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# Adsorptive stripping voltammetry of nickel with 1-nitroso-2-napthol using a bismuth film electrode

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ABSTRACT

A sensitive procedure is presented for the voltammetric determination of nickel. The procedure involves an adsorptive accumulation of nickel 1-nitroso-2-napthol (NN) complex on a bismuth film electrode prepared ex situ by electrodeposition. The most suitable operating conditions and parameters such as pH, ligand concentration ($C_{NN}$), adsorptive potential ($E_{ads}$), adsorptive time ($t_{ads}$), scan rate and others were selected and the determination of nickel in aqueous solutions using the standard addition method was possible. The adsorbed Ni–NN complex gives a well defined cathodic stripping peak current at −0.70 V, which was used for the determination of nickel in the concentration range of 10.0–70.0 $\mu g\,L^{-1}$ (pH 7.5; $C_{NN}$ 6.5 $\mu mol\,L^{-1}$; $E_{ads}$ −0.30 V; $t_{ads}$ 60 s) with a detection limit of 0.1 $\mu g\,L^{-1}$. The relative standard deviation for a solution containing 10.0 $\mu g\,L^{-1}$ of Ni(II) was 3.5% ($n = 4$). The proposed method was validated determining Ni(II) in certified reference waste water (SPS-WW1) and Certified Reference Water for Trace Elements (TMDA 51.3) with satisfactory results. Then lake water samples were analyzed.

## 1. Introduction

The increasing utilization of heavy metals in modern industries leads to increased environmental burden. Nickel represents a good example of a metal whose use is widening 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 fibrosis, variable degrees of kidney and cardiovascular system poisoning, and stimulation of neoplastic transformation [1]. Considering the low content of nickel in natural water, sensitive analytical techniques are required.

Stripping analysis has been widely recognized as a powerful tool for trace metal analysis. Its remarkable sensitivity is attributed to the combination of a preconcentration step coupled with pulse measurements. Adsorptive stripping voltammetry (AdSV) is more adequate for nickel than anodic stripping voltammetry (ASV) because of its low solubility on the mercury electrode and its irreversible reduction behavior at very negative potential. Mercury electrodes have been traditionally used for achieving high reproducibility and sensitivity of the stripping technique. However, because of the toxicity of mercury, the use of bismuth thin films, deposited in situ on platinum or glassy carbon substrates, has been proposed as a possible alternative to mercury [2–12]. In the case of Ni(II) determination, complexes with dimethylglyoxime or nioxime have been the most commonly studied [13–18].

In the present study, we used a bismuth film electrode (BiFE) formed ex situ and applied it to Ni(II) determination by AdSV in the presence of 1-nitroso-2-napthol (NN). This ligand has been widely used as chromospheres reagent in spectroscopic techniques for the determination of several metal ions at trace level; however there are not reports in adsorptive stripping voltammetry with BiFE. The method was validated using certified reference waters (SPS-WW1 and TMDA 53.1) and was applied to the analysis of natural water of Lake Caren (Chile).

## 2. Experimental

### 2.1. Instruments

Square wave adsorptive stripping voltammetry (SWAdSV) was carried out on a CHInstrument Voltammetry analyzer (CHInstrument). A 10 mL capacity measuring cell was equipped with Ag/AgCl/KCl 3 mol $L^{-1}$ reference electrode, a glassy carbon working electrode (3 mm diameter, BAS, USA), and an auxiliary platinum

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electrode. For pH measurements an Orion 430 pH meter was used. All measurements were performed at room temperature.

### 2.2. Reagents

All solutions were prepared with ultra pure water from a Millipore Milli-Q system (Milford, MA, USA). The chemicals were analytical grade from Merck (Darmstadt, Germany). Standard stock solutions with 1.0 or 0.1 mg L$^{-1}$ of Ni(II) were prepared from standard Ni(II) 1000 mg L$^{-1}$ solutions (Merck). Bi(III) standard solutions were prepared from standard Bi(III) 1000 mg L$^{-1}$ solutions (Merck). The ligand was prepared by dissolving appropriate amounts in deionized water. Certified reference waste water (SPS-WW1) containing Al 2.00; As 0.1; Cd 0.02; Co 0.06; Cr 0.20; Cu 0.40; Fe 1.00; Mn 0.4; Ni 1.0; P 1.00; Pb 0.1; V 0.1 and Zn 5.00 mg L$^{-1}$ and certified reference water for trace elements (TMDA 51.3) containing Al 93.8; Sb 13.8; As 5.7; Bi 12.9; Cd 25.8; Cr 67.5; Co 71.5; Cu 89.2; Pb 73.3; Mn 84.9; Mo 58.4; Ni 68.3, Zn 137 μg L$^{-1}$, and others were used for validation measurements. Britton Robinson (BR) buffers (pH 2.0–10.0) were prepared by mixing equal volumes of 0.1 mol L$^{-1}$ orthophosphoric acid, acetic acid and boric acid. The pH was adjusted with NaOH 0.1 mol L$^{-1}$ solution.

### 2.3. Preparation of BIFE

The surface of the glassy carbon electrode (GCE) was cleaned and polished to a mirror-like appearance with an alumina slurry (0.3 μm) on a polishing cloth and then rinsed with deionized water in an ultrasonic bath. The GCE was then inserted in a cell containing an aqueous solution of Bi(III) (100 mg L$^{-1}$) in 0.1 mol L$^{-1}$ acetate buffer (pH 5.0). A constant film of bismuth was obtained by plating at −1.0 V for 120 s. After the plating procedure, the BiFE was rinsed with water and immersed into the test solution. Neither cleaning nor activating procedures were needed to pretreated the electrode between individual runs. The same electrode surface was used for each series of measures without new generation of a bismuth film.

### 2.4. Procedure

All bottles and containers used for standards and samples were thoroughly cleaned with 5% nitric acid before use. Filtration was carried out through 0.45 μm membrane filters. Surface water samples were obtained from Lake Caren (Santiago, Chile). Samples were obtained at different times of the year: in June 2008 (cold and rainy winter season), September 2008 (temperate spring season), and January 2008 (dry and warm summer season)

All voltammetric measurements were carried out in 0.10 mol L$^{-1}$ Britton Robinson (BR) buffer (pH 7.5) at room temperature (23 ± 2 °C) containing 6.5 μmol L$^{-1}$ of NN as complexing agent. An accumulation potential ($E_{\text{ads}}$) of −0.30 V was applied to the working electrode. The solution was stirred during the deposition step, and after an equilibration period of 10 s the voltammogram was recorded by applying a negative-going potential scan between −0.30 and −1.20 V. Square wave voltammetry was carried with an amplitude of 25 mV, a frequency of 15 Hz, and a potential step of 5 mV.

### 2.5. Limit of detection (LOD)

The LOD was calculated using the approximation of Miller and Miller [19] for calibration curves. The minimum signal ($y_{\text{min}}$) was calculated from $y_{\text{min}} = a + S_{y/x}$, where $a$ = intercept and $S_{y/x}$ = standard deviation of the calibration curve.

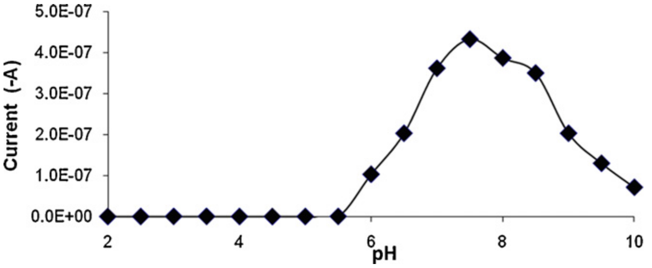

**Fig. 1.** Effect of pH on the peak current of Ni(II)–NN complex (supporting electrolyte 0.1 mol L$^{-1}$ BR buffer). Conditions: Ni(II) 10.0 μgL$^{-1}$; $C_{\text{NN}}$ 5.0 μmol L$^{-1}$; $E_{\text{ads}}$ −0.30 V; $t_{\text{ads}}$ 60 s.

## 3. Results and discussion

### 3.1. Effect of pH

The formation and stability of the complexes are strongly dependent on the pH of the solution. The influence of pH on the peak current of the Ni–NN complex was studied in the 2.0–10.0 range in BR buffer. The Ni(II) and $C_{\text{NN}}$ concentrations were 10.0 μgL$^{-1}$ and 6.5 μmol L$^{-1}$, respectively ($t_{\text{ads}}$ = 60 s, $E_{\text{ads}}$ = −0.30 V). The peak current vs. pH plot is presented in Fig. 1. It is seen that the peak height of nickel increased greatly in the pH range 5.5–7.5 and decreased at pH values greater than 7.5, perhaps due to the formation of hydroxo compounds. On the other hand, the peak potential was shifted to more negative values. The profile indicated that pH 7.5 offers the most favorable performance for Ni determination. Then, phosphate buffer (0.1 mol L$^{-1}$) was tested for its suitability in the determination of nickel, getting the same results as with BR buffer.

### 3.2. Effect of adsorptive potential ($E_{\text{ads}}$)

The adsorption of a complex on BiFE depends strongly on the potential to which the preconcentration process is carried out. In the case of the Ni(II)–NN complex, of an organic nature, adsorption does not depend only on the potential but also on the sign and intensity of the electric charge on the electrode, as well as on the supporting electrolyte. Complexes with positive charge will be adsorbed strongly on surfaces with negative charges, and vice versa. The optimum for adsorption of the neutral compound occurs when the potential of zero charge (PZC) is reached. The effect of adsorption potential on the peak current of the Ni(II)–NN complex (10.0 μgL$^{-1}$) was studied in the range between −0.30 and −1.00 V (Fig. 2). Peak current increased from −0.30 to −0.40 V and then decreased; over −0.60 V the current did not change. The accumulation potential of −0.30 V was used in all further AdSV measurements.

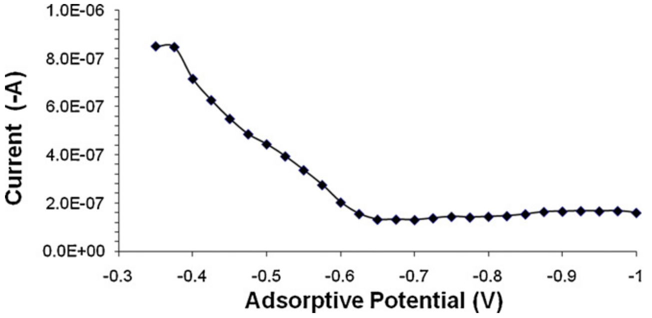

**Fig. 2.** Effect of adsorptive potential on the peak current of the Ni(II)–NN complex. Conditions: Ni(II) 10.0 μgL$^{-1}$; $C_{\text{NN}}$ 5.0 μmol L$^{-1}$; pH 7.5 (0.1 mol L$^{-1}$ BR buffer); $t_{\text{ads}}$ 60 s.

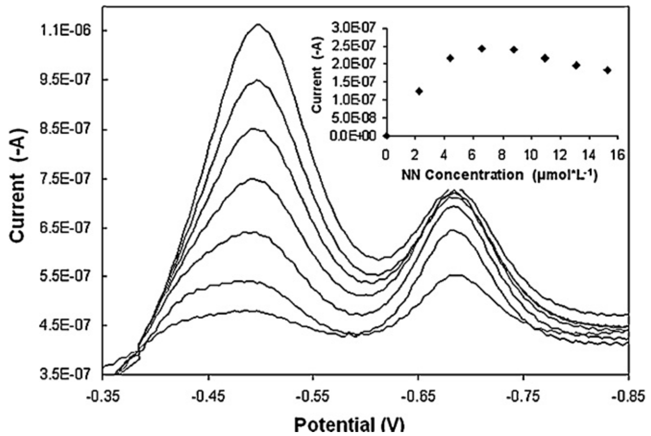

**Fig. 3.** Adsorptive stripping voltammograms of different concentrations of 1-nitroso-2-naftol and plot of $I_p$ vs. $C_{NN}$. Conditions: Ni(II) 10.0 μgL$^{-1}$; pH 7.5 (0.1 mol L$^{-1}$ BR); $E_{ads}$ −0.30 V; $t_{ads}$ 60 s. Amplitude 25 mV; frequency 15 Hz; and stirring speed 700 rpm in the accumulation step.

### 3.3. Effect of ligand concentration ($C_{NN}$)

The dependence of the Ni(II)–NN peak current on complexing agent concentration was tested. The ligand concentration ranged from 0.0 to 16.0 μmol L$^{-1}$ in the presence of 10.0 μgL$^{-1}$ Ni(II) (pH 7.5). The results (Fig. 3) show that the peak current of the Ni(II)–NN complex ($E_p$ = −0.68 V) increased with increasing ligand concentration up to 6.5 μmol L$^{-1}$. At higher concentrations the current peak decreased slightly as a consequence of competitive adsorption of free ligand and Ni complex. Consequently, an optimum NN concentration of 6.5 μmol L$^{-1}$ was selected for further experiments.

### 3.4. Effect of adsorption time ($t_{ads}$)

The time required for accumulation of the metal complexes on the electrode depends on the concentration of the complex, with less time required for higher concentrations. The accumulation time was changed from 10 to 240 s, and it was found that the peak current increased linearly with accumulation time up to 60 s, remained constant until 100 s, and then decreased (Fig. 4). For further study the accumulation time of 60 s was chosen.

### 3.5. Linear range and limit of detection

To verify the linear relationship between peak current and nickel concentration, a calibration graph was constructed under optimum conditions (pH 7.5 BR buffer; $C_{NN}$ 6.5 μmol L$^{-1}$; $E_{ads}$ −0.30 V; $t_{ads}$ 60 s), adding aliquots of Ni(II) solution, with of 0.9 μg L$^{-1}$ concentration increments until 200.0 μg L$^{-1}$. The results of this study (Fig. 5) indicated that current increased with Ni(II) concentration; but two slopes were observed. One of these was from 15.0 to 70.0 μg L$^{-1}$ and the other from 80 to 200.0 μg L$^{-1}$. The LOD was 0.10 μg L$^{-1}$ [19]. The relative standard deviation for a solution containing 10.0 μg L$^{-1}$ of Ni(II) was 3.5% ($n$ = 4).

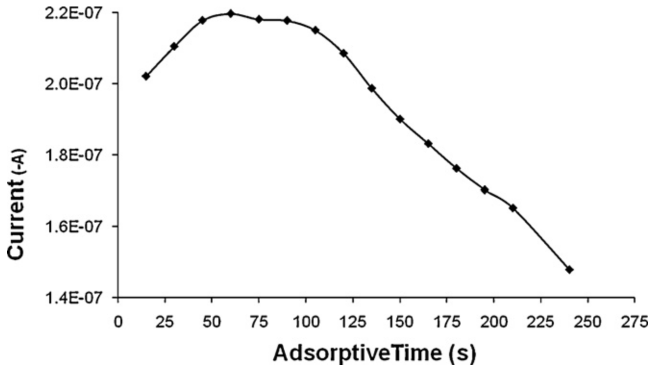

**Fig. 4.** Effect of adsorption time on the peak current of the Ni(II)–NN complex. Conditions: Ni(II) 10.0 μgL$^{-1}$; $C_{NN}$ 6.5 μmol L$^{-1}$; pH 7.5 (0.1 mol L$^{-1}$ BR buffer); $E_{ads}$ −0.30 V.

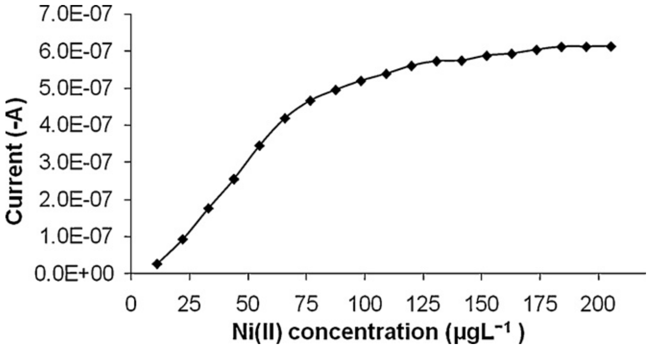

**Fig. 5.** Dependence of peak current of Ni–NN complex on Ni(II) concentration. $C_{NN}$ 6.5 μmol L$^{-1}$; pH 7.5 (0.1 mol L$^{-1}$ BR buffer); $E_{ads}$ −0.30 V; $t_{ads}$ 60 s.

### 3.6. Interferences studies

Possible interference by other metal ions on the adsorptive stripping voltammetry of nickel was investigated by the addition of the interfering ion to a solution containing this metal using the optimized conditions. When a solution containing Al(III), As(III), Bi(III), Cu(II), Cd(II), Cr(III), Mo(VI), and Zn(II) in a 100 μg L$^{-1}$ concentration coexists with 20.0 μg L$^{-1}$ of Ni (II) and 6.5 μmol L$^{-1}$ of NN (pH 7.5) the peak current of the Ni(II)–NN complex was not affected.

### 3.7. Analysis of certified reference water

The accuracy of the method designed employing the BiFE was assessed by analyses of two types of certified water: SPS-WW1 (waste water) and TMDA 51.3 (water with trace metals) with different contents of Ni(II) using the standard addition procedure. Three replicate analyses were performed for each sample. The results for Ni(II), 1014.0 ± 48.7 μg L$^{-1}$, for SPS-WW1 and 70.4 ± 2.4 μg L$^{-1}$ for TMDA 51.3, agreed well with the respective certified values of 1000.0 μg L$^{-1}$ and 70.0 ± 2.7 μg L$^{-1}$. The results obtained indicate that the proposed procedure can be applied to the determination of Ni(II) in natural water samples containing amounts of Ni(II) greater than 0.1 μg L$^{-1}$.

### 3.8. Real water samples

The method was also applied to three real water samples from Lake Caren. The samples were analyzed without prior treatment. Depending on the level of Ni(II) in the samples different aliquots were added to the voltammetry cell and completed up to 10.0 mL with deionized water. The results are presented in Table 1.

**Table 1**
Analysis of lake water samples.

| Sample | Found SWASV (μg L$^{-1}$) | Found ICP-EOS (μg L$^{-1}$) |
|---|---|---|
| S1 ($n$ = 4) | 10.8 (1.4%) | 10.0 (2.0%) |
| S2 ($n$ = 4) | 1.8 (3.0%) | 2.0 (3.8%) |
| S3 ($n$ = 4) | 20.4 (4.8%) | 20.0 (2.9%) |

## 4. Conclusions

Nickel can be effectively analyzed by square wave adsorptive stripping voltammetry using 1-nitroso-2-napthol as ligand. The accuracy and repeatability are satisfactory as well. It was found that electrode stability was excellent for measurements made without any additional pretreatment (SD 3.5%, $n = 4$).

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