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Development of a New Method for Determination of Lead in Urine by Anodic Stripping Pulse Voltammetry in Methanol

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A sensitive and selective anodic stripping pulse voltammetric method in methanol containing 0.1M HCl as supporting electrolyte at RDGCE was employed to determine traces of lead. The linear ranges were obtained at the concentration ranges of 6×10^{-8} to 2×10^{-6} M with 60 s deposition time and 50 mV amplitude pulse, 4×10^{-8} to 1×10^{-6} M with 60 s deposition time and 100 mV amplitude pulse and 4×10^{-9} to 9×10^{-8} M with 200 s deposition time and 100 mV amplitude pulse. The detection limit was 4×10^{-9} M with relative standard deviation equal to ±5.1%. Most of the metal ions do not interfere during the determination. The developed method was applied to lead determination in urine. The concentrations of lead in the urine samples ±SD, ranged from 248.40 ± 3.35 μg/L to 1045.33 ± 22.33 μg/L, while the urine lead materials show more troublesome particles at concentrations above 600 μg/L.

Key Words: **Lead, Anodic stripping pulse voltammetry, Urine.**

INTRODUCTION

Lead is a potentially toxic metal, in the form of inorganic and organic lead compounds. Provisional maximum tolerable limit for weekly intake of lead must not exceed 3 μg per kg body weight for adults and 25 μg per kg body weight for infants. The limit of lead in food is defined as a maximum of 1 mg/L[1]. Lead poisoning is currently considered a major environmental health hazard for children by the US Center for Disease Control. As the level of concern for lead in blood has dropped from 25 to 10 μg/dL (1.21–0.48 μM)[2], there is a need for improved methods for quantification of this metal. Among the various methods used for lead determination, graphite furnace atomic absorption spectrometry is perhaps the most accepted technique. On the other hand, electrochemical stripping techniques have continued to attract much attention because of their inherent sensitivity and especially because they are suitable for decentralized analysis due to the relatively compact and low-cost instrumentation needed and the possibility of employing inexpensive, disposable electrochemical cells such as screen-printed electrodes[3, 4].

Berzas *et al.*[5] and Sabry *et al.*[6] have examined the possibilities of applying differential pulse polarographic (DPP) signals to simultaneous determination of binary mixtures of inorganic ions cadmium(II)/indium(III), thallium(I)/lead(II) and tin(II)/lead(II).

Mercury-based electrodes, especially mercury-film electrodes, have been widely used in anodic stripping voltammetry[7, 8] for lead determination[9–11].

Stripping voltammetry was developed to increase the sensitivity of electroanalytical methods. Anodic stripping voltammetry (ASV) was developed to determine Pb(II) at a very low concentration by using many kinds of electrodes such as rotating Hg-coated glassy carbon split-disk electrode or rotating glassy carbon electrode with the absence of Hg^{2+}, where the limits of detection[12–17] were found to be 1.2×10^{-5} to 5×10^{-8} M.

However, on a carbon-glass-ceramic rotating disc electrode or on a glassy carbon electrode modified by using zeolite/poly(vinyl alcohol) or on a pyrolytic carbon film electrode or rotating Hg-amalgamated Cu-disk electrode. The limits of detection[18–22] were 3×10^{-7} to 2×10^{-9} M. In non-aqueous media such as acetonitrile, methanol, ethanol and ethyleneglycol were used to determine lead by anodic stripping voltammetry; the limit of detection was 2.5×10^{-7} M in ethanol[23].

In the present work, a new stripping voltammetry with superimposed constant amplitude pulses of negative polarity (SVPNP) of Pb(II) in non-aqueous solvents is developed and applied for determination of lead in urine.

EXPERIMENTAL

A pulse polarograph, model PRG-5 (Tacussel), with increasing amplitude pulses was used for differential detection of current and for superimposing constant amplitude pulses of negative or positive polarity and pulses of linearly increasing amplitude as the source of scanning voltage. A programmer model POLAROMAX-78, a recorder model ECOSRIPT (Tacussel) and an integrator model C-RBA (Shimadzu) were also used. RDGCE model ED165-14 and EM-EDI-CVJ was used as a working electrode. The reference electrode was calomel model BJC. The electrolysis vessel was provided with three electrodes (triple electrode). The solution was stirred with a rotating electrode and was kept in a thermostat at 45°C. The diluter/pipetter model DIP-1 (Shimadzu), having 100 μL sample syringe and five continuously adjustable pipettes covering a volume range from 2 to 5000 μL (model PIPTMANP, Gilson) was used for the preparation of experimental solutions.

The chemicals $Pb(NO_3)_2$, hydrochloric acid, methanol, ethanol, propanol, iso-propanol and butanol used in this work were all of analytical grade. Doubly distilled water was used also.

The standard solution of lead was prepared by dissolving 0.331 g of analytically pure $Pb(NO_3)_2$ (GR) in 100 mL distilled water which gives a concentration of 1×10^{-2} M. To prepare a solution, 1 mL of solution 1×10^{-2} M of Pb(II) and 0.84 mL of concentrated HCl was diluted to 100 mL with methanol.

Sample preparations

Urine samples were analyzed, without treatment: 1 mL of urine was prepared in 10 mL methanol containing 0.1 M of HCl.

Voltammetric measurements

A 10 mL aliquot of the standard solution of lead(II) (or sample) containing 0.1 M HCl was placed in the cell compartment. Nitrogen gas was bubbled for 15 min. The potential was increased from –1.0 V at a rate of 10 mV/sec until the anodic peaks were obtained. The time of deposition (τ) was 60 s for the concentration range 6×10^{-8} to 2×10^{-6} M and the pulse amplitude was 50 mV; for the pulse amplitude 100 mV the (τ) concentration range was 4×10^{-8} to 1×10^{-6} M and for the time deposition (τ) 200 s and pulse amplitude 100 mV, the concentration range was 4×10^{-9} to 9×10^{-8} M. The speed of rotating electrode was 375 r/min.

Quantitative results were obtained by the standard addition method. Appropriate aliquots of the standard solutions of lead were added to the urine sample and the concentration was evaluated.

RESULTS AND DISCUSSION

Stripping voltammetry with superimposed constant amplitude pulses of negative polarity (SVPNP) of Pb(II) in methanol, ethanol, propanol, iso-propanol and butanol in presence of 0.1 M HCl as supporting electrolyte using RDGCE were studied. Methanol was found to give the greatest sensitivity. Fig. 1 (a) shows the voltammograms obtained by SVPNP in the solvents used at the effective rate of 10 mV/s and deposition time of 60 s. The solution contains M of Pb(II). An anodic peak (E_p) was obtained at potentials –0.542, –0.562, –0.570, –0.596 and –0.636 V in methanol, ethanol, propanol, iso-propanol and butanol respectively. Fig. 1 (b) shows the effect of dialectical constant (ε) of alcohol on the peak potential of lead oxidation (E_p).

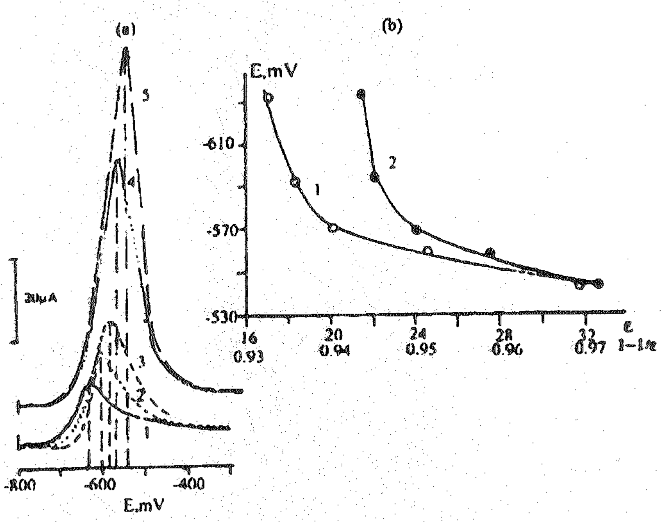

Fig. 1. (a) Anodic stripping voltammetry of lead using SVPNP method in the following alcohols: (1) butanol, (2) iso-propanol, (3) propanol, (4) ethanol, (5) methanol. (b) The effect of dielectrical constant (ε) of alcohol on peak potential of lead oxidation (E_p): (1) $E_p = f(\varepsilon)$, (2) $E_p = f(1 - 1/\varepsilon)$ ($C = 2 \times 10^{-6}$ M, $T = 60$ s, amplitude pulse = 100 mV, 45 ± 0.5°C and RDGCE)

The accuracy of SVPNP determinations, in general, depends on the potential applied during the preconcentration step. As seen in Fig. 2, the height of the reduction peak is strongly influenced by the accumulation potential. For signal –1.500 V in methanol and ethanol, –1.600 V in propanol and iso-propanol and –1.800 V in butanol represents the optimum potential for accumulation of lead in

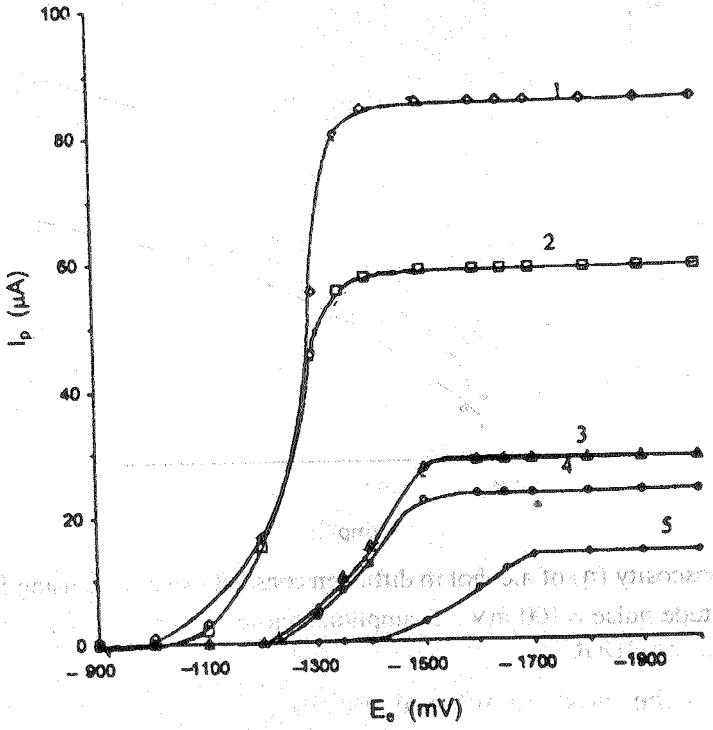

Fig. 2. The effect of deposition potential on peak current using SVPNP method: (1) methanol, (2) ethanol, (3) propanol, (4) propanol, (5) butanol ($C = 2 \times 10^{-6}$ M, $\tau = 60$ s, amplitude pulse = 100 mV, 45 ± 0.5°C and RDGCE)

RDGCE. Figs. 3 and 4 show the effect of dialectical constant (ε) and viscosity (η) of alcohols on the deposition potential and peak current (I_p) or diffusion current (K).

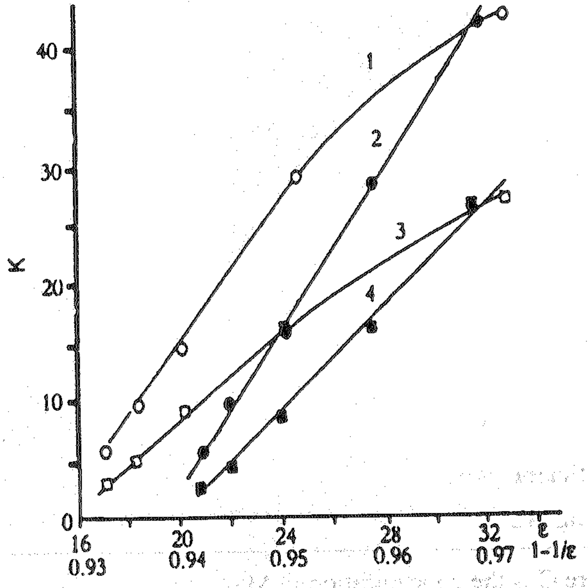

Fig. 3. The effect of dielectrical constant (ε) of alcohol in diffusion constant (K) of lead using SVPNP: (1 and 2) amplitude pulse = 100 mV, (3 and 4) amplitude pulse = 50 mV ($C = 2 \times 10^{-6}$ M, $\tau = 60$ s, 45 ± 0.5°C and RDGCE)

The effects of solvents, electrolyte concentration (HCl), speed changes of potential, amplitude pulses and temperature of the solution on the form and the current of anodic peak were studied and found that the most suitable conditions are:

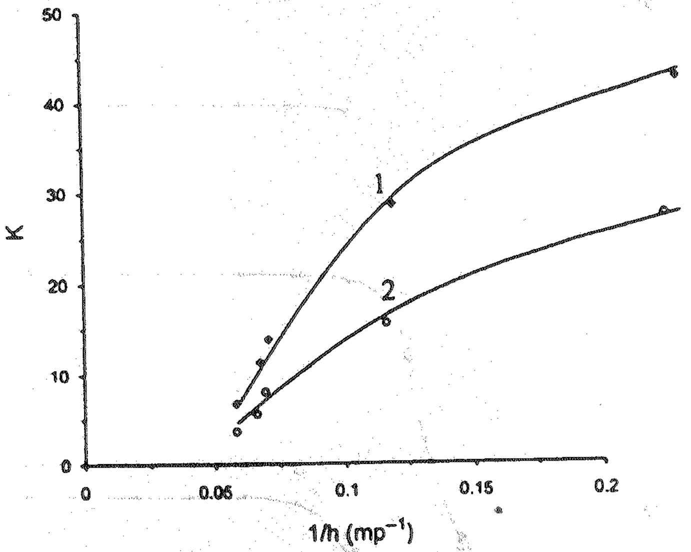

Fig. 4. Effect of viscosity (η) of alcohol in diffusion constant (K) of lead using SVPNP: (1) amplitude pulse = 100 mV, (2) amplitude pulse = 50 mV (C = 2 × 10^{6} M, τ = 60 s, 45 ± 0.5°C and RDGCE).

(i) Methanol is the most suitable solvent, (ii) 0.1 M HCl for the concentration of the electrolyte, (iii) 10 mV/s speed changes of potential, (iv) 100 mV amplitude pulses and 45 ± 0.5°C the temperature of analyzed solution.

Quantification: A linear relationship was found between peak current (I_p) and concentration of lead in the ranges given in Table-1. The correlation coefficients, intercepts and slopes for the calibration data for lead in methanol were calculated using the least-squares method.

TABLE-1
QUANTITATIVE PARAMETERS FOR DETERMINATION OF LEAD BY SVPNP

Parameters	MeOH
E_e (V)	−1.500
E_p (V)	−0.542
τ (s)	200
Optimum concentration range (M)	4 × 10^9 to 9 × 10^8
Regression equation*	
Slope (m)	0.5007
Intercept (b)	−0.0021
Correlation coefficient (r)	1
Detection limit (ng mL^{-1})	0.828

*A = mC + b, where C is the concentration in M.

Accuracy and precision: The precision and accuracy of the proposed method were tested by estimating five replicates of the eight standards. The standard deviation, relative standard deviation, standard analytical errors, recovery and 95% confidence limits determined from the calibration curve are given in Table-2.

TABLE-2
PRECISION AND ACCURACY OF THE PROPOSED METHOD

Taken, $C_{Pb} \cdot 10^8$ M	Found* $C_{Pb} \cdot 10^8$ M	SD (M)	RSD (%)	Standard error	Recovery (%)	Confidence limits
0.40	0.39	0.020	5.1	0.009	97.5	0.39 ± 0.025
0.50	0.51	0.023	4.6	0.010	102.0	0.51 ± 0.029
0.60	0.60	0.024	4.0	0.011	100.0	0.60 ± 0.030
1.00	1.00	0.036	3.6	0.016	100.0	1.00 ± 0.045
2.00	2.03	0.059	2.9	0.026	101.5	2.03 ± 0.073
4.00	4.00	0.100	2.5	0.045	100.0	4.00 ± 0.124
6.00	6.04	0.132	2.2	0.059	100.7	6.04 ± 0.164
10.0	9.98	0.320	3.2	0.143	99.8	10.0 ± 0.397

*Average of five determinations.

Analytical applications

The analytical procedure described above was used for the determination of lead in urine. The urine sample showed a distinct peak of lead(II). The concentration of lead in the urine was determined by the standard addition method. Solutions of known concentrations (2×10^{-8}, 5×10^{-8}, 10×10^{-8}, 20×10^{-8}, 50×10^{-8}, 70×10^{-8} M) of Pb(II) were added to the urine samples. Three determinations were made on each addition. The plot of peak current against lead concentration was linear ($r = 0.9998$) and the regression equation is $A = 0.5257C + 4.2634$.

The concentrations of lead in the urine samples, ±SD, ranged from 248.40 ± 3.35 μg/L to 1045.33 ± 22.33 μg/L, as seen from Table-3. Reaching the maximum value in sample VI, while the urine lead materials proved more troublesome, particle at concentrations above 600 μg/L.

TABLE-3
RESULTS FOR DETERMINATION OF LEAD IN THE SAMPLES OF URINE IN PRESENCE OF HYDROCHLORIC ACID IN METHANOL

Sample	Lead content ± SD (μg/L)	Recovery (%)
I	445.05 ± 5.56	99.96 ± 1.23
II	269.10 ± 2.70	99.40 ± 0.88
III	621.00 ± 6.58	100.20 ± 0.63
IV	600.30 ± 6.22	98.80 ± 0.92
V	341.55 ± 4.32	101.20 ± 1.10
VI	1045.33 ± 22.33	98.80 ± 0.93
VII	434.70 ± 6.85	99.50 ± 1.10
VIII	393.30 ± 5.32	100.50 ± 0.93
IX	248.40 ± 3.35	99.00 ± 0.68

Conclusion

A new chemically modified method has been developed by using 0.1 M HCl in methanol for the determination of lead(II) at trace levels by anodic stripping pulse voltammetry. Compared with other adsorptive stripping voltametric determination of lead(II)$^{7-23}$, the method presented here has a lower detection limit and is not interfered strongly by other metals, such as Mn, Zn, Cd, Mg, Co and Ni, which are normally associated with lead in urine.

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