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Adsorptive Stripping Voltammetric Determination of Cobalt (II) on the Carbon Paste Electrode

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Traces of cobalt (II) can be determined by adsorptive stripping voltammetry using Nitroso-S as complex forming reagent. First in acetate buffer pH 5.0, cobalt (II)-Nitroso-S complex was adsorbed on the carbon paste electrode with an accumulation potential of +0.1 V. Following this, adsorbed complex was detected by cathodic differential pulse voltammetric scan from +0.1 to -0.6 V. The effective parameters in sensor response were examined. The detection limit of Co(II) was 1.8 µg l^{-1} and relative standard deviations for 10 and 100 µg l^{-1} of Co(II) were 0.8 and 1.2%, respectively. The calibration curve was linear for 3.3-187.1 µg l^{-1} Co(II). This technique does not use mercury and therefore, has a positive environmental benefit. The method, which is reasonably sensitive and selective, has been successfully applied to the determination of trace amount of Co(II) in water samples.

Keywords: Carbon paste electrode, cobalt(II), adsorptive stripping voltammetry, nitroso-S.

1. INTRODUCTION

The quantitative determination of trace amounts of cobalt plays an important role in the field of environmental analysis, process control and medicine [1]. A preconcentration step is usually necessary to determine low concentrations of cobalt in natural samples [2–4]. 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. Additionally the analytical signal can be enhanced as a result of exploitation of catalytic processes [5]. HMDE [6–9] or mercury film [10–12] electrodes are usually used to determine trace concentrations of cobalt by AdSV. The disadvantage of mercury electrodes is the toxicity of mercury, so attempts to replace mercury by solid electrodes have also been reported [13-20].

The development and application of carbon paste electrodes have received considerable attention in recent years. These kind of electrodes are inexpensive and possess many advantages such as low background current, wide range of used potential, easy fabrication, and rapid renewal. A number of studies on the use of carbon paste electrodes for analytical determinations of different metal ions by stripping voltammetric measurements have been reported [18-20]. However, a few papers have appeared for the determination of metal ions using complex adsorption voltammetry at an unmodified CPE [21-22].

Nitroso-S, Fig 1, is a metal sensitive ligand and its sorption capacity was investigated for some heavy metal ions at different pH values [23-24]. To our knowledge, no application of Nitroso-S for electroanalytical aims has been reported.

The aim of this work was to develop a simple, selective and sensitive system for determination of Co(II) by stripping voltammetry on the unmodified CPE. The results obtained led to the development of a voltammetric method for the determination of Co(II) with a wide linear range, good reproducibility and low detection limit. The procedure was applied for determination of Co(II) in natural waters. The accuracy and precision of results were comparable to those obtained by flame atomic absorption spectroscopy (FAAS).

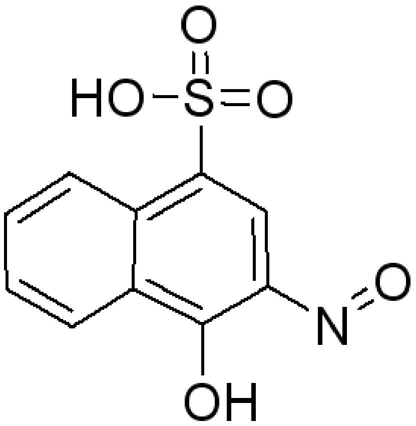

Figure 1. The structure of 2-nitroso-1-naphthol-4-sulfonic acid (Nitroso-S).

2. EXPERIMENTAL

2.1. Reagents

All reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used for all experiments. Nitroso-S was purchased from Fluka and its stock solution (10^{-2} M) was prepared by dissolving Nitroso-S in double distilled water. The stock solution of

1000 mg l^{-1} Co(II) was prepared from $Co(NO_3)_2$ in doubly distilled water. All other solutions were prepared using standard laboratory procedures.

2.2. Apparatus

All voltammograms were recorded with a three-electrode system consisting of an Ag/AgCl as the reference electrode, a platinum wire as the counter electrode, and a CPE as the working electrode. Voltammetric experiments were performed using a AutoLab Potentiostate/Galvanostate (Model PG-STAT12). A Metrohm 710 pH meter was used for pH adjustments. All measurements were carried out at room temperature (23±1 ^{o}C).

2.3. Preparation of CPE

Carbon pastes were prepared by mixing 0.25 g of paraffin oil with 0.75 g of high purity graphite powder and thoroughly hand-mixing in a mortar and pestle. The carbon paste electrode (CPE) was constructed by packing this paste into a glass tube (4 mm inner diameter) and providing it with a platinum contact. The electrode surface was smoothed by polishing on a piece of graph paper while a slight manual pressure was applied to the piston. For regeneration of the electrode after every determination, a thin layer of the surface was removed with a spatula, replaced by fresh paste and polished.

2.4. Stripping determination of Co(II) at CPE

For differential pulse (DP) stripping voltammetric experiments, a 20.0 ml volume of solution containing Co(II), 1 mM Nitroso-S and 0.1 M acetate buffer (pH 5.0) was pipetted into the electrochemical cell and deaerated by purging with high pure nitrogen for 5 min. The stirrer was switched on. The accumulation potential of +0.1 V was applied to a CPE for 20 s. Following the accumulation period, the stirrer was stopped, and after a rest period of 5 s, the DPV was recorded by applying a negative-going potential scan from +0.1 to -0.6 V at 25 mV s^{-1}, and the peak current of the copper was obtained at -0.3 V.

3. RESULT AND DISCUSSION

3.1. Electrochemical behavior of Nitroso-S-Co(II) complex on CPE

The behavior of the Co(II) – Nitroso-S complex on CPE was studied by DPV between +0.1 to -0.6 V versus Ag/AgCl as reference. Curves a and b in Fig 2 show typical DPV obtained for the CPE in only acetate buffer and acetate buffer including 200 µg l^{-1} Cobalt(II) ions, respectively. In absence of

Nitroso-S in the electrolyte solution, no well defined voltammetric wave attributable to the reduction of support electrolyte or metal ions was observed within the applied potential window. The adsorptive stripping voltammogram for the Nitroso-S is shown in curve c in Fig 2. As shown in this curve, one cathodic peak at -0.2 V was observed. Therefore it can be related with reduction of Nitroso-S. As shown in curve d in Fig 2, when cobalt(II) is added into the solution including Nitroso-S so decrease the peak current of the reduction of Nitroso-S. Also, a new peak in -0.3 V is observed. More experiments showed that currents of this new peak is proportional to Co(II) concentrations in solution.

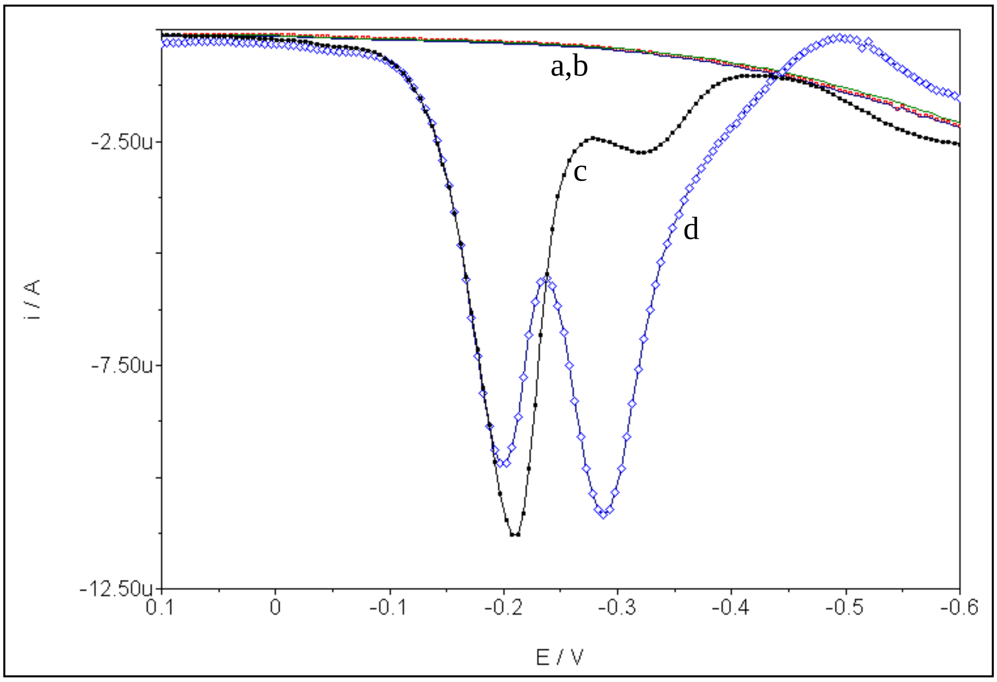

Figure 2. DPVs (scan rate 25 mV s^{-1}) at a CPE in acetate buffer solutions pH 5.0: (a) with no Co(II) and no Nitroso-S in solution, (b) with 200 µg l^{-1} Co(II) and no Nitroso-S in solution, (c) with no Co(II) and 1 mM Nitroso-S in solution, and (d) with 200 µg l^{-1} Co(II) and 1 mM Nitroso-S in solution.

3.2. Optimization of analytical parameters

Four media, namely phosphate buffer, Britton-Robinson buffer, acetate buffer and citrate buffer were tested as supporting media. It was found that acetate buffer was outstanding in terms of peak shape and sensitivity.

The chelating properties of Nitroso-S with metal cations have been demonstrated to be pH dependent [23-24]. Therefore, the effect of pH on the stripping peak currents of Co(II)-Nitroso-S complex was studied as shown in Fig 3A. The maximum stripping current is to be expected at pH 5.0. Therefore it was selected for the further studied.

The dependence of the voltammetric peak current on the pre-concentration potential was investigated over the potential range of -0.3 to +0.2 V. Maximum peak currents were obtained when the pre-concentration potential was set on +0.1 V. Therefore, +0.1 V was selected as the preconcentration potential for all measurements. Under this potential, the effect of varying the accumulation time for 50 µg l^{-1} Co(II) in the range from 0 – 100 seconds was studied. The peak current was found to increase with increasing pre-concentration time, indicating an enhancement of Co(II)-Nitroso-S complex uptakes at the electrode surface. Normally, the increase in the response current was continued until a maximum signal level after times 25 s for preconcentration time (probably corresponding to saturation of electrode surface). Therefore, preconcentration times of 25 s were used for all subsequent measurements.

As the accumulation of metal ions at CPE was based on formation of Co(II)-Nitroso-S complexes, the concentration of Nitroso-S in solution was expected to have a significant influence on the voltammetric response. The results showed (Fig 3B) the peak currents increased with the increasing concentration of Nitroso-S in the solution up to 1 mM. At Nitroso-S concentrations higher than 1 mM, the peak currents decreased probably due to the competition for adsorption of Nitroso-S with the Co(II)-Nitroso-S complex at the CPE. Therefore, concentrations of 1 mM were used for all subsequent measurements.

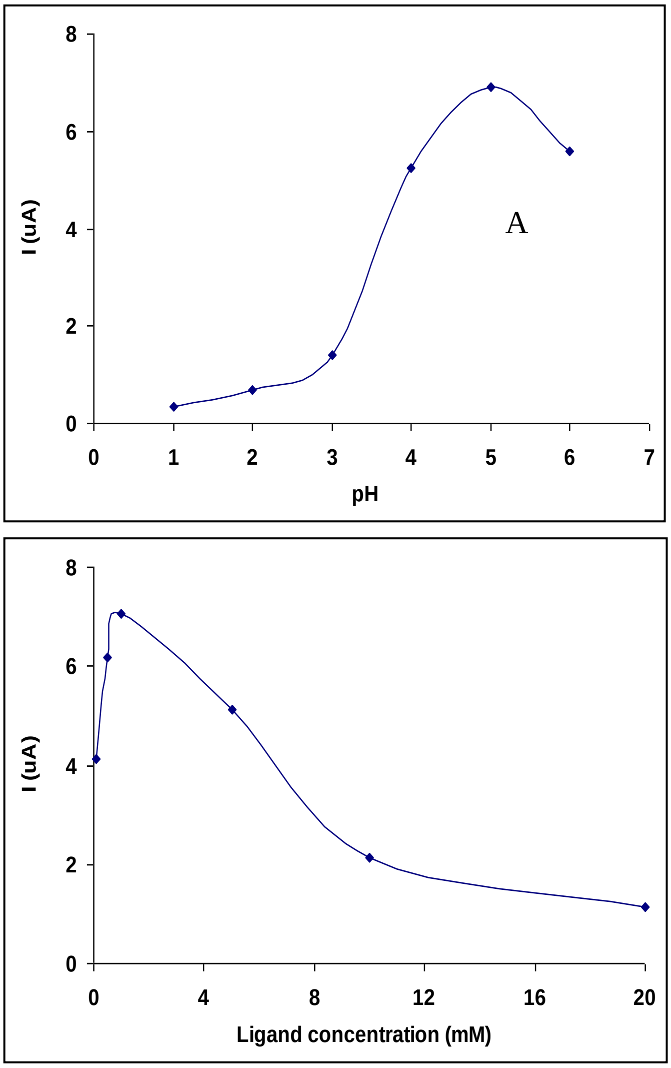

Figure 3. Plot of the cathodic stripping peak currents of Co(II)-Nitroso-S complex vs. (A) pH and (B) Nitroso-S concentration. Co(II) concentration was 150 µg l^{-1} and other conditions were the same as Figure 2.

3.3. Calibration curve, detection limit, reproducibility and selectivity

Standard solution containing different concentrations of Co(II) were prepared in pH 5.0 solutions and subjected to the optimized stripping voltammetric procedure. A linear calibration graph was obtained in the concentration range 3.3-187.1 µg l^{-1} (Fig 4). The detection limit was found to be 1.8 µg l^{-1} Co(II) and for five successive determinations of 10 and 100 µg l^{-1} Co(II) relative standard deviations were 1.2 and 0.8 %, respectively.

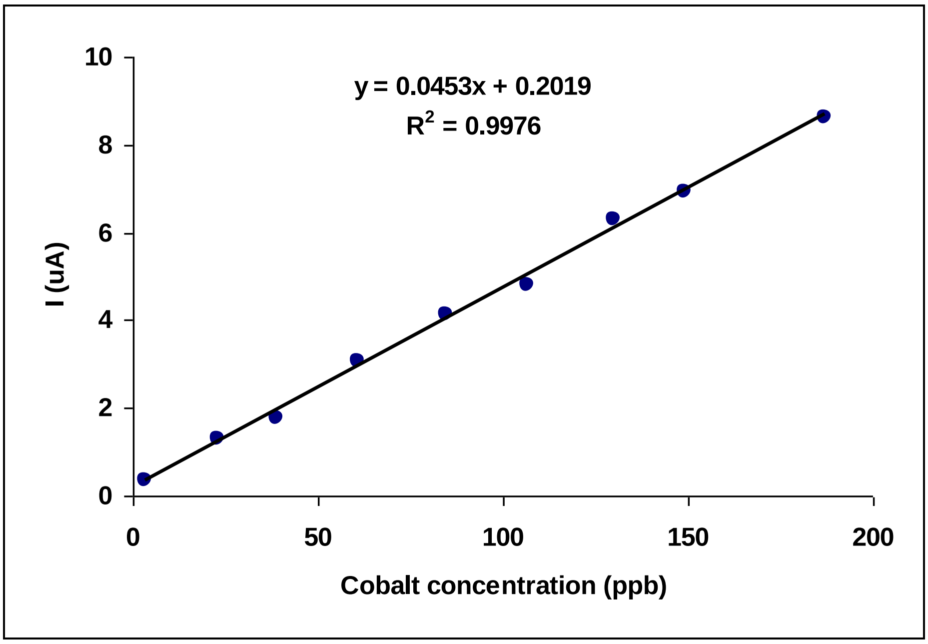

Figure 4. Plot of the cathodic stripping peak currents vs. Co(II) concentration. Other conditions were the same as Figure 2.

To check the selectivity of the proposed stripping voltammetric method for the Co(II) ions, various metal ions as potential interferents, were tested. Various salts and metal ions were added individually to a solution containing 50 µg l^{-1} of Co(II) and the general procedure was applied. Recoveries are given in Table 1. Among the salts and metal ions examined, most of them did not interfere at the high levels of concentration. As can be seen in Table 1, the presence of oxalate, citrate, thiosulfate or Pb(II) caused high depressions of the Co (II) peak. However, these compounds were not present in tested samples. Thus, the method is selective and useful for determination of Co (II) in real samples.

3.4. Real sample analysis

The developed method was applied to the determination of Co(II) in water samples. These waters were exchanged with distilled water used for the preparation of a acetate buffer (pH 5.0) and the general procedure was used on these resultant solutions. The standard addition method was applied for the determinations of cobalt ions. The results obtained by the proposed method were compared with FAAS method. Also, in order to evaluate the validity of the proposed method for the determination of Co^{2+}, recovery studies were carried out on samples to which known amount of Co^{2+} was added. The results were summarized in Table 2. Statistical comparison at the 95% confidence level showed no significant difference between the results obtained with the proposed procedure and those of the FAAS standard method.

Table 1. Effect of diver ions on the cobalt(II) determination

Interferent	Original compound	Recovery(%)
Na(I)	$NaNO_3$	100
K(I)	KNO_3	100
Fe(II)	$Fe(NO_3)_2$	103
Pb(II)	$Pb(NO_3)_2$	92
Cu(II)	$CuSO_4$	105
Zn(II)	$Zn(NO_3)_2$	97
Fe(III)	$Fe(NO_3)_3$	106
Oxalate	Na_2(oxalate)	93
Citrate	Na_2(citrate)	84
Thiosulfate	Na_2(thiosulfate)	110

[a] Cobalt(II) and interference concentrations are 50 and 500 μg l^{-1}, respectively and other conditions the same as Fig 2.

Table 2. The determination of Co(II) in water samples.

Sample	Present method (μg l^{-1}) [a]	FAAS method (μg l^{-1}) [a,b]	Recovery (%)	Spiked Co^{2+} (μg l^{-1})	Founded Co^{2+} (μg l^{-1}) [a]	Recovery (%)
Lab water	No detect	No detect	--	10.0	10.2 ± 0.3	102.0
				100.0	101.7 ± 1.4	101.7
Tab water	4.1 ± 0.1	4.3 ± 0.1	104.9	10.0	14.3 ± 0.4	101.4
				100.0	115.0 ± 1.4	100.8

(a) Mean of three determinations, ± standard deviation. (b) After vacuum evaporator concentration

4. CONCLUSION

This paper showed that the Nitroso-S is a useful ligand for the highly sensitive and selective determination of Co(II) by adsorptive stripping voltammetry at CPE. The cheap and nonpoisonous CPE was used instead of the severe toxic, expensive mercury electrodes in this method. Thus, it has excellent environmental and economical benefit. This method showed high selectivity and reproducibility. The procedure presented in this study could be used for the determination of cobalt in water samples with good accuracy and precision.

References

1. M. Haij, S. Dadfarnia, and K. Dehghan, *Talanta* 59 (2003) 719.
2. S. Cerutti, S. Moyano, J. A. Gasquez, J. Stripeikis, R. A. Olsina, and L. D. Martinez, *Spectrochim. Acta part B: Atom. Spect.* 58 (2003) 2015.
3. V. A. Lemos, J. S. Santos, and P. X. Baliza, *Separ. Sci. Technol.* 39 (2004) 3317.
4. N. Tokman, S. Akman, and Y. Bakircioglu, *Microchim. Acta* 146 (2004) 31.
5. A. Bobrowski, and J. Zarebski, *Electroanalysis* 12 (2000) 1177.
6. Bobrowski, *Anal. Chem.* 61 (1989) 2178.
7. Bobrowski, and A. M. Bond, *Electroanalysis* 3 (1991) 157.
8. M. Vega, and C. M. G. Berg, *Anal. Chem.* 69 (1997) 874.
9. A. Bobrowski, *Anal. Lett.* 23 (1990) 1487.
10. A. Economou, and P. R. Fielden, *Analyst* 118 (1993) 47.
11. A. Economou, and P. R. Fielden, *Talanta* 46 (1998) 1137.
12. M. A. Brett, A. M. O. Brett, and L. Tugulea, *Electroanalysis* 8 (1996) 639.
13. M. Korolczuk, A. Moroziewicz, and M. Grabarczyk, *Anal. Bioanal. Chem.* 382 (2005) 1678.
14. E. A. Hutton, S. B. Hocevar, B. Ogorevc, and M. R. Smyth, *Electrochem. Commun.* 5 (2003) 765.
15. A. Krolicka, A. Bobrowski, K. Kalcher, J. Mocak, I. Svancara, and K. Vytras, *Electroanalysis* 15 (2003) 1859.
16. M. Morfobos, A. Economou, and A.Voulgaropoulos, *Anal. Chim. Acta* 519 (2004) 57.
17. N. Y. Stozhko, and O. V. Inzhevatova, *J. Anal. Chem.* 59 (2004) 854.
18. X. Lu, Z. Wang, Z. Geng, J. Kang, and J. Gao, *Talanta* 52 (2000) 411.
19. Z. Gao, G. Wang, P. Li, and Z. Zhao, *Anal. Chem.* 63 (1991) 953.
20. M. R. Khan, and S. B. Khoo, *Analyst* 123 (1998) 1351.
21. M. A. Taher, M. Esfandyarpour, S. Abbasi, and A. Mohadesi, *Electroanalysis* 20 (2008) 374.
22. A. Mohadesi, M. A. Taher, and F. Majidi, *J. Anal. Chem.* in proof (2010).
23. M. A. Taher, and B. K. Puri, *Talanta* 48 (1999) 355.
24. M. A. Taher, A. Mostafavi, B. K. Puri, and S. Puri, *Anal. Chim. Acta* 367 (1998) 5