

Use of programmed time-potential inputs in anodic stripping voltammetry with *in situ* sodium amalgamation[§]

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Abstract. Enhanced sensitivity for the determination of amalgamable metals by anodic stripping voltammetry with *in situ* sodium deposition is obtained by making use of programmed time-potential inputs. The usefulness of this simple approach in lowering the limits of determination is illustrated by using zinc and cadmium samples for stripping analysis.

Keywords. Amalgamable metals; anodic stripping voltammetry; *in situ*; programmed *E-t* inputs; zinc and cadmium sulphate.

1. Introduction

An improved anodic stripping voltammetric technique in which the potentialities of *in situ* sodium deposition (using a cyclic potential-time, CV, input profiles) on a hanging mercury drop electrode (HMDE) as a means of enhancing the sensitivity of stripping analysis for different metal ions, viz. Ga^{3+} , Cu^{2+} and Cd^{2+} ions, has been examined using a cyclic potential-time input profile (Prabhakara Rao and Varadharaj 1983). The simplicity of the experimentation, the advantage in dispensing with the pre-electrolysis step (lasting several minutes under reproducible experimental conditions) for effecting the accumulation of the metal in HMDE—an important pre-requisite of the conventional ASV procedures—and the resulting time saving in the analysis, make it an attractive alternative in trace analysis. In this communication, we report briefly the usefulness of the programmed time-potential inputs in the estimation of individual metal ions of Zn^{2+} and Cd^{2+} which further lowers the limit of their determination.

2. Experimental

A conventional glass electrolysis cell with provision for inlet and outlet for deaerating the solution with N_2 gas is used. A three-electrode system consisting of a saturated calomel electrode (SCE), a hanging mercury drop electrode (HMDE) supplied by Metrohm of Switzerland and a pool of mercury counter electrode is employed. All the solutions are prepared from analar grade reagents and double distilled water. A solution of 0.5 M sodium carbonate, the pH of which is kept at 8 by adjustment with H_2SO_4 , has been chosen as the supporting electrolyte for all the experiments (Kemula *et al* 1959).

[§] Dedicated to Prof. K S G Doss on his eightieth birthday.

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A Wenking potentiostat (Model LB75M) coupled with a Wenking Scan Generator (Model VSG 72) is used for controlling the potential. The range of potentials covered in the CV experiments corresponds to 0 to -2.2 V vs SCE. An X-Y recorder (Digitronic Model 2000 series) is used to record the i - E curves. All the potentials are expressed vs SCE and the measurements are made at $32 \pm 1^\circ\text{C}$. Potential sweeps are effected with (i) equal slopes for forward and backward scans and (ii) unequal slopes for forward and backward scans.

3. Results and discussion

Figure 1A shows the ASV curves of 10^{-5} M ZnSO_4 solutions in which the forward cathodic sweep of the CF was extended to -2.2 V and they demonstrate the beneficial influence of *in situ* deposited sodium on the anodic peak current obtained in the reverse scan. The potential sweep rate has been kept constant in both

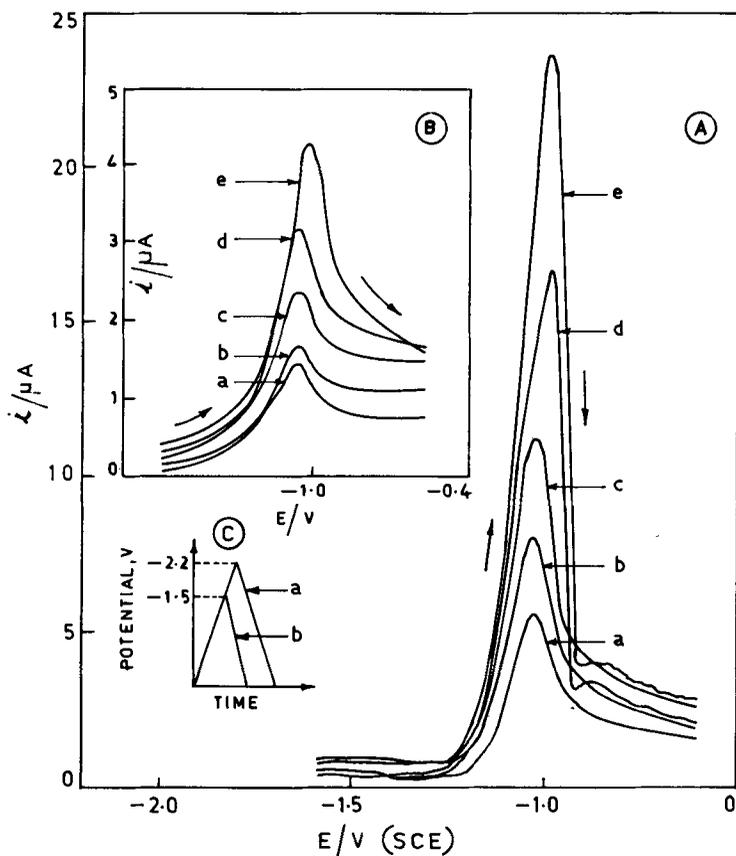


Figure 1. (A) Anodic stripping curves obtained for a solution containing (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10×10^{-5} M ZnSO_4 . Voltage scan rate is 100 mV Sec^{-1} in both forward and backward directions. Lower limit of the potential sweep is -2.2 V. (B) As (A) but lower limit of the potential sweep is -1.5 V. (C) Symmetrical cyclic potential-time profiles used as inputs in recording the curves in (A) and (B).

forward and backward directions of CV (See inset of figure 1c for the input time profile). For comparison, the ASV curves of the same solution in which the forward cathodic potential sweep was limited to -1.5 V only (thus ensuring the absence of sodium deposition) and the resulting anodic sweep voltammograms are shown in figure 1B (inset). The observed anodic peak currents were also linear and thus directly proportional to the concentration of the metal ion in solution. A comparison of such calibration plots, obtained in the presence and in the absence of sodium amalgamation, have been given in figure 2, and it clearly reveals the anodic signal enhancement in the case of forward scan extended to sodium deposition potential.

Confirmation for the involvement of *in situ* sodium deposition and its role in the enhancement of the anodic peak currents has been verified by running CVs using a supporting electrolyte which is completely devoid of sodium ions, viz., tetramethyl ammonium chloride again taking the case of cadmium as an example (Prabhakara Rao and Varadharaj 1983). The proportionality in the increase of the anodic peak height obtained to the concentration of the sodium ion in solution in the case of mixed supporting electrolyte of tetraalkyl chloride and sodium carbonate and inclusion of sodium deposition potential has also been verified (Varadharaj 1984).

These anodic peak currents are expected to respond to the scan rate of the potential, their magnitudes increasing with the increase in sweep rate for a given concentration. However, it may be realised that such peak heights will not bear a square root dependence on the scan rate expectations based on Randles-Sevcik equation (Randles 1948; Sevcik 1948), because the concentration of the metal in the amalgam available for stripping differs in each case from one sweep rate to the other arising out of different amounts of metal being deposited and exchanged

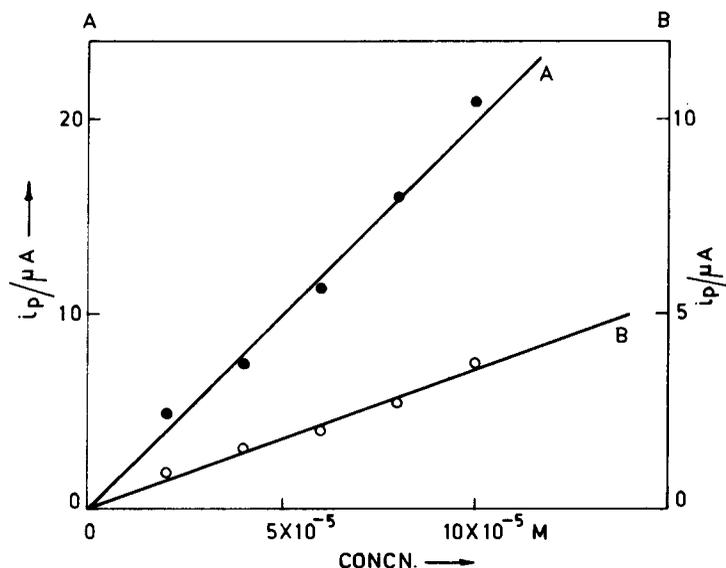


Figure 2. (A) Calibration plot of Zn^{2+} obtained by plotting i_p vs concentration. Lower limit of potential sweep is -2.2 V. (B) As (A) but lower limit of the potential sweep is -1.5 V.

through the sodium displacement in proportion to the time of scan rate, i.e., the time of contact of the amalgam with the metal ion in solution (Kozun *et al* 1981). Programmed time-potential inputs using a common forward sweep rate followed by reverse scans having different sweep rates have been employed with a view to see whether the expected linearity of i_p with potential scan rate could be achieved. This is done by keeping the forward scan rate identical in a series of experiments and varying only the reverse scan rate (conditions favourable for Randles-Sevcik equation to hold good for the anodic stripping peak). Experimental results obtained on cadmium have conformed to these expectations. In figure 3 typical anodic stripping curves for Cd^{2+} obtained using programmed time-potential inputs are shown. A plot of i_p vs $\nu^{1/2}$ constructed from the data in figure 3 is found to be linear.

Further, in order to demonstrate the utility of this programmed i - E inputs for effecting enhanced sensitivity for analysis, the stripping curves of Cd^{2+} and Zn^{2+} ions are recorded using the programmed inputs and compared with the normal linear cyclic potential inputs (identical sweep in forward and backward directions) and are given in figures 4 and 5 respectively. It is seen clearly that the enhancement of the anodic signal is substantial and significant when programmed inputs are used. The corresponding plots of anodic peak current vs concentration in figures 6 and 7 for Cd^{2+} and Zn^{2+} ions are linear.

Using the programmed time-potential inputs in the system the limits of determination in the case of Cd^{2+} ions is found to be 10^{-8} M CdSO_4 solution and in the case of Zn^{2+} ion it is found to be 10^{-7} M ZnSO_4 solution under the experimental conditions described. The calibration plots of the anodic peak current vs concentration of the respective metal ion in solution have been found to be linear

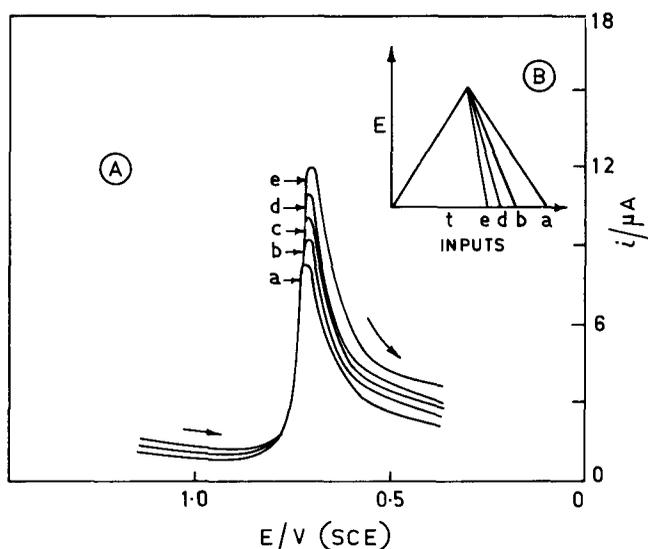


Figure 3. (A) Stripping curves recorded for 10^{-4} M Cd^{2+} ion in solution using programmed time-potential inputs. Scan rate for the forward scan is 100 mV Sec^{-1} whereas the reverse scan is varied as (a) 100, (b) 140, (c) 200, (d) 250 and (e) 300 mV Sec^{-1} . (B) Typical potential input profiles for recordings the curves in (A).

over the concentration range from 5×10^{-8} M to 10×10^{-8} M for Cd^{2+} ions and 2×10^{-7} M to 10×10^{-7} M for Zn^{2+} ions in solution.

It may be noted that the limits of determination are influenced by the factors (i) electrochemical kinetics of deposition and dissolution of the metal in Hg, (ii) the

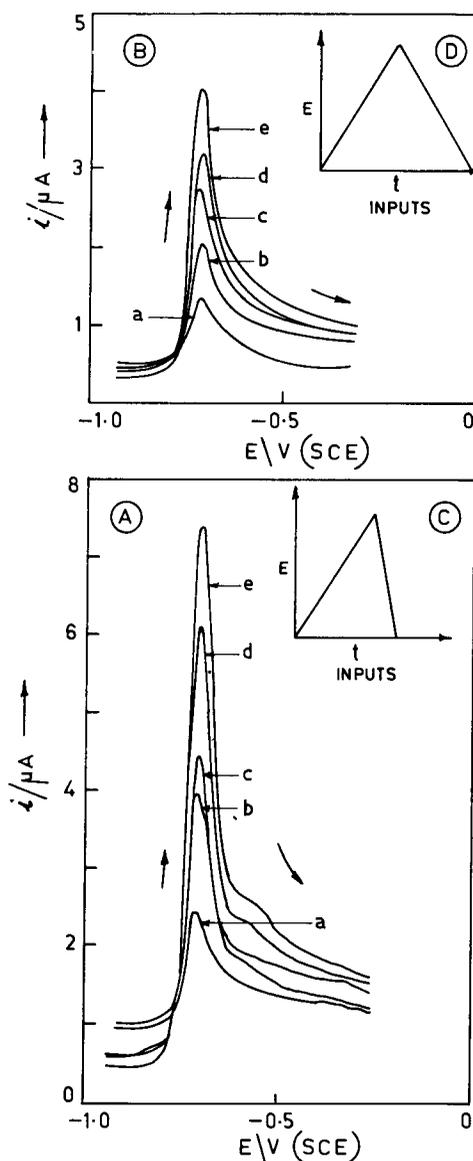


Figure 4 (A) Anodic stripping curves obtained for a solution containing (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5 μm CdSO₄ and using programmed time-potential inputs. Sweep rate of forward scan is 50 mV Sec⁻¹ and reverse scan is 100 mV Sec⁻¹. (B) As (A) but using inputs in which sweep rates of forward and reverse scan are identical i.e. 50 mV Sec⁻¹. (C) and (D) Potential input profiles for recording the curves in (A) and (B) respectively.

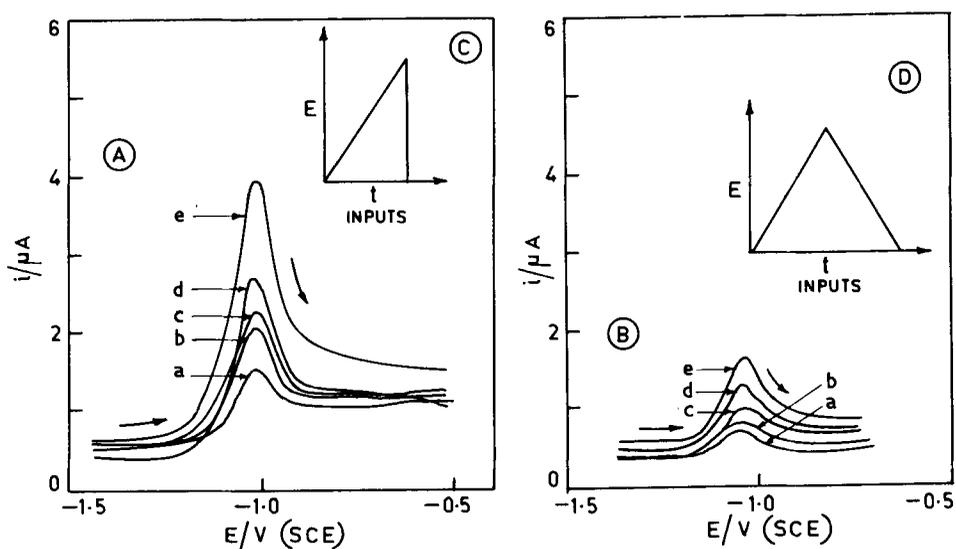


Figure 5. (A) Stripping curves obtained for a solution containing (a) 2, (b) 3, (c) 4, (d) 5 and (e) 6 μM ZnSO_4 and using programmed time-potential inputs. Sweep rate of forward scan is 50 mV Sec^{-1} and reverse scan is 200 mV Sec^{-1} . (B) As (A) but using inputs in which sweep rates of forward and reverse scan are identical i.e. 50 mV Sec^{-1} . (C) and (D) are potential input profiles for recording the curves in (A) and (B) respectively.

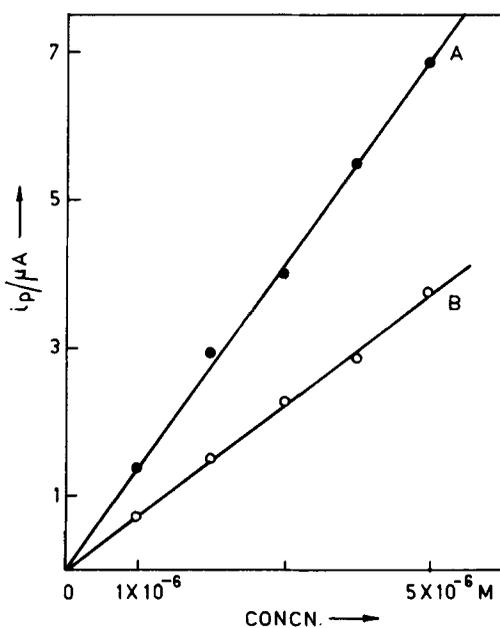


Figure 6. (A) Plot of i_p vs concentration of Cd^{2+} ion obtained using programmed inputs. Sweep rate of forward scan is 50 mV Sec^{-1} and reverse scan is 150 mV Sec^{-1} . (B) As (A) but using inputs in which sweep rates of forward and reverse scan are identical i.e. 50 mV Sec^{-1} .

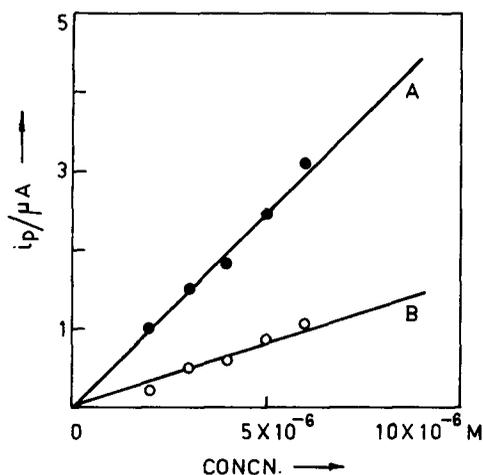


Figure 7. (A) Plot of i_p vs concentration of Zn^{2+} ion obtained using programmed inputs sweep rate of forward scan is 50 mV Sec^{-1} and reverse scan is 200 mV Sec^{-1} . (B) As (A) but using inputs in which sweep rates of forward and reverse scan are identical i.e. 50 mV Sec^{-1} .

rate of exchange reaction taking place between the metal ion in solution and the sodium in amalgam, (iii) solubility considerations for the respective metal in Hg, and (iv) the rate of potential sweep of the forward scan (which is analogous to the time of pre-electrolysis in the conventional ASV).

From the above experimental data one can conclude that a good enhancement of the anodic signal is possible in ASV by favouring additional accumulation of metal ion in HMDE via a displacement reaction between sodium metal in mercury and metal ions present in solution, the former being generated *in situ* on HMDE using a programmed time-potential input. This technique, besides enhancing estimation of individual metal ions at low levels, could also be expected to work well in the case of a mixture of metal ions in the solution under consideration.

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