Asian Journal of Chemistry Vol. 18, No. 2 (2006), 957–960

Voltammetric Analysis of Ni^{2+} Ions Concentration in Watt's Electrolytic Bath

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The present results prove that Ni/Ni^{2+} system has an irreversible behaviour, $Ep_c = -1.01$ volt, in electrolytic formula as Watt's bath. It is possible to measure the Ni^{2+} ions concentration by CV, DPP and ASV voltammetric methods. Our investigations show that DPP method is the most convenient, because it is much faster than the volumetric and gravimetric methods. In comparison with spectroscopic methods, DPP is more selective, because inorganic impurities have less interference with Ni^{2+} peak potential. Finally, DPP is more sensitive to CV, because residual current is minimized and also faster than ASV, because DPP dose not need preelectrolysis.

Key Words: **Voltammetry, Spectroscopy, Peak potential, Standard addition.**

INTRODUCTION

Modern electroanalytical methods have wide applications in chemical based industries[1-5]. In this work, we have examined the determination of the Ni^{2+} quantities in Watt's electrolytic bath by voltammetric methods as CV, DPP and ASV[6,7] because this control is very important in order to obtain smooth and nonporous deposits. We have measured the Ni^{2+} concentration, by usual methods, as spectroscopy (AAS, visible), volumetry (direct and indirect) and gravimetry[8,9], on the same electrolytic solution. This study was performed comparatively in order to identify a more convenient method.

EXPERIMENTAL

Voltammetric experiments (CV, DPP, ASV) were carried out with polarecord 747 VA stand and 746 VA trace analyzer (Metrohm Swiss), using Ag/AgCl/KCl 3M as reference electrode and DME as a working electrode. AAS measurement was carried out with Philips PU 9100 (UK) and spectrophotometric determinations by Unicam 8700 series (UK). All chemicals were of analytical grade (Merck); solutions were prepared with distilled water and experiments were

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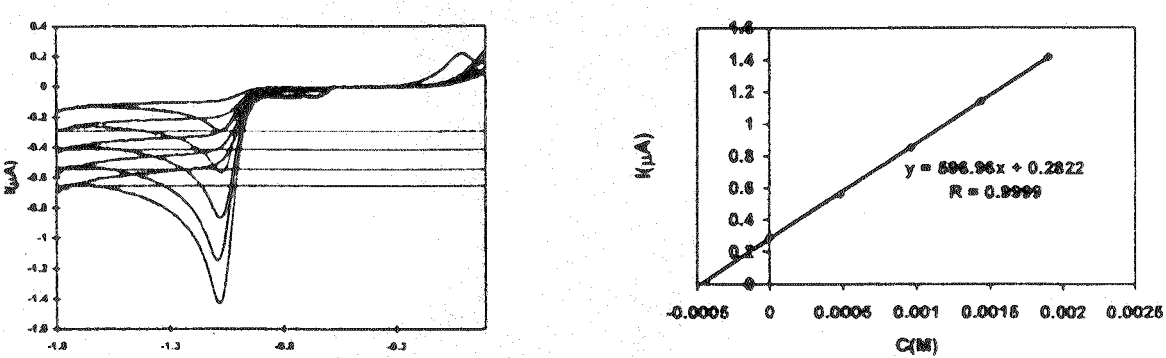
conducted at 25°C. Watt's nickel electrolytic bath contains nickel ions (40–58 g L^{-1}), boric acid (35–45 g L^{-1}), chloride ions (35–50 g L^{-1}) and pH = 4–5.

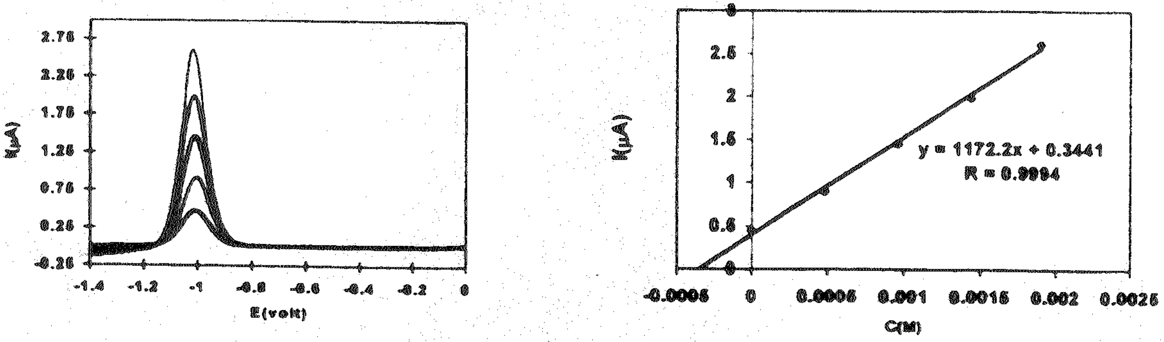
RESULTS AND DISCUSSION

Present results show that Ni/Ni^{2+} system has an irreversible behaviour in Watt's electrolytic bath ($Ep_c = -1.01$ volt). But detailed studies by varying scan rate show that peak current, I_p, increases linearly with $v^{1/2}$ (scan rate) which is indicative of a diffusion control process. We have presented CV, DPP and ASV voltammogram of Ni^{2+} on Figs. 1a, 2a and 3a, respectively and also, calibration curves, by standard addition method, for these methods on Figs. 1b, 2b and 3b. In these comparative investigations, we have determined the concentration of Ni^{2+} in a solution with the same composition as Watt's electrolytic bath, by spectroscopic (AAS, visible), gravimetric and volumetric methods. Spectrogram of visible spectroscopy and calibration curves, standard addition, for visible and AAS methods are presented, respectively, on Figs. 4a, 4b and 5. We have performed spectroscopic measurements, respectively, at $\lambda = 341.5$ and 545 nm, in AAS (using a nickel lamp) and visible methods.



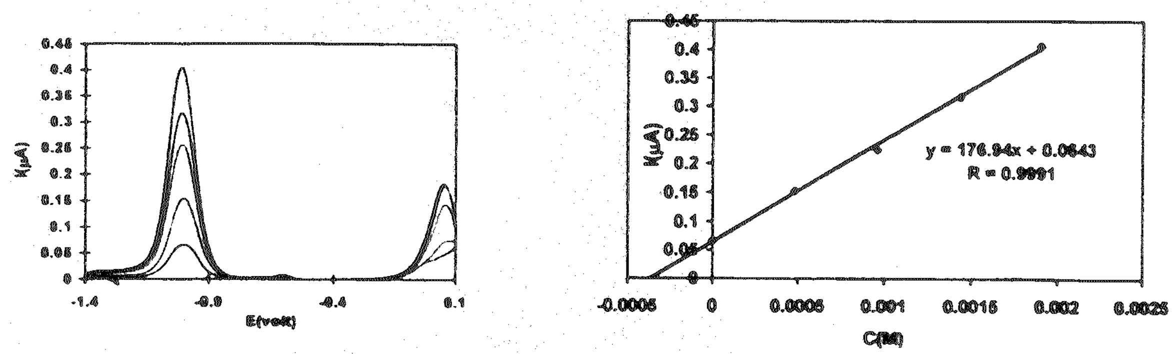
(a) (b)

Fig. 1. (a) Standard addition CV of unknown Ni^{2+} solution, (b) Standard addition calibration curve



(a) (b)

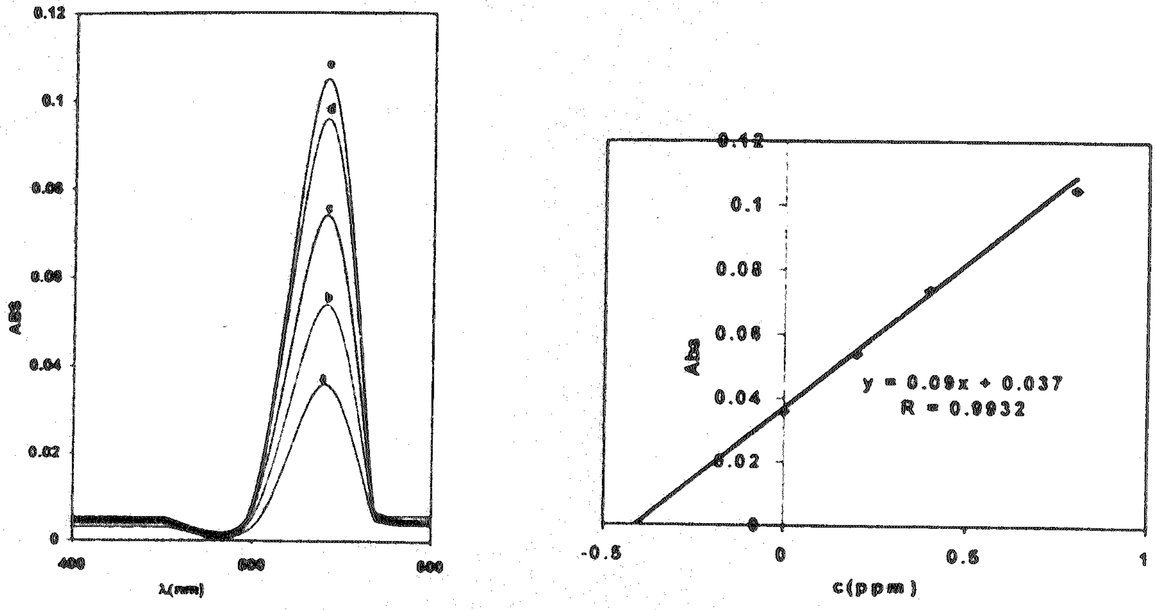
Fig. 2. (a) Standard addition DPP of unknown Ni^{2+} solution, (b) Standard addition calibration curve



(b)

(a)

Fig. 3. (a) Standard addition ASV of unknown Ni^{2+} solution, (b) Standard addition calibration



(a) (b)

Fig. 4. (a) Visible absorption spectrogram of unknown Ni^{2+} and standard solutions with concentration a: 0, b: 0.2, c: 0.4, d: 0.6, e: 0.8 ppm with standard addition method in distilled water blank, (b) standard addition calibration curve

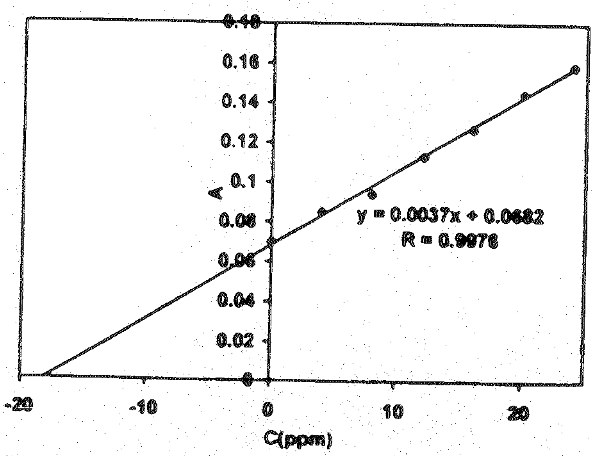


Fig. 5. Standard addition calibration curve for standard solutions 0–24 ppm in wavelength 341.5 nm in distilled water blank

We have given all the analytical results of these methods in Table-1.

TABLE-1
COMPARATIVE ANALYTICAL RESULTS FOR DETERMINATION OF Ni^{2+} QUANTITY IN WATT'S ELECTROLYTIC BATH

Per cent error	Ni^{2+} (g/L)*	Analytical results (standard addition method)	Method	
+2.80	50.0	$Ep_c = -1.01$ volt	CV	Voltammetry
+0.46	43.2	$Ep_c = -1.01$ volt	DPP	
+7.52	46.5	$Ep_c = -1.01$ volt	ASV	
+3.48	44.5	$\lambda = 341.5$ nm	AAS	Spectroscopy
−4.11	41.3	$\lambda = 545$ nm	ES	
−3.02	41.7	—	Direct	Volumetry (EDTA)
−4.31	40.2	—	Reverse	
+2.55	44.1	—	Gravimetry (dimethyl glyoxime)	

*Peak potentials were obtained *vs.* Ag/AgCl/KCl 3 M

According to these results, we concluded that DPP method is faster than volumetric and gravimetric methods, because it does not require reagents and it is more selective method than spectroscopic methods, because inorganic impurities present in the electrolytic bath could not interfere easily in voltammetric methods that are performed at constant potential. Finally, DPP is more sensitive to CV, because the residual current is minimized in DPP and in comparison with ASV, it does not need a preelectrolysis treatment.

Conclusion

Our results prove that Ni/Ni^{2+} system has an irreversible behaviour in Watt's nickel electrolytic bath. Determination of Ni^{2+} concentration is possible by DC, DPP and ASV methods. But DPP is faster than volumetric, gravimetric and ASV; also more selective than spectroscopic methods and finally more precise than the CV method.

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(*Received*: 14 March 2005; *Accepted*: 12 December 2005) AJC-4514