

ELECTROCHEMICAL DETERMINATION OF ZINC METAL IN VEGETABLES

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ABSTRACT

Electrochemical method was developed for the trace determination of zinc metal in vegetables using simple polarography by mercury drop electrode. This apparatus has three electrode assembly, dropping mercury electrode as working electrode, calomel as reference electrode and platinum as counter electrode. Dropping mercury electrode had the characteristics $m = 2.422$ mg/sec, $t = 2.5$ sec and $h = 60$ cm, under the conditions of Amplitude 50 mV and 6 mV/S scan rate was used for electro analysis measurements. Electro analysis of zinc metal in vegetables was performed in HCl buffer (pH=2.5) quantities of Zn was determined. Half wave potentials were 1.02 Volt for zinc. A considerably higher amount of zinc was found in all the vegetables, which vary from approximately 0.894 to 6.914 ppm. Highest amount of zinc was recorded in Luffa cylindrical of site-I (6.914) followed by Brassica oleracea var. botrytis.

Keywords: Zinc, Dropping Mercury Electrode, DC Polarography, Vegetables.

Introduction

One of the main sources of pollution in the environments is metallic compounds. Metals and metalloids have long been mined and used in numerous applications. This has led to a significant increase of metal pollutions. Metals can accumulate in all environmental matrices at either high or trace levels of concentration. Therefore amount of various kinds of metals are present in soil, plants, air, lakes, animals, oceanic regions, even in foodstuffs and human beings. Their widespread distribution, especially heavy metals, became serious problems because of their toxicities for animals and human beings. Although some metals such as manganese, iron, copper and zinc are essential micronutrients, many such as mercury, cadmium, lead are not required even in small amount by any organism. Man had started using metals ever since civilization has started. Metals generally enter in the ecosystem in a relatively non-toxic form and generally become intrinsic components of the environment in such a way that it is difficult to remove them from the environment. Some of them are converted into toxic forms through the environmental reactions involving various micro-organisms and non-biological pathways. For example, methylated compounds like dimethyl mercury, $(\text{CH}_3)_2\text{Hg}$, are more toxic than their inorganic forms. In the present investigation more attention has been given to heavy metals like lead, cadmium, nickel and zinc. Although, the term "heavy metals" refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include Pb, Cd, Hg, As, Cr, and Ti etc¹⁻³. According to United Nation Development Programme (UNDP), human development report there was about 185.4 million people during 1988-93, who were not having access of safe drinking water.

According to a survey published in "The Hindu" (Nov. 23, 2002), at present about 15,000 habitations in the country have no potable drinking water, while two lakhs are partially covered and 2-17 lakh villages are identified with problem with quality of water. Lakes like Dal and Nagin in Kashmir, Loktak in Manipur and Hussain Sagar in Hyderabad have seriously choked by aquatic weeds due to eutrophication. Sukh-tal and Saria tal represent high pollution level in Kumaun region. In urban sector also, the drinking piped water is not safe. Many experiments found industrial pollutants, e.g., lead, mercury, chemical wastes and other toxic substance in piped water. Arsenic species are determined in water, soil and plants⁴. Mercury pollution was found in the Tapajos River basin Amazon⁵. Aluminium, Pb,

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Cd have been determined in water samples⁶⁻⁹. The heavy metals like lead, mercury, synthetic chemicals and some hazardous wastes dissolve in water in a manner that it is quite difficult to detect and separate them in the purification process. Thus problem of deteriorating water quality and thus aquatic ecosystem is worst where rivers pass through large cities or areas having industrial establishment which discharge effluents, solid wastes, particles and other hazardous wastes, which account for one-third of the total water pollution. In rural and semi-urban sectors having less number of industrial establishments, water pollution is mostly due to human wastes and agricultural runoff. Utilization of contaminated water causes many water borne diseases. The tendency of heavy metals to concentrate in the sediments may result in a persistent source of the contamination to various tropic levels in the aquatic environment¹⁰. Zinc is an essential trace element that poses great importance in human dietary nutrition and health. Therefore, it is known to be the second most abundant trace metal in human body after iron. It is consisting 2-4 g within a human body mass with plasma concentration of 12-16 μM . The role of zinc on human health was originally observed and reported by Prasad *et al.* Since there is no specialized Zn storage system in human body, daily intake of Zn is necessary to maintain a steady state. The objective of this review is to summarize the role of Zn in human physiology, the hazard of its enrichment and its appearance in commonly consumed vegetables.

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 Amplitude 50 mV and 6 mV/S scan rate. Elico digital pH meter.

Reagents

All reagents used were of analytical reagent grade purity (AR). The mercury used in the dropping mercury electrode was obtained from Merck. Britton-Robinson (BR) universal buffer solutions containing a mixture of equal amounts (0.08 mol/L) of phosphoric, boric and acetic acids with sodium hydroxide (0.02 mol/L) were applied as supporting electrolyte and to provide the various pH values. Standard Stock solutions (1×10^{-4} mol/L) of pesticides (technical grade, 21.5% w/w) were made up in ethanol. A series of standard solutions of pesticides were prepared by diluting the stock solution with distilled water in presence of few drops of ethanol to prevent turbidity. 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 2.0 M nitric acid for at least 7 days, washed three times with distilled deionized water, soaked in 0.1 M hydrochloric acid until ready for use. In distilled deionized water and finally soaked.

Sampling Locations

To find out heavy metal contamination in vegetables of industrial and educational Jaipur city, vegetables samples were collected from three different selected sites in rainy season and summer season of year 2020. **1. Lalkothi Vegetable Market**-Lalkothi vegetable market was selected as study area where vegetables grown in various parts of Jaipur city are brought for sale. They can be grown in such agricultural fields, which receive untreated water from sewerage and also from textile industries and transformer manufacturing industries. Jaipurites consume these vegetables and products of other crop plants. **2. Site-I, Amanishah Drainage, near Gurjar ki Thadi, Jaipur City** (a) Site-I, in summer season (b) Site-I, in Rainy season **3. Site-II, 1.5 kms Away from Site-I** (a) Site-II, in summer season (b) Site-II, in Rainy season.

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 E1/2 values confirming the presence of Pb, Cd, Ni and Zn in Vegetables sample solution. In order to combat water pollution, we must understand the problems and become part of the solution. Here, direct current polarographic evaluations of toxic heavy metals (Pb, Cd, Ni and Zn) in the water sample of Amanishah drainage (Gurjar ki Thdi Jaipur City) are shown in Fig.5.35 (A) to 5.38(A). Calibration curve of standard additions of metals are given in Fig. 5.35(B) to 5.38(B). It was found that among all the metals Zn was found in maximum concentration followed by Cadmium and Nickel.

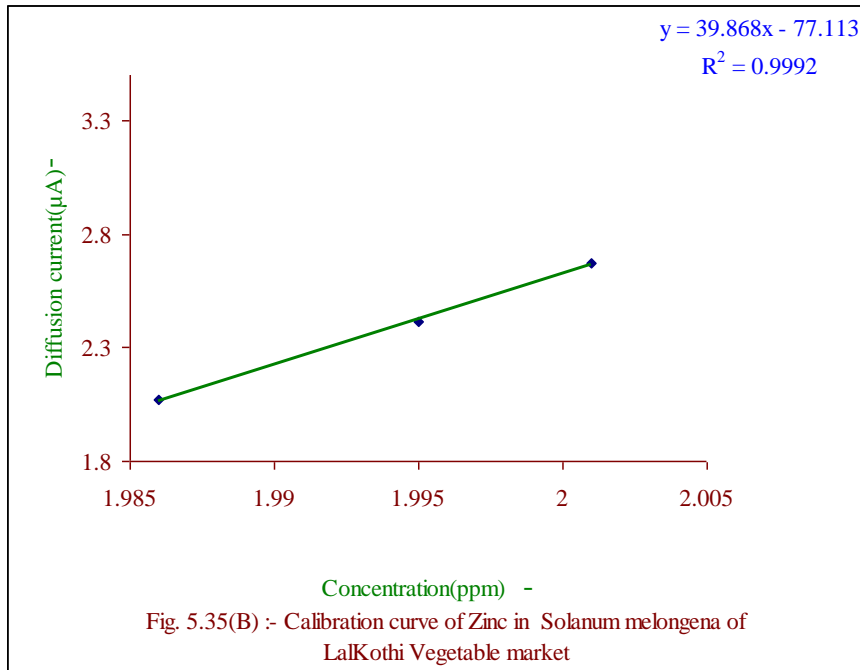
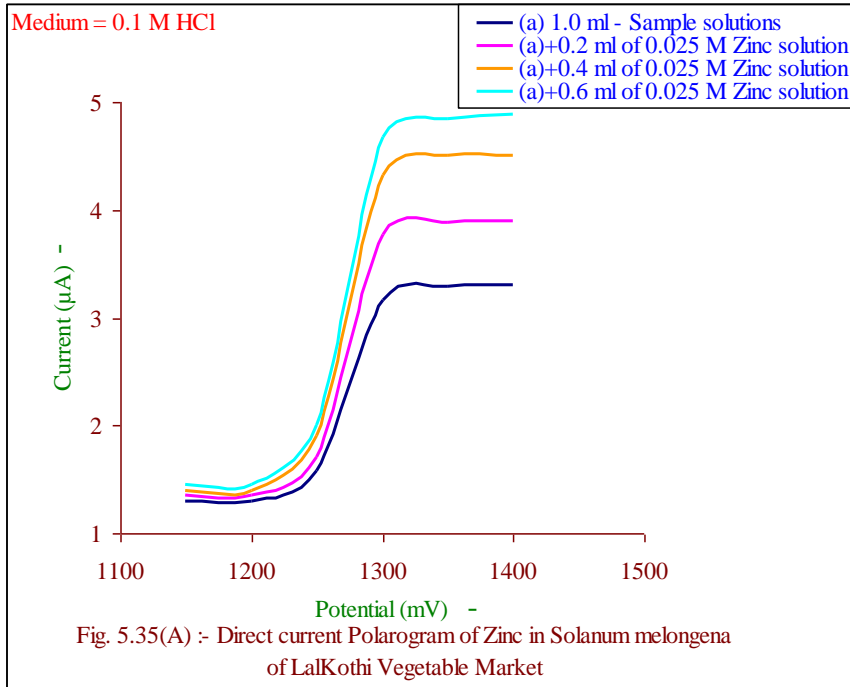


Table 1: Trace analysis of zinc in different vegetables in Lalkothi vegetable market

Vegetable sample	Buffer/ Supporting electrolyte	Half wave potential as E1/2	Conc. in ppm			% Error	Mean deviation	Standard deviation
			Taken	Observed	Mean			
1. Brassica oleracea var. botrytis	0.01M HCl	-1.02 V	1	1.000 1.090 1.108	1.066	0.066	0.044	0.057
2. Ablmoschuss eschlentus	0.01M HCl	-1.02 V	1	0.987 0.995 1.001	0.994	0.006	0.004	0.006
3. Luffa cylindrical	0.01M HCl	-1.02 V	1	0.986 0.994 1.003	0.994	0.006	0.005	0.008
4. Spinacia olerarica	0.01M HCl	-1.02 V	2	1.985 1.995 2.002	0.994	0.006	0.005	0.008
5. Solanum melongena	0.01M HCl	-1.02 V	2	1.986 1.995 2.001	1.994	0.003	0.005	0.007

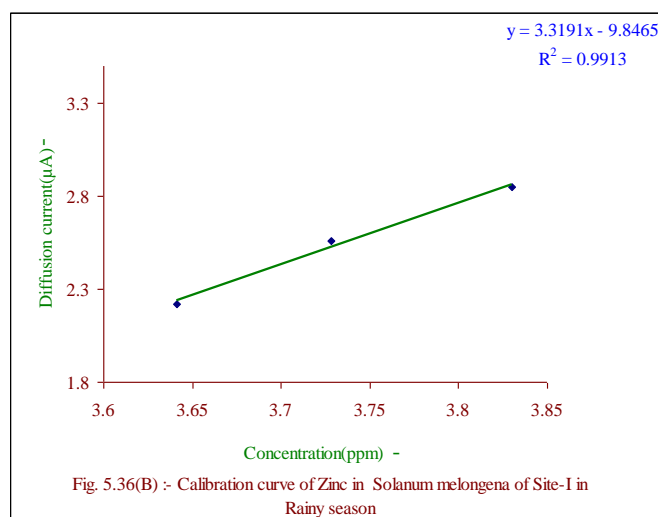
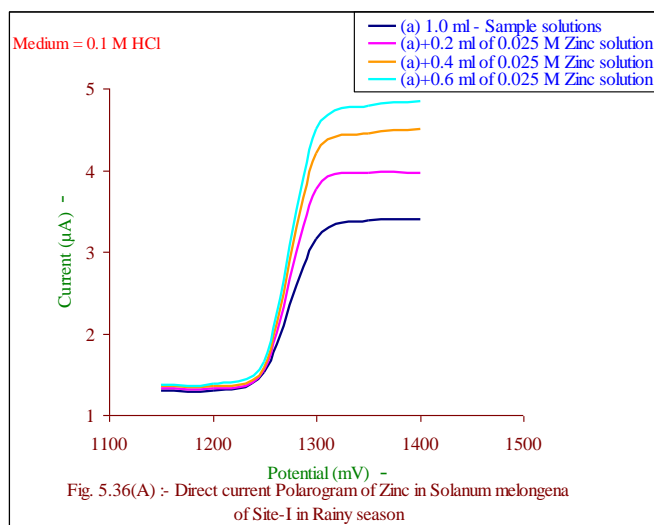
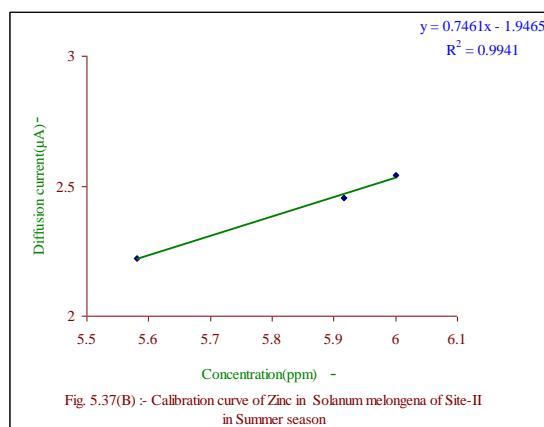
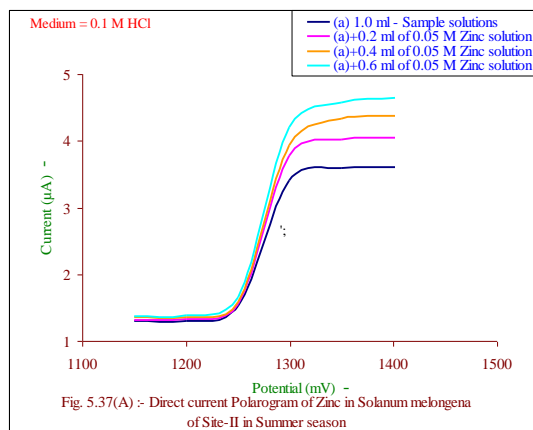


Table 2: Trace Analysis of Zinc in Different Vegetables in Site – I

Vegetable samples	Buffer/ Supporting electrolytes	Half wave potential as E _{1/2}	Conc. in ppm			% Error	Mean deviation	Standard deviation
			Taken	Observed	Mean			
1. Brassica oleracea var. botrytis (Summer season)	0.01M HCl	-1.02 V	5	4.619 4.930 5.001	4.850	0.030	0.154	0.203
2. Brassica oleracea var. botrytis (Rainy season)	0.01M HCl	-1.02 V	3	2.900 2.970 3.200	3.023	0.007	0.117	0.156
3. Abmoschuss eschlentus (Summer season)	0.01M HCl	-1.02 V	6	5.897 5.970 6.200	6.022	0.003	0.118	0.158
4. Abmoschuss eschlentus (Rainy season)	0.01M HCl	-1.02 V	4	3.600 3.975 4.082	3.885	0.028	0.190	0.253
5. Luffa cylindrical (Summer season)	0.01M HCl	-1.02 V	7	6.805 7.087 7.150	7.014	0.002	0.139	0.183
6. Luffa cylindrical (Rainy season)	0.01M HCl	-1.02 V	5	4.960 4.987 5.000	4.982	0.003	0.014	0.020
7. Solanum melongena (Summer season)	0.01M HCl	-1.02 V	5	4.960 4.980 5.102	5.014	0.028	0.058	0.076
8. Solanum melongena (Rainy season)	0.01M HCl	-1.02 V	4	3.641 3.728 3.830	3.733	0.066	0.064	0.094



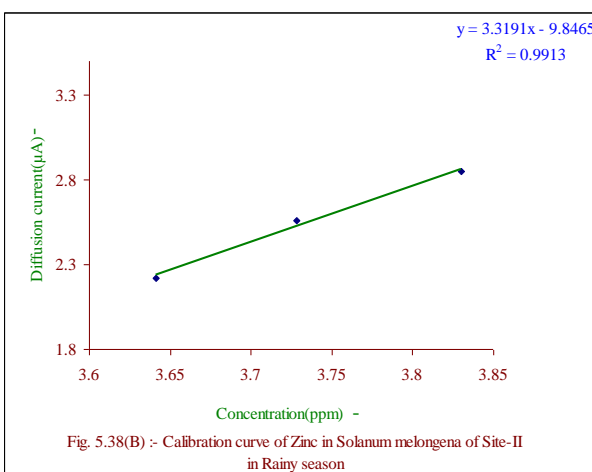
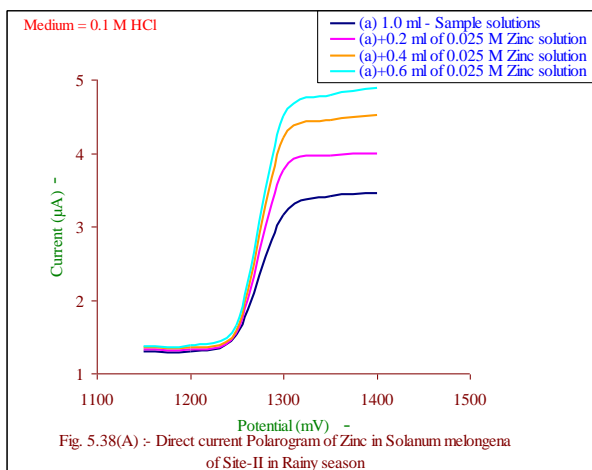


Table 3: Trace Analysis of Zinc in Different Vegetables in Site - II

Vegetable samples	Buffer/ Supporting electrolyte	Half wave potential as E1/2	Conc. in ppm			% Error	Mean deviation	Standard deviation
			Taken	Observed	Mean			
1. Brassica oleracea var. botrytis (Summer season)	0.01M HCl	-1.02 V	7	6.457 6.720 6.885	6.687	0.044	0.153	0.215
2. Brassica oleracea var. botrytis (Rainy season)	0.01M HCl	-1.02 V	5	4.932 4.986 5.102	5.006	0.001	0.063	0.086
3. Ablmoschuss eschlentus (Summer season)	0.01M HCl	-1.02 V	6	5.520 5.614 5.856	5.663	0.056	0.128	0.173
4. Ablmoschuss eschlentus (Rainy season)	0.01M HCl	-1.02 V	5	4.975 4.998 5.023	4.998	0.000	0.016	0.024
5. Luffa Cylindrica (Summer season)	0.01M HCl	-1.02 V	5	4.975 4.998 5.023	4.998	0.000	0.016	0.024
6. Luffa Cylindrica (Rainy season)	0.01M HCl	-1.02 V	5	4.963 4.995 5.023	4.993	0.001	0.020	0.030
7. Solanum melongena (Summer season)	0.01M HCl	-1.02 V	6	5.581 5.917 6.000	5.832	0.138	0.167	0.221
8. Solanum melongena (Rainy season)	0.01M HCl	-1.02V	4	3.641 3.728 3.830	3.733	0.183	0.064	0.094

Results and Discussion

The results obtained from the study of toxic metals in vegetables samples in part per million ranges are presented in table 1 to 3. Direct current polarograms for zinc in *Solanum melongena* of Lalkothi vegetable market, Site-I, and Site-II in summer season and rainy season are shown in Fig. 5.35(A), 5.36(A), 5.37(A) and 5.38(A) (as representative polarograms) and calibration curves of standard additions of metal are given in Fig. 5.35(B), 5.36(B), 5.37(B) and 5.38(B).

Similar DC polarograms for zinc in other vegetable samples of different sites (Lalkothi vegetable market, Site-I, and Site-II) were obtained and the calibration curves of the standard addition of metals were drawn. The metal concentration obtained are reported in table- 1, 2 and 3. The heavy metals concentration was found more in summer season than rainy season this is because during the rainy season waste water flows away with rain water, so heavy metals like zinc concentration gets decreased. A considerably higher amount of zinc was found in all the vegetables, which vary from approximately 0.894 to 6.914 ppm. Highest amount of zinc was recorded in *Luffa cylindrical* of site-I (6.914) followed by *Brassica oleracea var. botrytis*. 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 (i_d) 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 (14-15).

Conclusion

The described DCP method for the determination Zn in vegetables 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. Zn is crucial for both industries and human physiology. It involves in various important biological processes. However, Zn would be toxic to human health in excessive concentration. Therefore, constant close monitoring of Zn levels in commonly consuming vegetables are crucial in public health viewpoint. The Zn concentration can be elevated due to the application of chicken manure fertilizer, mining and smelting activities. Zn in vegetable tissues were also been discovered to have a correlation with other chemical elements, such as Fe, Mn and Cd, indicating Zn enrichment could impact a vegetable by altering the level of other biologically significant elements. Finally, the human health risk assessment on Zn should take Zn speciation in food biomass into account.

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References

1. Lingane, J. J. and Loveridge, B. A.; *J. Am. Chem. Soc.*, **66**, 1425, 1944.
2. Tomes, J.; *Collection Czechoslov. Chem. Commun.*, **9**, 1281, 1937.
3. Lingane, J. J.; *J. Am. Chem. Soc.*, **61**, 2099, 1939.
4. Hoyt and Stegeman; *J. Phys. Chem.*, **38**, 753, 1934.
5. Pearce and Eversole; *J. Phys. Chem.*, **32**, 209, 1928.
6. Stackelberg, M. V.; *J. Electrochem.*, **45**, 466, 1939.
7. Demassieux, M. and Heyrovsky, J.; *J. Chem. Phys.* **26**, 219, 1929.
8. Heyrovsky, J. and Kalousek, M.; *Collection Czechoslov. Chem. Commun.*, **11**, 464, 1939.
9. Ashok, K.; *Bull Electrochem.*, **13**, 209-212, 1997.
10. Lakhani, R. and Joshi, A. P.; *J. Ind. Chem. Soc.*, **64**, 380-381, 1987.

