Glassy Carbon Electrode Modified with Alizarin Red S as a Working Electrode for the Analysis of Cobalt in Water and Hair Using Adsorptive Stripping Voltammetry

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In the present work, glassy carbon electrode (GCE) modified with Alizarin Red S (ARS) was employed for the determination of cobalt in waters and human hair by square wave cathodic adsorptive stripping voltammetry (SW–CASV). The method is based upon the selective and interfacial accumulation of Co (II) ion on GCE surface treated by Alizarin Red S. The parameters influencing on the determination efficiency e.g. pH and type of supporting electrolyte, accumulation potential and time, scan rate, and ionic strength were discussed and optimized systematically. The method submitted in the current study is able to track ultra-trace concentrations of Cobalt in variety of samples where the limit of detection (LOD) was 0.14 ± 0.006 pM, while, the linearity was in the range of $2.00 – 80.00$ pM at optimezed conditions. The evaluation of the proposed method was successfully carried out by the analysis of cobalt content in natural waters and human hair and the results were compared with standard ICP method.

1. INTRODUCTION

Cobalt is an essential element in some biological compounds such as vitamin B_{12} and some metalloprotein. From the analytical chemistry point of view, monitoring cobalt concentration in real samples represents a big challenge for chemical analyst since cobalt concentration level in environmental and biological samples is at ppb levels or less. The most common technique for the determination of low concentrations of cobalt is graphite furnace atomic absorption (GFAAS) after

carrying out a preconcentration step. However, multiple steps in this technique increase the probability of loss or contamination of the sample.

Among the various analytical techniques, adsorptive stripping voltammetry (AdSV) technique has high performance efficiency and good analytical characteristics e.g. speed of analysis, good selectivity and sensitivity, suitability for the determination of analytes even in saline samples like sea waters and also simultaneous analysis of mixtures [1]. On the other hand, the preconcentration step used in AdSV technique involves the adsorption of analyte as a complex on working electrode surface, therefore, the probability of loss or contamination of the sample is very poor. The catalytic adsorptive stripping voltammetry (CAdSV), in which AdSV is combined with a catalytic process, is suitable for the determination of ultra-trace concentrations of analytes [2]. Thus, several stripping voltammetric methods either AdSV or CAdSV have been developed for the trace determination of cobalt [3 – 7]. However, AdSV is characterized by good selectivity and sensitivity, in addition to simplicity and versatility. Preconcentration step in AdSV is based upon non – electrolytic adsorptive accumulation process combined with advanced measurement techniques like DP or SW [8 – 12]. Therefore, analytes are collected on the electrode surface by adsorptive accumulation at open circuit without charge transfer. Hence, surface – active species, that are not collected electrolytically, may be determined by AdSV because the adsorption allows them to be interfacially accumulated on the electrode surface. Thus, AdSV technique has had different applications in the field of metal ions and organic compounds analysis [13 – 17]. Therefore, our work in the present paper well be focused on developing a simple, low cost and selective adsorptive stripping voltammetric (AdSV) procedure for the analysis of ultra-trace concentrations of cobalt (II) ions using glassy carbon electrode modified with Alizarin Red S (Fig. 1). The work was also aimed to investigate the nature, kinetics and mechanism of the electrode reactions.
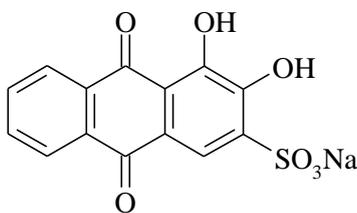
Figure 1. The chemical formula of Alizarin Red S.

2. EXPERIMENTAL

2.1. Apparatus

All voltammetric measurements were carried out using EG&G Princeton Applied Research 273 A potentiostat (PAR Princeton, NJ, USA), controlled by the model 270/250 electrochemical software (version 4.30). The electrodes used in this study were glassy carbon electrode that was prepared as previously reported in [18] as working electrode, double-junction Ag/AgCl (saturated KCl

solution) as a reference electrode, and platinum wire (BAS model MW-1032) as a helping electrode. An electrochemical cell with capacity of 10 mL was employed for carrying out the measurements since the solutions were transferred to this cell via a digital-micro-pipette (Biohit). All pH measurements were made with VWR scientific products model 2000, USA.

2.2. Reagents and solutions

All chemicals used in the present study are of analytical reagents grade and met Committee Specifications of Analytical Reagents in the American Chemical Society. An appropriate weight of cobalt nitrate (Merck, BDH) required for preparation of 1000 µg mL^{-1} of Co (II) ions was dissolved in deionized water and the volume was then completed to 100 mL in measuring flask. This solution was then titrated complexometrically by EDTA [19] to find out the concentration of Co (II) ions accurately. The concentration of 1×10^{-4} mol L^{-1} of Alizarin Red S (Fig.1) was prepared, and employed for the carbon paste electrode modification[20].

2.3. The adsorption of Alizarin red S on the electrode surface.

GCE was immersed in Alizarin red S solution (1×10^{-4} mol L^{-1}) for 20 seconds. After adsorption of Alizarin red S on the electrode surface, the electrode became ready to use.

2.4. Recommended SW–CASV procedure for Co(II) determination.

10 mL of supporting electrolyte (0.15 mol L^{-1} phosphate buffer, pH 9.0) was placed and stirred in the electrochemical cell, then nitrogen gas was passed though the cell for 10 min before recording background square wave voltammogram. The stirrer was stopped and after equilibration time (≈15 s), the square wave voltammogram was recorded from – 0.35 to – 0.7 V versus Ag/AgCl at accumulation potential of – 0.35 V. After recording the background voltammogram, aliquots of the standard cobalt solutions (2.00 – 60.00 pM) or real samples solutions (natural waters, and human hair) were added to supporting electrolyte solution pre-existing in electrochemical cell, and the mixture was then stirred and the voltammogram was recorded at open circuit conditions. A renewed Alizarin red S – glassy carbon electrode was used for each measurement.

For determination of Co(II) ion in natural waters 30 µL of sample was added to (10 mL 0.15 mol L– 1 phosphate buffer, pH 9.0). 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. Water samples were collected from different places (Red sea water & River water), all water samples were filtered by a suitable filtration paper like 0.45µm cellulose paper and stored in LDPE bottles prior to the analysis.

Also, for hair sample was digested using silica crucibles heated by muffle furnace (450 ^{0}C, 6 h) [21]. The residue (a white powder) was dissolved by 0.15 mol L^{-1} HCl and stored in polyethylene bottles. 30 µL of this solution was added to 10 mL 0.15 mol L^{-1} phosphate buffer (pH 9.0), and the concentration of cobalt in human hair was analyzed by recommended SW–CASV procedure.

3. RESULTS AND DISCUSSION

3.1. The study of voltammetric behavior and mechanism of working electrode reactions.

Alizarin Red S (ARS) ligand may be adsorbed on GCE surface, therefore, Co(II) ions may coordinate with this ligand to form a surface complex [22]. The chemical structure of Co(II) – ARS complex formed on electrode surface is proposed in [Fig.2. A]. It is well known that Co(II) ion has the coordination number of 6, therefore, the formula of Co(II) – ARS complex should contain 4 water molecules when the Co(II) ion is coordinated with two sites of the ligand as shown in [Fig.2. A].

The stripping peak near $E_{max} = -0.518V$ is most likely attributed to the catalytic-adsorptive current associated with Co(I) – (ARS) complex formation due to electrochemical reduction of Co(II) to Co(I). The chemical structure of Co(I) – (ARS) complex is shown in [Fig.2. B]. Therefore, the possible mechanism of working electrode reactions is as follow:

(i) The preconcentration step:

Co(II) (solution) + (ARS) (adsorbed on surface) → [Co(II) – (ARS)] (adsorbed on surface)　　　(1)

(ii) The reduction step:

Co(II) – (ARS) (adsorbed on surface) + e⁻ → Co(I) – (ARS) (adsorbed on surface)　　　(2)
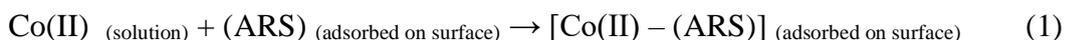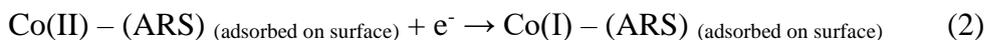
Because of the catalytic reaction nature, the trace concentrations of Co(II) – (ARS) complex adsorbed on the electrode surface can begin the whole process producing a large amount of hydrogen gas. On the other hand, when reversing the electrode potential towards the positive direction, a back oxidation of the [Co(I) – (ARS)] to [Co(II) – (ARS)] occur .The stripping step happens according to the following proposed mechanism:

Co(I) – (ARS) (adsorbed on surface) → Co(II) – (ARS) (adsorbed on surface) + e⁻　　　(3)
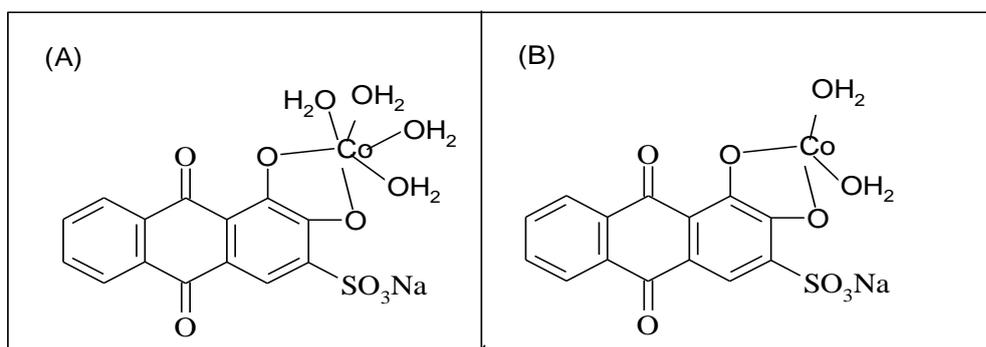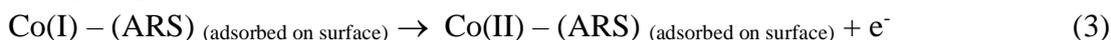
Figure 2. The proposed chemical structures of (A) Co(II) – (ARS) and (B) Co(I) – (ARS) complexes.

3.2. The influence of supporting electrolyte type and pH.

The influence of supporting electrolyte type on peak current (I_p) of Co(II) – (ARS) complex was examined using different kinds of supporting electrolytes e.g. potassium chloride, sodium nitrate, sodium perchlorate acetate buffer, phosphate buffer and Britton – Robinson. However, the peak height and peak shape should be taking into consideration when selecting buffer type. Thus, phosphate buffer was selected as a supporting electrolyte for determination of Co(II) using the proposed method because

the best analytical signal (I_p) was obtained only when using this buffer. On the other hand, the influence of phosphate buffer pH on I_p value when determination of Co(II) at concentration level of 60.00 pM was tested in the pH range (3 – 11). As shown in Fig. 3, the highest value of I_p was observed at pH 9.0, with increasing pH over than 9.0, the cathodic potential of the Co(II) – (ARS) complex is shifted linearly towards less negative values. Therefore, the solution pH was adjusted at pH 9.0 using phosphate buffer in the subsequent experiments.
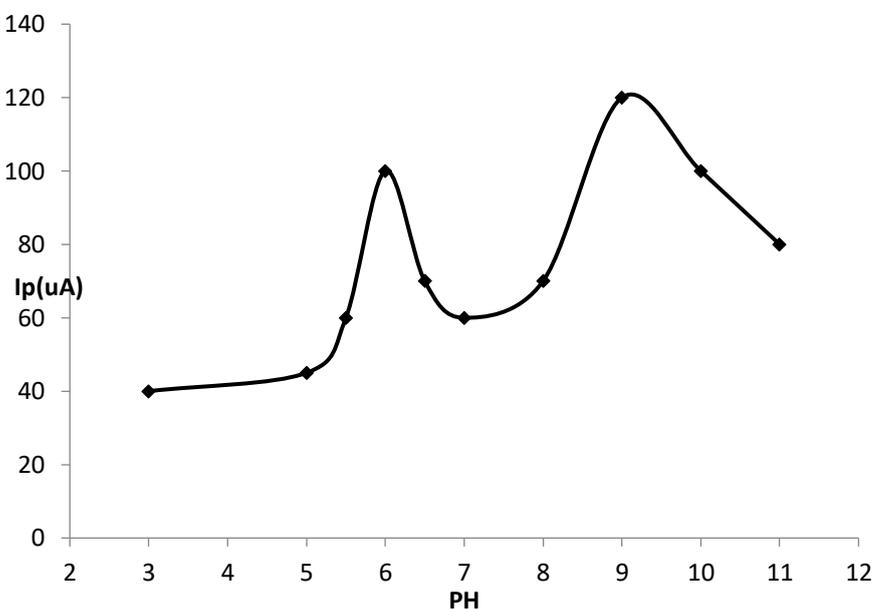
Figure 3. The plot of I_p versus phosphate buffer pH in presence of 60.00 pM of Co(II) ion.

3.3. The ionic strength influence.

The influence of ionic strength on I_p of Co(II) – (ARS) complex was investigated using different ionic strengths from 0.02 to 0.5 mol L^{-1} of phosphate buffer, while, the concentration of Co(II) was 60.00 pM. Therefore, 0.1 mol L^{-1} of phosphate was selected in the subsequent work for cobalt(II) analysis since this concentration provides a maximum sensitivity.

3.4. The influence of accumulation potential.

The influence of accumulation potential on I_p at -0.518V versus Ag/AgCl reference electrode was investigated over the potential range from $+0.1$ to -0.7V versus Ag/AgCl reference electrode after 15 s accumulation time of the analyte at glassy carbon electrode modified with Alizarin Red S. Fig. 4 revealed that the stripping peak current of 60.00 pM of Co(II) ion at -0.518 V enhanced dramatically by increasing accumulation potential in negative side until -0.35 V then no change in I_p was observed. Therefore, the accumulation of potential of -0.35 V was selected for the next study.
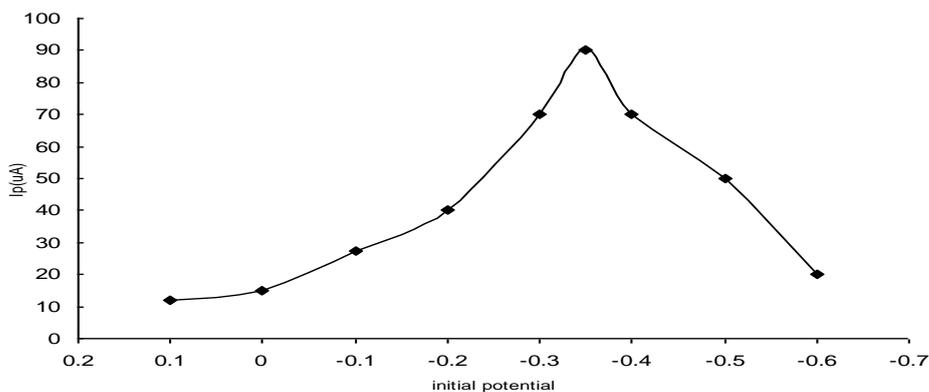
Figure 4 The plot of I_p versus different initial potentials in the presence of 60.00 pM of Co(II) ion at pH = 9.0

3.5. The effect of accumulation time.

The relationship between the accumulation time (5 – 170 s) and the I_p measured at –0.518V versus Ag/AgCl reference electrode was systematically studied at concentration level of 60.00 pM of Co(II) ions. **Fig.5** shows a linear relationship between I_p and an accumulation time, however, after 150 s, a decrease in I_p was observed. The phenomenon of drop in peak current when a longer adsorption time is the characteristic feature of adsorptive stripping with the stirred solutions due to the saturation of electrode surface. Hence, to enhance the sensitivity of method, the accumulation time of **150 s** was adopted in the subsequent work.
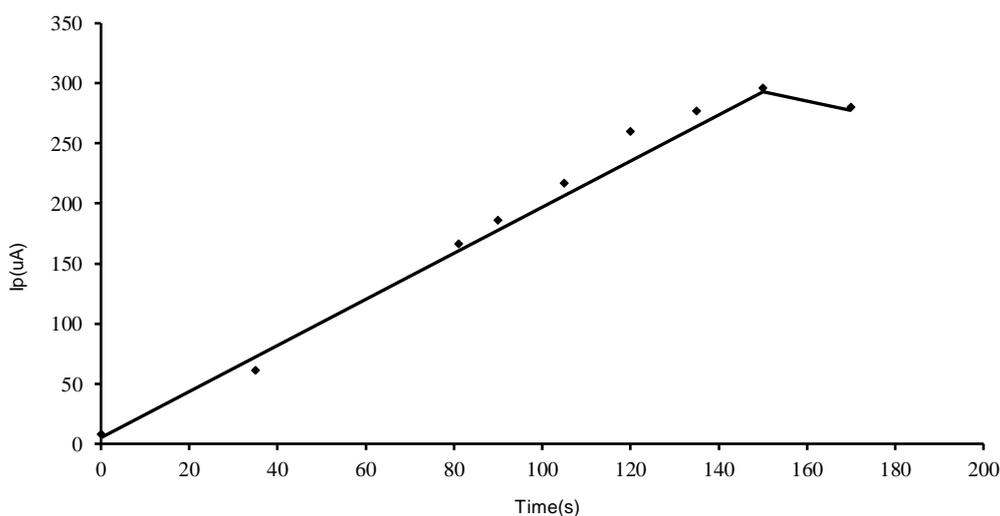
Figure 5. Plot of the peak current versus different pre-concentration times in presence of 60.00 pM of Co(II) ion at optimum conditions.

3.6. The analytical efficiency of the developed SW–CASV.

The analytical performance of Co^{2+} ions determination using the proposed SW–CASV procedure was examined under the optimized experimental conditions. The SW–CASV

voltammograms recorded at – 0.518V versus Ag/AgCl reference electrode of different concentrations of Co(II) ions are demonstrated in Fig.6. However, the calibration curve (Fig.7) was linear in the range of 2.00 – 60.00 pM at optimezed conditions. According to IUPAC [23, 24, 25], the lower limits of detection (LOD) and quantitation (LOQ) were calculated as follows:

$$LOD=3b/S \tag{3}$$

$$LOQ=10b/S \tag{4}$$

where b is the standard deviation of blank at five replicates measurements (n = 5), whereas, S is the method sensitivity, or in another meaning, the calibration curve slope. However, The LOD and LOQ were 0.14 ± 0.006 pM and 0.67 ± 0.005 pM, respectively for five replicate measurements. The correlation coefficient of calibration curve was 0.9996 for five replicate measurements at the accumulation time of 150 s. **Table.2** shown a comparison between proposed electrode with other reported electrodes.
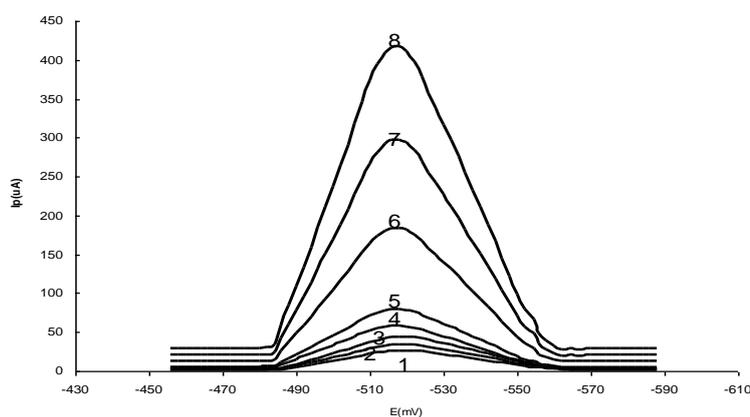
Figure 6. The typical SW–CASV voltammograms recorded by glassy carbon electrode modified with Alizarin Red S as a working electrode at different concentrations of Co(II) ions at acumulatuion time 150 s Britton Robinson Buffer(pH 9.0) : 2.00 pM (1) ; 4.06 pM (2) ; 5.93 pM (3) ; 7.97 pM (4) ; 10.00 pM (5) ; 20.00 pM (6) ; 40.00 pM (7) ; 60.00 pM (8).
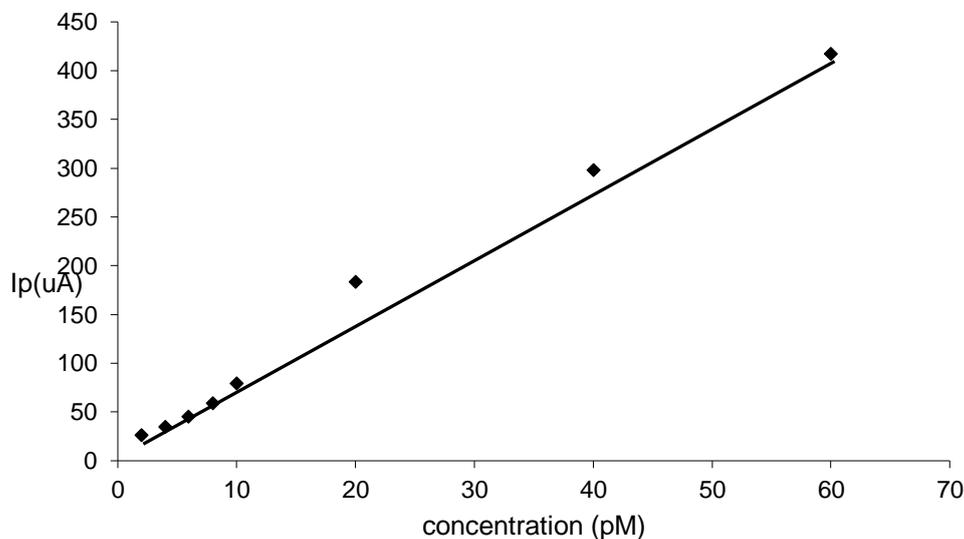
Figure 7. The calibration curve of cobalt (II) determination by the proposed electrochemical method**.** Concentrations are given in the pM unit

Table 2. Comparison of the proposed electrode with the reported electrodes.

Reference No.	Working Electrode	Concentration Range (M)	Detection Limit (M)	Electrochemical Method
This work	Glassy carbon electrode (GCE)	2×10^{-12}- 6×10^{-11}	1.4×10^{-13}	Catalytic Adsorptive stripping voltammetry
30	Pencil-based renewable Zn/Al-CPPA nanocomposite electrode	1.0×10^{-3} - 1.0×10^{-8}	1.26×10^{-8}	Cyclic voltammetry
33	Nitroso-S complex carbon paste electrode	1.871×10^{-4} - 3.3×10^{-6}	1.8×10^{-6}	Adsorptive stripping voltammetry
34	Hanging mercury drop electrode	-	7.0×10^{-9}	Adsorptive stripping voltammetry
35	Hanging mercury drop electrode	-	7.0×10^{-9}	Catalytic Adsorptive stripping voltammetry
36	Hanging mercury drop electrode	3.0×10^{-9} - 5.0×10^{-11}	1.7×10^{-11}	Adsorptive stripping voltammetry
20	Carbon paste electrode (CPE)	2×10^{-12}- 6×10^{-11}	2×10^{-13}	Adsorptive stripping voltammetry

3.7. The proposed method selectivity.

The influence of some ions and compounds commonly present in some real samples e.g. cations: Al^{3+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{3+}, Cd^{2+}; anions: SO_4^{2-}, SCN^-, NO_3^-, CO_3^{2-}, Cl^-, Br^-, PO_4^{3-} ; compounds: Glycine, DL- arginine , DL – Valine , Ascorbic acid, Glucose, and Urea on cobalt determination by the developed procedure was systematically examined. The tolerance limit is an error of less than $\pm5\%$ in the value of I_p at -0.518 V versus Ag/AgCl that arises as a result of addition of foreign ions or compounds. Among the studied ions, only Fe^{3+}, Al^{3+}, and Cd^{2+} significantly interfere by decreasing I_p at -0.518 V. However, such interferences were quantitatively solved by adding drops of NaF or KCN (0.1% w/v) into investigated samples solutions prior to measurement. On the other hand, the amino acid e.g. Glycine, DL- arginine , and DL – Valine, and the other compounds e.g. Ascorbic acid, Glucose, and Urea interfered by either increase or decrease of I_p at -0.518 V only when they have very high concentrations that are usually not found in the real samples.

3.8. The validation of proposed method by real samples analysis.

The electroanalytical method submitted in the present study was validated by the estimation of cobalt in some real samples e.g. natural waters [26 – 32] and human hair.

The cobalt content was then determined by the recommended SW–CASV procedure. The statistical comparison at the 95% confidence level between our results and those obtained from standard ICP method has demonstrated that no significant difference between two methods (Table 3).

Table 3. The results of cobalt analysis in chosen samples e.g. water and human hair *samples*

Sample	Present method, ng/mL or µg/g for hair	ICP method, ng/mL or µg/g for hair	Recovery of ICP, %	Spiked Co^{2+}, ng/mL	Found Co^{2+}, ng/mL	Recovery of ICP , %
Red sea water	0.151±0.05	0.16 ± 0.06	94.37	100	99.44 ± 1,67	99.44
River water	0.033 ± 0.17	0.035 ± 0.03	97.14	100	102± 0.08	102
Human hair	0.17± 0.035	0.18 ± 0. 08	96,71	-	-	-

4. CONCLUSION

The electroanalytical method provided in this work can be considered as an excellent alternative approach for the determination of cobalt at ultra – trace concentration levels (Nano or Pico molar) because of its sufficient precision and accuracy. The proposed method has been successfully applied for cobalt determination in natural waters and human hair with excellent recovery percent (always higher than 95%). Our work in future will be focused on the use of on-line estimation of inorganic cobalt species in environmental samples.

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