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SIMULTANEOUS DETERMINATION OF ZINC, CADMIUM, LEAD AND COPPER IN WATER BY POTENTIOMETRIC STRIPPING ANALYSIS

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Analysis of zinc (Zn) cadmium (Cd), lead (Pb) and copper (Cu) in drinking and irrigation waters by potentiometric stripping analysis (PSA) is described. The pH and EC of waters were also determined. The results for zinc and copper were compared with those obtained by atomic absorption spectrophotometry (AAS) which indicated a significantly ($P<0.01$) strong correlation ($r = 0.994$ and 0.984 for Zn and Cu). The waters widely varied in pH, EC, Zn, Cd, Pb and Cu contents. The range values observed were; pH (7.5–8.7), EC (3.2–16.6 μmhos cm^{-1} x100), Zn (18.2–89.2 ppb), Cd (0.5–2.9 ppb), Pb (1.3–10.3 ppb) and Cu (9.2–70.2 ppb). Water of river–Kabul contained generally higher levels of heavy metals and lower EC than others. Lowest Pb was in the tubewell water at Nowshera.

INTRODUCTION

The determination of heavy metals in foods, and drinking and irrigation waters has become an important part of most studies concerned with environmental pollution and occupational health hazards. Although it is difficult to classify trace metals into essential and toxic groups, yet it is well known that an essential metal becomes toxic at sufficiently high intakes (Khurshid and Qureshi, 1984). Heavy metals can be determined by several techniques such as neutron activation analysis, atomic absorption spectroscopy (AAS), anodic stripping voltammetry and potentiometric stripping analysis (Jagner, 1979; Qureshi *et al.*, 1984; Satzger *et al.*, 1984 and Benzo *et al*.,1984). Potentiometric stripping analysis (PSA) is an electrochemical approach for the assay of trace metals (Jagner and Graneli, 1976). It appears to be widely applicable as stripping voltammetry and differential pulse stripping voltammetry (Jagner and Westerlund, 1980). PSA is particularly well suited in liquid samples since normally no pretreatment of such samples is necessary unlike biological materials where organic material must be destroyed prior to determination by any technique (Sattar *et al.*, 1989). High correlations between atomic absorption spectrophotometry (AAS) and PSA technique for the analysis of heavy metals in biological materials and sea water have already been described (Jagner and Aren, 1979). The objective of this study was to determine concentration of Cd, Pb, Cu and Zn in some drinking and irrigation waters available around Peshawer using the PSA.

MATERIALS AND METHODS

Sampling: The drinking and irrigation waters were collected thrice at week interval and pooled. The samples were acidified with HCl to 0.1 M immediately after sampling and stored in polyethylene flasks.

Chemicals: All chemicals used, except mercury (II) nitrate were of suprapure (merck) grade. The 1000 ppm mercury (II) nitrate solution contained less than 0.2 μg L^{-1} of Zn, Cd, Pb and Cu.

Analytical procedures: Simultaneous determination of cadmium, copper, lead and zinc was carried out by the potentiometric stripping technique (Danielsson *et al.*, 1983) using the Tecator Striptec system comprising glassy carbon electrode, saturated calomel electrode (SCE) and platinum wire as counter electrode. To 50 ml of the acidified sea water sample, mercury (II) ions were added to give a total concentration of 2–4 mg L^{-1}. The sample was placed in the analyser, the stirrer started and a stream of N_2 passed through the sample at a rate of about 200ml $min.^{-1}$. The analytical signal for each element is taken as the interval of time between two consecutive equivalence points on the time – potential curve (Fig. 1). The stripping curves were measured at potential – 1.1 volt vs SCE and 180 seconds plating time for Cd, Cu and Pb while – 1.3 volt vs SCE and 180 seconds plating time for Zn. The concentration of the metal in the samples was evaluated by means of the standard addition technique ; the 1–min preelectrolysis/stripping cycle being repeated after each addition. In comparison to calibration curves, the standard addition method is considered to be appropriate especially when the samples are of varying type and origin. In most experiments, two standard additions were used and the concentration of the standard addition solution was chosen so that the first addition almost doubled the concentration of the analyte. The stripping time for the element considered was prolonged in proportion to the added amount. Then the unknown content in the acid digest and finally the sample was determined by simple calculations. Details of the methodology are available elsewhere (Jagner, 1978; Lagner and Aren, 1979). The assays for Zn and Cu were also made by the atomic absorption spectrophotometry using Hitachi model 170–10 atomic absorption spectrophotometer for comparison of results. The water samples were also analysed for pH and EC (USSLS, 1954).

RESULTS AND DISSCUSSION

The accuracy of the method was initially estimsted by comparison with the results from the analysis of 16 samples of different concentrations. Closeness of the relation between these two methodologies measured by the linear correlation and regression. The correlation coefficients and regression equations of the data were measured. The test statistics indicated presence of a strong correlation for Zn and Cu between these two analytical techniques. The relationship was expressed by significant linear ($P < 0.05$) regression of the forms:

$$Y = 1.456 + 0.960\,X \text{ for Zn} \quad (r = 0.994)$$
$$Y = 0.180 + 0.997\,X \text{ for Cu} \quad (r = 0.984)$$

where X was the amount of AAS analysis and Y was that of PSA. The results obtained by both of the methods were almost similar. It was because the determinations were made on standard samples, similar observations have been made for heavy metals such as Zn, Cd and Cu except Pb for which significantly higher values by PSA than AAS analysis were found (Jagner and Aren, 1979). These wide differences in sea–water were considered to be the result of contamination on board analysis.

The characteristics and heavy metal contents of different waters are presented in Table 1. The analysis of distilled water was also conducted for comparison, which of course exhibited lower pH, EC and contents of different heavy metals. The reason for unexpectedly higher amounts of zinc in the distilled water is not clear. It may perhaps be the result of some contamination from the distillery. The pH of these waters ranged 7.5–8.7 and the EC was found to vary between 3.2 and 16.6 μmhos cm^{-1} x 100. The highest EC was in the tube–well water obtained from Taru followed by those of Pulosi Nowshera , and Regi. The lowest EC was in the water obtained from the river Kabul. The concentration of Pb ranged 1.3–10.3 ppb; highest level was in the water sample obtained from a canal near Tarnab (10.8 ppb) followed by river–Kabul (7.9 ppb). The amount of Pb in waters obtained from the well Pulosi, tubewell Tehkal and tubewell NIFA were higher than other waters tested. The concentration

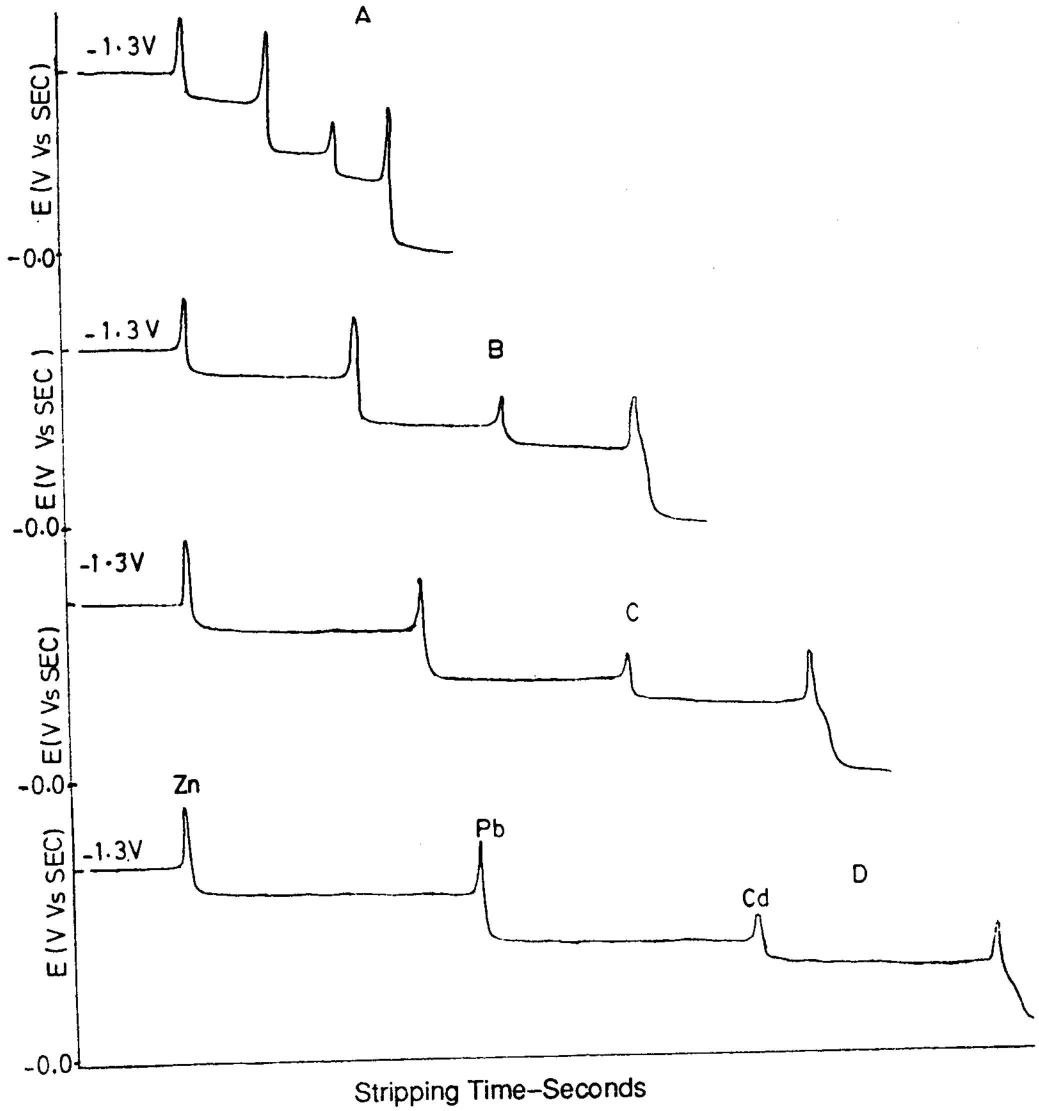

Fig. 1. Potentiometric stripping curves obtained for Zn, Pb and Cd with 250, 500, 750 and 100 ppb in curves A, B, C and D respectively

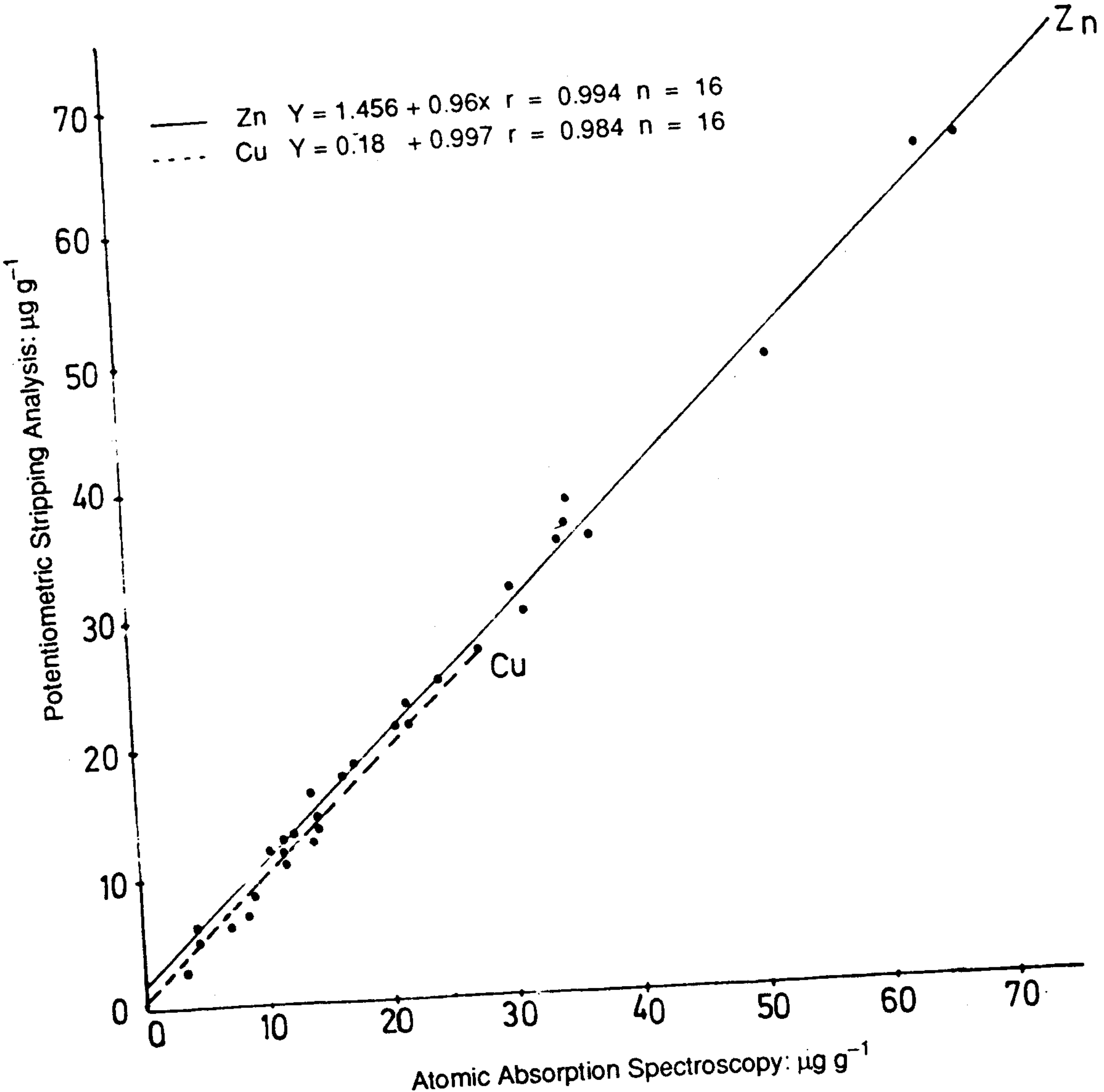

Fig. 2. Correlation between the results abtained by AAS and PSA

Table 1. The characteristics and heavy metal content of different waters

Waters	pH	EC	Lead	Copper	Cadmium	Zinc
		µmhos cm–1 x 100	ppb			
Water– distilled	7.1	0.03	1.0	6.5	0.5	16.8
Tube–well–NIFA	7.8	7.5	5.6	32.0	1.5	22.2
Canal–Tarnab	8.5	7.1	10.3	22.0	2.9	28.0
Well–Regi	7.5	8.4	4.2	16.5	0.9	25.7
Well–Pulosi	8.0	10.5	6.5	19.2	1.2	18.8
Tube–well–Tehkal	7.9	4.7	5.2	15.8	1.9	20.9
Tube–well–Taru	8.7	16.6	1.9	9.2	0.5	16.5
Tube–well–Nowshera	7.8	9.0	1.3	20.1	0.7	18.2
River–Kabul (Amangar)	7.7	3.2	7.9	70.2	3.4	89.2
CV	6.13	63.16	64.4	80.84	70.0	81.14

of Cu ranged between 9.2–70.2 ppb. The water obtained from river Kabul was found to contain highest level of Cu than other waters. The lowest Cu was in the water from tubewell at Taru. The amounts of Cd ranged 0.5–3.4 ppb among all the waters. The sample obtained from river Kabul had highest levels of Cd. Similarly the water of this river had highest level of Zn (89.2 ppb). However, the concentration of Zn in other water samples was found between 16.8 and 28.0 ppb. It was interesting to find, that water of river Kabul invariably contained higher levels of these heavy metals. The measurements of CV. revealed wide variation in Zn followed by Cu, Cd, Pb, EC and pH among these water samples. The drinking waters generally had appreciable amounts of essential trace metals but low contents of toxic metals such as Pb and Cd. This is useful for the people from nutrition point of view.

In view of the importance of heavy metals in the health and nutrition of human beings and animals, several studies have been carried out in Pakistan and foreign countries (Sattar *et al.*, 1989; Jaffar and Saleem, 1987; Jelinek, 1982; Wolnik *et al.*, 1985; Marletta *et al.*, 1986). However, little work has been done on the heavy metal contents of food materials and waters in Pakistan, specially in the N.W.F.P. According to the Food and Nutrition Board (1974), the average daily requirements for human beings of Cu and Zn are 2 mg and 15 mg respectively. The joint FAO/WHO Expert Committee (1972) had set tolerable weekly intake limits for Pb and Cd as 3 mg and 315–330 µg respectively per person. Reliable base line data for heavy metals are not available in developing countries. The background values are needed for evaluating the toxicological and nutritional significance of consumption of these elements and their possible increase due to pollution.

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