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An evaluation of integration procedures for improving the precision of a.c. polarography

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Two integration procedures for improving the precision of a.c. polarography have been studied. Both methods are single electrode techniques and involve integration of the rectified a.c. current over the complete peak or at the peak potential respectively. The time integration procedure was found to be seriously influenced by small variations in the reference electrode potential and applied voltage, resulting in poor reproducibility between different samples. In the area integration procedure, however, where the accurate control of potential is less critical, the standard deviation between replicate samples was found to be within the statistically expected limits and this method was therefore preferred. Standard deviations were measured for a range of inorganic and organic species and typical values of ±0·25% at the optimum concentration level ($4{\cdot}10^{-4}$M) were obtained.

Introduction

The major factor limiting the precision attainable by polarographic methods is the accuracy of the current measuring system. There have been several approaches to the problem of improving the precision. Various integration procedures and digital read-out devices have been proposed. Perone *et al.* [1] and Stephens and Harrar [2] have both described instruments with digital read-out of the peak current for fast sweep polarography. A precision of ±0·1–0·2% at the 10^{-3}M level was obtained in both cases. Time integration procedures applied to classical d.c. polarography have been studied by Lingane [3] for increasing precision (approx. ±0·1–0·2%) and by Matsuda *et al.* [4] for increasing the detection limit.

Barker and Faircloth [5] have described the use of twin electrodes for square wave polarography to increase the precision, while more recently Rooney [6] has used a digital voltmeter to give a digital read-out for pulse polarography.

In the present work two methods are described for increasing the precision of a.c. polarography by means of integration with digital read-out. Both methods are single electrode techniques and involve measurement of the area of the a.c. peak (area integration) or integration of the peak current for a given period (time integration), the latter method is analogous to Lingane's d.c. polarographic procedure. A procedure of this type which involves integration over a large number of drops has the advantage of averaging out any irregularities in drop time, this giving an increase in precision.

Theoretical discussion

The peak shaped response of a.c. polarography coupled with the ability to discriminate the species of interest from more easily reducible species as well as the low sensitivity to oxygen make it ideally suited as a precision technique. The a.c. technique is rather more complex than the d.c. method, however, in that the magnitude of the peak current is influenced by several factors.

The peak current (i_p) of a fundamental harmonic a.c. polarogram is given by equation (1) [7].

$$i_p = \frac{n^2F^2Ac(\omega D)^{\frac{1}{2}}\Delta E}{4RT}\sin(\omega t + \mathrm{II}_4) \qquad (1)$$

Thus for a given concentration (c) i_p will depend on the amplitude of the applied sinusoidal voltage (ΔE), the square root of the frequency (ω) and the area of the electrode surface (A). In order to obtain reproducible values of i_p, ω and ΔE must be kept constant. In the case of a D.M.E. the electrode area (A), while not constant, varies periodically in a reproducible manner. Unlike d.c. polarography, i_p is unaffected by the mercury reservoir height. The temperature coefficient of the a.c. process is also generally less than that for the corresponding d.c. process.

The time integration procedure requires the d.c. applied potential (E_{dc}) to be equal to E_p (peak potential of the a.c. polarogram), any variation in E_{dc} will cause an error. The permissible error in E_{dc} for a given precision can be calculated from equation (2) [7].

$$E_{dc} = E_{\frac{1}{2}} + \frac{2RT}{nF}\ln\left[\left(\frac{i_p}{i}\right)^{\frac{1}{2}} - \left(\frac{i_p - i}{i}\right)^{\frac{1}{2}}\right] \qquad (2)$$

where $E_{\frac{1}{2}}$ = half wave potential, i = a.c. current at potential E_{dc}.

It can be seen from Fig. 1 that this imposes a serious limitation to the method, as even under the best potentiostatic conditions any slight drift in reference electrode potential will result in error.

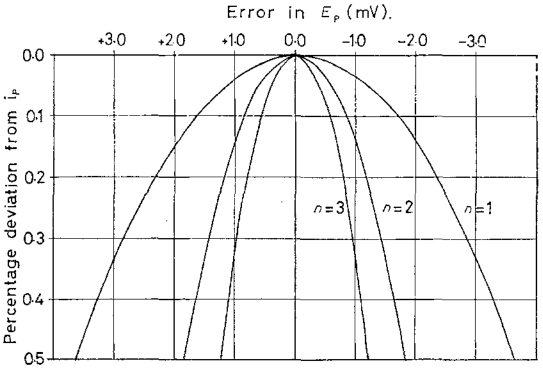

Fig. 1. Dependence of peak current on applied voltage.

In principle the method of area integration will be relatively unaffected by changes in the value of E_{ref} *between* successive measurements (Fig. 2(a)), where E^{I} and E^{II} are the initial and final potentials of the integration period respectively. It is apparent that any small change in E_{ref} resulting in the initial and final potentials being E^{III} and E^{IV} will have little influence on the area. In many cases the a.c. polarogram will be non-ideal in shape (Fig. 2(b)) and therefore any change in E_{ref} will affect the area of integration. The situation becomes more complicated when E_{ref} varies during the course of a single measurement; in this case both types of integration procedure are seriously affected.

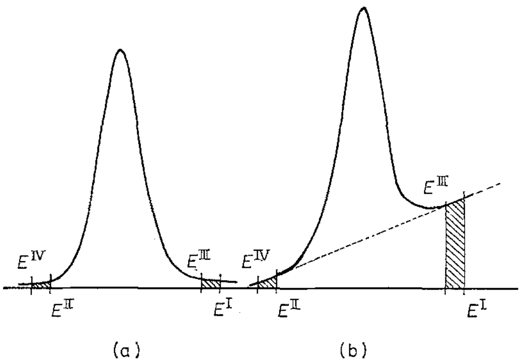

Fig. 2. Effect of potential drift on integration procedures.

One further source of complication with this type of procedure arises through depletion of the electroactive species during successive measurements on the same solution. This problem has been considered by Lingane [3] and must be allowed for when the absolute precision of the method is being established. Under normal analytical conditions, however, where sample and standard are compared this effect is eliminated.

Experimental

Apparatus

Integrating polarograph. A schematic diagram of the equipment, showing the various connections, is given in Fig. 3. The a.c. polarograph consisted of the Cambridge general purpose polarograph in conjunction with the Univector attachment (both Cambridge Instruments, London). The Univector was run off a 240 V 'Advance Volstat', thus improving the noise level by a factor of five or more. The output of the polarograph (terminals +M and −M) which is normally connected to a low impedance galvanometer or recorder was connected to a current follower. The current follower consisted of an Analog Devices 232(J) chopper stabilized amplifier with a 2 MΩ±1% resistor in the feed-back loop. The voltage output was then displayed on the Y axis of an XY recorder (Model 22000 Bryans, Surrey, England) as well as integrated with respect to time by means of a voltage to frequency converter and scaler. An RC (1 to 4 sec) smoothing circuit was connected to the recorder to reduce the drop oscillations. The X axis of the recorder was connected to terminal C− on the general purpose polarograph via a voltage follower consisting of a μA709C operational amplifier. An RC (approx. 0·8 sec) smoothing circuit was required at the X input to remove the 35 Hz signal present. The low voltage required for the general purpose polarograph was obtained from a stabilized power supply and the normal 6 V supply replaced by a 3 V supply in order to give a scan rate of 1·35 mV/sec. The two operational amplifiers were powered from the power unit (Harwell model 2015B) required for the scaler.

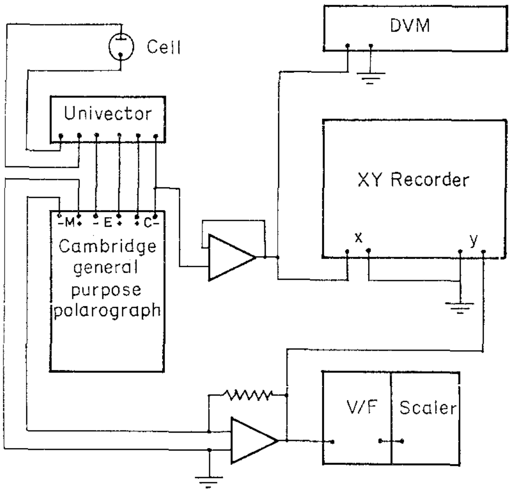

Fig. 3. Schematic diagram of the integrating polarograph.

Voltage to frequency converter (*V*/*F*). The circuit for the *V*/*F* converter and associated power supply [8] is based on a G.E.C. Circuit. The *V*/*F* converter only accepts positive voltage levels up to approximately 4·0 V and gives output pulses of −3·5 V with a half width of 8 μsec. The linearity was measured over the range 0·5 mV to 3·0 V and found to be ±0·07% with a slope of 1·358 Hz/mV. The zero drift, which was due mainly to ambient temperature changes, represented approximately 1 mV/°C with respect to the input, and in practice amounted to approximately 0·3 mV/h under the present experimental conditions. The output pulses were fed straight into a type 1 input on a Harwell 2117B scaler.

Dropping mercury electrode. This was a modified conventional dropping mercury electrode. The end of the capillary was ground by hand on a dry oil stone to a point (0·2 mm diameter). The capillary characteristics measured at 0·0 V applied in 1M KCl were t = 2·88 sec, m = 2·48 mg/sec at h = 52 cm.

Cells. Two types of cell were examined; the first contained a mercury pool reference electrode with a surface area of 7 cm^2 and the second type was a H cell with a separated S.C.E. (surface area 5 cm^2). The limbs of the H cell were divided by a 2 cm diameter No. 3 glass sinter. A 1 cm agar/KNO_3 plug was formed against the sinter on the reference electrode side. In order to minimize vibration the cell and D.M.E. were rigidly clamped and the cell itself immersed in a water bath at 25±0·15°C.

Reagents. The standard solutions for the comparative work were prepared by weighing out aliquots (approximately 5 g) of a standard 10^{-2}M Cd^{2+} in 1N HCl solution and diluting to 250 ml with 1N HCl. The same volumetric flask was used for all the solutions.

Organomercury compounds were prepared by treating the appropriate olefinic compound with an excess of methanolic mercuric acetate [9, 10]. After addition of the supporting electrolyte (NaOH) the solutions were allowed to stand for 1–2 h to allow any mercuric oxide formed to precipitate out. The solutions of 1,2 diphenyloxytriazine were prepared as described. The behaviour of this compound was previously studied in some detail [11] and under the experimental conditions employed a well-defined 2-electron reversible wave is obtained.

Procedure

Area integration. The sample under examination was deoxygenated for 5 mins with nitrogen presaturated with the supporting electrolyte. During the actual measurement the nitrogen was directed over the surface of the solution. The starting potential on the polarograph was set at a value some 50 mV more positive than the initial integrating voltage. The scan is initiated and when the voltage (as indicated on the digital voltmeter, Fig. 3) reached the first integrating voltage the scaler, switched on, and then finally switched off at the second integrating voltage. The count is recorded and the sample replaced by a standard solution of similar concentration and a polarogram recorded. Similarly a blank determination is made.

Time integration. In the time integration procedure the applied d.c. potential was adjusted until it coincided with the peak potential and then the counts recorded for a period of 300 sec.

The concentration of the sample (c) is given in both cases by

$$c = \frac{N_S - N_B}{N_R - N_B} \times C_R$$

where N_S = sample count; N_R = standard count; N_B = blank count and C_R = concentration of standard. The above equation assumes a linear calibration curve for the species of interest over the measured concentration range.

Results and discussion

The stability of the experimental assembly was initially measured by replacing the polarographic cell by resistors of various values. With a dummy cell resistance of 100 kΩ (corresponding approximately to 5×10^{-6}M Cd^{2+}) the variation of the output frequency from the V/F converter showed a standard deviation of ±0·54%. For a resistance of 10 kΩ or less the standard deviation was ±0·03%. With area integration the reproducibility of the d.c. scan rate is also of importance and was shown to be ±0·1% or better.

The use of a conventional blunt-ended D.M.E. was found to give poor reproducibility due to the trapping of small bubbles of N_2 under the D.M.E. tip. Lingane [3] has circumvented this problem by not introducing the D.M.E. until after deoxygenation and using magnetic stirring when required. It was found in this present work that the use of a pointed D.M.E. also effectively eliminated the problem. The reproducibility of the a.c. polarogram for successive scans of the same solution is shown in Fig. 4. When the measurements were repeated on two separate solutions the standard deviation between the three samples was within the statistically expected limits. The data obtained from the other systems studied also followed this pattern.

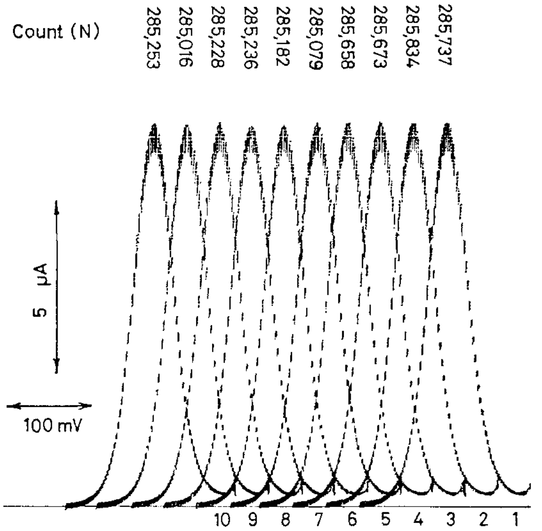

Fig. 4. Reproducibility of a.c. polarogram. $1 \cdot 10^{-3}$M $[Fe(C_2O_4)_3]^{4-}$, 0·5 M H_2C_2O

The data summarized in Table 1 illustrate the reproducibility obtained for the area integration procedure with various inorganic ions undergoing 1-, 2- or 3-electron processes, as well as a number of organic compounds. It can be seen that the instrument stability contributes very little error when compared to the overall reproducibility other than for $1 \cdot 0 \times 10^{-5}$M solutions and that the optimum concentration is around 1–4×10^{-4}M level. With concentrations as high as 10^{-3}M the current is generally large enough to upset the stability of the reference electrode which is often evidenced by a progressive change in the results. This situation will also occur when in addition to the species of interest a large excess of a more easily reducible species is present. This effect is shown in Table 2, and is

Table 1. Experimentally measured standard deviations using the area integration procedure

Species	*Standard deviation—single scan* ± %[a]				*Supporting electrolyte*	*Cell*
	$10^{-3}M$	$4\times10^{-4}M$	$10^{-4}M$	$10^{-5}M$		
$[Fe(C_2O_4)_3]^{4-}$	0·11	0·19	0·27	3·5	0·5 M $H_2C_2O_4$	b
Cd^{2+}	0·54	0·19	0·23	1·3	1 M HCl	b
Cd^{2+}	0·20	0·29	0·25	1·2	1 M HCl	c
Cd^{2+}	0·21	0·25	0·22	0·82	1 M HCl	d
Pb^{2+}	0·47	0·20	0·13	0·51	1 M HCl	b
Bi^{2+}	0·48	0·20	0·24	0·88	1 M HCl	b
Benzil	0·25	0·33	0·42	2·0	0·5 M NaOH 50% EtOH	c
Benzil	0·28	0·37	0·84	1·6	0·5 M NaOH 50% EtOH	b
1,2 diphenyloxytrizine	0·84	0·30	0·40	3·1	0·2 M HCl 50% EtOH	b
4-methyl-1-pentene/Hg^{2+}	—	0·20	0·32	0·49	0·1 M NaOH 90% MeOH	c
Allyl alcohol/Hg^{2+}	—	0·27	0·35	1·4	0·1 M NaOH 90% MeOH	c

[a] Values calculated on 9 degrees of freedom.
b Internal mercury pool.
c H cell.
d H cell, no mixing between scans.

Table 2. Effect of a pre-reduction process on the standard deviation for Cd^{2+} (area integration—H cell)

	Concentration of Bi^{3+}				
	$10^{-4}M$	$10^{-3}M$	$2\times10^{-3}M$	$3\times10^{-3}M$	$5\times10^{-3}M$
S.D. for $10^{-4}M$ Cd^{2+} in 1N HCl	0·22	0·28	0·68	0·69	3·0

more pronounced for a cell possessing an internal mercury pool reference electrode rather than a separated S.C.E. If an internal mercury pool reference electrode is used its stability will be considerably influenced by the nature of the anions present in solution. For example 4×10^{-4}M 1,2 diphenyloxytriazine in 0·2N H_2SO_4 gave counts varying from 149,000 to 172,000 and a shift in E_p (apparent) was easily observable; however, in a 0·2N HCl medium the reproducibility (s.d. = ±0·3%) is typical for the organic compounds examined. The use of the H cell with a separated S.C.E. does not always circumvent these problems; for example, with the $[Fe(C_2O_4)_3]^{3-}/[Fe(C_2O_4)_3]^{4-}$ system in 0·05M $H_2C_2O_4$ a distorted and unstable a.c. polarogram is obtained due to traces of chloride diffusing through the reference junction.

It is also noticeable (Table 1) that the $[Fe(C_2O_4)_3]^{3-}/[Fe(C_2O_4)_3]^{4-}$ system gave very acceptable results at the 10^3M level when compared with Cd^{2+}, Pb^{2+} or Bi^{3+}; this is of course a direct consequence of the dependence of the fundamental harmonic a.c. current on n^2.

Table 3 gives the results obtained by the time integration procedure using an integration period of 300 sec. The data were collated by making four measurements on each of three solutions in order that the sample changing reproducibility could be found. Comparison with Table 1 indicates com-

Table 3. Experimentally measured standard deviations for a single integration using the time integration procedure

Species	*Standard deviation* ± % $10^{-3}M$	$4\times10^{-4}M$	$10^{-4}M$	$10^{-4}M$	*Supporting Electrolyte*	*Cell*
Cd^{2+}	0·27 (9·4)	0·25 (11)	0·33 (2·3)	0·51 (42)	1N HCl	H
Bi^{2+}	0·14 (1·8)	0·17 (9·4)	0·66 (2·3)	0·83 (2·3)	1N HCl	H
4-methyl-1-pentene/Hg^{2+}	—	0·23 (10·6)	0·24 (4·2)	0·88 (7·9)	0·1N NaOH 90% MeOH	H

Initial value calculated on 9 degrees of freedom. 3 sets of four 300 sec integrations. Values in parentheses show calculated *F* values for comparison of averages of sets; critical *F* value 4.3.

Table 4. Determination of Cd^{2+} by comparative area integration a.c. polarography

Solution	*Taken*	*Count*[a]	*Found*	*Error*
1	$2{\cdot}0390\times10^{-4}$M	161,862	standard	—
2	$2{\cdot}1077\times10^{-4}$M	167,016	$2{\cdot}1053\times10^{-4}$M	−0·11%
3	$2{\cdot}0704\times10^{-4}$M	164,396	$2{\cdot}0716\times10^{-4}$M	+0·06%
4	$1{\cdot}9985\times10^{-4}$M	158,409	$1{\cdot}9946\times10^{-4}$M	−0·20%
5	Blank	3,402	—	—

[a] Average of three scans.

parable results to that of area integration, however the reproducibility from one sample to another is rather poor and clearly indicates the difficulties associated with locating E_p.

From the results it is evident that the area integration procedure is to be preferred and has the added advantage that it could be readily automated by the introduction of gating circuits to actuate the scaler at the preselected voltage levels.

The results obtained by the comparative area integration technique are shown in Table 4.

The technique is probably capable of further refinement by the use of a 3-electrode system to eliminate the need for a current carrying reference electrode. Errors due to drop time irregularities could be reduced by the use of a mechanically controlled drop time.

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