INSTRUCTION MANUAL
FOR

DROP LIFE TIMER
Type DLT1

TABLE OF CONTENTS

	page
SECTION A - GENERAL DESCRIPTION	3
1. The Drop Life Timer, DLT1	3
2. Rapid Polarography and Tast Polarography	4
3. The Operating Principle	5
SECTION B - THE CONTROLS	7
SECTION C - SPECIFICATIONS	10
1. Drop Life Timer, DLT1	10
SECTION D - OPERATING INSTRUCTIONS	12
1. Preparing the Equipment	12
2. Rapid Polarography	12
3. Recording a Tast Polarogram	15
4. Derivative Tast and Rapid Polarography	17
SECTION E - EXAMPLES OF APPLICATIONS	19
1. Examples	23

DROP LIFE TIMER
TYPE DLT 1

Section A. General Description

1. The Drop Life Timer, type DLT1,

The Drop Life Timer, type DLT1, is used in conjunction with a polarographic setup consisting of the Polariter, type PO4, and the Electrode Assembly, type E65, for dc polarography employing a dropping mercury electrode.

Use of the Drop Life Timer allows for purely electrical control of the drop life from 0.1 second and up to 10 seconds, provided that the natural life of the mercury drop does not prohibit the choice of the slowest drop rate settings.

Apart from controlling the actual drop rate, the DLT1 makes it possible to divide the drop life into a blanking period an a subsequent recording period, so that the DLT1

Fig.1: The Drop Life Timer, type DLT1

can be utilized both for Rapid Polarography (i.e. polarography based on short drop lives) and for Tast Polarography (i.e. polarography in which the polarographic current is recorded only during the final part of the drop life). It should be noted, however, that the polarographic setup is still suitable for polarographic recordings by the conventional method.

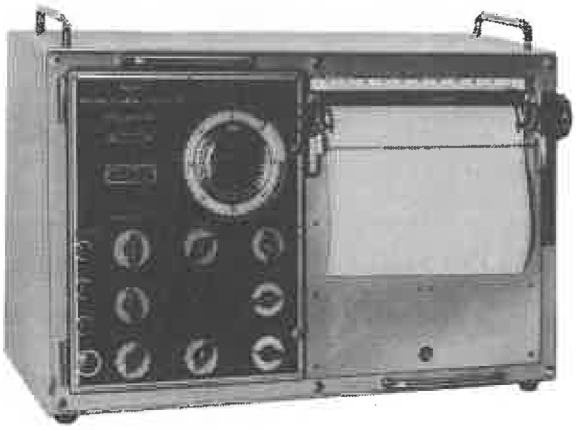

Fig. 2. The Polariter, type PO4

Before setting up the Drop Life Timer, type DLT1, with the polarographic equipment, it is necessary to modify the PO4 Polariter proper if this instrument is of the type PO4 f, or of a still earlier series. The installation of the Modification Kit (900/213 for PO4 d & f; 900/213-900/214 for PO4 a, b & c) should be carried out at a service shop authorized to service Radiometer instruments.

The Electrode Assembly, type E64, used for conventional dc polarography can be modified into the above mentioned Electrode Assembly, type E65, by means of

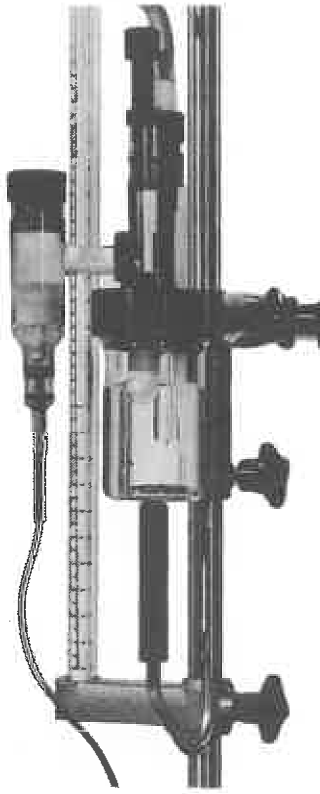

Fig. 3. The Electrode Assembly, type E64

the Kit for Drop Life Control, type D453, which includes a drop detaching mechanism for the mercury capillary electrode. The modification is easily carried out and can be done by any laboratory technician.

2. RAPID POLAROGRAPHY AND TAST POLAROGRAPHY

In conventional polarography the drop life varies with the polarographic voltage, so that the drop life in aqueous solutions, for instance, is shortened considerably at voltages exceeding 1.2 V.

Polarography by means of controlled drop

Fig.4. The Electrode Assembly, type E65

life, however, renders the drop life independent of the polarographic voltage, so that polarographic recordings can be accomplished in a voltage range which – in the cathodic direction – is restricted solely by the decomposition of the electrolyte medium (i.e. usually incipient liberation of hydrogen).

A further advantage of using controlled drop life for rapid and tast polarography lies in the fact that much less damping is required than for conventional polarography under otherwise identical operating conditions, so that a polarogram recorded in this manner will provide a more accurate reproduction of the polarographic current. Incidentally, by applying only very slight damping it is possible to obtain an almost smooth polarographic curve when the depolarization concentrations are greater than 10^{-4} M, thus facilitating accurate evaluation of polarograms in routine analyses.

Examples are given in Section E page 19.

3. THE OPERATING PRINCIPLE

Embodied in the DLT1 is a stabilized power supply that provides the voltages -24V and +5.6V with respect to chassis to a series of pulse circuits whose main functions are illustrated in the block diagram Fig.5.

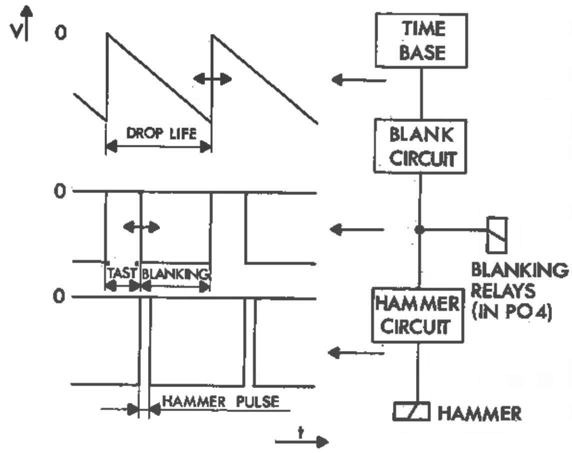

Fig. 5. Simplified Block diagram of the Drop Life Timer, type DLT1, with indication of the electrical signals from the different units.

In addition, the DLT1 is equipped with a synchronizing circuit to ensure that drop life, Tast period, and blanking period actually are whole multiples of the periodic time of the line voltage used.

Besides the blanking relay shown in the block diagram, the PO4 unit is equipped with a relay for the purpose of slightly reducing the amount of damping when the PO4 is used for rapid or Tast polarography.

Section B. The Controls

Note: The encircled numerals refer to the drawing.

a. Cables, Plugs, and Jacks.

The Back Panel

Power cord, cable with multiplug for connecting to front panel of the PO4 unit, and grounding jack are located on the back panel.

The Front Panel

1 Jack for hammer D4562
2 Jack for synchronizing generator (peak value: less than 50 V)

b. Power Switch, Selector Switches and Controls

3 and 4 DROP LIFE

The drop life is controlled by means of a pushbutton switch and a rotary pointer knob at its right side. The dial of the pointer knob indicates the approximate life of each drop in tenths of a second when the left pushbutton is depressed, and in full seconds when the right pushbutton is depressed.

The drop life can be set to any value between 0.1 and 10 seconds.

5 and 6 BLANKING TIME

The blanking period is controlled by means of the bottom pushbutton switch and a rotary pointer knob at its right side. With pushbutton 0 depressed, the PO4 will register the polarographic current throughout the drop life, and consequently the only difference from conventional polarography is the fact that operations in the present case are carried out with controlled drop life and reduced damping. This, then, is the pushbutton setting used in simple rapid polarography.

By depressing the pushbutton 30-80 and manipulating the rotary pointer knob, it is possible to control the length of the blanking period, viz. that interval in

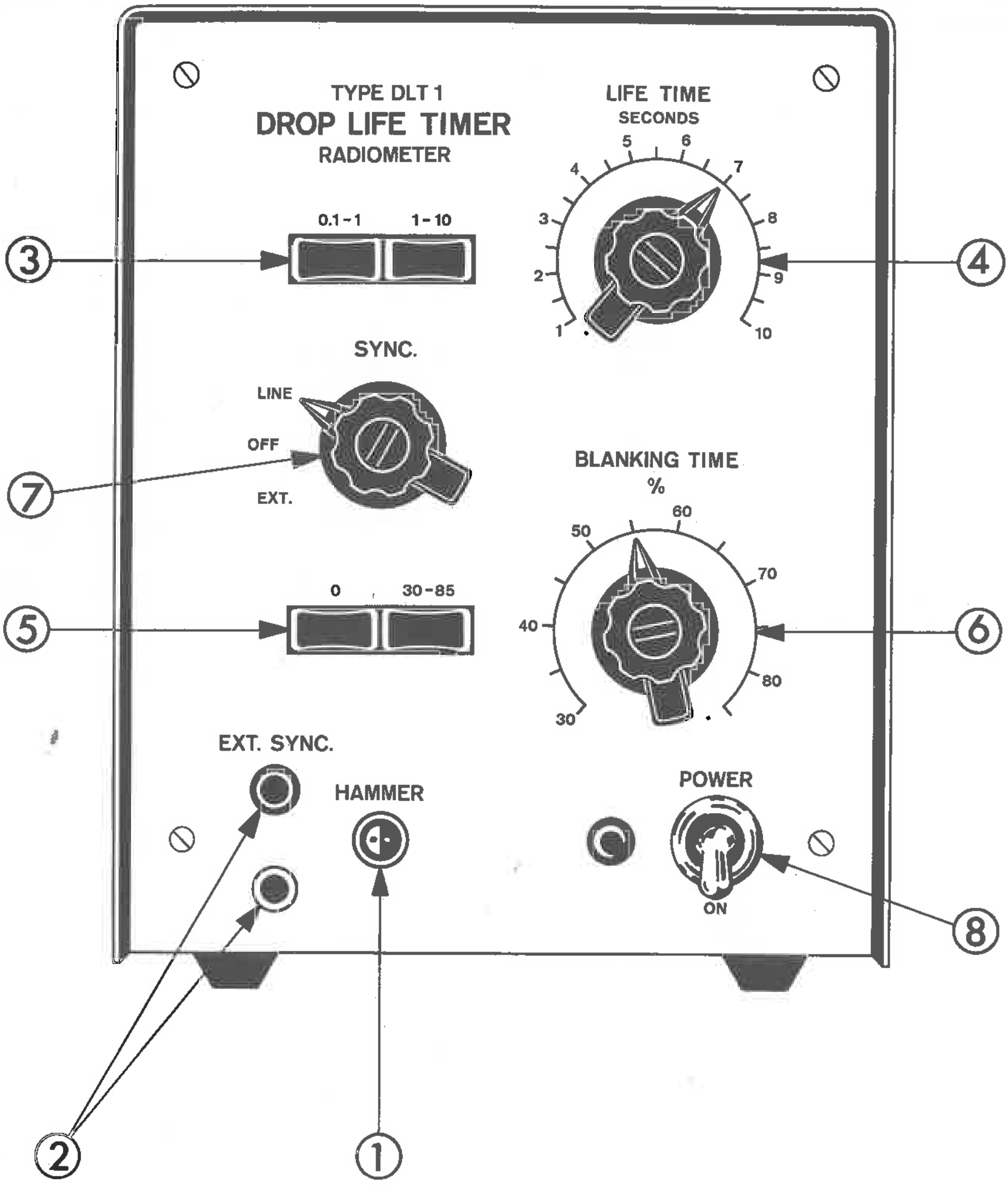

Fig.6. Front plate of DLT1

the early life of the drop during which the PO4 does not record the polarographic current. The duration of the blanking period can be read on the pointer knob dial as a percentage of the drop life. This, then, is the setting used in Tast polarography.

⑦ SYNC

Three positions are provided.

LINE

Normally, the synchronization switch is set to position LINE, which means that drop life and blanking period are controlled by the line frequency, whose stability is a determining factor for the reproducibility of drop life and blanking period. In this case drop life and blanking period constitute a whole number of line periods, so that the drop life control occurs stepwise at intervals of approx. 0.02 second.

OFF

Continuous, free-running regulation of drop life as well as blanking and Tast periods is possible.

EXT

When the synchronization switch is in position EXT., the DLT1 can be controlled by means of an external ac voltage. The generator is connected to the two jacks marked EXT. SYNC. on the lower left-hand side of the front panel.

(8) POWER

In position OFF, the PO4 may be used for conventional polarography without removing the hammer or the cable inserted in the front panel of PO4.

In position ON, hammer and blanking relay will operate according to the settings of the controls. Simultaneously, the damping within the servomechanism will be reduced to about half its normal value. This signifies that the effective damping for PO4 during a recording of a Tast polarogram with 50% blanking will be almost the same as the normal damping (DLT1 POWER OFF) without changing the position of the DAMPING switch. As regards damping in the ranges 0.02, 0.03, and 0.05 µA full scale, see Appendix "Technical Information".

Section C. Specifications

1. Drop Life Timer, type DLT1

DIMENSIONS:

Height 190 mm

Width 145 mm

Depth 220 mm

Weight 3.2 kilos

Power Supply

115V ±20%

220V ±20%

45-65 cps

Power Consumption 10 W

Ambient Temperature 0-50°C

Drop Life 0.1 - 10 seconds

Tolerance: ±10% of scale reading

Dependence on Line Voltage:

Typically 3% for changes from 20% undervoltage to 20% overvoltage

Dependence on Ambient Temperature:

Typically 1 - 2% for variations from 0°C to 50°C

Short-time Stability: Typically 0.05%.

Blanking Time

30 - 85% and 0%, the accuracy obtained depending on the setting - thus:

	Actual Bl.	
Set Blanking %	Min.	Max.
30	20	40
85	81	89

The dependence on line voltage and temperature and the short-time stability are practically the same as quoted for the drop life.

Synchronization

Provision for synchronizing with frequencies above 10 cps. Required synchronizing voltage (sinusoidal ac voltage): approx. 3 V_{eff} at 50 cps. The amplitude of the ac voltage must not exceed 50 V.

Synchronization with the line frequency can be carried out internally.

Hammer Pulse 24 V Duration 18–27 ms

In case the DLT1 is to be used for some purpose that does not require the original blanking relay and hammer, the following loading requirements must be observed:

Connection to Blanking output (3–4 in the multiconnector P101) min. 1.2 kΩ.

Connection to Hammer output: min. 130 Ω (residual current from hammer output is lower than 1 mA).

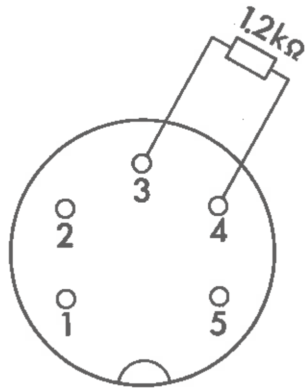

Fig.7. Multiconnector P101 with a resistor of 1.2 kΩ

Section D. Operating Instructions

1. PREPARING THE EQUIPMENT

1) Connect the Polariter PO4 and the Drop Life Timer DLT1 to a power line.

2) Insert the multiplug of the gray cable leading from the back panel of DLT1 into the multipole socket situated beneath the electrode terminals on PO4.

3) Mount the electrode assembly (see Appendix of PO4 Instruction Manual or Manual for Electrode Assembly E65).

4) Connect the leads from the mercury reservoir and the calomel electrode of the electrode assembly to the electrode terminals on PO4.

5) Connect the lead from the hammer of the electrode assembly to the hammer jack on the front panel of DLT1.

6) Switch on power of PO4 and DLT1.

2. RAPID POLAROGRAPHY

Recording a Rapid Polarogram of the Test Solution, Type S3001.

(1) Set up the PO4 (see PO4 Instruction Manual, Section 2.2).

(2) Set up the Electrode Assembly (see Appendix BI and Appendix B2.2 of PO4 Instruction Manual).

(3) Set up the DLT1 as described above (Preparing the Equipment).

(4) Make the following settings of PO4:

a) SELECTOR:
ZERO

b) CHART FEED:
OFF

c) A-gear:
0.1 V per cm

d) CHARTFEED B:
8 cm per min. (FORWARD)

e) SENSITIVITY
20 μA full scale

f) DAMPING:
1

g) DERIVATIVE CIRCUIT:
OFF

h) SET ZERO:

corresponding to a recorder reading at approx. 10%

i) COMPENSATION:

None

(5) Prepare the sample

(a) Pour 15-20 ml of the test solution, type S3001, into the vessel of the Electrode Assembly.

(b) Add with a spatula a small amount of sodium sulfite (abt. 200 milligrams) to the sample and stir. After a few minutes the sample will be deoxygenated.

(c) Mount the vessel on the Electrode Assembly.

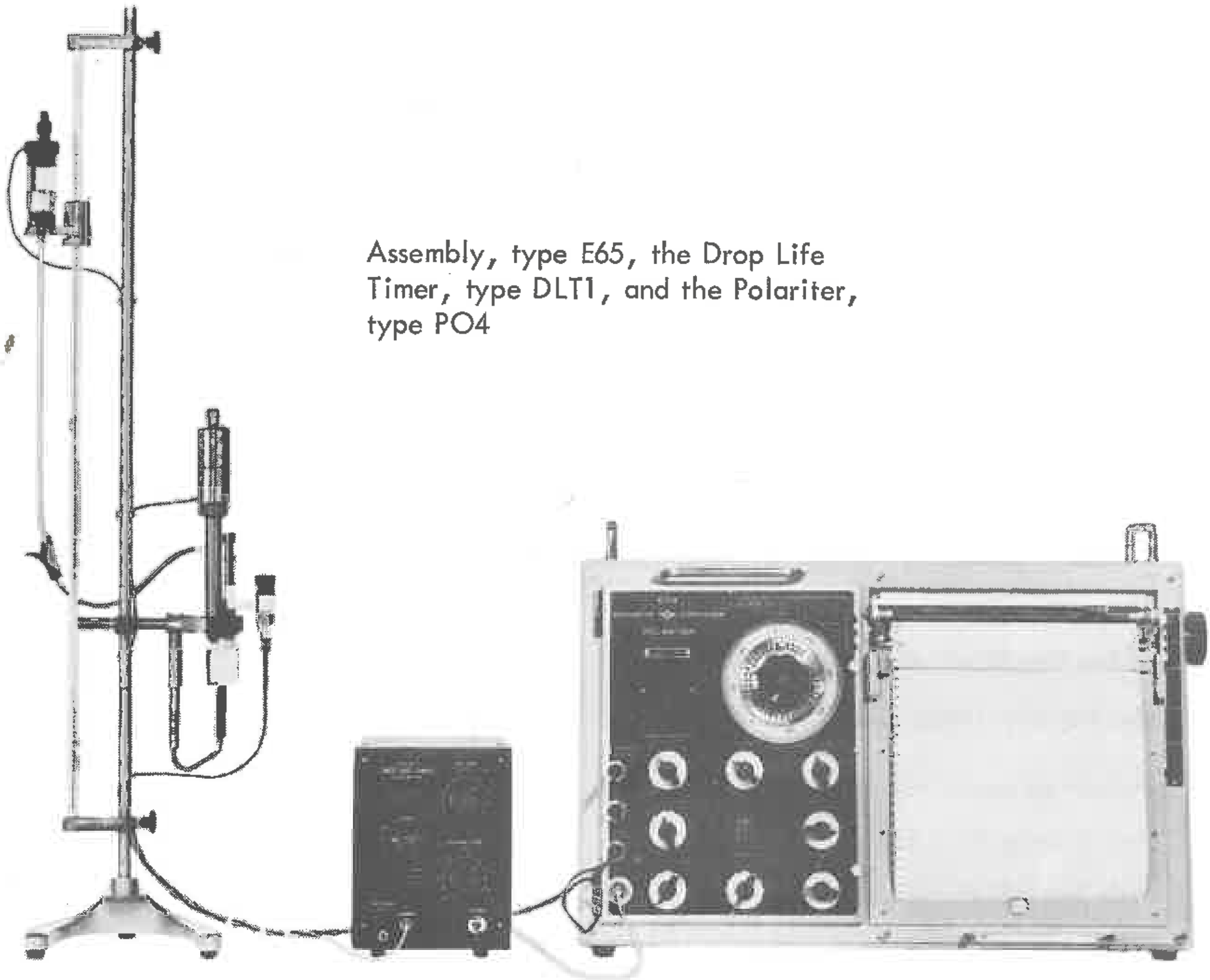

Fig.8. Setup showing the Electrode Assembly, type E65, the Drop Life Timer, type DLT1, and the Polariter, type PO4

(6) Make the following settings of DLT1:

(a) Top pushbutton switch:

Depress 0.1-1

(b) DROP LIFE control:

2 (~0.2 sec.).

(c) Bottom pushbutton switch:
Depress 0.

(d) BLANKING control:
Any position.

(e) SYNC switch:
LINE

NOTE:
For most operations it is recommended that the synchronization switch be set to position LINE in order to avoid interference phenomena between drop frequency and line frequency.

(7) Set EMF dial of PO4 to -0.56 V.

(8) Raise the mercury reservoir of the Electrode Assembly until the mercury about reaches the 50 cm mark of the scale.

(9) Open the clamp on the plastic tube of the capillary and make sure that the mercury drops evenly.

(10) Adjust screw at top of hammer so that a drop will fall at each stroke with the SELECTOR switch set to CELL.

Unscrewing (i.e. counter-clockwise) will increase the length of stroke of the hammer and thereby provide greater impact.

The customary procedure is to select an impact force which will result in an efficient detachment of the drops for the full duration of the recording, and which yet does not cause unnecessary vibrations to be transmitted to other parts of the setup.

NOTE:
It appears that the greatest impact is required near an electro-capillary maximum. Adjustment of the hammer impact ought consequently to be made whilst the electrodes are immersed in the test solution, and the polarographic voltage should then be set to a value corresponding to the electro-capillary maximum.

(11) Insert a knurled screw at the -0.2V mark in the outer circle of holes in the EMF dial of PO4.

(12) Turn the EMF dial counter-clockwise as far as it will go.

(13) Set the SELECTOR switch to CELL.

(14) Release the pen so that it writes.

(15) Set CHART FEED to ON.

(16) Lift the pen off the paper when the recording is finished at about -1.2 V on the dial.

(17) Set CHART FEED to OFF.

(18) Set SELECTOR to ZERO.

(19) Rotate the paper conveyance knob one full turn clockwise and cut off the paper.

(20) Reset the EMF dial to -0.2 V.

The recording of the Rapid Polarogram may be repeated in accordance with the instructions (13) through (20).

a. General Instructions for Recording a Rapid Polarogram

Proceed according to the instructions given above, but adapt steps (4) through (11) - and, of course, steps (16) and (20) - to the prevailing conditions.

Compared with the settings used for conventional polarography, the settings for rapid polarography differ in the following respects (ref. also step (4) of the instructions above):

I) Settings of PO4:

d) CHART FEED B:
usually 8 cm per min.

f) DAMPING:
low - usually 1 or 2

i) COMPENSATION:
a higher value of CONDENSER CURRENT COMPENSATION may be needed.

II) Settings of DLT1

The settings of controls a,c,d, and e, are the same as in (6) above since only DROP LIFE control is adjusted in Rapid Polarography - for normal work: to values between 1 and 5, corresponding to drop lives from 0.1 to 0.5 seconds.

NOTE:
It is essential that the settings of both PO4 and DLT1 are the same when measuring the unknown sample and the standard solution.

If natural drop lives are required for the analysis, one of the two following methods can be adopted:

a) Switch off power switch of DLT1.
PO4 will now operate as though it were not connected up to DLT1.
This method is recommended in most cases.

b) Withdraw the hammer plug from DLT1.
This will ensure that the reduced damping, as utilized in connection with controlled drop life, is retained.

NOTE:
In case (b), be sure to depress the 0-button of the blanking pushbutton switch.

3. RECORDING A TAST POLAROGRAM OF THE TEST SOLUTION, Type S3001

(1) Set up the PO4 (see PO4 Instruction Manual, Section 2.2).

(2) Set up the Electrode Assembly (see Appendix BI and Appendix B2.2 of PO4 Instruction Manual).

(3) Set up the DLT1 as described above (Preparing the Equipment).

(4) Make the following settings of PO4

a) SELECTOR:
ZERO

b) CHART FEED:
OFF

c) A-gear:
0.05 V per cm.

d) CHART FEED B:
4 cm per min.

e) SENSITIVITY:
20 μA full scale

f) DAMPING:
2

g) DERIVATIVE CIRCUIT:
OFF

h) SET ZERO:
corresponding to a recorder reading at approx. 10%.

i) COMPENSATION:
None

(5) Prepare the sample.

(a) Pour 15-20 ml of the test solution, type S3001, into the vessel of the Electrode Assembly.

(b) Add with a spatula a small amount of sodium sulfite (abt. 200 milligrams) to the sample and stir; after a few minutes the sample will be deoxygenated.

(c) Mount the vessel on the Electrode Assembly.

(6) Make the following settings of DLT1:

(a) Top pushbutton switch:
Depress 1-10

(b) DROP LIFE control:
1 (~1 sec.)

(c) Bottom pushbutton switch:
Depress 30-80

(d) BLANKING control:
70

(e) SYNC switch:
LINE

(7) Set EMF dial of PO4 to -0.56 V.

(8) Raise the mercury reservoir of the Electrode Assembly until the mercury level about reaches the 50 cm mark of the scale.

(9) Open the clamp on the plastic tube of the capillary and make sure that the mercury drops evenly.

(10) Adjust screw at top of hammer so that a drop will fall at each stroke with the SELECTOR switch turned to CELL. (See also item 10, page 14).

(11) Insert a knurled screw at the -0.2 V mark in the outer circle of holes in the EMF dial of PO4.

(12) Turn the EMF dial counter-clockwise as far as it will go.

(13) Set the SELECTOR switch to CELL.

(14) Release the pen so that it writes.

(15) Set CHART FEED to ON.

(16) Lift the pen off the paper when the recording is accomplished at about -1.2 V on the dial.

(17) Set CHART FEED to OFF.

(18) Set SELECTOR to ZERO.

(19) Rotate the paper conveyance knob one full turn clockwise and cut off the paper.

(20) Reset the EMF dial to -0.2 V.

The recording of the Tast Polarogram may be repeated by following the instructions (13) through (20).

a. General Instructions for Recording a Tast Polarogram

Proceed according to the instructions in section 3 above, but adapt steps (4) to (11) - and, of course, steps (16) and (20) to the prevailing conditions.

Compared with conventional polarography the settings for Tast polarography differ in the following respects (ref. also step (4) in the above instructions):

I) Settings of PO4:

In most cases the same as for conventional polarography, although less DAMPING is permissible. As a rule compensation of the condensor current is not required.

II) Settings of DLT1:

No particular settings of top push-button switch and DROP LIFE control can be stated as typical settings in Tast Polarography, but in most cases the range from 0.5 sec. to 2 sec. should be recommended.

Keep button 30-80 of bottom push-button switch depressed during all kinds of Tast recordings.

Set BLANKING control to that percentage of the drop life which is to be blanked out during the blanking period. The longer the blanking lasts, the more will the Tast polarogram differ from a conventional recording.

4. DERIVATIVE TAST AND RAPID POLAROGRAPHY

Derivative polarography involving the DLT1 is carried out on lines laid down in Section 4.3 of the Instruction Manual for PO4, but it should be noted that quite as much damping as stipulated in the said instructions need not as a rule be applied when derivative polarography is combined with Tast or rapid polarography.

NOTE:

Certain properties of the electrical circuitry within PO4 discourage the use of damping settings 1 and 2 as long as the DERIVATIVE CIRCUIT switch is in position ON.

5. USING THE COMPENSATORS of PO4

a. Use of the Condenser Current Compensation

Compensation of the condenser current is carried out as described in section 3.241 of the PO4 Instruction Manual.

Considerably higher values of condenser current must be expected in rapid polarography than in conventional polarography; in fact, for very short drop lives efficient compensation of the condenser current cannot be achieved in certain supporting electrolytes.

b. Use of Diffusion Current Compensation

Compensation of a constant current level - caused, for instance, by diffusion currents emanating from previous polarographic steps - can be carried out as described in section 3.242 of the PO4 Instruction Manual.

In Tast and Rapid Polarography this expedient will often serve admirably to allow for a better examination of details in the polarographic curves than is possible by conventional polarography, since the smoother curves that usually are obtained permit a greater increment of SENSITIVITY.

Section E. Examples of Applications

(cf. illustrations at back of this manual)

1. Example 1 (series A, I):

A Tast polarogram of a solution of 1.0 x 10^{-3} mol/liter TlCl and 0.5 x 10^{-3} mol/liter $CdCl_2$ in an ammonia-ammonium chloride buffer (Radiometer Test Solution, type S3001).

The polarogram has been recorded in nearly the same way as the conventional polarogram described in the PO4 Instruction Manual, the only differences being that the damping control of the PO4 Polariter is set in position 2; that the drop life is 1 second; and that "tasting" is carried out during the last 30 per cents of the drop life.

It will be seen that the Tast polarogram reveals the same two steps as does the conventional polarogram, but that variations in the polarographic current are smaller (abt. 1/3) in the present case. Strict proportionality exists between the height of the polarographic step (the diffusion current) and the concentration of the corresponding depolarizor down to depolarizor concentrations of approximately 10^{-5} M.

2. Example 2 (Series A, II, III & IV)

A rapid polarogram of the above mentioned test solution, type S3001, recorded both as a direct polarogram and as a derivative polarogram, is shown at the back of the manual. The polarogram is recorded with the damping control set in positions 1, 4, and 3, respectively, and in all three cases with a drop life of 0.2 seconds.

The recorded curves are almost quite smooth, and predominantly in connection with derivative recordings it is a marked improvement that the damping can be substantially reduced. A further conclusion emerges from the recording, viz. that Tast polarography is ideally suited also for producing derivative polarograms. (It must be borne in mind, however, that although the derivative polarogram as a consequence is in fair accord with the theoretical curve, the peak height is not strictly proportional to the depolarizor concentrations).

In order to elucidate both merits and demerits of rapid and Tast polarography, it is necessary to resort to Ilkovic's equation expressing the instant value of a diffusion current:

$$i_d = 706 \cdot n \cdot D^{1/2} \cdot C \cdot m^{2/3} \cdot t^{1/6}.$$

At the same time, the condenser current, that also contributes to the polarographic current, must be considered from the equation.

$$i_c = 0.00567 \cdot k \cdot (E_{max} - E) \cdot m^{2/3} \cdot t^{-1/3},$$

in which k denotes microfarads per cm^2 of the double layer on the surface of the mercury drop; E_{max} is a characteristic value of the polarographic voltage - the so-called electro-capillary maximum; i_c is measured in micro-amperes, and m and t are measured respectively in mg/sec and sec.

It will be observed that shorter drop lives give rise to a less favourable ratio between diffusion currents and condenser currents. On the other hand, the condenser current decreases rapidly towards the end of the drop life, or, in other words: is greatly reduced with t (i.e. time elapsed since the instant of detachment of the previous drop), so that the above ratio will be much improved by employing Tast polarography for sensing the current in a short period before the drop falls off.

Generally speaking however, the application of this method instead of conventional dc polarography will not improve the sensitivity, but it does greatly facilitate the study of details in a polarographic curve.

3. Example 3 (Series B):

Polarographic curves of a mixture of cadmium chloride and indium chloride in 1 M potassium chloride at pH = 1, using methyl red as maximum suppressor.

Curve I: Conventional polarography
Curve II: Tast polarography
Curve III: Derivative polarography
Curve IV: Derivative Tast polarography

It will be seen that neither conventional polarography nor Tast polarography (curves I and II) is able to disclose the presence of two components. On the other hand, it will be noted that derivative polarography (curve III) is very useful for this purpose. Nevertheless, in cases as the present where only small differences in half-wave potentials occur (approx. 50 mV), it is essential that only very slight damping be applied, and this requirement can only be fulfilled when either Tast or rapid polarography (curve IV) is employed.

4. Example 4 (Series C):

Polarogram of a brass alloy (58 Cu, 40 Zn, and 2 Pb)

The objective of this test is to determine the quantity of lead contained in the alloy. Around -0.4 V the polarographic current is dominated by the copper content (curve I & II) so that it is necessary to use a compensation of the diffusion current in order to obtain a lead-step on the curve. In conventional polarography (curve III) this method will yield an inferior measurement, whereas far better results are produced by rapid and Tast polarography (curve IV), although a somewhat increased condenser current must be taken into account when rapid polarography is employed.

Incidentally, it should be noted that it is possible by purely chemical measures to displace the half-wave potential of copper by simply adding potassium cyanide, so that the lead-step can be recorded at a high degree of sensitivity without recourse to compensation of the diffusion current. However, a polarogram recorded in this manner cannot be used for determining the content of zinc.

Additional information on the subject of rapid polarography and Tast polarography and their uses will be found in the following papers:

1) E. Wåhlin: Acta Chemica Scandinavica 10, pp. 935-956 (1956)
2) K. Kronenberg, H. Strehlow, and A.W. Elbel: Leybold Polarographische Berichte V, pp. 62-77 (1957).
3. D. Wolf: J. electroanal. Chem. 5, pp. 186-194 (1963).

Appendix. Technical Information

The following points must be carefully observed if very accurately recorded polarograms are required.

1) A certain amount of drift will occasionally be observed during the blanking period. It is caused by leakage currents in the PO4 and cannot totally be eliminated. It is advisable, therefore, to allow the PO4 to warm up for about 1 hour prior to use. Afterwards the drift will normally be less than 0.05% per second in all positions of the DAMPING control.

2) To a certain extent (as a rule less than 0.5%), the zero-position of the pen is dependent on the setting of BLANKING TIME. Consequently, neither POWER SWITCH nor BLANKING TIME controls should be manipulated immediately before a recording is started.

3) With DLT1 in position POWER ON, the damping within PO4 is as a rule reduced to about half its normal value (i.e. POWER OFF). This reduction is not entirely uninfluenced by the sensitivity setting, although it is in the three most sensitive ranges only (0.05, 0.03, and 0.02 µA full scale) that the influence becomes noticeable.
As the SENSITIVITY control is switched to still higher settings, the damping will gradually approach the normal value. Consequently, no reduction of the damping occurs in the range 0.02 µA f.s.