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THE CONSTRUCTION AND OPERATION OF A METER FOR MEASURING THE QUALITY OF ZINC ELECTROLYTES

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EXTRACTION METALLURGY DIVISION

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THE CONSTRUCTION AND OPERATION OF A METER FOR MEASURING THE QUALITY OF ZINC ELECTROLYTES

by

R.C. Kerby[*], J.M. Brannen[**] and T.R. Ingraham[***]

ABSTRACT

The construction and operation of a meter for automatically measuring the quality of zinc electrolytes, in relation to zinc electrodeposition, is described. The meter consists essentially of a small zinc electrolysis cell and a gas detection unit for measuring the hydrogen evolved during electrolysis. The amount of hydrogen evolved provides a measure of current efficiency during zinc electrolysis. The meter can be used to provide a continuous record of the quality of the zinc electrolyte which is used in the cell room of a zinc electrolytic plant.

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Direction des mines

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LA CONSTRUCTION ET LE FONCTIONNEMENT D'UN COMPTEUR POUR MESURER LA QUALITÉ DES ÉLECTROLYTES DE ZINC

par

R.C. Kerby*, J.M. Brannen** et T.R. Ingraham***

RÉSUMÉ

Les auteurs décrivent la construction et le fonctionnement d'un compteur pour mesurer automatiquement la qualité des électrolytes de zinc, en relation avec l'électrodéposition de zinc. Le compteur se compose essentiellement d'une petite pile d'électrolyse de zinc et d'une unité pour la détection de gaz pour mesurer l'hydrogène dégagé pendant l'électrolyse. Le montant d'hydrogène dégagé fournit une mesure d'efficacité du courant pendant l'électrolyse de zinc. Le compteur peut être utilisé pour fournir un rapport continuel sur la qualité de l'électrolyte de zinc qui est utilisé dans une pile d'une installation d'électrolyte de zinc.

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...cont'd

INTRODUCTION

The development of a method of automatically determining the quality of zinc electrolyte entering the tank house is of major importance to the electrolytic zinc industry. Several methods have been developed and are listed in References 1 and 2, but none of these methods have been used extensively in Canada.

A program was initiated at the Mines Branch in 1967 to develop a meter capable of measuring the quality of zinc electrolyte and which could also be used to automatically control the quality of zinc electrolyte entering the cell room. Testing programs using doped acid zinc solutions(1) and zinc electrolytic solutions obtained from a commercial zinc electrolysis plant(2) confirmed that the meter was capable of quickly and accurately measuring the quality of zinc electrolytes. This report describes the construction and operation of the meter.

BACKGROUND

The presence of harmful impurities in the zinc electrolyte entering the tank house of an electrolysis plant can result in large losses in current efficiency, due to increased production of gaseous hydrogen at the cathodes. Because the increase in the evolution of hydrogen from the cathode is approximately proportional to the decrease in zinc electrodeposition, the amount of hydrogen evolved during electrolysis can be used as a convenient measure of the decrease in current efficiency of zinc electrodeposition and therefore as a measure of the purity of the zinc electrolyte.

A thermal conductivity cell (TCC) can be used for accurately measuring the changes in gas flow composition. It is based on the principle that because gases have different thermal conductivities, they will cool heated filaments at different rates and thereby change the resistance of the filaments. The filaments are connected into a Wheatstone bridge circuit, with a carrier gas flowing over two filaments to act as reference while the gas mixture flows over the other two filaments. The differential signal from the Wheatstone bridge. circuit is proportional to the difference in thermal conductivity between the carrier gas and the gas mixture.

Nitrogen is a good carrier gas for the detection of hydrogen gas in a TCC, because the thermal conductivities of the two differ by a factor of seven. This large difference in thermal conductivity is easily picked up by the TCC, making it very sensitive to small changes in hydrogen concentration in the gas flow.

CONSTRUCTION OF THE METER

The zinc electrolysis meter can be divided for clarity into two major components, the zinc electrolysis unit and the hydrogen gas detection unit. Both components were mounted in a cabinet (20" x 16" x 10") to permit easy portability.

A. Zinc Electrolysis Unit

The zinc electrolysis cell is shown in Figure 1. It consists of a glass U-tube, which provides separate cathode and anode campartments. The U-tube is held by two adjustable clamps, allowing it to be removed for cleaning after each test.

The flow of zinc electrolyte through the cell is from the cathode campartment to the anode compartment. This ensures that there is always a fresh solution of zinc electrolyte flowing over the cathode. The zinc electrolyte, after being filtered and acidified with H_2SO_4 , is stored in a sample jar connected to the cathode compartment by rubber tubes (Figure 2). A Teflon stopcock is used to control the solution flow. The waste zinc electrolyte from the anode compartment is collected in an Erlenmeyer flask.

The cathode (Figure 3) consists of an aluminum rod, mounted in a rubber stopper, to which is attached a disposable aluminum strip on which the zinc is electrodeposited. The anode consists of a lead strip permanently mounted on an aluminum rod. Both anode and cathode strips are immersed into the zinc electrolyte to a depth of 2.5 cm.

A direct current density of 10 mA/cm^2 is used to deposit the zinc on the cathode. The electric circuit diagram of the direct current supply is shown in Figure 4. Circuit connections to the electrodes are made by clips which attach to the aluminum rods. The current is controlled by the "cell current" switch on the front of the cabinet (Figure 5).

The hydrogen gas produced during the electrodeposition of zinc is collected by a measured flow of nitrogen carrier gas and taken to the thermal conductivity cell. The schematic flow diagram for this operation is shown in Figure 6. After the nitrogen gas has collected the effluent hydrogen gas, it is passed through Drierite to remove water vapour before arriving at the thermal conductivity cell. Nitrogen gas is provided from a cylinder of high-purity nitrogen. The nitrogen flow is controlled by accurate regulating valves on the nitrogen cylinder.

B. Hydrogen Gas Detection Unit

A Gow-Mac Thermal Conductivity Cell (TCC) is used to measure the hydrogen gas evolved from the zinc electrolysis cell. The TCC is heated to 110°C by a heating tape controlled by the "TCC heater" switch on the front of the cabinet (Figure 5). The TCC is heated to prevent any dilute sulfuric acid from condensing on the filaments.

A direct current of 70 mA is supplied to the filaments of the TCC (Figure 7). The electric circuit diagram of the direct current supply is shown in Figure 8. The TCC current is controlled by a switch and a 100-ohm variable resistance located on the front of the cabinet (Figure 5). The current is read on a dc milliammeter. Balance in the Wheatstone bridge circuit is controlled by a 4-ohm resistor connected to the "zero" dial on the front of the cabinet.

The resulting signal fron the Wheatstone bridge circuit of the TCC is amplified by an Acromag D.C. amplifier. The amplification is approximately linear up to a 1-mV input signal. The amplified signal is read on a 500-mV meter. The signal is controlled by a switch and a 250-ohm variable resistor connected to the "sensitivity" dial (Figure 5). The switch is used to reduce the amplified signal by a factor of 10, so as to facilitate the initial balancing of the Wheatstone bridge circuit with the zero knob.

The overall circuit diagram for the meter is given in Figure 9. The location of the various electrical components in the cabinet is shown in Figure 10. The electrolysis cell power supply is located in the bottom left-hand corner, the TCC power supply and the amplifier are located in the bottom right-hand corner, and the TCC is located in the top right-hand corner of the cabinet as shown in the figure.

OPERATION

(a) Installation

The zinc electrolysis meter was made as self-contained as possible while still being portable. Therefore only a minimum of bench space is needed to set it up.

The meter should be close to an ac 110-volt power source so that it can be plugged in using the extension cord. The sample jar was made to sit on the side of the meter, however other arrangements for supplying the zinc electrolytic solution to the meter can be made. The waste flow of electrolyte from the cell is collected in a container. It should be remembered that the electrolyte is highly acidic. A nitrogen cylinder with good flow regulators should be set up close to the meter to provide a gas flow to the thermal conductivity cell.

(b) Operation Procedure

The zinc electrolyte to be used for testing should be filtered to remove any solid particles that could block passage of the zinc solution through the electrolytic cell. It should then be acidified to the same conditions as used in the cell rooms.

Fresh aluminum cathode strips should be used for each test to ensure reproducibility of the results. The aluminum strips can be cleaned by dissolving the deposited zinc with a sulfuric acid solution.

The electrolysis cell should be cleaned before each test, because the meter is very sensitive to any metallic impurities which might be present from previous tests. The cell is easily detached by loosening the clamps and removing the electrodes. A tray is provided under the cell to catch any solution which might be spilled.

It is important that there is always a flow of nitrogen through the thermal conductivity cell while the TCC current is on. If there is no gas flow, the filaments in the TCC will heat up and possibly burn out. The flow-meter is situated between the electrolysis cell and the TCC to provide a check that the nitrogen flow is not being lost in the electrolysis cell.

The meter is calibrated initially to indicate current efficiency by comparing the weight of deposited zinc, after drying, with both the expected amount of zinc and the rate of hydrogen gas evolution associated with the electrodeposition of zinc.

(c) Procedure in Routine Operation

The following suggestions are included as a guide for operating the meter.

1. Place all toggle switches in their "off" position and connect the line cord to a 110-V ac supply.
2. Flip the TCC heater to the "on" position to heat the thermal conductivity block to its operating temperature. About 3/4 hr is required for it to stabilize. During this time

the cell and the cathode and anode strips can be cleaned.

3. When the TCC block has reached operating temperature, the anode and cathode should be tightly fitted into their respective stoppers and the stoppers should then be installed in the cell as shown in Figures 1 and 3. The power lines should be attached (negative to aluminum).
4. Place between 200 and 300 ml of filtered and acidified zinc sulfate solution in the reservoir and slowly open tap to fill the cell.
5. Turn on the nitrogen flow and adjust the ball to a height of 8 on the rotameter flow-meter. This corresponds to 50 cc/min. If the flow is slower, the readings of the meter will be high and vice versa. This flow should be checked periodically.
6. Only when the nitrogen is flowing through the cell should the current to the filaments be turned on (TCC current switch). The filaments may burn out without a flow of gas. A preliminary adjustment of current to 70 mA (7 on the dial - note red strip) should now be made. It will require a slight readjustment after about 5 minutes as the cell is re-equilibrated.
7. After the 5 minutes has elapsed, rotate the "sensitivity" knob to its end position in a clockwise direction, then adjust the "zero" dial until the dc millivoltmeter reads

zero. Flip the switch to read on the 1-mV range of the meter and readjust the zero if required.

8. When no drift of the zero is evident after rechecking a few minutes later, switch on the power to electrolize the solution. Gassing at the anode will be evident. The amount of gassing at the cathode will depend on the purity of the solution. It may be barely visible. After 15 to 20 minutes the cell equilibrates to the electrolysis and the meter gives a steady reading. Readings above 100 generally indicate that impurity level is too high for the efficient recovery of zinc from the solution. With the aid of a calibration chart (Figure 11) the approximate current efficiency which might be expected from any particular solution may be estimated.
9. To turn the meter off at the end of a test, first turn off the power to the electrolysis cell. Then switch off the TCC current, the TCC heater, and the flow of zinc electrolyte.

PARTS LIST

A list of the more important components used in constructing the meter are given below.

<u>Zinc Electrolysis Unit</u>

U-tube:	Drying tube, U-shaped with side tubes, 150 mm long, Fisher Cat. No. 9-240.

Drierite tube: Drying tube, straight, one bulb, 100 mm long, Fisher Cat. No. 9-215.

Flow-meter: Fischer and Porter Tri-flat flowmeter, Tube 08F-1/16-16-4 Float SA-16.

Separatory funnel: 250-ml capacity with Teflon plug.

Power Supply: constructed in workshop using Hammond 167Q power transformer (see Figure 4).

Hydrogen Gas Detection Unit

Thermal Conductivity Cell: Gow-Mac Type WX, tungsten fil filament.

Power Supply: Acopian Variable dc Power Supply.

D.C. Amplifier: Acromag dc to dc Amplifier.

D.C. Milliammeter: Simpson Model No. 25, 10 milliamperes.

D.C. Millivoltmeter: Simpson Model No. 1329SC, 500 millivolts.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Mr. J. Herbert in the construction of the meter.

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1. Kerby, R.C. and Ingraham, T.R., Mines Branch Research Report R 243 (1971).
2. Ingraham, T.R. and Kerby, R.C., Can. Met. Quart. 11(2), 451-454 (1972).

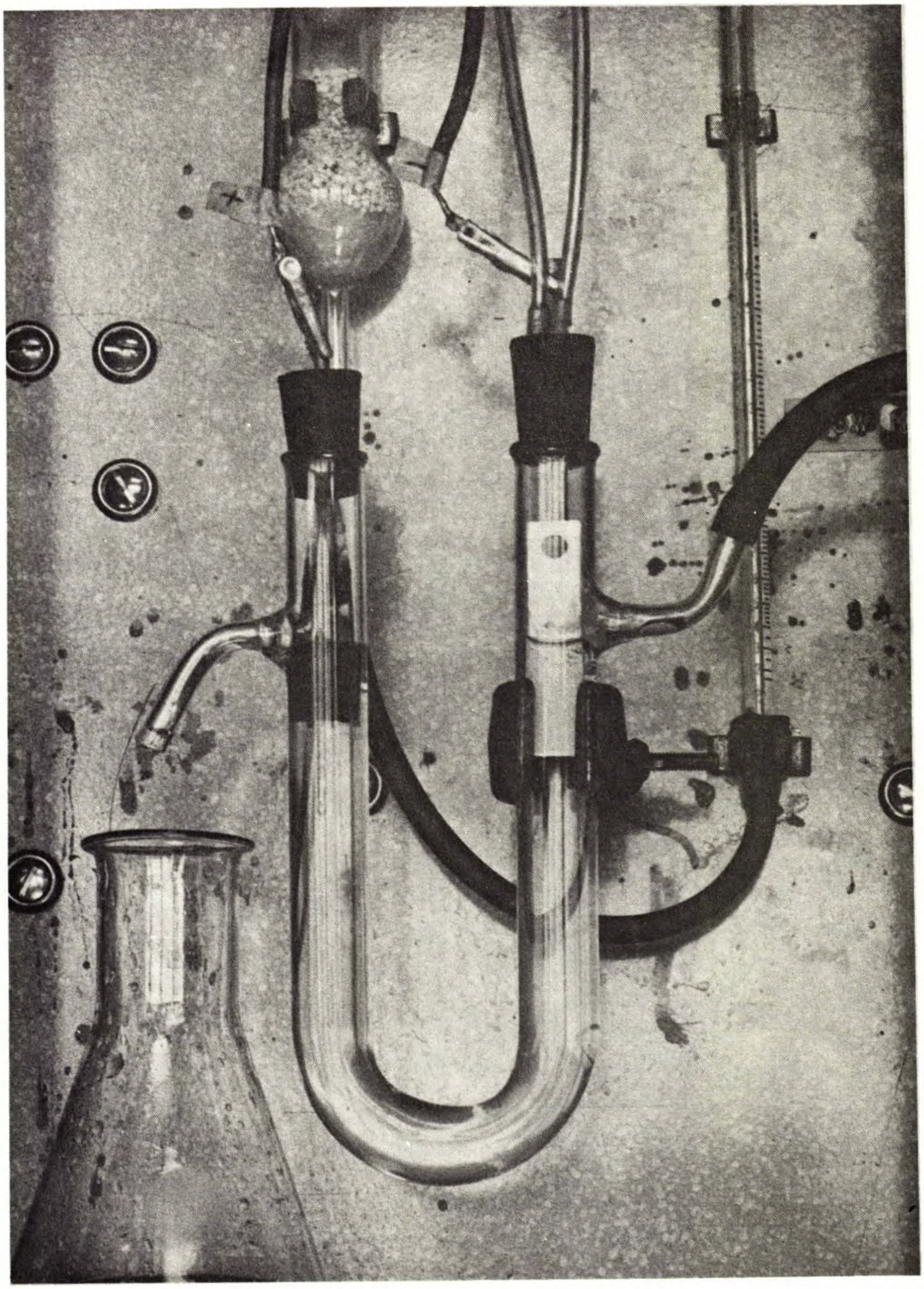

Figure 1: View of the zinc electrolysis cell.

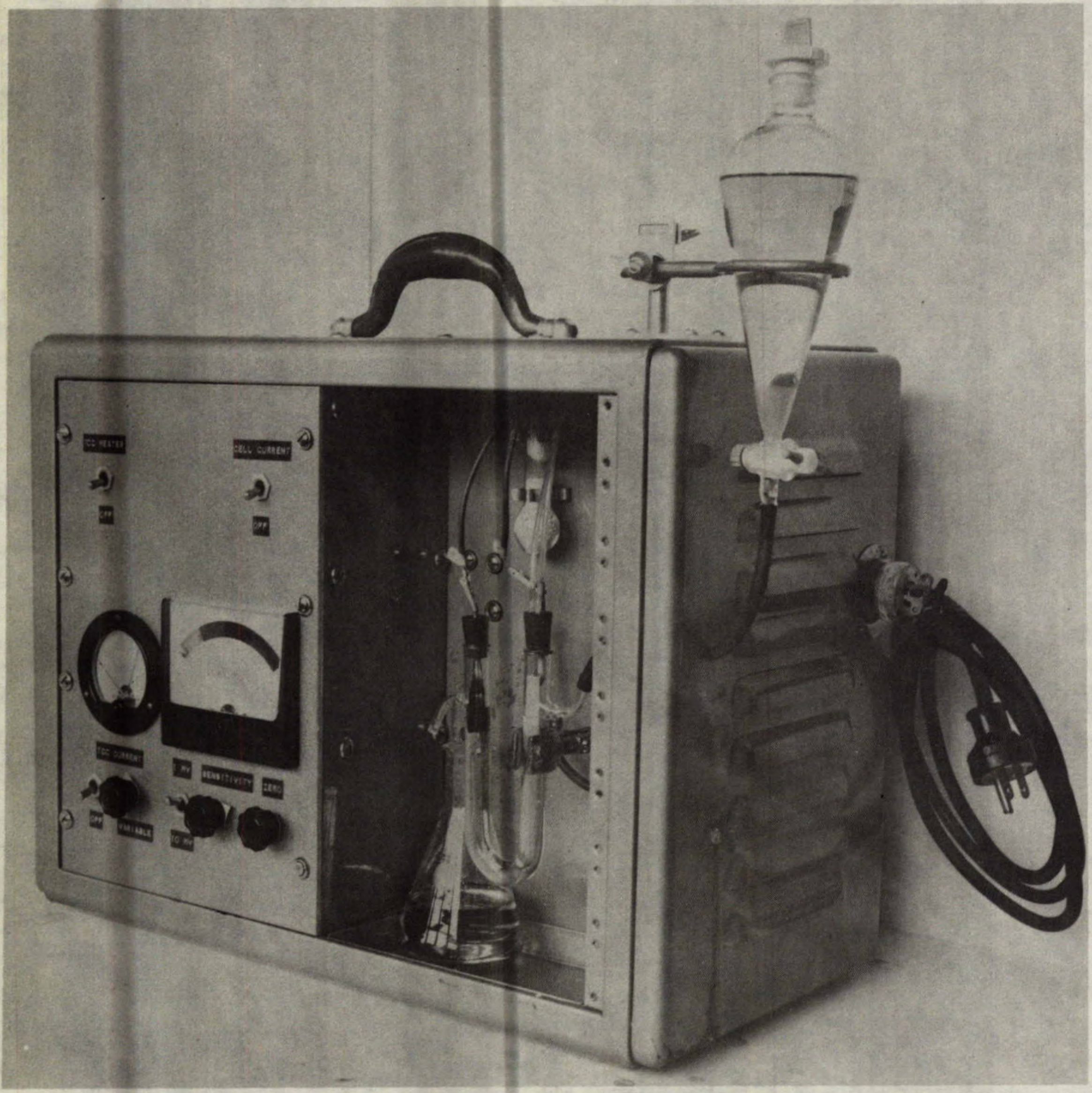

Figure 2: General view of the meter, showing the mounting of the sample jar.

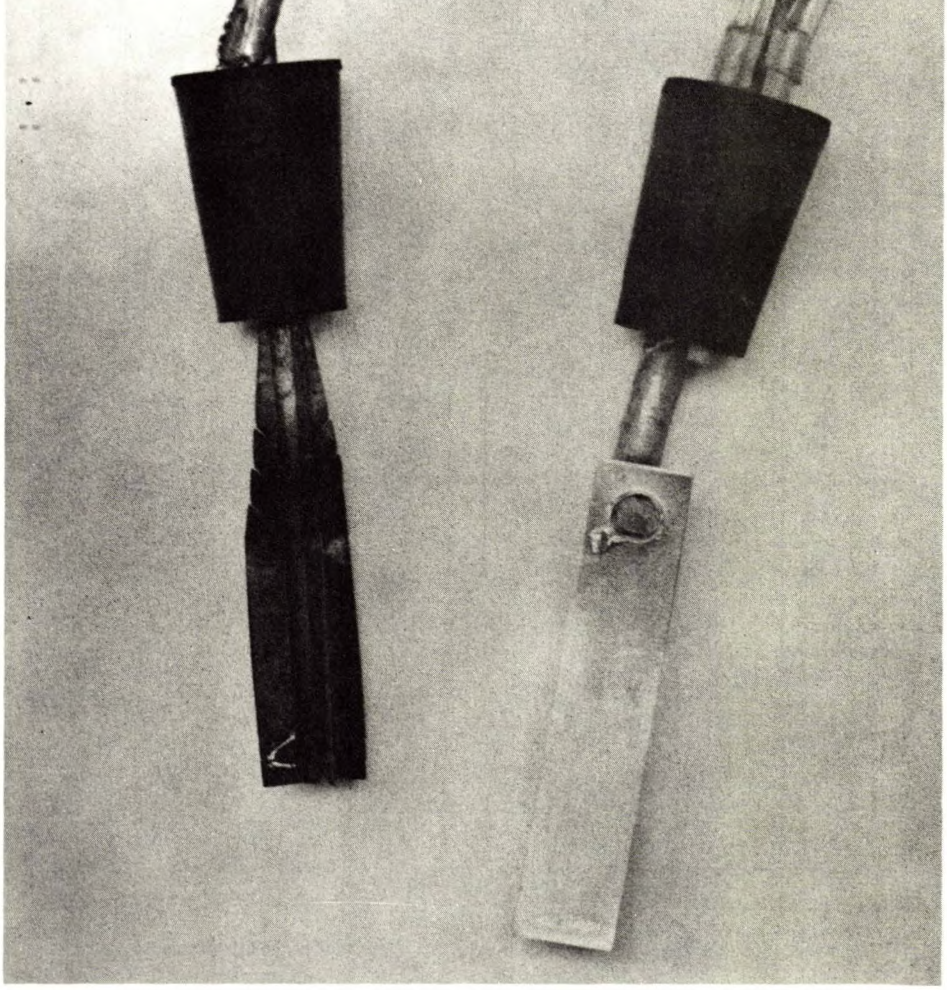

Figure 3: Aluminum cathode (right) and lead anode (left).

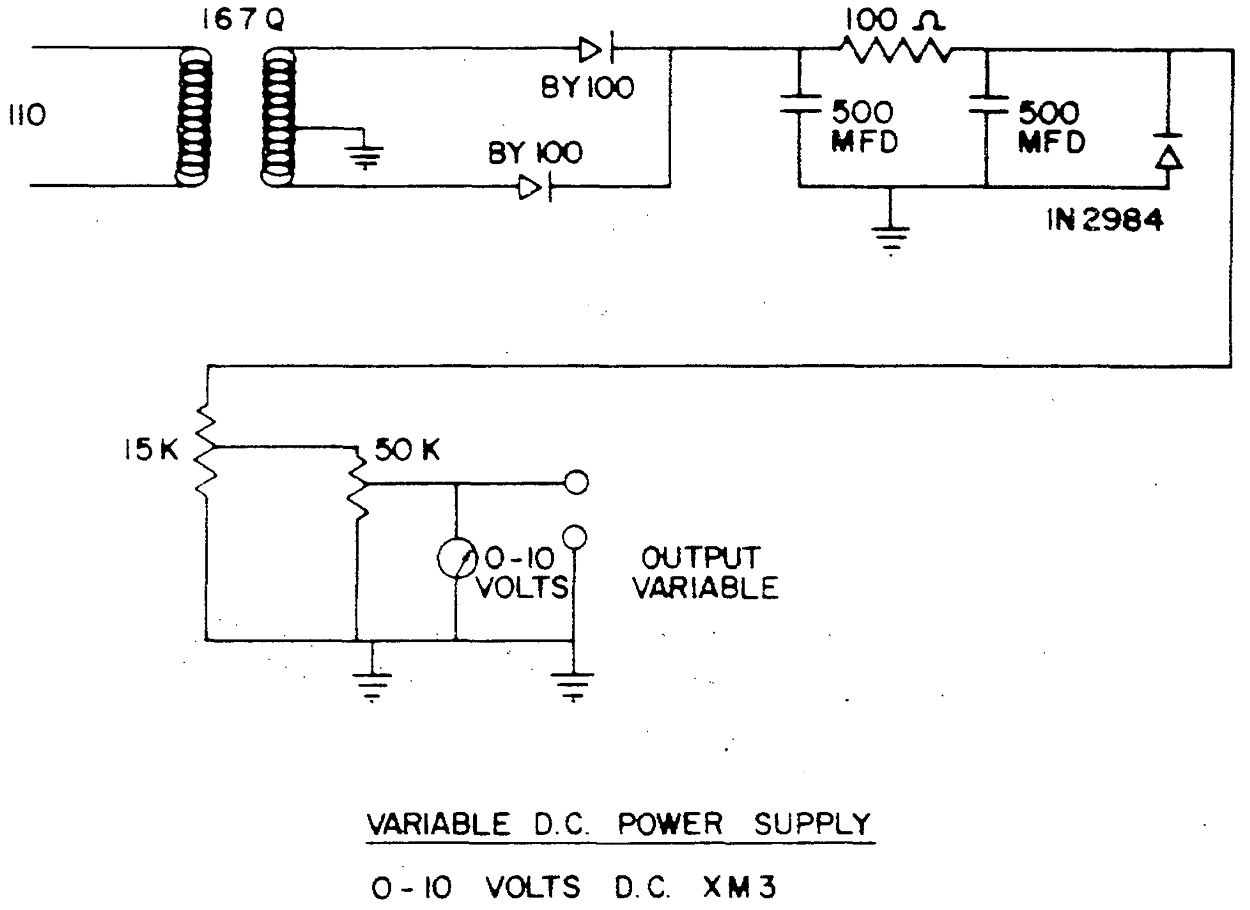

Figure 4: Electrical circuit diagram of the Hammond dc power supply.

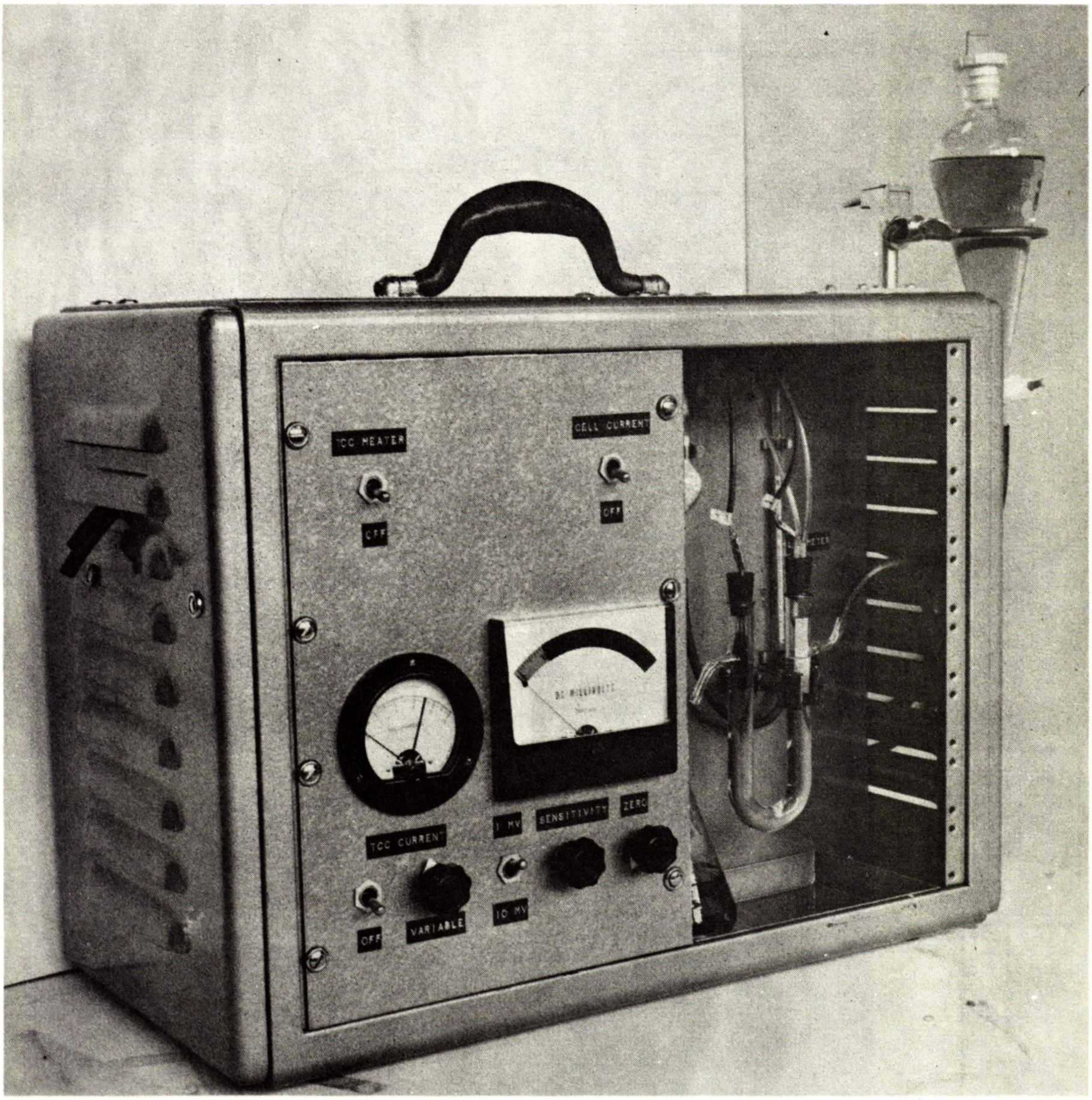

Figure 5: General view of the meter, showing the control panel.

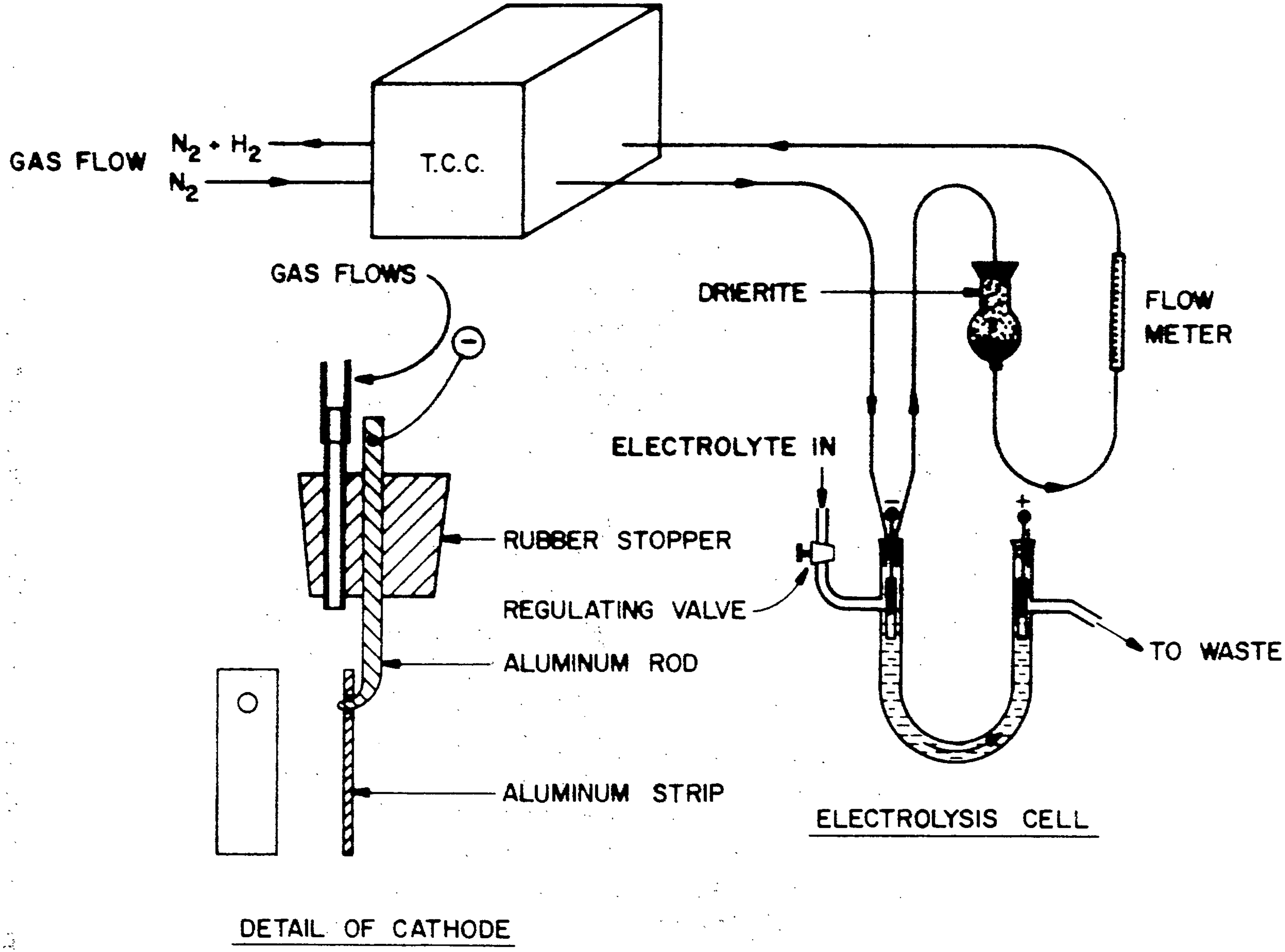

Figure 6: Schematic diagram of the apparatus used to measure cathodic hydrogen evolution during zinc electrolysis.

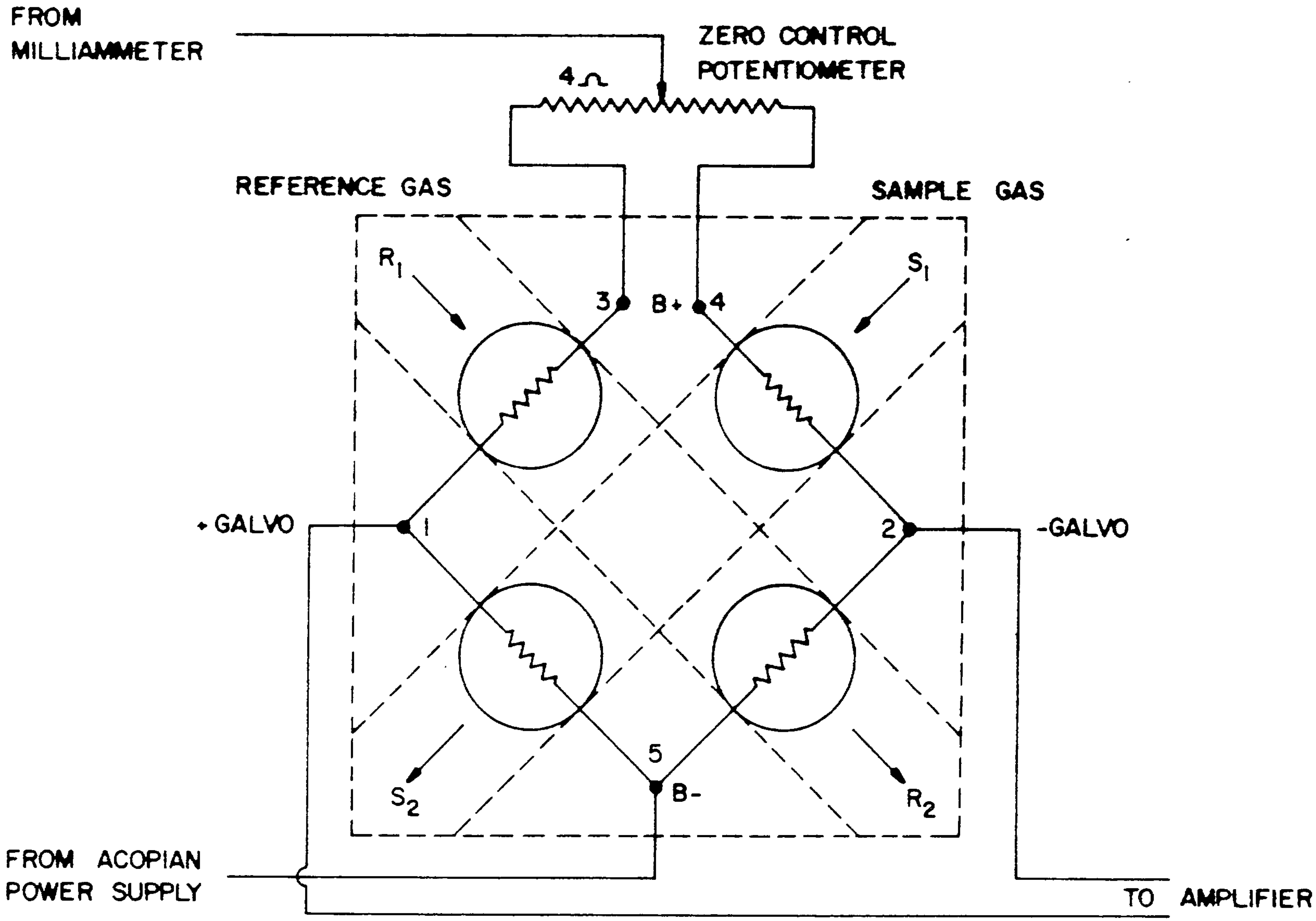

Figure 7: Electrical circuit diagram of the Thermal Conductivity Cell (TCC).

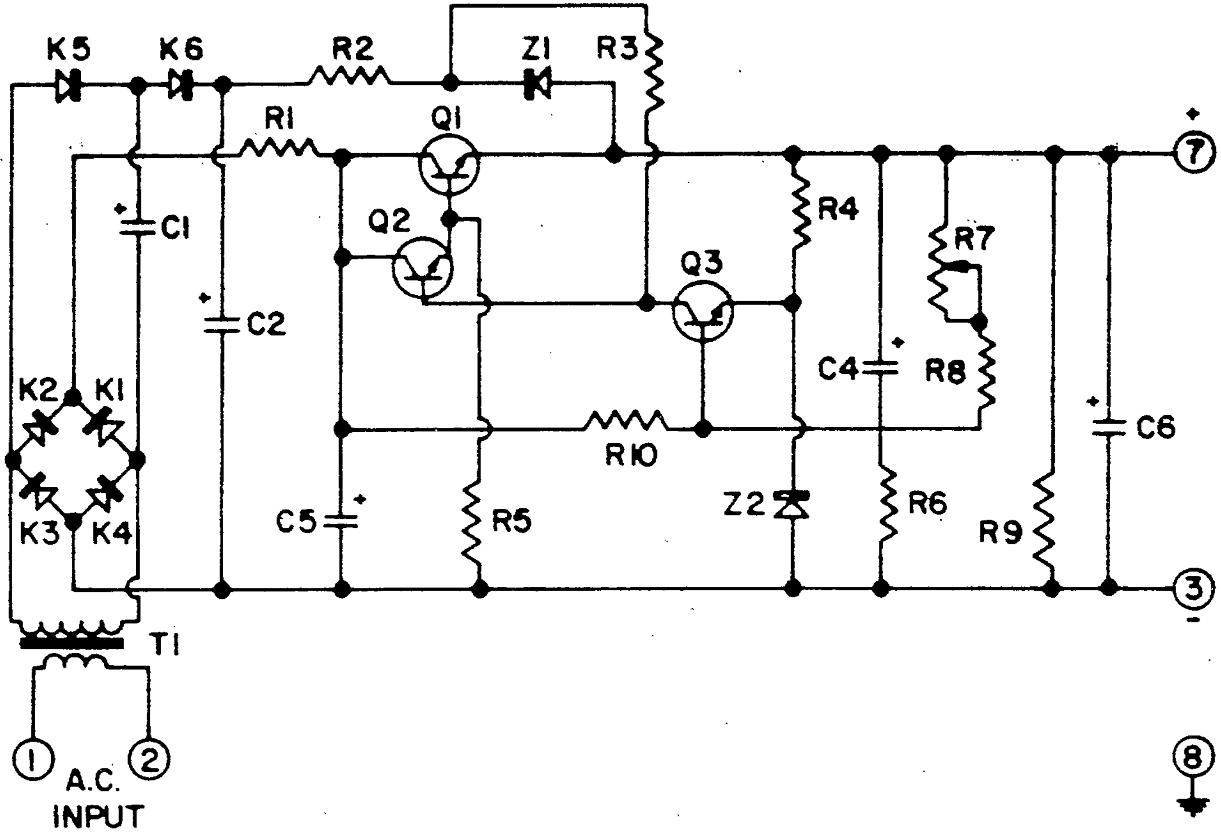

Figure 8: Electrical circuit diagram of the Acopian dc power supply.

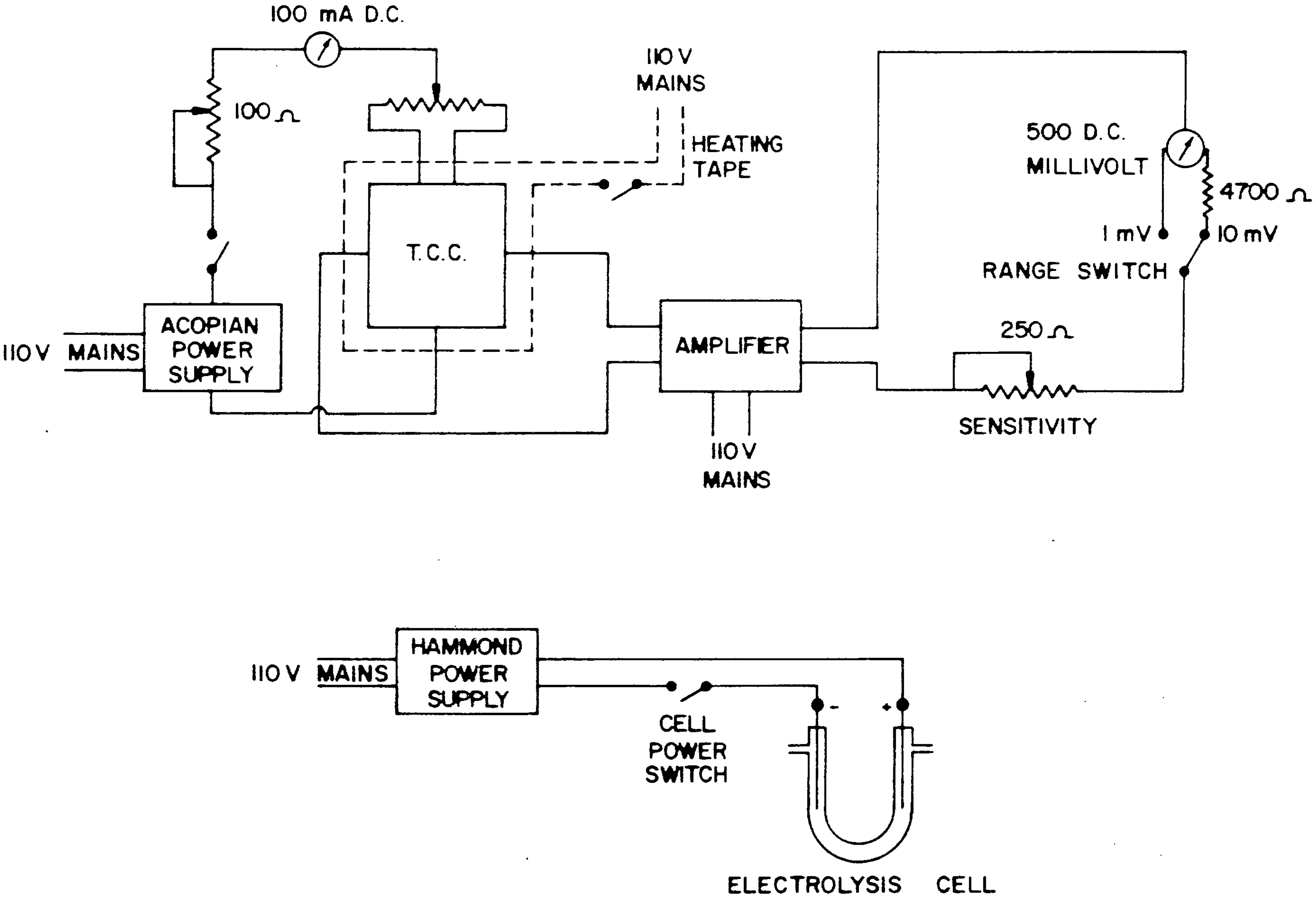

Figure 9: Circuit diagram for the zinc electrolysis meter.

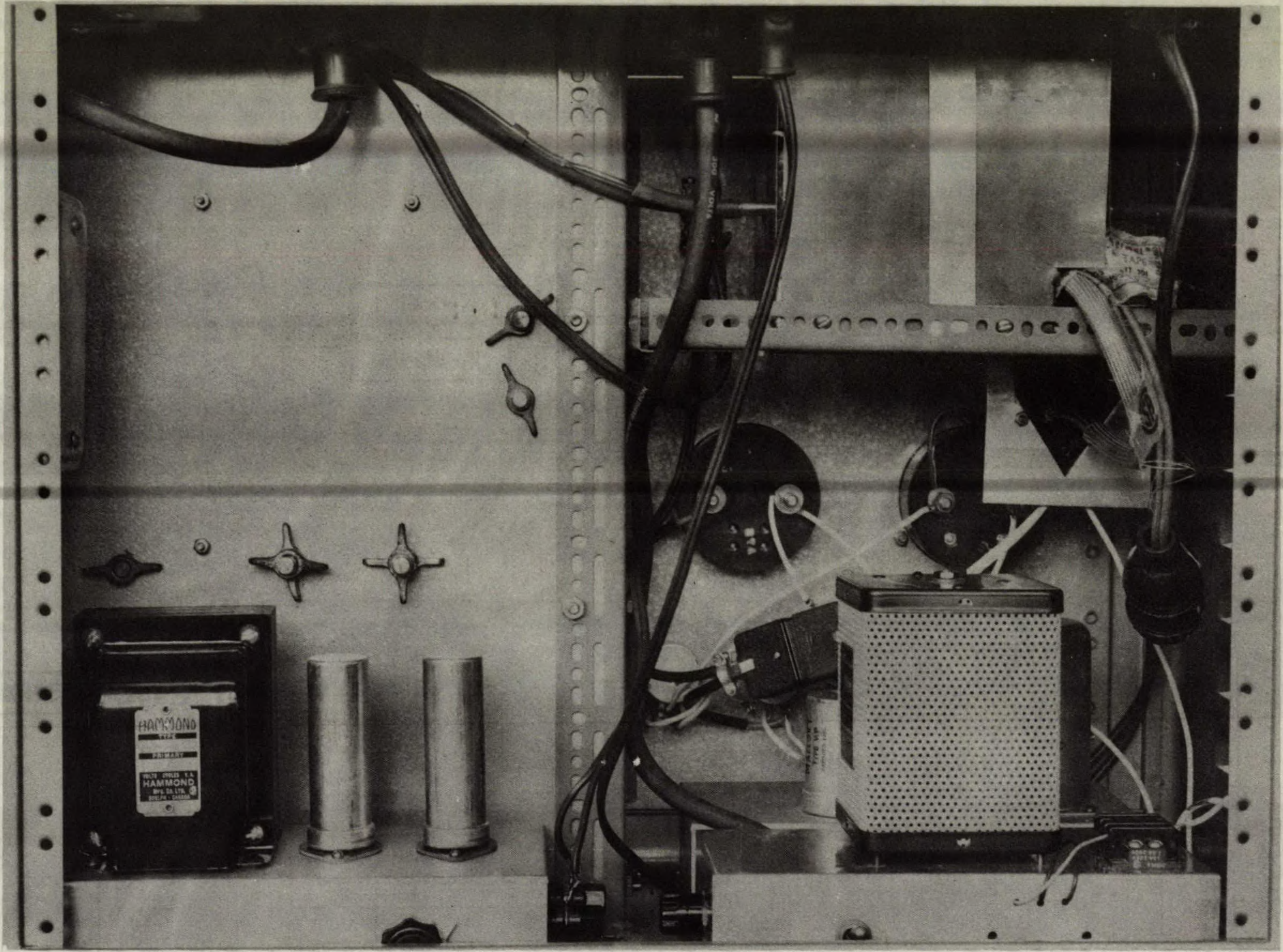

Figure 10: View of the rear of the meter, showing the location of the various electrical components in the cabinet.

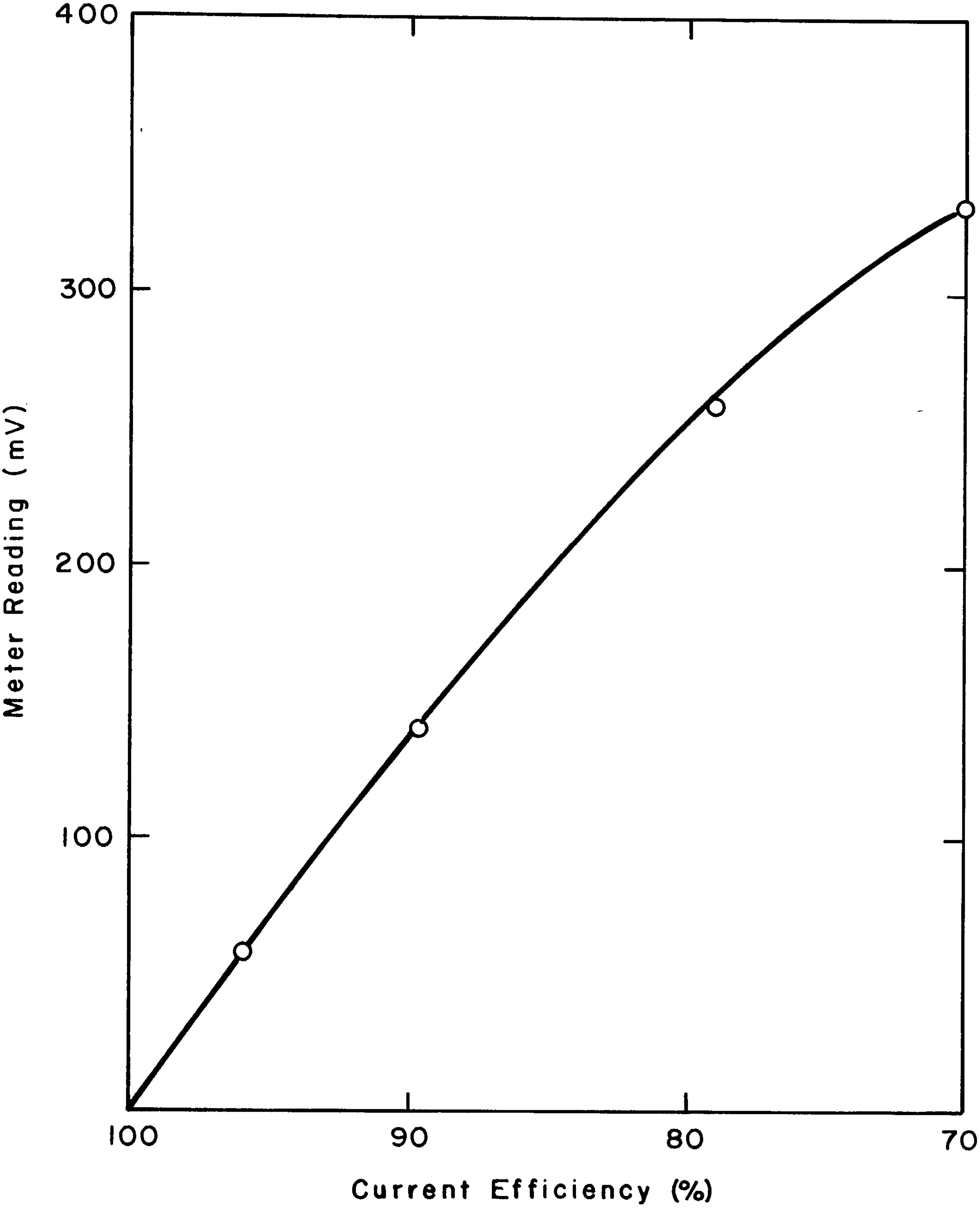

Figure 11: Example of a calibration chart for calculating the current efficiency associated with any meter reading.