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# Determination of Toxic Trace Metals Pb, Cd, Ni, and Zn in Soil by Polarographic Method

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**Abstract :** The concentrations of toxic trace metals in the soil sample collected from Jaipur, India, have been determined using Direct current Polarography (DC- Polarography). Using DC polarograms of dry digested Soil sample in acetate buffer (pH=4.7) and HCl (pH=2.5), quantities of Pb, Cd, Ni and Zn were determined. Half wave potentials were -1.00 V, -0.61 V, -0.41 V and -0.91 V for zinc, cadmium, lead and nickel, respectively. The heavy elements quantities in digested soil samples were as follows: Pb about 7.70 ppm, Cd 7.35 ppm, Ni 2.41 ppm and Zn 2.68 ppm.

**Keywords:** Soil pollution, Pb, Cd, Ni and Zn, DC-Polarography, Jaipur soils, India.

## Introduction:

Heavy metal contamination has received much attention with regard to accumulation in soils, uptake by plants, and contamination of aquatic environments[1]. The rapid development of industry and the use of chemical substances in many industrial activities have caused a steady increase of trace- metal pollution in soil[2]. Soils receive potentially toxic elements from both natural and wide range of anthropogenic sources, including the weathering of primary minerals, mining, fossil fuel combustion, the metallurgical, electronic, and chemical industries, and waste disposal. Soils consist of heterogeneous mixtures of organic and inorganic substances as well a variety of soluble substances[3]. The ecological effects of heavy metals in soil are closely related to the distribution of species in the solid and liquid phase of the soil. A comprehensive knowledge of the interactions between the trace elements and the soil matrix is required to judge their environmental impact. Total metal content can be a starting point for developing control strategies to obtain better environmental quality and is a key to assess soil quality. Extensive investigations of urban soils have been carried out recently in some countries[4].

It is well known that metals, reaching excessive levels, can exert serious impact on humans, animals, and plants[5]. The human health impacts of pollution of soils by metals are primarily related to bioaccumulation of the metals into the food items. Certain heavy metals constitute, in spite of their low concentrations in the environment, a class of environmental chemicals with great significance in ecochemistry and ecotoxicology. Some of these act below their respective threshold levels essentially for man and mammalians, and display progressively toxic actions above these levels. Examples include Cu, Zn, Se, Co, etc. Other trace metals, such as Cd, Hg, and Pb, belong to a priori toxic metals. From the toxicological viewpoint, these metals are insidious because they have the tendency to accumulate in vital organs of man and mammalians, e.g. brain renal system, liver, intestinal tract and bones, and are only slowly excreted.

Atmospheric trace metals from both local and distant sources impact the environment in the from of dry and wet deposition[6]. The leaves of plants can directly take up toxic trace metals or they are at first accumulated in the soil and reach the plants through their roots. The uptake of metals by the soil depends on the chemicals properties of the metals and of the soil, especially on its acidity and the content of humic substances. Some metals, such as Pb or Hg, are rather firmly bound to humic substances in the soil, whereas others, such as Cd, can easily remobilize from the soil. Thus the monitoring of toxic heavy metals in the soil becomes a task of high priority and significance in environmental research and protection, particularly in view of the rate at which chemicals are at present introduced into the terrestrial environment. Therefore, soil has been selected for analysis in the present work due to its importance in the environment.

Public health and environment concerns have emerged concurrently with improvements in techniques for the measurement and monitoring of contamination. Atomic absorption spectroscopy (AAS) has been widely used for the determination of trace metal levels in soils[7-8]. With the growing demands on the accuracy of analytical data in environmental protection with respect toxic trace metals, Polarography, especially in under the conditions of 150 mV per minute span rate and 100 nA per division sensitivity, provides a significant and attractive alternative to AAS[9]. In our early work we determined cadmium, nickel and cobalt in soil samples using polarographic techniques[10-12]. Polarographic techniques appear to be very suitable, versatile and rapid for multi component determinations, having both good selectivity and without requiring metal enrichments before the analytical measurements[13-14]. In the present work we used the method developed previously in our lab for soil samples.

## Experimental

### Apparatus

A digital DC Recording polarograph CL-357 was used for the measurement of current-voltages data. This apparatus has three electrode assembly, dropping mercury electrode as working electrode, and calomel as reference electrode and platinum as counter electrode. DC polarograms were recorded by the Strip chart recorder LR-101P, under the conditions of 150 mV per minute span rate and 100 nA per division sensitivity. Elico digital pH meter was employed to measure the pH of solution.

### Reagents

All reagents used were of analytical reagent grade purity (AR). The mercury used in the dropping mercury electrode was obtained from Merck. Standard stock solutions (0.05 M) of Pb, Co, Ni, and Zn were prepared with triply distilled water from their nitrate and sulfate salts. The C-V data for test solution were recorded after passing pure nitrogen gas in the test solution and 0.001%triton-X-100 was used as maxima suppressor.

### Glassware

All glassware were soaked in 2 M nitric acid for at least 7 days, washed three times with distilled deionizer water, soaked in 0.1 M hydrochloric acid until ready for use. In distilled deionizer water and finally soaked

## Procedure

### Sampling and Digestion

Soil sample was collected from the area of Amanisha nala near Gurjar ki Thadi Jaipur city (Rajasthan India). The soils at the sites studied are sandy clay loams. These soils vary from brown to grey brown. Soil samples were collected from the topsoil horizon (10-15 cm). The pH of the study area varies from 7.5 to 8.5. A V-shaped hole was dug and sliced from the three sides and this sample was placed in a polythene bag. Six such individual samples following a random sampling pattern were collected. This was representative of the entire area selected.

After collection of the soil samples, the lumps were broken and stones removed. In the laboratory, the soil samples were dried at ambient temperature (22-25$^0$C), crushed in a porcelain mortar and sieved through a 2-mm screen. The air-dried samples were stored in polyethylene bags at 5$^0$C for subsequent analysis. Then it's digested by dry ash method,

### Electro Analytical Determination

A total of 10 ml electrolyte was de-aerated by a stream of nitrogen gas (99.999 %) for about 15 min. Polarograms were taken by scanning the potential in the negative direction from 0.0 to –1.5 V, depending on pH, at a scan rate of 5 mV/s. to the sample solution taken in Pyrex polarographic cell including 2.0 ml. of suitable buffer solution we add 0.1 ml. of 0.001% triton-X-100 and remaining required volume of distilled water. After that the polarographic cell was de-aerated by a stream of nitrogen gas for about 15 minutes. To ascertain the presence of the metal ions in the sample, a known quantity of stock standard solution of each metal ion was added to the analyte and polarograms were recorded. An increase in the wave height of the ion signal was observed without any change in its $E^{1/2}$ values confirming the presence of Pb, Cd, Ni and Zn in Soil sample solution.

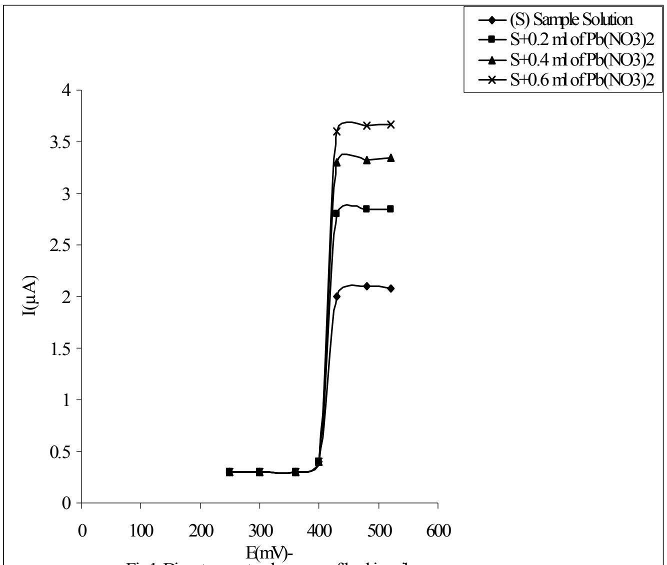

Fig. 1-Dirrect current polarogram of lead in soil

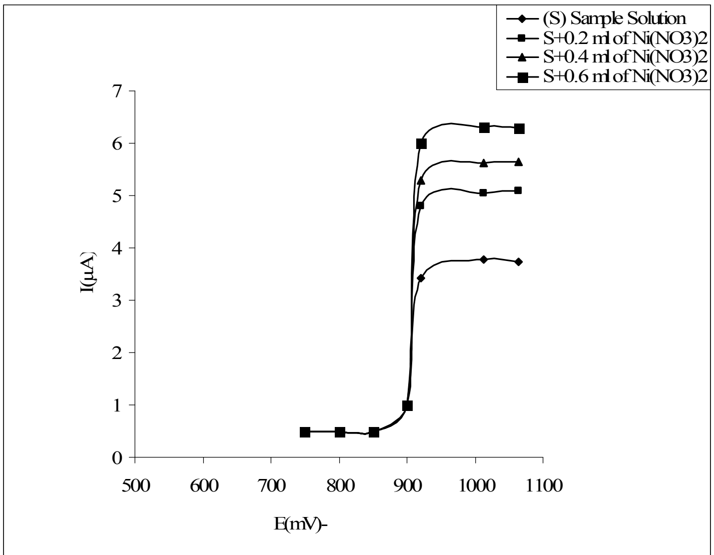

Fig.3-Dirrect Current Polarogram of Nickel in Soil

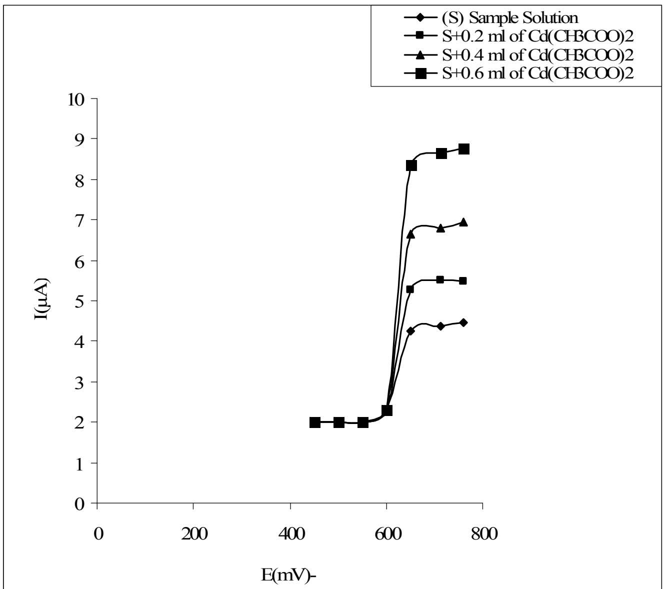

Fig.2-Dirrect Current Polarogram of Cadmium inSoil

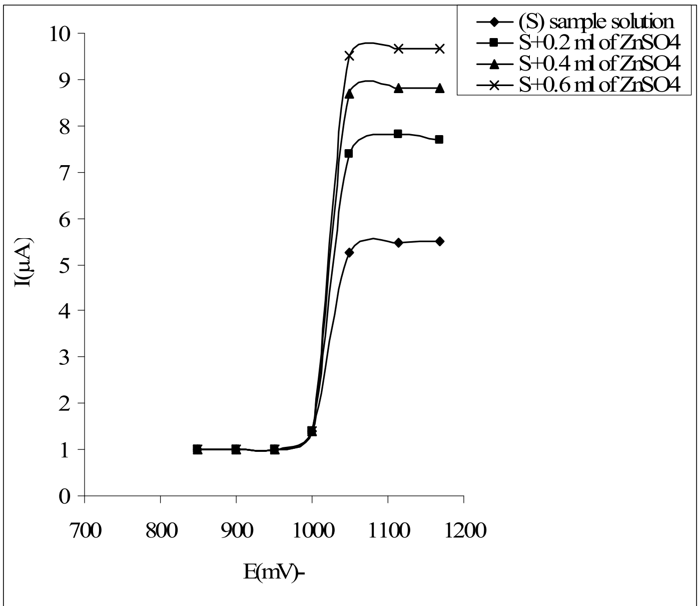

Fig.4-Dirrect Current POlarogram of Zinc in Soil

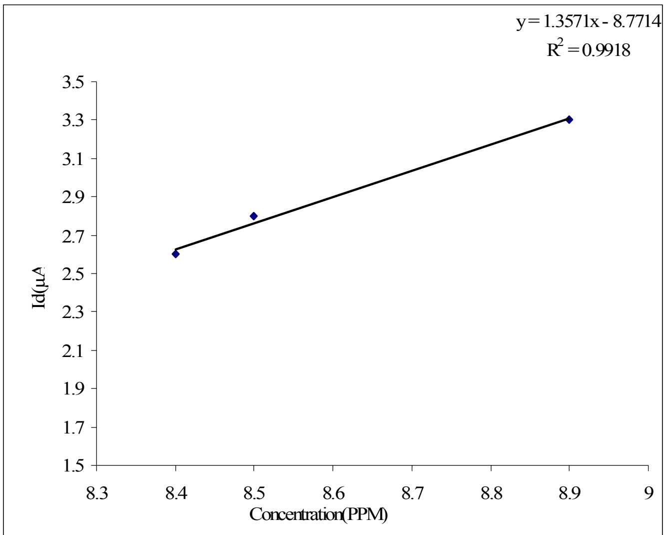

Fig.5-Calibration Curve Of Lead in Soil

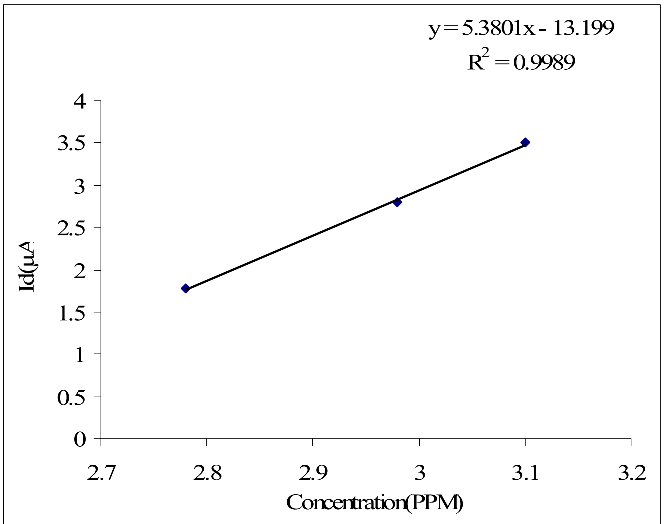

Fig.6-Calibration Curve Of Cadmium in Soil

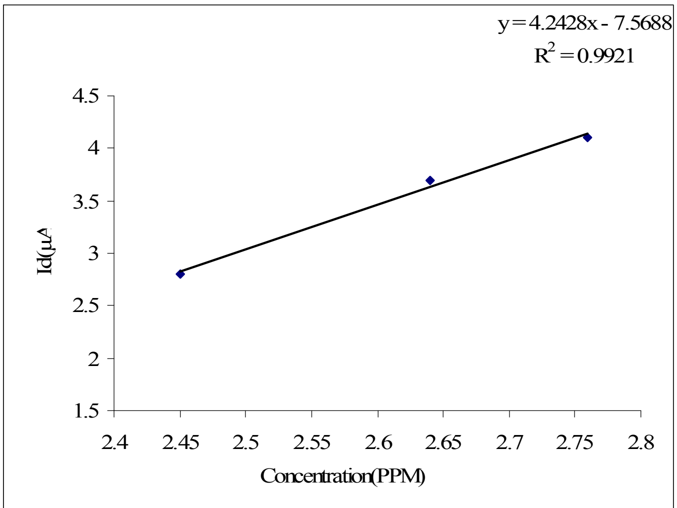

Fig.7-Calibration Curve Of Nickel in Soil

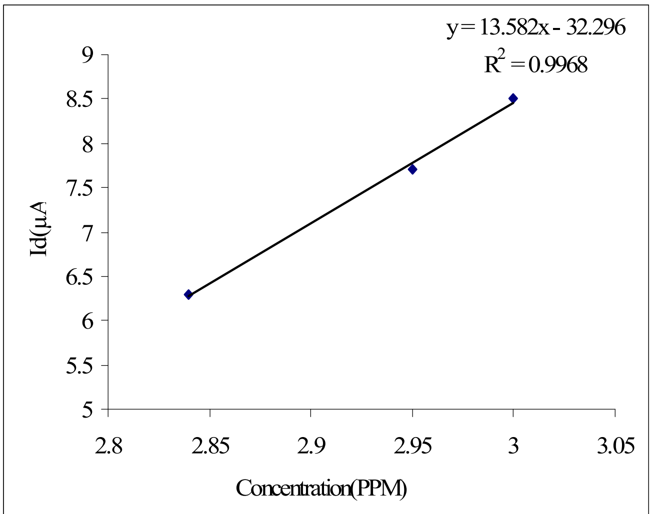

Fig.8-Calibration Curve Of Zincl in Soil

## Results and Discussion

The results obtained from the study of toxic metals in soil samples in part per million ranges are presented in table 1. Which shows mean concentration in ppm as 8.613, 7.857, 2.617, 2.930 and percentage error is small as 0.043, 0.018, 0.128, 0.023respectively for Pb, Cd, Ni and Zn in acetate buffer and HCl buffer. Mean deviation is found to be 0.197778, 0.124444, 0.11111, 0.08 and standard deviation is found to be 0.260832, 0.161967, 0.156312 and 0.108167 respectively for Pb, Cd, Ni and Zn. Linearity of calibration curves was obtained in all cases with the value of correlation factor (r) near to one . Linear relationship between concentration and diffusion current (Id) has been proved statistically by applying straight line equation to all calibration curves.

Heavy metals are important environmental pollutants they are a threat to the environment and to human health, because they are not biodegradable as they are retained indefinitely in the ecological systems and in the food chain[15-16]. The allowed values of metals given table no.-2 are not harmful, but whenever the concentration of these metals exceeds from this value, it may pose harmful effects on soil as follows

**Table1: Trace analysis of Pb, Cd, Ni and Zn in Soil Sample**

| Heavy metal | Supporting Electrolyte | Half wave Potential as $E_{1/2}$ in volts | Conc. in ppm | Mean | % Error | Mean deviation | Std. deviation |
|---|---|---|---|---|---|---|---|
| Pb | Acetate buffer | 0.41 | 8.42<br>8.51<br>8.91 | 8.613 | 0.043 | 0.197778 | 0.260832 |
| Cd | Acetate buffer | 0.61 | 7.67<br>7.94<br>7.96 | 7.857 | 0.018 | 0.124444 | 0.161967 |
| Ni | Acetate buffer | 0.91 | 2.45 2.64<br>2.76 | 2.617 | 0.128 | 0.11111 | 0.156312 |
| Zn | HCl | 1.00 | 2.84<br>2.90<br>3.05 | 2.930 | 0.023 | 0.08 | 0.108167 |

As a result of soil pollution with heavy metals, a microbiological activity disturbance occurs, which is expressed by a significant depletion of bacteria and actinomycetes. Actually dehydrogenase activity is decreased to a zero level. Also, pollution with heavy metals caused a drastic depletion of the number of oribatidae and collembolles, while, dipterous larvae, population increased revealing a very reduced bio-conversion activity of the substances. The acidification and the microbiological activity disturbance directly effect the quality of organic matter by the increase of fulvic acids weight up to 3.6 times to the prejudice of humic acid. A fast effect of this process is heavy metals mobility intensification up to 3-4 times, as compared to the non-polluted soil.

The second effect is the decrease of the humification intensity, because the organic matter has low nitrogen content and high carbon content. The loss of basic elements, especially calcium from the colloidal complex under the condition of low organic matter contents causes soil structure deterioration.

To assess the pollution levels in our study area, the results were compared with world averages[17-21].

## Conclusion:

The described DCP method for the determination of Pb, Cd, Ni and Zn in soil is specific, sensitive and rapid with a simple approach comprising low cost instrumentation compared to the mass spectrometry and atomic absorption spectrophotometry. The results obtained by DCP are quantitative and in good agreement in terms of precise measurement.

## Acknowledgement:

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**Table2. Metal concentrations from literature (mg/kg)**

| Elements | Zn | Cd | Pb | Reference No. |
|---|---|---|---|---|
| World average earth crust | 75 | 0.11 | 14 | 17 |
| United States average soil | 60 | _ | 19 | 18 |
| World average soil | 50 | 0.06 | 10 | 19 |
| World average soil | 50 | 0.06 | 10 | 20 |
| Common range of Ni elements | 5-500 **(mg/kg)** | | Reference No.21 | |

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