

SIMULTANEOUS DETERMINATION OF Cd, Pb, Cu AND Zn IN DIFFERENT MATERIALS USING DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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A simple digestion method with subsequent simultaneous analysis of Pb, Cd, Cu and Zn by differential pulse anodic stripping voltammetry (DPASV) in different types of materials has been developed for environmental pollution control studies. The applicability of the procedure was proved by analysing different types of samples. The accuracy of the method was verified by analysing standard reference materials from NBS. Using this method different environmental samples were analysed and results are reported.

Key words: Trace analysis of Pb, Cd, Cu, Zn, Voltammetry, Environmental pollution.

Introduction

Many of the heavy metals are toxic even at very low levels while the others become toxic after certain threshold levels [1,2]. Input of these metals into the environment have increased significantly due to industrialization and other activities [3]. From the environment these toxic metals take their way to man through different food chain systems [3]. Lead and cadmium are toxic even at very low levels. To avoid the toxicity hazards there is a need to monitor different environmental samples for these toxic metals. For monitoring of environmental samples, sensitive, reliable, rapid and simple analytical methods are required. For environmental pollution studies, atomic absorption spectroscopy (AAS) voltammetry and many other techniques are being used [4]. Most frequently used method is AAS [5] and it is also not without problems at trace and ultratrace level analysis [6-7]. Voltammetry has been mostly used for water systems [8]. This limited application of voltammetry in spite of its high sensitivity, reliability and very low costs was mainly due to the interferences during measurement from the normally digested solution as used for AAS. These interferences are created by some dissolved organics. Voltammetry requires complete digestion and destruction of all dissolved organics and any other complexing substances. After the development of one of the first complete digestion methods for solid biological materials [9] its application for trace analysis of metals has increased significantly [10-13], but still there is a need to develop simpler digestion methods and to investigate the application of this technique for a variety of environmental samples.

In this work a convenient analytical procedure is presented with a simple digestion method and simultaneous determination of Cd, Pb, Cu and Zn in different types of samples using differential pulse anodic stripping voltammetry (DPASV) at the hanging mercury drop electrode. A variety of

environmental samples have been analysed and results are reported.

Experimental

Apparatus. Polarographic Analyzer Model 174A with hanging mercury drop electrode model 303A both from Princeton Applied Research, Princeton, NJ, U.S.A. were used for voltammetric measurements and X-y recorder used was Model 0074 from Hewlett Packard. A Ag/AgCl saturated electrode was used as reference electrode and platinum electrode was used as counter electrode. All the glasswares used were mostly of pyrex glass or quartz glass.

Chemicals. Proanalysis grade acids from E. Merck, West Germany were further purified by distillation and used for digestions. Nanopure water was used after purification with Nano-purifier of Barnstead, U.S.A. Stock solutions of Cd, Pb, Cu and Zn are prepared of 1000 ppm concentrations from oxides or salts of these metals and acidified. Dilute standards of different concentrations were prepared every fortnight and acidified with 0.02N HCl. Labware and glassware was cleaned by soaking in or boiling with 10-20% HNO₃ at least three times.

Sampling. Each sample was usually taken from a bulk of the material after mixing thoroughly. Samples were collected from Rawalpindi-Islamabad area. Cereal samples after collection were washed with de-ionized water, dried and grinded. Vegetable samples were washed with de-ionized water, freeze dried with freeze dryer Model Beta A of Martin Christ of West Germany. After freeze drying the samples were grinded, packed and stored at -20°.

Digestions. Although the digestion procedures were slightly varied depending upon the nature of every sample but main approach remained the same. 0.1- 0.5 g of the dried homogenised sample was taken in a glass vessel of about 30 ml volume specially prepared for this purpose. 2.0 ml of

HNO₃ and 0.5 ml of HClO₄ were added to the vessel and covered with watch glass. At first the sample was heated at about 80° till most of it dissolved. Then the temperature was raised to 150–200° and heating continued till complete dissolution and brought near to dryness. Now the temperature was raised to 250° and heated to complete dryness. After cooling the crucible de-ionized water was added to it and 1–2 drops of HCl (for soil sample 1.0 ml of HCl) and heated at 100–150° for one to two hours. In case of incomplete dissolution some more acids were added during the second step.

Voltammetric analysis. The digested solution was made upto 10 ml. 5.0 ml of the 0.02N HClO₄ background electrolyte was taken in the voltammetric cell and blank solution was measured for any contamination after deaeration with nitrogen. 0.1–2.0 ml of the sample solution (depending upon the concentrations) was added to the cell, deaerated with nitrogen and Zn, Cd, Pb and Cu were measured simultaneously. To get appreciable peak heights appropriate sensitivities were selected for every metal. For the evaluation of the metal contents at least two standard additions were done.

Results and Discussions

For reliable trace analysis purposes sampling and sample preparation is a major problem [14] and it is particularly true for voltammetric analysis. Voltammetric trace analysis requires the complete destruction of any dissolved organics and residual carbon. It is reported that complete destruction of residual carbon cannot be achieved by pressurized digestion even after heating for 25 hours [11]. The combination of pressurized digestion followed by UV-irradiation with the addition of H₂O₂ achieves complete digestion [9,11] but this method involves two steps, one digestion and the other UV-irradiation which increase the chances of contamination at trace levels. Secondly it requires strong UV-irradiation lamps and all the solutions must be handled in quartz glass vessels because UV-irradiation cannot pass easily through pyrex glass vessels and quartz glass vessels are costly. Low temperature ashing (LTA) method also achieves full destruction of organic matter, but it also cannot be used as a routine method because of its high price and long decomposition times and risks of contamination. Mixture of nitric acid and perchloric acid has been recommended to achieve complete digestion but danger of explosions has been reported [10, 11]. In this work a very simplified digestion method has been developed which can be used in any laboratory. Concentration of perchloric acid in the digestion acid mixture has been decreased and volume of the digestion vessel has been slightly increased to

successfully eliminate the dangers of explosions. Digestion takes place under slight pressure created by the weight of relatively heavier watch glasses. By adopting these measures not even a single explosion occurred during digestions in this laboratory. Care must be taken that enough nitric acid should be present in the vessel to react with biological matter. Usually blackening of the digestion mixture indicates the shortage of nitric acid. This method can be very successfully applied for routine analysis of environmental samples by voltammetry. This digestion procedure can also be used for atomic absorption measurements with advantage because low acid concentrations in the digested solution will increase the life of graphite tubes and will also reduce unnecessary background interferences during measurement. As relatively low amounts of acids are used, therefore, contaminations from the reagents (acids) are also reduced.

Voltammetric method is very sensitive and precise for trace analysis. Sensitivity of this method can be increased by many factors by just increasing the deposition times for the metal. In Fig.1 are given deposition times versus peak height curves for Cd, Pb, Cu and Zn. It can be seen that the curves are quite linear which means that any deposition time can be selected and it will not affect the analytical results. For samples with higher concentrations of metals deposition times were kept low and for samples with lower concentrations of metals deposition times were increased to get better peaks. Linearity range of voltammetric method is very high for most of the metals. In Fig.2 are given concentration versus peak height curves for Cd, Pb, Cu and Zn from 0- 900 ppb which are quite linear.

Accuracy of the analytical procedure was checked by analysing standard reference materials from National Bureau of Standards, U.S.A. Certified reference values of spinach SRM-1570 and river sediment SRM-1645 and measured values in this laboratory for Pb, Cd, Cu and Zn are compared in Table 1. It can be seen that the measured values are in quite good agreement with the certified values and it is an ample proof of the reliability of the method.

A typical voltammogram as obtained for the simultaneous analysis of Pb, Cd, Cu and Zn in cauliflower

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

Elements	Spinach NBS-1570		River sediment NBS-1645	
	Reference value (µg/g)	Measured value (µg/g)	Reference value (µg/g)	Measured value (µg/g)
Zn	50 ± 2	45.20 ± 1.17	1720 ± 169	1702 ± 32
Cd	(1.5)	1.28 ± 0.11	10.2 ± 1.5	10.1 ± 2.0
Pb	1.2 ± 0.2	1.16 ± 0.29	714 ± 28	692 ± 17
Cu	12 ± 2	12.51 ± 0.10	109.0 ± 19.0	110 ± 9

sample is shown in Fig 3. Voltammograms are taken for the sample and two standard additions in duplicate for each. Production of clear interference free, well defined and

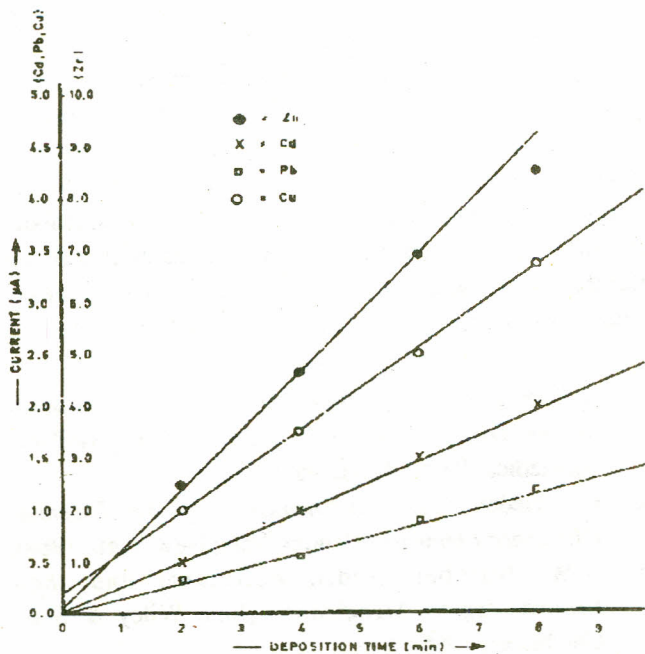


Fig.1 Deposition time versus peak height curves of Zn, Cd, Pb and Cu. Concentration of each element is 17ng/ml.

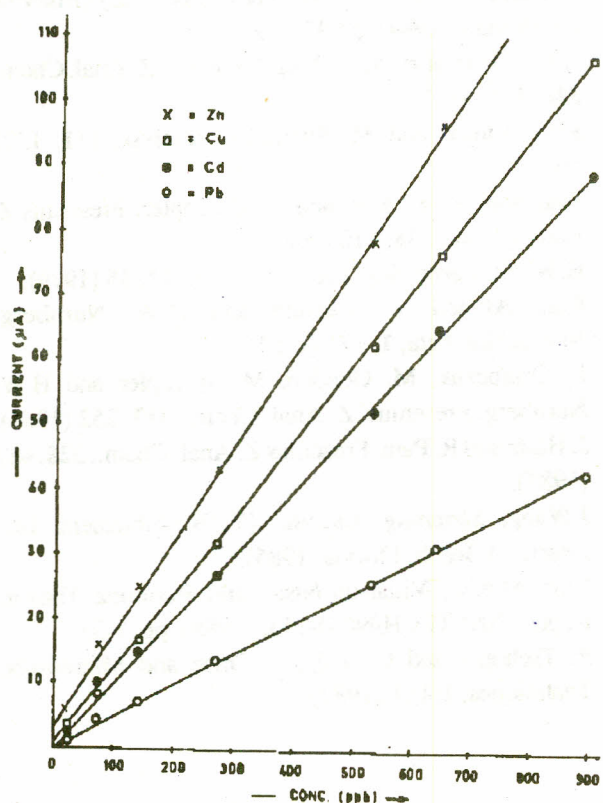


Fig.2. Concentration versus peak height (current) curves for Cd, Pb, Cu and Zn.

reproducible peaks for Pb, Cd, Cu and Zn proves the reliability of the procedure. Now most of the natural environmental samples contain different concentrations of metals. Voltammetry has an added advantage that one can change the sensitivities for each element during simultaneous analysis in the same run without any problem because it has wide linearity range for all the elements. It can be seen from the voltammogram (Fig. 3) that the concentrations of Cd, Pb, Cu and Zn vary from each other by many orders of magnitude without interfering with the analysis of the others. Thus for the simultaneous analysis of Cd, Pb, Cu and Zn in all types of samples, voltammetry is one of the most suitable methods. Because of the toxicity and importance of these elements in environmental pollution the voltammetric method attains special significance. Moreover voltammetric instruments are much cheaper as compared to other analytical techniques [10]. For example polarographic analyzer is many times cheaper than an electrothermal AAS system which is necessary for trace analysis.

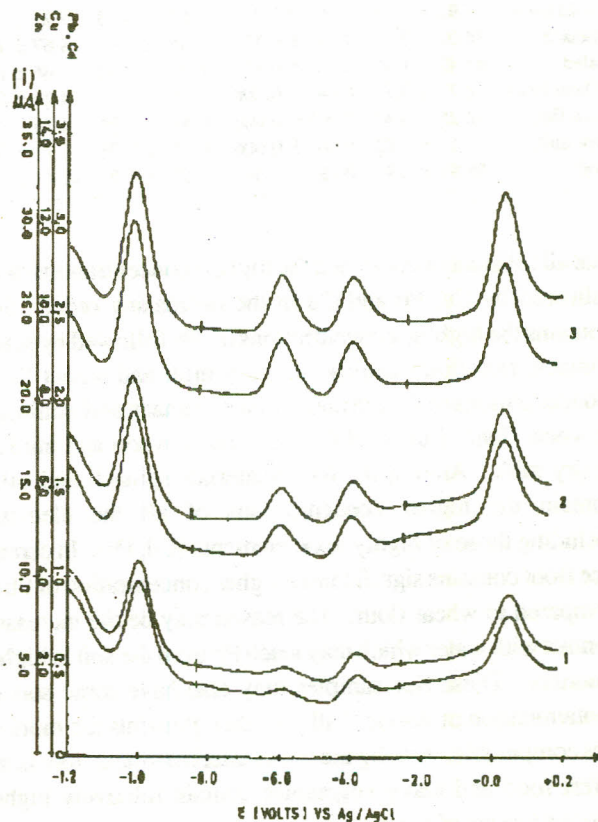


Fig.3. Differential pulse stripping voltammograms of Zn, Cd, Pb and Cu in the analyte from the digested cauliflower sample. 5.0 ml of 0.02N HClO₄ Background electrolyte + 1.0 ml of digested sample. Deposition time = 2.0 min, scan rate = 10 mv/sec, pulse height 50 mv. (1), sample (2), first standard addition of Zn = 42 ng/ml, Cd = 1.67 ng/ml, Pb = 1.67 ng/ml, Cu = 16.7 ng/ml; (3), second standard addition of Zn = 84 ng/ml Cd = 3.34 ng/ml, Pb = 3.34 ng/ml Cu = 33.4 ng/ml.

Using this method different types of samples were analysed. The samples were selected keeping in view two factors (a) the samples should represent different types of materials to see the applicability of the analytical method for nearly all types of materials (b) the samples should represent those materials which are usually exposed to environmental pollution and are abundantly consumed by human beings. In these samples cauliflower, spinach and salad represent the class of vegetables, wheat flour and rice flour represent cereals, milk is also consumed very much and soil is the major recipient of all types of pollution and also many food materials are grown on soil which may take up contaminations of the soil. All these substances were analysed by the above mentioned voltammetric method and the results are given in Table 2. It can be seen from the table

TABLE 2. CONCENTRATIONS OF Zn, Cd, Pb AND Cu IN DIFFERENT TYPES OF ENVIRONMENTAL SAMPLES.

Sample	Zn ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)
Cauliflower	17.95 \pm 2.14	0.10 \pm 0.01	0.54 \pm 0.13	6.21 \pm 0.80
Spinach	38.02 \pm 2.1	1.08 \pm 0.12	1.65 \pm 0.15	8.67 \pm 1.32
Salad	48.42 \pm 1.52	0.70 \pm 0.10	2.01 \pm 0.32	7.46 \pm 0.21
Wheat flour	18.77 \pm 0.77	0.04 \pm 0.008	0.06	4.24 \pm 0.14
Rice flour	22.25 \pm 0.42	0.067 \pm 0.006	0.587 \pm 0.05	4.25 \pm 0.27
Dry milk	37.11 \pm 0.62	0.06 \pm 0.006	0.161 \pm 0.01	1.71 \pm 0.18
Soil	56.87 \pm 2.91	0.18 \pm 0.04	13.58 \pm 0.9	25.41 \pm 2.06

that all substances contained the highest concentrations of Zn followed by Cu, Pb and Cd in the decreasing order. Soil contains the highest concentrations of Pb followed by salad, spinach, rice flour, cauliflower, dry milk and wheat flour. Concentrations of Cd are maximum in spinach and minimum in wheat flour. Levels of Cu are highest in soil and minimum in dry milk. Among the food materials spinach and salad contain the higher concentrations of all the elements including those of highly toxic elements (Cd, Pb). In cereals rice flour contains significantly higher concentration of Pb as compared to wheat flour. The reason may be the increased contact with water which may leach Pb from the soil in higher amounts. These rice samples may also have some sort of contamination of lead and all the other elements are more or less comparable. Among the food materials wheat flour is the safest food and leafy vegetables contain relatively higher concentrations of toxic elements.

Conclusions

With industrialization, environmental pollution is bound to increase. To monitor the environmental pollution levels, sensitive, reliable and easily accessible analytical methods are required. Voltammetric method is one of the most attractive methods because it is sensitive, reliable and many times cheaper than atomic absorption method. It can be accessible to all medium types of laboratories even in developing countries. Voltammetric method is applicable for all types of environmental samples. Preliminary results about the levels of toxic metals in different food materials indicate that they are still within the permissible levels in Pakistan but detailed studies for specific industrialized areas are required.

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