

## Differential Pulse Polarography and Voltammetry with an Automated Microprocessor-based Polarograph and a Static Mercury Drop Electrode

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### ABSTRAK

*Polarografi denyut pembeza dengan menggunakan penganalisis polarografik yang berdasarkan kepada pemeroses mikro automatik dengan elektrod raksa pegun statik telah dinilai terhadap amplitud denyut, kadar skan, masa menitik ( $t$ ), dan luas titik. Didapati perubahan punca arus ( $i_p$ ) dengan luas titik dan  $t^{-1/2}$ ; perubahan punca keupayaan ( $E_p$ ) dengan amplitud denyut bersetuju dengan teori secara sederhana. Akan tetapi didapati pengantungan  $i_p$  dan  $E_p$  kepada kadar skan dan amplitud denyut yang besar dan terkecil telah didapati menyimpang daripada teori. Keputusan aliran yang serupa juga ditemui untuk voltametri melucut anodik apabila langkah melucut denyut pembeza digunakan. Kepresisian kedua-dua teknik itu adalah baik. Kuprum disadurkan secara individu semasa voltametri melucut anodik.*

### ABSTRACT

*Differential pulse polarography using an automated, microprocessor-based polarographic analyzer equipped with a static mercury drop electrode has been evaluated with respect to pulse amplitude, scan rate, drop time ( $t$ ), and drop area. Variation of peak current,  $i_p$ , with drop area and  $t^{-1/2}$ , with some pulse amplitudes agree reasonably well with theory. However, dependence of  $i_p$  and  $E_p$  on scan rate and on pulse amplitude at very large and very small amplitudes was found to deviate from theory. Similar trends were also found for anodic stripping voltammetry when differential pulse stripping was used. The precision attainable by both techniques was good. Copper peaks demonstrated good precision only when copper was plated out individually during anodic stripping voltammetry.*

### INTRODUCTION

The utility and novelty of computerized systems for electrochemical analysis using on-line mini computers have been well documented (Keller and Osteryoung, 1971; Smith, 1972). However, its high cost and complexity have prevented its widespread use. Recently, due to the advent of reasonably priced microprocessors ( $\mu p$ ), there is an upsurge of interest in the incorporation of digital microcomputers in electro-analytical devices (Bond and Grabaric, 1977;

Barrett *et al.*, 1980; Anderson and Bond, 1981, 1983). These computerized systems enable digital methods of data acquisition, data analysis, instrument control and hence some degree of automation.

The first generation up-based polarograph constructed by EG & G Princeton Applied Research Corporation (PARC) was the PARC model 374. Its performance characteristics for differential pulse methods and anodic stripping voltammetry (ASV) have been described by

Bond and Grabaric (1977). Most of the details were concerned with the consequences of the short drop times available from a pressurized dropping mercury electrode (PARC model 302) and the comparison of direct current (DC), normal pulse (NP) and differential pulse polarography (DPP), also at short drop times ( $< 1$  sec), and the DC distortion effect using the most recently introduced electrode system, the static mercury drop electrode (SMDE) (Peterson, 1979; Bond and Jones, 1980; Anderson *et al.*, 1981). A laboratory built up-controlled polarograph which could generate only staircase voltammetric and NP mode waveforms was reported and evaluated by Barrett *et al.* (1980). Results for the reduction of Cd(II) closely follow theoretical trends. An improved version of a up-controlled polarograph was later constructed by Anderson and Bond (1983) which has the capability to generate square wave, alternating current (AC), DC, and pulse polarograms.

Analytical evaluation of pulse polarographs was first reported by Parry and Osteryoung (1965) on their laboratory built analog polarograph using a DME. The reported instrumental artifacts in the PARC model 174 (Instruction Manual) has been substantiated by Christie *et al.* (1973). Anodic stripping voltammetry, which has gained much popularity recently and is especially useful for determining trace elements at the subppb level, has also been evaluated by many workers (Copeland *et al.*, 1974; Batley and Florence, 1974; Valanta *et al.*, 1977) using the analog units, the PARC model 174 and 174A, incorporating a hanging mercury drop electrode (HMDE) or mercury film electrode. Stripping techniques reported include DC, staircase, square wave and differential pulse.

A recent review in Analytical Chemistry (Ryan and Wilson, 1982) emphasized the need to evaluate theoretically and experimentally those computerized pulse techniques which can impress a variety of different potential waveforms.

Thus far there is no report pertaining to a more thorough experimental verification of

theory for DPP and differential pulse anodic stripping voltammetry (DPASV) using the second generation  $\mu$ -p based polarographic analyzer (PARC model 384) equipped with a SMDE. This study is essential for this fully automated instrument before it can be used for routine analysis. The analytical evaluation, which is the theme of this paper, is also done with the future user of this particular instrument in mind.

Based on the Cottrell equation for linear diffusion to a planar electrode, several theoretical treatment for DPP have been described (Barker and Gardner, 1958; Parry and Osteryoung, 1965; Keller and Osteryoung, 1971; Anderson *et al.*, 1981) for a simple, reversible process. A more general and less complicated expression for the differential pulse current,  $\Delta i$ , was put forward by Parry and Osteryoung (1965). In their theoretical treatment, maximum  $\Delta i$  ( $\Delta i_{\max}$ ) or  $i_p$  is described by the following:

$$\Delta i_{\max} = nFAC \sqrt{\frac{D}{\pi t'}} \frac{\sigma - 1}{\sigma + 1} \quad (1)$$

where  $\sigma = \exp\left(\frac{E_2 - E_1}{2} \frac{nF}{RT}\right)$ ,  $t'$  = time

interval between pulse amplification and current measurement and  $E_2 - E_1 = \Delta E$ , the pulse amplitude ( $\Delta E$  is negative for reduction). Other parameters have their usual meaning. If  $\Delta E/2$  is smaller than  $RT/nF$ , equation 1 is simplified to:

$$\Delta i_{\max} = \frac{n^2 F^2}{4RT} AC(-\Delta E) \left(-\sqrt{\frac{D}{\pi t'}}\right) \quad (2)$$

These expressions have neglected the contribution from the dc term,  $\Delta i_{dc}$ . A more specific  $\Delta i$  expression which takes into account this term was described recently by Anderson *et al.* (1981) for a stationary electrode like the SMDE. The contribution from both  $i_p$  and  $\Delta i_{dc}$  are strictly additive for the reversible electrode process. The effect of dc distortion using a SMDE has been well documented in the work reported by Anderson *et al.* (1981). The  $\Delta i_{dc}$  term can be minimiz-

ed and hence neglected when reasonably long drop times ( $>0.5$  sec) and large  $\Delta E$  values ( $>5$  mV) are used. For these reasons and also its simplicity, the theory of DPP described in equation 1 is used in this work. A similar expression has been successfully used by other workers to test their instrument (Parry and Osteryoung, 1965; Christie *et al.*, 1973; Blutstein and Bond, 1976).

According to equation (1),  $(\Delta i)_{\max}$  (or  $i_p$  as determined experimentally) obtained from a reversible reduction process of a simple system, is expected to be a linear function of the concentration of electroactive species, drop area, inverse square root drop time (for constant drop area),  $\frac{1-\sigma}{1+\sigma}$  and pulse amplitudes ( $\Delta E$ ). Peak

potential is given as  $E_p = E_{1/2} - \Delta E/2$  (3)

Even though equation (1) does not take into account the variation of  $i_p$  with scan rate ( $\nu$ ), certain predictions can be made from the treatment of other similar techniques. According to Sevcik (1948) and Roundles (1948), the relationship between  $i_p$  and  $\nu$  in linear sweep voltammetry was described by equation (4):  $i_p = K \times \nu^{1/2}$  where  $K$  is proportionality constant. Peak current increase with  $\nu$ . No peak shifting should occur when scan rate is varied. The validity and hence the usefulness of the instrument which performs DPP and DPASV shall largely depend on the above relationship between  $i_p$  and the various related parameters. Peak position and peak width should also conform to the theoretical expectation.

## MATERIALS AND METHODS

### Apparatus

The polarographic and voltammetric experiments described here were performed using an EG & G PARC model 384 second generation microprocessor-based polarographic analyzer equipped with an EG & G PARC model 303 SMDE. The differential pulse mode was used throughout. The 20 ml capacity cell used was made of quartz glass. A three electrode system was used. It consisted of a working electrode

(DME and HMDE modes in SMDE system were used throughout for the DPP and DPASV experiments respectively), a platinum auxiliary electrode, and a Ag/AgCl (saturated KCl) reference electrode. In DPASV, the stirring was done with a teflon covered magnetic stirring bar which was run by the PARC model 305 magnetic stirrer. The polarograms and voltammograms were recorded by a digital plotter, PARC model RE0082.

### Reagents and Procedures

Reagent grade chemicals were used. A 0.10 M stock solution of Cd(II) was prepared by dissolving CdCl<sub>2</sub> in deionized, distilled water (DDW). DDW was prepared by running laboratory prepared distilled H<sub>2</sub>O through a Millipore water purification system and used for sample preparation as required. A more dilute solution of Cd(II) was prepared by 1 : 10 dilution of the stock solution. 0.10 M KNO<sub>3</sub> was used as a supporting electrolyte. The nitrogen used to deoxygenate the solution was purified by passage through activated molecular sieve and deionized, distilled water.

The blank was initially run on a 10.0 ml 0.10 M KNO<sub>3</sub> solution followed by stepwise addition of 10 to 100  $\mu$ l of Cd(II) stock solution as required. Blank subtraction was done instrumentally for all experimental runs. Tangent fit, an iterative numerical routine which fits the best tangent to the baseline of each peak was used throughout to measure peak heights. For sensitivity and reproducibility studies, nine experimental runs were performed using prepared Cd(II) standard and 0.10 M KNO<sub>3</sub> supporting electrolyte.

## RESULTS AND DISCUSSION

In this work, peak currents for  $6.0 \times 10^{-5}$  M and  $1.0 \times 10^{-3}$  M Cd(II) solutions were obtained for the various scan rates ( $\nu$ ) available (2, 4, 6, 8 and 10 mV/s) at 5, 10, 25, 50 and 100 mV pulse amplitudes using a 1 sec drop time. These data are summarized in Tables 1 and 2. Fig. 1 is a plot of  $(\Delta i)_{\max}$  or  $i_p$  vs scan rate for various values of  $\Delta E$ . In general, any linear

TABLE 1  
Dependence of peak current and peak potential on scan rate and pulse amplitude at constant drop time of 1 sec. and Cd(II) concentration of  $1.0 \times 10^{-3}$  M during DPP

Scan rate		2 mV/s		4 mV/s		6 mV/s		10 mV/s	
$\Delta E$ (mV)	$\frac{1 - \sigma}{1 + \sigma}$	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)
5	0.097	1.24	556	0.795	564	0.645	560	0.447	540
10	0.193	2.69	555	1.70	560	1.40	566	0.970	550
25	0.453	5.93	548	3.68	556	3.21	554	2.12	550
50	0.750	10.69	534	6.97	540	6.35	548	4.80	540
100	0.960	13.73	508	14.2	536	13.3	536	10.5	520

TABLE 2  
Dependence of peak current and peak potential on scan rate and pulse amplitude at constant drop time of 1 sec. and Cd(II) concentration of  $6 \times 10^{-5}$  M during DPP

Scan rate		2 mV/s		4mV/s		6mv/s		8 mV/s		10 mV/s	
$\Delta E$ (mv)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	$i_p$ ( $\mu A$ )	$E_p$ (mV)	
5	0.085	556	0.065	556	0.049	554	0.039	548	0.032	530	
10	0.190	552	0.145	552	0.099	554	0.083	548	0.062	548	
25	0.422	546	0.325	548	0.251	548	0.190	548	0.139	540	
50	0.771	532	0.635	532	0.505	530	0.396	532	0.319	530	
100	0.954	508	0.867	508	0.840	506	0.733	504	0.623	510	

region seems to be confined to the range of 4 – 8 mV/s for various  $\Delta E$ . At all the  $\Delta E$  values studied,  $i_p$  decreases with scan rates contrary to what is expected from theory (refer equation (4)). The increase in scan rate is also associated with peak shifting in a rather irreproducible manner deviating somewhat from theory. The non-constancy of peak potential with respect to the change in scan rate and pulse amplitude could be attributed to the interplay of the following effects: DC distortion associated at low pulse amplitudes with peak broadening at higher scan rates; peak broadening at large pulse amplitudes and high scan rates (Fig. 2a, b). These effects

cause some difficulty in locating accurately the peak potential.

A deviation from theoretical behaviour was also observed when  $i_p$  was plotted against  $\frac{1 - \sigma}{1 + \sigma}$ .

In theory, a linear relationship should be observed for all scan rates studied. However, Fig. 3 demonstrates clearly that linearity was observed only at low scan rates ( $\leq 4$  mV/s). The deviation from linearity increases with an increase in scan rate. Fig. 4 shows that current increases proportionally with  $|\Delta E$  up to about 60 mV pulse and increases slowly for large pulses. This is in agree-

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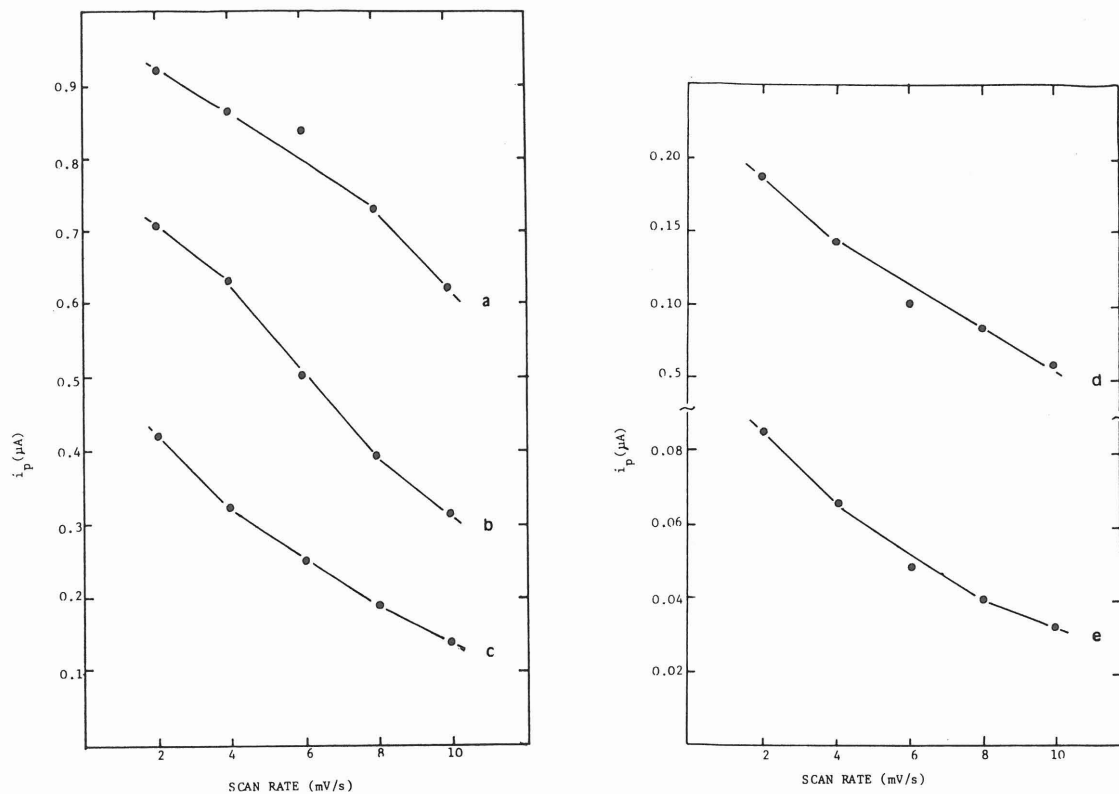


Fig. 1. Peak current as a function of scan rate for various pulse amplitudes.  
 $[Cd(II)] = 6.0 \times 10^{-5} M$ , drop time = 1.0 s,  
 a = 100 mV, b = 50 mV, c = 25 mV, d = 10 mV, e = 5 mV

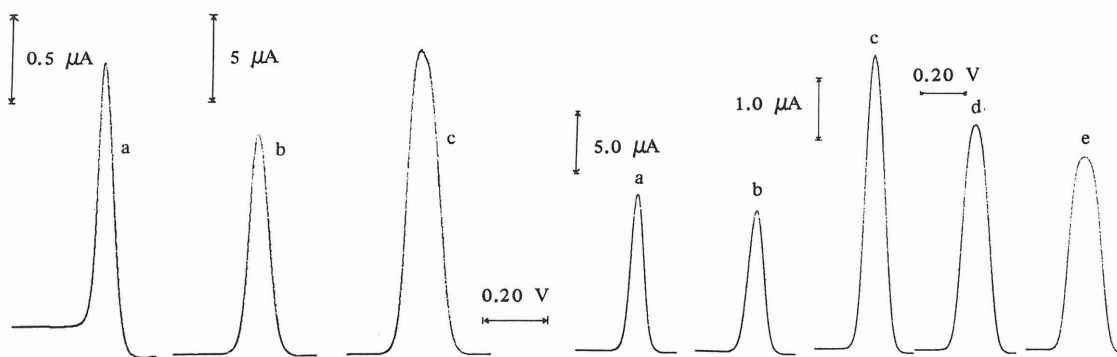


Fig. 2. (a) Comparison of differential pulse polarograms of 1.0 mM Cd(II) for various pulse amplitudes.  
 $v = 2 \text{ mV/s}$ , a = 5 mV, b = 50 mV, c = 10 mV  
 (b) Comparison of differential pulse polarogram of 1.0 mM Cd(I) for various scan rates.  
 $\Delta E = 50 \text{ mV}$ , drop time = 1 s  
 a = 2 mV/s, b = 4 mV/s, c = 6 mV/s, d = 8 mV/s, e = 10 mV/s

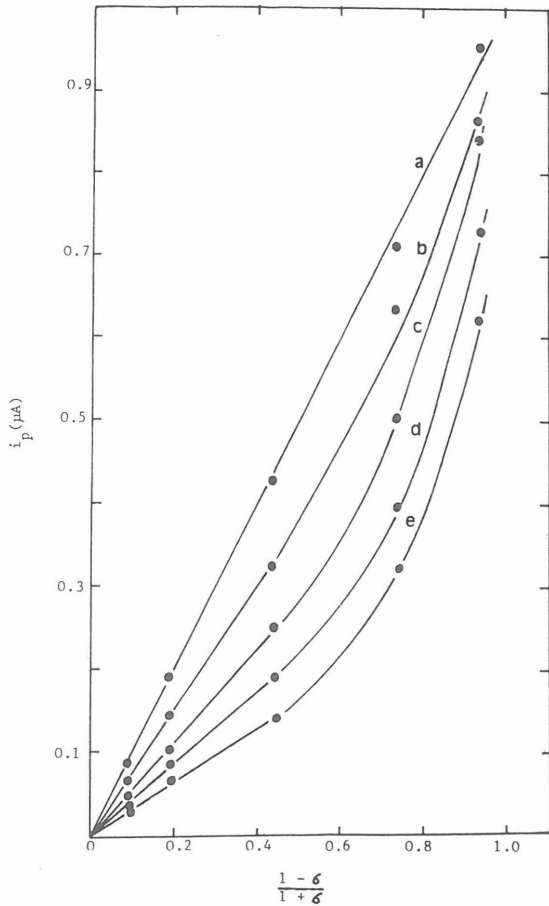


Fig. 3. Dependence of peak currents on  $\frac{1 - \sigma}{1 + \sigma}$  for various scan rates.  
 drop time = 1 s,  $[Cd(II)] = 6.0 \times 10^{-5} M$ ,  
 : a = 2 mV/s,            b = 4 mV/s,  
   c = 6 mV/s,            d = 8 mV/s,  
   e = 10 mV/s

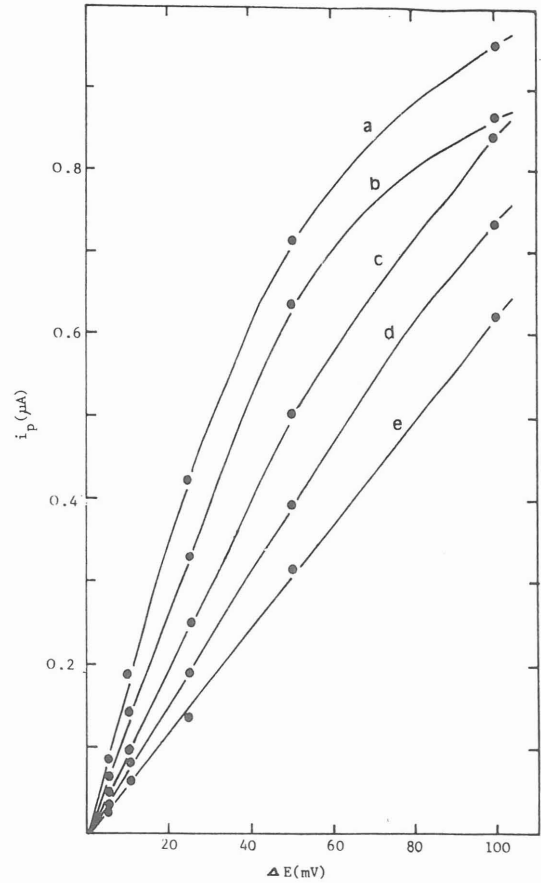


Fig. 4. Dependence of peak current on pulse amplitudes for various scan rates.  
 Other parameters: same as in Fig. 3.

ment with equation 2 for small pulse amplitude. Christie *et al.* (1973) and Blutstein and Bond (1976) also observed a divergence from theory for large pulse amplitude and large scan rates in their analog polarograph. They attributed the discrepancies to an instrumental artifact which arises from the small ratio of the sampling interval to the rather long time constant of the memory circuit. The long time constant was used to improve signal to noise ratio in very dilute solutions. However, in this  $\mu p$ -based polarograph, the discrepancies observed be-

tween theory and practical results could be due to the instrumental artifact mentioned above or to the combination of the  $\mu p$  and the instrumental artifact inherent in the polarograph or to a faulty mathematical model for the behaviour of the electrode processes. No attempt is made to identify the real cause of these discrepancies.

According to equation (3),  $E_p$  should be shifted anodically for a cathodic wave with an increase in  $\Delta E$ . The slope for  $E_p$  vs  $\Delta E$  graph should be  $-\frac{1}{2}$  for theory to hold. Fig. 5 shows

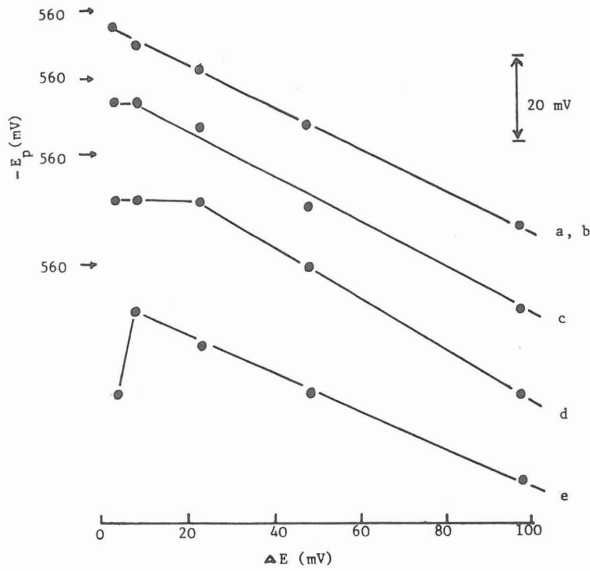


Fig. 5. Dependence of peak potential as a function of pulse amplitudes for various scan rates. Other parameters: same as in Fig. 3.

results which conform reasonably well with theory for all  $\Delta E$  values studied except for  $\Delta E \leq 10$  mV and  $\nu \geq 8$  mV/s. This is expected as peak broadening sets in at a high scan rate. This effect leads to error in peak location as explained above. DC distortion, evident in Fig. 2a, may have had an effect on the cathodic peak shifting at small pulse amplitude of 5 mV.

According to Baker and Gardner (1958)  $W_{1/2} = 3.52 RT$ . This gives a  $W_{1/2}$  of 90.4, 45.2

and 30.1 mV for 1, 2 and 3 electron reaction respectively at 25°C. Table 3 depicts the effect of  $\Delta E$  on  $W_{1/2}$ . For small  $\Delta E \leq 50$  mV,  $W_{1/2}$  is  $50 \pm 2$  mV, agreeing reasonably well with theory for  $n = 2$ . Peak broadening which sets in at  $\Delta E > 50$  mV is also to be expected from the theoretical treatment of Parry and Osteryoung.

For a stationary electrode system, faradaic current decays inversely as  $t^{1/2}$  where  $t$  is the drop time or experimentally the interval between pulse steps. Fig. 6 demonstrates this relationship which holds true for this automated polarograph as  $i_p$  vs  $t^{1/2}$  (at constant  $\nu$ ) produces a straight line passing through the origin. The  $i_p$  was also found proportional to drop area when the drop size was regulated by the SMDE as it should be (Fig. 7).

Differential Pulse Anodic Stripping Voltammetry (DPASV)

The effects of various parameters commonly associated with DPP on  $i_p$ ,  $E_p$  and  $W_{1/2}$  in DPASV were found to follow similar trends to those discussed above for DPP (Fig. 1-7). Besides these parameters, electrolysis time which includes deposition time ( $t_{dep}$ ) and equilibrium period ( $t_{eq}$ ) also determines the performance of DPASV. Deposition time exerts a direct control on the amount of metal plated onto the electrode while  $t_{eq}$  controls the homogeneity of amalgam formation in the electrode. Theoretically the

TABLE 3  
Effect of scan rate and pulse amplitude on half-peak width ( $W_{1/2}$ )

(a) $\Delta E$ (mV)	$W_{1/2}$ ( $\pm 2$ mV)		(b) $\nu$ (mV/s)	$W_{1/2}$ ( $\pm 2$ mV)	
	DPP	DPASV		DPP	DPASV
5	50	48	2	63	56
10	50	48	4	71	72
25	50	48	6	94	96
50	63	56	8	113	120
80	—	80	10	150	232
100	105	96			

(a)  $\nu = 2$  mV/s  
(b)  $\Delta E = 50$  mV

$[Cd(II)] = 1.0 \times 10^{-3} M$  for DPP  
 $8.9 \times 10^{-5} M$  for DPASV

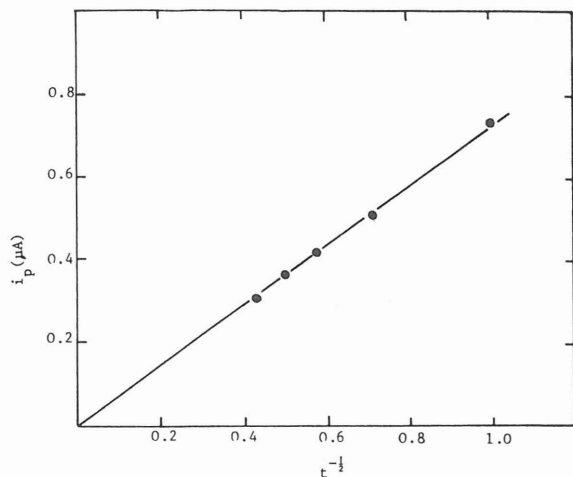


Fig. 6. Plot of peak current as a function of  $t^{-1/2}$  (proportional to electrode area) at constant scan rate.

$[Cd(II)] = 1.0 \times 10^{-3} M$ ,  $\Delta E = 50 mV$ ,  
 $v = 2 mV/s$

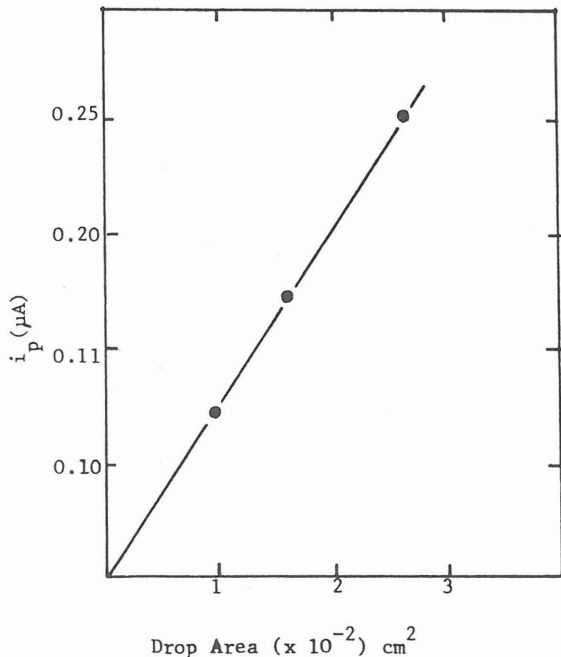


Fig. 7. Plot of peak current against electrode area regulated by SMDE. Other parameters; Same as in Fig. 6.

observed  $i_p$  should be directly proportional to the electrolysis time. However, this is not often the case in practice.

Fig. 8, 9 depict the dependence of  $i_p$  on  $t_{dep}$  and  $t_{eq}$ . Direct proportionality between  $i_p$  and the electrolysis time was maintained up to deposition time of 120 sec and equilibrium period of 300 sec. The increase in electrolysis time was also associated with an anodic shift in  $E_p$ . It appears that an equilibrium surface concentration is reached when longer deposition times are used (Fig. 8). Also sensitivity can be increased by increasing  $t_{dep}$  and  $t_{eq}$ . This approach would have little merit since it would require a rather long analysis time. More over it would lead to elec-

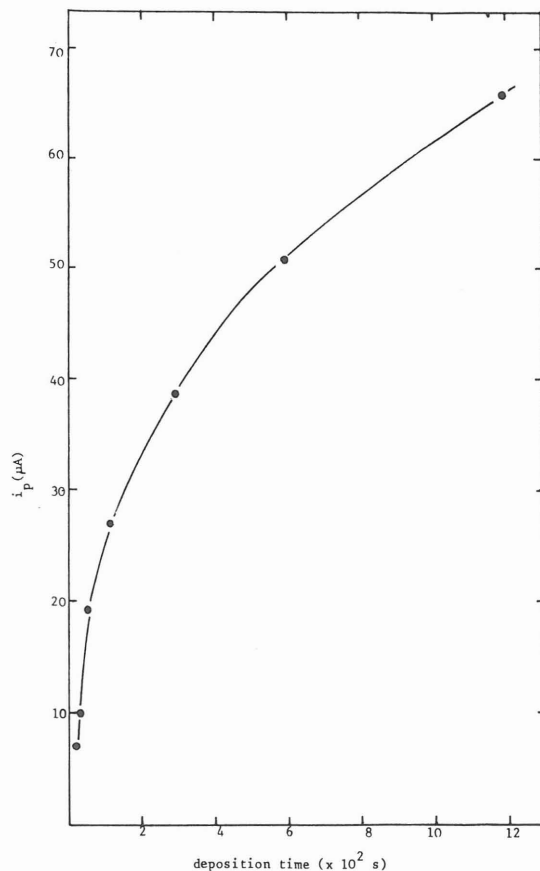


Fig. 8. Plot of peak current as a function of deposition time during DPASV.  $[Cd(II)] = 8.9 \times 10^{-5} M$ ,  $v = 2 mV/s$ ,  $\Delta E = 50 mV$ ,  $t_{eq} = 30 s$ .



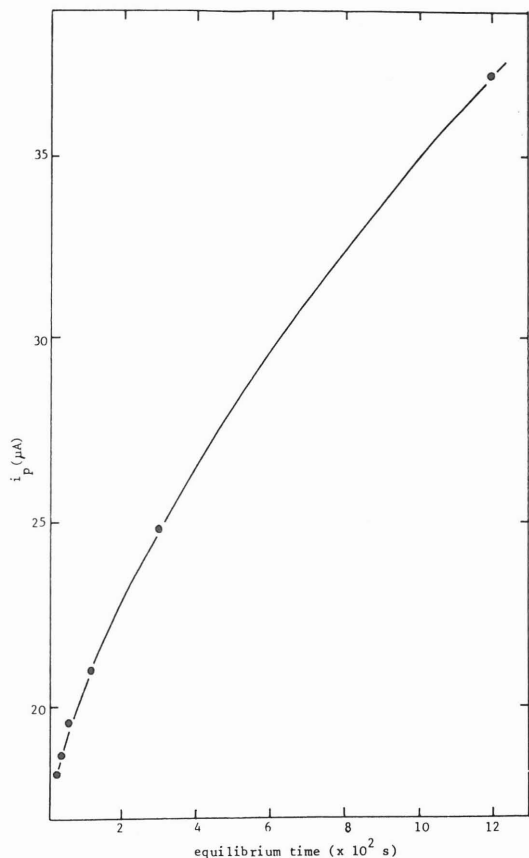


Fig. 9. Plot of peak current as a function of equilibrium time during DPASV.  
 $[Cd(II)] = 8.9 \times 10^{-5} M$ ,  $v = 2 mV/s$ ,  
 $\Delta E = 50 mV$ ,  $t_{dep} = 60 s$ .

tronic instabilities which may explain the increase in anodic shift of  $E_p$  with  $t_{dep}$  and  $t_{eq}$ . With electrodes formed by a mercury drop hanging on a mercury column as used in this work, back diffusion also plays a part. This phenomenon causes peak broadening (as observed in this work) and partial loss of the metal pre-electrolysed, thus leading to an apparent decrease in  $i_p$  and peak shifting.

From sensitivity and reproducibility studies, it was found that DPASV is still by far a more sensitive technique than DPP due to the preconcentration step of DPASV. Fig. 10a, b shows

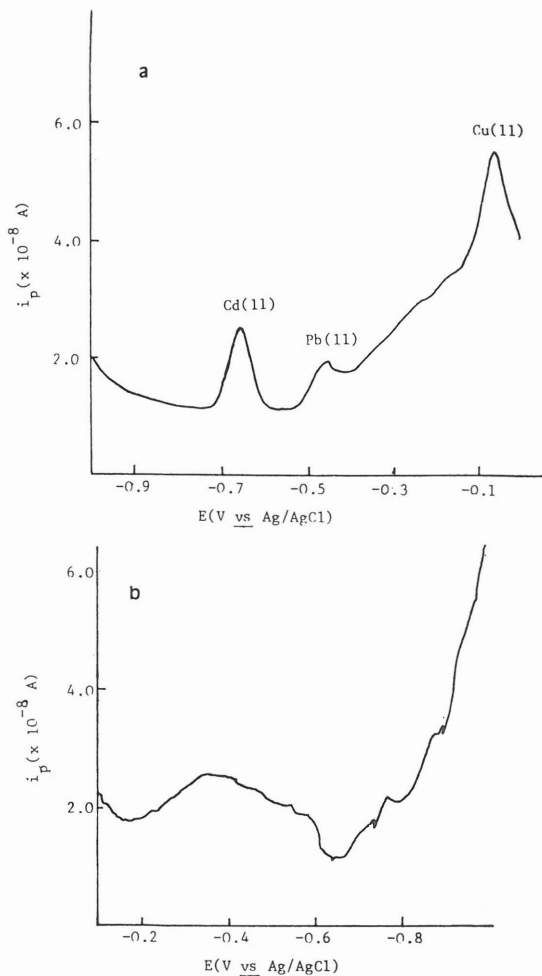


Fig. 10. Comparison of (a) differential pulse anodic stripping voltammograms and (b) differential pulse polarograms of Cd(II), Pb(II) and Cu(II) in  $0.10 M KNO_3$  background solution.

$v = 2 mV/s$ ,  $\Delta E = 50 mV$ ,  
 drop area =  $2.61 \times 10^2 cm^2$ ,  
 $t_{dep} = 60 s$ ,  $t_{eq} = 30 s$ .

that DPASV, but not DPP, can easily pick up three distinct peaks of Cd(II), Pb(II) and Cu(II) even at a concentration of  $\sim 10^{-8} M$ . From reproducibility studies involving nine duplicate runs, DPP shows a precision of 3 and 1% relative standard deviation (RSD) for  $i_p$  at a level of  $1 \mu M$  Cd(II) and  $11 \mu M$  Cd(II) respectively. In DPASV, when nine duplicate runs, each with

one analysis on one mercury drop, was considered RSD of  $i_p$  at a level of  $10^{-8}$  M Cd(II) and Pb(II) were 9.3 and 12.7% respectively. However, when nine duplicate runs, each with three analyses on different mercury drops and its means considered, the RSD for determining Cd(II) and Pb(II) improves to 8.0 and 6.8% respectively.  $\Delta E_p$  remains reasonably constant i.e.  $\pm 2$  mV for Cd(II) and Pb(II) in both techniques. However, when Cu(II) is plated out together with Cd and Pb, the RSD is as high as 34% for  $i_p$  and  $E_p$  fluctuates greatly from  $-0.086$  to  $-0.058$  V ( $\pm 28$  mV). A possible reason for this anomaly is the interference between metals. Many studies have shown that Cd and Cu may form an intermetallic compound when plated out simultaneously (Whitfield, 1975). When Cu(II) in 0.1 M  $\text{KNO}_3$  was plated out individually, its RSD for  $i_p$  and  $E_p$  improved to 6.1% and 4.4% respectively. From a standard addition study, the amount of Cu(II) present in the 0.10 M  $\text{KNO}_3$  supporting electrolyte was estimated to be  $1.8 \times 10^{-8}$  M or 1.1 ppb.

### CONCLUSION

The dependences of  $i_p$  on  $\frac{1-\sigma}{1+\sigma}$  at high

and of  $i_p$  and  $E_p$  on scan rates were found to deviate from theory. These would inevitably prevent the use of this polarograph in the investigation of electrode mechanisms. However, variation of  $i_p$  with drop time at constant scan rate and drop size, and of  $i_p$  with drop area agree well with theory indicating the validity of using expression (1) for the SMDE using the PARC 384. Peak potential was also found to vary with most pulse amplitudes employed in accordance with theory. Peak half-width is acceptable only for pulse amplitudes smaller than about 50 mV. Peak broadening occurs at large pulse amplitudes and scan rates.

In general, the PARC 384 and PARC 303 SMDE make a good combination as an essentially fully automated system. There is also the added features of background subtraction and tangent fitting which help to remove difficulty in extrapolating distorted based lines commonly

associated with dc distortion and high matrix effects. The time saving capability and the commendable precision attainable would undoubtedly enhance the status of differential pulse techniques especially DPASV for trace analysis at ppb or subppb level.

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