A MODIFIED METHOD FOR MEASURING THE WAVEHEIGHT OF THE POLAROGRAM

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Summary

1. An improved method has been described to measure the waveheights of photo-recorded polarograms and the accuracy obtained by this method is practically the same as in the case of manually operated polarograph. The improvements are effected (i) by introducing a vernier, (ii) by measuring the top and the bottom of the polarogram to determine the mean and (iii) by fixing the wet photographic paper on a sheet of glass.

2. The modified method can also be employed to obtain the log plots and the half-wave potentials.

Since photo-recording was introduced into polarography a number of attempts have been made to improve the accuracy during the measurement of [illegible] in the photo-recorded polarograms. Buckley and Taylor[1] estimate that the value of i_d is reproducible within 0·5 to 4%, while Mueller[2] states that an accuracy of [illegible] can be reached using the average of several polarograms of the same solution. To minimise errors, Jablonski and Moritz[3] suggest the use of microscope for [illegible] the waveheight. Kolthoff and Lingane,[4] Zlotowski and Kolthoff,[5] and Lingane and Meites[6] on the other hand, prefer manual polarography to enhance the [illegible] of measurements. Taylor[7] has described a device employed for accurate measurement of the waveheights recorded on photographic paper and gets an [illegible] of ±1·2%.

The present method employed for measuring the waveheight is a modification of the device developed by Taylor. The device consists of a drawing board (12″ 10″), to the short parallel edges of which are attached two plain rectangular wooden strips (10″ × 2″ × 1/5″) over which the transparent plexi-glass arm of the T-square moves. The wooden strip on the left has a millimeter scale attached on it and the vernier is attached to the vertical arm of the T-square and enables one to measure heights correct to 0·02 mm. A thin line is drawn on the lower surface of the arm to serve as an index line. The photographic paper is wetted with water and placed on a sheet of glass (7″ × 4″) with the emulsion side touching the glass sheet and pressed with a squeezing roller to remove excess water. The polarogram is then placed on the drawing board underneath the arm of the T-square. In Taylor's method,[7] the polarogram remains fixed and the inclination of the arm of the T-square is altered to any desired degree. In the present method, the T-square is

not adjusted but the position of the polargoram is initially adjusted to make the graph line of the polarogram coincide with the index line. This procedure has the advantage of simplicity in manipulation and avoids the rubbing of the T-square against the sensitive side of the photographic paper. A thin piece of mirror is placed on the glass plate to avoid the errors due to parallax. While measuring the waveheight, it is usual to take the mean position of the base line and the average of the galvanometer oscillations, as judged by the eye. The present author found that the visual judgment of the position of the mean would introduce an error of 0·2 mm. In order to avoid this error, the readings at the upper and the lower portions of the base line and those of the galvanometer oscillations are taken to calculate the mean values.

In order to verify the precision in the measurement of waveheight using the modified apparatus, polarograms were taken for cadmium solution (1·034 millimolar) using 0·1 N hydrochloric acid and 0·1 N potassium chloride in the base solution. The method employed for measuring the waveheight is as follows: The index arm is adjusted parallel to the horizontal lines on the photographic paper graphed by the automatic method incorporated in the instrument. Two points are chosen, one before (− 0·50 V *vs.* S.C.E.) and the other after (− 0·80 V *vs.* S.C.E.) the completion of the wave. The mean heights of the polarogram at these two points are measured and the difference gives the waveheight. Table I indicates the reproducibility of the values for the waveheight.

The results in Table I indicate that for the same curve the mean position can be measured with a precision of $\pm$ 0·06%.

The overall accuracy of the measurements was also verified by taking different concentrations of the cadmium solution and changing the sensitivity of the galvanometer to have nearly the same values for the waveheight. In these experiments the drop-time, the amount of mercury flowing out per second and the temperature have all been maintained constant correct to $\pm$ 0·1%. The blank lines (corresponding to the base solution only, *i.e.*, 0·1 N HCl, 0·1 N KCl) for each sensitivity of the galvanometer are also run and the corresponding corrections are applied to the waveheights. This procedure is essential because in the polarograph supplied by the Cambridge Instrument Co., even when the counter-current dial is set at zero, the galvanometer zero line is not parallel to the horizontal line of the graph but is inclined downwards. Thus, the correction may be either positive or negative. Table II gives the results obtained.

The results of Table II indicate that the overall error (W.H. × S)/concn. introduced in the analysis of cadmium is about 0·25%.

Ladisch and Balmer[8] have pointed out that the photographic paper expands to an extent of 2% when the humidity is varied from 12 to 97%. In order to avoid the error, he has two fixed lines drawn under standard conditions to compare the polarographic heights measured. In the present method, however, this error is overcome by having 100% humidity (*i.e.*, by wetting the photographic paper in

TABLE I

Waveheight for 1·034 millimolar cadmium solution in 0·1 N potassium chloride + 0·1 N hydrochloric acid

Sensitivity S/30

Height for 50 graph divisions	Observation No.	Base line reading at −0·50 V			Diffusion current plateau reading at −0·80 V			Height of the wave (6−3)	Height of the wave in graph divisions
		Top 1	Bottom 2	Mean (1 & 2) 3	Top 4	Bottom 5	Mean (4 & 5) 6	7	8
54·12 mm.	A_1	3·38	2·64	3·01	62·70	59·00	60·85	57·84	53·43
	A_2	1·98	1·28	1·63	61·36	57·50	59·43	57·80	53·39
	A_3	2·16	2·92	2·54	62·24	58·42	60·33	57·79	53·39
54·03 mm.	A_4*	65·30	66·12	65·71	125·29	121·64	123·46	57·75	53·46
	A_5*	72·95	72·12	72·53	132·01	128·45	130·23	57·70	53·40
	A_6*	86·07	85·24	85·65	145·15	141·59	143·37	57·72	53·43

* The values were determined by attaching a steel millimetre scale and vernier, reading correct to 0·01 mm after re-setting the cadmium polarogram.

TABLE II

Effect of concentration on the corrected waveheight at different sensitivities of galvanometer

Concn. of cadmium (millimolar)	Sensitivity	Height of the wave at −0·80 V (mm.)	Blank value			Corrected wave height	W.H.×S / Concn.
			Reading at −0·80 V	Reading at −0·50 V	Correction factor (mm.)		
1·034	S/30	57·82	11·38	11·46	+0·08	57·90	1680
3·114	S/100	51·96	11·16	11·54	+0·38	52·34	1681
5·170	S/150	57·29	13·76	14·26	+0·50	57·79	1677
					Average ..		1679 ± 2

water and removing the excess of water under standard conditions). In order to verify this experimentally, the distance between 50 divisions in different photographic papers graphed by the automatic method, was measured and the results are given in Table III.

TABLE III

Effect of wetting on the expansion error of the photographic paper

Paper	Distance between 50 divisions	Deviation from the mean value
1	54·80	0·57
2	54·28	0·05
3	54·28	0·05
4	54·24	0·01
5	54·20	−0·03
6	54·04	−0·19
7	54·14	−0·09
8	54·18	−0·05
9	54·34	0·11
10	54·24	0·01
11	54·20	−0·03
12	54·24	0·01
13	54·00	−0·23
14	54·18	−0·05
15	54·10	−0·13
16	54·24	0·01
Mean Value	54·23	

The results in Table III indicate that the error introduced by the present method is not greater than $0{\cdot}5\%$. Even this error can be eliminated by [illegible] the distance between the graphed divisions for every [illegible]

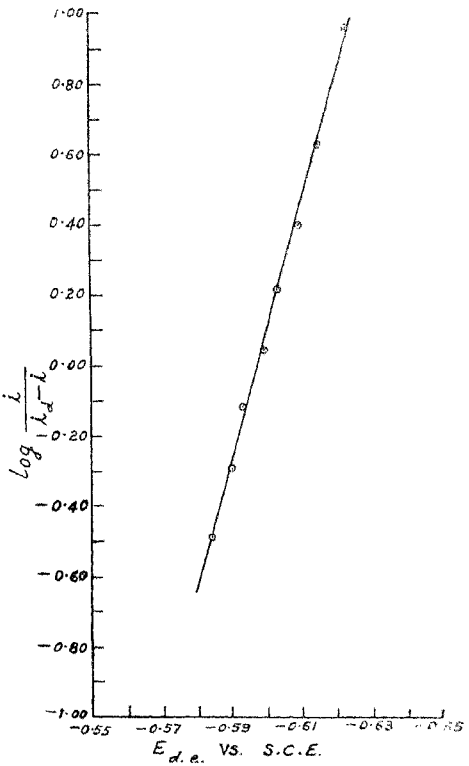

FIG. 1. Plot of $\log \frac{i}{i_d - i}$ *vs.* $E_{d.e.}$ of 1·034 Millimolar cadmium chloride in 0·1M hydrochloric acid & 0·1 M potassium chloride solution.

It is generally assumed that the photographic method gives results correct to $\pm 2\%$.[1] In order to avoid the uncertainties and to obtain a high degree of accuracy, the measurement of diffusion current was carried out by Meites and Meites[8] by the

manual method when the error got reduced to $\pm 0{\cdot}16\%$ for the cadmium polarograms. The improvements introduced in the present work (1) by employing a vernier, (2) by measuring the top and the bottom of the polarograms in calculating the mean value and (3) by fixing the photographic paper to the glass plate under standard conditions of humidity, have enabled the present author to obtain an accuracy of $0{\cdot}25\%$ for cadmium by the photographic method. The value of the diffusion current constant obtained by the modified Ilkovic equation[10] is 2·98 (25° C.) as compared with a value of 3·03 obtained by Meites and Meites[9] by the manual polarographic method. It can, therefore, be concluded that reliable analytical results can be obtained even by the photo-recording method when suitable precautions are taken.

The present method can also be employed for getting the current-potential curves which are needed to get the plot of log $i/(i_d - i)$ *vs.* potential and also to get the values of the half-wave potentials after incorporating the iR drop corrections. In the polarograms obtained with the Cambridge Instrument Co. Polarograph, the span of 0·1 volt is about 5 mm. and the maximum error in the measurement is of the order of 0·05 mm. corresponding to $(0{\cdot}05/5) \times 0{\cdot}1 = 0{\cdot}001$ volt. As the potentiometric drum is run at a low speed, there is negligible falsification of the half-wave potential. Even this small falsification is eliminated by standardizing against a cadmium solution, the half-wave potential of which is known with great accuracy. Figure 1 gives the log plot obtained for the polarogram of 1·034 millimolar cadmium in 0·1 N hydrochloric acid and 0·1 N potassium chloride. The slope of the line is 0·028 V indicating a reversible two-electron process. The accuracy of the method is indicated by the fact that all the points lie on a straight line. This method has been extensively used by the present author for different systems and the results are quite satisfactory.

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