when gaseous or liquid refrigerants are constantly circulated around the enclosed sample. In the particular cell arrangement shown here the sample chamber is 6.5 cm. long, with an inside diameter of 2.5 cm. and an outside diameter (including the jacket) of 5.0 cm. The sodium chloride windows are 0.6 cm. thick and 4.7 cm. in diameter. Evacuated compartments are 1.0 cm. wide.

During construction, the end surfaces of the cell body are ground flat and thin lead amalgam gaskets (0.05 mm.) are pressed on. Sodium chloride windows are then sealed onto the gaskets with clear Glyptal varnish (General Electric No. 1202). Before use, the complete cell must be baked at 125° C. for at least 24 hours, preferably in a vacuum oven. This method for low temperature seals to sodium chloride was first described by L. G. Smith [*Rev. Sci. Instr.* **13,** 65 (1942)].

The most important consideration in operating the cell is preventing uneven cooling or heating in the fragile windows. Cooling to 0° C. can be fairly rapid, but any lower temperature must be approached slowly to prevent cracks. Approximately 10 minutes are required to reach −20° C. and 20 minutes are recommended for −60° C. The cell described here can be used for several hours at −20° C. without danger of condensation on the outside windows. For −60° C. operation, however, the 1.0-cm. vacuum insulation must be replaced with 3.0-cm. compartments.

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Leeds & Northrup Electrochemograph as a Recording Alternating Current Polarograph

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THIS COMMUNICATION describes the modifications which we have made to a Leeds & Northrup Electrochemograph Type E to provide for the recording of alternating current (a.c.) polarograms.

Recording a.c. polarographs based upon the manual circuit of Breyer, Gutmann, and Hacobian (*3*) have been described by Buchanan and Werner (*4*), Ishibashi, Fujinaga, and Saito (*6*), Tachi and Senda (*12*), and others. Miller (*9*) has described the modification of the Sargent Model XXI Polarograph for a.c. polarography. Polarograms obtained with Miller's instrument can only have relative significance as the magnitude of the measured alternating current will be dependent upon its phase angle. This makes the instrument suitable only for analytical work, the purpose for which it was designed.

Niki (*10*) has reported details of the a.c. bridge polarograph. In the Univector polarograph unit the base current is cancelled by a phase selective process (*7*). Smith and Reinmuth (*11*) have also described an a.c. polarograph incorporating a phase selective circuit. Although these instruments are very sensitive to traces of electroactive substances they are not, in general, suited to the investigation of the mechanisms of electrode reactions as in this work the magnitude of the base current, which they eliminate, is of interest (*2, 5*).

Walker, Adams, and Alden (*13*), and Kelley *et al.* (*8*) have described instruments for alternating current voltammetry which control both the d.c. and a.c. potential of the working electrode. These instruments are fundamentally superior to ones of the Breyer type (*3*).

Walker, Adams, and Juliard (*14*), have reported a modification of the Leeds & Northrup Electrochemograph Type E for a.c. voltammetry. Their circuit is similar to the one described here but they have not given any details of their connections to the Electrochemograph. In the modification described below no alteration to the Electrochemograph wiring is necessary as all connections are made at outlets already available on the instrument case.

Our circuit (Figure 1) is based on that of Buchanan and Werner (*4*). The potentiometer is the motor driven polarizing slide-wire of the Electrochemograph, powered from an 8-volt accumulator.

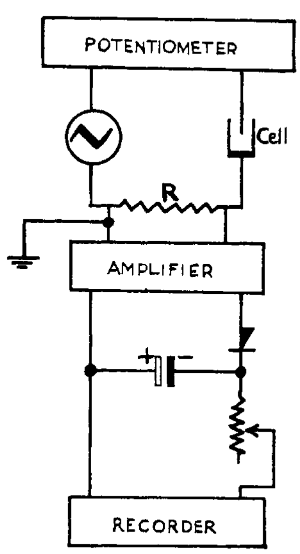

Figure 1. Block diagram of recording a.c. polarograph

The voltage developed across *R*, which is in series with the conventional polarizing circuit, may be amplified by any suitable a.c. amplifier (gain × 10^4 to 10^5). For convenience we have used a Philips GM 4574 preamplifier coupled in cascade with a Radiometer RV33b vacuum tube voltmeter (V.T.V.M.). The output from the amplifier is rectified by an OA85 germanium diode, filtered and fed through a series rheostat, the sensitivity control, to the cell terminals of the Electrochemograph.

The output of the Electrochemograph polarizing slide-wire is isolated by connecting the external leads from the octal socket located at the rear of the instrument in the following way: Pin 3 to pin 4, pin 7 to pin 8, and pin 1 to pin 6. The polarizing voltage is obtained across pins 5 and 2. This connection also completes the Electrochemograph polarizing circuit, omitting the polarizing slide-wire, so that the rectified current when applied to the cell terminals will be indicated on the recorder. The details of the modifications are shown in the full circuit diagram and the specifications given in Figure 2. The a.c. polarogram may be recorded at the slow polarizing rates provided by the Leeds & Northrup auxiliary polarizing unit by suitable connection of the units through a junction box (Figure 3).

Because the polarizing slide-wire has such a low resistance (*viz.* 40 Ω) there is no need for the shorting condenser that is used across the potentiometer in the circuit of Buchanan and Werner (*1, 4*). The use of such large value condensers across the potentiometer in a.c. polarography causes unreproducibility in the polarizing potential. This is probably caused by memory effects in the elec-

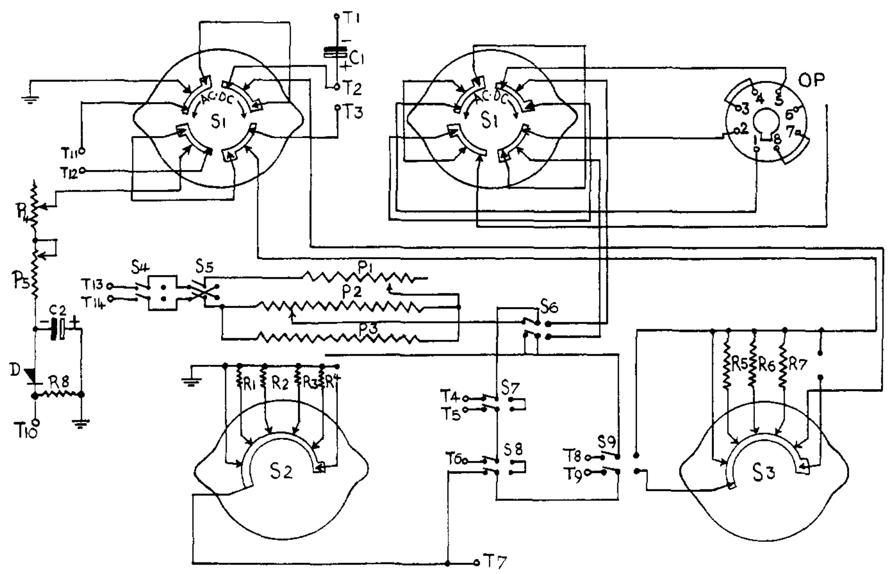

Figure 2. Circuit diagram of additions to Electrochemograph

S_1: 2-position, 8-pole switch
S_1,S_3: 6-position, single-pole switch
S_4,S_5,S_6,S_7,S_8: D.P.D.T. switch
S_9: 3-position, 2-pole switch
P_1: 50 Ω 10-turn Helipot
P_2: 100 Ω, 10-turn Helipot
P_3: 25 Ω, 10-turn Helipot
P_4: 2M Ω, 2W, carbon potentiometer
P_5: 200 KΩ, 2W, carbon potentiometer
R_1: 5 Ω, 1% tolerance, 1W high stability cracked carbon resistor
R_2: 10 Ω
R_3: 20 Ω
R_4: 100 Ω
R_5: 500 Ω
R_6: 1500 Ω
R_7: 250 Ω
R_8: 200 Ω
C_1: 2000 μF, 4-volt, electrolytic condenser
C_2: 4 μF, 25-volt, electrolytic condenser
D: 0A85 germanium diode
OP: octal plug to Electrochemograph
T_1,T_2 T_3: cell terminals
T_4,T_5: galvanometer terminals
T_6: alternating voltage input terminal
T_7: preamplifier input terminal
T_8,T_9: Weston standard cell terminals
T_{10}: amplifier output terminal
T_{11},T_{12}: recorder input terminals

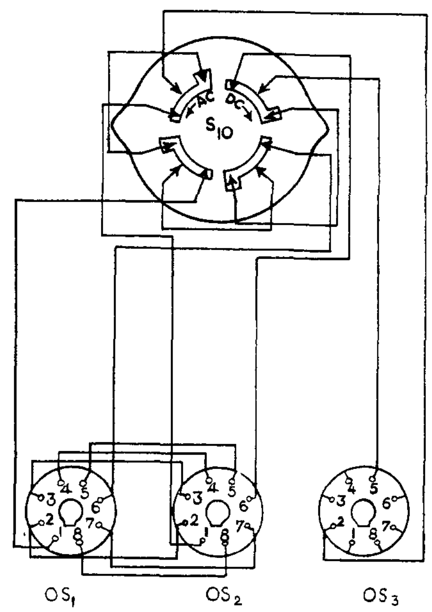

Figure 3. Circuit of junction box for connection of Leeds & Northrup auxiliary polarizing unit for a.c. and d.c. polarography

S_{10}: 2 position, 4-pole switch
OS_1: Octal socket to Electrochemograph
OS_2: Octal socket to Leeds & Northrup auxiliary polarizing unit
OS_3: Octal socket to a.c. Polarograph unit

trolytic condensers of the capacitance necessary for this purpose.

The alternating voltage for the polarizing circuit is supplied from either an oscillator (Hewlett Packard 200CD) working into an attenuator of output impedance 0 to 10 Ω or a mains operated step down transformer and a similar attenuator. The amplitude is normally 15 mv. (root mean square).

It is essential that the entire circuit be connected to the earth at one point only; otherwise large hum voltages will be developed by the earth loops. The input to the preamplifier is rather arbitrarily selected as this point of connection to earth. All leads external to the instrument cases are shielded, and shielded terminals are used wherever possible.

The polarizing circuit, rectifier, and filter are built into an instrument case which also houses a manual potentiometer which can take the place of the Electrochemograph slide-wire for manual a.c. polarography. Provision for the connection of a galvanometer and standard cell to the polarizing circuit is also made for the same purpose.

When the AC-DC switch is set on DC, pin 1 of the octal socket is connected to pin 2, and pin 5 to pin 6, and the polarographic cell is connected directly to the cell terminals of the Electrochemograph. The instrument may now be used in the normal way.

For a.c. polarography the AC-DC switch is set on AC, the amplifier gain is suitably adjusted and the current range switch is set on 20 μa. One of the calibrating resistors is switched in and the potentiometers P_4 and P_5 are adjusted until the recorder reads a suitable value when compared with the reading obtained with a V.T.V.M. at the output of the preamplifier. The polarographic cell is then brought into the circuit and the a.c. polarogram may be recorded. The damping switch on the Electrochemograph may be used to damp the recorder response as usual.

Any other setting of the current range switch may be used, depending upon the gain of the amplifier. In our arrangement it is more convenient to alter the sensitivity of the a.c. polarograph at the amplifier input. Furthermore altering the current range switch changes the response time of the recorder, as it alters the time constant of the resistance-capacitance network formed by the 4-microfarad filter condenser (Figure 1) and the current range resistor in the Electrochemograph.

This instrument has been in use in this laboratory for 6 months and the results are comparable with those obtained from manual a.c. polarographs for both faradaic and tensammetric waves. The speed of the polarizing motor is sufficiently slow to give a good indication of the peak current of all but the sharpest of waves. Accurate measurements of these peak currents can be made using the slow polarizing rates.

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