INSTRUCTION AND OPERATING MANUAL

FOR

Type PO4

POLARITER

ePO4
Title page

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of

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INSTRUCTIONS FOR USE OF THE DROPPING Hg ELECTRODE ASSEMBLY, TYPE E63

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APPENDIX B

SECTION 1
GENERAL DESCRIPTION

1.1 USES

Polarographic analysis, which covers a wide area in the general field of chemical analysis, is based on measurement of the diffusion current of the electrolytic process in a chemical system with a well-defined reduction potential. The electrolytic process may very often be the reduction of inorganic compounds, such as metallic ions, oxygen or oxidizing compounds, but many organic compounds, such as aldehydes, ketones, sugars, unsaturated acids, peroxides, nitro compounds, and azo compounds, can also be determined in aqueous solutions.

The PO4 Polariter can be used for:

(1) Conventional and derivative polarography

The PO4 Polariter is designed primarily for use in quantitative polarographic analysis, by which it is possible to determine unknown components in concentrations down to about 10^{-6} mol per liter. Simultaneous detection and determination of several compounds or ions are possible, but in that case the sensitivity will not be optimal for all compounds.

For conventional polarography the PO4 uses a polarographic cell with a dropping mercury electrode, such as the cells of the Electrode Assemblies types E63 and E64.

For derivative polarography the PO4 can be used directly with the electrode assemblies mentioned.

(2) Polarography with controlled drop frequency (Tast Polarography or Rapid Polarography)

For these purposes the PO4 can be used with the Electrode Assembly E64. Some extra accessories are required, viz. a Drop Life Timer, type DLT1, and a Kit for Drop Life Control, type D453.

(3) Polarography utilizing the hanging drop technique

For this kind of polarography the PO4 is used with the Kemula Equipment, type E69 (extra accessories). When using the Kemula method, a very increased sensitivity is obtained, so it is possible to detect metal ions at concentrations down to 10^{-9} moles per liter.

(4) Amperometric measurements with a fixed voltage across the electrode terminals, such as utilized in amperometric titrations.

Also for such purposes the PO4 is useful. In many cases the standard mercury electrode is often replaced by a rotating platinum electrode such as the Radiometer type SMP1/D131/P141.

The PO4 Polariter is a completely line operated instrument primarily designed for precision work in the research field. However, it can also be used to advantage in the routine laboratory because it has various devices that facilitate this kind of work considerably.

1.2 THE PRINCIPLE OF (CONVENTIONAL) POLAROGRAPHY

The polarographic method was introduced in chemical analysis by professor Jaroslav Heyrovsky in about 1925. In it, the current of an electrolysis in an aqueous solution is measured while the electrolysis voltage is gradually increased. The voltage is varied linearly with time during the recording of a standard polarogram.

The properties of the electrodes differ widely. The anode is a calomel electrode that must be able to keep a constant reference potential even at currents of the order of 100 μA, and the cathode is an easily polarizable micro electrode. Generally it is designed as a dropping mercury electrode.

The dropping mercury electrode has been chosen because

(1) The surface of the electrode is constantly renewed, thus maintaining the good polarizability.

(2) The mercury electrode can operate on a wide voltage range because mercury is a relatively precious metal and has a comparatively high overvoltage to hydrogen.

If the electrolysis current is recorded as a function of the impressed voltage, the result is a curve, the so-called polarogram. The current recorded will, of course, vary with the size of the mercury drop, so the curve will be indented, having an indent frequency which is equal to the drop frequency. Leaving this detail out of consideration, a polarogram consists of a stepped curve, if components are present that can be reduced or oxidized in the potential range covered by the mercury electrode. The potential that corresponds to the middle of a step of the curve is called the half-wave potential. This is a characteristic quality of the above reduction or oxidation process and serves to identify the analyzable components of the sample.

The diffusion current is an equally characteristic quality of the quantitive determination of analyzable components. The diffusion current is measured as the height of the step in a polarogram. It is proportional to the concentration in the sample so that, by comparing the height of the steps in the polarograms of an unknown solution with those of a standard solution, it is easy to find the concentration in the unknown solution. If several electrode reactions occur, the polarograms of the individual components will generally be superposed in the polarogram.

As mentioned above, a half-wave potential is a characteristic quality of the actual electrode reaction. In the reduction of metal ions there is an evident relation between the half-wave potential and the location of the metal in the electromotive series. The location of the half-wave potentials, however, depends on the chemical conditions of the sample, such as the possibility of the formation of complexes. In certain cases this can be utilized to separate steps in the polarogram which under other conditions would interfere with each other.

E x a m p l e (see polarogram at the back of the manual)

Polarogram of solution of

$$1.0 \times 10^{-3} \text{ mole/l TlCl and } 0.5 \times 10^{-3} \text{ mole/l } CdCl_2$$

The solution contains an ammonia-ammonium chloride buffer to ensure that a stable pH and a good electrolytic conductance between the mercury electrode and the calomel electrode.

The polarogram has 2 steps, one at approximately -480 mV corresponding to the half-wave potential for the process

$$Tl^{+} + \theta \longrightarrow Tl\,(Hg)$$

and another step at approximately -800 mV corresponding to

$$Cd^{++} + 2\,\theta \longrightarrow Cd\,(Hg)$$

As appears from the polarogram at the back of the manual, the diffusion current is constant in a wide potential range when the half-wave potential has been passed.

This is because it is not the electric field strength around the drop that determines the flow of ions to the mercury electrode, but exclusively the thermal diffusion of ions (and possibly other depolarisers) to the electrode surface. The problem can be dealt with mathematically, and the relation between the diffusion current and the concentration, the rate of flow of mercury, and the drop time is expressed in Ilkovic's equation:

$$i_d = 605\, n\, D^{1/2}\, C\, m^{2/3}\, t^{1/6}$$

where i_d is the average current in microamps during the life of a drop, n is the number of equivalents that are transferred by the reaction of a mole in the electrode reaction, D is the diffusion coefficient of the reducible or oxidizable substance in the unit $cm^2\ sec^{-1}$, C is its concentration in millimoles per liter, m is the rate of flow of mercury from the capillary expressed in the units $mg\ sec^{-1}$, and t is the drop time in seconds.

The diffusion coefficient can be determined once and for all for a specified ion in a specified supporting electrolyte at a specified temperature (when recording polarograms of a standard solution of the ion concerned). The unknown concentration of the ion can then be computed on the basis of the diffusion current measured, as the quantities m and t are readily accessible for measurement. Using Ilkovic's equation when shifting to another capillary makes it possible to theoretically calculate the new standard curve. As the diffusion current is dependent on the temperature, the drop time, and the quantity of mercury issued per time unit, these factors must be kept constant during the recording of a polarogram.

For further details on the theory and practice of polarographic analysis, we refer the reader to the vast literature on the subject:

M. L. Domange: "Elements de Polarographie Société d'editions pharmaceutiques & scientifiques",
Paris 1950, 39 p.

J. Heyrovský: "Polarographie",
Springer-Verlag, Wien 1941, 514 p.

J. Heyrovský: "Polarographisches Praktikum",
Springer-Verlag, Berlin-Göttingen-Heidelberg 1948, 118 p.

I. M. Kolthoff & J. J. Lingane: "Polarography", vol. I & II.,
Interscience Publishers, New York 1952, 990 p.

L. Meites: "Polarographic Techniques",
Interscience Publishers, New York 1952, 317 p.

G. W. C. Milner: "The Principles and Applications of Polarography",
Longman, Green & Co., London, New York, Toronto 1957, 729 p.

O. H. Müller: "Polarographic Method of Analysis",
Chemical Education Publishing Co., Easton, Pennsylvania 1951, 209 p.

M. V. Stackelberg: "Polarographische Arbeitsmethoden",
Walter de Gruyter & Co., Berlin 1950, 477 p.

A. Scholander: "Introduction to Practical Polarography",
Jul. Gjellerup, Copenhagen 1950, 77 p.

L. Tosi: "Al Método Polarografico de Analisis",
Editorial Universitaria, Santiago del Chile 1952, 172 p.

1.3 THE OPERATING PRINCIPLE

The construction of the Polariter, type PO4, can be divided into 4 main elements: the power supply, the recorder unit, the amplifier, and the input controls for the amplifier. The simplified diagram at the back of the manual shows the operating principle of the instrument. The stabilized power supply, details of the amplifier and the recorder, and test circuits have been omitted from the diagram.

From the power supply a stabilized d-c voltage is supplied across the APPLIED EMF potentiometer in the lower left-hand corner of the diagram so that the potential at the CALOMEL terminal can be varied between +3195 mV and -605 mV synchronously with the chart feed of the recorder (indicated in the diagram by the dotted line to $\boxed{A}$).

The polarographic current in the cell flows to the Hg-terminal of the PO4 and through the CELL-ZERO-TEST selector to the variable resistor, SENSITIVITY. The voltage drop across this resistor is proportional to the polarographic current. The voltage at the top of this resistor is fed - through the DAMPING network, a 2-stage RC low-pass filter - to the input of the amplifier, i.e. the upper contact of the vibrator. The amplifier acts as a phase-sensitive null-detector, so when the output is fed to a servomotor, this motor runs in a direction that corresponds to the phase of the input, with the result that the voltage at the bottom of the SENSITIVITY resistor due to movement of the servopotentiometer has changed by exactly the same value as the voltage drop across the resistor. In this way the potential at the top of the resistor is kept constant.

To summarize the function of the servosystem of the PO4:

(1) The input of the amplifier is again zero so that the motor does not run.

(2) The potential of the Hg-terminal remains unchanged from the potential found when no current flows so that a cancellation of the voltage drop across the SENSITIVITY resistor is obtained.

The two main advantages obtained in this way are:

(1) The position of the pen corresponds exactly to the current flowing through the SENSITIVITY resistor.

(2) The APPLIED EMF, i.e. the potential of the CALOMEL terminal, is identical to the voltage across the pair of electrodes of the polarographic cell.

The zero of the amplifier is controlled by the ZERO potentiometer by means of which the potential of the lower pole of the vibrator can be kept at an adequate value.

The networks CONDENSER CURRENT and DIFFUSION CURRENT can supply an additional current component besides the polarographic current through the SENSITIVITY resistor and the SERVO potentiometer. The CONDENSER current network is supplied with a d-c voltage from a potentiometer moved synchronously with the APPLIED EMF potentiometer. Therefore the current from the network is proportional to the voltage across the polarographic cell. In this way the condenser current, which roughly is proportional to the voltage across the cell, can be compensated by using the CONDENSER CURRENT network.

The DIFFUSION CURRENT network supplies a current that is independent of the voltage across the cell. A constant current component of the polarographic current can be compensated by means of this network.

The PO4 has also a DERIVATIVE CIRCUIT, that is, an RC-network following the SENSITIVITY resistor. In ON-position the current through this differentiation network is directly recorded after being amplified.

1.4 THE CONTROLS

Note: The encircled numbers refer to the drawing at the back of this manual.

1.41 Terminals

1 DROPPING Hg ELECTRODE

2 CALOMEL ELECTRODE

3 E
Chassis terminal

A jack for grounding the PO4 is located on the back panel.

1.42 Switches, dials, knobs, and buttons

4 Applied EMF POTENTIOMETER

This potentiometer controls the voltage of the DROPPING Hg ELECTRODE terminal referred to the CALOMEL ELECTRODE terminal as a zero potential. This voltage is directly shown on the scale of the dial, ranging from +0.5 to -3.0 volts. The dial may be operated by hand or coupled synchronously to the recorder.

In the dial are two rows of holes. A knurled screw inserted in a hole in the outer row of holes will limit the counter-clockwise movement of the dial, so it can be used for fixing the starting voltage of the range to be covered in the polarogram.

A knurled screw inserted in a hole in the inner row of holes operates the switch of a built-in buzzer, which will indicate the ending of the recording (the dial and the recorder will automatically stop moving shortly after the buzzer has been switched on).

(5) Knob for manual feed of the chart paper

(6) CHART FEED

ON-OFF switch that operates the chart motor.

(7) A

Lever for selecting the synchronization between the movements of the chart motor and the APPLIED EMF potentiometer.

It has 3 positions:

upper: 0.05, giving 0.05 V/cm chart
center: 0, APPLIED EMF kept constant
lower: 0.1, giving 0.1 V/cm chart

(8) B

Switch for setting the chart speed. It has 3 positions: 2, 4, and 8 cm per minute.

(9) FORWARD - REVERSE

Lever that controls the direction of rotation of the paper drive.

(10) ON-OFF

Power switch

(11) SELECTOR

Four-position selector for selecting the input:

(a) CELL (input from the electrode circuit)
(b) ZERO (electrode circuit opened, no current input)
(c) TEST 1 (current input 0.4 μA/V of applied EMF)
(d) TEST 2 (current input 40 μA/V of applied EMF)

(12) TEST 3

Button for testing the sensitivity of the recorder directly.

13 CURRENT SENSITIVITY, uA FULL SCALE

This selector controls the input sensitivity of amplifier in 25 steps from 0.02 to 200 µA for the full 25 cm scale of the recorder.

14 DAMPING

Selector with 9 positions used to diminish the oscillations of the polarographic current when recorded. The higher the setting, the higher the time constant of the damping network.

15 SET ZERO

Knob for controlling the zero on the recorder. The zero can be selected continuously over the whole range from 0 to 100% of the recorder.

16a & 16b DIFFUSION CURRENT COMPENSATION

Compensation of diffusion current is controlled by a switch 16a and a continuous knob adjustment 16b . The current compensated is equal to the product of the two settings. The possible compensations range from -20 µA to 100 µA.

17 CONDENSER CURRENT COMPENSATION

This knob provides for continuous compensation of condenser current or of currents that are proportional to the applied EMF from 0 µA/V to 0.5 µA/V.

18 DERIVATIVE CURRENT

ON-OFF switch for the derivation network:

OFF: Conventional polarography (i versus E)

ON: Derivative polarography ($\frac{di}{dE}$ versus E)

1.43 The recorder

19 Pen and pen holder

The pen and pen holder are locked together when the red-point end of the bar of the pen holder is pressed in. The pen is released when the green-point end is in.

20 Knife for cutting the chart paper.

SECTION 2
MOUNTINGS

2.1 SPECIFICATIONS

2.11 1 Polariter type PO4

Dimensions (over-all):

Height:	270 mm
Width:	710 mm
Depth:	350 mm

Weight:

42 kilos

Power supply:

110, 127, 150, 200, 220, or 240 volts, 40-60 cps.
Power consumption: 100 watts.

2.12 Standard accessories supplied with the PO4

1 line cord	type 12K21
1 bottle, 50 ml, quick-drying recording ink	- S7015
1 bottle, 250 ml, test solution	- S3001
1 bottle, 50 ml, sodium sulfite	- S4048
5 rolls chart paper	- 980-A3
1 box containing:	
2 pens with cleaning needles	- D192
2 cleaning needles	
4 INFA wrenches (1.5 - 2 - 2.5 - 3)	
2 fuses T-0.63 amps	- 520
2 fuses T-1.25 amps	- 520
1 instruction manual	

2.13 Extra accessories used with the PO4 for ordinary polarography

Electrode assembly	type E63
Electrode assembly	- E64

2.14 Extra accessories used with the PO4 for special polarographic applications

KEMULA equipment	type E69
Kit for Drop Life Control for E64	- D453
Drop Life Timer	- DLT1

2.2 MOUNTINGS

2.21 General

Adjust the line voltage selector and connect the line cord. Apply the separate GROUND connection, if the line socket does not provide for ground connection to the red lead of the line cord.

2.22 Mounting the electrode stand

See appendices A and B: Instructions for use of the Electrode Assembly, type E63, and the corresponding instructions for Electrode Assembly, type E64.

2.23 Inserting the chart paper

(1) Tilt the drum assembly on its lower edge by pulling the two red knobs of the recorder.

(2) Release the roller.

(3) Mount the chart roll on the roller and place it in the spring bearings again (Note: the chart roll must turn from back to front back to front when the paper is being unwound).

(4) Open the springs that hold the paper on to the drum and pull a strip of paper over the drum.

(5) Make sure that the lines of the paper are parallel to the axis of the drum, and turn the paper holder on to the drum.

(6) Push the drum assembly back into position (both the red knobs must snap).

Note: In cutting off the chart paper slide the knife 20 along the steel wire. The tiny wheel in the knife must run on the horizontal rail below the drum. If not, press the small tip on the knife and press the knife into position.

2.24 Servicing the pen

(1) Mounting the pen: Press the red dot of the indicator slide. Insert the pen on the left-hand side of the indicator slide with its arm below the suspension wire and the edge of the chassis. Push the pen to the right until it is coupled together with the indicator slide. Fill the pen with a few drops of ink.

(2) Removing the pen: Press the green dot of the indicator slide, pull the pen slide to the left, and lift it off the suspension wire.

(3) Interrupting the recording: Lift the container until it is caught by the arm on the right-hand side of the indicator slide. In the case of long periods: Press the green knob and pull the pen slide to the left. Keeping the pen on to the paper like this prevents clogging.

(4) When out of use for more than a day or so: empty the container and rinse with distilled water. Suck the capillary tube empty by means of a suction pump, a pipette, or filtering paper.

(5) If required, clean the pen by means of water with an admixture of detergent and apply vacuum or air pressure to the capillary tube. A o.15Ø mm wire can also be used for cleaning.