

Square Wave Catalytic-Adsorptive Stripping Voltammetric Determination of Ultra trace Cobalt with Magneson Modified Carbon Paste Electrode

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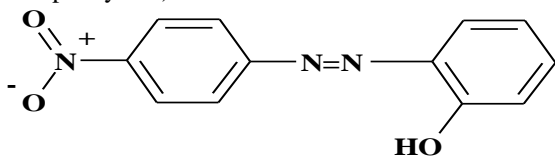
ABSTRACT

A simple, reliable and selective square wave cathodic Adsorptive stripping (SWCAS) voltammetric method at modified carbon paste electrode (CPE) for determination of Cobalt(II) has been developed and evaluated. Square wave Cathodic Adsorptive Stripping Voltammetric (SWCASV) mechanism is proposed to interpret the amplified sensitivity. The procedure is based on the interfacial preconcentration of Cobalt (II) ion on magneson through a surface coordination effect. Different parameters such as medium, pH, accumulation potential, scan rate, accumulation time and ionic strength were tested to optimize the conditions for the determination of Cobalt(II) ion. The adsorbed form is reduced irreversible at optimal conditions viz; 0.15M Britton–Robinson universal buffer (pH~9.5). Linear concentration range 2×10^{-12} - 6×10^{-11} M (0.00012 – 0.00354 ng/mL) at 60s, can be determined successfully. The interferences of some common interfering species and some metal ions were studied. The application of the procedure in Lab tap water sample demonstrates that it is possible to determine Co(II) ion at a level as low as 5.13×10^{-10} mol/L (0.03 ng/mL) in real sample with a recovery of 103%, a standard deviation (triplicate measurements) of 3.08%, and a confidence level of 95%. The concentration of Co(II) in lab tap water sample was confirmed by analysis the sample by using Inductively Coupled Plasma Emission Spectrometer.

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Introduction

Magneson (2-Carboxy-2'-hydroxy-5'-sulfoformazyl-benzene monosodium salt) 4-(4-Nitrophenylazo) Resorcinol.



Structure of (Magneson)

Cobalt (Co) as an important element in environment is an essential element in biological compounds like vitamin B₁₂ and some metalloprotein. Since the concentration of cobalt is extremely low in various natural samples, a sufficient and selective analytical procedure for the reliable determination of cobalt in natural sample would be of great interest. The most common technique for determination low concentration of cobalt is application of Graphite furnace atomic absorption (GFAAS) after a preconcentration step. This technique has difficulties achieving the sensitivity required for the determination of the low level of cobalt in natural water and includes a high risk of sample contamination or loss of analyte during the several sample preparation steps involved.

Amongst the various analytical methods, adsorptive stripping voltammetry (AdSV) technique [1] is becoming a widely accepted analytical tool, as a high sensitive and economic method in determination of some ions in water and in addition the metal preconcentration is performed in this case is performed in situ. The preconcentration step used in AdSV involves adsorption of a complex with a specific chelating agent on a hanging mercury drop electrode (HMDE). The sensible

combination of adsorptive stripping voltammetry (AdSV) and catalytic process produced a remarkably sensitive method named catalytic adsorptive stripping voltammetry (CAAdSV) suitable for ultra trace measurement of certain metals [2]. Several stripping voltammetry methods were reported for trace determination of cobalt [3-7].

Many of the adsorptive stripping voltammetric (AdSV) approach features such as sensitivity, selectivity, simplicity and versatility attributed to the combination of an effective preconcentration step based on non-electrolytic adsorptive accumulation process with an advanced measurement procedures such as DP or SW [8-12]. Unlike conventional stripping approaches (anodic and cathodic stripping voltammetry), which are based on an electrolytic nature of preconcentration step, AdSV approach in contrast is based on adsorptive accumulation of the analyte on the electrode at open circuit with no charge transferred. Consequently, for a wide range of surfaceactive organic and inorganic species, which cannot be preconcentrated electrolytically, the adsorption approach allows these analytes to be interfacially accumulated on the electrode and hence analysed. There have been many reviews devoted to emphasize and illustrate the wide spectrum and scope of AdSV applications and potentialities in the analysis of metal ions [13, 14] organic analytes [15] and pharmaceutical drugs and biomedical compounds [16, 17].

This work presents a catalytic adsorptive stripping voltammetry method for the determination of Cobalt(II), using Magneson as a ligand in presence of 0.15M Britton–Robinson universal buffer. This system provides the lowest detection limit 2×10^{-13} M ever reported for determination of Co(II). Furthermore, we introduce a new method as a very sensitive

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technique for determination of 10^{-10} M concentration of Co(II) in some real samples.

Experimental

Apparatus

All voltammeter experiments were performed with EG&G Princeton Applied Research (PAR Princeton, NJ, USA) Model 273 A potentiostat, controlled by the model 270/250 electrochemical software version 4.30. A three-electrode cell was employed incorporating a hand-made working carbon paste electrode that prepared as previously mentioned [18], an Ag/AgCl (saturated KCl) reference electrode and platinum wire was used as a counter electrode. Mass transport was achieved with a Teflon-coated bar at approximately 400 rpm using a magnetic stirrer (KIKA Laborotechnik, Germany). All pH measurements were made with VWR scientific products model 2000, USA.

Reagents and solutions

All chemical used were either analytical or primary standard grade and were used without further purification. Bi-distilled water and Ethanol were used throughout Standard free sodium hydroxide solution 0.2 M; the sodium hydroxide solution was standardized against standard potassium hydrogen phthalate. The solution of Co(II) ion (Merck, BDH) as nitrate was prepared and titrated complexometrically by EDTA [19]. The magneson solution, with a concentration of 1×10^{-4} mol/L, was prepared for the electrode modification.

Methods

Electrode modification

Carbon paste electrode 15% was prepared by mixing with 4.25 gm of pure carbon with 0.75 gram paraffin oil. This electrode was then immersed in a 1×10^{-4} mol/L magneson solution for about 20 seconds to let magneson adsorb on the electrode surface. The electrode is then ready for the cobalt preconcentration step.

Voltammetric procedure for Co(II) determination

The preconcentration step was performed by immersing the carbon paste electrode in stirring 15 ml sample solution for a given period of time at potential rang from (-0.35) to (-0.6) V for Co(II) ion, then stop the stirring and delay period of 15 sec to the stele the solution and decrease the background current, square wave voltammogram was recorded in the potential direction. A renewed magneson - carbon paste surface electrode was used for each measurement.

For determination of Co(II) ion 30 μ L, 2×10^{-6} M (containing 117.86 ng/mL) of Co(II) metal was added to 15 ml 0.15M universal buffer pH = 9.5. The solution was stirred at 400 ramps at open circuit conditions and the square wave voltammogram was recorded.

For determination of Co(II) ion in lab tap water sample 30 μ L of water sample added to 15 ml 0.15 M universal buffer pH = 9.5. After that different concentrations of Co(II) were added by using Standard addition method. In all measurements the square wave voltammogram was recorded in negative potential direction. The optimum operational parameters selected for the determination of Co(II) by SWCASV using modified CPE illustrated in Table 1.

Table 1. The optimum operational parameters selected for the determination of Co(II) by SWCASV at modified GE

Parameter	Selected value
Accumulation potential	-0.35 V
Final potential	-0.6 V
Modulation time	10 S.
Frequency	50 HZ
Scan increment	2 mV

Accumulation time	Various
PH	9.5
Buffer type	0.15M Britton – Robinson buffer

Results and Discussion

Voltammetric Response and possible mechanism.

The possible mechanism for the formation of the Co(II)-magneson complex on the electrode surface [20], the magneson molecule can be strongly adsorbed on a carbon paste surface coordinating with the cobalt ion to form a surface complex. The molecular structures of the formed surface Co(II) complex and its one-electron reduction product the Co(I)-magneson and complex is proposed in Fig(1), based on fact the metal ion has a coordination number of 6.

The formula for the compound should therefore contain 4 water molecules if the central ion is bonded to only two sites of the ligand molecule.

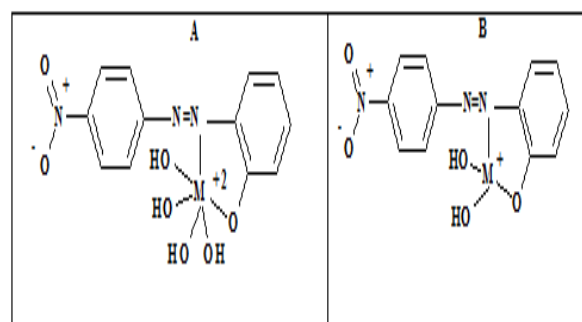


Figure1. Proposed molecular structures for (A) Co(II) - magneson and (B) Co(I)- magneson complexes

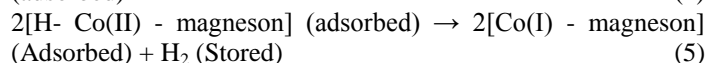
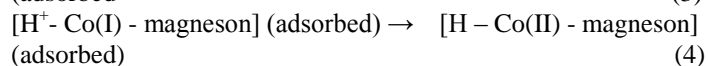
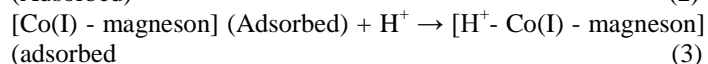
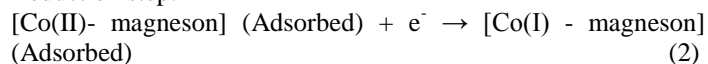
The stripping peak near $E_{\max} = -0.518$ V is believed to be the catalytic-adsorptive current associated with the preconcentrated Co(I) - magneson complex.

The possible mechanism for the whole process may be proposed as follows for Co(II)– magneson Complex.

Preconcentration step:

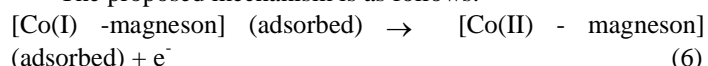


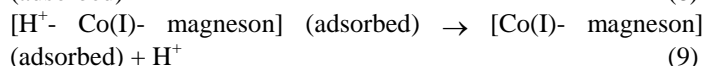
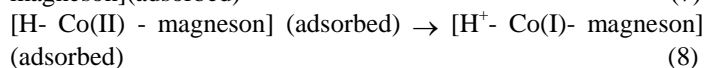
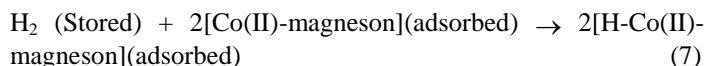
Reduction step:



In the reduction step, the catalytic formation of an adduct between hydrogen and the Co(I)- magneson complex by reactions (3), (4) and (5) may combine together to form H_2 , which is then stored in the space between the electrode surface and the Co(II) - magneson layer. In reaction (5), the adsorbed Co(I) - magneson complex will continuously carry on the catalytic reaction cycle from reactions (3) to (5). Due to the nature of the catalytic reaction, a trace surface Co(II) - magneson complex can start the whole process and produce a large quantity of H_2 . In the preconcentration period, the quantity of formed H_2 should continuously increase as the catalyst surface quantity increases. After the preconcentration and reduction steps, when the electrode potential is scanned toward a positive direction, the stripping step.

The proposed mechanism is as follows:





The formed $[\text{Co(I)-magneson}](\text{adsorbed})$ in reaction (9) would be oxidized back to $[\text{Co(II)-magneson}](\text{adsorbed})$ according to reaction (6), making a continuous catalytic reaction cycle from reactions (6) to (9).

Effect of Supporting Electrolyte, pH

The influence of supporting electrolyte on peak current response of Co(II) ion with ligand (magneson) was examined using different supporting electrolytes such as Potassium Chloride, Sodium nitrate, sodium Perchlorate Acetate buffer, Phosphate buffer and Britton – Robinson universal buffer on the analytical signal was tested. Both the peak height and peak shape were taking into consideration when choosing type of buffer.

The Britton – Robinson (universal buffer) solution was selected for determination of these trace ions Co(II) with ligand (magneson) as optimum conditions. The effect of pH of universal buffer solution on square wave stripping voltammetry of trace ions Co(II) metal 2×10^{-6} M (117.86 ng/mL) in 0.15M Britton – Robinson (universal buffer) at different pH range (3–11) was studied respectively, as shown in Fig.(2).

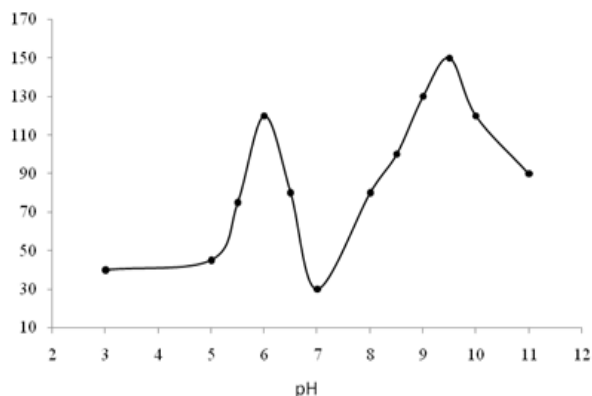


Fig 2. Plot of Ip versus pH using Britton–Robinson buffer solution in presence of 2×10^{-6} M (117.86 ng/mL) Co(II) ion at -0.35V accumulation potential and 15s accumulation time

A small current was observed at (pH = 6) which increased gradually up to pH = 9.5 which used in all measurements. The cathodic potential of the Co(II)- magneson complex is shifted linearly towards less negative values with increasing the pH over than 9.5 the best medium used for studying the stripping analysis of Co (II) - magneson is 0.15M Britton – Robinson universal buffer (pH = 9.5).

Effect buffer concentration

The influence of buffer concentration of universal buffer of pH 9.5 on the square wave stripping voltammetry of trace ions Co(II) was investigated. The study utilizing (117.86 ng/mL) Co(II) with magneson using different ionic strength from 0.02-0.6 M of Britton– Robinson universal buffer. Figure (3) illustrate the plot of peak current versus buffer concentration, the study revealed that the best medium used for studying the stripping analysis of Co(II) ion is 0.15 M Britton – Robinson universal buffer (pH= 9.5).

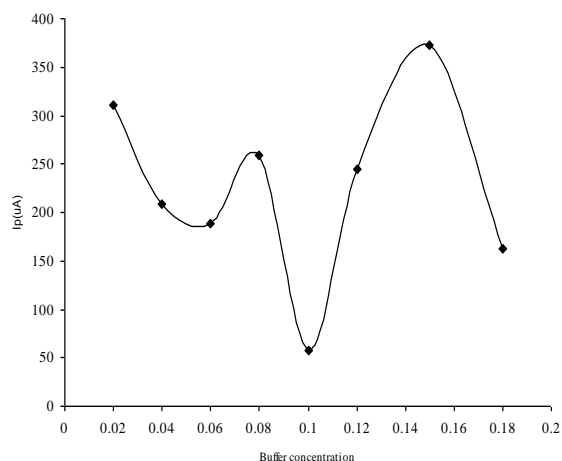


Fig 3. Plot of Ip versus buffer concentration in presence 117.86 ng/mL of Co(II) ion and magneson on electrode surface at (pH=9.5.), -0.35V accumulation potential and 15 s accumulation time

Effect of accumulation potential

The effect of accumulation potential on stripping peak current for 2×10^{-6} M (117.86) Co(II) ion at pH = 9.5 was also investigated in potential range from +0.1 to (-0.6)V at 15 s. The peak current of stripping signal complex increase in the range +0.1 to (-0.35) V potential and decrease with negative shifting from (-0.35) to (-0.6) V. The peak current has its maximum value at initial potential (-0.35) V, which was used in the subsequent examination of other decencies. Plot of peak current versus initial potential is shown in Fig. (4).

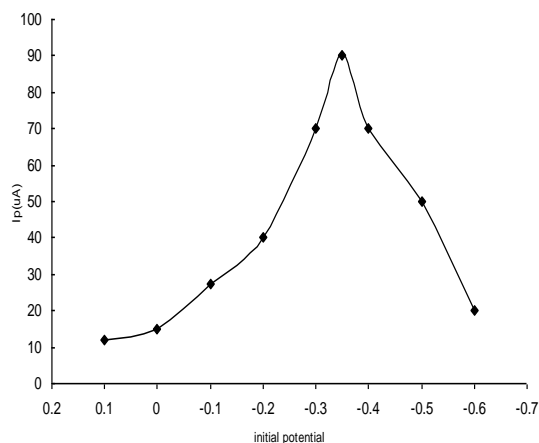


Fig 4. Plot of Ip versus different initial potentials (V) in presence of 117.86 ng/mL of Co(II) ion at (pH = 9.5)

Effect of Accumulation Time and Reproducibility

The dependence of the peak current an accumulation time was studied for one level of concentration named as 2×10^{-6} (117.86 ng/mL) of Co(II) at 0.15M Britton – Robinson buffer (pH = 9.5). The stripping signal increased linearly with increase accumulation time up to 176 s after that occur a decrease in the stripping signal. Figure 5, show plot of peak current versus different of accumulation times.

Effect of Concentration and detection Limit

The square wave cathodic stripping peak for Co(II) ion with (magneson) complex yields a well-defined peak concentration dependence using Square Wave Cathodic Stripping Voltammetry (SWCASV) method. Calibration plots over the Co(II) with magneson concentration range, following different preconcentration times were investigated.

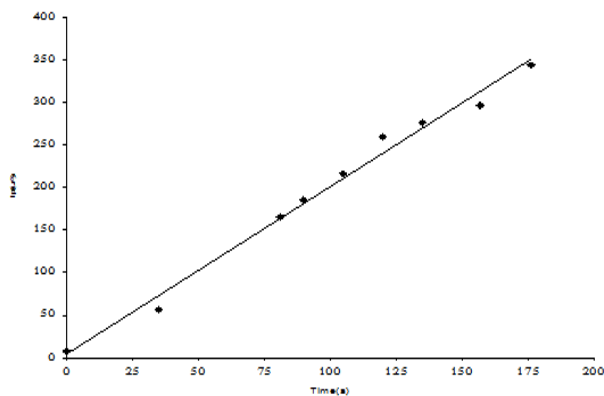


Fig 5. Plot of the peak current versus different pre-concentration times in presence of (117.86 ng/mL) of Co(II) ion at optimum conditions

The quantitative evaluation is based on the dependence of the peak current on Co (II) concentration. A well-defined peak was observed with the stirring at (-0.518V) of Co(II) ion is shown in Fig.6, at 60 s. A linear concentration ranges were 2×10^{-12} - 6×10^{-11} M (0.00012 - 0.00354 ng/mL) at 60s. If the Co(II) ion concentration is higher than 0.0035 ng/mL, a deviation from linearity is observed. The Calibration plot of the peak current versus different concentrations is shown in Fig.8. However, the detection limits estimated as $3\sigma/b$ [21, 22, 23], where b is the slope and σ = standard deviation (SD) of the intercept, quantitative limits was computed as $10\sigma/b$. The results obtained from the proposed method show that Co(II) ion can be detected for 2×10^{-13} M with relative standard deviation $\pm 0.01\%$, Correlation coefficient $r = 0.9996$ for Co (II) ($n = 5$) at accumulation time 60 s .

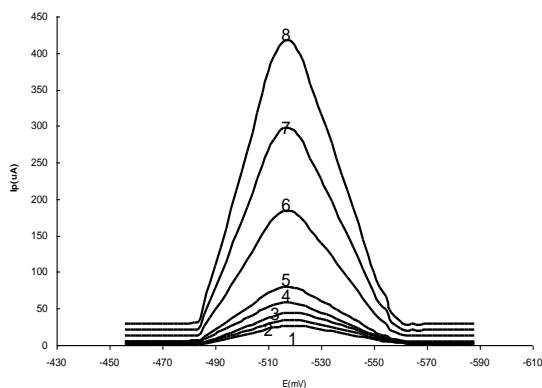


Fig 6. Typical SWCAS voltammograms of Co(II) ion at different concentrations of Co(II) ion in presence of magneson modified electrode, 0.15M universal buffer (pH= 9.5) , 60s accumulation time ,and (1): 0.00012 ng/mL,(2): 0.00024 ng/mL, (3): 0.00035 ng/mL, (4): 0.00047 ng/mL , (5): 0.00059 ng/mL, (6): 0.00118 ng/ml, (7): 0.00236 ng/ml And(8): 0.00354 ng/ml of Co(II) ion

Effect of interferences

To investigate the efficiency and selectivity of the proposed analytical method for determination of Co(II) ion with magneson complexes formulation, a synthetic solution containing a fixed amount trace ions of Co(II) ion, 2×10^{-6} M was spiked excess amount of some common interfering species (10:1) the interfering species Glycine, DL- arginine, DL - Valine (amino acids), Ascorbic acid, Urea, Glucose, Fe(III), pb(II), Na(I) and Cd (II). These interfering species were added to voltammetric cell to study the effect of such interfering species under the optimum experimental conditions.

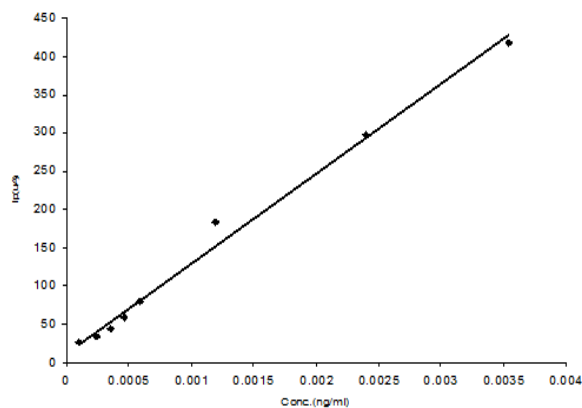


Fig 7. Plot Ip versus concentration of Co(II) ion in presence of magneson on electrode surface, 0.15M Britton- Robinson buffer (pH = 9.5) at 60 s accumulation time

Effect of same amino acids

Different concentrations Glycine, DL- arginine and DL - Valine ranged 2×10^{-6} - 2×10^{-5} M were added to 2×10^{-6} M of Co(II) - (magneson) complex then the voltammograms were recorded. The results showed that the addition of 2×10^{-6} - 2×10^{-5} M of Glycine, DL- arginine and DL-Valine increase in the current peak by about 12.16 - 13.63%, 61.28 -79.08% and 63.49 -76.19 % for Glycine, DL- arginine and DL-Valine, respectively.

Effect of Ascorbic acid, urea and Glucose

Also, different concentrations of Ascorbic acid, urea and Glucose ranged from 2×10^{-6} - 2×10^{-5} M were added to 2×10^{-6} M of Co(II)-(magneson) complex, and then the voltammograms were recorded. The results showed that a significant interference. The addition of 2×10^{-6} - 2×10^{-5} M from Ascorbic acid, urea and Glucose to Co(II)-(magneson) complex, showed the peak current increase by about 10.71–26.5 % , 12.19–53.04 % and 10.97–13.04 % for Ascorbic acid, urea and Glucose, respectively.

Effects of some metal ions

The effect of some metal ions such as Fe (III), Pb (II), Na (I) and Cd (II) on the peak response of 2×10^{-6} M of Co(II)-(magneson) complex were studied. Different concentrations of Fe(III), pb(II), Na(I) and Cd(II) ranged from 2×10^{-6} - 2×10^{-5} M were added. In the presence of Fe (III) the current peak response decrease by (-30.58-(- 21.49) %).In the case of Pb(II) increase in the current peak by about 23.56–27.48 %.

For Cd(II) and Na (I) the peak current response increase by about 11.30–31.5 % and 25.43-30.43 % , respectively .

Determination of Co (II) in lab tap water sample

In order to measure the sensitivity of the present method through a calibration curve, a procedure was applied for determination of Co(II) in the a tap water sample. After that, a standard addition method was used to analyze the water samples. A linear standard addition curve was obtained Fig.8. The Co(II) concentration could be determined from 2×10^{-10} - 6×10^{-10} mol/L level, adjusted by the equation $I_p (\mu A) = 1.90 (\pm 0.13) + 0.37 (\pm 0.08) \times [Co(II)] \text{ mol/L}$, with $r^2 = 0.9997$ and $n = 1$. Practical samples Co(II) Lab Tap water showed a medium value of 5.13×10^{-10} mol/L (0.03 ng/mL) with a recovery of 103 % , a standard deviation of 3.08 % , and a confidence level of 95 % . The concentration of Co(II) in lab tap water sample was confirmed by analysis the sample by using Inductively Coupled Plasma Emission Spectrometer (icap 6200) in central laboratory for chemical analysis , Faculty of Agriculture Assiut University

The concentration of Co(II) in lab tap water sample was 7.12×10^{-10} mol/L (0.042 ng/mL).

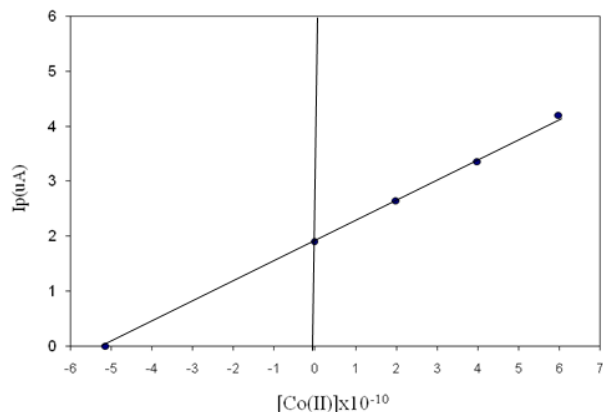


Fig 8. Plot I_p versus standard concentration of Co(II) ion in presence of Lab tap water sample at optimum Conditions: 0.15M Britton – Robinson buffer pH = 9.5 at the preconcentration time 176 s

Conclusion

An extremely high sensitivity for Co(II) analysis at a level of 10^{-13} M has been achieved in this study using (magneson) as a coordination ligand on the electrode surface to facilitate the Co(II) preconcentration process. It is believed that this sensitivity may be amplified by a catalytic-adsorptive stripping mechanism.

The present study demonstrates that the procedure developed here offers a simple method for the determination of low levels of cobalt in real sample. In conclusion, therefore, the above system can be a potential candidate for practical use of Co(II) determination with high sensitivity, selectivity, simplicity and speed.

References

- [1]. Wang J., Analytical Electrochemistry, 2nd edn, Wiley-Vch, New York, 2000.
- [2]. Bobrowski, A., Zarebski, J.: Electroanalysis, (2000)12, 1177.
- [3]. Gao Z. Siong Siow, K.: Talanta , 43, (1996), 43, 255.

- [4]. Vega M., van den Berg C.M.G., Anal. Chem., 69, (1997), 874.
- [5]. Safavi, A., Shams, E. Talanta, 51, (2000), 1117
- [6]. Bobrowski, A., Bond, A.M. Electroanalysis, 3, (1991), 157.
- [7]. Donat, J.R., Bruland K. W. Anal. Chem. 60, (1988), 240.
- [8]. Wang J., Analytical Electrochemistry (2nd Edition), VCH Publishers, inc., New York (1994) 44 -54.
- [9]. Brainina K. H. and Neyman E., Electroanalytical Stripping Methods, John Wiley and Sons, New York '1; (1993) 71-120.
- [10]. Wang J., Stripping Analysis: Principles, Instrumentation and applications, VCH Publishers Inc., Florida, 1985.
- [11]. Kalvoda R., Adsorptive Stripping Voltammetry in Analytical Chemistry II, (J. Zuka, Ed.), Ellis Horwood, New York, 1996.
- [12]. Wang J., Electroanalytical Techniques in Clinical Chemistry and Laboratory Medicine, VCH Publishers Inc., New York, (1988) 17-20.
- [13]. Zaitsev P. M., Salikhdzhanova R. M. and Zaitsev N. K., Indus. Lab Diagno. Mater., 65, (1999), 1-15.
- [14]. Abu Zuhri A. Z. and Voelter W, Fresenius J. Anal. Chem., 1998: 360, 1-9.
- [15]. Brainina K. H., Malakhova N. A. and Stojko N. Y., Fresenius J. Anal. Chem., : 368,(2000), 307-25.
- [16]. Alghamdi A. H., areview, J. Saudi Chem Soc., 6, (2002), 185-98.
- [17]. Vire J. C., Kauffmann J. M. and Patriarche G. J., J. Pharma. Biomed. Anal., 7, (1989), 1323-35.
- [18] Farghaly O.A., Talanta 63 (2004) 497–501.
- [19]- Amrallah A.H., Abdalla N.A. and El-Haty, Talanta, 46 (4) (1998) 491-500.
- [20]- Cassandra R. B. C., Aldaléa L. B.M., Edmar P. M., William S.C. and Jiujun Zhang, Int. J.Electrochem. Sci., 1(2006)343-353
- [21]-O. A. Farghaly, Microchemical Journal 75 (2003) 119-131.
- [22]- Ali A. M., Farghaly O. A. and Ghandour M. A., Anal.Chim. Acta 412 (2000) 99-110.
- [23]-Farghaly O. A., Abd El-Wadood H. M. and Ghandour M. A., J. Pharm. Biomed. Anal., 21 (1999) 233-240.