Pak. j. sci. ind. res., vol. 37, nos. 1-2, Jan-Feb 1994

DETERMINATION OF HEAVY AND TOXIC METALS Zn, Cd, Pb AND Cu IN VEGETABLES BY VOLTAMETRY

VIQAR-UN-NISA, RIAZ AHMED AND M. MUHAMMAD*

Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan

(Received November 3, 1991; revised September 25, 1993)

A simple and reliable voltametric procedure has been developed for trace metal analysis in vegetables. Different varieties of vegetables were analyzed for the contents of Zn,Cd, Pb and Cu and results are reported. Comparison between different vegetables showed that leafy vegetables have higher concentrations of metals as compared to other vegetables. Peels of vegetables have higher contents of metals. Distribution patterns of metals in soil, stem and leaves of vegetables are discussed.

Key words: Vegetables, Voltametry, Analysis of Cd, Pb, Cu and Zn.

Introduction

Toxic and heavy metals have a great significance in ecochemistry and ecotoxicology because of their toxicity at low levels and tendency to accumulate in vital human organs over prolonged time periods [1-3]. Food is the major intake source of toxic metals by human beings. Among different food systems, vegetables specifically leafy vegetables are relatively the most exposed foods to environmental pollution because of their large surface areas. Vegetable are consumed enormously in many countries and thus constitute one of the important food sources. It is, therefore, necessary to monitor vegetable samples and establish their heavy metal levels.

Search for simpler, reliable, quicker and inexpensive analytical methods is continuing due to the ever increasing demand of trace metal analysis particularly for environmental problems and in routine consumer protection. Until recently most of the trace metal analysis work in biological material was done mostly by atomic absorption spectroscopy [4] and voltametry was mostly used for water systmes [5]. Actually voltametry is one of the best methods for the analysis of toxic and heavy metals because of its high sensitivity, precision, inherent accuracy and cheap instrumentation [6,7]. Problems encountered for voltametric analysis were usually the incomplete destruction of organic matter during diges-tions,which adsorb on the electrodes during measurements. With the development of better digestion procedures [8-13] application of voltametry for the the analysis of biological materials have increased significantly but still there is a need to improve the procedures.

In this work, a simpler and reliable voltametric method has been developed for the analysis of vegetables. Levels of toxic and heavy metals in many vegetable samples from Rawalpindi–Islamabad area are reported and effects of environmental pollution are discussed.

Experimental

Instrumentation. The measurements were done using polarographic analyzer model 174A from Princeton Applied Research(PAR) and X-Y recorder model RE 0074. Hanging mercury drop electrode model 303 with magnetic stirrer 305 also from PAR was used. Reference electrode used was saturated Ag/AgCl electrode and a platinum wire served as counter electrode. Nitrogen gas was used for deaeration purposes. Pyrex glass crucibles of 30 ml volume were used for digestions and were covered with watch glasses during digestions.

Reagents. Nitric acid and perchloric acid were from E. Merck of p.a. quality and were purified before use by distillation. Thirty percent H_2O_2 from E. Merck of p.a. quality was used as such. Standard stock solutions of all the metals (1000–µg/g) were prepared by dissolving their respective compounds and preserved with 0.02 M HCl. Dilutions from stock solution were done weekly with 0.02M HCl. Glassware was washed with about 20% boiling nitric acid at least three times.

Sampling and sample preparation. Fresh vegetable samples were purchased at random from different shops in Rawalpindi and Islamabad in 1988-89. Samples of the same vegetable were thoroughly mixed, washed with deionized water and freeze dried in freeze dryer model Beta-A from Martin Christ, West Germany, homogenized and stored in precleaned and dried polyethylene bottles at-20°. Digestions were done using a nitric acid, perchloric acid and hydrogen peroxide mixture [12]. The dried vegetables 0.4 g were taken into crucible. Two ml conc. HNO_3 and 0.5 ml of conc. $HClO_4$ were added to the crucible and heated at about 100°. After

* Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan.

dissolution samples were cooled and 0.4ml of 30% H_2O_2 were added and heated again to dryness at 250-300°. Vessels were cooled to 100°, deionized water and 0.1 ml $HClO_4$ were added, heated, cooled and volume was made to 10 ml. Blanks were also run in the same way.

Voltametric procedure. After properly washing the electrodes and cell, 5.0 ml of 0.02M $HClO_4$ was taken in the cell, deaerated with pure nitrogen for 5 mins. Conditions for voltametric measurements were

Deposition potential	=	-1.2 V
Deposition time	=	4 mins.
Scan rate	=	10 mv/sec.
Clock time	=	0.5
Pulse height	=	50 mV

After taking the voltamogram of the blank, a measured aliquot of the sample solution ranging from 0.01 to 1.0 ml was added to the blank and measured for Zn,Cd,Pb and Cu. Then standard additions were done to the sample and measured and concentrations of metals in the samples were calculated. Typical voltamograms are given in Fig.1.

TABLE 1. ANALYSIS OF Zn, Cd, Pb AND Cu IN STANDARD REFERENCE MATERIALS.

Element	Citrus leaves NBS-1572		Spinach NBS-1570	
	Measured value (μg/g)	Reference value(μg/g)	Measured value(μg/g)	Reference value(μg/g)
Zn	30.26± 0.20	29.0 ± 2.0	48.71± 2.1	50±2
Cd	0.04± 0.01	0.03± 0.01	1.34± 0.08	1.5
Pb	12.45± 0.62	13.3 ± 2.4	1.44± 0.21	1.2± 0.2
Cu	13.91± 0.65	16.5 ± 1.0	10.61± 1.10	12± 2

Results and Discussion

Precision and accuracy. Studies were done [14] to optimize the voltametric method regarding the linearity curves of concentration versus peak heights (currents) and deposition times versus peak heights (currents) and all were found linear in the measuring range. Blanks were also run along the samples and were subtracted from the sample. Two standard reference materials of spinach and citrus leaves from National Bureau of Standards, USA were analysed to check the accuracy of results. In Table 1 are compared the measured values with the reference values. The measured values are in quite good agreement with the reference values which indicates the accuracy of the analytical procedure.

Concentration of metals in different vegetables. After optimizing the analytical procedure a variety of vegetable samples

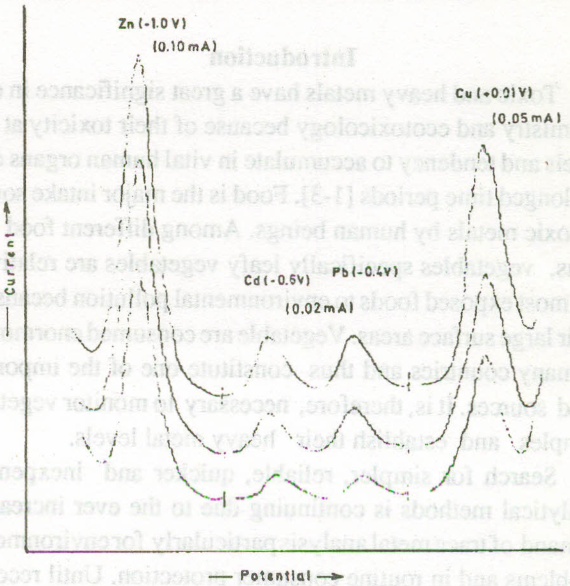

Fig. 1. Voltammograms of Zn, Cd, Pb and Cu in spinach sample.

TABLE 2. CONCENTRATION OF METALS IN DIFFERENT VEGETABLES.

S. No.	Common name	Botanical name	Zn (μg/g)	Cd (μg/g)	Pb (μg/g)	Cu (μg/g)
1.	Spinach	*Spinacea oleracia*	42.2 ± 2.81	1.08 ± 0.17	1.60 ± 0.19	12.6 ± 0.61
2.	Coriander	*Coriandrum sativum*	38.1 ± 4.33	1.03 ± 0.25	1.86 ± 0.25	9.16 ± 0.22
3.	Salad	*Lactuca sativa*	46.2 ± 2.84	0.94 ± 0.12	2.10 ± 0.08	9.22 ± 0.32
4.	Mint	*Mehtha piperita*	35.6 ± 0.59	0.92 ± 0.11	2.54 ± 0.48	11.99 ± 0.03
5.	Brassica	—	38.00 ± 3.53	1.25 ± 0.12	1.60 ± 0.31	15.00 ± 1.20
6.	Cauli flower	*Brassica oleraceae*	46.66 ± 5.03	0.82 ± 0.11	2.52 ± 0.21	5.32 ± 0.69
7.	Cabbage	*Brassica oleracea*	16.95 ± 3.2	0.13 ± 0.02	0.55 ± 0.05	5.12 ± 1.2
8.	Peas	*Pisum sativum*	9.6 ± 0.5	0.81 ± 0.13	2.47 ± 0.64	2.18 ± 0.10
9.	Bitter gourd	*Memordice chorantic*	15.98 ± 0.74	0.11 ± 0.02	0.40 ± 0.01	4.10 ± 0.24
10.	Lady finger	*Hibiscus esculentas*	86.14 ± 3.44	0.26 ± 0.05	0.78 ± 0.06	2.82 ± 0.41
11.	Turnip	*Brassice rapa*	14.44 ± 1.31	0.61 ± 0.04	2.85 ± 0.08	2.75 ± 0.7
12.	Tomato	*Lycopersicon*	13.49 ± 1.21	0.12 ± 0.01	0.37 ± 0.02	5.64 ± 0.09
13.	Aubergine	*Solanum melongena*	51.45 ± 4.6	0.25 ± 0.07	2.72 ± 0.8	6.81 ± 1.15
14.	Marrom	*Luffa aegyptica acutangula*	49.6 ± 1.2	0.18 ± 0.09	1.46 ± 0.05	12.17 ± 0.12
15.	Potato	*Solanum tuberosum*	6.50 ± 0.82	0.01 ± 0.008	0.25 ± 0.01	2.39 ± 0.55
16.	Potato peals	—	17.50 ± 1.21	0.25 ± 0.13	1.56 ± 0.08	9.84 ± 1.10

TABLE 3. ESTIMATED DAILY INTAKE OF Zn, Cd, Pb AND Cu THROUGH VEGETABLES.

Element	Average conc. of 15 vegetables (µg/g)	Intake by human-beings (µg)
Zn	34.06	1703.0
Cd	0.568	28.4
Pb	1.60	80.0
Cu	7.15	357.5

were analysed to see the levels of heavy metals for Rawalpindi - Islamabad area. In Table 2 are reported the values of metals analysed in different vegetables. Fifteen types of vegetables were analysed which are mostly consumed in this region. It can be seen from Table 3 that leafy vegetable (spinach, corriander, salad, mint, brassica and cauli flower) have higher concentrations of metals as compared to other vegetables. Lady finger, has relatively higher concentration of zink. Cabbage, bitter gourd, Lady finger, tomato and potato have low concentrations of all metals and particularly Pb and Cd. Here all the values are on dry weight basis and only the eatable parts of the vegetables were taken. Potato is a very common vegetable and consumed overall the world extensively. It is eaten mostly without peels. Here potatos without peels were analysed and peels were anlysed separately. It can be seen from Table 3 that essential metals Zn and Cu are lost appreciably in the peels and levels of toxic metals are also not very high. Levels of metals in all the vegetables are not high except, a few samples where slight Pb contamination is suspected. Mint, cauli flower, turnip, aubergine and peas have relatively higher concentrations of Pb. Mint and cauli flower being leafy vegetables may accumulate slightly higher concentrations of Pb, but peas and turnips normally should not contain higher concentrations of Pb.

In Table 3 are given the approximate daily intake values of metals by human beings from mixed vegetables. These intake values are calculated by taking the average value of metals in all the fifteen types of vegetables and considering that each person consumes approximately 200g (fresh weight), 50 g (dry weight) of vegetables per day. Although different vegetables are consumed variably by different people at different times throughout the year, yet it may be a good estimate for the average intake of metals from vegetable. It can be seen from Table 3 [1] that intake of toxic metals from vegetables is not high and is within the permissible limits.

Distribution of metals in soil, stem and leaves. To see the distribution pattern of trace metals in soil, stem and leaves of vegetables, some samples from the suburbs of the city were collected and analysed. Samples of spinach and corriander were taken an results are shown in Table 4. In both types the concentrations of Cd and Pb were highest in soil followed by stem and leaves. Leaves have much more surface area than stems, if there would have been some atmospheric pollution, then leaves should have higher concentrations of these elements, but here it is not the case, it shows that presently there is no atmospheric pollution in the suburbs of the city where most of the vegetables are grown. Distribution of copper and zinc does not entirely follow the pattern of Cd and Pb. The reason may be that the movement mechanism of these elements in the plant from soil may be different or higher concentrations of these elements in the atmosphere may be the contributing factors.

TABLE 4. ANALYSIS OF TRACE ELEMENTS IN SOIL, STEM, LEAVES OF THE VEGETABLES.

S. No.	Elements (µg/g)	Root soil		Stem		Leaves	
		Spinach	Coriander	Spinach	Coriander	Spinach	Coriander
1.	Cd	2.30 ±0.17	2.78 ±0.16	–	1.38 ± 0.25	1.1 ±0.14	0.7 ±0.01
2.	Pb	19.03 ±1.4	17.4 ±1.18	–	1.86 ± 0.12	1.21 ±0.21	1.11 ±0.04
3.	Cu	20.53 ±1.04	21.88 ±1.87	–	6.04 ± 0.23	7.17 ±0.16	9.1 ±0.05
4.	Zn	32.68 ±2.63	34.7 ±2.09	–	26.02 ± 1.11	36.6 ±0.72	27.24 ± 1.1

References

1. L. Friberg, G.F. Nordberg, B. Vouk (eds.), *Handbook on the Toxicity of Metals* (Elsevier/North Holland, Biomedical Press, Amsterdam, 1984).
2. H.W. Nurnberg (ed.), *Pollutants and their Ecotoxicological Significance* (John Wiley & Sons. Chichester, 1985).
3. S.S. Brown, F.S. Mitchell and D.S. Young (eds.), *Chemical Diagnosis of Disease* (Elsevier/North Holland, 1979).
4. J.A.C. Brokaert, G. Tolg, Fresenius, Z. Anal. Chem, **326**, 495 (1987).
5. H.W. Numberg, Sci. Tot. Environ., **37**, 9 (1984).
6. M. Stoeppler and H.W. Nurnberg, *Hazardous Metals in Human Toxicology*, A. Vercruysse (ed.) (Elsevier, New York, 1984), pp. 95.
7. J. Wang, *Stripping Analysis, Principles, Instrumentation and Applications* (VCH Publishers, Inc. Deerfield Beach, 1985).
8. R. Ahmed, P. Valenta, H.W. Numberg, Mikrochim. Acta., **I**, 171 (1981).

9. P. Ostapczuk, M. Godde, M. Stoeppler and H.W. Nurnberg, **317**, 252 (1984).
10. J. Hertz and R. Pani, Fresenius, Z. Anal. Chem., **328**, 487 (1987).
11. R. Ahmed and Viqar-un-Nisa, Pak. j. sci. ind. res., **32**, 639 (1989).
12. Viqar-un-Nisa and Riaz Ahmed, Mikrochim. Acta, **106**, 137 (1992).
13. R. Ahmed and Roomina Tanwir, Pak. j. sci. ind. res., **36**, 232 (1993).
14. R. Ahmed, Viqar-un-Nisa, R. Tanwir, PINSTECH/NCD-113, 1(1988).