BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 499—500 (1974)

Computer-assisted In-phase AC Polarography: Determination of Cadmium(II) Ions

Shizuo Fujiwara, Michio Hirota, Katsuhiko Sawatari,
Hiroyuki Kojima, and Yoshio Umezawa
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received August 17, 1973)

Synopsis. An on-line polarograph is used to detect the in-phase component of the ac response. The applied ac voltage and resulting current are sampled simultaneously and multiplied and then integrated. The detection limit of Cd(II)(0.1 M KCl) is 1.85×10^{-7} M by accumulation.

In ac polarography, two kinds of electrolytic currents flow at the mercury solution interface: one is the faradaic current which has in-phase and out-of phase components with applied alternating voltage, and the other is the charging current, which is an out-of-phase component. Both phase components provide meaningful information about the electrode kinetics. In quantitative analysis, the in-phase component of the ac electrolytic current must be selectively detected without the superposition of any out-of-phase charging current, because the elimination of the charging current plays the most decisive role in enhancing the signal-to-noise (S/N) ratio. In view of the above conciderations, analog-type phase-sensitive ac polarography has successfully been used in trace analysis.[1-8)]

In the present study, a computer-assisted on-line polarograph was used to perform phase-sensitive(in-phase) ac polarography. In recent years, many instruments have been interfaced for purposes of sampling, handling, and data collecting and processing. With the availability of such systems, the purchase of various pieces of hardware is sometimes no longer necessary; *i.e.*, a digital computer sometimes performs functions numerically similar to those of hardware.[9)]

Method

Figure 1 shows the principle of the present method. By means of two channels of an analog to digital(A/D) converter, the polarographic current $I(t_i)$ and the applied alternating voltage $\Delta E(t_i)$ are sampled at the same time. The product of $I(t_i)$ and $\Delta E(t_i)$ is then integrated over the period of each cycle of the alternating voltage. The summed-up products give the in-phase (sine) component of the fundamental current.[1,3)] It is a great convenience that the method does not require any troublesome adjustment of the timing circuit which triggers the start of sampling at the time when the applied alternating voltage is zero.[10)] Furthermore, the limitation of the detection may be improved by the aid of the accumulation(ensemble average).

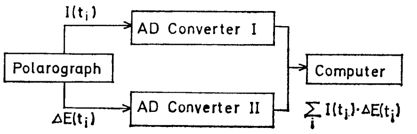

Fig. 1. The principle of the in-phase ac polarography.

Experimental

Apparatus. The block diagram of the present system is shown in Fig. 2. The polarograph used in the present work was built in our laboratory. The alternating voltage is applied by means of a Yokogawa Hewlett-Packard(YHP) function generator Model 3310B. Trigger pulses from a YHP frequency counter Model 5326B are fed into the computer to initiate the sampling.

Computer. Model JRA-5 of JEOLCO is used. The memory capacity of this computer is 4096 words, and the basic cycle time is 20 μs. The output voltage of the puncher-driving circuit is used to control the drop synchronizer. The waiting time before sampling can be set beforehand. The reference voltage signal and the current signal are input to a two-channel A/D converter, converted into 8-bit digital data, and stored in the memory. These two channels of the A/D converter are conveniently used in the present ex-

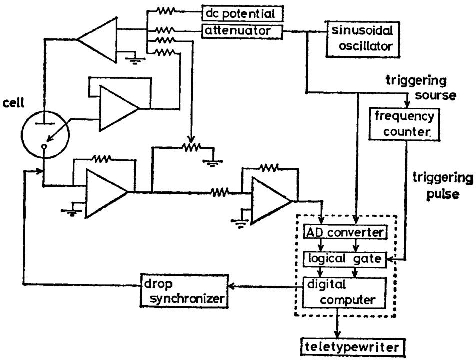

Fig. 2. The block diagram of the apparatus.

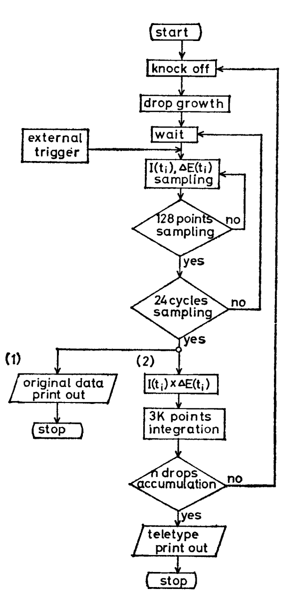

Fig. 3. The flow chart of the program.

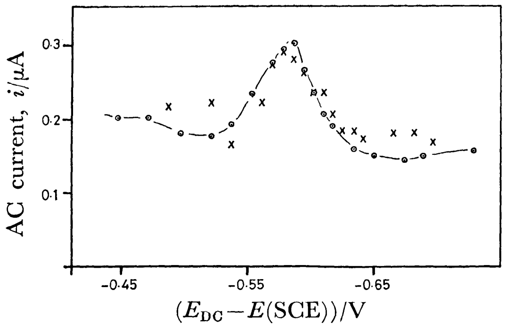

Fig. 4. In-phase ac polarogram of cadmium(II); the effect of accumulation.
$[\mathrm{Cd}^{2+}]=7.5\times10^{-6}$ M, [KCl]$=0.1$ M,
frequency$=27.9$ Hz, peak-to-peak voltage$=30$ mV,
○: ensemble average for 4 drops.
×: 1 drop.

periment to perform a simultaneous sampling of both the polarographic current $I(t_i)$ and the applied alternating voltage $\Delta E(t_i)$. These two digitalized signals($I(t_i)$ and $\Delta E(t_i)$) are multiplied, and the product is integrated over n cycles, where $n=24$. The output of the computer is usually typed on a teletypewriter or is converted into analog voltages and written on the chart paper of a recorder. In addition, the experimental data can be perforated on paper tapes in the digital form of 6 holes if necessary.

Program. A machine language is used for programing in which the number of instructions are 17, including the orders for A/D and D/A conversions. The flow chart of the present experiment is shown in Fig. 3.

Conditions. An alternating voltage of 27.9 Hz and 30 mV (peak-to-peak) was superposed on the direct voltage. The mercury reservoir height was 35.0 cm. The measurements were done at (25.0±0.5)°C.

Procedure

(1) Fix the electrode potential at an appropriate value.
(2) Knock off a mercury drop with a pulse from the computer.
(3) Wait $200n$ μs and then begin to sample the analog data of both the polarographic current and applied voltage simultaneously every $(180+20m)$ μs, where $n=2^{14}$ and $m=5$. Thus, 3072 words of the data storage capacity of the computer are occupied.
(4) Calculate Eq. (1) by means of the computer:

$$X=\sum_i I(t_i)\cdot\Delta E(t_i) \tag{1}$$

(5) In order to calculate the average of many drops, repeat the above procedures(2—4) and add the results.
(6) Write the results using a teletypewriter.

The above procedure is repeated above 20 times by changing the applied dc potential every 10 mV around the peak potential.

Results

The working curve of the present method was obtained by taking the Cd^{2+} ion in a 0.1 M KCl solution as an example. The peak current in this case is linearly proportional to the concentration of the Cd^{2+} ion in the range from 10^{-6} M to 5×10^{-4} M. As has been mentioned, in the present method, the calculation of the ensemble average of the output data for many drops easily be performed by means of the computer. A typical example showing the effect of ensemble average for 4 drops is demonstrated in Figure 4, where as appreciable enhancement of S/N ratio can be observed. The detection limit of this system was found to be 1.85×10^{-7} M for an accumulation of 8 drops, which is almost equivalent to that of conventional analog-type phase-sensitive ac polarography. For obtaining a larger S/N ratio, an accumulation of many more mercury drops would be necessary. Even with the advantages presented above, it should be mentioned that new developments which would avoid some time-consuming processes in the experiment are strongly desired: i) If much larger bit numbers of an A/D converter were available, the data for many mercury drops could be directly accumulated as they are, resulting in a decrease in the total experimental time. ii) A decrease in the cycle time of the computer would effectively reduce the time needed for the experiment.

References

1) D. E. Smith, *Anal. Chem.*, **35**, 1811 (1962).
2) J. W. Hayes and C. N. Reilley, *ibid.*, **37**, 1322 (1965).
3) D. E. Smith and W. H. Reinmuth, *ibid.*, **37**, 1892 (1965).
4) D. E. Smith, in A. J. Bard (ed.), "Electroanalytical Chemistry," Marcel Dekker, New York (1966), Vol. 1, p. 122.
5) R. F. Evilia and A. J. Diefenderfer, *Anal. Chem.*, **39** 1885 (1967).
6) R. de Levie and A. A. Muskovsky, *J. Electroanal. Chem.*, **20**, 181 (1969).
7) K. Matsuda, K. Takahashi, and R. Tamamushi, *Sci. Papers Inst. Phys. Chem. Research*, **64**, 62 (1970).
8) D. L. McAllister and G. Dryhust, *Anal. Chim. Acta*, **58**, 273 (1972).
9) G. M. Hieftje, R. I. Bystroff, and R. Lim, *Anal. Chem.*, **45**, 253 (1973).
10) H. Kojima and S. Fujiwara, This Bulletin, **44**, 2158 (1971).