SECTION 3
INSTRUCTIONS FOR POLARITING

3.1 RECORDING A POLAROGRAM OF THE TEST SOLUTION, type S3001

The test solution contains 1 mM Tl^{+} and 0.5 mM Cd^{++} in an ammonia-ammonium chloride buffer with a small amount of Triton x-100 used as a maximum suppressor.

(1) Mount the Polariter (follow the instructions in 2.2)

(2) Mount the Electrode Assembly (see appendices A2.2 or B2.2)

(3) Set SELECTOR to ZERO.

(4) Set power switch to ON. Make sure the CHART FEED is in position OFF.

(5) Pour 10-20 ml of test solution, type S3001, into the vessel of the Electrode Assembly.

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

(7) Mount the vessel on the Electrode Assembly.

(8) Connect the lead from the calomel cell to the CALOMEL ELECTRODE binding post of the Polariter.

(9) Connect the lead from the mercury capillary electrode to the binding post DROPPING Hg ELECTRODE.

(10) Set DAMPING to 4.

(11) Set all compensations to zero.

(12) Set DERIVATIVE CIRCUIT to OFF.

(13) Turn SET ZERO to get a recorder reading near zero, for instance 10%.

(14) Set SENSITIVITY to 20 µA.

(15) Insert a knurled screw in the outer row of holes in the EMF dial (4) at the -0.2 V mark.

(16) Set the lever to the left of the recorder to A=0.1 (i.e. 0.1 V per cm).

(17) Set the levers to the right of the recorder to FORWARD and 4 cm per Min.

(18) Turn the EMF dial counterclockwise till it stops.

(19) Raise the mercury reservoir of the Electrode Assembly until the mercury level is at about the 50 cm mark of the scale.

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

(21) Set the SELECTOR switch to CELL.

(22) Release the pen so that it writes.

(23) Set CHART FEED to ON.

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

(25) Set CHART FEED to OFF.

(26) Set SELECTOR to ZERO.

(27) Turn the paper conveyance knob one turn clockwise, and cut off the paper.

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

The recording of a polarogram may be repeated in accordance with the instructions from (21) to (28).

3.2 GENERAL INSTRUCTIONS FOR RECORDING A POLAROGRAM

3.21 Preparing the solution containg the medium to be analyzed

The medium to be analyzed is to be dissolved in a solution of a suitable electrolyte. The concentration of this electrolyte is usually (fairly) high (that is, about 0.1-1 mol per liter) to ensure a good conductivity. To prevent deposition of the medium and to get it in a good condition for polarography, the supporting electrolyte should be chosen with great care. Sodium hydroxide, hydrochloric acid, different buffer solutions and inactive salt solutions are often used, but in some cases the best conditions for polarography are present if the electrolyte forms a complex with the component to be analyzed. Very often the shape of the polarogram can be improved by adding a small amount of a maximum suppressor-gelatin, Triton x-100, or other surface-active media.

The concentration of the medium to be analyzed should preferably be about 10^{-3} mols per liter, but generally the PO4 Polariter will work, if the concentration of the medium is in the range 10^{-6} to 10^{-2} mols per liter.

The sample must be deoxygenated before the recording. In an alkaline and neutral solution sodium sulfite may be used, if the concentration of the medium is not too low. Otherwise deoxygenate by bubbling with pure nitrogen for 10-15 minutes.

3.22 Recording the polarogram

(1) Mount the Polariter and the Electrode Assembly and connect the electrodes to the instrument.

(2a) Using the Electrode Assembly, type E63: Prepare a 10- to 15 ml sample in a vessel, type V500, and mount the vessel in the electrode assembly.

(2b) Using the Electrode Assembly, type E64: Prepare a 20-ml sample in a vessel, type V518, and mount the vessel in the electrode assembly.

Note: In the case of deoxygenating by bubbling with nitrogen, connect the reduction valve of the nitrogen cylinder to the gas inlet of the electrode assembly by means of a piece of tubing.

In the electrode assemblies, type E63 and E64, the nitrogen flow can be controlled by means of a needle valve or an adjustable screw compressor and can be humidified, if required.

The bubbling is performed for 10 to 15 minutes till the sample is freed from oxygen. Next raise the gas inlet tube in the vessel to that the nitrogen flows over the surface of the sample without bubbling through it.

(3) Check the following settings:

(a) SELECTOR at ZERO
(b) DERIVATIVE CIRCUIT at OFF
(c) COMPENSATIONS at 0
(d) CHART FEED at OFF
(e) FORWARD-REVERSE lever at FORWARD

(4) Set power switch to ON.

(5) Raise the mercury reservoir of the Electrode Assembly to give an adequate drop time. (Generally 3 to 4 sec/drop).

(6) Adjust the EMF dial to indicate the starting voltage.

Note: If required, the starting voltage can be fixed by means of a knurled screw inserted in a hole in the outer row of holes in the dial. In the same way a clockwise limitation in the dial movement can be obtained by a screw inserted in the inner row of holes.

(7) Set the SENSITIVITY
(If you have no idea what the polarogram will be like, choose a fairly low sensitivity, i.e. turn the SENSITIVITY switch well counter-clockwise).

(8) Set the DAMPING. High damping will give a smooth but distorted polarogram, so in the case of unknown samples, positions from 3 to 6 are to be preferred.

(9) Turn SET ZERO to get an adequate zero of the recorder. Generally select the zero well to the right on the recorder, for instance 10%.

(10) Set the chart speed by means of the lever B to the right of the recorder.

(11) Synchronize the rate of changing the APPLIED EMF with the chart speed by means of the lever A to the left of the recorder.

(12) Set the SELECTOR to CELL.

(13) Release the pen.

(14) Set CHART FEED to ON.

(15) Lift the pen off the paper when the recording is finished.

(16) Set CHART FEED to OFF.

(17) Set the SELECTOR to ZERO.

(18) Reset the APPLIED EMF dial.

(19) Turn the paper drum a little forward and cut off the paper.

The Polariter is now ready to repeat the polarographic analysis according to the above instructions from (6) to (19).

3.23 After use

(1) Follow the instructions AFTER USE in item A3.2 or B3.2 of the Appendices.

(2) Set the power switch to OFF.

(3) Follow the instructions for servicing the pen, item 2.

3.24 Compensations

3.241 Condenser current compensation.

(1) Record the uncompensated polarogram of the sample or, in difficult cases, of a blank, as described in item 3.32.

(2) Calculate the condenser current in the voltage range of the polarogram, you want it compensated.

Note: Use for the calculation a part of the polarogram where no, or at least a constant limit current (diffusion current) is expected. The condenser current is simply $\Delta i / \Delta E$, i.e. the average slope of the polarogram measured in $\mu A / V$-units.

(3) Set the CONDENSER CURRENT knob to the calculated $\mu A / V$.

(4) Record the compensated polarogram in accordance with item 3.32 from (9) to (19). Do not change the drop frequency.

3.242 Diffusion current compensation

(1) Record the uncompensated polarogram or the polarogram with compensated condenser current.

(2) Calculate from the recorded curve the value of constant current to be compensated.

Note: Read the deviation from the set zero of the level to be compensated and use the full scale calibration (SENSITIVITY) to convert it into μA.

(3) Switch the left-hand DIFFUSION CURRENT knob to a value just above the calculated current to be compensated.

(4) Adjust with the right-hand DIFFUSION CURRENT knob to such a value that the product of the two settings equals the calculated current.

(5) Record the compensated polarogram in accordance with item 3.32 from (6) to (19). Keep in mind that the starting voltage is to be readjusted. If required, change the SENSITIVITY to a higher value (a position with a lower value of μA for full scale).

SECTION 4
SPECIFIC INSTRUCTIONS

4.1 PEAK CURRENT RECORDING POLAROGRAPHY

In certain respects peak current polarography offers some advantages: Low damping can be used to give higher accuracy in determining half-wave potentials. In most cases peak current will be referred to the polarographic current immediately before the drops fall off, which means that the condenser current contribution is eliminated to a great extent.

The principal disadvantage of peak polarography carried out as described here is that the recorder cannot follow the complete peak current curve in the case of polarographic maxima or in other cases when the peak current is not steadily increasing with the applied EMF.

How to record a peak current polarogram

Follow the instructions in item 3.32 except for items (8) and (13) which should be changed as follows:

(8) Set the DAMPING. Use position 1 or 2.

(13) Release the pen and press the green-dot end of the bar of the pen holder.

Note: Take care not to overcompensate the condenser current when compensations are used.

The actual condenser current is not so strong as that in ordinary polarography, and overcompensation will artificially give ranges in the polarogram where the current decreases, when the voltage increases, i.e. ranges where this method of recording cannot be used.

4.2 REVERSE POLAROGRAPHY

In ordinary polarography reverse polarography can be used to eliminate errors caused by the damping when half-wave potentials are to be determined.

Proceed as follows:

(1) Record the normal polarogram in accordance with the instructions in 3.32 from the beginning to (14).

(2) When the end of the voltage range being recorded has been reached, switch the lever (9) from FORWARD to REVERSE.

(3) When the starting voltage is reached again, lift the pen off the paper.

(4) Set CHART FEED to OFF.

(5) Set SELECTOR to ZERO.

(6) Turn the paper drum so that the entire polarogram is visible again.

(7) Cut off the paper.

(8) Reset the lever (9) to FORWARD.

In damped polarograms the polarographic waves are somewhat delayed, depending on the setting of the DAMPING and the speed of the APPLIED EMF dial. High damping and high paper speed will give a long delay, but if the mean values of the half-wave potentials in FORWARD and REVERSE polarograms are used, the errors caused by these delays will eliminate one another. The principal error in the $E_{1/2}$ - determination is then the RI-drop in the polarographic cell used in the experiment.

4.3 DERIVATIVE POLAROGRAPHY (see illustration at the back of the manual)

The built-in DERIVATIVE CIRCUIT provides an easy way of recording derivative polarograms, i.e. $E - \frac{di}{dE}$ curves. In derivative polarography the polarographic waves are recorded as peaks around the half-wave potentials, and the ranges with a constant (diffusion) current will be on the zero line. Derivative polarography is useful in qualitative analysis, but is not recommended for general quantitative determinations, because the peak heights and the concentration of the depolarizers are not completely proportional when the derivation of the polarographic current takes place in an RC-circuit as is the case in PO4.

As the derivation is really a derivation against time and thus only indirectly against the polarographic voltage, the settings of chart speed B, synchronization A, and to some extent DAMPING, are important to the real sensitivity in addition to the settings of the SENSITIVITY itself.

To record a derivative polarogram, follow the instructions in item 3.32, however with the following alterations:

(3)(b) DERIVATIVE CIRCUIT at ON.

(7) Set the SENSITIVITY.

In case the original polarogram is recorded with 0.8 V per minute, do not increase the SENSITIVITY more than by a factor of 2, or keep the SENSITIVITY unchanged. In other cases increase the SENSITIVITY inversely proportional to the APPLIED EMF per minute.

(8) Set the DAMPING to a rather high valve, 6 or more.

This is necessary to suppress the oscillations due to the drop falls in proportion to head lines of the polarogram.

4.4 AMPEROMETRIC TITRATIONS

Many titrations can be made with the PO4. The electrode setup may be the type E63 or E64 Electrode Assembly that uses a dropping mercury cathode, but whenever possible a rotating platinum electrode, type SMP1/D131/P141, should be used, because it reduces the condenser current and gives a smooth titration curve.

The PO4 is used with gear control A at 0 and the APPLIED EMF dial preset at the required voltage, so that it can record the current at a constant voltage against time.

The types of titration can be divided into three main groups:

(1) Precipitation titrations
(2) Redox titrations
(3) Complex-formation titrations

In the amperometric titration the constant voltage impressed across the electrode circuit must be chosen well above the half-wave potential of the component to be determined, but not so high that waves from impurities and supporting electrolyte will interfere. The diffusion current is recorded during the dosage of the reagent, which must give no diffusion current itself. When the polarographic current does not change, the end-point of the titration has been reached.

4.5 USING THE PO4 WITH THE KEMULA EQUIPMENT

For some polarographic analyses, especially analyses of metallic ions, a higher sensitivity can be gained by using the Kemula Equipment, type E69, for anodic stripping polarography on a hanging mercury electrode.

The KEMULA EQUIPMENT, type E69, consists chiefly of the Electrode Assembly including accessories to stir the sample and to control the flow of inert gas through the cell and the Damping Adapter, i.e. a unit with an RC-damping circuit to be used with the Electrode Assembly. The hanging-drop electrode is directly connected to the terminal DROPPING Hg ELECTRODE of the Polariter by means of a shielded cable. The shield is connected to the terminal E, the chassis of the PO4. The calomel electrode is connected to the Damping Adapter and through the resistor of the damping circuit connected to the CALOMEL terminal of the Polariter. The condenser of the Damping Adapter is inserted between the calomel electrode and the E terminal.

The polarographic analysis performed with the KEMULA EQUIPMENT has 3 steps:

I The electrolyzing period
II The stand-by period
III The recording period

In the first period a constant electrolyzing voltage is supplied to the electrode circuit from the Polariter. The electrolysis takes place while stirring, and the applied voltage must exceed the decomposition voltages of the metal ions that the analysis concerns. The duration of the electrolyzing period should be measured and a similar period used for the standardizing.

In the second period the stirring has stopped. While waiting for the movements in the sample to set, the Polariter is prepared for recording. This preparation comprises: setting the SENSITIVITY, displacing the zero to the left of the chart paper, inspection of the settings of the levers that control the paper transportation, and making sure that enough paper for a REVERSE polarogram has been turned forward.

While the recording takes place in the third period, the ions decomposited and accumulated in the first period will be liberated, when

the voltage during reversing passes the half-wave potentials of the metals concerned. An anodic current peak will then be recorded around the half-wave potential.

The peak heights or, in more accurate work, the peak areas are used as a measure of the concentrations of the metal ions in the sample, but care must be taken to maintain the same electrolysis conditions, that is, voltage, period duration, and stirring efficiency, when standardizing.

For further details on the KEMULA method, see the instruction manual for E69.

4.6 POLAROGRAPHY WITH CONTROLLED DROP LIFE TIME

By means of the Kit for Drop Life Control, type D453, and the Drop Life Timer, type DLT1, the PO4 + E64 can be used for different kinds of polarography with controlled drop life time. The DLT1 provides for setting the drop life directly in seconds and for setting the duration of the knock-off pulse fed to the Kit for Drop Life Control, type D453. When selecting a short drop period (half a second or less), this is the setup for rapid-polarography.

Rapid-polarograms are smoother than ordinary polarograms. However, the sensitivity of rapid-polarography is a little decreased, because the condenser current contributes more to the polarographic current.

Also for "tast" polarography this equipment provides a useful setup. In the Drop Life Timer, type DLT1, the drop period can be divided in a blank period and a registration (tast) period. As the registration period is at the end of the drop life, "tast"-polarography gives polarograms in which the condenser current contribution is very much reduced, and furthermore the tast-polarograms are smoother than ordinary polarograms, because the variation of the diffusion current is very slow at the end of the drop period (see the Ilkovič equation in item 1.2).

For further details see the manual for Drop Life Timer, type DLT1.

SECTION 5
TESTING

This section deals with the use of Tests 1, 2, and 3 for checking the SENSITIVITY and the calibration of the Applied EMF.

Tests 1 and 2 described below enable the operator to verify that the instrument as a whole is operative. The tests are based upon a current derived from the EMF device through one of two position resistors (2.5 MΩ ±1% and 25 kΩ ±0.1%) and fed into the current amplifier.

Correct results of tests 1 and 2 do not exclude that current sensitivity and EMF have identical deviations (of opposite signs) from the correct values. Therefore a third test is available by which the EMF device can be checked against a built-in standard-cell.

5.1 TEST 1 AND TEST 2

(1) Set SENSITIVITY to 0.5 µA
- DAMPING to 3
- DERIVATIVE CIRCUIT to OFF
- SELECTOR to ZERO
- ZERO to 10% recorder deflection
- APPLIED EMF to 1.0 V

If a recording is wanted:

Set GEAR CONTROL A to 0
- GEAR CONTROL B to 4 CM PER MIN
- CHART FEED to ON

(2) Switch SELECTOR to TEST 1
Recorder should deflect to 90 ±1.5 degrees

(3) Reduce SENSITIVITY to 50 µA
Switch SELECTOR to TEST 2
Recorder should deflect to 90 ±0.8 degrees

Other SENSITIVITY settings can be tested by varying APPLIED EMF to suitable values.

5.2 TEST 3

(1) Set DERIVATIVE CIRCUIT to OFF
- SELECTOR to ZERO
- ZERO to 10% recorder deflection

(2) Press the button TEST 3 and make sure that the recorder deflection is within 8 to 12 degrees.

(3) If deflection deviates more than 2 degrees from 10, readjust slotted screw P2 until the condition is fulfilled. (The drum assembly is to be opened by pulling the two red knobs).

Note: A more comprehensive description of testing all the functions and controls of the Polariter, type PO4, is found in "Bulletin on B-test of the type PO4 Polariters from serial number 22652".