# A New Method for the Precise Measurement of the Polarographic Current and Its Application in Digital Polarography

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In order to increase polarographic precision and sensitivity, the oscillopolarographic current was digitized and stored in a 100-channel pulse-height analyzer (PHA) operated in the multi-scaler mode (MS mode). An oscillopolarograph which could sweep the DC potential rapidly was combined with the PHA. The digitized oscillopolarographic current was repeatedly stored in the PHA, so that the statistical noise was reduced and the signal-to-noise ratio of the oscillopolarographic current was increased. Also, the drift due to the change in the experimental conditions was removed effectively by shortening the measurement time. Therefore, precision was efficiently improved by means of accumulation. The relative deviation was 0.25% at the concentration of the $5 \times 10^{-7}$ M cadmium ion. As an example of the application, trace amounts of copper, lead, and cadimum in 99.99% indium metal were analyzed.

Recent developments in electronics have resulted in various improvements of polarography, such as those of radio-frequency polarography and pulse polarography. Besides, digital accumulation and processing[1)] have been introduced to permit a high rate of data collection and greater accuracy, resolution, and precision. A small computer[2)] has been employed online in an electrochemical system to provide semiautomated polarographic measurements.

Recently several reports have been published concerned with the precise measurement of the polarographic current at a low concentration using an accumulator or a digital computer. Perone and Harrar *et al.*[3)] applied a rapid potential sweep and thus repeatedly accumulated the polarographic current. The relative deviation of their result was 0.1% at the concentration of 1 mM and 1.3% at the concentration of $2 \times 10^{-7}$ M. Matsuda and Tamamushi[4)] reported that the long-term integration of diffusion currents was reasonably accurate even at concentrations as low as $10^{-6}$ M. Shults, Fisher and Schaap[5)] demonstrated that a precision and accuracy of about 0.1% could be obtained by using the mode of comparative polarography and by measuring the difference between the diffusion currents of unknown and standard solutions. Lingane[6)] measured the diffusion current up to 0.1% and integrated it over an exactly known time which covered 50 or more mercury drops.

The detection limit in square-wave polarography is about $10^{-8}$ M, restricted by the capillary effect. If the statistical noises arising from the power supply, the capillary effect, etc. are sufficiently reduced by means of accumulation, a sensitivity of more than $10^{-8}$ M can be expected.

In this experiment, the oscillopolarographic current was digitized and a train of pulses proportional in number to the current was accumulated in the PHA. The statistical noise decreases in proportion to $1/\sqrt{n}$, where n is the number of repeated samplings. The coefficient of the variation in the oscillopolarographic current was improved by the accumulation.

## Experimental

*General.* A block diagram of the apparatus is shown in Fig. 1. The rapid DC potential sweep, on which the square-wave voltage is superimposed, is used; the alternating faradaic current is measured through the gate circuit, which is used to eliminate the charging current. After the alternating faradaic current is rectified, amplified, and converted into the voltage, the output voltage is changed into a train of pulses proportional in number to its voltage by using a digital voltmeter. The train of pulses is stored in the 100-channel PHA. The beginning of the channel scanning of the PHA is synchronized with the start of the potential sweep, so that each oscillopolarographic current in the same state of the mercury drops and at the same applied potential is repeatedly stored in the same channel of the PHA. Therefore, the channel advance corresponds to the potential sweep

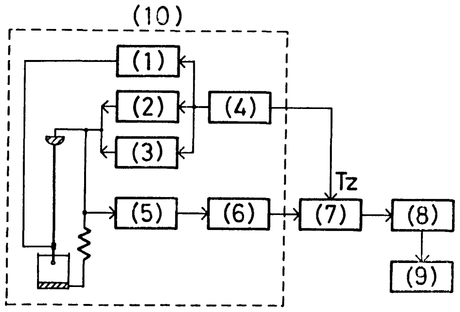

Fig. 1. The block diagram of the digital polarograph.
(1) Drop dislodger circuit, (2) Sweep potential generator, (3) Superimposed SW voltage generator, (4) Timing circuit, (5) Gate circuit, (6) Tuned rectifying detector, (7) Digital voltmeter, (8) Pulse height analyzer, (9) Digital printer, (10) Oscillopolarograph.
Tz is the start signal of the potential sweep.

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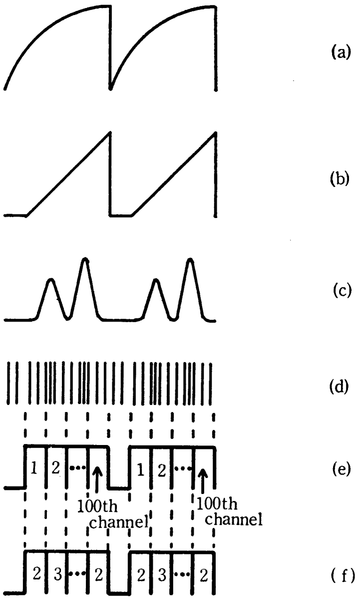

Fig. 2. The time sequence of the operation.
(a) Drop current, (b) Potential sweep, (c) Oscillographic SW polarogram, (d) Output of digital voltmeter, (e) The PHA has 100 channels., (f) Output of digital printer.

and the accumulated numbers of the pulses correspond to the oscillopolarographic current at a given value of the applied potential. The numbers of pulses stored in each channel of the PHA are printed out by a digital printer at the end of a predetermined number of scannings. The digital data thus obtained can be plotted as is shown in Fig. 5. The time sequence of the operation is shown in Fig. 2.

*Instrumentation.* *Oscillopolarograph (Yanagimoto digital polarograph PE 21)*: An oscillographic square-wave polarogram and an oscillographic direct-current polarogram can be measured. A mercury drop is detached by the drop dislodger, and the start time of the potential sweep is synchronized with the dislodgement of the mercury drop. The oscillopolarographic current is converted into voltages from 0 mV to +50 mV, which is proportional to its current.

*Digital Voltmeter (Takeda Riken 6154 B digital voltmeter)*: In this experiment, the digital voltmeter is used as a voltage-to-frequency converter. The output voltage from the oscillopolarograph is introduced into the digital voltmeter and then converted into a train of pulses proportional in number to its voltage. This digital voltmeter converts the input voltage of 100 mV into the frequency of 10 kHz. The height of the output pulse from the digital voltmeter is 4 V, and the rise time of the pulse is about 1 μs.

*Multichannel Pulse-height Analyzer*: A Toshiba 100-channel PHA (EDS-34206) is connected to a plug-in unit M (type UE 730-007); thus, the measurement can be performed in the multi-scaler mode (MS mode). The train of pulses from the digital voltmeter is stored in the PHA from the 1st channel to the 100th channel. In Fig. 3 the time sequence of the operation of the PHA is shown. The capacity of the PHA is $(10^5-1)$pulses/channel.

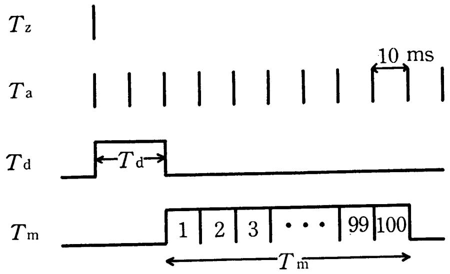

Fig. 3. The time sequence of the operation of the PHA.
$T_z$: The signal for the start of the measurement.
$T_a$: The signal for the channel advance.
$T_d$: The delay time of the scanning of the PHA.
$T_m$: The operating time of the PHA. When the sweep reaches the 100th channel, it goes back to the 1st channel and waits for the next $T_z$ signal.
All the time of the PHA refers to the clock signal generated by a 1 M Hz Xtal oscillator.

*Experimental Conditions.* In order to reduce the fluctuation of the current arising from the depleting effect,7) which was caused by the fact that the concentration of the depolarizer in the vicinity of the electrode decreased during the electrolysis, the actual measurement was started after electrolysis over 10 mercury drops using the same potential sweep as the actual measurement. The decrease due to the depleting effect was most marked at the beginning of the electrolysis; it reached a constant value after 10 mercury drops.7) Also, gelatin was added at 0.01% in order to decrease the variation in the current arising from the fluctuation of the solution. The temperature was controlled within ±0.01 °C by surrounding the cell with lagging material in order to limit the variation in the oscillopolarographic current due to temperature change within 0.015%. All the solutions were deoxygenated by passing pure nitrogen through for at least 10 min.

## Results and Discussion

It is impossible to avoid the error arising from quantization when the train of pulses is sampled repeatedly at definite intervals. The relation between the coefficient of the variation and the number of repeated samplings is shown in Fig. 4. In the actual measurement, other statistical noises arising from the power supply, the capillary effect, etc. are added. In order to measure the oscillopolarographic current at a low concentration, the residual current had to be elimi-

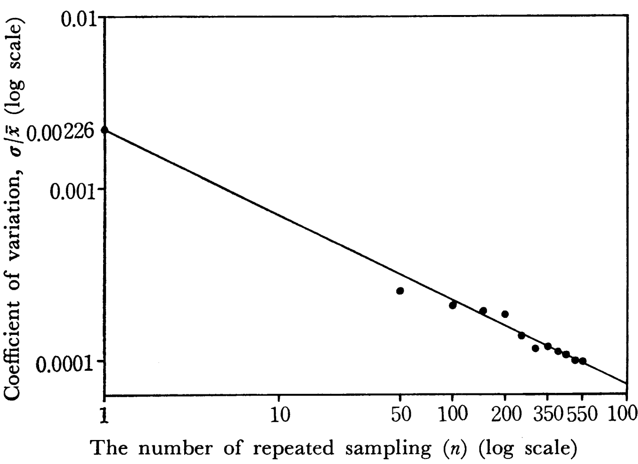

Fig. 4. The decrease of the coefficient of variation by accumulation.
Straight line: $\log \sigma/\bar{x} \propto -1/2 \log n$, $n$ is the number of repeated sampling.
●: Experimental

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TABLE 1. THE RELATION BETWEEN THE CONCENTRATION OF CADMIUM ION AND THE COEFFICIENT OF VARIATION OF THE OSCILLOPOLAROGRAPHIC CURRENT

| Concn. (M) | Method | $\bar{x}$ | $\sigma$ | $\sigma/\bar{x}$ | $m$ (mg/s) | $N$ |
|---|---|---|---|---|---|---|
| $10^{-3}$ | DC | 1171 | 1.10 | 0.0009 | 1.11 | 10 |
| $10^{-3}$ | SW | 1996 | 1.05 | 0.0005 | 1.11 | 10 |
| $5\times10^{-5}$ | SW | 2774 | 2.68 | 0.0010 | 1.11 | 16 |
| $5\times10^{-6}$ | SW | 3015 | 5.59 | 0.0017 | 1.11 | 20 |
| $5\times10^{-7}$ | SW | 1308 | 3.32 | 0.0025 | 1.09 | 25 |

Concn.: Concentration, $\bar{x}$: The accumulated numbers of pulses which correspond to the height of the cadmium peak by oscillopolaography, $\sigma$: Standard deviation, $\sigma/\bar{x}$: The coefficient of variation, $m$: Mercury flow rate, $N$: The number of repeated sampling.

nated. At first, the solution of the supporting electrolyte was scanned and the digitized residual current was stored in the PHA, whose channels were related to the applied potential. Next, after changing the sign of the memory, the solution containing the supporting electrolyte plus the sample was scanned under the same conditions as in the first scan. Consequently, an oscillopolarogram in which the residual current had been subtracted could be obtained. Table 1 shows the precision of the current measurements on solutions containing various concentrations of the cadmium ion. The relative deviation was 0.05% at a concentration of the 1 mM cadmium ion; this value was obtained by integrating the oscillographic square-wave polarographic current over 10 mercury drops. The relative deviation was 0.25% at a concentration of the $5\times10^{-7}$ M cadmium ion; this value was obtained by accumulating the oscillographic square-wave polarographic current over 25 mercury drops. It is evident that the statistical noise was reduced efficiently by accumulation. The change in the time constant of the square-wave oscillator, which changed the wave form of the superimposed SW voltage, had little effect on the precision of the current measurement (Table 2). The change in the amplitude of the superimposed SW voltage also had little effect on the precision of the current measurement (Table 3). Therefore, it is profitable to use the large amplitude of the superimposed SW voltage (30 mV), because the square-wave polarographic current is in proportion to the amplitude of the superimposed SW voltage. Table 4 indicates that the precision of the current measurement decreased as the rate of the potential sweep increased. Therefore, the sweep rate of 0.2 V/s was used in this experiment. As an example of application, trace amounts of copper, lead, and cadmium in 99.99% indium metal were analyzed. The indium metal was dissolved in concentrated nitric acid. The solution which contained the indium ion was heated until the indium nitrate had crystallized. The reduction potentials of the cadmium ion and the indium ion are

TABLE 2. THE RELATION BETWEEN THE TIME CONSTANT OF SW OSCILLATOR (SW Frequency-200 Hz) AND THE COEFFICIENT OF VARIATION

Sample 1 mM $CdSO_4$ in 1 M KCl

| Time const. (ms) | $\bar{x}$ | $\sigma$ | $\sigma/\bar{x}$ |
|---|---|---|---|
| 110 | 2995 | 3.25 | 0.0011 |
| 210 | 2876 | 3.13 | 0.0011 |
| 310 | 2796 | 2.62 | 0.00094 |
| 410 | 2743 | 5.08 | 0.0019 |
| 510 | 2709 | 3.18 | 0.0012 |
| 610 | 2673 | 2.11 | 0.00079 |
| 710 | 2649 | 2.83 | 0.0011 |
| 810 | 2623 | 2.78 | 0.0011 |
| 910 | 2605 | 1.73 | 0.00067 |
| 1010 | 2572 | 3.30 | 0.0013 |

TABLE 3. THE RELATION BETWEEN THE AMPLITUDE OF THE SUPERIMPOSED SW POTENTIAL AND THE COEFFICIENT OF VARIATION

Sample 1 mM $CdSO_4$ in 1 M KCl

| $\Delta E$ (mV) | $\bar{x}$ | $\sigma$ | $\sigma/\bar{x}$ |
|---|---|---|---|
| 1 | 2917 | 3.45 | 0.0012 |
| 2 | 1976 | 1.92 | 0.00097 |
| 5 | 2482 | 2.52 | 0.0010 |
| 10 | 2507 | 1.94 | 0.00077 |
| 20 | 2002 | 3.50 | 0.0017 |
| 30 | 2485 | 3.00 | 0.0012 |

$\Delta E$: The amplitude of the superimposed SW potential.

TABLE 4. THE RELATION BETWEEN THE RATE OF POTENTIAL SWEEP AND THE COEFFICIENT OF VARIATION

Sample 1 mM $CdSO_4$ in 1 M KCl

| Pot. (V) | $R$ (V/s) | $\bar{x}$ | $\sigma$ | $\sigma/\bar{x}$ |
|---|---|---|---|---|
| −0.439 | 0.1 | 3674 | 2.04 | 0.00065 |
|  | 0.2 | 2981 | 2.33 | 0.00078 |
|  | 0.3 | 2667 | 3.90 | 0.0015 |
| −0.001 | 0.3 | 1745 | 3.11 | 0.0018 |
|  | 0.5 | 1356 | 3.40 | 0.0025 |

Pot.: The initial potential (*vs.* Hg-pool), $R$: Sweep rate.

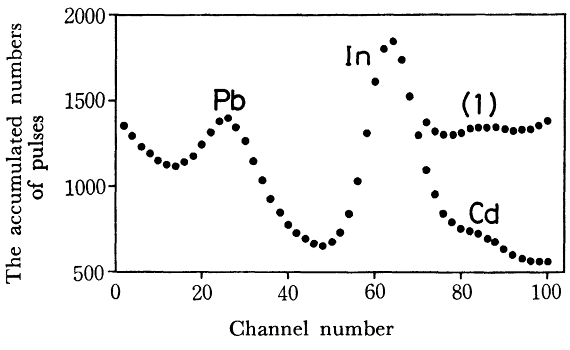

Fig. 5. The oscillographic SW polarogram of $1.5\times10^{-7}$ M cadmium ion, $2\times10^{-6}$ M lead ion and indium ion in 0.025 M $In(NO_3)_3$ and 1 M $H_3PO_4$.
$m=1.17$ mg/s, $T=21\pm0.01$ °C
Peak pot. ($Pb^{2+}$) = −0.402 V *vs.* SCE
Peak pot. ($In^{3+}$) = −0.530 V *vs.* SCE
Peak pot. ($Cd^{2+}$) = −0.594 V *vs.* SCE
(1): 0.025 M $In(NO_3)_3$ in 1 M $H_3PO_4$+0.54 M $HNO_3$
Peak pot. ($In^{3+}$) = −0.510 V *vs.* SCE
Peak pot. ($Cd^{2+}$) = −0.598 V *vs.* SCE

close together, and the waves overlap in almost all the supporting electrolytes. However, indium forms a complex with phosphate ions in phosphoric acid,[8] so the half-wave potential of the indium complex deviates from that of the indium ion. Fig. 5 shows an oscillographic square-wave polarogram of the cadmium ion, the lead ion, and the indium ion in 0.025 M indium nitrate plus 1 M phosphoric acid. The appearance of the indium peak may be attributed to the fact that the quantity of indium is so large that the complex formation can not mask the indium peak completely. However, if 0.54 M nitric acid is added, the cadmium peak appears distinctly (Fig. 5). The half-wave potentials of indium and cadmium differ by 63 mV in 1 M phosphoric acid, while the half-wave potentials differ by 88 mV in 1 M phosphoric acid plus 0.54 M nitric acid. In Figs. 6 and 7, oscillographic square-wave polarograms of the copper(I) ion and the lead ion in 0.025 M indium nitrate plus 1 M phosphoric acid are shown. The oscillographic square-wave polarograms of the supporting electrolyte are shown at the same time. It is obvious that very small amounts of the copper(I) ion and the lead ion are present in 1 M phosphoric acid. In Fig. 8 the relation between the accumulated numbers of the pulses and the concentrations of the cadmium ion is shown. Table 5 shows the quantitative analytical data of trace amounts of copper, lead, and cadmium in 99.99% indium metal.

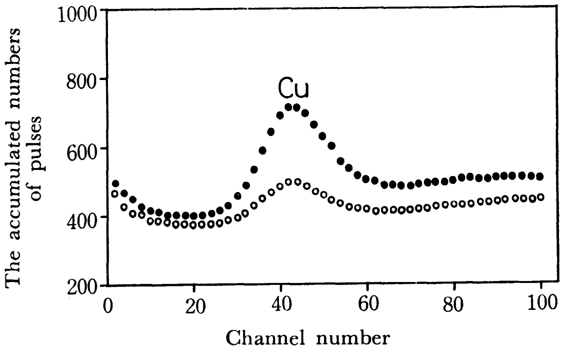

Fig. 6. The oscillographic SW polarogram of $8\times10^{-7}$ M copper(I) ion and indium ion.
●: in 0.025 M $In(NO_3)_3$ and 1 M $H_3PO_4$
○: in 1 M $H_3PO_4$ only
$m=1.14$ mg/s, $T=21\pm0.01$ °C
Peak pot. ($Cu^+$) = +0.018 V *vs.* SCE

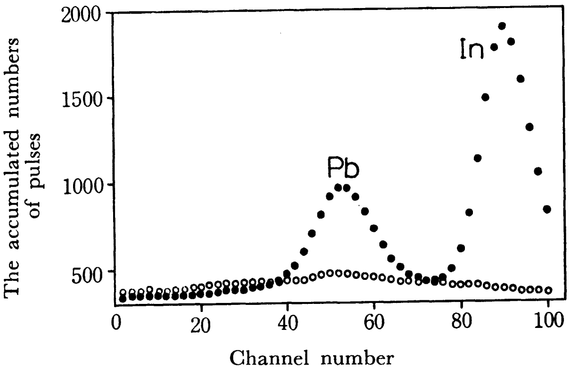

Fig. 7. The oscillographic SW polarogram of $2\times10^{-6}$ M lead ion and indium ion.
●: in 0.025 M $In(NO_3)_3$ and 1 M $H_3PO_4$
○: in 1 M $H_3PO_4$ only
$m=1.16$ mg/s, $T=21\pm0.01$ °C
Peak pot. ($Pb^{2+}$) = −0.402 V *vs.* SCE

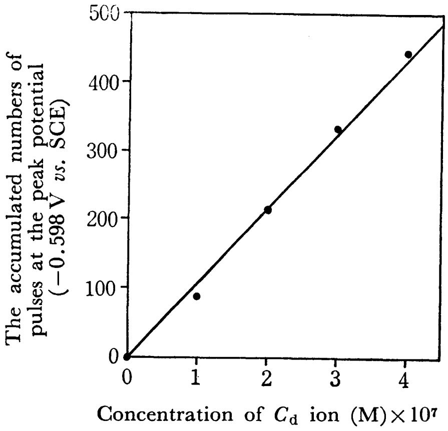

Fig. 8. The relation between the concentrations of cadmium ion and the accumulated numbers of pulses.

Table 5. The quantitative analytical data of trace amounts of copper, lead, and cadmium in 99.99% indium metal

| Metal | Contents (ppm) |
|---|---|
| Cu | 16 |
| Pb | 129 |
| Cd | 6 |

## Conclusion

As has been indicated in the quantitative analysis of a trace amount of cadmium in indium metal, the precise measurement of $10^{-7}$ M could be performed in this experiment. If the statistical noise is decreased sufficiently, a sensitivity as high as $10^{-8}$ M or even higher can be expected in the near future.

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