Errors in Measuring the Wave-Height of Polarogram. II. Practical Errors of Graphical Construction

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(Received June 16, 1954)

Introduction

In the previous work[1] the errors in measuring the wave-height on a polarogram were mathematically discussed, and it was concluded that the relative errors in graphical construction on a polarogram might vary with the transformation of the polarogram by the changes of span voltage and sensitivity. In this paper the practical variations of errors are investigated for the sake of comparison with the mathematical conclusion.

Experimental

The intersections of tangents were constructed by ten polarographists on the polarograms printed photographically with a same printing ratio (0.45) from variously transformed original polarograms which were recorded of the same samples with various span voltages and sensitivities.

The original polarograms were recorded of the following three samples after oxygen removal with tne initial voltage of –0.3V vs. Hg-pool; and the span voltage and sensitivity are shown in Table I.

Sample A: $1\times10^{-4}N$ $Pb(NO_3)_2$+$2\times10^{-2}N$ $CdCl_2$
Sample B: $1\times10^{-4}N$ $Pb(NO_3)_2$+$1\times10^{-2}N$ $CdCl_2$
Sample C: $4\times10^{-4}N$ TlCl+$8\times10^{-3}N$ $CdCl_2$
(Each sample contains $1\times10^{-1}N$ KCl as an indifferent salt)

TABLE I
NOTATIONS OF POLAROGRAMS TAKEN WITH VARIOUS SPAN VOLTAGES AND SENSITIVITIES

		Sensitivity microamp./mm.		
		High	Medium	Low
Polarogram	A	0.004	0.010	0.020
	B	0.006	0.015	0.030
	C	0.008	0.015	0.030
Span Voltage	3V	00	01	02
	1V	10	11	12
	0.5V	20	21	22

The polarograph used here was Sargent Model XXI Polarograph, on whose recorder-paper the 1 mm.-scales on current-axis are printed and so

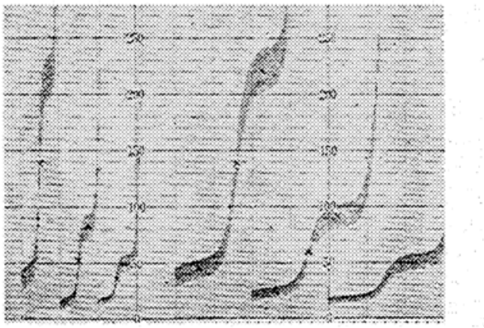

Fig. 3.

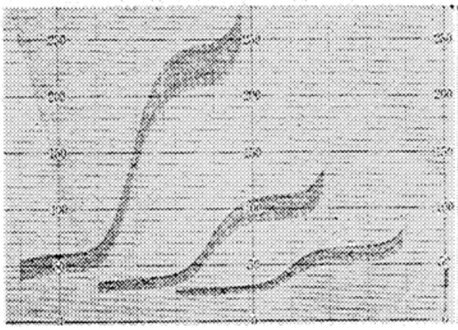

Fig. 4.

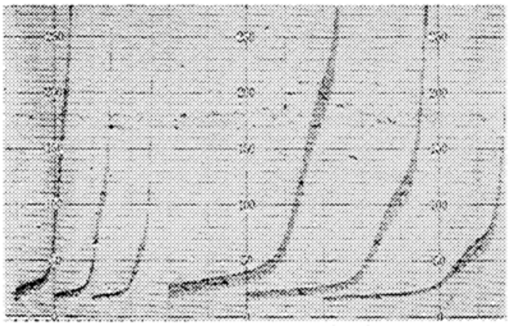

Fig. 5.

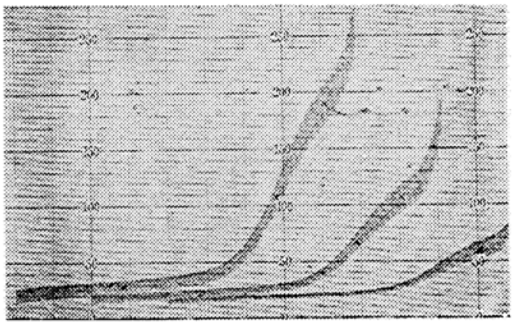

Fig. 6.

1) Y. Yasumori, This Bulletin, **27**, 554 (1954).

the positions of intersections of tangents could be read with these scales.

The tangents in polarogram A (Fig. 3 and 4) and B (Fig. 5 and 6) were drawn through the marked points corresponding to the inflexion-points. In Table II are shown the positions of intersections, in Table III the mean squares of relative deviations of positions of the points from their median to the respective wave-height and in Table 4 the mean squares of relative deviations of thh wave-heights from their median to the respective wave-height.

(The figures in Tables III & IV are values multiplied by 10^4 of the above mentioned.)

TABLE II

THE POSITIONS OF INTERSECTIONS

			Constructer									
Sample	Point	Polaro-gram	A	B	C	D	E	F	G	H	I	J
A	Y	00	208.1	210.8	208.1	209.0	202.9	205.0	209.3	208.6	209.0	202.3
		01	77.7	79.3	80.0	83.1	79.8	80.3	79.8	81.0	81.1	80.6
		02	48.1	49.7	47.7	50.0	48.2	47.4	48.5	48.8	49.6	49.4
		10	215.0	216.4	214.4	219.8	214.2	210.9	215.0	216.8	215.2	212.5
		11	86.9	90.8	89.2	91.9	89.0	88.7	89.3	89.9	90.2	88.4
		12	48.2	48.7	49.4	50.3	50.3	49.2	48.3	49.8	49.3	49.2
		20	214.0	222.8	214.3	221.2	218.2	218.2	216.1	219.1	219.4	220.2
		21	98.3	97.7	97.1	100.9	100.0	98.3	97.3	98.9	98.5	97.5
		22	57.5	57.9	57.6	58.0	57.6	57.2	57.2	57.9	57.0	57.2
	X	00	44.4	49.9	47.8	46.0	46.3	47.7	47.7	45.7	45.7	49.0
		01	18.8	17.9	19.3	18.6	18.3	18.2	19.7	17.3	18.7	18.4
		02	18.0	19.1	18.5	18.4	18.7	18.5	18.1	17.3	18.0	17.2
		10	51.0	54.8	54.0	51.1	50.2	52.4	51.3	48.6	50.0	52.9
		11	26.8	27.4	27.0	25.7	26.7	26.9	26.2	25.9	26.1	21.8
		12	19.7	18.9	19.1	18.8	17.9	19.3	19.3	18.3	18.5	18.9
		20	55.2	57.2	58.3	53.9	53.4	56.3	56.0	54.2	55.3	55.6
		21	36.2	36.7	36.1	36.0	36.2	37.0	37.6	35.8	35.5	37.0
		22	28.9	28.3	28.3	28.3	28.1	28.4	28.3	28.0	29.9	28.3
B	Y	00	174.1	174.6	175.9	177.0	179.2	175.3	176.0	181.2	178.4	173.5
		01	74.3	74.8	74.0	76.9	75.9	73.8	76.4	77.6	77.7	73.7
		02	37.0	38.7	38.5	39.4	39.4	39.4	37.7	39.8	39.2	37.9
		10	191.2	195.3	192.2	198.8	191.0	191.3	194.1	194.6	194.8	189.3
		11	74.0	75.2	72.4	76.2	74.1	74.0	73.8	74.8	75.3	72.9
		12	35.8	35.9	36.1	37.0	35.1	36.9	35.9	36.8	37.0	35.9
		20	198.4	196.9	195.3	199.2	194.4	192.4	191.7	196.3	193.4	191.8
		21	75.1	76.8	75.7	77.9	76.3	78.3	77.2	78.7	76.8	75.8
		22	37.9	37.2	38.2	38.9	39.9	38.6	38.2	38.8	37.1	38.0
	X	00	46.9	49.2	51.1	47.5	46.6	49.2	50.1	44.3	49.9	50.1
		01	31.1	31.3	31.9	29.3	32.0	29.9	31.5	29.1	29.6	32.2
		02	17.2	18.9	18.7	15.8	15.8	15.9	17.6	15.1	16.2	17.1
		10	86.8	83.2	87.8	82.2	85.3	84.6	83.9	85.1	85.2	84.7
		11	30.1	30.1	31.8	28.3	31.8	30.6	31.0	29.0	30.5	31.0
		12	14.3	15.2	14.7	13.3	14.8	14.2	14.0	14.1	14.2	13.8
		20	85.0	80.1	86.4	82.8	84.8	84.2	83.4	78.3	83.0	88.4
		21	31.2	34.9	33.3	34.9	32.9	33.1	32.2	32.2	34.1	33.4
		22	14.5	17.0	16.0	15.3	15.7	16.0	16.5	15.9	16.0	16.0
C	Y	00	175.0	176.5	158.6	180.7	187.8	166.0	152.2	194.0	167.6	185.5
		01	104.2	99.9	87.2	97.1	99.7	87.0	96.8	100.1	90.0	95.9
		02	59.0	58.8	45.9	60.0	54.9	63.3	62.1	56.2	55.2	55.0
		10	173.8	174.8	155.1	180.9	164.0	166.2	169.5	179.0	184.1	153.4
		11	96.0	97.2	88.8	97.4	96.0	89.9	96.0	97.8	104.0	91.0
		12	55.8	55.8	51.5	55.1	54.0	53.9	53.0	54.5	58.9	56.0
		20	151.4	170.0	164.1	181.8	168.8	172.1	169.5	178.2	178.0	165.1
		21	88.8	100.9	98.6	101.9	94.4	103.0	94.1	96.9	99.8	92.2
		22	53.4	57.0	54.2	56.9	59.1	57.2	57.0	57.7	55.0	55.3
	X	00	33.7	32.5	34.3	31.8	32.4	32.4	33.0	32.4	31.4	32.3
		01	25.7	25.0	25.6	23.4	24.3	24.7	24.4	24.7	24.9	24.8
		02	21.4	20.7	21.9	20.8	20.9	20.7	20.7	21.7	21.1	21.3
		10	40.1	40.1	41.2	40.0	41.9	40.0	40.8	38.8	40.9	40.0
		11	25.2	25.9	26.6	26.3	26.2	26.8	26.4	25.2	26.3	26.4
		12	20.6	21.4	20.5	20.1	21.4	21.7	21.4	20.6	21.7	21.1
		20	36.0	36.4	37.7	34.7	34.5	35.3	39.1	35.1	34.4	35.6
		21	28.2	27.2	26.7	26.5	28.3	27.1	28.2	27.3	27.7	27.1
		22	22.4	21.0	21.9	21.6	20.7	21.0	21.9	21.3	22.1	20.6

TABLE III

THE MEAN SQUARES OF RELATIVE DEVIATIONS OF POSITIONS OF POINTS FROM TMEIR MEDIANS

Span Voltage	Sample	Sensitivity: High		Medium		Low		Sum	
		Y	X	Y	X	Y	X	Y	X
3V	A	3.31	0.98	4.58	2.62	8.01	3.53	15.90	7.13
	B	3.50	2.76	11.56	5.95	24.80	30.47	39.86	39.18
	C	78.3	0.17	62.1	0.74	126.3	1.39	302.7	2.30
1V	A	1.96	1.28	4.41	0.83	5.29	2.69	11.66	4.80
	B	5.95	2.02	6.40	5.06	9.18	5.48	21.53	12.56
	C	54.9	0.40	38.2	0.61	32.1	3.10	125.2	4.11
0.5V	A	2.79	0.85	3.50	1.10	1.35	0.79	7.64	2.74
	B	5.29	6.15	6.60	6.71	12.67	8.29	24.56	21.15
	C	37.7	1.21	38.4	0.77	25.3	3.20	101.4	5.18
Sum	A	8.06	3.11	12.49	4.55	14.65	7.01	35.20	14.67
	B	14.74	10.93	24.56	17.72	46.65	44.24	85.95	72.89
	C	170.9	1.79	138.7	2.12	219.7	7.69	529.4	11.59

TABLE IV

THE MEAN SQUARES OF RELATIVE DEVIATIONS OF WAVE-HEIGHTS FROM THEIR MEDIANS

Span Voltage	Sample	Sensitivity: High	Medium	Low	Sum
3V	A	4.54	6.35	12.53	23.42
	C	82.8	67.1	191.0	340.9
1V	A	4.04	5.43	13.91	23.38
	C	61.9	35.2	29.9	127.0
0.5V	A	4.84	6.55	7.02	18.41
	C	44.9	46.4	36.2	127.5
Sum	A	13.42	18.33	33.46	65.21
	C	189.6	148.7	257.1	595.4

Discussion of the Results

(1) **Polarogram A.** — (*a*) *Intersection Y.* The values of respective sums in Table III become smaller with increasing sensitivity and decreasing span voltage. So this result is coincident with the mathematical result obtained with the assumption (2) in the previous paper. But in the high level of sensitivity and the low level of span voltage, this is not valid. In these levels the errors appear not to vary after such a manner that the assumption (2) alone holds.

(*b*) *Intersection X.* The values of the respective sum in Table III varies after the same manner as in (1, -a). But this is not valid in each level except the low level of sensitivity and the high level of span voltage. In this case, as each value is so small that the error in reading of the intersection may not be ignored, this result cannot be compared with the mathematical result.

(*c*) *Wave-height* (*h*). The values of respective sums in Table IV become smaller with increasing sensitivity, but they are not so affected by the change of span voltage. The cause for this seems to be, that the effect of error e_θ on construction of tangent through a inflexion-point of wave becomes more overwhelming with decreasing span voltage. For the errors of Y and X caused by e_θ are not independent of each other. If the errors of Y and X are independent of each other, the sum of these errors in a certain sensitivity and span voltage in Table III will be equal to the error of wave-height in the corresponding sensitivity and span voltage in Table IV[2], but if these errors are not independent of each other and further errors of Y and X are of the same sign, the sum of these errors will be smaller than the error of wave-height. It is obvious that the effect of error e_θ becomes more pronounced with decreasing span voltage, when the values in Tables III and IV are compared with each other on this standpoint.

(2) **Polarogram B.** — Polarogram B has almost the same wave-form as Polarogram A but its inflexion-points have not been marked on it previously.

(*a*) *Intersection Y.* The values of respective sums in Table III become smaller with increasing sensitivity, but they are not so much affected by the change of span voltage. And each value is greater than the corresponding value in Polarogram A. Perhaps the magnitude of error on construction of tangent may not vary after such a manner as discussed mathematically previously, where the point is not fixed, through which the tangent is to be drawn. The error of construction without the fixing of a point is greater than with the fixing of a point and this tendency becomes more effective when the span voltage and sensitivity are low.

(*b*) *Intersection X* The result is analogous to (2, -a).

(3) **Polarogram C.** — (*a*) *Intersection Y.* The values of respective sums in Table III

2) P. G. Hoel, "Introduction to Mathematical Statistics," (translated into Japanese by G. Taguchi) Kagaku-Shinko-Sha (Tokyo) (1950) p. 159.

become smaller with decreasing span voltage, but the effect of sensitivity is irregular. And the result in the medium level of span voltage is coincident with the mathematical result with the assumption (1), where the error in construction of a tangent along the curve just after the wave, is more remarkable. Nevertheless, the results in other levels of span voltage are inconsistent with the mathematical result with the assumption (1). In the high level of span voltage, the error in construction of a tangent through the inflexion-point of a wave may become more predominant with decreasing sensitivity.

(*b*) *Intersection X.* Each value in this case is so small that it may be nonsense to discuss this result with the above mathematical result.

(*c*) *Wave-Height h.* When the corresponding values in Table III and IV are compared with each other, it will be found that the error of wave-height is affected mainly by one of intersections (Y), but where the span voltage is low, by both intersections (Y and X), which are not independent of each other.

Summary

When the construction of tangent η on the curve just after the wave in a poralogram is more difficult, but the construction of other tangents are less difficult, it is concluded as follows.

In the case that the construction of η is a little more difficult, a polarogram with high sensitivity is desirable in order to minimize the relative error in measuring the wave-height. And here low span voltage is, to some extent, effective, but a polarogram too enlarged in abscissa is ill-conditioned. Next, in the case of the very difficult construction of η, the relative error of wave-height is minimum, when a polarogram is taken with lowered span voltage, in which the slope of a tangent is tan 45°. Here the error is not always minimum if the polarogram is recorded with lowered sensitivity.

The author wishes to express his hearty thanks to Prof. I. Tachi for his kind encouragement. The authors' thanks are also due to the members of the Polarographic Group in the Faculty of Agriculture, Kyoto University for their kind help in the construction.

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