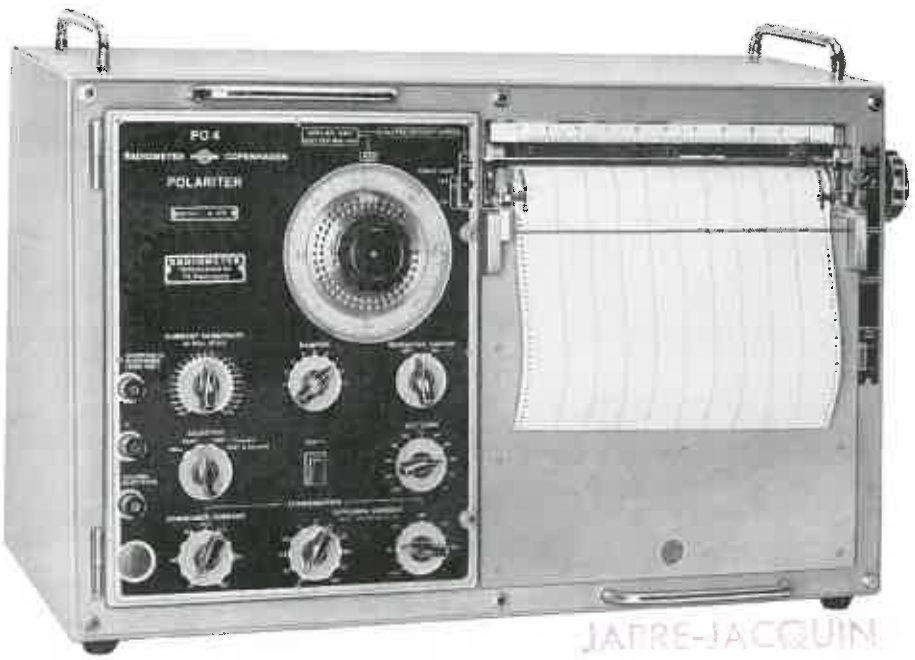
POLARITER P03

RADIOMETER

POLARITER P03
POLARITER P04

POLAROGRAPHIC ANALYZERS



POLARITER P04

The principle of polarography

The principle of a polarographic setup is shown in fig. 1. The electrolysis cell is located in the upper left corner of the diagram. The beaker contains the test solution. *K* represents a dropping mercury electrode consisting of a narrow capillary from which mercury emerges at a rate of 20-30 drops per minute. *A* is a non-polarizable electrode, e. g. a mercury pool at the bottom of the beaker. (Instead of this it is quite common to use a calomel half-cell).

The polarographic method is based on observations of the variations in the current flowing through the electrolysis cell as the potential between the electrodes is

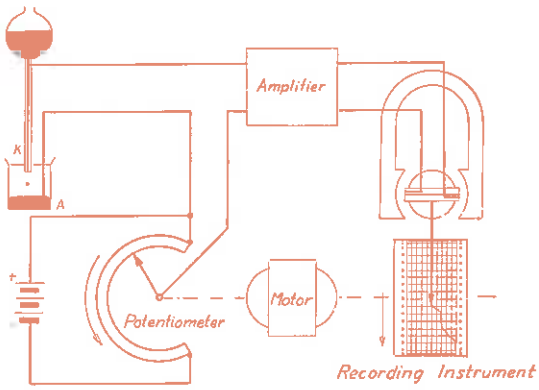


Fig. 1

gradually increased from one value to another, e. g. from 0 to 2 volts. This process is accomplished by the motor, which simultaneously drives the potentiometer and feeds the chart paper on which the electrolysis current is recorded as a function of the electrolysis voltage. Fig. 2 represents a polarogram of a solution containing copper, cadmium, and zinc. The electrolysis current is practically zero until the potential reaches a certain value at which the current starts to increase rapidly. The increase is brought about as an increasing number of Cu^{2+} ions are discharged at the dropping mercury electrode. The current will soon reach a constant value which is governed by the velocity of diffusion at which the Cu^{2+} ions are transferred to the cathode. In the presence of a suitable content of sup-

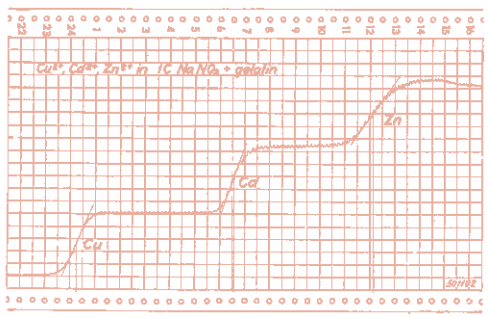


Fig. 2
Polarogram of a solution containing Cu^{2+}, Cd^{2+}, and Zn^{2+}.

porting electrolyte and at constant temperature this velocity of diffusion depends on the difference between the Cu^{2+} concentration of the bulk of the solution and that of the solution at the mercury surface of the cathode. This difference reaches its maximum value (i. e. the Cu^{2+} concentration of the bulk of the solution) when the Cu^{2+} ions are discharged as fast as they appear at the mercury cathode. This means that the height of the copper wave is proportional to the Cu^{2+}

Radiometer Instruments for Polarography

Ever since 1922, when J. Heyrowsky published his first papers on polarography, the tendency has been to widen the fields of application of this instrument. Naturally this development is primarily due to the general advantages of the polarographic method. Particularly tempting are the speed and the accuracy of

PO 1, 1938

polarography and the fact that several components can be determined simultaneously and practically without the use of material. Furthermore the polarographic method in many instances offers the only possible solution to an analytical problem.

The first Radiometer instrument for polarographic analysis was built in 1938. In order to increase the speed of the method the instrument was equipped with a recorder which could draw a line with pen and ink on the chart. Thus for the first time it was possible to avoid the use of photographic paper in connection with polarographic work. This

PO 3, 1940

first direct-recording instrument for polarography, type P01, was soon followed by new developments, and in 1940 it was possible to put its successor, type P03, on the the market. To the best of

our knowledge this instrument was the first commercially available mass-produced direct-recording polarographic analyzer.

The introduction of a direct-recording instrument into the field of polarography naturally meant a considerable time saving, but what is more important, no darkroom work or wet processing was required, and thus the risk of warping and shrinking was eliminated. Furthermore, direct recording made it possible to watch the polarograms as they were being drawn, and in some cases this very feature no doubt represented the most striking advantage. In view of this and the reception which the P03 got on its first appearance, it is perhaps no exaggeration to say that this instrument has contributed notably to the general acceptance of the polarographic method.

Since the completion of the first specimen of the P03 the general design of this model has not changed appreciably. Naturally improvements have been made

PO4, present model

from time to time in order to keep the instrument up to date with the latest developments. Right from the beginning the P03 was received particularly well by research institutes, but the number of customers in industry clearly proves that the design of the instrument makes it equally suitable for production laboratories and for research laboratories. Due to the continued success of the instrument it remains a very important item in the Radiometer production scheme.

As time went by, researchers in particular increased their requirements for sensitivity and other characteristics of the instrument used for polarography. Consequently the model P04 made its appearance in 1956 as the result of intensive development work. This instrument combines the reliability and convenient operation of the P03 with a number of important features that make the P04 particularly suitable for advanced polarographic work.

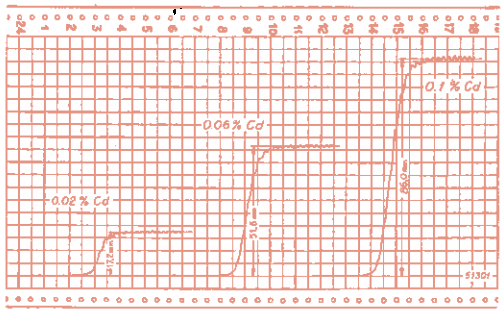


Fig. 3
Proportionality between wave height and concentration.

concentration. As the potential is increased further, the Cd^{2+} ions will begin to discharge at the cathode. A wave corresponding to the Cd^{2+} concentration will result. The Zn^{2+} wave is recorded at a still higher potential.

It can be seen that the height of the wave corresponds to the concentration of the ion concerned, whereas the potential at which the wave is produced is characteristic of the ion.

Fig. 3 illustrates the proportionality between the wave height and the concentration of Cd^{2+} ions.

Many organic compounds behave in a similar manner. Nitro-benzene is a very good example.

Fig. 4 and fig. 5 are polarograms of aniline hydrochloride solutions containing 0.002 and 0.003% nitro-ben-

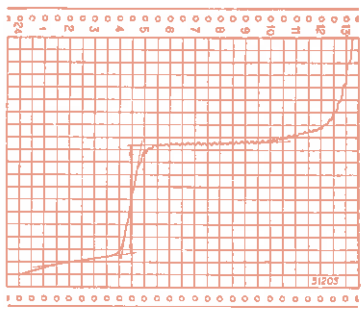


Fig. 4
0.002% nitro-benzene in aniline hydrochloride, wave height 43 mm.

zene, respectively. The proportionality between wave height and concentration of nitro-benzene is apparent when the polarograms are compared.

Further information on the polarographic method and its applications can be found in the abundant literature on this subject.

For preliminary instruction the following book is recommended: Axel Scholander: "Introduction to Practical Polarography", Jul. Gjellerups Forlag, Copenhagen. 77 pages.

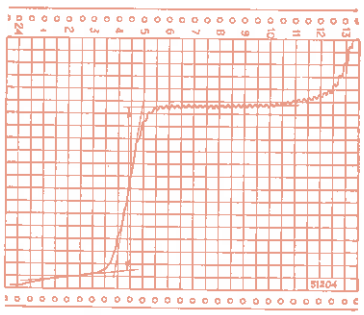
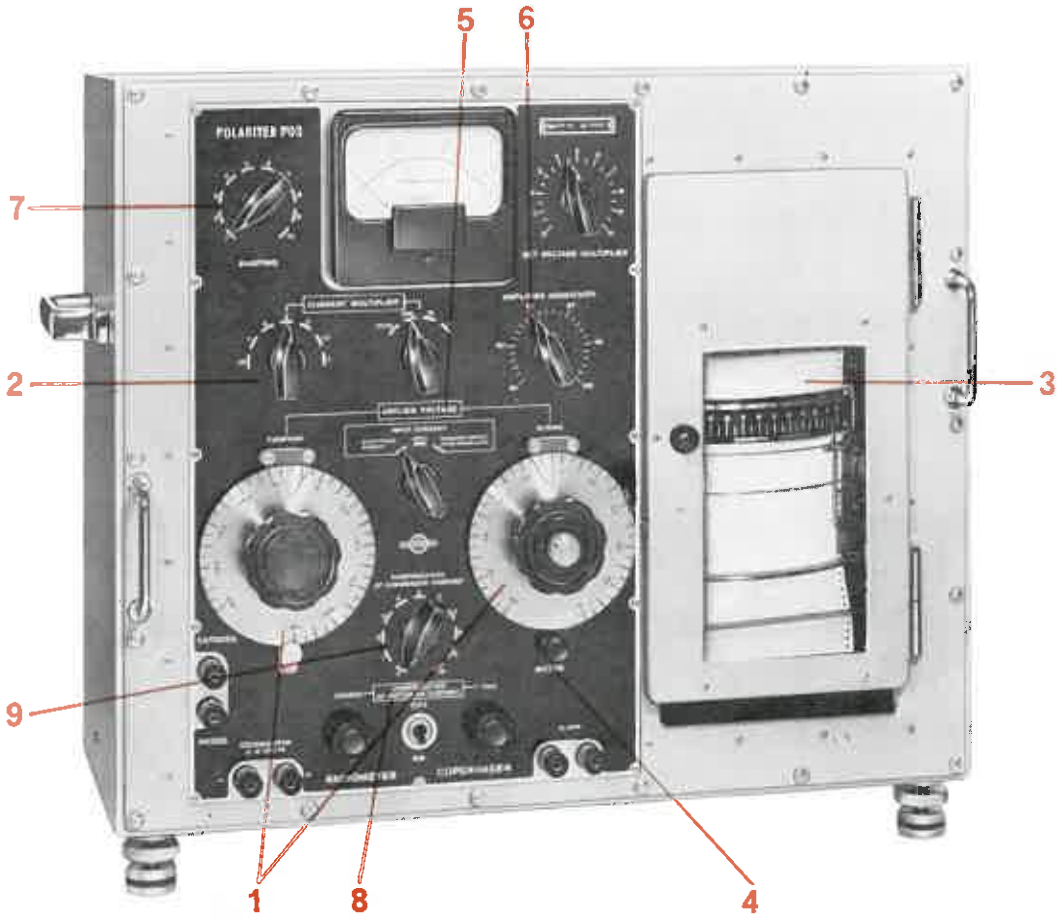


Fig. 5
0.003% nitro-benzene in aniline hydrochloride, wave height 65 mm.



PO 3

POLARITER PO 3

Polarographic Analyzer

The type PO 3 Polariter is line-operated and electronically stabilized. It is provided with all devices required for polarography and amperometric titration. It is simple and well-arranged and suitable for production laboratory analyses and the like.

Specifications:

1 Electrolysis voltage:

Continuous voltage: 2 volts, corresponding to 200 mm on the chart paper. Speed of variation: 0.4 volts per minute. The voltage variation can be adjusted to starting in the interval −1 to +1 volt. By means of a rheostat the above voltages can be multiplied by factors from 0.5 to 1.5. The multiplication factor is read on a built-in meter.

2 Current sensitivity:

Maximum: 1 mm deflection equals 3.5×10^{-10} amps. The full recording width is 100 mm. The sensitivity can be reduced from 1 to 10,000 in 25 steps.

3 Recorder:

Built-in moving coil ink recorder with a 100-mm working width. Within ½% the deflection of the moving coil system is directly proportional to the electrolysis current. This linearity has been maintained in the recording, because the paper is stretched across the surface of a cylinder when it passes the pen.

4 Paper drive:

The paper is driven by a special motor at a speed of 40 mm per minute. The paper drive is mechanically coupled to the main potentiometer from which, however, it can be disengaged. After the completion of a polarogram the paper drive is automatically switched off.

Other features:

5 Absolute calibration in microamps per mm deflection.

6 Special devices for standardizing against different capillaries so that identical polarograms are obtained with the same solution.

7 Variable damping (of current oscillations from the dropping mercury electrode) by means of R-C link. Adjustable in 10 steps.

8 Compensation of diffusion current (to eliminate unwanted lower waves in the polarogram).

9 Compensation of condenser current (compensation proportional to electrolysis voltage).

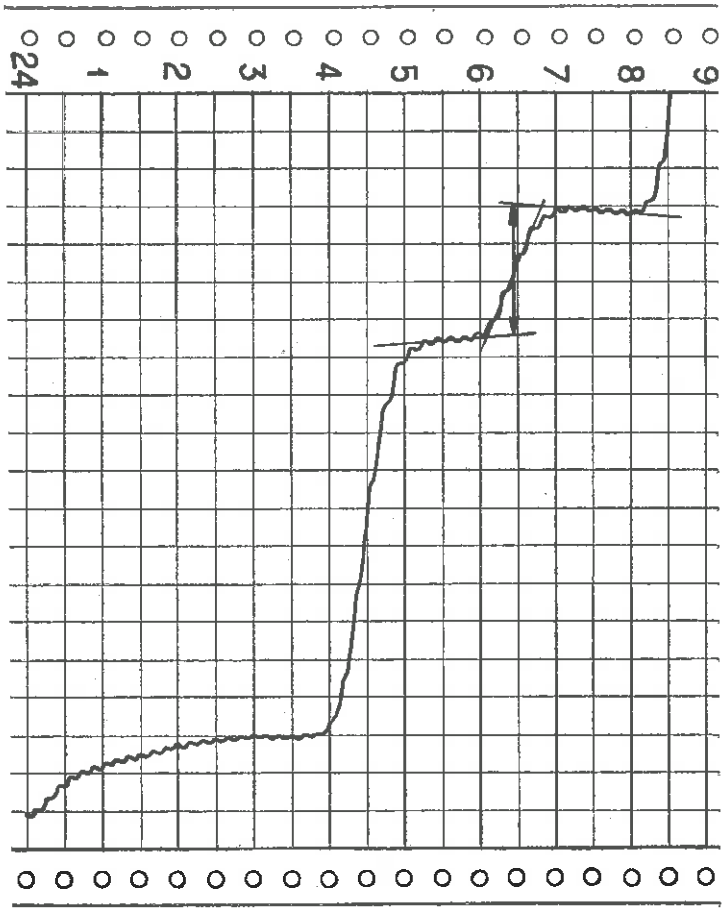


Fig. 8 0.007 % Pb^{2+} and 0,0013 % Cd^{2+} in 99,99 Zn.
Condenser current compensated. Full size polarogram.

Compensation of condenser current

Due to the fact that each drop of mercury carries with it a certain charge of electricity from the cathode to the anode, a so-called condenser current will occur. As far as comparatively concentrated solutions are concerned, this condenser current will have no influence at all, but when the higher sensitivities are employed, in the case of dilute solutions, it may interfere with the diffusion current, making it difficult to interpret the polarograms. The Radiometer Polariter can compensate the condenser current, a fact that makes the instrument particularly suitable for determinations of traces or impurities otherwise impracticable.

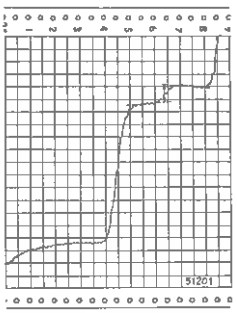


Fig. 6
With compensation.

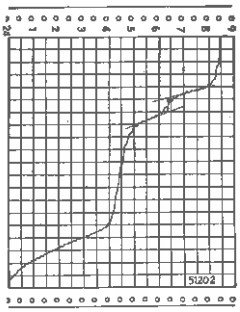


Fig. 7
Without compensation.

Purity determination of 99.99 % zinc represents a striking example of the importance of this feature. Fig. 6 shows a polarogram of Pb and Cd in very pure zinc. The sensitivity was 1/20 of maximum, and compensation of condenser current was applied. Fig. 7 shows a polarogram of the same solution, but without the application of condenser current compensation. Owing to the slope arising from the condenser current, it was necessary to reduce the sensitivity to 1/30 of maximum and, as appears, the interpretation of the polarogram is impaired. The polarogram fig. 8 was made in a way similar to that of fig. 6, but 0.0008 % Cd was added to the test solution in order to ascertain the unknown Cd content, which was found to be 0.0005 %. By following the same procedure (the standard addition method) the lead content was determined to be 0.007 %.

10 A bell or a buzzer can be connected to the instrument to indicate the completion of a polarogram.

Power supply:

110, 127, 150, 200, 220, 240 volts, 50-60 cycles.
Consumption: 60 watts.
Battery (for electrolysis voltage) 4 to 6 volt (capacity at least 20 a. h.)

Mounting:

Metal cabinet finished in grey enamel.

Dimensions (over-all):

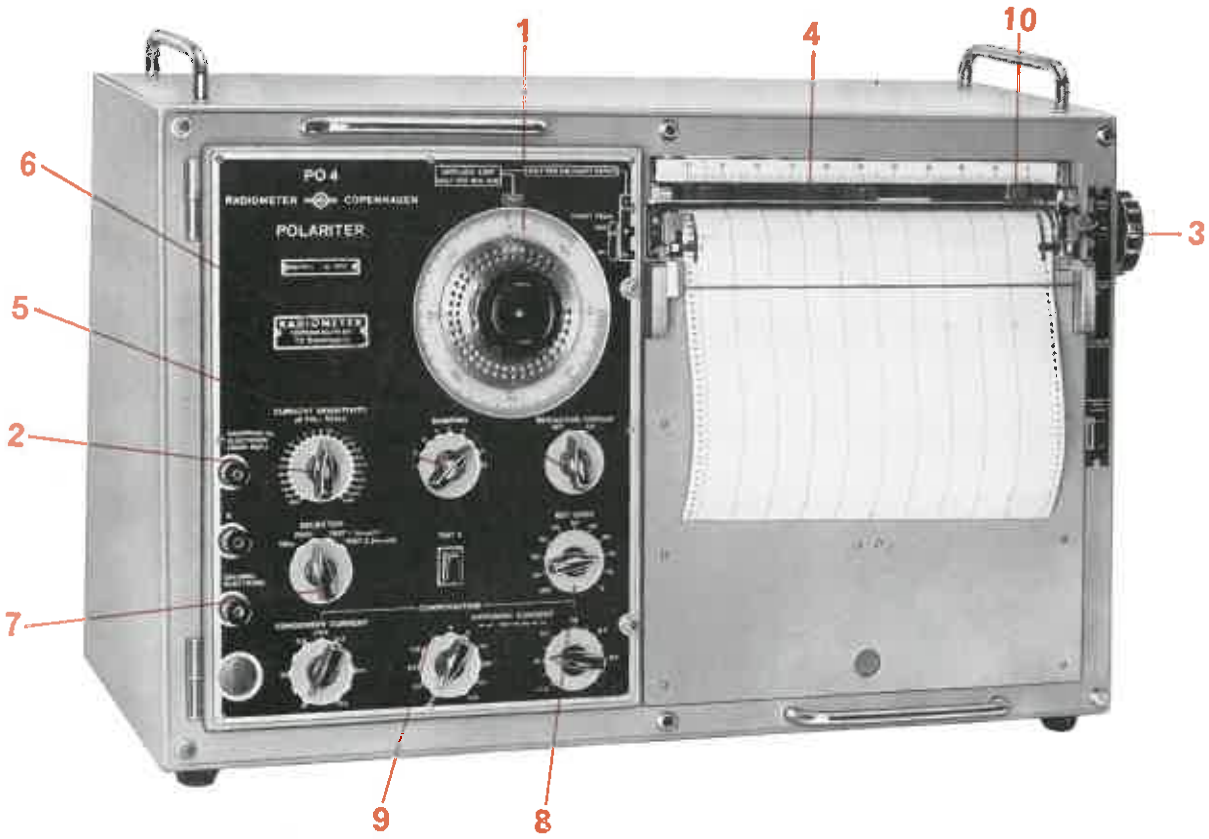
Height: 500 mm. Width: 650 mm. Depth: 300 mm.
Weight: 35 kilos.

Tube complement:

1 EF 40 – 2 EF 42 – 1 85 A2 – EZ 40

Standard accessories:

1 line cord.
1 battery lead.
2 pens.
5 rolls chart paper.
1 bottle quick-drying ink (50 ml) with screw-on stopper with pipette.
1 bottle test solution.
1 bottle sodium sulfite
1 instruction manual.
1 manual on polarography (A. Scholander: Introduction to Practical Polarography).



PO 4

POLARITER PO 4

Polarographic Analyzer

The type PO 4 polarographic analyzer is completely line-operated and is designed for precision work. Its versatility and accuracy make the instrument ideal for research purposes. It is, however, also provided with various devices that facilitate routine laboratory analyses considerably.

Specifications:

1 Electrolysis voltage:

The main potentiometer which is wound with a special gold alloy controls the voltage range from + 0.5 to – 3.0 volt (cathode voltage). The voltage is supplied by a built-in highly stabilized rectifier. The potentiometer is driven by a synchronous motor. The voltage variation can be set between 100 and 800 mV per minute in 4 steps, or to zero. The potentiometer dial is provided with bushings which will take starting and stop pins thus facilitating the routine work.

2 Current sensitivity:

The maximum sensitivity corresponds to 8×10^{-11} amps per millimeter recording height and the minimum sensitivity corresponds to 8×10^{-7} amps. 23 different settings of the sensitivity are available between these values. The sensitivity control is provided with precision resistors having an accuracy of 0.2 % except for the smallest and the largest decade, for which the accuracy is 0.5%.

3 Paper drive:

The paper drive can be set to a speed of 2, 4 or 8 cm per minute. The potentiometer and the paper drive are operated by a common synchronous motor. In proportion to the paper drive the potentiometer drive can be shifted in the ratio 1:2 or be switched off entirely. Both movements are reversible. The paper and the potentiometer can be adjusted by hand and independently of each other.

4 Recorder:

The instrument is provided with a built-in potentiometer ink recorder which requires 2 seconds for full deflection at a setting accuracy of better than 0.1%. The effective working width is 250 mm.

5 Damping:

An R-C link can be varied in 9 positions to damp the current oscillations of the mercury electrode.

6 Derivation:

A built-in derivation device provides for recording of derivative polarograms which in special cases offer a better separation of related elements.

7 Adjustment control:

Built-in control resistors and a built-in standard cell provide for the control of the setting value of the instrument.

8 Zero setting:

The zero can be shifted within some 30% of full deflection.

9 Compensation current:

By means of calibrated potentiometers, the charging current and the diffusion current can be extensively compensated. It should be noted that the charging current compensation is independent of the sensitivity. The maximum compensation of the charging current is 0.5 μA/V and that of the diffusion current is 100 μA.

10 »Peak Current« recording:

The design of the pen holder provides for easy recording of the maximum of the electrolysis current at any time. This device provides for the recording of undamped polarograms without the oscillations caused by the mercury drops.

Cutting device:

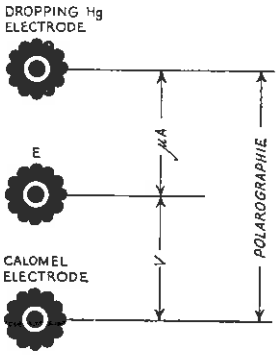
The instrument is provided with a convenient cutting device.

11 Amplifier:

The instrument incorporates a modulated d-c amplifier, the excellent stability of which has been obtained by means of negative feedback. Line surges of up to ±10% will not affect the amplification by more than 0.2%.

12 Terminals:

Two of the three input terminals, viz. those marked DROPPING Hg ELECTRODE and CALOMEL ELECTRODE are used for connecting the polarographic cell. The electrolysis voltage is present across these terminals and the current thus agitated is picked up by the instrument.



The terminals »E« and DROPPING Hg ELECTRODE are used when measuring or recording μA without using any voltage. The voltage corresponding to the position of the main potentiometer can be drawn from the terminals »E« and CALOMEL ELECTRODE.

Power supply:

105, 110, 127, 200, 220, 240 volts, 40-60 cycles.
Consumption: 100 watts.

Mounting:

Metal cabinet finished in grey enamel.

Dimensions:

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

Weight: 42 kilos.

Tube complement:

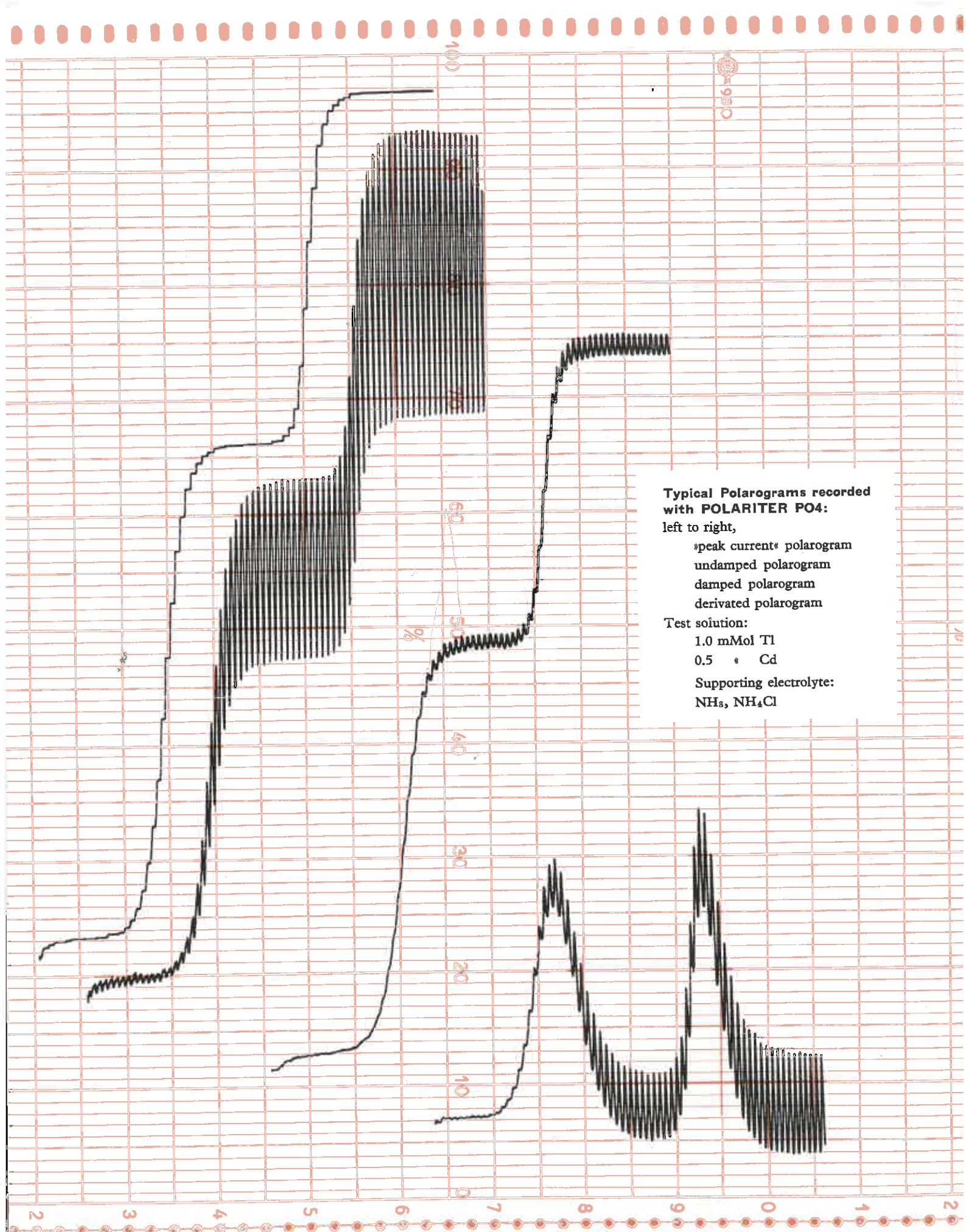
1 E80CC
3 E80F
1 E80L
2 E85A2
2 PL81
1 GZ34

Standard accessories:

2 pens.
5 rolls chart paper with a recording width of 250 mm. 30 m per roll.
1 bottle quick-drying recording ink.
1 bottle test solution.
1 bottle sodium sulfite, crystals.

Electrode Assemblies:

Dropping Mercury Electrode Assembly, type E63
Dropping Mercury Electrode Assembly, type E64
Kit for Drop-Life Control for E64, type D453
Drop-Life Timer, type DLT1



Typical Polarograms recorded with POLARITER PO4:

left to right,

»peak current« polarogram
undamped polarogram
damped polarogram
derivated polarogram

Test solution:

1.0 mMol Tl
0.5 « Cd

Supporting electrolyte:

NH_3, NH_4Cl