

Determination of Pb(II) by Anodic Stripping Pulse Voltammetry (ASPV) Using Platinum and Glassy Carbon Electrodes

A.A. RAMADAN,* H. MANDIL and A.A. KAMEL

*Department of Chemistry, Faculty of Science
University of Aleppo, Syria*

Determination of Pb(II) by Anodic Stripping Pulse Voltammetry (ASPV) in aqueous solutions of 0.01 M CH₃COOH and 0.1 M NaCl using Rotating Disk platinum Electrode (RDPE) and Rotating Disk Glassy Carbon Electrode (RDGCE) has been studied. A number of supporting types of pulses have been examined and stripping voltammetry with superimposed constant amplitude pulses of negative polarity (SVPNP) found to give the greatest sensitivity. The relative standard deviation is 5.0% at very low concentration of 4×10^{-6} M on RDPE. The simultaneous discharge-ionization of lead with or without 5×10^{-5} M Hg²⁺ has also been studied by SVPNP on RDGCE. It is shown that the sensitivity increased from 4×10^{-8} M without Hg²⁺ to 1×10^{-10} M with 5×10^{-5} M Hg²⁺. The relative standard deviations are 4.4% and 5.9% respectively. This developed method gives the possibility of determination of Pb(II) on bare RDPE. Up to 4×10^{-6} M, the sensitivity increased from 5×10^{-8} M in previous works to 1×10^{-10} M on RDGCE in presence of 5×10^{-5} M Hg²⁺

INTRODUCTION

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 a rotating Hg-coated glassy carbon split-disk electrode or rotating glassy carbon electrode with the absence of Hg²⁺, where the limits of detection were 1×10^{-5} M– 5×10^{-8} M.^{1–6}

However, on 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 were 3×10^{-7} M– 2×10^{-9} M.^{7–10}

Inverse-voltammetric and ASV were developed to determine Pb(II) using glassy carbon electrode where the conditions of the deposition of metals and their anodic oxidation on the surface of the solid electrode without Hg film were studied^{11, 12}.

One problem was associated with using bare solid metal electrodes, such as Au and Pt in stripping analysis for the determination of heavy metal ions like Pb

and Cu ions in diluted solutions. The problem was that underpotential deposition (UPD) gave multiple stripping peaks in the analysis. These peaks were often overlapped and cannot be conveniently used for analysis. Thus, a rotating Pt electrode modified by deposition of PbO_2 on its surface or a Pt sphere electrode with Hg coated film was used. The range of concentrations was $2 \times 10^{-4} \text{ M} - 1.5 \times 10^{-8} \text{ M}$.¹³⁻¹⁷

In the present paper we report a method for the determination of Pb(II) in aqueous solutions in the presence of 0.01 M CH_3COOH and 0.1 M NaCl by anodic stripping pulse voltammetry (ASPV) on RDpTE and RDGCE.

We have also studied the effect of Hg(II) on the determination of Pb by ASPV in aqueous solutions in the presence of 0.01 M CH_3COOH and 0.1 M NaCl on RDGCE.

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. RDpTE model ED165-14 or RDGCE model ED165-14 and EM-EDI-CVJ was used as a working electrode. The reference electrode was Argenthal 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 50°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 the preparing experimental solutions.

A standard solution of lead was prepared by dissolving 0.331 g of analytically pure (GR) $\text{Pb}(\text{NO}_3)_2$ in 100 mL distilled water which gives a concentration $1 \times 10^{-2} \text{ M}$.

The standard solution of mercury was prepared by dissolving 0.3426 g of analytically pure (GR) $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 100 mL of 1M CH_3COOH which gives a concentration $1 \times 10^{-2} \text{ M}$.

The standard solution of 0.1 M NaCl.

The standard solution of 1 M CH_3COOH .

All the other reagents and solvents were of GR grade.

Procedure: A 10 mL aliquot of the standard solution of lead(II) or its mixture with Hg(II) in aqueous solution containing 0.01 M CH_3COOH and 0.1 M NaCl was placed in the cell compartment. Nitrogen gas was bubbled for 15 min. The potential was increased from 0.7 V at a rate of 10 mV/sec until the anodic peaks were obtained. The pulse amplitude was 50 mV and the time of deposition (τ) was 200 sec using RDpTE and 150 sec using RDGCE. The speed of rotating electrode was constant (1375 r/min).

RESULTS AND DISCUSSION

Stripping Voltammetry with Superimposed constant amplitude Pulses of Negative Polarity (SVPNP), Stripping Voltammetry with Pulses of Linearly Increasing Amplitude (SVPLIA) and Stripping Differential Pulses Voltammetry (SDPV) of Pb(II) in presence of 0.01 M CH₃COOH and 0.1 M NaCl as electrolyte by using RDPtE, RDGCE and RDGCE with 5×10^{-5} M Hg²⁺ were studied. Stripping voltammetry with superimposed constant amplitude pulses of negative polarity were found to give the greatest sensitivity. An anodic peak was obtained at potential varying between -0.430 V to -0.460 V on RDPtE, -0.480 V to -0.500 V on RDGCE, and -0.450 V to -0.460 V on RDGCE in presence of 5×10^{-5} M Hg²⁺ due to the oxidation of lead(I) to lead(II) (Fig. 1).

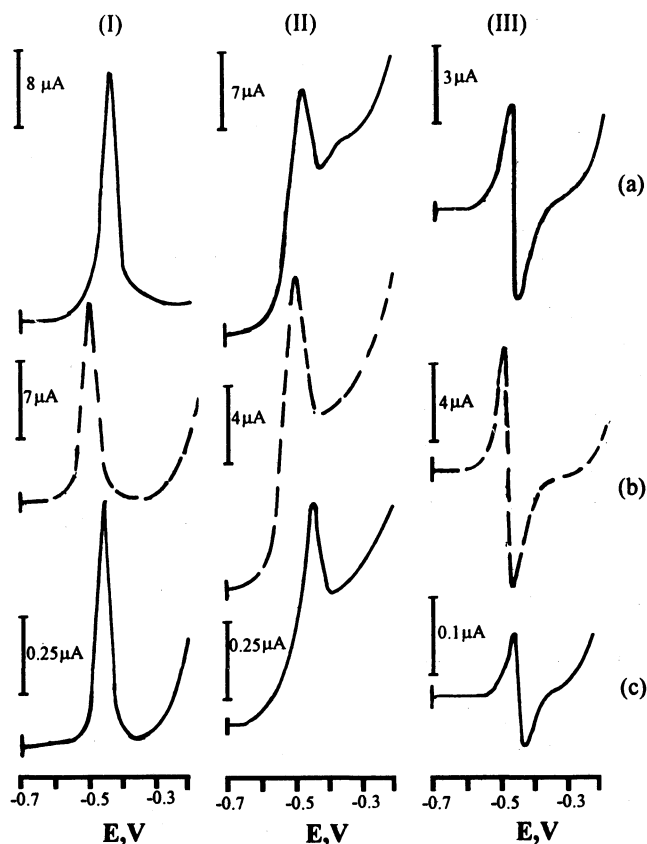


Fig. 1. Anodic stripping voltammetry of lead by SVPNP (I), SVPLIA (II) and SDVP (III) methods at various concentrations of Pb(II): (a) 1×10^{-5} M on RDPtE, (b) 4×10^{-7} M on RDGCE, (c) 1×10^{-8} M on RDGCE with the presence of 5×10^{-5} M Hg²⁺.

The variation of peak current (I_p) with deposition potential (E_d) was studied. It was found that the optimum deposition potential -0.55 V, -1.40 V and

-1.20 V on RDPtE, RDGCE and RDGCE in presence of 5×10^{-5} M Hg^{2+} respectively (Fig. 2).

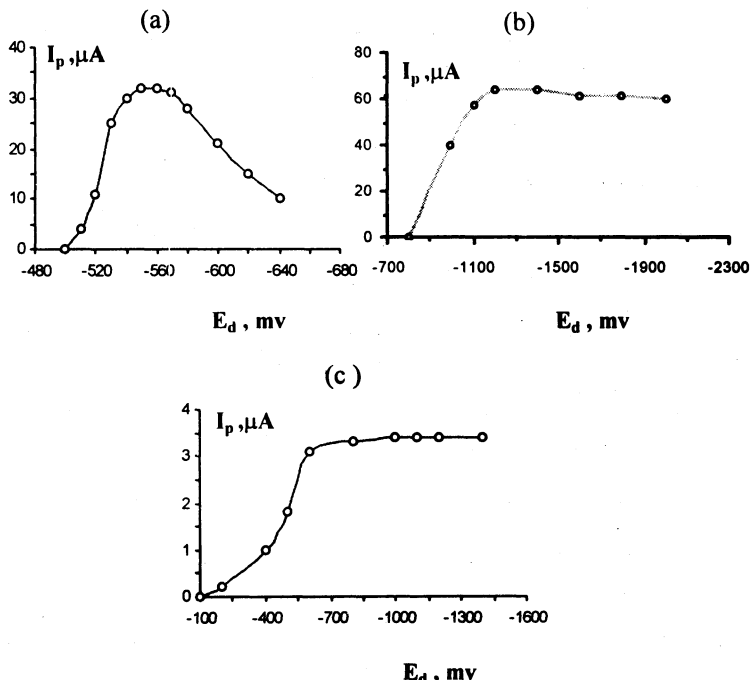


Fig. 2. Effect of deposition potential in the peak currents using SVPNP method:

- (a) On RDPtE ($C_{\text{Pb}}^{2+} = 2 \times 10^{-5}$ M, $\tau = 100$ sec), (b) On RDGCE ($C_{\text{Pb}}^{2+} = 2 \times 10^{-6}$ M, $\tau = 60$ sec), (c) On RDGCE in presence of 5×10^{-5} M Hg^{2+} ($C_{\text{Pb}}^{2+} = 8 \times 10^{-8}$ M, $\tau = 90$ sec).

We have studied the effect of electrolyte concentration (CH_3COOH , NaCl), speed changes of potential, temperature of the solution and amplitude pulses on the form and the current of anodic peak. We found that the most suitable conditions on the different electrodes are:

- 0.01 M CH_3COOH and 0.1 M NaCl for the concentration of the electrolyte.
- 10 M v/s speed changes of potential.
- 50°C the temperature of the analyzed solution.
- 50 mV amplitude pulses.

The variation of the peak current (I_p) against deposition time (τ) was studied. The relationship between I_p and τ showed linear proportionality in different anodic stripping voltammetry methods. The deposition time range was 40 to 200 sec for the concentration range of 4×10^{-6} to 2×10^{-5} M on the RDPtE, 60 to 150 sec for the concentrations range of 4×10^{-8} to 6×10^{-7} M on RDGCE and 50 to 300 sec for the concentrations range of 8×10^{-8} to 1×10^{-10} M on RDGCE in the presence of 5×10^{-5} M Hg^{2+} .

RESULTS AND DISCUSSION

The present work involved the use of SVPNP on RDPtE, RDGCE and RDGCE with 5×10^{-5} M Hg^{2+} to study the relation between I_p and lead concentration [$I_p = f(C_{\text{Pb}}^{2+})$]. This relationship was found to be linear over the concentration range 4×10^{-6} M to 2×10^{-5} M on RDPtE, 4×10^{-8} M to 6×10^{-7} M on RDGCE and 1×10^{-10} M to 1×10^{-9} M on RDGCE in presence of 5×10^{-5} M Hg^{2+} , (Fig. 3).

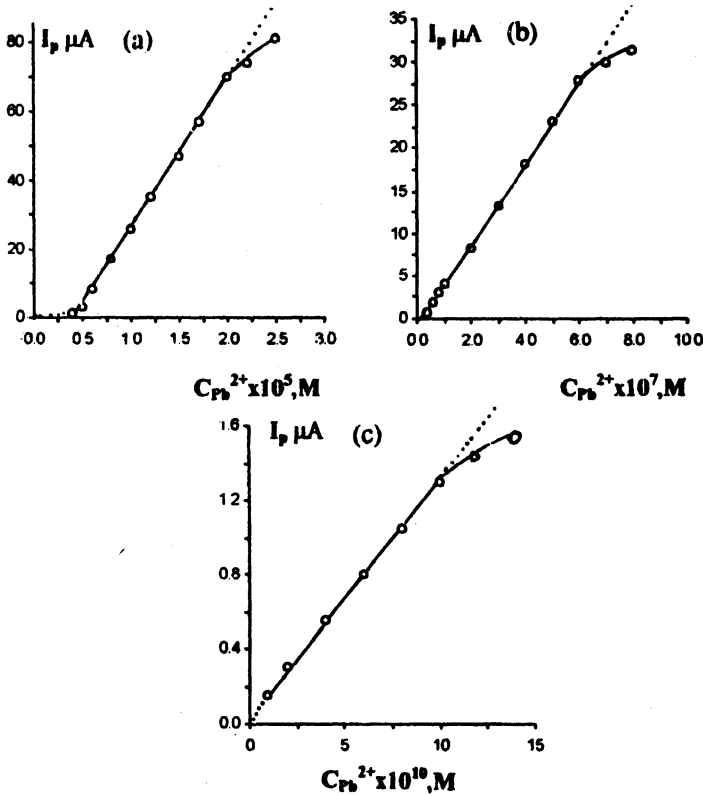


Fig. 3. Correlation of I_p and lead(II) concentrations by SVPNP method:
 (a) On RDPtE ($\tau = 200$ sec), (b) On RDGCE ($\tau = 150$ sec),
 (c) On RDGCE in presence of 5×10^{-5} M Hg^{2+} ($t = 300$ sec).

The relative standard deviation (RSD) for the determination of Pb(II) by the analytical curves at very low concentration 4×10^{-6} M on RDPtE, 4×10^{-8} M on RDGCE (Table-1) and 1×10^{-10} M on RDGCE in presence of 5×10^{-5} M Hg^{2+} did not exceed 5.0%, 4.4% and 5.9% respectively (Table-2).

This developed method gives the possibility determination of Pb(II) up to 4×10^{-6} M on bare RDPtE where it was impossible to be determined by the references.¹³⁻¹⁷

The sensitivity for determination of Pb(II) increased from 5×10^{-8} M in previous works^{6,10} to 1×10^{-10} M of Pb(II) on RDGCE in presence of 5×10^{-5} M Hg^{2+} . The relative standard deviation did not exceed 5.9%.

TABLE-1
DETERMINATION OF Pb(II) BY SVPNP ON RDPtE (a) AND RDGCE (b)

(τ DEPOSITION TIME)

$C_{\text{Pb(II)}} \times 10^6 \text{ M, taken}$	(a) $\tau = 200 \text{ sec}$		(b) $\tau = 150 \text{ sec}$		
	$C_{\text{Pb(II)}} \times 10^6 \text{ M, found}$		$C_{\text{Pb(II)}} \times 10^8 \text{ M, taken}$	$C_{\text{Pb(II)}} \times 10^8 \text{ M, found}$	
	\bar{C}	RSD%		\bar{C}	RSD%
4.00	4.10	5.0	4.00	4.00	4.4
5.00	5.00	3.3	6.00	6.10	4.0
6.00	6.00	2.5	8.00	8.00	3.3
8.00	8.00	1.7	10.0	10.1	2.5
10.0	10.0	1.2	15.0	15.0	2.5
12.0	12.0	1.0	20.0	20.0	2.4
15.0	15.0	0.70	30.0	30.0	2.3
20.0	20.0	0.60	40.0	40.0	1.6
—	—	—	50.0	50.0	1.3
—	—	—	60.0	60.0	1.1

TABLE-2
DETERMINATION OF Pb(II) BY SVPNP ON RDGCE WITH THE PRESENCE OF
 $5 \times 10^{-5} \text{ M Hg}^{2+}$, (τ deposition time)

$C_{\text{Pb(II)}} \times 10^9 \text{ M, taken}$	$C_{\text{Pb(II)}} \times 10^9 \text{ M, found}$			
	$\tau = 150 \text{ sec}$		$\tau = 300 \text{ sec}$	
	\bar{C}	RSD%	\bar{C}	RSD%
0.10	—	—	0.10	5.9
0.20	—	—	0.21	5.0
0.40	—	—	0.40	4.0
0.60	—	—	0.60	3.3
0.80	—	—	0.80	2.8
1.00	1.00	5.0	1.00	2.5
4.00	4.00	4.0	—	—
8.00	8.00	3.0	—	—
10.0	10.0	2.6	—	—
20.0	20.0	2.0	—	—
40.0	40.0	2.0	—	—
60.0	60.0	2.0	—	—
80.0	80.0	1.5	—	—

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