

Electrochemical Determination of Lead and Cadmium Traces in Zinc Oxide and Magnesium Stearate Used as Pharmaceutical Products

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Trace amounts of cadmium and lead were determined in zinc oxide and magnesium stearate by differential pulse anodic stripping voltammetry (DPASV) at hanging mercury drop electrode. Measurements were performed on zinc oxide samples without previous treatment whereas magnesium stearate samples were digested at 400°C for 12 h. The mean recoveries were more than 95 %. Detection limits for cadmium and lead were 0.1 and 0.2 ppb, respectively, for deposition time of 90 s. The precision (RSD %, n = 10) for 5 ppb of the metals were below 6 % with the correlation coefficient of 0.997.

Key Words: Lead, Cadmium, Differential pulse anodic stripping voltammetry, Traces analysis.

INTRODUCTION

The need for regular monitoring of toxic trace elements in pharmaceutical products and cosmetics, to minimize the exposure of consumers to these elements, has led to an increasing demand for suitably sensitive and selective analytical techniques with multi element capabilities. The regulatory agencies have lowered the acceptable exposure limits¹ to 0.5 µg/d. A prime concern is to minimize the exposure of consumers to these elements. Although these elements could be detected by various analytical techniques, their concentrations in many samples are so low that their determination is difficult². Neutron activation techniques have high sensitivity, but they are not frequently used because of the specialized techniques, skills, time and costs involved³.

Other accessible techniques capable of multi element determination, such as atomic emission spectroscopy with inductively coupled plasma excitation (AES-ICP), graphite furnace atomic absorption spectroscopy (GF-AAS), mass spectrometry with inductively coupled plasma (ICPMS),

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and X-ray fluorescence (XRF), are very expensive^{3,4}. Ultraviolet spectroscopy (UV), also does not offer sufficient sensitivity for accurate determination of most elements at the trace to ultra trace concentrations, usually, encountered in pharmaceutical and cosmetics products⁵.

Voltammetric techniques such as differential pulse polarography (DPP), anodic stripping voltammetry (ASV), or cathodic stripping voltammetry (CSV) and the more recent approach of adsorption voltammetry (AV) require relatively inexpensive instrumentation, are capable to determine accurately elements at trace to ultra trace levels and have demonstrated ability for multi element determination³⁻⁶.

Our results demonstrate a simple stripping voltammetric method for determination of cadmium and lead traces in magnesium stearate and zinc oxide. In this proposed method, there is no need for sophisticated instruments, tedious separation procedure and limitations.

EXPERIMENTAL

Differential pulse anodic stripping voltammetry (DPASV) was performed with a record 747 VA stand and 746 VA trace analyzer for a multi mode electrode used the hanging mercury drop electrode (HMDE) mode (Metrohm, Swiss). A platinum rod and an Ag/AgCl, KCl (3 M) electrodes were used as auxiliary and reference electrodes, respectively.

All chemicals were of analytical reagent grade (Merck) and doubly distilled water was used throughout for preparing of solutions. Acetate buffer (0.1 M, pH 4.6) was prepared by dissolving 8.203 g of sodium acetate monohydrate in water and glacial acetic acid was added until pH of solution was 4.6, then diluting to 500 mL with water. A 1000 ppm mixed stock solution was prepared by dissolving lead nitrate and cadmium acetate de hydrate in water. Oxygen free nitrogen gas (99.99 % N₂) was used for purging dissolved oxygen from solution.

Procedure: Zinc oxide samples were prepared by dissolving 0.5 g ZnO in acetic acid (1 %) and then the solution was buffered to pH 4.6 and diluted to 50 mL with doubly distilled water and 0.1 mL of the sample was added into 10 mL blank solution in the polarographic cell. Dissolved oxygen was removed by 5 min nitrogen purge, the electrode potential was held at -0.8 for 90 s and the solution was rotated at 200 rpm. After a 10 s quiescent period the stripping step was performed by applying an anodic differential potential sweep (scan rate = 60 mV/s; pulse height = 50 mV; deposition time = 90 s) from -0.8 to -0.2 V.

Magnesium stearate samples were digested by dry ashing at 400°C. 0.5 g of sample and 1 mL HNO₃ (1 %) was transferred into a crucible and then heated very gently on a hot plate. This mixture was heated until nitrogen oxides (brown fumes) were given off. This procedure was repeated for

three times and between each addition of acid the sample was cooled for about 2 min. After heating the sample to 400°C for 12 h, the digested sample was cooled to room temperature and dissolved in 10 mL nitric acid (1 %) and the solution pH was adjusted in 4.6 with acetate buffer. The solution was diluted to 50 mL with doubly distilled water and 1 mL of this solution was added into 9 mL blank solution in the polarographic cell and the voltammetric measurements were carried out by DPASV method as described for zinc oxide samples.

RESULTS AND DISCUSSION

In order to obtain the maximum sensitivity for determination of cadmium and lead, the influence of a number of analytical parameters (pH, deposition potential, deposition time) was examined as described below: A 10 μ L blank solution (0.1 M acetate buffer) was spiked with 50 μ g/L cadmium and 50 μ g/L lead. Pulse height and time, scan rate and stirrer speed were also optimized.

Effect of pH: The influence of pH on the peak currents of Pb^{2+} and Cd^{2+} was investigated. As the pH increased from pH 2 to 8, Cd^{2+} peak current increased and reached to a maximum value near pH 5. Whereas the peak current for lead decreased by increasing pH from 2 to 8. Continuous increasing of pH led to a decreasing of peak current which is due to the hydrolysis of Pb^{2+} and Cd^{2+} in basic solution⁷. As the result, pH of 4.6 was selected as the optimum pH for determination of Pb^{2+} and Cd^{2+} (Fig. 1).

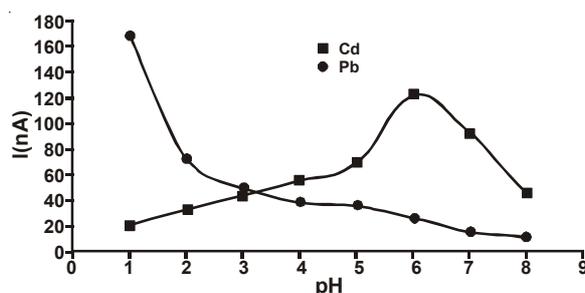


Fig. 1. Effect of pH on the peak current for 50 μ g/L cadmium and lead in 10 mL of 0.1 M acetate buffer

Effect of deposition potential and deposition time: Deposition potential is an important parameter for stripping techniques and has non-negligible influence on the sensitivity of measurement⁷. The effect of deposition potentials on the stripping peak current of Pb^{2+} and Cd^{2+} is shown in Fig. 2.

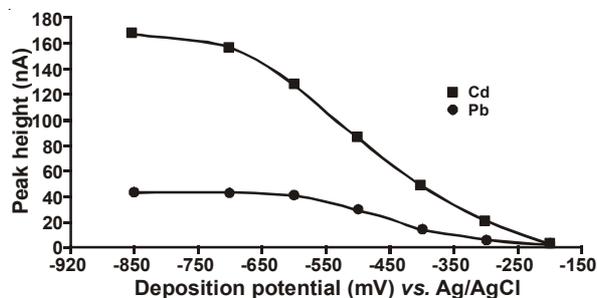


Fig. 2. Effect of deposition potential on the cadmium and lead peak current for 50 $\mu\text{g/L}$ cadmium and lead in 10 mL of 0.1 M acetate buffer

The negative shift of potential prove obviously more reduction of Pb^{2+} and Cd^{2+} on the surface of the electrode and increasing the peak currents. However, the peak current changes little when deposition potentials are more negative than -800 mV. For this reason a deposition potential of -800 mV was selected as the optimum condition for determination of Cd^{2+} and Pb^{2+} .

The effect of deposition time on the peak heights for Cd^{2+} and Pb^{2+} was examined in the range of 30-300 s, in the presence of 50 $\mu\text{g/L}$ Cd^{2+} and Pb^{2+} . As the results in Fig. 3, the peak currents increase with increasing of deposition time from 30 to 90 s. With further increase of deposition time, the peak currents were nearly constant. This observation at long deposition times is caused by the saturation of HMDE surface³. Consequently, we have chosen the deposition time 90 s in this work.

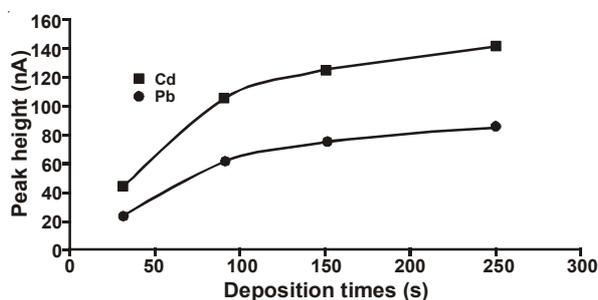


Fig. 3. Effect of deposition time on the cadmium and lead DPASV peak height for 50 $\mu\text{g/L}$ cadmium and lead in 10 mL of 0.1 M acetate buffer

The optimum conditions for anodic stripping voltammetry are summarized in Table-1.

TABLE-1
OPTIMUM CONDITIONS FOR ANODIC STRIPPING VOLTAMMETRY

Supporting electrolyte	0.1 M acetate buffer
pH	4.6
Deposition potential	-0.8 V vs. Ag/AgCl
Stripping potential	-0.8 to -0.2 V
Deposition time	90 s
Pulse height	50 mV
Purge time	5 min
Pulse time	40 ms
Scan rate	60 mV/s
Stirrer speed	200 rpm

Calibration graph and precision: Using the optimum conditions, a series of voltammograms of mixed standard solutions of cadmium and lead (1.25, 2.5, 5, 10, 15, 20, 25, 30, 50 and 100 µg/L) was investigated. The linear ranges, calibration equations, R^2 and detection limits are presented in Table-2. The theoretical detection limit of the instrument was also evaluated using the expression $3\sigma/S$, where σ is the base noise and S is the sensitivity obtained from the regression line of each analyte⁸.

TABLE-2
CALIBRATION DATA FOR MIXED SOLUTION OF CADMIUM

Element	Linear range	Equation	R^2	Detection limit (µg/L)
Cd	0.5-100	$y = 2.309x + 0.357$	0.9997	0.08
Pb	1.0-100	$y = 1.418x + 1.222$	0.9997	0.16

The recovery of the method was tested in the presence of 5, 10 and 15 µg/L of Cd^{2+} and Pb^{2+} (as a solution of cadmium acetate and lead nitrate) to the sample. The recoveries are presented in Table-3.

Precision of the methods was evaluated by 10 replicate determinations of 5 µg/L of each element in a mixed standard solution. The relative standard deviations of cadmium and lead were found to be 2.9 and 6, respectively.

Analysis of samples: Quantitative analysis were carried out by the method of standard addition. The zinc oxide and magnesium stearate voltammogramms are depicted in Figs. 4 and 5.

TABLE-3
RECOVERY ($\mu\text{g/L}$) OF CADMIUM AND LEAD ADDED TO A SAMPLE
OF MAGNESIUM STEARATE

Original	Added	Found	Recovery (%)
Cadmium			
2.8 ± 0.16	5	7.52 ± 0.4	94.34
2.8 ± 0.16	10	12.44 ± 0.5	96.45
2.8 ± 0.16	15	17.38 ± 0.7	97.21
Lead			
7.47 ± 0.4	5	12.24 ± 0.7	95.40
7.47 ± 0.4	10	17.15 ± 0.7	96.85
7.47 ± 0.4	15	22.30 ± 0.9	98.86

n = 5

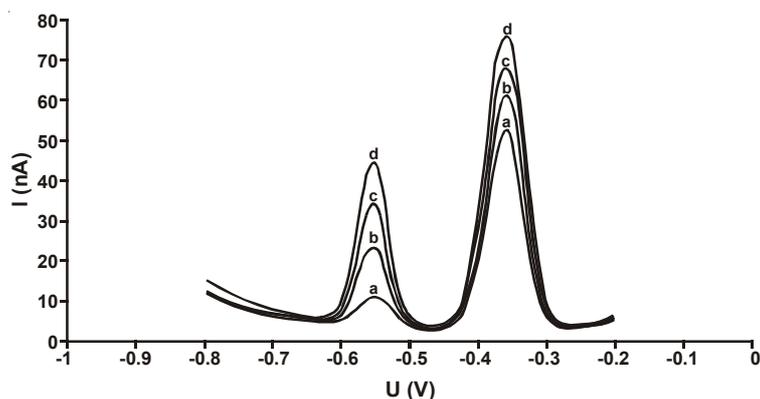


Fig. 4. Anodic stripping voltammograms for zinc oxide sample, using the optimum conditions. (a) sample, (b) after addition of 5 ppb of cadmium and lead, (c) after addition of 10 ppb of cadmium and lead, (d) after addition of 15 ppb of cadmium and lead

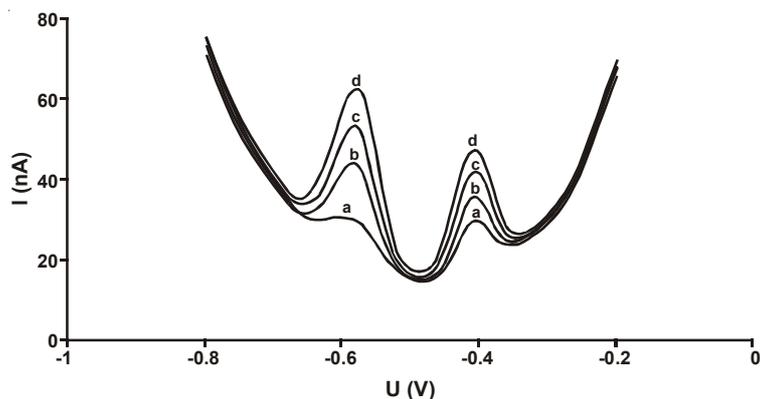


Fig. 5. Anodic stripping voltammograms for magnesium stearate sample, using the optimum conditions. (a) sample, (b) after addition of 5 ppb of cadmium and lead, (c) after addition of 10 ppb of cadmium and lead, (d) after addition of 15 ppb of cadmium and lead

The regression lines for analysis of magnesium stearate and zinc oxide are shown in Fig. 6. The determination coefficients and equation lines confirm good linearity in the range of concentrations examined.

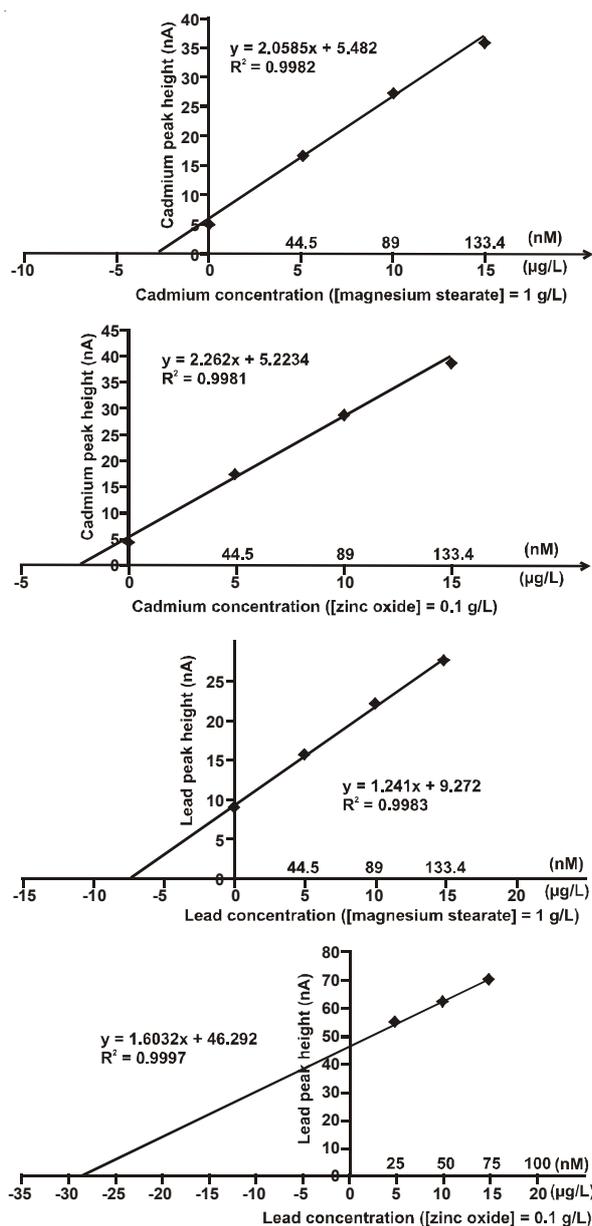


Fig. 6. Regression lines for analysis of magnesium stearate and zinc oxide samples. (a) Cadmium in magnesium stearate (b) Cadmium in zinc oxide (c) lead in magnesium stearate (d) lead in zinc oxide

Reproducibility of the method was elevated by analyzing each sample three times. The results obtained are shown in Table-4. The low standard deviations obtained indicate the good reproducibility of the method.

TABLE-4
CONCENTRATION OF CADMIUM AND LEAD IN MAGNESIUM
STEARATE AND ZINC OXIDE WITH DPASV (n = 3)

Sample	Cadmium		Lead	
	($\mu\text{g/L}$)	Standard deviation	($\mu\text{g/L}$)	Standard deviation
Magnesium stearate				
1	2.89	0.09	7.52	0.33
2	2.63	0.08	7.87	0.34
3	2.65	0.10	7.27	0.29
Zinc oxide				
1	28.94	0.89	2.23	0.07
2	28.00	1.07	2.31	0.08
3	29.38	1.19	2.19	0.08

Conclusions

In this study we determined the amount of lead and cadmium in zinc oxide and magnesium stearate by differential pulse anodic stripping voltammetry at hanging mercury drop electrode. Measurement was performed on zinc oxide without previous treatment whereas magnesium stearate was digested by dry ashing at 400°C and the recoveries of the method were tested. Lead and cadmium measurements were carried out from a solution made 0.1 M with respect to sodium acetate, buffered to pH 4.6.

We optimized the analytical parameters for the analysis. Scan rate = 60 mv/s; pulse height = 50 mv; deposition time = 90 s; accumulation potential = -800 mv and the voltammograms, recorded between -0.8 to -0.2 V.

The technique as described is applicable to determine the concentrations of lead and cadmium in magnesium stearate and zinc oxide samples as low as 0.2 and 0.1 $\mu\text{g/kg}$, respectively and the relative standard deviations (RSD %) are below 7 %.

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