

Analytical Advantages of Electrodeposition for Determination of Cadmium by Atomic Absorption Spectroscopy

H. SALAR AMOLI* and J. BARKER†

Department of Chemical Industry, Iranian Research Organization for Science and Technology (IROST), Tehran, I.R. Iran
E-mail: salar@irost.org

This work utilizes preconcentration of the cadmium in environmental samples by electrodeposition technique prior to its determination by flame and furnace atomic absorption spectroscopy. Using the method it is possible to reduce detection limits in the range of $\mu\text{g/mL}$ for flame AAS and ng/mL for graphite furnace (GF-AAS) and the sensitivity improvements ranging from 8-15 fold have been obtained. The effect of the deposition time and thickness was investigated and optical microscope studies show that a thickness of 25-40 micron gives the best results. By the method describe here, matrix interferences could be overcome and quantitative deposition of cadmium onto the electrode for 15-25 min at the 5-7 V is achieved.

Key Words: Cadmium, Electrodeposition, Atomic absorption spectroscopy.

INTRODUCTION

Although analysis of cadmium in the range of $\mu\text{g/mL}$ and ng/mL could be obtained easily by techniques such as ICP-OES and ICP-MS, but these are relatively high cost analytical methods. The most inexpensive methods of the preconcentration are solvent extraction^{1,2} coprecipitation³, solid phase extraction^{4,5} and recently electrodeposition^{6,7}. The main benefit of preconcentration by electrodeposition procedures is the possibility to measure lower analyte concentration and avoid matrix effects and to use inexpensive facilities.

The high salt content of samples presents a major difficulties for direct GF-AAS and AAS analyses, many articles^{8,9} recognized the potential of electrodeposition as a unique technique for separation and preconcentration of trace metals from complex matrices.

Using electrodeposition technique, there are several ways to achieve the atomization of the deposited metal. Whenever the electrode is graphite, it can be powdered and the powder sampled in the atomizer¹⁰. The electrode on which the metals are deposited can be used as a part of the atomizer or can be completely inserted into the graphite cup¹¹ and finally, the metallic deposit can be stripped off by acids and resulting solution analyzed¹².

†School of Pharmacy and Chemistry, University of Kingston, Surrey, KT1 2EE, UK.

In this analysis, the electrolyte should be carefully adjusted to pH 2. Since the pH of the solution may change during the electrodeposition process, it should be checked frequently. A solution of sodium bisulphate and sodium sulphate electrolyte is widely used and shows an excellent buffering effect to ensure the pH range of the solution remained constant during the deposition of metal on electrode.

The aim of this work is to find the ability of electrodeposition technique for determination of heavy metal in a sample with highly salted matrices. To achieve this goal, the details of a complete deposition and the effect of coating thickness on electrode was studied. It is hoped that the information obtained by this research work will help to determine regulatory methods in analyzing elements in environmental sample.

EXPERIMENTAL

The standard solutions of the metals were either prepared from high purity metals dissolved in nitric acid or from analytical grade nitrate salt. Solutions with a concentration below 1 ppm were prepared just before use. The water used was deionized with an ion-exchange resin and distilled.

A thermo elemental AAS, SOLAR M5 model was used. The spectrometer equipped with a graphite furnace heated by a high-frequency induction generator. For thickness measurement an Olympus BX60 optical microscope was used.

Soil digestion: The ash of the soil sample (2 g) obtained by heating upto 550 °C was weighed into a PTFE beaker, 20 mL of 16 M HNO₃ were added to it and the mixture allowed to reflux for 3 h on a hot plate. After cooling, the sample was filtered through a PTFE millipore syringe filter and spiked with a known amount of cadmium. The procedure was carried out as mentioned in previous work¹³.

Electrodeposition: The schematic electrodeposition device was introduced in previous publications^{14,15}. Two mL of 0.36 M NaHSO₄ were added to the known amount of cadmium(II) nitrate solution and heated. After fuming, the beaker was washed with 2 mL of distilled water. 6 mL of 0.75 H₂SO₄ and a few drops of thymol blue indicator was added to beaker. The solution was transferred to the electrodeposition cell and the pH adjusted to a salmon pink end point. The two electrodes inserted to a distance about 0.5 cm of each other. This was followed by turning on the main power in present current. At the final step, the cell was disassembled and the electrode rinsed with distilled water, washed with dilute nitric acid and prepared for atomic absorption measurement.

RESULTS AND DISCUSSION

The high salt content of environmental samples presents serious difficulties for cadmium analyses. In this regards, application of electrochemical techniques as a mean of separation and preconcentration of trace cadmium from complex matrices is a unique method to overcome these difficulties.

Since the electrode should meet certain requirement with regard to its mechanical and electrochemical properties, in this work, various kind of electrodes have been examined. Due to its more surface area the effectiveness of the disc electrodes was found to be more than the rod electrodes. So, the absorption signal increased significantly owing to the increased area of the electrode. Among various types of electrodes, stainless steel and graphite were found to give the best results. Some researcher used smaller electrode to increase their capabilities to electrodeposition from volumes of the order of milliliters^{8,16}. However, it is necessary to maximize the deposition rate in order to compensate for the small electrode area and thus maintain high sensitivity of determination of cadmium.

It is found that the pH of the solution play an important role in deposition procedure. It may increase markedly during the deposition step, owing to the cathodic evolution of hydrogen. A pH of 2-2.5 was found to give the best results.

The time required to carry out an exhaustive electrolysis depends on the mass transfer rate, which could be controlled by stirring and on the ratio of electrode area to solution volume. In previous studies^{14,15}, a satisfactory sensitivity was obtained by using a long deposition period, but in this work due to use of electrodes with a higher surface area, just a deposition time of 15 min was enough to obtain required sensitivity. In Fig. 1 the effect of electrolysis time on the amount of cadmium deposited on the graphite electrode is shown. The amount deposited was determined by the graphite furnace atomic absorption spectroscopy.

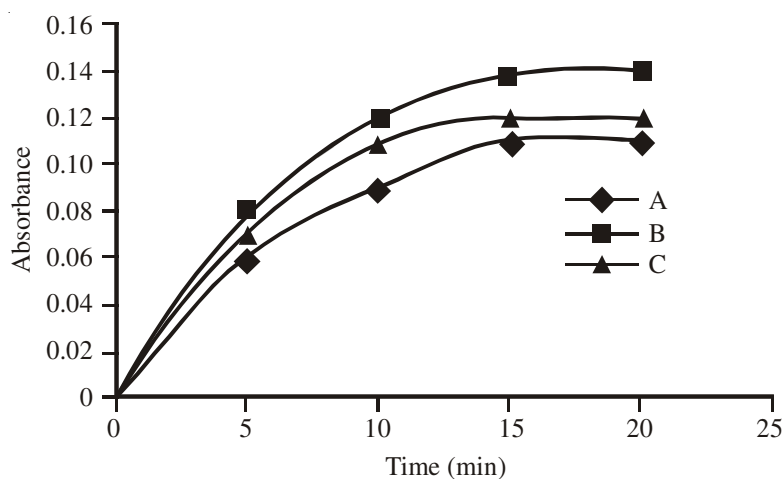


Fig. 1. Effect of electrolysis time on the amount of cadmium deposited on a graphite electrode (A = 600 ppb standard cadmium solution, B = soil sample No. 1, C = soil sample No. 2)

Thomassen *et al.*¹⁷ reported the choice of the deposition potential depends on the metals which are of interest. Table-1 shows the best voltage obtained at -7 V for stirred solutions for deposition of cadmium on graphite electrode.

TABLE-1
EFFECT OF APPLIED VOLTAGE DEPOSITION OF 1 PPM STANDARD
CADMIUM FROM STATIONARY OR STIRRED SOLUTIONS USING
GRAPHITE OR STAINLESS STILL ELECTRODES

Voltage (v)	Absorbance graphite electrode		Absorbance stainless steel electrode	
	Stirred	Stationary	Stirred	Stationary
2	0.00	0.000	0.00	0.000
3	0.04	0.030	0.25	0.020
4	0.07	0.050	0.05	0.035
5	0.09	0.075	0.08	0.065
6	0.12	0.105	0.09	0.080
7	0.16	0.145	0.13	0.115
8	0.14	0.130	0.12	0.090

In this research work the effect of film thickness on absorbance efficiency was investigated. Fig. 2 indicates the thickness was measured by an optical microscope. It was concluded that thickness of 25-40 μ which directly related to concentration of cadmium in solution, could produce accurate and repeatable absorbance.

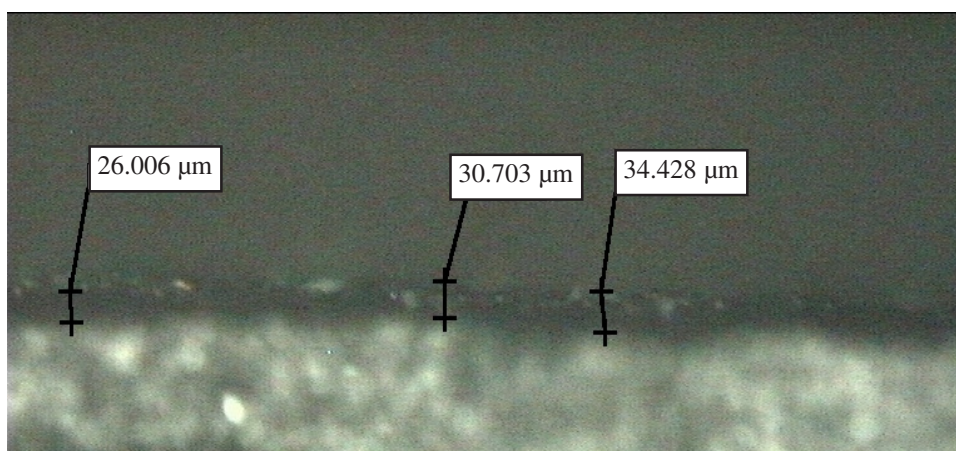


Fig. 2. Measurement of coating thickness on graphite electrode using optical microscope

Thickness less than 30 μ , has a very low absorbance which may be due to absorption of cadmium on the walls of the electrode or glass vessels for preparation for GF-AAS analysis.

The information obtained was applied for the determination of soil in environmental samples. Soil sample No. 1 was obtained from suburb of Tehran, zone 19 with a high rate of traffic. Soil sample No. 2, was also obtained from suburb of Tehran, zone 22, with a medium rate of traffic. Table-2 indicates that the method was successfully applied for determination of cadmium in these areas.

TABLE-2
AMOUNT OF CADMIUM IN SOIL SAMPLES 1 AND 2,
USING ELECTRO DEPOSITION/GFAAS

Soil sample	Cadmium found (ppm)	Average	RSD (%)
Soil sample (2)	1.40	1.67	9.6
	1.55		
	1.85		
	1.90		
Soil sample (2)	1.20	1.28	7.2
	1.35		
	1.20		
	1.40		

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