



## VOLTAMMETRIC SENSOR FOR TRACE DETERMINATION OF NICKEL AND COBALT IN FISHES

**R. M. Jugade**

*Dept. of Chemistry, RTM Nagpur University, Nagpur – 440033, India.*

### **Abstract**

Differential pulse adsorptive stripping voltammetric method has been for the trace determination of nickel and cobalt using 1-nitroso-2-naphthol as a complexing agent. Various parameters have been optimized in order to get high sensitivity, selectivity and reproducibility. Under optimum conditions of concentration of supporting electrolyte, pH, accumulation potential, accumulation period, drop time, pulse amplitude and scan rate, the detection limit of  $3.4 \times 10^{-9}$  mol L<sup>-1</sup> (0.2 ppb) has been achieved. The developed method has been applied to the determination of nickel and cobalt in fish samples collected from local markets of Nagpur and Mumbai, two cities in India.

### **Introduction**

Heavy metals present in water get accumulated in the bodies of aquatic animals called bioaccumulation. The bioaccumulation factor varies from metal to metal<sup>1</sup>. The damage caused to different organs of fish varies with the order of toxicity of the metal<sup>2</sup>. Contents of heavy metals in lake sediments have been investigated<sup>3</sup> and found to be dozens of times higher than background values. These values have been correlated with the concentration of metals in fish samples<sup>3</sup>.

Various methods like spectrophotometry<sup>4</sup>, flame AAS<sup>5</sup>, ETAAS<sup>6,7</sup>, ICPAES<sup>8</sup> and XRF<sup>9</sup> are known for the simultaneous determination of Ni(II) and Co(II). The voltammetric investigations of nickel and cobalt using ligands like DMG<sup>10,11</sup>, 2,2'-bipyridine<sup>12,13</sup>, nioxime<sup>14</sup> and 2-quinolinethiol<sup>15</sup>, have also been reported. In the present work, 1-nitroso-2-naphthol developed by us<sup>16</sup> has been used for determination of Ni(II) and Co(II) in fish samples.



## Experimental

**Apparatus:** Differential Pulse Adsorptive Cathodic Stripping Voltammetric (DPAdCSV) studies were carried out using Metrohm Polarecord E-506 serie-03 working on 220 volts stabilized AC mains. To it was connected the Metrohm polarography stand E-505. The instrument was kept in an air-conditioned room maintained at  $25 \pm 1^\circ\text{C}$  and humidity between 50 to 60.

The electrode assembly consisted of the hanging mercury drop electrode (Kemula type) as the working electrode, Ag/AgCl (sat. KCl) electrode as reference electrode and a platinum electrode as an auxiliary electrode. Nitrogen gas was used for deaeration and micropipette ( $25\mu\text{l}$ ) was used for addition of Ni(II) and Co(II) solutions. Mercury was purified by aeration method and then distilled under reduced pressure in a mercury distillation unit.

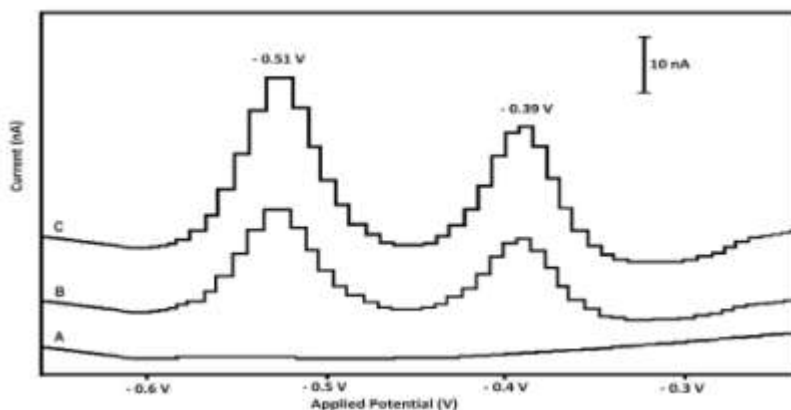
**Reagents and Solutions:** All the chemicals used were of AR grade. The solutions were prepared in double distilled water. Stock solutions of 100 ppb Ni(II) and Co(II) were prepared and desired dilutions were made as per the requirements. A 1mM solution of 1-nitroso-2-naphthol was prepared in 100 ml absolute alcohol. 0.1M  $\text{NH}_4\text{Cl}$  solution was prepared by dissolving A.R. grade salt in double distilled water.

## Results and Discussion

A 25 ml supporting electrolyte which is 0.01M  $\text{NH}_4\text{Cl}$  was taken in a polarography cell,  $25\mu\text{L}$  of 1mM solution of 1-nitroso-2-naphthol (ligand) was added using micropipette so as to make the ligand concentration  $1\mu\text{M}$ . The solution was deaerated for 10 minutes with nitrogen gas and voltammogram was recorded. To this solution,  $25\mu\text{L}$  of  $0.85 \times 10^{-4}\text{ mol L}^{-1}$  solutions of Ni(II) and Co(II) were added and voltammograms are recorded again. Various parameters like concentration of  $\text{NH}_4\text{Cl}$ , pH, concentration of ligand, drop time, pulse amplitude, scan rate, accumulation period, accumulation potential etc were varied and all of these parameters were optimized.

Highly reproducible and distinct peaks were obtained under the following conditions. Concentration of  $\text{NH}_4\text{Cl} = 0.01\text{M}$ ;  $\text{pH} = 9.5$ ; concentration of ligand

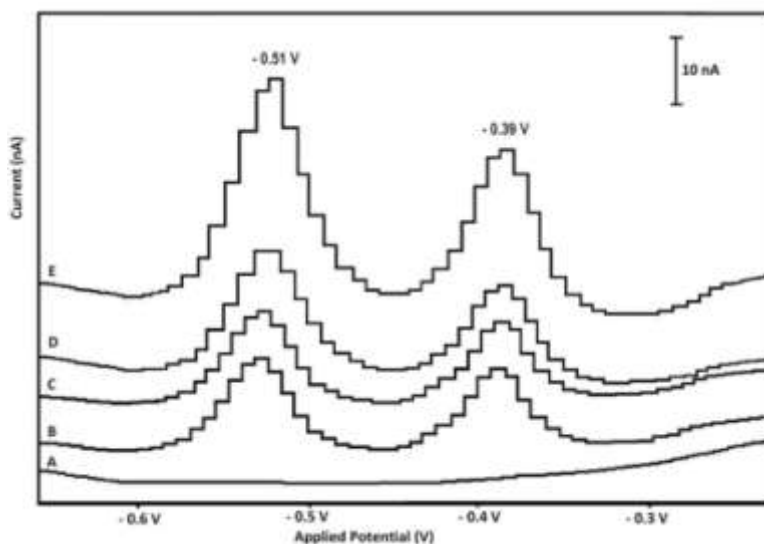
$=1.0\mu\text{M}$ ; accumulation potential =  $-0.2\text{ V}$ ; accumulation period =  $30\text{ s}$ ; rest period =  $30\text{ s}$ ; drop size =  $1.4\text{ mm}^2$ ; scan rate =  $20\text{ mV/s}$  and pulse amplitude =  $30\text{ mV}$ . Under these conditions, the peak current was found to increase linearly with the concentration of nickel and cobalt up to  $4.25 \times 10^{-7}\text{ mol L}^{-1}$  ( $25\text{ ppb}$ ). The  $3\sigma$  detection limit was found to be  $3.4 \times 10^{-9}\text{ mol L}^{-1}$  ( $0.2\text{ ppb}$ ) for Ni(II) as well as Co(II). Correlation coefficients were found to be  $0.9996$  and  $0.9988$  for Ni(II) and Co(II) respectively. Equation of regression lines are ( $Y_{nA} = 4.05X_{ppb} + 0.04$ ) and ( $Y_{nA} = 3.25X_{ppb} + 0.02$ ) for Ni(II) and Co(II) respectively. It shows a good current-concentration correlation for both the metal ions. Typical voltammograms are shown in Fig. 1.



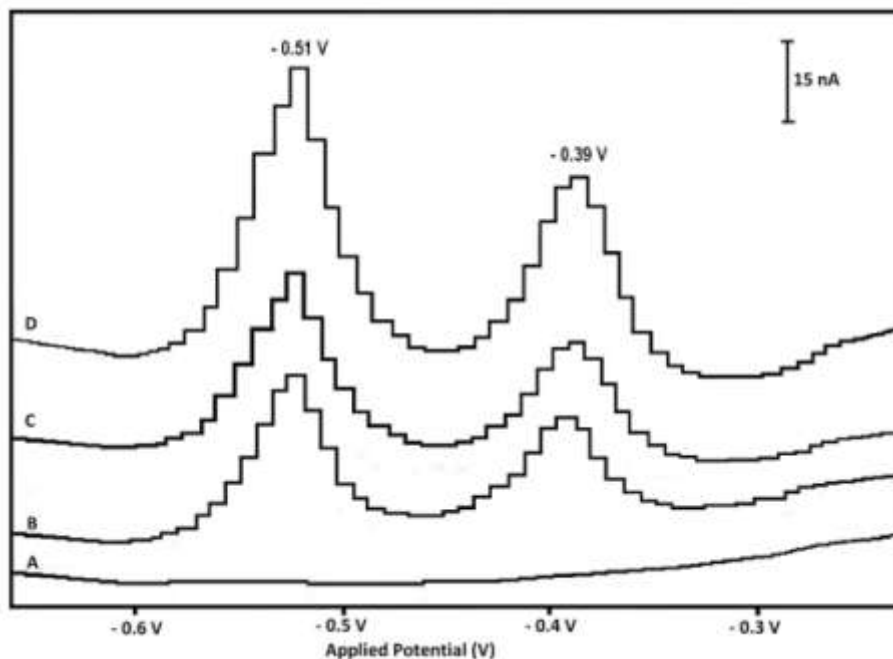
**Fig.1:** Voltammograms of the solution containing (A)  $0.01\text{ M NH}_4\text{Cl}$  and  $1\mu\text{M}$  1-nitroso-2-naphthol (B) with  $5\text{ ppb Ni (II)}$  and  $5\text{ ppb Co(II)}$  (C) with  $10\text{ ppb Ni(II)}$  and  $10\text{ ppb Co(II)}$

The optimized method was applied to analysis of fish samples. Fish samples were collected from local markets in Nagpur and Mumbai, two cities in India. The fish were cleaned with double distilled water. Muscles were taken out and dried in sunlight. These were crushed to a fine powder form.  $0.5\text{ g}$  of the sample was weighed,  $10\text{ ml conc. HNO}_3$  and  $0.4\text{ g}$  magnesium nitrate and a few porcelain pieces were added and allowed to predigest for  $18\text{ hours}$  at room temperature. It was then digested on hot plate for  $5\text{ hours}$ . The beaker was placed in muffle furnace at  $500^\circ\text{C}$  for  $30\text{ minutes}$ . After cooling,  $10\text{ ml}$  of  $6\text{ M HCl}$  was added and heated on water bath until the white residue dissolved. Volume was made up to  $50\text{ ml}$ .

Suitable aliquots were taken in 25 ml volumetric flasks. 2.5 ml of 0.1 M  $\text{NH}_4\text{Cl}$  and 25  $\mu\text{L}$  of 1 mM 1-nitroso-2-naphthol solutions were added. pH was adjusted to 9.5 using dilute ammonia solution and volume made up to the mark. The solution was transferred to polarography cell, deaerated with nitrogen for 10 minutes to remove dissolved oxygen. Adsorptive accumulation of the complexes was carried out on HMDE at  $-0.2$  V for 30 s while the solution was stirred. The potential was scanned cathodically after a rest period of 15 s in differential pulse mode. Scan rate of 20 mV/s and pulse amplitude of 30 mV were used and the voltammograms were recorded. They are shown in Fig. 2 and Fig. 3. The results obtained by present method and checked by AAS method are shown in Table 1.



**Fig.2:** Voltammograms of the (A) reagent blank and for fish samples from Nagpur (B) crabs (C) marrel (D) vogte (E) prawn



**Fig.3:** Voltammograms of the (A) reagent blank and for fish samples from Mumbai (B) sukhat (C) shilat (D) jalva

**Table 1:** Concentration of Nickel and Cobalt in Fish Samples

| Sr. No. | Name of fish | Place  | Conc. of Nickel / $\mu\text{g g}^{-1}$ * |                  | Conc. of Cobalt / $\mu\text{g g}^{-1}$ * |                 |
|---------|--------------|--------|--|------------------|--|-----------------|
|         |              |        | Present method                           | AAS method       | Present method                           | AAS method      |
| 1       | Crabs        | Nagpur | $9.23 \pm 0.06$                          | $9.05 \pm 0.05$  | $4.96 \pm 0.06$                          | $5.00 \pm 0.05$ |
| 2       | Marrel       | Nagpur | $9.11 \pm 0.11$                          | $10.10 \pm 0.03$ | $5.40 \pm 0.19$                          | $5.50 \pm 0.10$ |
| 3       | Vogte        | Nagpur | $10.22 \pm 0.08$                         | $10.30 \pm 0.10$ | $5.06 \pm 0.15$                          | $5.00 \pm 0.07$ |
| 4       | Prawn        | Nagpur | $16.90 \pm 0.18$                         | $18.30 \pm 0.11$ | $5.99 \pm 0.25$                          | $5.70 \pm 0.31$ |
| 5       | Sukat        | Mumbai | $11.25 \pm 0.21$                         | $11.20 \pm 0.30$ | $8.83 \pm 0.11$                          | $8.90 \pm 0.07$ |
| 6       | Shilat       | Mumbai | $15.64 \pm 0.35$                         | $16.30 \pm 0.22$ | $8.23 \pm 0.35$                          | $8.50 \pm 0.41$ |
| 7       | Jalva        | Mumbai | $16.45 \pm 0.32$                         | $18.80 \pm 0.13$ | $9.34 \pm 0.26$                          | $8.90 \pm 0.02$ |

\*(Avg $\pm$ SD) of 4 observations



The results obtained by the voltammetric method have been found to be in good agreement with those obtained by AAS method. The method has an important advantage that the sample treatment is not very complex. Once the sample is digested, it can be analyzed directly without any preconcentration at sub-ppb level. Also, an accumulation period of 30 seconds is sufficient to achieve such a low detection limit.

### **Acknowledgement**

The author is thankful to Alexander von Humboldt Foundation of Germany, for the donation of Metrohm Polarograph and UGC, New Delhi for Start-up Grant.

### **References**

- G. Masters, (1995) "*Introduction to Environmental Engineering and Science*", Prentice Hall of India, New Delhi.
- K. Krishnani, I. Azad, M. Kailasam, A. Thirunavukkarasu, B. Gupta, K. Joseph, M. Muralidhar and M. Abraham, (2003) *J. Environ. Sci. Health Part A Tox. Hazard. Subst. Environ. Eng.*, 38, 645.
- A. Lukin, V. Dauvalter, N. Kashulin, V. Yakovlev, A. Sharov and O. Vandysh, (2003) *The Sci. of Total Environ.*, 306, 73.
- J. Yun and H. Choi, (2000) *Talanta*, 52, 893.
- A. Turker, R. Cokun and B. Huseyin, (2000) *Spectrochimica Acta Part B: Atomic spectroscopy*, 55, 1099.
- M. Gonzalez, M. Gallego and M. Valcarcel, (1999) *Talanta*, 48, 1051.
- G. Pavlovska, D. Undeva and T. Stafilov, (2000) *Separation Science and Technology*, 35, 2663.
- S. Ferreira, C. Brito, A. Dantas, N. Arango and A. Costa, (1999) *Talanta*, 48, 1173.
- H. Sawatari, T. Hayashi, E. Fujimordi, A. Hirose and H. Haraguchi, (1996) *Bull Chem Soc Japan*, 69, 1925.
- B. Pihlar, P. Valenta and H. Nurnburg, (1981) *Fr Z Anal Chem*, 307, 337.



- S. Adeloju, A. Bond and H. Briggs, (1984) *Anal Chim Acta*, 164, 181.
- H. Suwamoto, (1981) *Daigaku Kyoikugakubo Kenkyn Hokoku*, 33, 9.
- H. Kavel and f. Umland, (1986) *Fr Z Anal Chem*, 325, 191.
- J. Donat and k. Bruland, (1988) *Anal Chem*, 60, 240.
- M. Paneli and A. Voulgaropoulos, (1991) *Fr Z Anal Chem*, 341, 716.
- R. Jugade and A. Joshi, (2003) *Ind. J. Chem. Sec. A*, 42 A, 94.