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## Simultaneous quantitation of nickel and zinc in an industrial effluent using differential pulse polarography

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### ABSTRACT

A simple and precise electroanalytical method for the quantitation of nickel and zinc simultaneously from an industrial effluent has been established using differential pulse polarography. With this technique it was possible to quantitate nickel and zinc simultaneously with a validated method. The polarogram recorded for the industrial effluent in potassium thiocyanate as a supporting electrolyte showed two cathodic peaks at -0.63 V and -0.93 V vs. saturated calomel electrode which were confirmed to be of nickel and zinc by the method of standard addition. The linear dynamic range for nickel and zinc was 0.652 µg/mL to 13.5438 µg/mL and 0.7265 µg/mL to 13.078 µg/mL respectively. © 2012 Trade Science Inc. - INDIA

### KEYWORDS

Differential pulse polarography;  
Industrial effluent;  
Nickel;  
Zinc;  
Potassium thiocyanate.

### INTRODUCTION

Rapid industrialization and abnormal population growth has enhanced water pollution. Monitoring the metal ions and organic compounds in aquatic environment has been a subject of great concern over the last few decades and will continue to be so, as increasing number of metal ions in increasing amounts and a diverse array of organic compounds form a part of an industrial effluent. Metal ions are the most common electroactive species present in the industrial effluents. 'Heavy metals' is a general collective term applied to the group of metals such as Pb, Cr, Cu, Ni and Zn which are commonly associated with pollution and toxicity problems. Some of these elements may be micronutrients for many living organisms and are required in small amounts for normal healthy growth, but any metal ion in large amount will always cause acute or chronic toxicity.

Trace determinations of metals by voltammetric methods with modified electrodes has been reported<sup>[1, 2, 3]</sup>. Complexation of the metal ions in waste water was also studied by differential pulse cathodic stripping voltammetry<sup>[4, 5]</sup>. Simultaneous determination of Zn(II) and Ni (II) was also studied in the presence of crown ethers by D.C. polarography<sup>[6]</sup>. Metals present in industrial effluents and sludge samples have been separated and concentrated by using other techniques like electro dialysis, coulometry and photocatalysis<sup>[9]</sup>. However, less work has been done in the area of environmental chemistry especially on separation and quantitation of electroactive species present in industrial effluents.

### Objective

The main objective of the study was to provide a simple, rapid, efficient, precise and economical method

for the simultaneous determination of Ni(II) and Zn(II) from an industrial effluent using differential pulse polarography. The developed method has been validated as per ICH guidelines<sup>[6,7]</sup>.

## MATERIALS AND METHODS (EXPERIMENTAL)

### Introduction to the workstation



All the measurements were performed on a fully automated computerized electroanalytical workstation, an electrochemical system PG STAT 30 with 663 VA electrode stand manufactured by Metrohm. It includes 3 electrode system viz. hanging mercury drop electrode as a working electrode, saturated calomel electrode as a reference electrode and platinum electrode as an auxiliary electrode.

### Reagents

Merck A.R grade  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and KSCN were used.

### Preparation of standard solution

28 mg of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  and 28.75 mg of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  were accurately weighed and dissolved in minimum amount of double distilled water and made

up to the mark in a 100 mL volumetric flask. The solution so prepared contained 58.69  $\mu\text{g/mL}$  of Ni and 65.39  $\mu\text{g/mL}$  of Zn respectively. All the other standard solutions containing both Ni and Zn were prepared using this stock solution.

### Voltammetric method

18 mL of distilled water and 2.0 mL of 1 M KSCN were placed in the dry, clean cell. The solution was purged with pure nitrogen gas for 180s. The potential scan between 0.0 V to -2.0 V vs. S.C.E was applied. The operational parameters were as follows: 1] Scan rate- 15  $\text{mVs}^{-1}$  2] Pulse amplitude- 50mV. After recording a polarogram of the blank, 0.4mL of standard solution of Ni and Zn were added in succession and polarograms were recorded and peak currents were measured and calibration curves were prepared.

### Preparation of sample solution

The sample was an effluent from an electroplating industry. The sample solution was centrifuged and filtered through Whatman paper no. 41. 50 mL of the sample was evaporated to dryness and extracted with water containing 0.2 mL of conc HCl and diluted to 50 mL in a volumetric flask with distilled water. Polarograms for the sample solutions were recorded under the same conditions used for the calibration curve. The amount of Ni and Zn were calculated from the measured peak currents and using the equation of the calibration curve. The equation of the calibration curve for Ni was  $y=38.2699x+4.0742$  and for Zn was  $y=96.5378x-2.3310$  where y is the current in nanoamperes and x is the concentration in  $\mu\text{g/ml}$ .

## ANALYTICAL METHOD VALIDATION<sup>[6,7]</sup>

### System suitability

System suitability tests were carried out to ensure reproducibility of the instrument. The system suitability test was carried out by recording polarogram for Ni and Zn at two different concentrations (2.257  $\mu\text{g/ml}$  and 6.288  $\mu\text{g/ml}$  for Ni and 2.515  $\mu\text{g/ml}$ , 7.006  $\mu\text{g/ml}$  for Zn) with five replicates and the mean current was used for the calculation. The % RSD in both cases was found to be less than 2%.

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### Specificity

The specificity of method was confirmed by comparing the polarograms of the combined standard solutions containing Ni and Zn with the sample solution. The peak potentials recorded for the sample solution were found to be identical to those obtained for the combined standard solution of Ni and Zn. The addition of the standard solutions of Ni and Zn to the sample solution did not change the characteristics of differential pulse polarogram but enhanced the peak current. This confirms the specificity of the method.

### Robustness

The robustness of the method was examined by observing the consistency of the peak height and the peak shape with the deliberately made small changes in the experimental parameters. It is a measure of the capacity of the method to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage. To determine the robustness of the proposed method, the following variations were made in the analytical parameters. The Scan rate was changed by  $\pm 0.5 \text{ mVs}^{-1}$  and the Pulse amplitude  $\pm 1.0 \text{ mV}$ . These parameters were deliberately changed one at a time and the effect of these changes on the peak shape and peak currents were studied. The proposed method was found to be robust.

### Linearity and dynamic range

The linearity for Ni and Zn in a solution containing the two was determined. In the concentration range,  $0.65 \mu\text{g/mL}$  to  $13.54 \mu\text{g/mL}$  for Ni and  $0.73 \mu\text{g/mL}$  to  $13.078 \mu\text{g/mL}$  Zn, a good linearity was obtained. The equation of the calibration curves is presented in (TABLE 1).

### Limit of detection and limit of quantitation

The limit of detection (LOD) and the limit of quantification (LOQ) for Ni and Zn were fixed at signal to noise ratio of 3:1 and 10:1 respectively. Twenty replicates of the blank solution were recorded and the mean current value at the peak potential of Ni (i.e. at  $-0.63 \text{ V}$ ) and Zn (i.e. at  $-0.93 \text{ V}$ ) were calculated. The concentration at which the peak current was found three times of mean blank current was taken as the limit of

detection and the concentration at which peak current was found to be ten times the mean blank current was selected as the limit of quantification. The LOD and LOQ of Ni and Zn were  $0.25 \mu\text{g/mL}$  and  $0.65 \mu\text{g/mL}$  and  $0.28 \mu\text{g/mL}$  and  $0.73 \mu\text{g/mL}$  respectively.

### Intraday and interday precision

The variability of the method was tested with the intra-day and inter-day precision. It was checked by recording the polarograms of standard solutions of Ni and Zn in the concentration ranges  $1.1507 \mu\text{g/mL}$  to  $8.095 \mu\text{g/mL}$  for Ni and  $1.282 \mu\text{g/mL}$  to  $9.019 \mu\text{g/mL}$  for Zn. Intra-day precision was tested by recording the polarograms at an interval of four hours and inter-day precision twice a day with a gap of three days. The mean % RSD for intra-day and inter-day precision for Ni was found to be 0.82% and 0.95% and for Zn 0.38% and 0.54%, respectively.

### Quantitation/Determination

The validated method was used for the determination of Ni and Zn. Polarograms were recorded under the optimum experimental conditions for the sample solution. Resulting peak currents for Ni and Zn were measured and the amount of Ni and Zn was calculated using calibration curve equations. The results are presented in (TABLE 2).

### Accuracy (Recovery)

The recovery technique was used to evaluate the accuracy of the method. The method of standard addition was employed for the purpose. A fixed volume of the standard Ni and Zn solution was added to the sample solutions and the mixed solutions so obtained were analyzed by the proposed method. The percentage recovery was determined at different percentage levels i.e. the added amounts ranging from 40% to 200% of the amount present in the sample. The results of the recovery analysis for Ni and Zn are presented in (TABLE 3)

## RESULT AND DISCUSSION

The present study provides determination of Ni and Zn from the industrial effluents using the technique of differential pulse polarography. The method was validated as per the ICH guidelines (TABLE 1-3). Before

**TABLE 1 : METHOD VALIDATION PARAMETERS FOR NICKEL AND ZINC**

Parameters	Values	
	Ni	Zn
System suitability (n=5)	0.75%	0.47%
%RSD	0.75%	0.47%
Linearity range ( $\mu\text{g/ml}$ )	1.1507 to 8.095 $\mu\text{g/ml}$	1.282 to 9.019 $\mu\text{g/ml}$
Slope (m) <sup>a)</sup>	38.2699	96.5378
Intercept(c) <sup>a)</sup>	4.0742	-2.3310
Correlation coefficient ( $R^2$ )	0.9993	0.9992
LOD ( $\mu\text{g/ml}$ )	0.2527 $\mu\text{g mL}^{-1}$	0.2815 $\mu\text{g mL}^{-1}$
LOQ ( $\mu\text{g/ml}$ )	0.652 $\mu\text{g mL}^{-1}$	0.7265 $\mu\text{g mL}^{-1}$
Intraday precision (n=5)	0.82%	0.38%
Interday precision (n=5)	0.95%	0.54 %
Recovery	98% to 102%	98% to 102%

a) Of the equation  $y = mx + c$ , where  $y$  is peak current,  $m$  is the slope,  $x$  is the concentration and  $c$  is the intercept

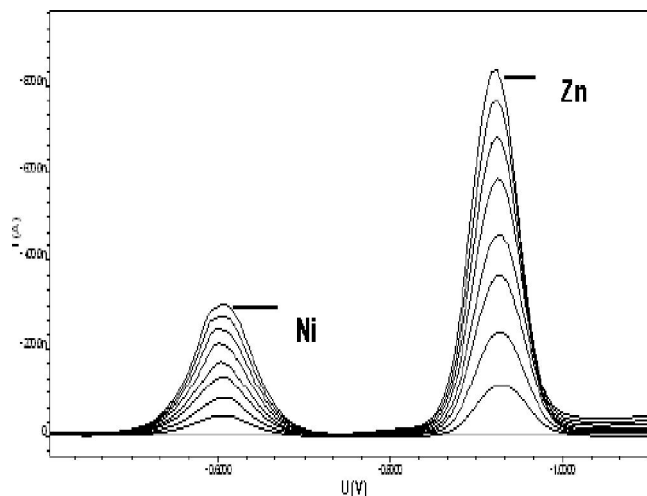
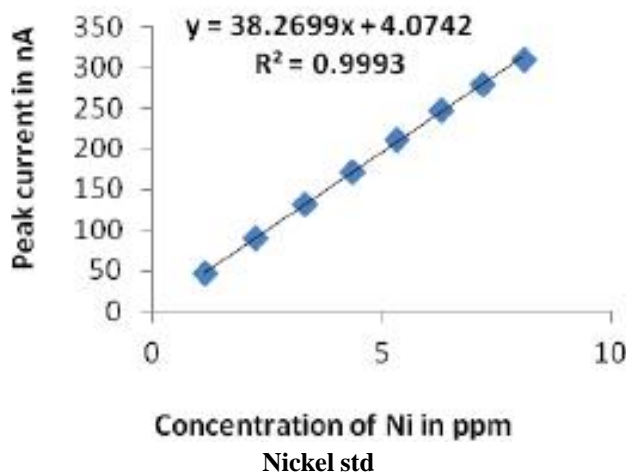
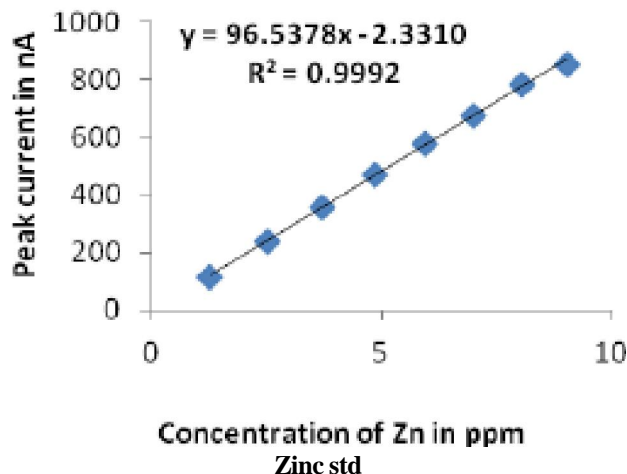
**TABLE 2 : RESULTS OF QUANTITATION STUDIES FOR NICKEL AND ZINC**

Name of Metal ions	Ni	Zn
Conc in $\mu\text{g/ml}$	2141.84	1016.8
% RSD (n=5)	0.66	0.86

**TABLE 3 : RESULTS OF RECOVERY STUDIES FOR NICKEL AND ZINC**

Standard Level	Conc. of std [ $\mu\text{g/ml}$ ]	Conc. of std Found [ $\mu\text{g/ml}$ ]	RSD (%) (n = 5)	Recovery (%)
Nickel	50%	1.684	0.58	99.30%
	80 %	2.755	0.57	101.48%
	100%	3.2757	0.47	101.30%
			Mean	100.69%
Zinc	40 %	0.638	0.25	100.66%
	110%	1.877	0.69	99.88%
	180%	3.0699	0.58	101.56%
			Mean	100.70%

validation, optimization of the conditions i.e. pH, supporting electrolyte, scan rate and pulse amplitude were optimized. The polarographic response of the sample for Ni and Zn in different supporting electrolytes has been studied. With KCl as the supporting electrolyte the sample showed only one peak for both Ni and Zn. However, two separate peaks were produced with KSCN as the supporting electrolyte.

**Figure 1 : POLAROGRAMS OF NICKEL AND ZINC****LWR for Ni****LWR for Zn****Figure 2 : LINEARITY GRAPHS FOR Nickel std Zinc std**

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Pulse amplitude of 50mV was chosen as the optimum as there is loss of resolution at high pulse amplitude. The Differential Pulse polarogram of Ni and Zn were recorded at various scan rates. At scan rates higher than  $15\text{mVs}^{-1}$  the width of peak increases, its height decreases and peak shape was distorted. At lower scan rates than  $15\text{mVs}^{-1}$  peak current was lower. So a scan rate of  $15\text{mVs}^{-1}$  was chosen as a best for the analysis.

### ABBREVIATIONS

Ni- Nickel

Zn- Zinc

KSCN- Potassium thiocyanate

### ACKNOWLEDGEMENT

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