

## DETERMINATION OF Zn, Cd, Pb AND Cu IN SOIL AND SLUDGE SAMPLES BY VOLTAMETRY

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(Received August 15, 1992; revised February 3, 1993)

A rapid and reliable analytical procedure has been developed for the simultaneous determination of traces of Zn, Cd, Pb and Cu in soils, after digestion with aqua regia, by differential pulse anodic stripping voltametry using a microprocessor controlled polarograph. Procedure was tested by analysing standard reference materials and comparing results with atomic absorption spectrometry. Soil and sludge samples from polluted and unpolluted areas were analysed. Soil samples from the road side showed the effects of vehicular traffic.

**Key words:** Soil and sludges, Voltametry, Pollution.

### Introduction

Importance of monitoring different types of samples for toxic metals to avoid health hazards has been well established [1-2]. Toxic metals reach man through food chain via dry and wet deposition from the polluted atmosphere [3-4] and sewage waters entering into the rivers and lakes [5]. Toxic metals first accumulate into soil to reach the plants through roots or are taken up by the leaves of the plants from the atmosphere [1]. Soil can also be contaminated with toxic metals by the run-off water from high ways and from the use of solid sewage sludge or water coming from waste-water treatment plants. Thus, monitoring of soil for toxic and heavy metals is very important. Over the years differential pulse polarography, differential pulse stripping voltametry, square wave voltametry and related voltametric techniques have developed into very reliable methods for trace metal analysis [5-9], because of their high sensitivity, accuracy and low costs especially for the analysis of many toxic and heavy metals [10-11]. Voltametric methods for the simultaneous determination of zinc, cadmium, lead and copper in soil have already been used by some workers [12-13]. These methods suffered from certain disadvantages such as lengthy digestion procedures [12] or use of high concentration of background electrolytes [13].

Present communication describes a reliable and rapid procedure for the analysis of cadmium, copper, lead and zinc in soils and sludge samples using a microprocessor controlled polarograph after digestion with aqua regia. Soil samples from polluted and unpolluted areas have been analysed and effects of traffic on environmental pollution have also been studied.

### Experimental

**Instrumentation.** VA-Processor 646 alongwith 675 VA sample changer (Metrohm, Switzerland) was used for voltametric measurements. Automatic washing of the cell and elec-

trodes thrice and change over to the next sample are controlled by microprocessor. For determinations by AAS Zeeman atomic absorption spectrometer, model 8000 of Hitachi, Japan was used.

**Reagents and chemicals.** HCl, HClO<sub>4</sub>, HNO<sub>3</sub> were used of pro-analysis grade from E. Merck, Germany Standard (1g/1) stock solutions of Zn, Cd, Pb and Cu were prepared using ZnCl<sub>2</sub>, CdCl<sub>2</sub> · H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub> and CuCl<sub>2</sub> · 2H<sub>2</sub>O (E. Merck) in 0.02M HCl. Required dilute standards were prepared fortnightly also in 0.02M HCl.

**Sample preparation.** Dried, homogenized soil sample (0.5 g) was taken in flask fitted with a reflux condenser, 3 ml of conc. HCl and 1 ml of HNO<sub>3</sub> were added to the sample and the flask was heated to boiling for 2-3 hrs near to dryness. About 0.5-1.0 ml of HCl was added and heated for some time to boiling. After cooling deionized water (5-10 ml) was added to the flask and heated at 100-150° for half an hour. The contents were cooled and transferred to a measuring flask and volume was made to 10 or 25 ml.

All the glass wares used were thoroughly cleaned with 20% hot nitric acid as described earlier [8-9].

**Voltametric determination.** 0.02N HClO<sub>4</sub> (15-20 ml) was taken in the cell as background electrolyte, to which 0.5-5.0 ml of the sample solution (depending upon the concentration of the trace elements) was added. Measurements were done on multimode Hanging Mercury Drop Electrode (HMDE) together with a Ag/AgCl reference electrode and platinum wire counter electrode. Deposition time for Cd, Pb and Cu was 90 sec. and for Zn 30 sec. and standing time for all the cases was 20 sec. Deposition potential for Cd, Pb and Cu was -0.8 V and for Zn was -1.2 V. As the concentration of metals varied considerably from each other in the actual samples therefore, the programme was divided into four segments. With computer controlled instrument, peak current measurements are

U Initial/mV	U. End/mV	Segment for	Measuring mode	Deposition time
Sweep 1-850	-550	Cd	DPASV	90 sec.
Sweep 2-600	-300	Pb	"	"
Sweep 3-300	-30	Cu	"	"
Sweep 4-1200	-850	Zn	"	30 sec.

always made in the adequate sensitivity range (autoranging) in each segment for the designated element. All the four elements were measured using differential pulse anodic stripping voltammetry. As the concentration of zinc in actual samples is higher than the other three elements, therefore, zinc was measured in the same solution independent of the other three elements. It also improved the measurement of other three elements particularly cadmium which is present in low concentration in the sample. Programme for peak recognition, standard additions and calculation was selected optimally as suggested by the manufacturer. With the change in acid concentration in different samples, sometimes copper peak shifted considerably, therefore, its recognition potential had to be changed accordingly and it could be easily done even after the recording of polarograms. It did not affect the results of copper. The peak potentials of other three elements were not much affected by change in acid concentration and remained within the recognition criteria for calculation purposes by the instrument. A typical voltamogram obtained for the soil samples is given in Fig. 1. Concentrations of cadmium in the measured

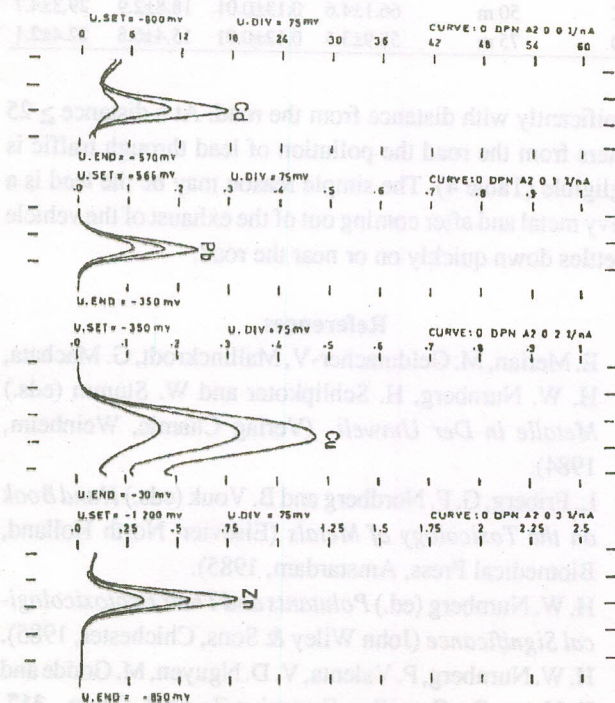


Fig. 1. Voltamograms of Cd, Pb, Cu and Zn in soil samples. Background electrolyte 0.02 N HClO<sub>4</sub>, working electrode (HMDE), reference electrode Ag/AgCl.

soil samples were usually low, but under the segmented programme of the microprocessor controlled equipment, there was no problem in its measurement and recording of peaks of any size.

## Results and Discussion

**Digestion method.** Different methods for the digestion of soil samples for voltametric analysis have been used [12-13]. Those methods are commonly used for routine analysis, which are simple, rapid and reliable. According to this criteria two methods using aqua regia [13] and HNO<sub>3</sub> + HClO<sub>4</sub> [11] look attractive. Both of these methods were compared for the digestion of soil samples Table 1, which shows that both of them are comparable. Method using aqua regia is less time consuming and easy to handle and reliable. It has been reported [13] that after digestion with aqua regia, it causes interference during voltametric measurements, therefore, high concentration acetate buffer was used to eliminate the interferences. During this modified method relatively small amount of aqua regia was used, which mostly evaporate during the digestion procedure. During the voltametric method small amount of sample solution was added to the background electrolyte, thus further reducing the acid concentration, therefore, no interference was observed during direct voltammetric measurements after digestion with aqua regia. It helped to avoid relatively high concentrations of background electrolyte of acetate buffer which may also be a source of contamination for trace metals. Although the described digestion method using aqua regia for soil analysis is rapid and reliable for routine analysis, but is not good for soil samples having high concentrations of oil or organics. For soil samples containing high concentrations of organics, digestion with nitric and perchloric acid mixture with hydrogen peroxide is recommended [9].

**Precision and accuracy.** To check the precision and accuracy of the modified method, a standard reference material of

TABLE 1. COMPARISON BETWEEN DIFFERENT DIGESTION METHODS FOR THE ANALYSIS OF Zn, Cd, Pb, Cu IN SOIL.

Sample	Element	Digestion methods	
		Aqua regia µg/g	HNO <sub>3</sub> + HClO <sub>4</sub> µg/g
S	Zn	55.0 ± 8.9	65.4 ± 7.2
	Cd	0.39 ± 0.11	0.48 ± 0.05
	Pb	41.5 ± 11.9	45.8 ± 10.4
	Cu	35.3 ± 5.45	29.8 ± 2.69
F	Zn	66.1 ± 5.7	73.7 ± 7.08
	Cd	0.19 ± 0.01	0.24 ± 0.02
	Pb	18.8 ± 2.9	22.15 ± 5.51
	Cu	29.3 ± 4.7	24.5 ± 1.83

river sediment NBS-1645 from National Bureau of Standards USA was digested with aqua regia according to the prescribed method and measured. It was measured using differential pulse anodic stripping voltametry and also atomic absorption spectrophotometer (AAS). In Table 2 the measured values by both the techniques are comparable with the reference values. Measured values and reference values are quite comparable with each other. Comparing voltametry and AAS techniques (Table 2), the values obtained by voltametry are relatively more precise and values obtained by AAS are relatively higher. It shows a definite edge of voltametry on AAS in terms of precision and reliability, but AAS has its own other advantages.

*Analysis of soil and sludge samples.* After optimizing the analysis method a number of soil and some sludge samples were analysed. Result of some of the selected soil and sludge samples from polluted and unpolluted areas are given in Table 3. It can be seen from Table 3 that soil samples from polluted areas contain higher concentrations of all the elements as compared to unpolluted area, but the concentration of lead is many times higher as compared to other elements, which shows higher lead pollution. Samples from city area and from busy road also contain higher concentration of lead, while the concentrations of other elements are comparable. All these samples were collected from Rawalpindi. It shows that in Rawalpindi there is only problem of lead pollution and pollution through cadmium and copper is negligible. Sewage sludge samples were taken from water treatment plant of Islamabad. This sludge is obtained from the primary clarifier and is usually sold as a manure for gardening and plants. It can be seen from Table 3 that levels of zinc in sludge are very high, but the levels of other metals are not very high and are comparable to the unpolluted sample. Use of this sludge as manure is not that harmful. Low levels of toxic metals in sewage sludge from Islamabad may be due to the reason that there is no major industry in the city.

*Effect of traffic and soil.* Some soil samples were collected from Islamabad high way. Samples were collected from the middle of the high way and at distance of 25, 50 and 75 meters from the high way. Concentrations of zinc, cadmium, lead and copper are given in these samples in Table 4. Concentrations of zinc do not change with distance from the road. Changes in cadmium and copper levels with distance from road are very small. Concentration of lead in sample taken from the middle of the road is nearly ten times more than the concentration of lead in sample taken from the road side at a distance of 25 meters. It clearly indicates pollution of lead from vehicular traffic, because lead compounds are used as antiknocking agent in petrol. Pollution of lead through traffic is mainly on the road or near the road and it decreases

TABLE 2. DETERMINATION OF Cd, Pb, Cu AND Zn IN RIVER SEDIMENT STANDARD REFERENCE MATERIAL NBS-1645.

Method	Cd ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
Voltametry	9.3 $\pm$ 0.14	730 $\pm$ 14.6	121 $\pm$ 5.4	1749 $\pm$ 20.8
AAS	11.3 $\pm$ 0.28	798 $\pm$ 15	130 $\pm$ 26	1800 $\pm$ 244
Reference Value	10.2 $\pm$ 1.5	714 $\pm$ 28	109 $\pm$ 19	1720 $\pm$ 169

TABLE 3. CONCENTRATIONS OF Zn, Cd, Pb AND Cu IN SOIL AND SLUDGE SAMPLES.

Soil sample	Collection site	Zn ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )
1	Unpolluted area	71.5 $\pm$ 2.3	0.13 $\pm$ 0.01	24.7 $\pm$ 2.1	37.2 $\pm$ 2.6
2	Busy road	71.8 $\pm$ 1.2	0.22 $\pm$ 0.03	162.2 $\pm$ 9.1	35.8 $\pm$ 1.9
3	Industrial area	238.0 $\pm$ 3.6	0.34 $\pm$ 0.04	670.5 $\pm$ 16.8	85.2 $\pm$ 1.2
4	City area	97.6 $\pm$ 2.5	0.53 $\pm$ 0.02	84.4 $\pm$ 3.4	24.1 $\pm$ 3.2
<i>Sludge sample</i>					
1	Sewage plant Islamabad	547 $\pm$ 5.0	0.41 $\pm$ 0.07	34.6 $\pm$ 2.6	39.1 $\pm$ 1.2
2	"	528 $\pm$ 26	0.47 $\pm$ 0.07	32.9 $\pm$ 2.4	40.6 $\pm$ 0.8

TABLE 4. CONCENTRATIONS OF Zn, Cd, Pb AND Cu IN SOIL SAMPLES TAKEN FROM THE HIGH WAY.

Soil sample	Distance from road	Zn ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )
A	Middle of double road	68.3 $\pm$ 3.7	0.25 $\pm$ 0.03	241 $\pm$ 13	39.7 $\pm$ 0.5
B	25 m	60.3 $\pm$ 2.9	0.26 $\pm$ 0.04	23.3 $\pm$ 4.5	30.2 $\pm$ 1.2
C	50 m	66.1 $\pm$ 4.6	0.13 $\pm$ 0.01	18.8 $\pm$ 2.9	29.3 $\pm$ 4.7
D	75 m	58.9 $\pm$ 3.5	0.12 $\pm$ 0.01	15.4 $\pm$ 0.8	22.4 $\pm$ 2.1

significantly with distance from the road. At a distance  $\geq$  25 meters from the road the pollution of lead through traffic is negligible (Table 4). The simple reason may be the lead is a heavy metal and after coming out of the exhaust of the vehicle it settles down quickly on or near the road.

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