for determining the ratio of Cr(III) in seawater and species.

To overcome the problem mentioned above a better condition of adsorptive stripping voltammetry is needed to get a selective and sensitive method. The parameters investigated was variations of calcon concentration, variation of pH solution, accumulation potential and accumulation time. To determine the precision and accuracy of method, relative standard deviation (RSD) and recovery were determined. The method at optimum condition was applied for the direct determination of Fe(III), Co(III), Ni(II) and Cr(III) in seawater around of Bungus district, tap water and environmental water of Lubuk Minturun district of Padang city, Indonesia.

EXPERIMENTAL

Reagent and Instruments

The reagents used for this study were analytical grade namely, NH_4Cl , calcon, HNO_3 , CHCl_3 , acetate buffer, NH_4OH , methanol, nitrogen gas, double distilled water. Water sample are collected from Lubuk minturun and Bungus district. Various chemicals were purchased from Merck and the aqueous solution of Fe, Co, Ni and Cr 1000 mg/L was prepared by using the analytical grade.

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

Procedure

The aim of this study was to obtain the optimum condition of each metal ion Fe, Co, Ni and Cr by adsorptive stripping voltammetry. Therefore studied the effect of the following parameters namely, variations of concentration calcon of 0.2 mmol/L calcon to 0.9 mmol/L variation of pH 3 to pH 9, accumulation potential of - 0.2 V to - 1.1 V and accumulation time variation of 20 s to 100 s. To determine the precision and accuracy of method relative standard deviation (RSD) and recovery were determined [5]

RESULTS AND DISCUSSION

Variation of calcon concentration

From the results of previous studied, calcon showed a better complexing agent because it provides the highest peak current [5]. The effect of variation of calcon concentration on the adsorptive stripping peak current of standard solution of Fe(III), Co(II), Ni(II) and Cr(III) 10 µg/L was studied. The variation of calcon concentration in 20 mL test solution were: 0.1, -0.9 mM. The result can be seen in Fig. 1.

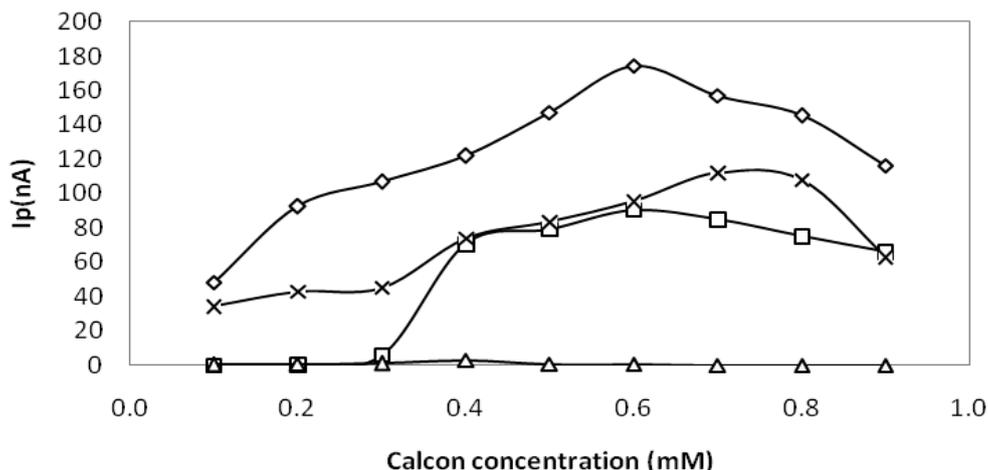


Figure 1: The effect of calcon concentration of peak current

- Fe 10 µg/L KCl 0.1 M, pH 6, accumulation potential -0.8 V
- × Co 10 µg/L KCl 0.1 M, pH 7, accumulation potential -0.4 V
- ◇ Ni 10 µg/L KCl 0.1 M, pH 6, accumulation potential -0.7 V
- △ Cr 10 µg/L KCl 0.1 M, pH 5, accumulation potential -0.5 V

The obtained results show that the adsorptive stripping peak current of Fe, Co, Ni and Cr-calcon complexes were improved by increasing the calcon concentration up to 0.6 mmol/L for ion Co(II) and Ni(II). Fig. 1 can be seen, the peak current increased with increasing concentrations of calcon, below 0.4 mmol/LM for Fe(III) peak current produced is very small. This is because there is very little ion Fe(III) which reacts with calcon to form complex compounds, while for ion Co(III) and Ni(II) the resulting current is large enough then it's complex formed between the metal ions with calcon. At concentrations above 0.4 mmol/L calcon up to 0.6 mmol/L increased peak current, especially for Fe(III) and Ni(II), while for the Co(III) to 0.7 mmol/L, mean complex is formed between the ion- The metal ions with calcon and adsorbed on the working electrode (HMDE). For ion Cr(III) concentration increased calcon resulting current does not change, except at a concentration of 0.4 mM produced peak current of 3.06 nA, then tended to decline and undetectable results can be seen in Figure 1. At concentrations above 0.6 mmol/L calcon for Fe and Ni ions and ion 0.7 mmol/L for Co(III) peak current decreased. This is due to the competition between ligands adsorbed on the electrode surface at the deposition step (pre-concentration) and forming complexes with metal ions. Peak currents generated as a result of the reduction of metal-ligand complexes are adsorbed 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-ligand complex

to be reduced so that the resulting peak current getting smaller. Therefore, the calcon concentration of 0.6 mmol/L was chosen as optimum value for determination of Fe(III) and Ni(II), 0.7 mmol/L for Co(III) and 0.4 mmol/l for Cr(III).

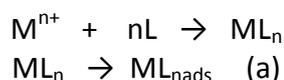
Table1: Measurement results of 10 ug / L Standard Solution of Fe(III), Co (II), Ni(II) and Cr(III)

Replicates	Peak current (nA)			
	Fe	Co	Ni	Cr
1	50.15	218.61	117.38	382.42
2	50.14	219.40	116.88	390.84
3	50.75	220.29	116.84	398.60
4	50.07	224.56	116.74	389.76
5	50.70	228.37	116.10	391.22
6	50.40	222.31	116.23	383.92
7	50.27	224.58	115.84	387.26
8	50.90	229.12	115.58	393.71
Average	50.33	223.40	116.44	389.71
SD	0.26	3.96	0.61	5.23
RSD	0.52 %	1.77 %	0.52 %	1.34 %

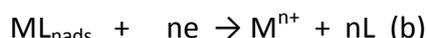
Variation of pH

The complex formation between the Fe(III), Co(III), Ni(II) ions and Cr(III) ions with calcon at accumulation step were affected by pH. The reaction process is described in reaction (a)

Accumulation step:



Stripping step:



At the proper pH it was expected more and more Fe-calcon, Co-calcon, Ni-calcon and Cr-calcon complexes formed at the electrode surface, so that they would produce optimum peak current at the time of measurement. The influences of pH on the adsorptive peak currents (Ip) of Fe, Co, Ni and Cr were studied in the pH range of 3 to 9. The result is shown in Fig. 2. At accumulation (pre-concentration) step, the complex formation between the Fe(III), Co(II), Ni(II) and Cr(III) ions with calcon were affected by pH. The results shown that the peak current of the Fe-calcon complex increasing pH from 3 to 6, while for Co-calcon and nickel-calcon until pH 7 and chromium at pH 5. The pH affected 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 for ion Fe(III), pH 7 for Co(II) and Ni(II) ions, while for Cr(III) ion at pH 5, because at these pH, there were many metals ions in the form of free ions, so that many Fe(III), Co(II), Ni(II) and Cr(III) got trapped on the electrode surface thus forming complexes with calcon. At pH 5 to 9 with the peak current decreased for Cr(III), while for Co(II) and Ni(II) at pH 7 to 9, this was due to complex formation between the ions Fe(III), Co(II), Ni(II) and Cr(III) 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 reacted to form metal

hydroxide, which reacted with calcon reduced. At a certain pH the metal ions formed precipitated as its hydroxide and consequently resulting smaller current.

This is because with the increasing pH of the solution, the more ions Fe(III), Co(III), Ni(II) and Cr(III) in the form of the free ions. As a result, the ions trapped on the surface of the working electrode and the metal complex-forming calcon, so that the resulting peak current increases. The pH also affects the stability of the complex formed, will also affect the concentration of the analyte is deposited on the working electrode as well as the resulting peak currents. Optimum high peak current occurs at pH 6 for ion Fe(III) and pH 7 for Co(III) and Ni(II) ions, while for Cr(III) at pH 5.

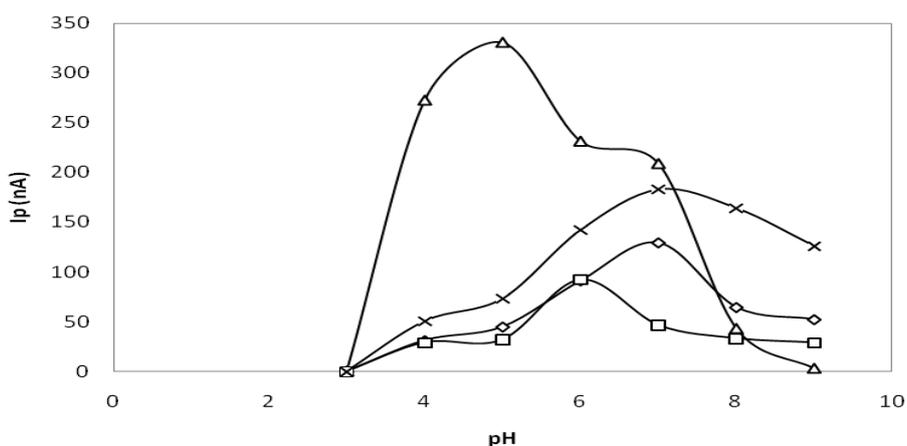


Figure 2. The relationship between variations of pH on peak current

- Fe 10 µg/L KCl 0.1 M, potent accumulation -0.8 V, 0.6 mM calcon
- x— Co 10 µg/L KCl 0.1 M, potent accumulation -0.4 V, 0.7 mM calcon
- ◇— Ni 10 µg/L KCl 0.1 M, potent accumulation -0.7 V, 0.6 mM calcon
- △— Cr 10 µg/L KCl 0.1 M, potent accumulation -0.5 V, 0.4 mM calcon

At pH 6 to pH 9 to Fe(III) and pH 7 to pH 9 to Co(III) and Ni(II) peak current decreased, this was due to the formation of complexes between the ion Fe(III), Co(III) and Ni(II) ions calcon be disturbed by the growing number of OH⁻ in solution with increasing pH.

Variation of accumulation potential

In this research, the determination of the relationship between the accumulation potential with peak currents of Fe(III), Co(III), Ni(II) and Cr(III) were tested in the range of -0.2 volts to -1.1 volts. Accumulation potential is the potential at the time of the analyte deposited on the working electrode. The result can be seen in Fig. 3 below.

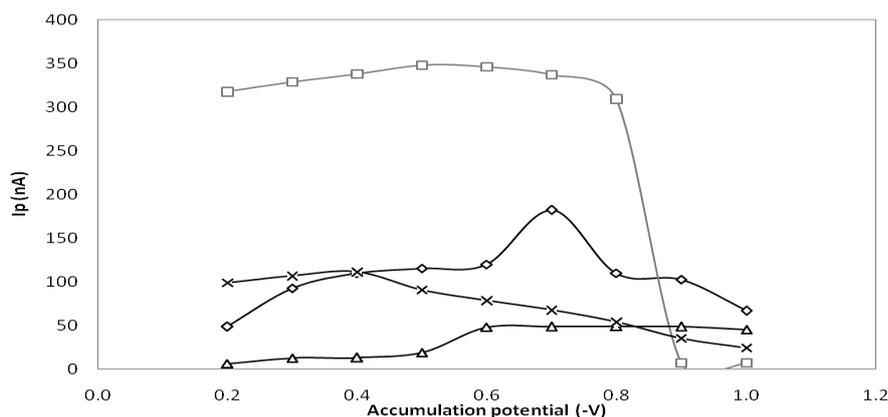


Figure 3. The relationship between accumulation potential on peak current

- Fe 10 µg/L KCl 0.1 M, pH 6, 0.6 mM calcon, 50 s
- ×— Co 10 µg/L KCl 0.1 M, pH 7, 0.7 mM calcon, 70 s
- ◇— Ni 10 µg/L KCl 0.1 M, pH 7, 0.6 mM calcon, 60 s
- △— Cr 10 µg/L KCl 0.1 M, pH 5, 0.4 mM calcon, 90 s

In the above curve can be seen, in every variation of accumulation potential were tested, giving values of different peak currents. For metal ions Fe(III) and Ni(II) at potentials -0.2 to -0.7 Volts peak current generated is increasing, while for ion Co(III) in the potential range -0.2 Volts to -0.4 Volt and for Cr(III) in the potential range -0.2 to -0.5 Volt. In the potential range -0.4 to -1.1 Volt curve down significantly, especially for metal ions Co (II). This suggests a process of deposition (accumulation) of analytes in complex working electrode surface reaches a maximum at -0.4 Volt to Co (II), while for Fe(III) and Ni(II) at -0.7 Volt. At -0.4 volt potential is optimum accumulation potential for Co (III), while for Fe (III) and Ni (II) -0.7V and -0.5 Volt to Cr (III) due to the resulting peak current maximum possible.

Variation of accumulation time

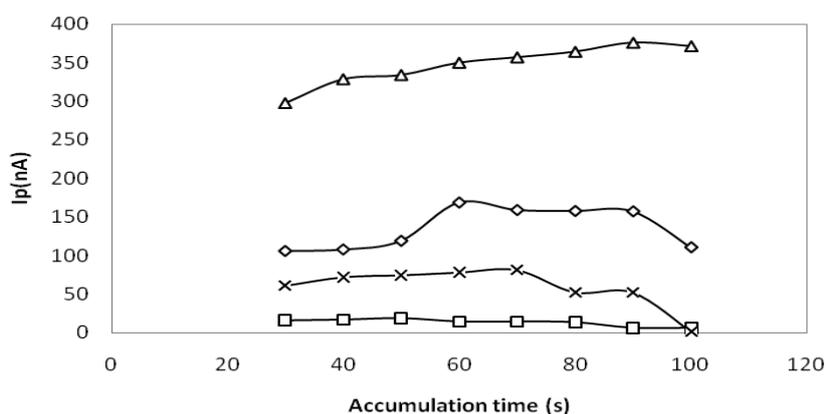


Figure 4. The relationship between time accumulation on peak current

- Fe 10 µg/L KCl 0.1 M, pH 6, 0.6 mM calcon, potential -0.8 V
- ×— Co 10 µg/L KCl 0.1 M, pH 7, 0.7 mM calcon, potential -0.7 V
- ◇— Ni 10 µg/L KCl 0.1 M, pH 7, 0.6 mM calcon, potential -0.4V
- △— Cr 10 µg/L KCl 0.1 M, pH 5, 0.4 mM calcon, potential -0.5 V

Accumulation time is the time when the analyte accumulated or deposited on the surface of the working electrode Drops Hanging Mercury Electrode (HMDE). Effect on the deposition time during the accumulation step (pre-concentration). At the accumulation time pre-concentration was useful to improved sensitivity and lower detection limit [16, 22]. The length of time the accumulation of Fe(III), Co (II), Ni(II) and Cr(III) affects the stability of the complex formed on the electrode surface. In this study, to determine the relationship between time accumulation with a peak current tested, by varying the accumulation time as follows: 30, 40, 50, 60,70, 80, 90 and 100 s. The result can be seen in Fig. 4.

Fig. 4, shows that the long time effect on the accumulation of high peak currents of Fe(III), Co (II), Ni(II) and Cr(III). High peak current increases at the longer accumulation time, except for the ion Fe(III) because of the length of time the accumulation of non-significant effect.

Relative Standard Deviation (RSD)

Relative standard deviation is used to look at the precision of the method is the same operating conditions. The determination of the relative standard deviation performed at optimum conditions have been defined above. At the optimum conditions with eight times replicates (n = 8) measurements of 10 ug/L standard solution of Fe(III), Co (II), Ni(II) and Cr(III) were : 0.52%, 1.77%, 0.52% and 1.34%. The result can be seen in Table 2.

According to the AOAC method, the value of relative standard deviation was smaller than 8% at concentration of 10 ug/L. That mean this method has a high degree of precision because the RSD obtained for each metals was smaller than 8%.

Table 2: Measurement results of concentration of Fe(III), Co(III), Ni(II) and Cr(III) in samples.

Samples	Concentration (µg/L)			
	Fe	Co	Ni	Cr
Seawater	697.62	255.64	509.66	232.06
Tap water	1046.71	139.48	112.57	180.17
Water of Lubuk Minturun	14.72	0.05	19.59	15.19

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 amount 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 Fe (III), Co (II), Ni (II) and Cr (III) by adsorptive stripping voltammetry at the optimum conditions, its value obtained were: 100.50%, 102.64%, 97.39% and 99.54%, respectively.

According to the AOAC method, the percent recovery for the solution with the concentration of 50 ug/L was in the range of 70% - 110%. That is, this method has high accuracy [22].

Analytical Application

The proposed method was successfully applied to the determination of Fe, Co, Ni and Cr in seawater from Bungus, water tap and water of Lubuk Minturun Padang City. It can be seen Table 2 and Fig 5, using the optimum conditions for measurement that had been obtained for each of metals ion them. The standard addition method was used, in order to eliminate the matrix effect. The data obtained for samples spiked with known amounts of Fe, Co, Ni and Cr showed good recoveries

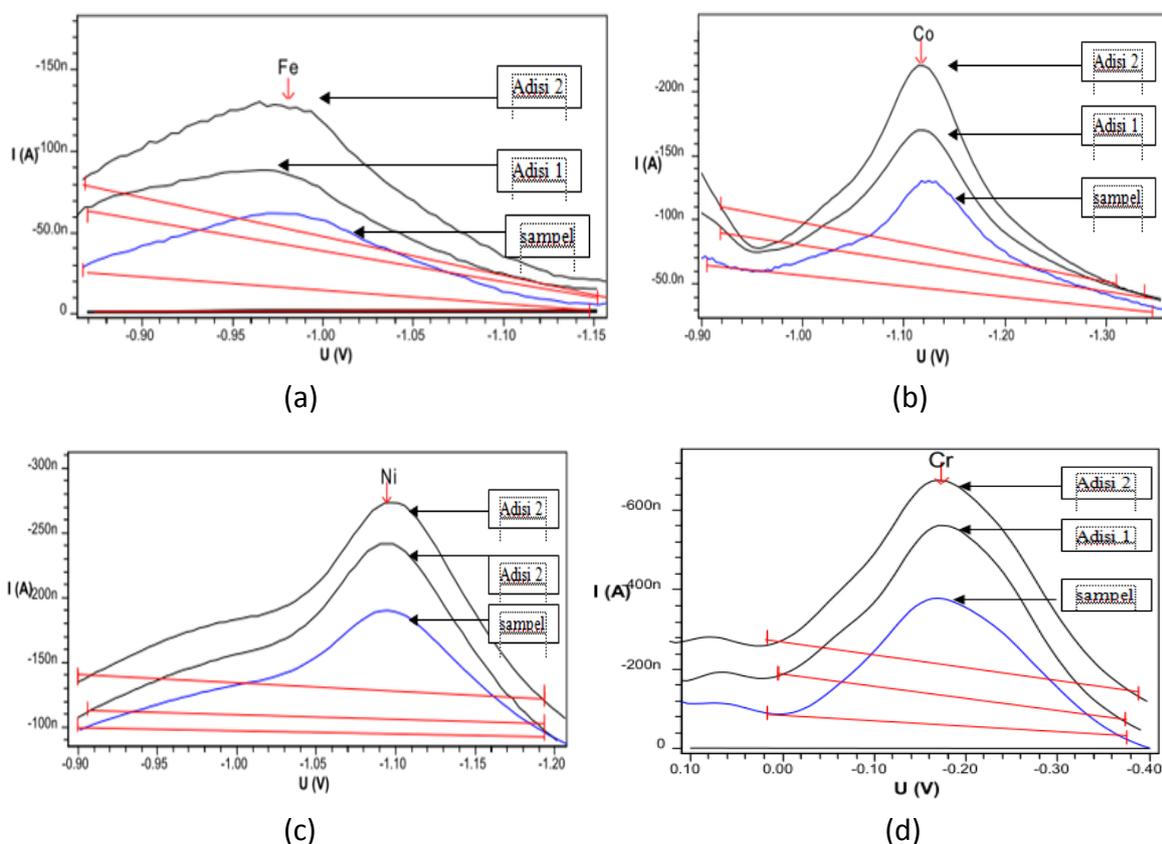


Figure 5. Voltammogram of Fe, Co, Ni and Cr in tap water samples from laboratory of Department of Chemistry Andalas University, by using standard addition method

CONCLUSION

It can be concluded that optimum conditions for measurement of Fe(III), Co (II), Ni(II) and Cr(III) by adsorptive stripping voltammetry were: calcon optimum concentration obtained for Fe(III) and Ni (II) 0.6 mM, Co (II) 0.7 mM, whereas for Cr(III) 0.4 mM, at pH 6 to Fe(III), pH 7 for Co(III) and Ni(II) and pH 5, the accumulation potential -0.8 Volt for Fe(III), -0,7 Volt for Ni(II), -0.4 Volt for Co (II) and -0.5 Volts for Cr(III), and the accumulation time of Fe(III) 50 s, Co (II) 70 s, Ni(II) 60 s and 90 s for Cr(III). At the optimum conditions, the relative standard deviation was obtained with a of eight replicated (n = 8) measurement

standard solution of Fe(III), Co(II), Ni(II) and Cr(III) 10 ug /L were: 0, 52%, 1.77%, 0.52% and 1.34%, respectively. This method was applied to the determination of Fe (III), Co (II), Ni (II) and Cr (III) directly in seawater around Bungus, water tap and water of Lubuk Minturun. The concentration obtained were of each metal ion of all three samples were aqual: 697.62 g/L, 1046.71 mg/L, 14.72 mg/L for Fe(III), 255.64 ug/L, 139.48 mg/L, 0.05 ug/L for Co (II), 509.66 ug/L, 112.57 mg/L, 19.59 mg/L for Ni(II) and 232.06 mg/L, 180.17 ug/L, 15.19 mg/L, with a recovery value for each Fe(III), Co (II), Ni(II) and Cr(III) were 100.50%, 102.64%, 97.39% and 99.54% for) respectively.

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