

## Determination of Trace Amounts of Nickel by Differential Pulse Adsorptive Cathodic Stripping Voltammetry Using Calconcarboxylic Acid as a Chelating Agent

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(Received 5 August 2003 Accepted 31 December 2004)

A method for the determination of nickel(II) by stripping voltammetry is described. The method is based on the adsorptive accumulation of nickel(II) calconcarboxylic acid complex onto a hanging mercury drop electrode (HMDE), followed by the reduction of the adsorbed complex using differential pulse voltammetry. The optimum operating conditions and parameters were found to be 0.05 M  $\text{NH}_3/\text{NH}_4\text{Cl}$  buffer (pH = 9.5) as the supporting electrolyte, a ligand concentration of  $1 \times 10^{-6}$  M, accumulation potential of -0.5 V (*vs.* Ag/AgCl) and accumulation time of 60 s. At the optimized conditions, the peak current is proportional to the concentration of nickel in the range of  $1.7 \times 10^{-9}$  to  $4.7 \times 10^{-7}$  M ( $0.1\text{-}28 \text{ ng ml}^{-1}$ ) with a detection limit of  $0.05 \text{ ng ml}^{-1}$ . The relative standard deviation ( $n = 10$ ) at nickel concentrations of 2, 10 and  $15 \text{ ng ml}^{-1}$  varies in the range 0.76 to 2.1%. Possible interferences by metal ions, which are of great significance in real matrices, have been studied. The method was successfully applied to the determination of nickel content in a chocolate sample.

**Keywords:** Adsorptive cathodic stripping voltammetry, (ACSV), Differential pulse voltammetry, Nickel, Calconcarboxylic acid

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### INTRODUCTION

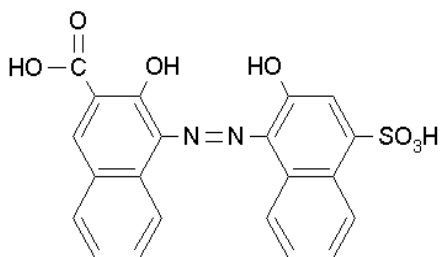
The determination of nickel is important due to its toxic nature, its important role in metallurgy for production of various types of ferrous and non-ferrous alloys, its widespread use in various industries such as electroplating industry, storage batteries and catalytic hydrogenation of vegetable oils, and its occurrence in various effluents. Nickel is also present at low concentrations in various foods of both animal and vegetable origin such as red meat, cotton seed, corn meal, saturated oils, chocolates, milk and milk products. It is among the toxic metals of significance for environmental surveillance, food control, and occupational medicine, toxicology and hygiene [1]. Nickel toxicity can cause acute pneumonitis, dermatitis, asthma, disorders of central nervous

system and cancer of nasal cavity and lungs [2]. Maximum admissible concentration of nickel in drinking water is  $0.1 \text{ mg l}^{-1}$  [3]. The carcinogenic action of nickel and its salts has been reported in numerous animal experiments over the years [4].

Consequently, many analytical procedures have been proposed for nickel determination, such as spectrophotometry [5-7], flame atomic absorption spectrometry after preconcentration [8], inductively coupled plasma (ICP) atomic emission spectrometry following a preconcentration step [9], potentiometry using nickel-selective electrodes [2,10,11], and adsorptive cathodic stripping voltammetry (ACSV) [12-19]. Among the different techniques, stripping analysis is one of the most powerful ones for trace metal analysis [20]. The ACSV methods are based on various ligands such as oxime derivatives [1,12-15,17], 8-hydroxyquinoline [14], hydroxynaphthyl blue [16] and dithiocarbamate derivatives [18,19]. Most other techniques generally require time

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**Fig. 1.** Structure of calconcarboxylic acid used as the ligand for DPACSV determination of nickel(II).

consuming preconcentration steps for trace and ultratrace analysis of nickel, before performing its determination. The ACSV method also includes an adsorption (preconcentration) step, but this is generally carried out over a short period (generally less than 1 min).

The applications of ACSV in the determination of trace and ultratrace metals have been reviewed elsewhere [21]. This method provides low detection limits due to its "built in" preconcentration step, during which the target metal ion is accumulated onto the surface of the working electrode [22].

Azo dyes are among the different classes of compounds that have been proposed for the ACSV determination of metal ions. Wang *et al.* [23,24] have used 4-hydroxy-3-(2-hydroxy-1-naphthylazo)benzene sulfonic acid, known as acid alizarin violet N, for the ACSV determination of several metal ions such as iron, aluminum and calcium. Abollino *et al.* [25] have recently investigated the behavior of several azo dyes of the naphthalene-hydroxy-azo sulfonic group as potential ligands for ACSV determination of several metal ions, and found that among Cd(II), Ni(II), Pb(II), and Mn(II), only Ni(II) complexes give an ACSV response.

In this work, we report the use of calconcarboxylic acid (CCA, Fig. 1) for the adsorptive cathodic stripping voltammetric determination of nickel(II) using a hanging mercury drop electrode (HMDE) in differential pulse modulation method. The proposed method was successfully applied to the reliable determination of nickel traces in a chocolate sample. The nickel(II)-CCA complex showed good adsorption onto the HMDE, leading to a detection limit of 0.05 ng ml<sup>-1</sup> (60 s accumulation), which is better than that obtained with many of the other ligands cited [16-19].

## EXPERIMENTAL

### Reagents and Solutions

All chemicals were purchased from Merck unless indicated otherwise. All solutions were prepared with doubly distilled water and reagent grade chemicals without further purification. Stock solution of nickel(II) (1000 µg ml<sup>-1</sup>) was prepared by dissolving 1.00 g of pure nickel foil (Aldrich) in nitric acid and diluting to 1 liter with distilled water. Standard solutions (1000 µg ml<sup>-1</sup>) of other cations, which were used to study their interference effects, were prepared from their corresponding nitrate or chloride salts, and those of anions were from their sodium or potassium salts. A stock 4 × 10<sup>-4</sup> M solution of CCA was prepared by dissolving 9.8 × 10<sup>-2</sup> g of the reagent in 10% (v/v) ethanol-water mixture. The pH adjustments were made using ammonia/ammonium chloride buffer (pH 9.5).

In all of the measurements, oxygen was expelled by purging the solutions with water saturated high purity argon gas at ~1 atm for 4 min prior to each experiment, and all experiments were performed under the argon atmosphere.

### Apparatus

Differential pulse stripping was conducted on a Metrohm 746 VA Trace Analyzer and a 747 VA Stand linked to a computer for data acquisition using Cacyvo 6.6017.100 and 693 VA backup Metrohm software. A conventional three electrode system comprised of a pneumatically operated Multi Mode Electrode (MME) for generation of the working HMDE, a platinum rod with plastic shaft as the counter electrode and an Ag/AgCl saturated KCl electrode as the reference electrode (all from Metrohm) was used in all experiments. The measuring cell was also equipped with a PTFE stirrer, which was used for stirring the solutions during the adsorptive process at a speed of 2000 rotations min<sup>-1</sup>.

The pH measurements were performed with a Metrohm model 692 pH-meter using a combined glass electrode. Atomic absorption measurements were carried out on a Shimadzu model AA-670 spectrometer with an air-acetylene flame.

### Preparation of Chocolate Sample

The general procedure for preparation of chocolate sample

was as following [10]. The chocolate sample, was weighed into a porcelain crucible and heated on a sand bath until fuming ceased. Then the crucible was transferred into a furnace at  $\sim 400\text{ }^{\circ}\text{C}$  for 3 h to ash the sample. After cooling, the residue was treated with 2 ml 1:1 nitric acid solution and gently heated on the sand bath to dryness. The crucible was transferred to the furnace again to remove traces of black residues. Then it was treated with 2-3 ml 1:1 nitric acid solution and heated to near boiling to dissolve the residue. The resulting solution was cooled, filtered and made up to 25 ml in a volumetric flask.

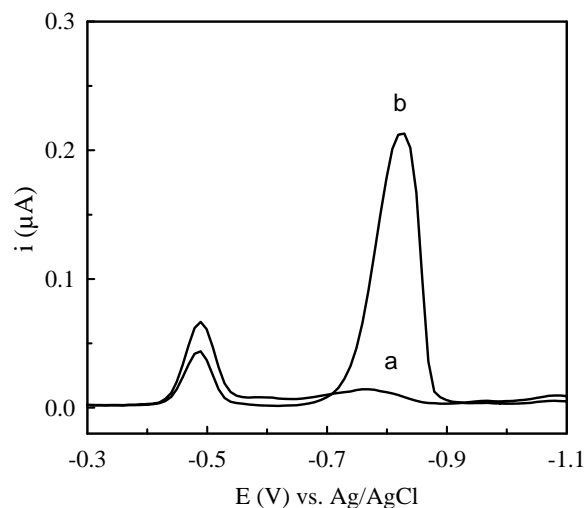
### Procedure

The general procedure used to obtain ACSV was as following. Ten ml of 0.1 M ammonia/ammonium chloride buffer, pH 9.5, 1.0 ml of  $2 \times 10^{-5}$  M CCA and an appropriate amount of standard or sample solution were made up to 20 ml in a volumetric flask. The solution was transferred into the voltammetric cell and purged with argon gas for 4 min. The accumulation potential of  $-0.5\text{ V vs. Ag/AgCl}$  was applied for 60 s to a fresh HMDE while the solution was stirring. Then stirring was stopped and after a pause of 10 s at the same potential to allow equilibration, the potential was scanned in the negative direction in the differential pulse mode from  $-0.6$  to  $-1.2\text{ V}$  using potential scan rate of  $50\text{ mV s}^{-1}$ , pulse amplitude of 50 mV, measuring time ( $t_{\text{meas}}$ ) of 15 ms, and pulse time ( $t_{\text{pulse}}$ ) of 20 ms. The nickel stripping peak was registered at about  $-0.8\text{ V}$  and its current used as a measure of analytical signal. Each scan measurement was repeated three times with a new HMDE for each analyzed solution and the mean of three peak currents obtained. All experiments were carried out at room temperature. The standard addition method was used for determination of nickel content in the sample.

## RESULTS AND DISCUSSION

### Voltammetric Behavior of Ni(II)-CCA System

Most of the reported ACSV methods for nickel are based on complexation with oxime derivatives. However, as recently reported by Abollino *et al.* [25], naphthalene-hydroxy-azo sulfonic species are good candidates for this purpose. Therefore, we were promoted to study the suitability of CCA for ACSV determination of nickel(II). Preliminary

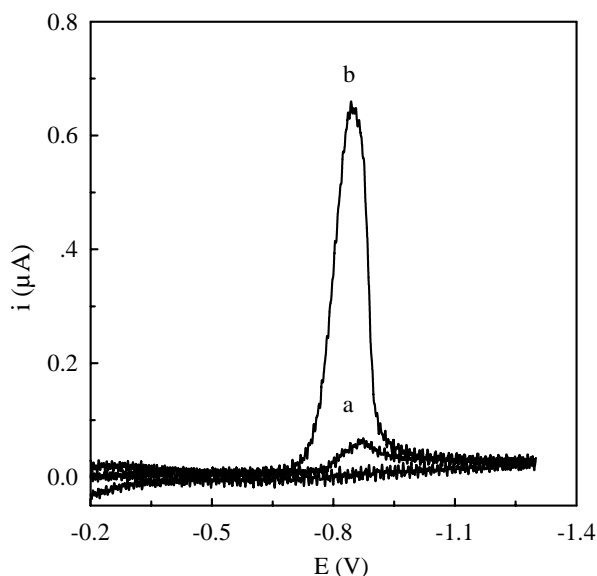


**Fig. 2.** Differential pulse ACSVs in 0.05 M ammonia buffer solution, pH 9.5, using an accumulation time of 60 s at  $-0.5\text{ V}$ ; (a)  $5\text{ }\mu\text{M}$  CCA; (b)  $5\text{ }\mu\text{M}$  CCA and  $10\text{ ng ml}^{-1}$  nickel(II).

experiments were carried out to identify the general characteristics and behavior of the nickel(II)-CCA system at the HMDE. Then the influence of experimental parameters such as pH, ligand concentration, accumulation time and potential, scan rate, pulse amplitude, pulse time and measuring time on the sensitivity of the differential pulse voltammograms were investigated.

The CCA can coordinate with some metal ions through its azo-nitrogen and phenolic oxygen sites. The carboxylate group, adjacent to one of the phenolic groups, can also influence the complexation of the ligand with metal ions [25]. The presence of an extended  $\pi$ -electron system in the structure of CCA increases its adsorption tendency. Figure 2 shows the ACSV for the ligand and nickel(II)-ligand systems in ammonia buffer solution, pH 9.5. As can be seen from Figure 2a, the CCA ligand gives rise to a differential pulse (DP) peak at  $-0.48\text{ V}$ . In the presence of small amounts of nickel ions (Fig. 2b) a well-defined DP peak appeared at  $\sim -0.8\text{ V}$ , while the intensity of the peak at  $-0.48\text{ V}$  decreased.

The actual occurrence of adsorption on the HMDE was confirmed by recording cyclic voltammograms with and without prior accumulation steps (Fig. 3). Much lower signals

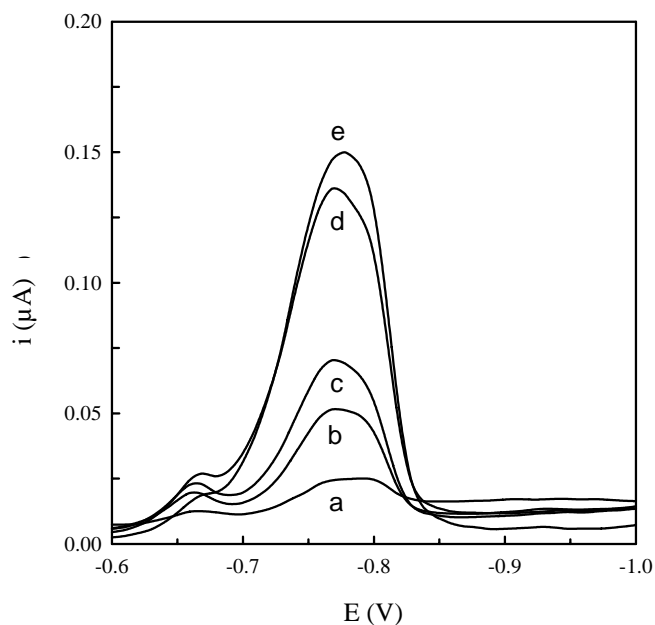


**Fig. 3.** Cyclic voltammogram for reduction of Ni-CCA complex in ammonia buffer of pH 9.5. Conditions: ligand concentration, 5  $\mu\text{M}$ ; Ni(II), 0.1  $\mu\text{g ml}^{-1}$ ; accumulation potential, -0.5 V; accumulation period, (a) 0 s and (b) 100 s.

were obtained in the later case (Fig. 3b). Cyclic and DP voltammograms showed an increase in the cathodic current by increasing accumulation time (Fig. 4). No peak was observed on the reverse (anodic) scan. A further indication of the adsorption process was obtained by recording repetitive cyclic voltammograms of Ni(II)-CCA after accumulation time of 60 s at a potential of -0.5 V. A strong cathodic peak was observed in the first sweep. Subsequent sweeps exhibited a substantial decrease in the peak current, showing that Ni(II)-CCA has adsorptive characteristics at the HMDE.

The peak observed in the presence of the ligand alone was due to the reduction of azo group to form hydrazo and finally to amine derivatives [26]. In the presence of nickel, a new DP peak appears at a more cathodic potential ( $\sim -0.8$  V) which can be related to the reduction of CCA in the Ni(II)-CCA complex, as has been reported for similar compounds [25].

The influence of scan rate on peak current and peak potential was investigated. Peak current increased almost linearly with potential scan rate up to 50  $\text{mV s}^{-1}$ . The peak



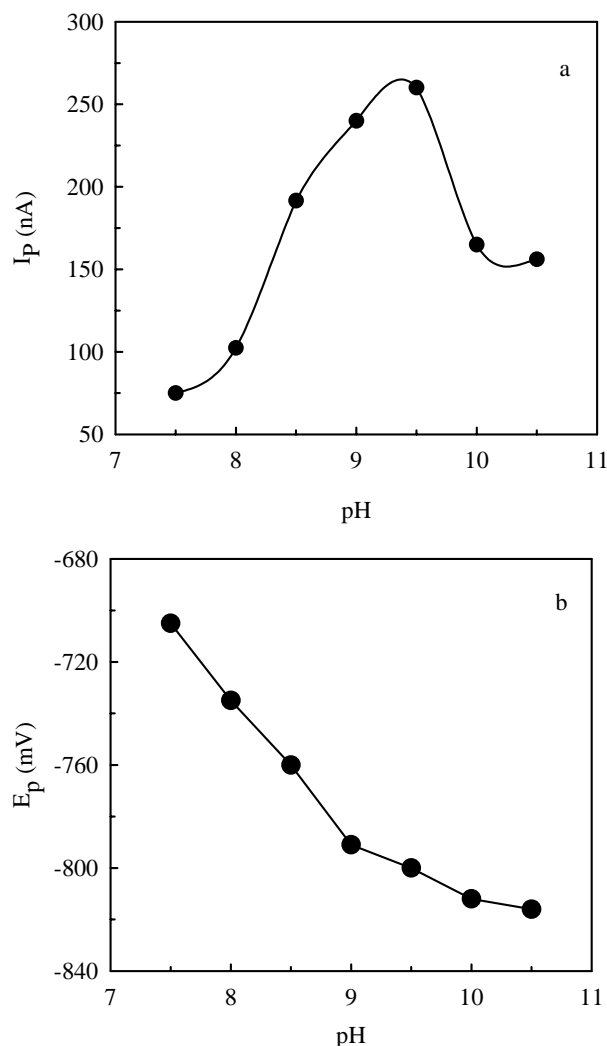
**Fig. 4.** Differential pulse ACSVs for reduction of Ni-CCA complex in ammonia buffer, pH 9.5 at different accumulation times: a, 0; b, 10; c, 20; d, 40; e, 60 s. Conditions: ligand concentration, 5  $\mu\text{M}$ ; Ni(II), 0.1  $\mu\text{g ml}^{-1}$ ; accumulation potential, -0.5 V.

potential for reduction of the ligand in the complex shifted to more negative potentials with increasing scan rate, with a  $\Delta E_p/\Delta \log(v)$  value of  $\sim -28$   $\text{mV}/\log(v, \text{mV})$ . Linear dependence of current on scan rate and a negative shift in potential are in line with expectation for an electrochemically irreversible charge transfer process of an adsorbed species.

### Effect of Various Parameters on the ACSV Sensitivity

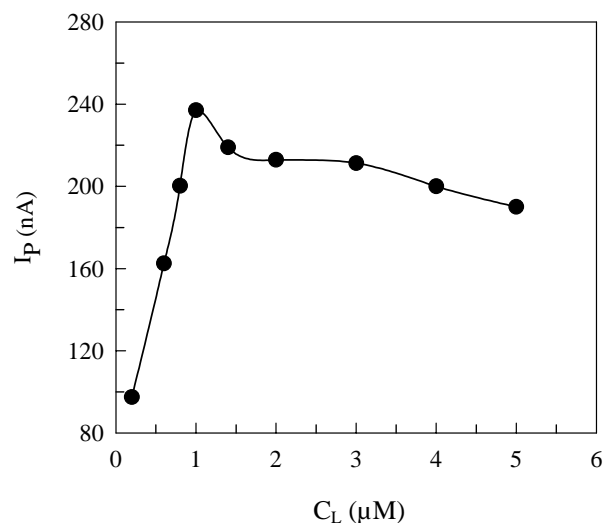
**Effect of buffer solution and pH.** Calconcarboxylic acid has four acidic groups. The sulfonic acid group completely dissociates in aqueous solutions, but the dissociation of other groups depends on the solution pH. Owing to the presence of these groups and competition between proton and  $\text{Ni}^{2+}$  ions for the binding sites in the ligand molecule, the pH is a very important parameter. The influence of pH on the ACSV peak of nickel was investigated for a solution containing  $1 \times 10^{-6}$  M CCA and 10  $\text{ng ml}^{-1}$   $\text{Ni}^{2+}$  in 0.05 M ammonia buffer, as

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**Fig. 5.** Effect of pH on the (a) peak current and (b) peak potential in 0.05 M ammonia buffer. Conditions: ligand concentration, 1  $\mu\text{M}$ ; Ni(II), 10  $\text{ng ml}^{-1}$ ; accumulation time, 60 s; accumulation potential, 0.5 V.

preliminary tests showed that this buffer improved the DP peak height and shape compared to phosphate and borax buffers. This can be related to the involvement of  $\text{NH}_3$  molecules as axial ligands for Ni(II), which is expected to form a planar complex with CCA. As can be seen in Fig. 5a, the DP peak height for nickel was strongly affected by pH, with a maximum at  $\text{pH} \sim 9.5$  and a sharp decrease at higher and



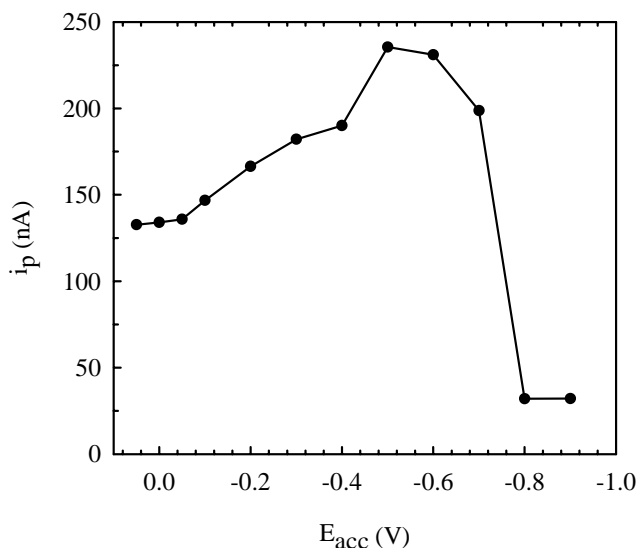
**Fig. 6.** Influence of CCA concentration on the ACSV sensitivity for 10  $\text{ng ml}^{-1}$  nickel(II) at pH 9.5. Other conditions are the same as in Fig. 2.

lower pH values. The reduction of peak currents at  $\text{pH} < 9.5$  can be related to protonation of coordination sites of the ligand whereas at  $\text{pH} > 9.5$  hydrolysis of the metal ion, in competition with formation of the electroactive complex, is probably the reason for declined peak heights. The reduction peak completely disappears at  $\text{pH} \leq 7$ , because the conditional stability constant of the complex is much smaller at these pH values.

The peak potential for the nickel complex is shifted to more negative potentials with increasing pH, as a result of complex stabilization, with a slope of  $\sim 60$  mV/pH unit in the range 7.5-10.5 (Fig. 5b).

**Influence of ligand concentration.** The concentration of CCA has a great influence on the sensitivity of nickel determination. As can be seen in Fig. 6, a large variation in the DP peak height occurs between 0.2 and 1  $\mu\text{M}$  of CCA. Beyond this concentration, the peak height decreases gradually, probably due to some competition of the ligand for adsorption at the electrode surface. Consequently, an optimum CCA concentration of 1  $\mu\text{M}$  was selected for further experiments.

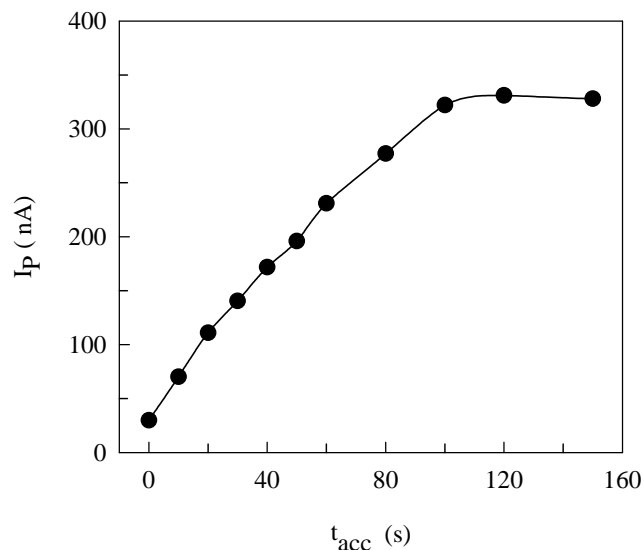
**Effect of accumulation potential and accumulation time.** The accumulation potential was varied between 0 and -



**Fig. 7.** Effect of accumulation potential on peak current for reduction of Ni-CCA complex in 0.05 M ammonia buffer containing  $1 \mu\text{M}$  CCA and  $10 \text{ ng ml}^{-1}$  nickel(II) using an accumulation time of 60 s.

0.9 V during a constant adsorption time of 60 s. The cathodic voltammetric scan was initiated after a pause of 10 s without stirring to allow the electrode to equilibrate before performing the measurement process. Maximum peak current was observed at accumulation potentials of -0.5 to -0.6 V (Fig. 7). This is close to the reduction potential of the ligand alone, which is also adsorbed to some extent at the electrode surface, but it is less than that required for reduction of the complex. It seems that reduction of the adsorbed ligand decreases its surface concentration and allows more room for the Ni(II)-CCA complex to adsorb at the electrode surface. At potentials higher than -0.7 V, reduction of the complex also occurs during the accumulation process, resulting in lower peak currents in the measurement step (Fig. 2). Generally, an accumulation potential of -0.5 V vs. Ag/AgCl was used for further investigations.

Variation of the accumulation time between 0 and 150 s at a deposition potential of -0.5 V showed that the DP peak height for reduction of the complex is increased linearly with the accumulation time, and reached a maximum after 100 s;



**Fig. 8.** Dependence of peak current on accumulation time at an applied potential of -0.5 V. Other conditions are the same as in Fig. 6.

leveling off is presumably due to saturation of the HMDE surface at longer accumulation times. The dependence of peak height on the deposition time is shown in Fig. 8. An adsorption time of 60 s was selected for nickel determination throughout this work as a compromise between high sensitivity and short analysis time. However, the sensitivity can be further increased by extending the accumulation period. The dependence of the peak heights on the deposition time is an evidence for the adsorption-controlled current. Addition of a small amount of Triton X-100, as a neutral surfactant, suppressed the peak current. This is a further indication that the observed current is due to reduction of an adsorbed species.

**Effect of DP parameters.** Increasing the DP scan rate from 2 to  $80 \text{ mV s}^{-1}$  at constant concentrations of the ligand ( $1 \mu\text{M}$ ) and nickel ion ( $5 \text{ ng ml}^{-1}$ ) in 0.05 M ammonia buffer, pH 9.5, using an accumulation period of 60 s at -0.5 V, caused the peak height to increase up to a potential scan rate of  $\sim 50 \text{ mV s}^{-1}$ . Other optimized DP parameters include pulse amplitude of 50 mV, measuring time ( $t_{meas}$ ) of 15 ms and pulse time ( $t_{pulse}$ ): of 20 ms.

### Performance Characteristics of the Method

Under the optimized conditions described above, (*i.e.*, pH 9.5 using 0.05 M ammonia buffer, 1  $\mu$ M CCA, accumulation period of 60 s at -0.5 V, potential scan rate of 50 mV s<sup>-1</sup> and pulse amplitude of 50 mV. Linearity was evaluated by increasing of nickel concentration up to 50 ng ml<sup>-1</sup>. The calibration plot thus obtained was linear over the range 0.1-28 ng ml<sup>-1</sup> with a correlation coefficient of 0.9996 ( $I_p$  (nA) = 9.74 + 24.76 [Ni<sup>2+</sup>] (ng ml<sup>-1</sup>), n = 12).

The limit of detection was calculated by carrying out the above procedure on 10 blank samples using the equation  $C_{DL} = 3SD_b/m$ , where  $SD_b$  is the standard deviation of the blank measurements and  $m$  is slope of the calibration plot. The  $C_{DL}$  thus obtained was 0.85 nM (0.05 ng ml<sup>-1</sup>), which is better than those reported for some spectroscopic (5-9) and ACSV methods (1,16-19).

The analytical precision of the method was estimated from the reproducibility of 10 determinations at several nickel concentrations; the relative standard deviations for 2, 10 and 15 ng ml<sup>-1</sup> of Ni(II) were in the range 0.76-2.1%.

### Interferences

Possible interference by other cationic and anionic species with ACSV determination of nickel was investigated by addition of the interfering ion to a solution containing 10 ng ml<sup>-1</sup> of nickel and carrying out the measurements at the optimized conditions. No interference was found in the presence of 1  $\times$  10<sup>4</sup> ng ml<sup>-1</sup> of Li<sup>+</sup>, Na<sup>+</sup>, Sr<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, 5  $\times$  10<sup>3</sup> ng ml<sup>-1</sup> of Cr<sup>3+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup> and Al<sup>3+</sup>, 1  $\times$  10<sup>3</sup> ng ml<sup>-1</sup> of Mg<sup>2+</sup>, 5  $\times$  10<sup>2</sup> ng ml<sup>-1</sup> of Cu<sup>2+</sup>, 2  $\times$  10<sup>2</sup> ng ml<sup>-1</sup> of Mn<sup>2+</sup> and 1  $\times$  10<sup>2</sup> ng ml<sup>-1</sup> of Fe<sup>3+</sup>. The interference from iron could be considerably reduced by masking it with sodium fluoride. Co(II) showed strong interference with the nickel determination at equimolar concentrations.

### Application to a Real Sample

To assess the applicability of the proposed DPACSV method to a real sample, an attempt was made to determine nickel in a chocolate sample. The sample was prepared for the analysis as described in the experimental section. The nickel content was measured by the standard addition method, and also by atomic absorption spectrometry (AAS). The amount of nickel obtained by voltammetry was 1.68  $\pm$  0.02 mg kg<sup>-1</sup> of the

solid chocolate sample (n = 5), which was in a good agreement with the results obtained from AAS measurement (1.62  $\pm$  0.04 mg kg<sup>-1</sup>).

### CONCLUSIONS

Our experiments show that the differential pulse adsorptive cathodic stripping voltammetric method based on nickel(II)-calconcarboxylic acid is suitable for determining low nickel concentrations, down to sub-nanomolar levels, after 60 s of deposition at an applied potential of -0.5 V. The sensitivity of the proposed procedure holds promise for its application in the determination of low nickel concentrations in biological samples. Further experiments are required to eliminate the interference from Co(II).

### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of this work by the University of Isfahan Research Council.

### REFERENCES

- [1] E.N. Iliadou, S.T. Girousi, U. Dietze, M. Otto, A.N. Voulgaropoulos, C.G. Papadopoulos, *Analyst* 122 (1997) 597.
- [2] V.K. Gupta, A.K. Jain, L.P. Singh, U. Khurana, *Anal. Chim. Acta* 31 (1997) 31.
- [3] U.S. Environmental Protection Agency Site at <http://www.epa.gov/safewater/dwh/c-ioc/nickel.html>
- [4] E. Berman, *Toxic Metals and Their Analysis*, Heyden & Sons, London 1980.
- [5] Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood, Chichester, 1986.
- [6] S.L.C. Ferreira, A.C.S. Costa, D.S. Jesus, *Talanta* 43 (1996) 1649.
- [7] S.L.C. Ferreira, A.C.S. Costa, D.S. Jesus, *Talanta* 43 (1996) 1649.
- [8] S.L.C. Ferreira, W.N.L. Santos, V.A. Lemos, *Anal. Chim. Acta* 445 (2001) 145.
- [9] S.L.C. Ferreira, C.F. Brito, A.F. Dantas, N.M.L. Araujo, A.C.S. Costa, *Talanta* 48 (1999) 1173.

- [10] M. Shamsipur, S.Y. Kazemi, *Electroanalysis* 12 (2000) 1472.
- [11] M. Mazloum, M. Salavati-Niassari, M.K. Amini, *Sens & Actuators B* 82 (2002) 259.
- [12] B. Pihlar, P. Valenta, H.W. Nürnberg, *Fresenius Z. Anal. Chem.* 307 (1981) 337.
- [13] J.R. Donat, K.W. Bruland, *Anal. Chem.* 60 (1988) 240.
- [14] C. Colombo, C.M.G. van den Berg, *Anal. Chim. Acta* 337 (1997) 29.
- [15] J. Golimowski, A. Tykarska, *Fresenius J. Anal. Chem.* 349 (1994) 620.
- [16] P.A.M. Farias, A.K. Ohara, I. Takase, S.L.C. Ferreira, *J.S. Gold, Talanta* 40 (1993) 1167.
- [17] W.R. Jin, V.D. Nguyen, P. Valenta, H.W. Nürnberg, *Anal. Lett.* 30 (1997) 1235.
- [18] S. Puri, R.K. Dubey, B.K. Puri, M.F. Hussain, *Anal. Lett.* 31 (1998) 283.
- [19] A.A. Ensafi, K. Zarei, *Talanta* 52 (2000) 435.
- [20] J. Wang, *Stripping Analysis: Principles, Instrumentation and Applications*, VCH, Deerfield Beach, FL, 1985.
- [21] M.G. Paneli, A.N. Voulgaropoulos, *Electroanalysis* 5 (1993) 355.
- [22] J. Wang, Jianyan Wang, B. Tian, M. Jiang, *Anal. Chem.* 69 (1997) 1657.
- [23] J. Wang, P.A.M. Farias, J.S. Mahmoud, *J. Electroanal. Chem.* 195 (1985) 165.
- [24] J. Wang, P.A.M. Farias, J.S. Mahmoud, *Anal. Chim. Acta* 172 (1985) 57.
- [25] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, *Electroanalysis* 11 (1999) 870.
- [26] G.W. Latimer Jr, *Talanta* 15 (1968) 1.