



MONITORING OF CADMIUM IN DRINKING WATER BY VOLTAMMETRY

*R. AHMED, T. YAMIN¹ and M.S. ANSARI¹

Nuclear Chemistry Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

¹ Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

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Cadmium, one of the most harmful elements is toxic at very low levels. The WHO recommended tolerance levels of cadmium in drinking water are 3 µg/L. Differential pulse anodic stripping voltammetry (DPASV) is quite a sensitive and accurate analytical technique, which can be employed to measure a number of metals including cadmium well below the tolerance levels in water samples. A DPASV method has been optimized for the analysis of cadmium in water. The initial standardization and optimization procedure using perchloric acid as the supporting electrolyte showed that for different deposition times vs. peak heights the results were linear which indicates that sensitivity of the method can be increased many fold by increasing the deposition times. Calibration curves between different concentrations of cadmium and peak heights are quite linear. A number of drinking water samples collected from various locations of Rawalpindi-Islamabad have been analysed. The levels of cadmium are in the ranges of 0.5-60 µg/L. Thus some of the samples have higher levels than the recommended values.

Keywords: Cadmium, Drinking water, Voltammetry

1. Introduction

Environmental pollution is one of the most important problems for human health [1]. The presence of toxic metals, metalloids and their compounds is a major concern due to their toxicity to many forms of life [2]. Pollution of water resources is a potential danger to human health and the environment [3]. Cadmium is highly toxic in nature [4]. The ingestion of cadmium in food or water can cause symptoms of nausea, vomiting, abdominal cramps and headache within minutes of ingestion. In severe cases diarrhea and shock can develop. Prolonged exposure to cadmium can cause anaemia and hypertension [5]. Cadmium and its compounds are widely used in electroplating, pigments, storage batteries, rubber, paints, plastics, semiconductors, brazing and low melting alloys, welding, fungicides, insecticides and in the reactor control rods etc. [3], therefore there is always a risk of cadmium contamination in water through the effluents released by the respective industries. Permissible limit of cadmium in water is 3 µg/L as recommended by WHO and it is beyond the detection limit of most of the analytical techniques. Cadmium can be analysed by different techniques. In vegetables, the levels of cadmium found can go as down to 0.11µg/g [6] and in milk these levels may reach down to 0.09 µg/L [7]. Atomic absorption spectrophotometry

has been employed to determine the levels of cadmium in waste waters [8, 9]. High resolution inductively coupled plasma mass spectrometry (ICP-MS) [10] and potentiometric stripping analysis [11] are other methods for trace analysis of cadmium. Voltammetry in general and DPASV in particular is a very sensitive method and can measure cadmium directly in natural and drinking water samples at very low levels [12-14]. In the present work a DPASV method has been optimized for the analysis of cadmium in drinking water samples collected from Rawalpindi and Islamabad areas and results are discussed.

2. Experimental

2.1. Apparatus and instruments

The model 174A polarographic analyzer with hanging mercury drop electrode model-303 from Princeton Applied Research, USA was used, for differential pulse anodic stripping voltammetry. Three electrode cell has been used in this work. The cell is usually a covered beaker of 5-50 mL volume and contains the three electrodes (working, reference, and auxiliary) which are immersed in the sample solution. pH meter used was from Metrohm model 605, Switzerland, while Wescan conductivity meter model 212, USA has been employed for conductance measurement.

* Corresponding author : riaz@pinstech.org.pk

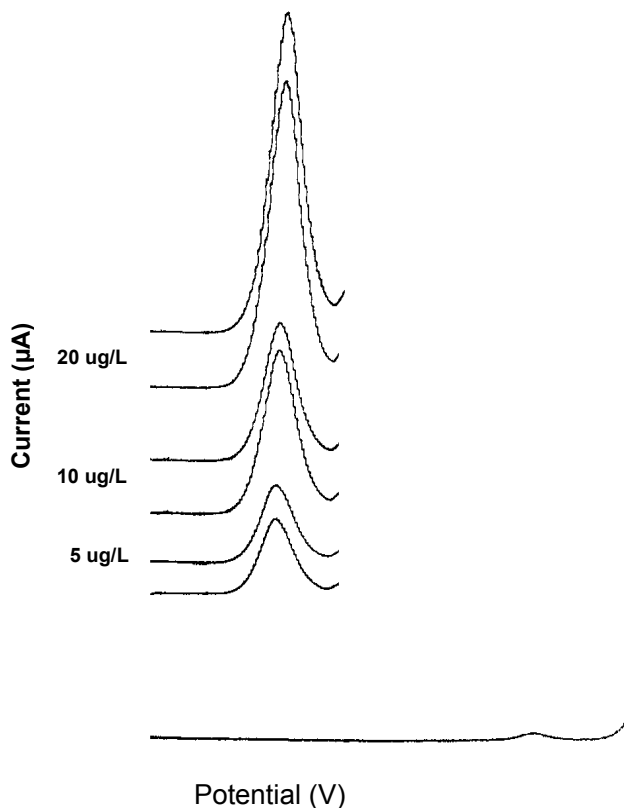


Figure 1. Voltammograms for 5,10 and 20 µg/L of Cadmium.

2.2. Chemicals and reagents

All chemicals employed were of analytical grade obtained from E. Merck, Germany and in most of the cases better than 99%. Solutions of cadmium of different concentrations were prepared from cadmium oxide in doubly deionized water and perchloric acid was added to make it 0.02 M in solution.

2.3. Procedure

To calibrate the instrument following parameters were set for DPASV measurements. (a) 0.02 M perchloric acid used as a background electrolyte, (b) Initial voltage was at -0.9 V(c) Potential scan rate was maintained at 10mV/S. (d) Voltage range was of 1.5 volt, (e) Modulation amplitude was 50mV (f) Operating mode was differential pulse. Current range was established as per response of cadmium ions in solution. For calibration, 50 ml of 0.02M HClO₄ was taken in the measuring cell. Instrument was adjusted as described above and a blank background reading

was taken to ensure that there was no peak appearing in the background, thus implying the absence of any sort of ion, or interfering substance in the system. Later 1000 µg/L solution of cadmium was diluted to have known concentration and measurements were carried out in triplicate. The concentrations of cadmium were enhanced, from 20 µg/L to 500 µg/L. Keeping deposition time equal to one minute a typical voltammogram for cadmium is shown in Fig.1.

3. Results and Discussion

DPASV can analyse cadmium upto less than µg/L levels, without interference from any other ion or radical present in the matrix. The voltammograms of different cadmium levels are shown in Fig.1. Calibration graph for cadmium concentration is drawn versus current. The calibration graph for Cd, and of current vs deposition time are shown in Figs. 2 and 3 respectively. Calibration curves are linear showing the precision of the method. Sensitivity of stripping voltammetric method may be increased to more

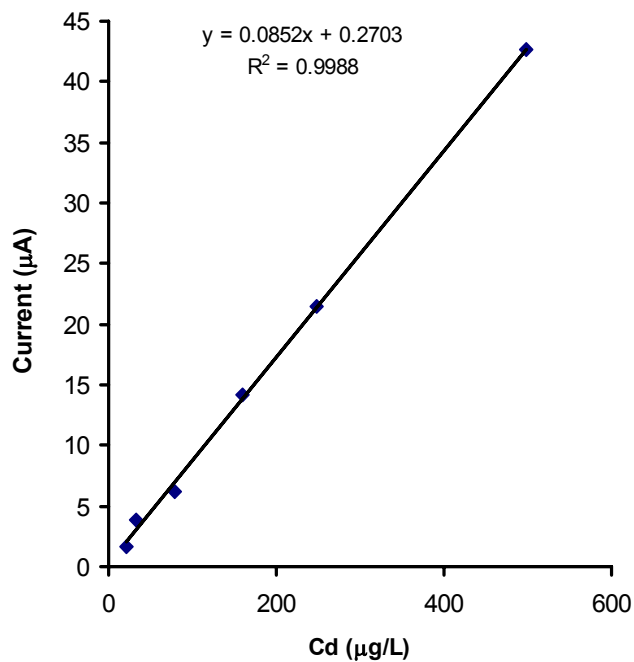


Figure 2. Calibration curve of cadmium.

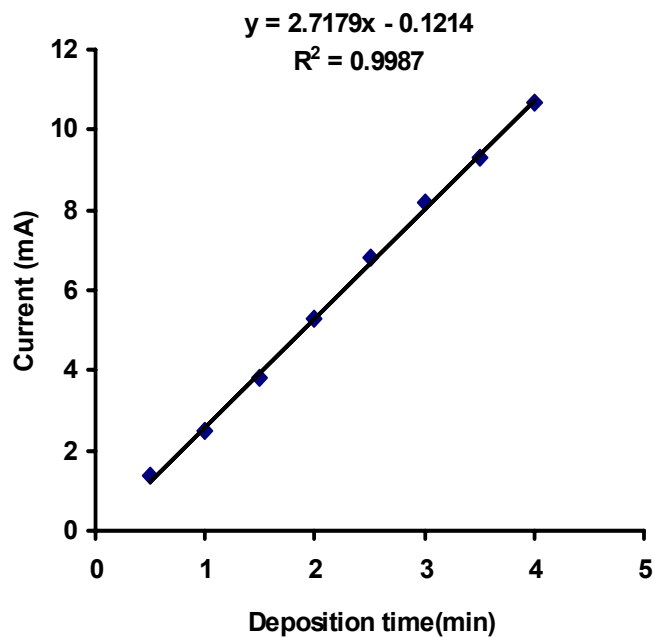


Figure 3. Calibration curve of deposition time vs peak height for cadmium

Table 1. Analysis of Cadmium in Standard Reference Materials.

No.	Reference Sample	Cadmium reference value ($\mu\text{g/g}$)	Cadmium measured by DPASV ($\mu\text{g/g}$)
1.	Wheat Flour NBS-1567	0.032 \pm 0.007	0.028 \pm 0.004
2.	Spinach NBS-1570	1.5	1.31 \pm 0.11
3.	River sediment NBS-1645	10.2 \pm 1.5	10.18 \pm 1.8
4.	Mixed human diet IAEA,H-9	0.031 \pm 0.004	0.024 \pm 0.002

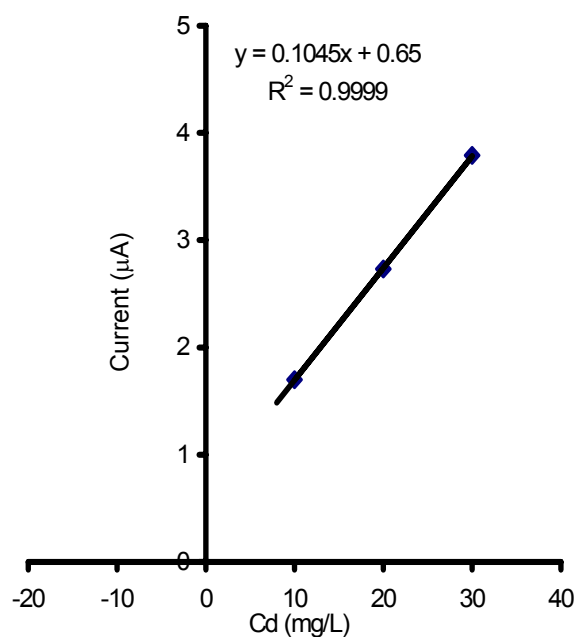


Figure 4. Calibration curve for standard addition method.

than thousand times compared to normal polarography and voltammetry. To check the accuracy of this method standard reference materials were analysed for cadmium. It can be seen from Table 1 that measured values are in very good agreement with the reference values which shows the accuracy and reliability of the method. Wheat flour and mixed human diet contain very low levels of cadmium whereas spinach contains relatively higher levels of cadmium. River sediment contains very high levels of cadmium. This voltammetric method was equally good for all levels of cadmium, which indicates its wide linearity range. After the calibration and optimization of the

method, the concentration of cadmium in various water samples was evaluated using standard addition method as shown in Fig. 4. In this procedure standards are added to the sample to remove any matrix effect. The results of cadmium are reported in Table 2 alongwith pH, conductance and total dissolved salt contents of these samples. Slightly basic pH of water is required for drinking purposes. In all the samples from various areas, the pH has been in an appropriate range, as shown in Table 2. pH of the drinking water significantly affects the levels of cadmium in water because acidic pH will increase the cadmium levels in water by leaching it from

Table 2. Levels of Cadmium, pH, conductance and TDS in different water samples.

Sample (S _{No.})	Original Source	Cd conc. (µg/L)	pH	Conductance (µ mhos)	TDS as KCl (µg/L)
QAU lab. (S ₁)	Simli Dam	0.5	8.1±0.09	334±0.98	176.0±0.25
NPD lab. (S ₂)	Simli Dam	6±0.25	8.2±0.08	345.5	182.0±0.7
Scheme 3. (S ₃)	Rawal Dam	0.5	8.0±0.005	375.7±2.9	198.0±1.56
NCD lab. (S ₄)	Simli Dam	1.5±0.5	8.1±0.001	336±1.5	178.0±0.8
I-8/2. (S ₅)	Tube Well	5.5±0.5	8.05±0.05	334±0.98	176.0±0.5
Qasimabad. (S ₆)	Tube Well	18.5±0.5	8.2±0.01	385±0.1	203.0±0.003
Holy Family. (S ₇)	Tube Well	40±1.58	8.06±0.05	335±0.35	177.0±0.18
Murree Road. (S ₈)	Home Well	59±1.0	8.09±0.01	381±0.97	203.0±0.4
Mughal Abad. (S ₉)	Home Well	20	8.2±0.04	375±0.02	198.0±0.001
Karachi Company (S ₁₀)	Simli Dam	53.5±2.5	8±0.009	396±2.0	209.0±1.1
Aabpara. (S ₁₁)	Simli Dam	5	8.2±0.04	392±0.5	207.0±0.3
G-6/4 (S ₁₂)	Simli Dam	16	7.4±0.05	337±0.8	179.0±0.45
Gulzar-e-Quaid (S ₁₃).	Tube Well	6.5±0.5	7.2±0.02	398±1.6	210.0±0.85
F-8/1 (S ₁₄)	Simli Dam	-	7.2±0.04	335±1.3	177.0±0.66
PAF, Base Chaklala. (S ₁₅)	Rawal Dam	44.5±1.5	7.3±0.02	382±0.2	202.0±0.14

sediments and other impurities into water. Environmental pollution and acid rain cause decrease in the pH levels which subsequently increase the levels of toxic metals. Therefore, in environmental pollution, acidity/ pH and toxic metals and their effects are inter-related. Conductance and TDS for all the samples were within the range of 330-400 µmhos, and 170-210 µg/ml. There is no apparent direct relation of cadmium levels with conductance or total dissolved salt content, however, these values do indicate the amount of salts present in a particular water sample. Higher TDS values would indicate higher ionic content of the ions of calcium, magnesium, carbonates and bicarbonates etc, which produce hardness in water. It has been reported [15] that cadmium toxicity may be lessened by the simultaneous ingestion of other metals. For example calcium, has an antagonistic effect to that

of cadmium. The infants who take milk regularly having high amount of calcium are less prone to get cadmium. In animals, cobalt, selenium and zinc chelates have this modifying effect. Itai-itai disease resulting from a combination of dietary calcium deficiency and tubular dysfunction is due to cadmium poisoning [5].

The analysis of cadmium in water samples has indicated somewhat random results. In some areas of Rawalpindi and Islamabad the levels of cadmium are high, while in some areas they are within the tolerance limits imposed by WHO, i.e., 3µg/L. In Rawalpindi Islamabad areas, drinking water sources are Rawal Dam, Simli Dam and tube wells. Samples were collected from all these sources at different distribution points. The levels of cadmium in surface water samples range from 0.5±0.06 µg/L to 53.5±2.5 µg/L and that of ground

water in the range of 5.5 ± 0.5 $\mu\text{g/L}$ to 59 ± 1.0 $\mu\text{g/L}$. Thus, levels of cadmium in ground water are relatively higher. The average levels of cadmium in ground water and surface water samples are 25 $\mu\text{g/L}$ and 14.2 $\mu\text{g/L}$ respectively. The daily intake of cadmium from these sources was calculated assuming that a person consumes about 3 liters of water daily and are 75 and 42.4 $\mu\text{g/day}$. It can be seen that due to high consumption of water, the daily intake values of cadmium increases significantly. Cadmium metal consumed is not excreted easily. It is stored in the human body particularly in liver and kidneys. Thus, our long-term cadmium consumption even at low levels leads to highly increased levels of cadmium in the body and toxicological effects may appear. It is, therefore, necessary that drinking water levels of cadmium must be analyzed regularly to avoid health hazards for human beings. In some areas water has high levels of cadmium while others have quite low levels. Starting from sample 1-5, the levels of cadmium are within the tolerance limit, or slightly higher, however as one moves towards more commercial areas, there are much more variations in the values. For example in S_6 sample cadmium is well above the tolerance limit. Similarly, S_7 , S_8 , S_{10} , S_{15} have values well above the tolerance levels. Water coming from tube wells also have higher levels of Cd^{2+} as shown by S_5 , S_6 , S_7 , S_8 , S_9 and S_{13} . There is no regularity as such in the levels of cadmium in different water samples, whether surface or ground, commercial or residential, but the highest levels of cadmium in surface water have been found in S_{15} . The source of this tap water is Rawal dam, but according to the residents of this area, the pipeline which directly supplies the water was broken twice, a few months prior to the collection of these samples. Contamination during the repair of pipeline could be one reason of these high levels. When the water tank, where the water is stored before running into the taps was checked, it was old and full of rust. This can be the other possible reason of such high levels because metals and rust (Fe_2O_3) etc. usually contain higher levels of toxic metals. Water from the Rawal dam does not have such high levels of cadmium, but the passage through which they pass, i.e., the pipelines, and domestic or commercial water tanks may be contaminated, therefore higher than usual levels of cadmium are observed.

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