Simultaneous Determination of Trace Amounts of Iron, Cobalt, Nickel and Chromium in Water Samples with Calcon as Complexing Agent by Adsorptive Stripping Voltammetry

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This paper presents a sensitive and selective method for simultaneous determination of iron, cobalt, nickel and chromium in water samples by adsorptive stripping voltammetry. The method is based on adsorptive accumulation of the complexes of Fe(III), Co(II), Ni(II) and Cr(III) ions with calcon [IUPAC name sodium-3-hydroxy-4[(E)(2-hydroxy-1-naphthyl)diazenyl]-1-naphthalenesulfonate (m.f. $C_{20}H_{13}N_2NaO_5S$] onto hanging mercury drop electrode (HMDE), followed by the reduction of the adsorbed species by differential pulse adsorptive stripping voltammetry. In this study the optimum reaction parameters and conditions study are investigated. Optimal conditions were obtained at pH 7.0, calcon concentration of 0.8 mM, the accumulation potential of -0.7 V and the accumulation time of 70 s. At the optimum conditions the relative standard deviation were 1.70, 2.40, 6.13 and 5.36 % for Fe(III), Co(II), Ni(II) and Cr(III), respectively for eight replicates (n = 8) measurements of 10 µg/L Fe(III), Co(II), Ni(II) and Cr(III). Under optimized conditions, linear calibration curves were established for the concentration of Fe(III), Co(II), Ni(II) and Cr(III) in the range 0.2-80.0; 0.2-120.0; 0.2-100.0 and 0.2-110.0 µg/L, respectively. The limit of detection of the method was 0.703 µg/L for Fe(III), 0.232 µg/L for Co(II), 0.974 µg/L for Ni(II) and 0.161 µg/L for Cr(III). The procedure was successfully applied to the simultaneous determination of iron(III), cobalt(II), nickel(II) and chromium(III) in water samples (sea water, tap water and river water) with recovery of 99.15, 103.73, 97.55 and 99.23 % for Fe(III), Co(II), Ni(II) and Cr(III) respectively.

Keywords: Iron, Cobalt, Nickel, Chromium, Calcon, Adsorptive stripping voltammetry, Water samples.

INTRODUCTION

Trace heavy metals are very important in the environment due to their serious toxicity although present at very low concentrations. The presence of heavy metals in the environment, including food ingredients is very dangerous, because of high level of toxicity[1,2]. The quantitative determination of trace amounts of cobalt plays an important role in the field of environmental analysis, process control and medicine. A preconcentration step is usually necessary to determine low concentrations of cobalt in natural samples. In the case of adsorptive stripping voltammetry (AdSV), a very low detection limit can be easily achieved owing to the preconcentration step included in this method[3]. Cobalt is an essential micronutrient for man, animals and plants and it is a component of cyanocobalamin or vitamin B$_{12}$. In environmental and biological samples, cobalt is present at a trace level[4]. The increasing utilization of heavy metals in modern industries leads to increased environmental burden. Nickel represents a good example of a metal used in modern technologies. As the result of accelerated consumption of nickel-containing products, nickel compounds are released

to the environment at all stages of production and utilization. Their accumulation in the environment may represent a serious hazard to human health. Among the known health-related effects of nickel are skin allergies, lung brosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation Considering the low content of nickel in natural water, sensitive analytical techniques are required[5].

Iron is an important element in environmental, industrial and medical applications as well as in biological studies. It presents in a variety of rock and soil minerals in oxidation states +2 and +3. However, Fe(II) and Fe(III) play different major roles in the biosphere. It is widely accepted that the presence of iron, alone or in combination, has beneficial or deleterious effects on the properties of many substances and the nature of various biological systems. It plays an important role in oxygen and electron transport; provides a fundamental structure of hemoglobin, myoglobin, hemenzymes and many co-factors involved in enzyme activities. In the industrialized world, the iron is the first metal in its usage and its compounds can justifiably be said to touch our daily lives[6]. Contamination of natural waters with chromium can be caused by anthropogenic

sources such as leather tanning, pigment production, electroplating industry and rinse waters, which mostly contain Cr(III) and/or Cr(VI). The toxicity of these two forms differs considerably: while Cr(III) is considered essential in mammals for the maintenance of glucose, lipid and protein metabolism for many living organisms. The Cr(VI) species are known to be toxic and carcinogenic, causing health problems such as liver damage, pulmonary congestions, vomiting and severe diarrhea[7]. It has been reported that Cr(VI) compounds are 10 to 100 times more toxic than Cr(III) compounds when both are administered orally. Sea water contains between 0.1 and 0.5 µg/L and unpolluted river water from 0.3 to 0.6 µg/L. The World Health Organization (WHO) and the European Community Directive (ECD) for drinking water has set the limit of total chromium not exceeding 50 µg/L, while the maximum concentration criterion for Cr(VI) in freshwater is 16 µg/L[3,4]. Since the concentration of chromium, mainly Cr(VI), is very low in many natural waters, a highly sensitive and selective method is required for its speciation.

In trace analysis, mainly of heavy metal ions, anodic stripping voltammetry (ASV) has been the most popular electro analytical technique because of its speed, good selectivity and sensitivity and low instrumentation cost compared to other techniques. Traditionally, the hanging mercury drop electrode (HMDE), due to its sensitivity has been used widely as the working electrode. However, Co, Ni and Cr do not form amalgams with mercury. In these cases adsorptive stripping voltammetry (AdSV) is the adequate technique for their determination in a variety of matrices. In adsorptive voltammetry high sensitivity of the determination can be achieved in the presence of catalytic systems. The catalytic reaction occurs at the surface of the electrode when the reduced analyte is oxidized to its previous by an oxidizing agent. A complete revision of catalytic adsorptive stripping voltammetry for cobalt determination using ligands as pyrogallol red[4]. Others ligands used in adsorptive stripping voltammetry of cobalt are: nitroso-S (3), quercetin[8].

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 µg/L, simple and easy sample preparation, rapid analysis, less infra structure[9,10]. In addition, with this method it is possible to learn chemical species of heavy metals[11,12] 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[13]. Simultaneous determination of Cd, Cu, Pb and Zn in sea water by AdSV[11], the simultaneous determination of copper, bismuth and lead in the presence of thymolphthalexone[14] and simultaneous determination of trace cadmium and zinc by using 5-phenyl-1,2,4-triazol-3-tion (PTT) as complexes agent[15]. 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 1 min[16].

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[9,17].

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 mol/L KCl supporting electrolyte[9]. 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 mol/L KCl as supporting electrolyte[18], the determination of Ni with dimethylglyoxime[19].

Santos-Echheandia[20] have reported the 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 Waridiyati[21] has been using 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[22] have reported a method for determining the ratio of Cr(III) in seawater and species, Deswati *et al.*[23] have reported the direct determination of Fe, Co, Ni and Cr in water samples by adsorptive stripping voltammetry in the presence calcon as a complexing agent.

The present paper describes an adsorptive stripping voltammetry procedure for simultaneous determination iron, cobalt, nickel and chromium in water samples using calcon (sodium-2-hydroxy-1-(2-hydroxy-1-naphthylazo)-naphthalen-4-sulfonate) as a complexing agent. To overcome the problem mentioned above a better condition of adsorptive stripping voltammetry is needed to get a selective and sensitive method. The parameters studied were: variations of calcon concentration, variation of pH solution, accumulation potential and accumulation time. To determine the precision, accuracy, sensivity and linearitas of method, relative standard deviation (RSD), recovery, limit of detection and correlation coefficient were determined. The method at optimum condition was applied for the direct simultaneous determination of Fe(III), Co(III), Ni(II) and Cr(III) in seawater around of Bungus, water tap and water of Lubuk Minturun, Padang city, West Sumatra, Indonesia.

EXPERIMENTAL

The materials used for this study were: NH_4Cl, calcon, concentrated HNO_3, concentrated HCl, acetate buffer, NH_4OH, methanol, nitrogen gas, doubly distilled water, Whatman filter paper and samples (sea water, water tap and water of Lubuk Minturun). 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 Merck product.

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 models 80 Griffin (Griffin & George Loughborough, UK), analytical balance Mettler AE 200, Toledo OH-USA and glassware commonly used in laboratory.

Methods: 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. Procedure used in this study were reported[9].

Sample preparation: Sea water samples were obtained from a beach around Bungus, Padang City, West Sumatera, Indonesia. The samples were placed in plastic bottles previously washed with 1 % HNO_3 solution. In the laboratory they were filtered through a 0.45 μm membrane filter and acidified with HNO_3 to pH close to 2. Tap water samples were obtained from the laboratory, Department Chemistry Andalas University, river water were obtained from Lubuk Minturun Padang City. Before the analysis all the samples were digested by UV irradiation for 90 min at 90 °C (10.0 mL of sample with 100 μL of 30 % H_2O_2).

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, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mmol/L. The results are shown in Fig. 1.
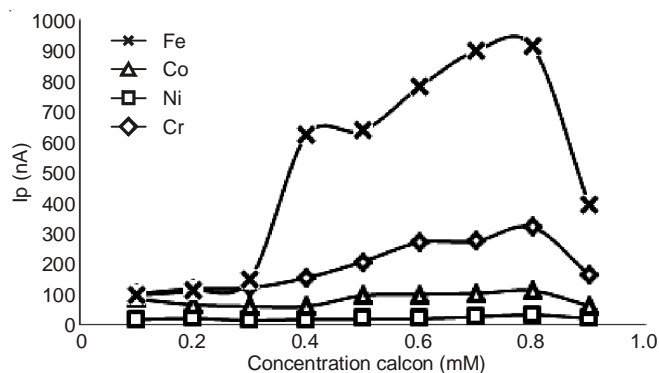

Fig. 1. Effect variations of concentration calcon on peak current (Ip); Condition: 10 mL mixed of Fe, Co, Ni and Cr 10 μg/L; 0.2 mL calcon; 0.2 mL KCl 0.1 M; Accumulation 60 s; accumulation potential -0.7 V; pH 6; scan potential 0 to -2.3 V

The 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 0.8 mM. The resulting peak current of the Fe(III) was the highest followed by Cr(III), Co(II) and Ni(II). This is due to complex formation between Fe(III) and calcon that more stable than of the other metal ions, where at these simultaneous conditions each competing metal ions form complexes with calcon. At the higher calcon concentrations above 0.8 mM the peak heights decreased due to the competition of calcon with Fe(III)-calcon, Co(II)-calcon,

Ni-calcon and Cr(III)-calcon complexes for adsorption on to the mercury drop electrode. At higher calcon concentration, it was difficult the metal-ligand complex to be reduced so that the resulting peak current getting smaller, indicating that the ligand does not compete with the complex for the surface of the mercury electrode ensure complete complex formation. Therefore, the calcon concentration of 0.8 mM was chosen as optimum value for the next experiments.

Effect of pH: The influences of pH on the adsorptive stripping peak currents of iron, cobalt, nickel and chromium, were studied in the pH range of 2 to 10. The results are shown in Fig. 2. At deposition (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 complex formation between the Fe(III), Co(II), 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:
$$M^{n+} + nL \rightleftharpoons ML_n$$
$$ML_n \longrightarrow ML_{nads} \quad (a)$$

Stripping step:
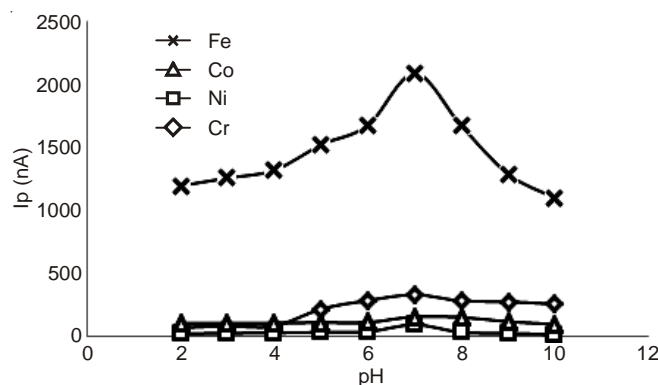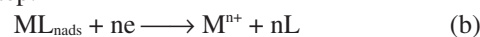$$ML_{nads} + ne \longrightarrow M^{n+} + nL \quad (b)$$

Fig 2. Effect of pH on peak current (Ip); Condition: 10 mL mixed of Fe, Co, Ni and Cr 10 μg/L; 0.2 mL 0.8 mM calcon; 0.2 mL KCl 0.1 M; accumulation time 60 s; accumulation potential -0.7 V; scan potential 0 -2.3 V

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. 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 Fe-calcon, Co-calcon, Ni-calcon and Cr-calcon complexes increasing pH from 2 to 7. 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 7 optimum for simultaneous determination Fe(III), Co(II), Ni(II) and Cr(III), 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 7 to pH 10 the resulting peak current tended to decrease for iron, cobalt, nickel and chromium ions, 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 to form metal hydroxide, which reacted with calcon reduced. At a certain pH the metal ions formed precipited as its hydroxide and consequently resulting smaller current. It appeared that pH 7 is adequate in obtaining sufficient sensitivity for iron, cobalt, nickel and chromium ions. Thus a pH of 7 was chosen for further studies. From the results of previous studied optimum pH for Fe(III) was 6, while for Co(II) and Ni(II) were pH 7 and Cr(III) was pH 5[23]. When compared to the results obtained with the previous study, the optimum pH for the simultaneous determination of Fe, Co, Ni and Cr using of calcon as a complexing agent by adsorptive stripping voltammetry was not significantly different.

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 -0.1 to -0.9 volt. Accumulation potential is the potential at the time of the analyte deposited on the working electrode. The result can be seen in Fig. 3. In above curve it is shown that in every variation of accumulation potential were tested, giving values of different peak currents. For metal ions Fe(III), Co(II) and Cr(II) at potentials -0.1 to -0.7 volt peak current generated is increasing, while for Ni^{2+} in the potential range -0.1 to -0.9 Volt peak current increase not significantly. In the potential range -0.7 to -0.9 Volt, especially for Fe(III) ions volt curve down significantly. This suggests a process of deposition (accumu-lation) of analytes in complex working electrode surface reaches a maximum at -0.7 volt. At -0.7 volt potential is optimum accumulation poten-tial for simultaneous determination of Fe(III), Co(II), Ni(II) and Cr(III) due to the resulting peak current maximum possible. Thus, an accumulation potential of -0.7 volt was selected as optimum accumulation potential.
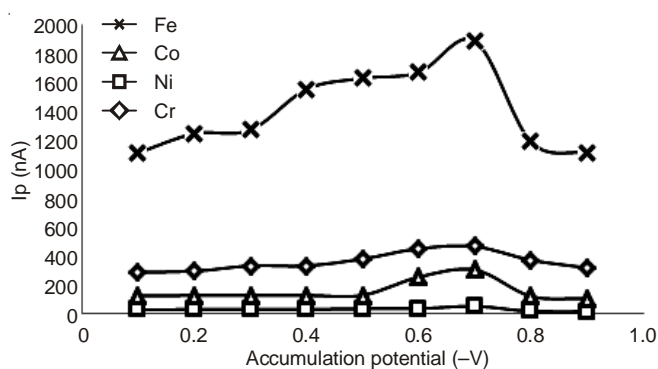

Fig 3.   Effect accumulation potential on peak current (Ip); Condition: 10 mL mixed of Fe, Co, Ni and Cr 10 µg/L; 0.2 mL 0.8 mM calcon; 0.2 mL KCl 0.1 M; accumulation time 60 s; pH 7; scan potential 0 to -2.3 V

Variation of accumulation time: 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[19,24]. 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: 20, 30, 40, 50, 60, 70, 80, 90 and 100 s. The result can be seen in Fig. 4. Fig. 4 shows that the influence of pre-concentration time or accumulation time on the stripping peak currents of Fe, Co, Ni and Cr in the range 20-100 s. At first, peak currents and desirability function increased with accumu-lation time up to 70 s. The peak current increased slightly for both Fe(III) and Cr(III) up to 70 s, indicating that, before adsorptive equilibrium was reached, the longer the accumu-lation time, the more metal-calcon was adsorbed and thus the peak currents became larger while the Ni(II) and Co(II) ions the peak current increased non significantly. Thus, an accumu-lation time of 70 s was selected as an optimum time for next experiments. Accumulation time of more than 70 s did not increase the peak current, even decreased longer accumulation time would cause saturation of electrode[11,17].
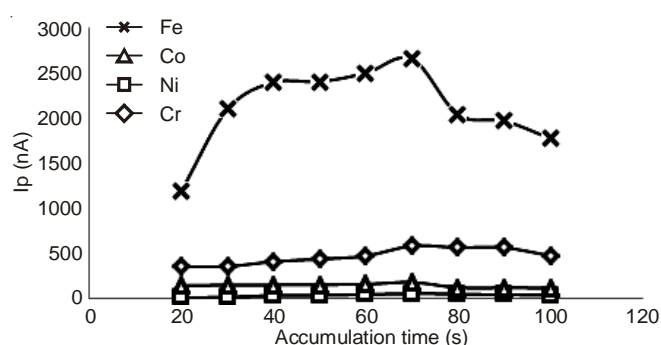

Fig 4.   Effect accumulation time on peak current (Ip); Condition: 10 mL mixed of Fe, Co, Ni and Cr 10 µg/L; 0.2 mL 0.8 mM calcon; 0.2 mL KCl 0.1 M; accumulation potential -0.7 V; pH 7; scan potential 0 to -2.3 V

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 µg/L mixed standard solution of Fe(III), Co(II), Ni(II) and Cr(III) were: 1.70, 2.40, 6.52 and 5.36 %. The result can be seen in Table-1.

TABLE-1
MEASUREMENT RESULTS OF 10 µg/L MIXED STANDARD
SOLUTION OF Fe(III), Co(II), Ni(II) AND Cr(III)

Replicates	Peak current (nA)			
	Fe	Co	Ni	Cr
1	1940	119.17	36.85	360.17
2	1966	122.8	31.31	377.2
3	1910	123.93	32.8	394.64
4	1910	126.8	34.11	480.89
5	1890	125.93	35.44	414.55
6	1980	120.21	35.65	405.36
7	1897	119.7	39.76	425.77
8	1915	120.26	38.07	413.21
Average	1926	122.35	34.873	398.97
SD	32.693	2.9616	2.1594	21.402
RSD (%)	1.70	2.40	6.20	5.36

According to the AOAC method, the value of relative standard deviation was smaller than 8 % at concentration of 10 µg/L. That mean this method has a high degree of precision because the RSD obtained for each metals was smaller 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 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: 99.15, 103.73, 97.55 and 99.23 %, respectively. According to the AOAC method, the percent recovery for the solution with the concentration of 50 µg/L was in the range of 70-110 %. Thus, it is suggested that this method has high accuracy[25].

Linear range and limit of detection: Under the optimized conditions, a linear relationship between the reduction peak current of the iron, cobalt, nickel and chromium complexes and the concentration of Fe(III), Co(II), Ni(II) and Cr(III) was obtained. To verify the linear relationship between peak current and metal concentrations, four calibration curves were plotted under optimum conditions (0.8 mM calcon, pH 7.0, accumulation potential of -0.7 Volt and 70 s accumulation time). The calibration equation, obtained by least-squares method, is $Ip = 3.928C + 11.56$ ($r^2 = 0.985$) for Fe(III), $Ip = 3.157C + 213.1$ ($r^2 = 0.990$) for Co(II), $Ip = 2.536C + 93.68$ ($r^2 = 0.998$) for Ni(II) and $Ip = 3.433C + 354.3$ ($r^2 = 0.981$) for Cr(III) determination, where C is the concentration of metal ions (µg/L) and Ip is the peak current (nA). The stripping peak current of Fe(III)-calcon, Co(II)-calcon, Ni(II)-calcon and Cr(III)-calcon complexes were found to be directly proportional to be the iron, cobalt, nickel and chromium concentration in the range of range 0.2-80.0; 0.2-120.0; 0.2-100.0 and 0.2-110.0 µg/L, respectively. The limit of detection (3s) of 0.703, 0.232, 0.974 and 0.161 µg/L were obtained of Fe(III), Co(II), Ni(II) and Cr(III) respectively.

Analytical application: The proposed method was successfully applied for 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.

TABLE-2
MEASUREMENT RESULTS OF CONCENTRATION OF Fe(III), Co(II), Ni(II) AND Cr(III) IN WATER SAMPLES

Samples	Concentration (µg/L)			
	Fe	Co	Ni	Cr
Sea water	547.62	154.64	439.26	342.06
Tap water	1044.12	87.17	115.68	174.96
Water of lumin	47.85	5.45	17.59	25.15

Conclusion

The present study demonstrates that adsorptive stripping voltammetry analysis of iron, cobalt, nickel and chromium in the presence of calcon as a complexing agent is an excellent
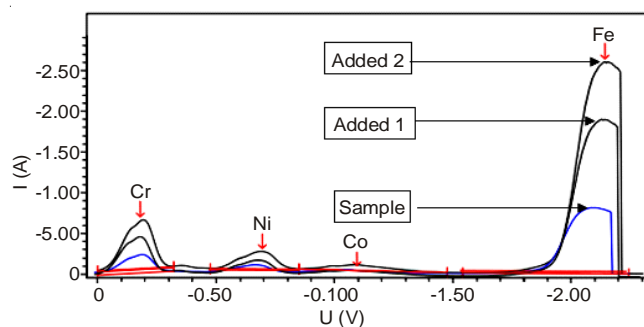

Fig 5. Voltammogram of Fe, Co, Ni and Cr in sea water samples from Bungus Padang City

method for the determination of trace amounts of these four metal ions in real samples. The above system offers a practical potential for simultaneous determination of iron, cobalt, nickel and chromium. This method has high sensitivity, precision, accuracy, simplicity and speed.

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