COMPUTERIZED KALOUSEK POLAROGRAPHY

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SUMMARY

A versatile online computer-based system for Kalousek polarography features simultaneous recording of oxidation and reduction currents, averaging over successive scans, and processing of the polarographic data by curve-fitting. The accuracy for determinations of cadmium, potassium and lithium down to 10^{-5} M is $\pm 5\%$ for pulse rates up to 25 Hz.

Kalousek polarography has received little attention in recent years [1], although Kinard et al. [2] outlined important analytical applications of the method, such as the ability to distinguish between reversible and irreversible systems and the possibility of determining reversible systems in the presence of proton discharge. The theoretical foundations of Kalousek polarography are well established. Kambara [3] was the first to solve the differential equations for the diffusion of compounds undergoing reversible oxidation/reduction during electrolysis with a square-wave voltage at a stationary plane electrode.

Koutecký [4] extended the theory to a dropping electrode; his general equations were modified by Ružić [1] to show the mean current versus potential relationships for the various types of Kalousek measurements.

Computerization of the Kalousek method was undertaken to make the technique available to general online computer owners who lack the complicated dedicated equipment for Kalousek polarography. Furthermore, this work was done to study the possibilities of automatic processing of the data, the accuracy that can be obtained by the computerized method, and the decrease in the detection limit obtained by averaging successive scans.

To be economically attractive, the method should work in a multi-user environment, for despite the decreasing cost of mini- and micro-computers themselves, mass storage devices and interfaces like A/D- and D/A-converters make up a large part of the total cost of a system. Only if these peripherals can be shared among a number of applications, e.g. titrations, coulometric and polarographic determinations, etc., can a general online computer system compete successfully with dedicated equipment for these techniques.

Additional advantages of replacing dedicated titrimetric and electroanalytical

equipment by an online computer are the great flexibility and the capability of data processing offered by the computer system.

Application of the theory of Kalousek polarography

Koutecký [4] derived the equation for the instantaneous current that flows when a square-wave potential with $E = E_1$ for $mT \leq t < (m + \frac{1}{2})T$, and $E = E_2$ for $(m + \frac{1}{2})T \leq t < (m + 1)T$ is applied to a dropping electrode where a reversible system undergoes reduction/oxidation:

$$i = nFq (7D_O/3\pi)^{\frac{1}{2}} t^{2/3} \left\{ \mu_1 t^{-1/6} + \sum_{j=1}^L (\mu_1 - \mu_2) (-1)^j / [t^{7/3} - (jV)^{7/3}]^{\frac{1}{2}} \right\} \quad (1)$$

(The symbols used are listed in Table 1.) In this equation, $2V = T$ and $L = 2N$ for the case $NT < t < (N + \frac{1}{2})T$; and $2V = T$ and $L = 2N + 1$ for the case $(N + \frac{1}{2})T < t < (N + 1)T$. Also

$$\mu_1 = \left\{ \exp \left[\frac{nF}{RT} (E_1 - E_0) \right] C_R^* - C_O^* \right\} / \left\{ 1 + (D_O/D_R)^{\frac{1}{2}} \exp \left[\frac{nF}{RT} (E_1 - E_0) \right]^{\frac{1}{2}} \right\}$$

$$\mu_2 = \left\{ \exp \left[\frac{nF}{RT} (E_2 - E_0) \right] C_R^* - C_O^* \right\} / \left\{ 1 + (D_O/D_R)^{\frac{1}{2}} \exp \left[\frac{nF}{RT} (E_2 - E_0) \right]^{\frac{1}{2}} \right\}$$

Formula (1) can be rewritten to show separately the time-dependent and potential-dependent factors:

$$i = A \{ F_1(t) \mu_1 + F_2(t) (\mu_1 - \mu_2) \} \quad (2)$$

with

$$A = nFq (7D_O/3\pi)^{\frac{1}{2}}, F_1(t) = t^{-\frac{1}{6}}$$

and

$$F_2(t) = t^{2/3} \sum_{j=1}^L (-1)^j / [t^{7/3} - (jV)^{7/3}]^{\frac{1}{2}}$$

F_1 and F_2 were calculated for instantaneous current measurement at the center of the last half-period of E_1 , as well as for the center of the last half-period of E_2 , for various numbers of pulses per drop life of 960 ms. The results are given in Table 2.

For a fixed value of E_1 , and for E_2 changing stepwise with time, eqn. (2) results in the familiar S-shaped polarogram also known in sampled d.c. polarography. Disregarding the sign of the current, the Kalousek polarographic data can be fitted to the equation

$$i' = i_i / \{ \exp [(E_2 - E_{\frac{1}{2}})/S] + 1 \} \quad (3)$$

where i_i is the height of the polarographic wave observed, $S = RT/nF$, and i' is measured with the foot of the wave as the zero line.

In the case where only the oxidized form of the electroactive component is present in the bulk of the solution, combination of eqns. (2) and (3) gives:

TABLE 1

List of symbols

C_O^*	Concentration of oxidised form (Ox.) in bulk of solution
C_R^*	Concentration of reduced form (Red.) in bulk of solution
D_O	Diffusion constant of Ox.
D_R	Diffusion constant of Red.
E	Voltage of the dropping mercury electrode
F	Faraday's constant
j, m	Integers
n	Number of electrons transferred between Ox. and Red.
q	Area of mercury drop at time t
R	Gas constant
T	Absolute temperature
t	Time elapsed since start of mercury drop
V	Half period of square-wave potential

TABLE 2

Factors for instantaneous current in Kalousek polarography

Number of pulses per droplife of 960 ms	F_1 measurement at E_1	F_1 measurement at E_2	F_2 measurement at E_1	F_2 measurement at E_2
2	1.29	1.09	0.65	-1.83
3	1.18	1.07	0.98	-2.10
4	1.13	1.05	1.24	-2.33
6	1.09	1.04	1.65	-2.72
12	1.05	1.03	2.57	-3.62
16	1.05	1.03	3.05	-4.09
24	1.04	1.03	3.86	-4.89
32	1.03	1.02	4.54	-5.56
48	1.03	1.02	5.67	-6.70
96	1.02	1.02	8.23	-9.26

$$i_l = A \cdot F_2 \cdot C_O^* \quad (4)$$

and

$$E_{\frac{1}{2}} = (RT/nF) \ln (D_R/D_O)^{\frac{1}{2}} + E_0 \quad (5)$$

EXPERIMENTAL

Chemicals

Cadmium chloride (Analar), potassium chloride (Merck, reagent grade), lithium chloride (Merck, Suprapur) and mercury (Drijfhout, polarographic grade) were used as received. Tetraethylammonium perchlorate (TEAP, Eastman) was recrystallized from ethanol (Merck, reagent grade) and dried in vacuo at 40°C.

Apparatus

The polarographic system consisted of a Radiometer polarographic stand (type E64) equipped with a drop-life timer (type DLT1). A PDP-11/10 (Digital Equipment Corp.) online computer system with 16K memory was used with a dual disk drive (RKO5), LPS system for A/D and D/A conversion, and a Decwriter. The specifications of the LPS system were: 12 bits A/D converter with dual sample and hold option, range ± 5 V and ± 1 V; 12 bits D/A converter, range ± 10 V at 10 mA max. Also available in this LPS system is a programmable real-time clock with rates up to 1 MHz. A Keithley model 301 operational amplifier was used to convert the polarographic current to the A/D converter input voltage.

A schematic diagram of the system is given in Fig. 1. The dropping mercury electrode (DME) had the following characteristics: $m = 2.58 \text{ mg s}^{-1}$, $t = 3.4 \text{ s}$ in 1 M KCl. Throughout all experiments a mercury pool was used as auxiliary electrode as well as reference electrode. For the lithium determinations, the DME characteristics were $m = 1.93 \text{ mg s}^{-1}$, $t = 4.83 \text{ s}$ (1 M KCl, open circuit).

Polarographic procedure

Treatment of the samples and the cell was as described earlier [5]. For concentrations from 10^{-4} to 10^{-5} M, averaging over 8 successive scans was applied before curve-fitting the data. For the cadmium determinations, the background electrolyte was 1 M potassium chloride, whereas potassium and lithium were determined in the presence of 0.1 M tetraethylammonium perchlorate. In all determinations the staircase potential step was 10 mV per drop time. The cadmium determinations were carried out with E_1 at -0.200 V and E_2 ranging from -0.200 to -0.800 V. For the potassium and lithium determinations these values were -0.800 and -0.800 to -2.500 ; and -2.000 with -2.000 to -2.700 V, respectively.

Fig. 1. Schematic diagram of equipment for computer-controlled Kalousek polarography.

COMPUTER PROGRAMS

The software for the fully computerized Kalousek polarography was developed as a set of several separate programs performing the following functions: control of the experiment and measurements; reduction of the experimental data to current versus square-wave amplitude tables; averaging of the current versus square-wave amplitude curves over successive scans; display of the polarograms on a strip-chart recorder or in digital form; curve-fitting of the polarograms to obtain limiting current, half-wave potential, and slope of the log plot.

The programs were to run under a 3-user real-time operating system with background facilities developed in this laboratory for the PDP-11/10. Under this operating system the real-time user has access to a software clock with a period of 120 ms derived from a line frequency clock and a programmable clock with rates up to 1 MHz. The programs for the control of the experiment and the display of the polarograms are written for the real-time environment while the other programs run in the background.

Kalousek polarography is mainly a matter of timing with regard to the pulses applied to the cell and the current measurement. In the real-time program that performs the Kalousek experiment, the square-wave voltage applied to the cell is generated under interrupt with the aid of the programmable clock from the LPS system. The number of pulses is restricted to the following set: 96, 48, 32, 24, 16, 12, 6, 4, 3 and 2 pulses per drop time. Current and cell voltage measurements are done simultaneously, but only during a time slice of 40 ms each 120 ms because of the nature of the operating system. They are initiated by the software clock. Current and cell voltage data are written to disk per drop lifetime. The most important routine in the program is the interrupt routine for the software clock; a flow diagram is given in Fig. 2. The main program senses continuously the flags MFLAG and DISKFLAG which are set by this interrupt routine.

When MFLAG is set, the main program performs the current and cell voltage measurements at a rate of about 2.5 kHz. The setting of DISKFLAG by this clock routine causes the main program to transfer the data from memory to disk. The software clock routine also controls the value of the pulse amplitude (VPULSE). The LPS-clock routine uses this value in combination with the value of the pulse base potential to generate square-wave voltage of the cell.

Timing diagrams for the square-wave voltage applied to the cell and the current measurements for 4 and 96 pulses per second are given in Figs. 3 and 4, respectively. Figure 5 shows the cell voltage versus time for 4 pulses/drop over the first 5 drops.

The next program reduces the current and cell voltage data acquired per drop in one or more 40-ms time windows to 3 values, i.e. current at the center of the last negative-going pulse half, current at the center of the last positive pulse half, and cell voltage at the center of the last pulse. To reduce

Fig. 2. Flow diagram of program for Kalousek polarographic experiment.

Fig. 3. Timing diagram for cell voltage generation and current-voltage measurements for 4 pulses per drop time of 960 ms.

the influence of line noise on the data, current values are averaged over that part of the half period where the charging current has decayed.

If required, the next program of the set can accumulate the constructed tables comprising the polarograms for averaging over a preset number of successive scans.

When the final polarograms are available, they are displayed by a real-time program on a chart recorder by outputting the current values normalized to

Fig. 4. Timing diagram for cell voltage generation and current-voltage measurements for 96 pulses per drop time of 960 ms.

Fig. 5. Cell voltage versus time for 4 pulses/drop over the first 5 drops.

fit the D/A converter connected to the recorder at fixed time increments. The data can also be presented in tabulated numerical form.

Finally the polarographic data are processed by a 3-parameter curve-fitting program to obtain limiting current, half-wave potential, and slope of the log plot. This program is the same as described earlier for the processing of sampled d.c. polarograms [5].

A block diagram of the various stages is given in Fig. 6.

Fig. 6. Flow diagram for complete set of programs for fully computerized Kalousek polarography.

RESULTS AND CONCLUSIONS

All determinations were carried out at a drop lifetime of 960 ms.

Table 3 shows the limiting currents measured at 48 and 16 pulses per drop for various concentrations of cadmium, potassium and lithium; there is a good linear relationship between limiting current and concentration for these Kalousek type II (Heyrovsky's [6] notation) measurements. In all cases the pulse base potential chosen was far more anodic than the halfwave potential, whereas the pulse amplitude was changed in 10 mV steps well into the cathodic limiting range.

For cadmium and potassium, the type I measurements also give useful results (Table 4). For lithium, the type I wave is completely masked by the hydrogen ion discharge wave.

The increase in sensitivity with higher pulse rates is demonstrated in Table 5 for potassium; the mean i_l^I/c and i_l^{II}/c values for the various numbers of pulses per drop, divided by the corresponding theoretically calculated F_2 values, are also given. The agreement between theory and experiment is better for the type I measurements than for the type II measurements. Despite the irregularities for 48 and 16 pulses per drop in the type II measurements, the theoretically calculated F_2 values serve to calculate the sensitivity that can be obtained at a given Kalousek frequency. The accuracy of the determinations decreases at pulse rates of 32 pulses per drop and higher; this may be caused by the relatively greater uncertainty in the location of the current measurements at the center of the pulse half periods.

As the reduction of oxygen at the DME is strongly irreversible, there is no interference from oxygen in the recording of type II waves. Table 6

TABLE 3

Kalousek type II limiting currents for Cd^{2+} , K^+ and Li^+

Cadmium					Potassium					Lithium				
48 pulses/ drop			16 pulses/ drop		48 pulses/ drop			16 pulses/ drop		48 pulses/ drop			16 pulses/ drop	
Conc. ^a	<i>i</i> _l ^b	<i>i</i> _l /c ^c	<i>i</i> _l ^b	<i>i</i> _l /c ^c	Conc. ^a	<i>i</i> _l ^b	<i>i</i> _l /c ^c	<i>i</i> _l ^b	<i>i</i> _l /c ^c	Conc. ^a	<i>i</i> _l ^b	<i>i</i> _l /c ^c	<i>i</i> _l ^b	<i>i</i> _l /c ^c
32.0	7.94	2.48	2.18	0.68	38.4	7.55	1.97	2.11	0.55	38.4	5.38	1.40	1.36	0.35
24.0	6.38	2.65	1.73	0.72	29.1	6.85	2.35	1.71	0.59	29.1	4.17	1.43	1.02	0.35
16.0	4.63	2.89	1.11	0.69	19.6	3.91	1.99	1.10	0.56	19.6	2.78	1.41	0.70	0.36
8.0	2.19	2.73	0.58	0.72	15.0	3.69	2.46			15.0	2.14	1.42	0.50	0.33
4.0	0.89	2.22	0.31	0.78	10.0	2.82	2.82	0.56	0.56	10.0	1.21	1.21	0.35	0.35
2.0	0.52	2.60	0.13	0.65	5.0	1.36	2.72	0.31	0.62					
Mean		2.57		0.71			2.38		0.57			1.37		0.35
<i>σ</i>		8%		6%			14%		5%			7%		3%

^a($\times 10^{-4}$ M), ^b μA , ^c($\times 10^4 \mu\text{A mol}^{-1}$).

TABLE 4

Kalousek type I limiting currents for Cd^{2+} and K^+

Cadmium					Potassium				
Conc. ^a	48 pulses/ drop		16 pulses/ drop		Conc. ^a	48 pulses/ drop		16 pulses/ drop	
	i_l^b	i_l/c^c	i_l^b	i_l/c^c		i_l^b	i_l/c^c	i_l^b	i_l/c^c
32.0	11.94	3.73	6.48	2.03	38.4	8.48	2.20	5.53	1.44
24.0	8.62	3.59	4.84	2.01	29.1	8.69	2.98	4.25	1.46
16.0	6.31	3.94	3.27	2.04	19.6	4.96	2.53	2.80	1.42
8.0	3.18	3.97	1.58	1.97	15.0	3.87	2.58		
4.0	1.36	3.40	0.84	2.10	10.0	2.79	2.79	1.38	1.38
2.0	0.69	3.46			5.0	1.69	3.38	0.71	1.42
1.0	0.30	3.00							
Mean		3.58		2.03			2.74		1.42
σ		9%		2%			15%		2%

^aFor footnotes, see Table 3.

TABLE 5

Sensitivity for Kalousek type I and II measurements at various pulse rates

No. of pulses per drop. ^a	Potassium				Cadmium			
	$i_l^I b$	$i_l^{II b}$	$i_l^I c$	$i_l^{II c}$	$i_l^I b$	$i_l^{II b}$	$i_l^I c$	$i_l^{II c}$
	c	c	cF_1^I	cF_1^{II}	c	c	cF_1^I	cF_1^{II}
48	2.74 ± 0.41	2.38 ± 0.33	0.41	0.42	3.48 ± 0.11	2.32 ± 0.19	0.52	0.41
32	2.00 ± 0.05	1.19 ± 0.10	0.36	0.26	2.79 ± 0.17	1.55 ± 0.06	0.50	0.34
24	1.84 ± 0.05	1.10 ± 0.01	0.38	0.29	2.28 ± 0.19	1.25 ± 0.05	0.47	0.32
16	1.42 ± 0.03	0.57 ± 0.03	0.35	0.19	2.05 ± 0.19	0.66 ± 0.02	0.50	0.22
12	1.07 ± 0.05	0.70 ± 0.01	0.30	0.27	1.69 ± 0.10	0.79 ± 0.03	0.47	0.31
6	0.96 ± 0.03	0.47 ± 0.02	0.35	0.28	1.22 ± 0.11	0.52 ± 0.03	0.45	0.32
3	0.75 ± 0.02	0.22 ± 0.02	0.36	0.23				

^aDrop time, 960 ms. ^b($\times 10^4 \mu\text{A mol}^{-1}$). ^c($\times 10^4 \mu\text{A mol}^{-1} \text{s}^{\frac{1}{2}}$).

shows the results of cadmium determinations of type II with and without prior removal of oxygen. Within the accuracy limits there is no difference in the limiting current data. However, there is a significant shift in half-wave potential from 651 ± 3 mV for the deoxygenated samples to 684 ± 3 mV in the presence of oxygen. A possible explanation is a reaction between cadmium ions and reaction products of the reduction of oxygen.

The improvement of the signal-to-noise ratio by averaging over successive scans, and the resulting increase in the accuracy of the determination of the limiting current, was found from a series of measurements of $2.91 \times 10^{-4} \text{ M K}^+$ in 0.1 M TEAP. For averaging over 8 scans, i_l^I was $3.40 \mu\text{A} \pm 3.0\%$; averaging over 64 scans gave $3.43 \mu\text{A} \pm 1.6\%$.

TABLE 6

Kalousek type II limiting currents for cadmium at 48 pulses per 960 ms drop time with and without prior removal of oxygen

Conc. ^a	Oxygen present		Oxygen absent	
	i_{II}^b	i_{II}/c^c	i_{II}^b	i_{II}/c^c
38.4	9.04	2.35	8.47	2.20
29.1	6.90	2.37	7.04	2.41
19.6	4.43	2.26	4.69	2.39
15.0	3.46	2.30	3.24	2.16
10.0	2.30	2.30	2.43	2.43
5.0	1.15	2.30	1.22	2.44
Mean		2.31		2.33
σ		2%		5%

^aFor footnotes, see Table 3.

Averaging over successive scans can also be used to lower the detection limit of the method. As there is practically no depletion of the bulk of the solution for Kalousek measurements at higher frequencies, time is the only limiting factor in this process. Some examples are given in Table 7 for cadmium determinations in the 10^{-6} M range for 48 pulses/drop. It will be clear that the method becomes impracticable for concentrations below 3×10^{-6} M.

As to the duration of the complete cycle of data acquisition and data processing, the following figures are typical values: experiment, 1–2 min for one scan; recording of the polarogram, 0.5–1 min; and the curve fitting, 1–3 min for one wave. This amounts to 1–6 min for the complete cycle.

TABLE 7

Determination of cadmium by Kalousek type II polarography with averaging over successive scans at 48 pulses per 960 ms drop time

Cd added ($\times 10^{-6}$ M)	Cd found ($\times 10^{-6}$ M)	Deviation (%)	No. of scans averaged
6.89	6.42	−7	47
3.33	3.53	+6	64
1.48	1.05	−29	128
1.00	1.77	+77	237

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