

## CHAPTER III

### EQUIPMENT AND PROCEDURE



#### 3.1 Equipment

The equipment used in this work consisted of the followings.

##### 3.1.1 D.C. power supply

The D.C. power supply was built in this work. It is of silicon rectifiers operating from A.C. main power 220 volts. A transformer steps the voltage down to 0 - 6 volts, the current is then passed through a silicon bridge rectifier, and finally through a smoothing filter circuit. (The rectifier contains) A variable resistance was used to contrall the direct current output, an ammeter and a voltmeter showed the amperage and voltage of the rectifier out put respectively

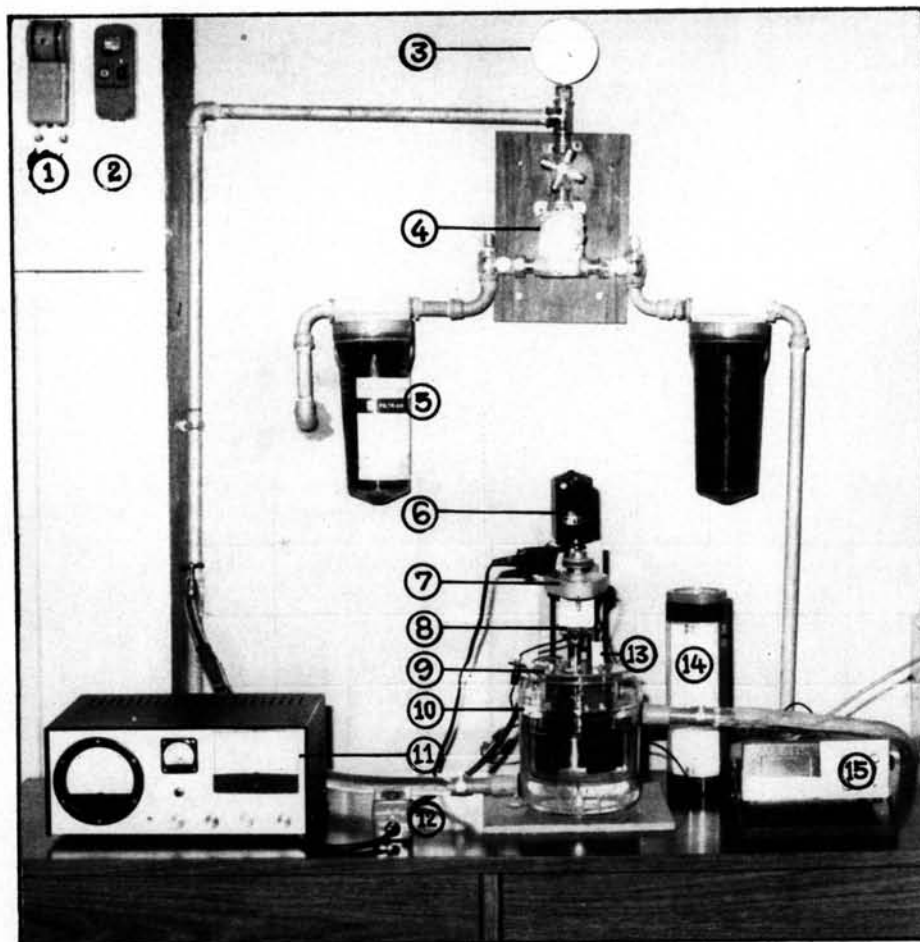
Specification : input 220 volt 60 cycle A.C.

output adjustable 0 - 6 volts,

0 - 5 amperes D.C.

##### 3.1.2 Electrolytic cell

Electrolytic test cell consisted of cell tank, water jacket, inner rotating cathode, fixed anode, A.C. motor, stand and electrode holder. The arrangement is shown in Figure 3.1, 3.2



- |                             |                            |
|-----------------------------|----------------------------|
| ① Water cooler switch       | ⑨ Electrolytic cell        |
| ② Water heater switch       | ⑩ Water jacket             |
| ③ Temperature indicator     | ⑪ D.C. power supply        |
| ④ Thermostatic mixing valve | ⑫ Electrolytic cell switch |
| ⑤ Water filter              | ⑬ pH electrode             |
| ⑥ A.C. motor                | ⑭ White light source       |
| ⑦ Electrode holder          | ⑮ Digital pH meter         |
| ⑧ Electrical connector      |                            |

Figure 3.1 Arrangement of experimental apparatus.

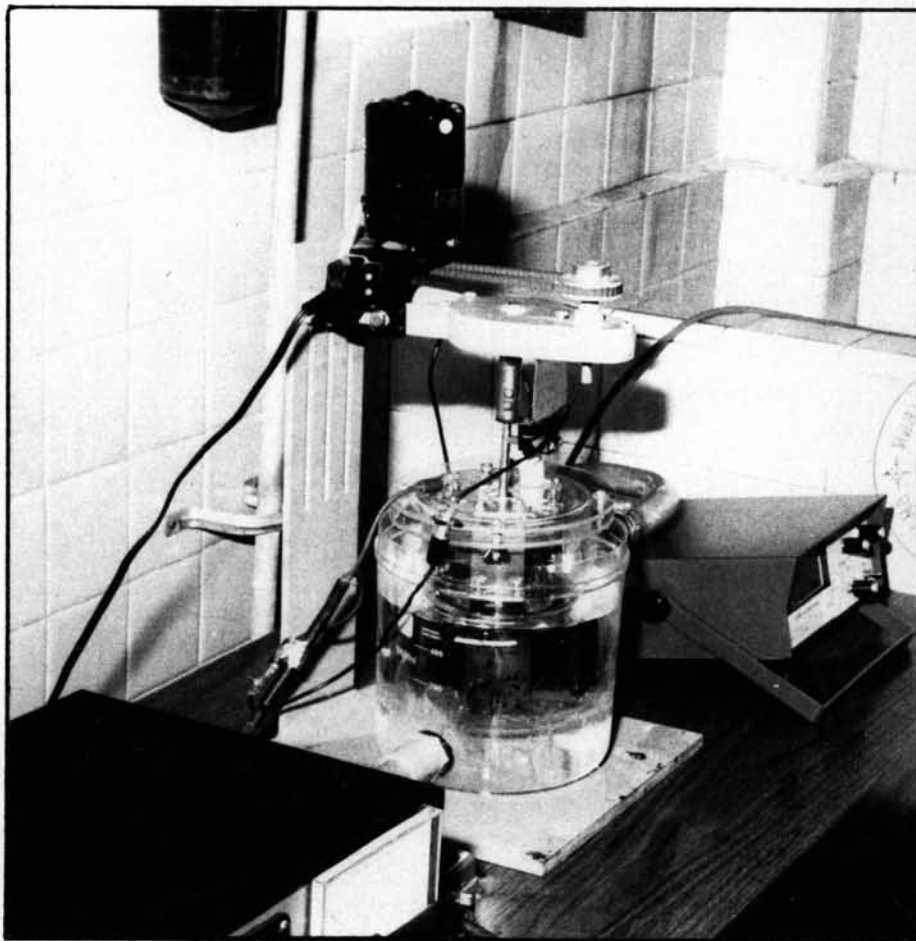


Figure 3.2 Photograph of electrolytic cell.

A 1,000 ml. beaker was used as the reactor. Water jacket was a plastic container having inlet and outlet for water at controlled temperature to keep the temperature of electrolytic test cell constant.

Inner rotating electrode is a hollow cylindrical electrode made of stainless steel type 316. Because the cathode must be corrosion resistant and also must be able to hold the silver deposit during electrolysis and release it completely during the stripping process, the usual cathode material is stainless steel. <sup>(20)</sup> Type 316 steel contains 16 to 26 percent chromium, 6 to 22 percent nickel, low carbon and 2.5 to 3.5 percent molybdenum, and is the most corrosion - resistant which can be work hardened. <sup>(21)</sup>

Characteristic :-

- Hollow cylindrical shape with radius = 2 cm.
- Height = 3.8 cm.
- Total surface area =  $100 \text{ cm}^2$  or  $1.0 \text{ dm}^2$
- Stainless steel Type 316 with thickness = 1.0 mm.

Anodes were made of graphite because of its high corrosion resistance and low electrical resistance. These anodes are readily available and are relatively inexpensive. <sup>(22)</sup> To obtain uniform current distribution around cylindrical cathode, the arrangement of anodes have to be radially symmetrical, by using four plates of rectangular graphite located around the cathode

equally spaced with stainless steel holder.

Characterestic :

- Graphite thickness = 4.0 mm.
- Length x width = 10 x 3.5 cm.
- Number of plates = 4
- Cylindrical arrangement with radius = 3.75 cm.
- Anode-cathode spacing\*\* = 1.75 cm.
- Total surface area = 307 cm<sup>2</sup> or 3.07 dm<sup>2</sup>  
(Anode : cathode surface area = 3 : 1)\*

A.C. motor was used to rotate the cathode with input : 90 watts, A.C. 220 volt 50 - 60 cycle per sec. and output : 42 watts, .46 amp., 7,000 r.p.m. The motor was manufactured by Phillips Co. The rotating speed can be controlled by electronic curcuit.

### 3.1.3 Digital pH meter

It was used for measuring pH of the solution. It was manufactured by Chemtrix Inc., Hillsboro, Ore, U.S.A. This pH meter was used with standard combination pH electrode, 0 - 14 pH and - 5 - 100°C, manufactured by EIL Chertsey - Surrey, Engl.

### 3.1.4 Tachometer

It was used for measuring the rotating speed of the cathode ; manufactured by Togohiseiki Co. Ltd., Japan.

### 3.1.5 Stop watch

It was used for timing ; manufactured by Heuer, Swiss.

\* Anode : cathode surface area of Electroplating and Electroforming of silver are in the range of 2 : 1 to 4 : 1<sup>(8)</sup>

\*\* In Electrolytic of metal anode-cathode spacing varies in the range of 0.5" - 3 1/2" (8)

### 3.1.6 Water temperature controlling system.

It consisted of water heater and water cooler manufactured by General electric Co. Ltd., U.S.A. The temperature of water is controlled by thermostatic mixing valve manufactured by Eastman Kodak Co. Ltd.

3.1.7 Atomic absorption spectrophotometer (model AA 120), manufactured by Varian Techtron PTY, Ltd, consisted of the following.

#### Lamp.

It is Hollow cathode lamp, tiller gas is Neon and window material is quartz. The purpose is to analyze silver concentration of the solution, then the wavelength at resonance line of silver element is  $3281^{\circ}\text{A}$ .

#### Burner.

Its flame atomizer is air-acetylene which has temperature about  $2,300^{\circ}\text{c}$ .

#### Monochromator.

It is Ebert type, plane gratting size 33 mm. x 22 mm. which consisted of 1276 lines/mm.

#### Photomultiplier.

It is HTV. type R. 213, manufactured by Mamatsu TV Co. Ltd. very sensitive with Ultraviolet and visible or the wauelength in range  $1930 - 7700^{\circ}\text{A}$ .

### 3.1.8 Electronic balance

### 3.1.9 Oven

### 3.1.10 Glass wares.

It consisted of Volumetric flasks, 250 ml., 100 ml. pipettes 1 ml., 20 ml. buret 50 ml. and glass funnel.

### 3.1.11 Syringe.

It is 2 ml. syringe, manufactured by Hamilton Co. Ltd., Nevada, U.S.A., used for dropping concentrate acid and base into solution to keep pH constant.

## 3.2 Chemicals.

The chemicals used in this work were as follows.

### 3.2.1 Standard silver nitrate solution for atomic absorption spectroscopy

- Manufactured by BDH chemical Ltd., Poole, Engl.
- Content 1 ml. = 1.00 mg. silver.
- Used as stock solution for preparing standard solution of silver by ten - fold dilution which have the following concentration 2, 4, 6, 8, 10 p.p.m.

### 3.2.2 Deionized water.

- double distilled water which had pass though ion exchange column.
- used as solvents for preparing standard solution.

## 3.2.3 0.1 N. Potassium thiocyanate solution (KSCN)

- analytical reagent, J.T. Baker chemical Co., Phillipsburg.
- preparation, about 10.5 g. of A.R. potassium thiocyanate was weighed out and dissolved in 1 litre of water in a volumetric flask, then shaken well.
- This is standardised by titration against standard 0.1 N. silver nitrate.

3.2.4 0.1000 N. Silver nitrate solution. ( $\text{AgNO}_3$ )

- analytical reagent, BDH chemicals Ltd., Poole, Engl.
- preparation : exactly 8.496 g. of  $\text{AgNO}_3$  was weighed out and dissolved in water, then made up to 500 ml. in volumetric flask.

## 3.2.5 12 N. Sodium hydroxide (NaOH)

- analytical reagent, BDH chemicals Ltd., Poole, Engl.
- preparation : about 120 g. was weighed out and dissolved in water, then made up to 250 ml. in a volumetric flask

3.2.6 Acetic acid gracial ( $\text{CH}_3\text{COOH}$ )

- analytical reagent, BDH chemicals Ltd., Poole, Engl.
- extra pure 99.5 %

3.2.7 0.1 M. Ammonium ferric sulphate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ 

- laboratory chemicals, May & Baker Ltd., Dagenham, Engl.
- preparation, about 9.644 g. was weighed out and dissolved in water, then made up to 100 ml. in a



volumetric flask.

3.2.8 Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ )

- laboratory chemicals, May & Baker Ltd. Dagenham, Engl.

3.2.9 Sodium sulphite anhydrous ( $\text{Na}_2\text{SO}_3$ )

- laboratory chemicals, May & Baker Ltd., Dagenham, Engl.

3.2.10 Potassium chloride (KCl)

- laboratory chemical, May & Baker Ltd., Dagenham, Engl.

### 3.3 Procedure

3.3.1 Procedure for quantitative analysis of silver from various fixing solution waste.

Concentration of silver were measured by atomic absorption spectrophotometer. A standard curve (see Appendix I) was first constructed. It was a plot of concentration in p.p.m. versus absorbance. Then, the various fixing solution waste was determined as follows.

After pH measurement, the sample was diluted by ten-fold dilution with deionized water to concentration region which could be measured. The absorbance of the dilute sample was measured and concentration was read from standard curve.

3.3.2 Preparation of pure silver complex ( $\text{NaAgS}_2\text{O}_3$ ) solution, silver concentration : 7.5 g /l.

Exactly 23.6207 g.  $\text{AgNO}_3$  was weighed out and dissolved in 200 ml. water, followed by adding 10.3657 g.  $\text{KCl}$ . Another solution was prepared by dissolving about 480 g.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1 litre of water at about  $125^\circ\text{F}$ . The two solutions were mixed together and made up to 2 litres in volumetric flask. The mixture was well shaken.

3.3.3 Preparation of used fixing solution, silver concentration : 7.5 g /l.

About 50 litres of used fixing solution having silver concentration of 7.5 g /l. was collected from Directorate of Photography, R.T.A.F, for the whole experiment. The stock solution was stirred vigorously before each sample was taken for experiment in 1,000 ml. beaker. The used fixing solution was clarified by filtration with paper filter.

3.3.4 Procedure for determination of decomposition potential

The experiment was carried out by mean of the apparatus arranged as shown diagrammatically in Figure 3.3. 500 ml. of sample was placed in the electrolytic cell. The rotating speed of the cathode was checked by a tachometer (this experiment was done at various speed). When the water temperature in the jacket was at  $30^\circ\text{c}$ , the applied voltage was gradually increased. The voltmeter and ammeter readings were noted after allowing a short time for the values to become steady. Upon plotting the current against the applied voltage, it was observed that there was a

sudden increase in current at a certain voltage. This is the decomposition potential.

3.3.5 Procedure for analysis of recovered silver products by Volhard method.

Exactly 0.500 g. of sample was weighed out, and placed into 100 ml. beaker. 25 ml. of deionized water was added, followed by 25 ml. of nitric acid. The mixture was heated vigorously on a hot plate for at least 10 minutes or until complete digestion to prevent drying and charring (Complete digestion is indicated by a relatively clear solution). Then the solution was allowed to cool to room temperature. After cooling, the sample was diluted to 100 ml. in a volumetric flask. 20 ml. of this solution was pipetted and titrated with 0.1 N potassium thiocyanate using a few drops of 0.1 M ammonium ferric sulfate as indicator. The end point was indicated by a salmon pink color ( $\text{FeSCN}^{++}$ ), and the volume of KSCN used was recorded.

Calculations:

Normality KSCN X ml. KSCN = milliequivalents of silver

(0.1) N x (X) ml. = (0.1 X)(0.10788) g. Ag

Weight of Ag in 20 ml. of sample =  $(0.005) \frac{\text{g}}{\text{ml}} (20) \text{ ml}$

Therefore percentage of purity =  $\frac{(0.1 X) (0.10788)(100)}{(0.005)(20)}$

= (10.788) X

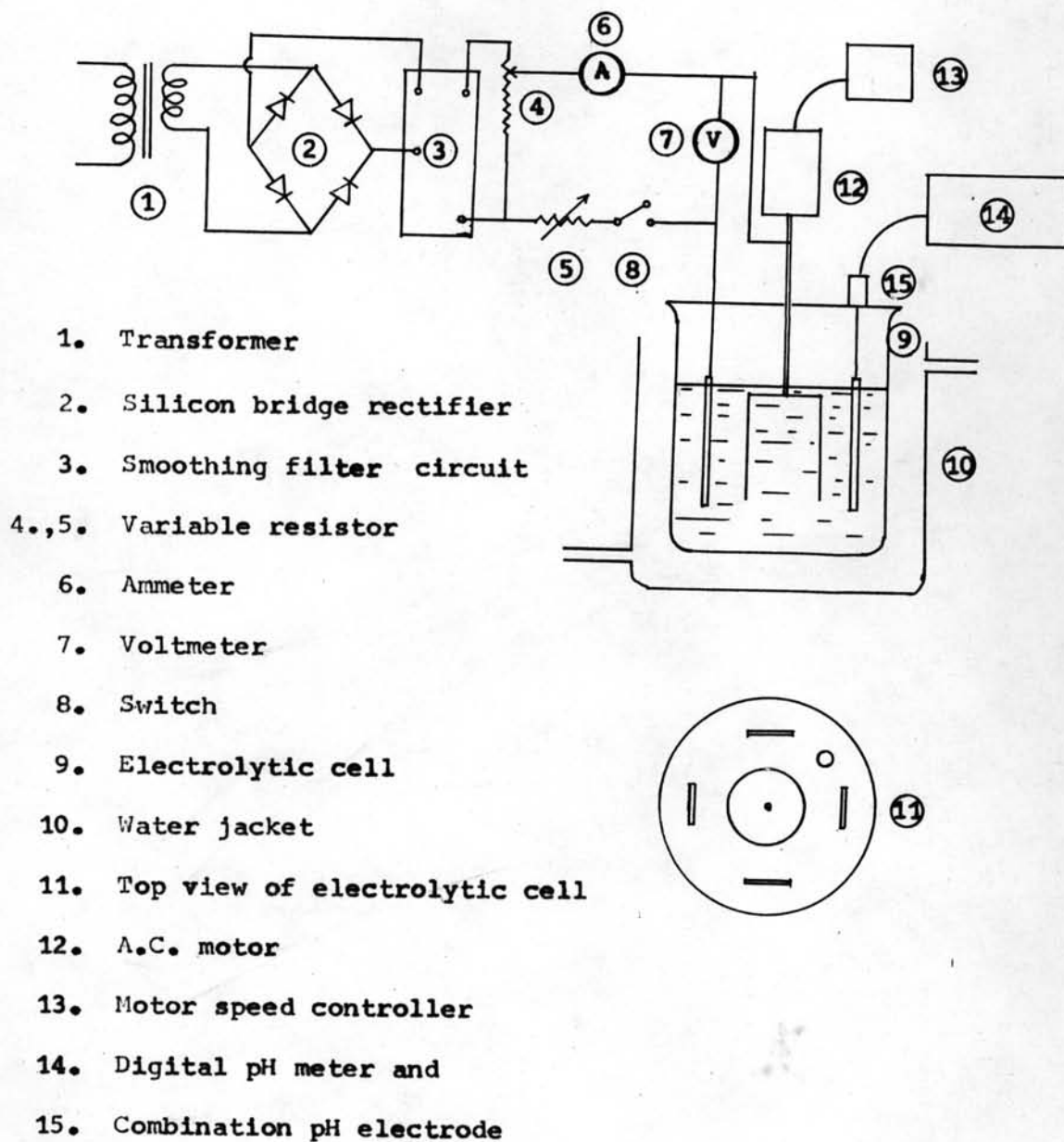


Figure 3.3 Diagrammatically arrangement of experimental apparatus.

### 3.3.6 Procedure for determination of current efficiency.

Arrangement of experimental apparatus is as shown in Figures 3.1 and 3.3. 500 ml. of sample was placed in the electrolytic cell, and the operating condition was controlled as followings.

Applied voltage : constant voltage was accomplished by voltage regulator in smoothing filter circuit, and shown on the voltmeter.

Current : constant current was accomplished by adjustment at variable resistor, and shown on the ammeter.

Cathode rotating speed : constant speed was accomplished by speed controller and was measured by the tachometer.

pH of solution : constant pH of solution was accomplished by dropping glacial acetic acid and 12 N. NaOH with a 2 ml. syringe, and its value was measured by the digital pH meter including standard combination pH electrode.

Temperature of electrolytic cell : constant temperature of electrolytic cell was accomplished by passing water of controlled temperature through the water jacket.

When all the operating condition had been set and under control switch was on to start operation and timing began with a stop watch. Weight of theoretical deposited silver ( $G_M, \text{theor.}$ )

can be calculated from the quantity of current (1 coulomb = 1.0788 mg. Ag) and the time used. Weight of the experimental deposited silver ( $G_M$ , expt.) was measured directly. The current efficiency was obtained by Equation 2.14

$$\eta = \frac{G_M, \text{ expt.}}{G_M, \text{ theor.}} \times 100$$

They are two methods to determine the weight of the experimental deposited silver.

3.3.6.1 Direct method : The fresh electrode was weighed out and recorded. After silver recovery operation, the electrode was dried in an oven at 60°C for 45 minutes, then allowed to cool to room temperature and weighed again. The experimental deposited silver was obtained by subtracting the weight of deposited silver electrode with that of the fresh electrode, and then multiplied with percentage purity of yield determined by the volhard method.

3.3.6.2 Indirect method : After silver recovery operation for  $t$ . minutes, the sample was analyzed to determine silver concentration by the atomic absorption spectrophotometer (to measure the absorbance and determine silver concentration from the standard curve). Then the experimental deposited silver were obtained from the following equation.

The experimental deposited silver =  $(C_o - C_t)V$

where  $C_o$  = Original silver concentration, g /l

$C_t$  = silver concentration after silver recovery  
operation for t. minute, g /l.

V = Volume of sample,  $\frac{1}{2}$  l

3.3.7 Procedure for determination of the minimum silver concentration at which silver sulfide appeared.

After setting operation condition for recovery silver from 500 ml. of the sample had been completed, the switch was on to start the operation, and timing began with a stop watch. During the operation, the change in color of deposited silver electrode which was illuminated by white light was observed. The change of color from white to black is the end point at which reaction to form silver sulfide occurs. The experiment was repeated two more times to ensure the end point. "The sample at the end point was analyzed to measure the silver concentration by the atomic absorption spectrophotometer. This silver concentration is the minimum concentration at which silver sulfide began to appear for each current density.