

RESEARCH ARTICLE

Study on Quality of Soil: Part-II. Simultaneous Determination of Cu, Pb, Cd, and Zn in Soil Samples of Bhusawal Area by Square Wave Voltammetry, Differential Pulse Polarographic and Differential Pulse-anodic Stripping Voltammetry

Manisha C. Patil^{1*}, C. J. Patil², Mrunmayee C. Patil³

¹Department of Zoology, Dr. A. G. D. Bendale Mahila College, Muktainagar, Jalgaon, Maharashtra, India,

²Department of Chemistry, Smt. G. G. Khadse Science and Arts College, Muktainagar, Jalgaon, Maharashtra,

India, ³Department of Pharmaceutical Science and Technology, Nathalal Parekh Marg, Institute of Chemical Technology, Matunga, Mumbai, Maharashtra, India

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ABSTRACT

Aim: The aim of this study is to determine the toxic trace metals Cu, Pb, Cd and Zn in soil samples from Bhusawal, employing electrochemical techniques viz. square wave voltammetry (SWV), differential pulse polarographic (DPP) and anodic stripping voltammetric (DP-ASV) at hanging mercury drop electrode (HMDE) and the calculation of concentration level of each metal in the collected samples. **Material and Methods:** The soil samples were collected from Bhusawal area, at five points, in the month of March 2016. Based on the pressurized wet digestion of the finely powdered soil sample in a mixture of HNO₃-HCl, also followed by UV-irradiation, before the direct analysis - to eliminate the interference effect of dissolved organic compounds, were used to prepare the analyte for the voltammetric analysis. The metals were made free from any interference and the applicability of the method has been proved by the analysis of soil samples from polluted and non-polluted area. Accuracy is verified by employing atomic absorption spectrometry (AAS). **Results and Discussion:** The relatively higher concentration of Zn in all the investigated samples may be due to the following factors, (i) The higher tendency of Zn metal to dissolution in aqueous media compared to other metals, (ii) Most of the food cans are probably made from alloy containing relatively higher percentage of Zn metal, (iii) The structural network of the pipes transferring the sewage to the treatment plant are Zn alloy made, (iv) Most of the food plants contain a higher concentration of Zn.

Keywords: Anodic stripping voltammetry, atomic absorption spectrometry, soil samples, square wave voltammetry, differential pulse polarography, trace metal

INTRODUCTION

Enormous rise in population, industrializations and agricultural growth cause the demand for greener soil in the city areas. In the dry dump areas, soil is polluted, soil also use has various impact on environment and possibly it can have an important role to play in irrigation. Furthermore, it has caused the soil pollution, erosion, and it may change some of the soil characteristics; hence, importance of soil testing is found to be continually increasing. In such case, soil characteristics must be carefully maintained and managed in economically feasible

manner. Varied applications will be accomplished if agricultural soil is managed properly.

Differential pulse polarography (DPP) and anodic stripping voltammetry (ASV) are well-established techniques for trace determination of heavy metals content in environmental samples, for example, soil samples.^[1] DPP has been applied for the determination of heavy metals in soil samples, animal tissues, and plants.^[2] DP-ASV has been applied for the determination of heavy metals in samples without previous treatment, UV-digest's samples of industrial soil, sugarcane spirit, urine of steel production workers, wet-digested samples of domestic waste, sea soil, and sediments.^[3-6]

The atomic absorption spectrometry (AAS) is one of the preferred techniques because of its rapidness, specificity, and comparatively inexpensiveness. However, pretreatments involved for sample

*Corresponding Author:

Manisha C. Patil

E-mail: manisha1999@rediffmail.com/

drcjpatil@yahoo.com.

are expensive or some of them are ineffective in overcoming the physical interferences and sometime require large volume of samples which are not available always. Recent, advancements in instrumentation results in the improved sensitivities of metals by reducing background. The excessive dilution will minimize the matrix effect, but the analyte of low concentration will be diluted to either below or near the detection limits of the analyte.

Literature survey indicated no reports come across on the polarographic and voltammetric techniques for trace metal detection from the soil. Recently, we have reported Patil *et al.*^[7] the simultaneous determination of the toxic heavy metals in soil from Bhavnagar area by employing DPP and DP-ASV technique. Keeping in view of all these facts, it was considered worthwhile look into a simple, rapid, accurate, and inexpensive method for the determination of many metals simultaneously at trace levels. The present work is put forth for the determination of the toxic heavy metals in soil using polarographic and voltammetric techniques are reported. The studies include simultaneous direct analysis of the post-irradiated samples by employing square wave voltammetry (SWV), DPP, and DP-ASV.

Experimental

The samples were collected and preserved properly as per the following method.

Sample collection and treatment

The sample collection area is depicted in Figure 1. The exact location of the samples collected is depicted in Figure 2. The samples were collected at the various locations from Bhusawal area, namely location-B1 was Satara in the West, location-B2 was Tapi Nagar in South, location-B3 was Railway colony in the East, location-B4 was additional MIDC area in North-East, and location-B5 was P. O. Nahata college area in the North of city [Figure 2]. The samples were collected in March 2016. Before the sampling, the sample bottles were removed from the plastic bags and rinsed several times with the deionized water. The soil samples were collected in the washed and dried Teflon PTFE bottles with a total weight of 1 kg. Sampling depths were 1.2 ft and 2.5 ft by scale measurement. The samples were collected and mixed properly to have uniformity.

The solutions of the collected soil were prepared in deionized water and subjected to pre-treatment by UV 254 mmHg lamp - Ushio UL 1-70 W was used for UV irradiation. An aliquot of 750 mL of sample was acidified with 1 ml of concentrated HNO₃, placed into a quartz bottle with a volume of 1 L, and irradiated for 36 h.

Reagents

All reagents A.R. grade were used as received without any further purification. The reagents used are HNO₃, Cu, Pb, Cd, and Zn and standard solutions in 1 gL⁻¹, all from Merck, sodium acetate buffer solution (pH 5.2, Aldrich), and standard buffer solutions pH 4 and pH 8 (Qualigence, India). Ammonium nitrate, 99% (Qualigence, India) and hydrochloric acid (35%, Aldrich). All solutions were prepared with soil deionized by ionic exchangers Millipore Milli Q until its specific resistance was 18.2 MΩcm. Calibration standard solutions were prepared for each element separately from stock solution.

Instrumentation

Polarographic and voltammetric measurements were made with model 384B equipped with Houston DMP-40 digital plotter of EG and G Princeton Applied Research Corporation (PAR), USA. PAR model 303A SMDE/hanging mercury drop electrode (HMDE) as working electrode and PAR 30S magnetic stirrer. A three-electrode polarographic/voltammetric cell was used.^[7] An area of the working mercury drop electrode was 0.16 mm². The large area bright platinum wire used as the counter electrode (auxiliary electrode) and Ag/AgCl/KCl(sat.) was the reference electrode in these measurements. The AAS of Chemito make Model AA 201 and acetylene gas was used for confirming the results of soil samples analysis. The pH meter Metrohm model pH M64 was used for pH measurements. UV 254 mmHg lamp - Ushio UL 1-70 W was used for UV irradiation of the collected soil samples.

Procedure

The measurement of pH was made for each sample using pH meter (Metrohm model pH M64) calibrated with buffer solutions of pH 4 and 8 before measurements.

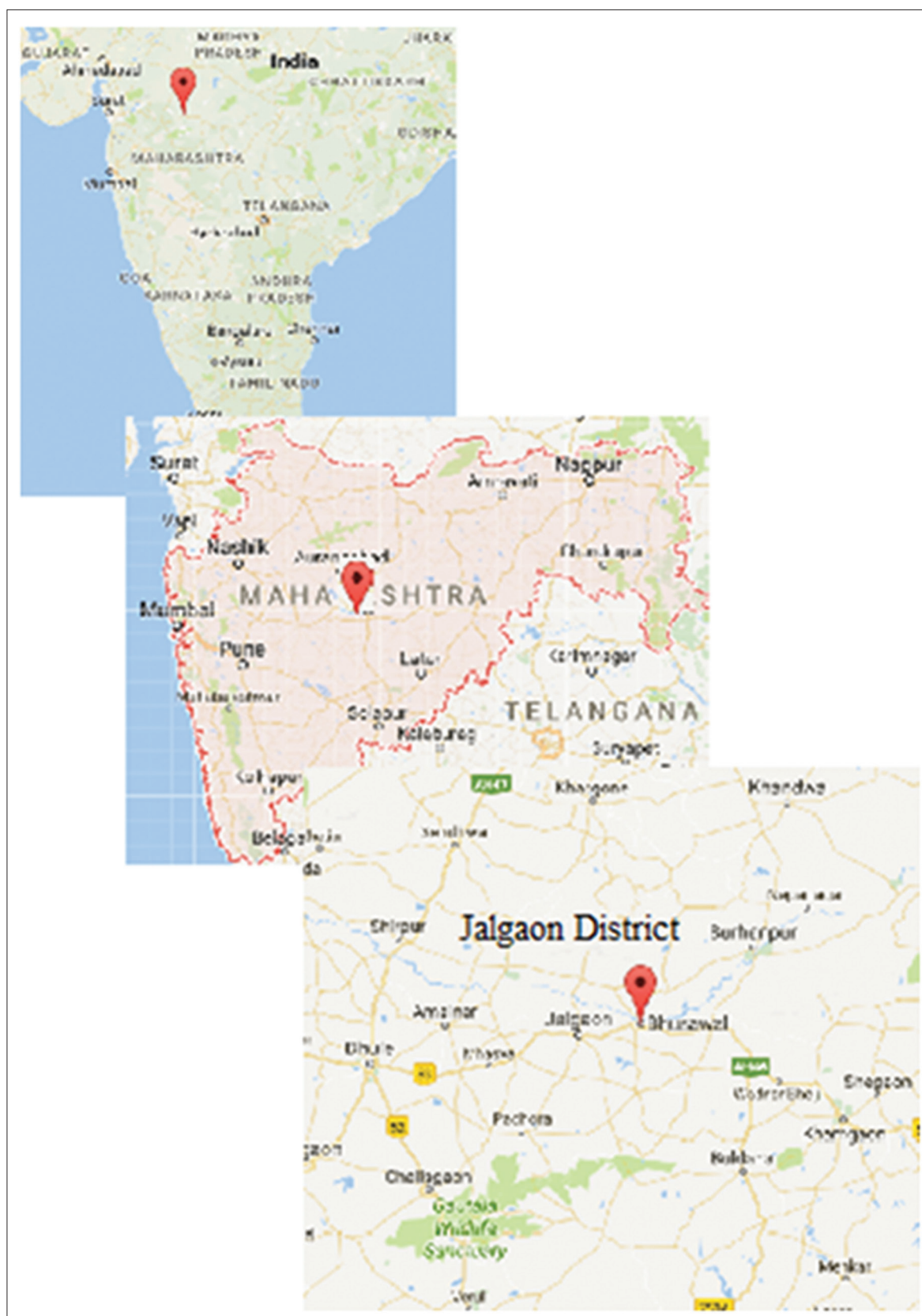


Figure 1: The map of Bhusawal Area (District Jalgaon, MS, India) showing study locations (drawn using Google Map)

Irradiation of the soil samples

10 g of soil sample solution containing 0.05 mol/L KCl and at pH = 3.2 was put in a 200 mL beaker at a distance 5 cm from the UV-L Hg lamp

for 8 h under an air cooling with fan. Sample temperature during irradiation was $25 \pm 1^\circ\text{C}$. The post-irradiated sample was kept in a polyethylene bottle before the polarographic and voltammetric measurements.



Figure 2: Detailed map showing locations for the collecting the soil samples (B1 to B5)

It should be mentioned that UV irradiation leads to photolytic decomposition of the organic compounds and humic acids.^[8] Therefore, interference of organic compounds and humic acid with heavy metal ions determination using DPP and DP-ASV was eliminated.

Extraction of the heavy metal in soil

The extraction of the trace metals from the soil samples with diethyldithiocarbamate into chloroform followed by back extraction with a Pb solution at pH 3.2.^[9]

Procedure for SWV, DPP, and DP-ASV

The 5 mL sample, after irradiation, was placed in the cell. The sample contains 0.05 mol/L KCl and the pH was adjusted at 3.2. Purified nitrogen gas was then purged for 10 min through the cell solution to remove dissolved oxygen. A polarogram was then recorded at the following conditions 30 s drop time, 50 mV pulse amplitude, and 2 mV/s or 5 mV/s scan rate. However, the ASV voltammograms were recorded using HMDE at $-1.3V$ starting potential and 300–420 s deposition time. For multistep

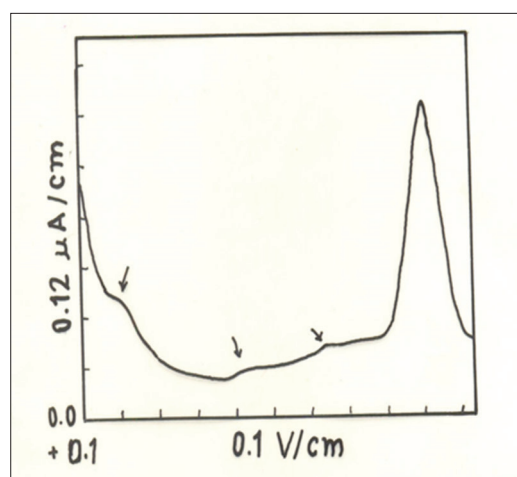


Figure 3: General differential pulse polarographic polarogram of soil sample - B1

standard addition method, different additives of the standard metal ion solution were added followed by recording the polarogram or voltammogram.

Analysis of the metals

The metals of interest were identified by their stripping potentials and quantified by the corresponding oxidation peak currents. The concentration of the various metals in the investigated samples was calculated.

Table 1: Typical identification of Cu, Pb, Cd, and Zn metals in soil sample B1

Meal ion	Potentials for standard metal solution in V	Potentials recorded for Test sample-B1 in V
Cu ²⁺	-0.071	-0.053
Pb ²⁺	-0.398	-0.393
Cd ²⁺	-0.602	-0.591
Zn ²⁺	-1.012	-0.997

Table 2: DPP* data for the determination of Cu, Pb, Cd, and Zn ion in soil samples - B1 to B5

Sample identification	Sample level	Zn (II), mg/L
Sample - B1	1.2 ft	0.1130
	2.5 ft	0.0940
Sample - B2	1.2 ft	0.1140
	2.5 ft	0.0990
Sample - B3	1.2 ft	0.1630
	2.5 ft	0.1325
Sample - B4	1.2 ft	0.1598
	2.5 ft	0.1495
Sample - B5	1.2 ft	0.1430
	2.5 ft	0.1155

*Concentration of Cu²⁺, Pb²⁺, and Cd²⁺, is below the detection level

RESULTS AND DISCUSSION

SWV and DPP analysis of soil samples

The DPP technique was applied for heavy metal ion analysis of soil samples - B1 to B5. The pH of the post-irradiated was adjusted to pH 3.2 and the ionic strength was kept constant by addition of solid KCl to give 0.05 mol/L KCl prepared in deionized water. Each time 5 mL of soil samples was subjected to DPP analysis and a typical polarogram was depicted in Figure 3. The polarogram of soil samples shows three small peaks at -0.053 V, -0.393 V, and -0.591 V and is correspond to the reduction of Cu, Pb, and Cd, respectively.

However, the soil sample exhibits only one cathodic reduction peak at -0.997 V, this peak correspond to the reduction of Zn to Zn (Hg). These peaks results were confirmed by spiking the sample solution with standard metal ion solutions [Table 1]. It was found that all peaks were increased nearby the same potential range, respectively. Furthermore, these results were confirmed by SWV analysis. The SWV of soil samples confirms the total four peaks at almost same potentials.

The DPP data related to sample - B1 to B5 were depicted in Table 2. The reduction, its behavior and the height of the reduction peak for the various

metal ions in the sample - B1 to B5 on the solution, and the other operational parameters were carefully investigated. This study was done to obtain the optimum conditions for the determination of the heavy metal ions in the sample using the DPP technique. It was found that the general optimum conditions are pH 3–4, scan rate 2 mV/s, drop time 30 s, and pulse amplitude 50 mV/s. Table 2 shows the results of application of the DPP determination of studied metal ions in the various sample - B1 to B5. Here, the metal ions Cu, Pb, and Cd cannot be determined using DPP due to relatively lower concentration of these ions.

DP-ASV analysis of soil samples

The interference of organic compounds on the DP-ASV determination of heavy metals in soil samples was eliminated successfully by irradiation with the low-pressure Hg lamp for 7 h. The irradiation process is a very good pre-treatment step to eliminate organic (and humic acid etc.) interference with the voltammetric determination of the heavy metals in the studied soil samples - B1 to B5. The decomposition of the organic compounds using low-pressure Hg lamp was carried out without added oxidizing agent and at room temperature, which eliminates loss of soil by evaporation at higher temperature.^[9]

The DP-ASV behavior of the pre-irradiated soil samples at pH 3.2 in 0.05 M KCl is shown in Figures 4a and b. At pre-concentration time (electrolysis time) 30 s and at -1.3 V electrolysis potential, the DP-ASV shows a very high and well-developed peak at about -1.0 V followed by two small peaks at -0.41 V and -0.123 V [Figure 4a]. However, at longer electrolysis time ca 300–420 s, the latter two peaks appeared as well-defined peaks and a new peak is obtained at -0.58 V [Figure 4b]. According to the previous reported results, the peaks located at -0.124 V, -0.414 V, -0.602 V, and -0.994 V at are corresponding to the anodic peak of the metal amalgam of Cu, Pb, Cd, and Zn, respectively. These results indicate that the sample under investigation contains mainly Cu, Pb, Cd, and Zn heavy metal at concentration level that could be determined using DP-ASV technique at the HMDE.

The time dependency of the anodic peak of Cu, Pb, Cd, and Zn at the mercury electrode surface was investigated. It was found that the height of the peak dependent on the concentration of metal. The effect of scan rate on the peak height of the anodic oxidation

Table 3: DP-ASV data for the determination of Cu, Pb, Cd, and Zn ion in soil samples - B1 to B5

Sample identification	Sample level	Cu ²⁺ , mg/L	Pb ²⁺ , mg/L	Cd ²⁺ , mg/L	Zn ²⁺ , mg/L
Sample - B1	1.2 ft	0.0840	0.3150	0.0252	0.2011
	2.5 ft	0.0719	0.2800	0.0178	0.1725
Sample - B2	1.2 ft	0.0618	0.2305	0.0358	0.1988
	2.5 ft	0.0710	0.2165	0.0127	0.1650
Sample - B3	1.2 ft	0.0819	0.3250	0.0365	0.2410
	2.5 ft	0.0726	0.2898	0.0229	0.2024
Sample - B4	1.2 ft	0.0766	0.1876	0.0341	0.2622
	2.5 ft	0.0972	0.1989	0.0265	0.2133
Sample - B5	1.2 ft	0.0663	0.2084	0.0353	0.1850
	2.5 ft	0.0572	0.1673	0.0379	0.1525

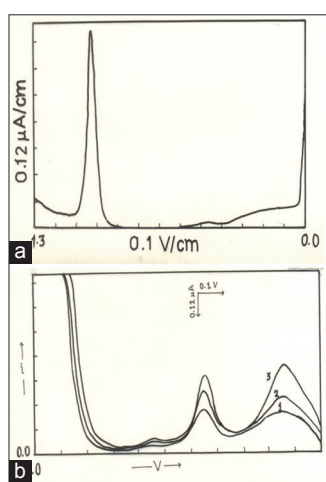


Figure 4: (a) - The differential pulse anodic stripping voltammetric behavior of the soil sample - B1 at pH 3.2 in 0.05 M KCl, at $E_s = -1.3$ V; and $t_s = 30$ s. (b) the differential pulse anodic stripping voltammetric behavior of the soil sample -B1 at pH 3.2 in 0.05 M KCl, at $E_s = -1.2$ V; and $t_s = 300$ s [1], 360 s [2], and 420s [3]

peak of the four metals (Cu, Pb, Cd, and Zn) was investigated, and it was found that the slower scan rate, for example, 5 mV/s is suitable to study the voltammetric behavior of the investigated samples and for trace determination of the various metals.

The obtained results are shown in Table 3 and were verified by AAS method, and on comparison, the results are in concurrence with that of the electrochemical method, namely DP-ASV. Table 3 shows DP-ASV data and the range of studied four metals, namely Cu, Pb, Cd, and Zn in the soil for samples - B1 to B5.

CONCLUSION

Results of the present study show the method for the identification and determination of Cu, Pb, Cd, and Zn in five samples of soil collected from Bhusawal area using DPP and DP-ASV. Metals have high tendency to accumulate in industrial

area than civil soil. This result could be explained by the fact that the main source of metals in the city area is mainly because of very low levels of soil (and hence more rock) a slight contribution of industrial areas of Bhusawal city.

The relatively higher concentration of Zn in all the investigated samples may be due to the following factors: (i) The higher tendency of Zn metal to dissolution in aqueous media compared to other metals, (ii) most of the food cans are probably made from alloy containing relatively higher percentage of Zn metal, (iii) the structural network of the pipes transferring the sewage to the treatment plant is Zn alloy made, and (iv) most of the food plants contain a higher concentration of Zn.^[10]

Scope

The method can be suitable when one has to determine many metals simultaneously, in the presence of the other metal ions.

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