# CHAPTER 2

## Techniques & Graphical Analysis

# EXPERIMENTAL TECHNIQUES

## 2.1 INTRODUCTION:

Several experimental techniques were employed during the course of this work. Excellent accounts are available on crystal growth (Gilman), (1) optical microscopy (Carl Zeiss(2), Clark(3), Martin & Johnson (4), Thompson(5)) indentation technique (Mott(6)), electrolytic conductivity (Harris(7)), and electron microscopy (Venables(8)). Hence only a brief description together with their salient features are presented here.

## 2.2 CRYSTAL GROWING TECHNIQUES:

There are several methods developed for growing crystals of different types of materials. They are as follows:

### 2.2.1 Growth from solution:

1) Growth from aqueous solution:

a) By progressively (regularly) lowering the temperature to reduce the solubility of solute and produce crystallization under controlled conditions (e.g. inorganic salts, such as alkali halides, Rochelle salts, etc.)

b) At constant temperature:

i) By progressively decreasing the amount of solvent by evaporation and

ii) By increasing the amount of solute.

2) Growth from flux (two component system) (Ruby and other refractory materials)

2.2.2 Hydro thermal Growth (Calcite, Zincite, etc)

2.2.3 High pressure Growth (Boron nitride)

2.2.4 Growth by gel method

2.2.5 Growth by electrodeposition

2.2.6 Growth from melt - one component system where no solvent is present.

a) Bridgmann - stockbarger method

b) Zone melting method

c) Verneuil flame fusion method

d) Czochralski - Kyropoulos method

2.2.7 Growth from vapour (gas) phase.

2.2.8 By chemical decomposition method

2.2.9 By strain - anneal method

2.2.10 From high temperature solution

2.2.11 From low temperature solution

The present work is a study of the growth of single crystals of ammonium hydrogen d-tartrate (d-AHT) in a gel medium. Several parameters affecting the growth of d-AHT were studied. The details are given in the concerned chapters.

## 2.3 SEMI-MICRO BALANCE:

For accurate weighing of the chemicals used in the gel method Mettler (E-Mettler, Zurich, made in Switzerland) semi micro balance was used. The least count was $10^{-5}$grms. The balance utilizes the principle of weighing by substitution and the constancy of sensitivity for all loads.

The latter feature distinguishes it from an ordinary beam balance where the sensitivity depends on load, i.e. it changes with the load in a way which reflects the relative positions of the three knife edges, viz. left, central and right on which the beam rests. Further in contrast to the ordinary balance, the present one is fully loaded when used.

## 2.4 pH- METER:

Gel pH is one of the important factors controlling the growth of a crystal, in a gel medium. It is therefore necessary to use a pH - meter to determine the gel pH of solution before gelation. The pH value or hydrogen ion concentration is a measure of the acidity or alkalinity (basicity) of a solution. For this purpose a digital pH meter manufactured by Elico Private Limited, Hyderabad, of the Model LI-120 was used. As compared to earlier methods, the pH meter gives quick measurement continuously and without disturbance to the solution whether by contamination or by withdrawal of any significant volume.

The basic principle of this meter is as follows:
If a set of properly designed electrodes are immersed in a solution and properly connected externally, they generate a complex voltage containing a component which is a linear function of pH level. It was standardised for different ranges (acidic and alkaline) using buffer solutions prepared from the given tablets.

## 2.5 VERTIVAL INCIDENT LIGHT MICROSCOPE:

For observing fine features on a crystal surface an optical microscope was used.

The vertival microscope manufactured by Carl Zeiss is one of the best and sophisticated instruments amongst the metallurgical microscopes. It can be used for different types of illuminations. Further, its utility is enhanced by providing different attachments which can be fitted to this microscope such as the hardness testing unit, polarizing accessories, multiple beam interference accessories etc. For efficient use of this instrument it is imperative to be familiar with various parts, arrangements for adjustment of coarse motion brake and illuminating unit incorporating bright field and dark field, for the co-ordination of concave mirror condensers etc. Excellent account of the above is given in the instruction manual (2) supplied by the manufacturer. The basic unit of microscope (Fig.2.1) consists of 1) the illuminating system; 2) the stage for placing the specimen; 3) the body of the microscope carrying the objective and 4) the monotube or binocular tube arrangement (Fig.2.1). The ray diagrams for bright and dark field illuminations are shown in figures (Fig. 2.2 & 2.3). The focussing arrangement is simple. It consists of a fine focussing and a coarse one. It is necessary to adjust the coarse motion brake.

a) Adjustment of the coarse motion brake (Fig.2.1):

The instrument is usually, supplied with the coarse motion brake released; hence the smoothness of the coarse motion mechanism has to be adjusted by the users. This is done by holding fast one pinion head (1) and moving the other one in clockwise direction until the desired smoothness has been attained.

b) Adjustment of illumination equipment:

Having switched on the lamp, set switching knob (2) to bright field (see para (d)) and on opening diaphragms (3 & 4) a bright circle becomes visible on the protective plate. This circle can be observed without eye-peice or even better after detaching angular tube. By turning the fixable knob so as to be loosened and moving pull-rod (not shown in Fig.2.1) in axial direction the filament image is focussed on protective plate as critically as possible. The pull-rod is then again clamped in position and the filament image is centered by actuating centering screws (5).

c) Co-ordination of concave mirror condensers:

The co-ordination of concave mirror condensers to the objectives is to be followed according to the instructions of the manufacturer. The concave mirror and slide especially adapted for objective 25 X /0.50 are marked with black point and those for objective 50 X/0.80 with a white point. The following magnification values refer to the equipment of carrier VERTIVAL (factor 0.63x) with regular tube (factor 1.6x) and monocular or binocular tube (factor 1x).

TABLE 2.1

| OBJECTIVE | CONCAVE MIRROR CONDENSER | EYE-PIECE PK 8X | PK 10X | PK 12.5X | PK 16X |
|---|---|---|---|---|---|
| 6.3X/0.12 | 11 | 50X | 63X | 80X | 100X |
| 12.5X/0.25 | 12 | 100X | 125X | 160X | 200X |
| 25X/0.50 | 12 | 200X | 250X | 320X | 400X |
| 50X/0.80 | 12 | 400X | 500X | 630X | 800X |
| HI 100X/1.30 | -- | 800X | 1000X | 1250X | 1600X |

d) Bright field (Fig.2.2)

For carrying out examinations in bright field the switching knob (2) has to be turned until the point to be found on it does no longer face the observer. Attention should be paid to the diaphragm slide (6) with an arrangement for luminous-field stop to bring it in centre, being inserted into the carrier to reach the maximum insertion point for proper alignment. A green filter, an attenuation filter or frosted glass may be introduced optionally or in a combined form into the filter slide (7). This slide is provided with a free passage. Filter and shutter slides have to click indistinctly.

The luminous field diaphragm is centered by actuating the two centering screws (8) and the aperture diaphragm by making use of socket wrenches to be put on to the two centering screws (9). The image of the luminous field diaphragm is to be seen within

the image of the objective sharply depicted and that of closed aperture diaphragm in the exist pupil of the objective after having removed eye-piece.

e) Dark Field (Fig.2.3):

For investigations in the dark field the objective corresponding to the desired magnification has to be fitted with the concave mirror condenser co-ordinated to it as mentioned above in (c). Switching knob (2) has to be set in such a way that the point to be found on it, faces the observer. The luminous field and aperture diaphragm are opened completely by actuating knurled wings ( 3 & 4).

f) Camera attachment (Fig.2.4):

For taking photomicrographs of samples, camera is attached to the microscope. The arrangement is shown in Fig.2.4. The advantage of this method is that it is possible to observe the sample while taking photographs.

## 2.6 VICKERS PROJECTION MICROSCOPE (FIG.2.8):

It is desirable to have bigger size films (i.e. 8.5 cm x 6.0 cm and 12.0 cm x 9.0 cm) to obtain photographs with useful magnification of the etched surfaces. Since this facility is not available with vertival microscope, it was decided to utilize the Vickers Projection Microscope.

It is an inverted metallurgical type of microscope and carries

two different systems for the optical examination of the crystals - one of them being the transmission and the other, the reflection system. In the present work, only the reflection system was used.

## 2.7 INDENTATION TECHNIQUE (FIG.2.5):

Hardness is one of the important mechanical properties and is the mechanism which is least understood. Static indentation technique using mhp 160 microhardness tester is employed (Fig.2.5).

The indenting device (19) and the threaded socket for objective (20) are mounted on a common carriage, which can be moved to and fro laterally by the handle (21) in the slide (22) until it meets the stops. This makes it possible to place either the indenter device or the objective above the test specimen. The threaded socket also has a threaded collar for concave mirror condensers, so that the indentation can be also be measured with peripheral dark field illumination.

A filament is attached to the upper surface of the slide for mounting the microhardness tester in the corresponding mount of an upright incident light microscope. The indenter device is suspended from two springs, so that it is rather sensitive to vibrations, which are manifested by continuous or intermittent swings of the indent lines on the force scale. If the vibrations exceed the tolerable level or (what is rarely the case) have a frequency that is in resonance with the natural frequency of the microhardness tester, provision must be made for absorbing the

vibrations of the microscope or else the latter must be set up in a part of building subject to little vibrations. Otherwise, the necessarily inaccurate application of the force, on the one hand, and the boring action of the indenter on the other would result in errors that might affect the hardness readings considerably.

Various diamond indenters may be used with mhp 160 microhardness tester. Regular four-sided Vickers indenter and the Knoop pyramidal indenter with a rhombic base are employed in the present investigation. They are kept in small screw top cases when not in use. One of them can be inserted into the tester mounting by means of a special clamp. A study on the mounting and a corresponding slot in the indenter hold provide for a correct alignment. The mhp 160 microhardness tester is a sensitive instrument that requires careful handling. Dropping it will certainly result in ruining its adjustment. The microhardness tester should always be kept in a closed case when not in use to avoid dust setting on it. For optimum utilization of the tester, detailed instructions for its adjustment, etc. are given below:

1. Level the stage (14) by using highly sensitive spirit level.

2. Focus microscope (without microhardness tester) on to an object having striking features or on to a centering cross. The object must be flawlessly prepared (naturally or artificially) and mounted on the object stage (use plane field achromatic objective and eye-piece with cross line or measuring rod).

3. Move the object until striking features or intersection of centring cross coincides with eye-piece cross.

4. Exchange upper tube section having eye-piece for special tube with eye-piece screw micrometer and adjust.

5. By turning the centring screws (23 & 24) bring the apex of fixed (left) measuring arm of eye-piece screw micrometer to coincide with the striking features of object or centring cross. Both measuring arms form a cross (zero position)(Fig.2.6).

6. Remove the objective with its slide.

7. Insert microhardness tester with diamond indenter.

8. Now screw formerly used objective into microhardness tester and place it in observation position. Critically focus on to the specimen.

9. Centre the objective by turning setting screws (25 & 26) with socket wrench until the striking features of the object (or centring cross) is again coinciding with the apex of the fixed measuring arm of the dashed figure in the micrometer eyepiece. (Fig.2.6).

10. Turn the knurled knob in a counter clockwise direction (27, Fig.2.5) to lock the indenter.

11. Move the change-over slide to indenter position.

12. Observe the horizontal bright index line of the load indicator in the eye-piece. If it is not seen, turn the rear knurled knob (28, Fig.2.7) on microhardness tester until it is seen.

13. Focus the line, if necessary, by adjusting the micrometer eye-piece.

14. Turn knurled knob until the index line coincides with the horizontal line in the eye-piece. Should the eyepiece be oblique to the line, turn eyepiece. This fixes the initial position of the index line.

15. Apply the suitable load.

16. Observe the (upward or downward) motion of the index line within the image field.

17. Observe with naked eye the tip of the indenter and simultaneously turn the fine motion knob of the microscope so that the image of the tip is seen on the specimen.

18. Now observe through the eyepiece and turn the fine motion knob so that the indenter just touches the specimen.

19. When the indenter touches the specimen the index line starts moving back. Turn the fine motion knob uniformly until the index line coincides with the original reference line.

20. Turn fine motion knob in the reverse direction until the index line goes back to the same position (upward or downward).

21. Now lower the stage considerably.

22. Release the indenter by actuating knurled knob (27) in clockwise direction.

23. Remove the load.

24. Move the indenter device to its operating position and lock it.

25. Turn the knurled knob, if necessary, so that the bright index line coincides with the horizontal line in the eyepiece.

26. Observe the indentation mark through the eyepiece and measure the length of the indentation mark with the micrometer eyepiece.

27. Compute the hardness number by using the necessary formula.

## 2.8 ETCH METHOD (CHEMICAL):

This method consists of carefully preparing crystal surfaces and solutions of desired composition and concentration and of dipping the prepared crystal surface in the still solution for definite time at a constant temperature of etching and then gently washing it in a solvent in which the crystal is not soluble. It is known that rinsing may deform the crystal if there is an appreciable change of temperature occurred at the time of rinsing. Hence adequate care in the present work was taken during rinsing of the crystal.

It was observed that ammonia gas also chemically reacts with d-AHT. Gel grown crystals of d-AHT were cleaved in the usual way i.e. by keeping a sharp razor along the cleavage direction and then giving a sharp blow. Every time freshly cleaved crystal surfaces were used for etching work in a still etchant.

## 2.9 SILVERING TECHNIQUE:

For better reflectivity of the crystal surface, it was coated with a highly reflecting layer of silver under high vacuum ($10^{-5}$torr) for microscopic studies. The principle of this method is to thermally evaporate silver onto the specimen at a very low pressure.

A commercial vacuum coating unit "Hind Hivac" 12 A4 was used for this purpose. The vacuum chamber was evacuated by a three stage silicon oil diffusion pump backed by an oil rotary pump. The vacuum at different stages was measured by the pirani gauge and the penning ionisation gauge incorporated in the unit. The surfaces were thoroughly cleaned by amyl acetate before the deposition of silver.

When the pressure was about $1x\ 10^{-5}$torr, pure silver was evaporated from a molybdenum boat by passing a low tension high current. In order to protect the surfaces to be coated from receiving the vapours of the burnt impurities while heating the boat, it was covered with an adjustable shutter. Silver was deposited for the required time by removing the shutter from above the boat. The specimens were then optically studied.

## 2.10 ERROR ANALYSIS:

No physical measurement is absolutely correct. It is always associated with an error. The final result in an experiment is obtained after a computation involving different physical quantities which are measured in the course of the experiment. It depends on the refinements of the experimental techniques and on the method of treatment given to different observations (9)(10). Relationships between different physical quantities, in an experiment should be made as simple as possible, preferably linear and should be amenable to graphical analysis (11)(12)(13).

In the present work, relations between applied load and diagonal of indentation mark on a cleavage surface and as grown faces of single crystals of d-AHT or a suitable combination of different physical quantities for obtaining a straight line are graphically studied. Data are plotted on a graph with carefully chosen scales along the axes so that details are not bunched together over a small range and are commensurate with accuracy and precision of observations of the variables along the axes so as to minimize the unwanted magnification of errors associated with each observation. In the present analysis of observation, linear relationships between different physical quantities exist or are created by having suitable combinations of these quantities. Obviously the plot between variables having linear relation is a straight line. It is necessary to obtain the estimation of the best straight line. For this several methods are known.

They are as under:

i) Estimation of the best straight line by eye;

ii) Estimation of Y= mx+c by the method of zero sum;

iii) Centroid method to estimate y = mx+c;

iv) Estimation of y= mx+c from data used in a specific manner;

v) Statistical estimation of a best straight line.

In the present work, the statistical estimation of a best straight line was utilized to analyse the data on hardness of d-AHT crystals. The straight line plots obtained are presented in the concerned chapters. The details of the statistical estimation is briefly described here.

## 2.11 STATISTICAL ESTIMATION:

There are two ways of estimating statistically the best straight line viz.

a) Regression of Y on X and

b) Regression of X on Y.

In both these methods one variable is assumed to be free from error.

### a) Regression of Y on X:

The best straight line is one for which the squares of the deviation of every point measured parallel to y-axis and summed for all points is a minimum. This is known as regression of Y on X. Suppose there are n pairs of observations $(x_1, y_1), (x_2, y_2), \ldots (x_n, y_n)$.

For each known x, it is required to predict the best value of by using all observations.

Let $Y_1 = m_1x+c$ .....(1)

where $Y_1$ is not the observed value, $y_1$, corresponding to $x_1$, but it is the best value considering all the observation. The difference between the actual and predicted values of y is:

$y_1 - Y_1$, for $y=y_1$ .....(2)

Assuming the equation of the form

$y = m_1x+c$

for which values of $m_1$ and c are required such that,

$(y-Y)^2 = E$ .....(3) is a minimum.

$y-Y = y-(m_1x+c)$

$\therefore E = \sum_1^n [y-(m_1x+c)]^2$

$= \sum_1^n [y^2 - 2y(m_1x+c)+m_1^2X^2 + 2m_1xc + c^2]....(4)$

For E to be minimum,

$dE/dm = 0$ , $dE/dc = 0$

Differentiating E, w.r. to m yields,

$dE/dm_1 = \sum_1^n (-2yx + 2m_1x^2 + 2xc) = 0$

$= \sum_1^n 2(m_1x^2 + xc-xy) = 0$

$\therefore \sum_1^n xy = m_1 \sum_1^n x^2 + c \sum_1^n x$ .....(5)

Now differentiating E, w.r to c gives

$dE/dC = \sum_1^n (-2y+2m_1X+2c)$

$= \sum_1^n 2(m_1X+c-y)$

For minimum E,

$dE/dc = 0$

$$\sum_i^n y = \sum_i^n c + m_1 \sum_i^n x$$

$$= nc + m_1 \sum_i^n x \quad \ldots\ldots\ldots\ldots (6)$$

solving the equations for

$$c = (\Sigma y - m_1 \Sigma x)/n$$

$$= \Sigma y/n - m_1 \Sigma x/n$$

$$c = \bar{y} - m_1 \bar{X} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where $\bar{x} = \Sigma x/n$ and $\bar{y} = \Sigma y/n$. $(\bar{x}, \bar{y})$ represent the mean of all coordinates x and y. The best straight line passes through the mean of all coordinates. Substituting the value of c from (7) in equation (5) gives,

$$\Sigma xy = m_1 \Sigma x^2 + (\bar{y} - m_1 \bar{x}) \Sigma x$$

$$= m_1 \Sigma x^2 + \bar{y} \Sigma x - m_1 \bar{x} \Sigma x$$

$$= m_1 \Sigma x^2 + (\Sigma y \ \Sigma x)/n - m_1 (\Sigma x)^2/n$$

$$= m_1 \Sigma x^2 + (\Sigma y \ \Sigma x)/n - m_1/n \ (\Sigma x)^2$$

$$\therefore \Sigma xy - \Sigma x . \Sigma y/n = m_1 (\Sigma x^2 - (\Sigma x)^2/n)$$

$$\therefore m_1 = (\Sigma xy - \Sigma x . \Sigma y/n) / \Sigma x^2 - (\Sigma x)^2/n$$

$$\therefore m_1 = (\Sigma (x-\bar{x}) \ (y-\bar{y}))/ \Sigma (x-\bar{x})^2 \quad \ldots\ldots\ldots (8)$$

It is well known that two conditions determine a straight line. Having obtained the values of slope (m) and intercept (c) the best straight line for n pairs of observations is

$$y = m_1 x + c \quad \ldots\ldots\ldots\ldots\ldots (9)$$

where $m_1$ is called regression coefficient of y on x.

b) Regression of X on Y:

The best straight line is the one for which the squares of the deviation of every point measured parallel to the x-axis and summed for all points is a minimum. This is known as regression of X on Y. It is thus clear from the above definition of the best line that equations similar to the ones derived above in (a) can be obtained by interchanging x and y and X and Y. Thus the mean coordinates are:

$$\bar{X} = \Sigma x/n \quad \ldots\ldots\ldots\ldots \quad (10)$$

$$\bar{Y} = \Sigma y/n \quad \ldots\ldots\ldots\ldots \quad (11)$$

and the intercept c and slope $m_2$ are,

$$c = \bar{x} - m_2\bar{y} \quad \ldots\ldots\ldots \quad (12)$$

and

$$m_2 = [\Sigma (x-\bar{X}) \quad (y-\bar{Y})] \; / \; \Sigma(y-\bar{Y}) \quad \ldots \quad (13)$$

and the best straight line is,

$$x = m_2 y + c \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

where c and $m_2$ are given by the equations (12) and (13). $m_2$ is a regression coefficient of x on y.

The condition for a best straight line is that the correlation coefficient r, should be nearly unity, which is defined as,

$$r = \sqrt{m_1 m_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

If r = +/- 1, the correlation between x and y is perfectly linear. If r = +1, the line has a positive slope and if r = -1, the line has a negative slope.

In the present work, the author has utilized, in various chapters, the conditions expressed by (15) for each straight line plot in such a way that the correlation coefficient r is unity or is much nearer unity.

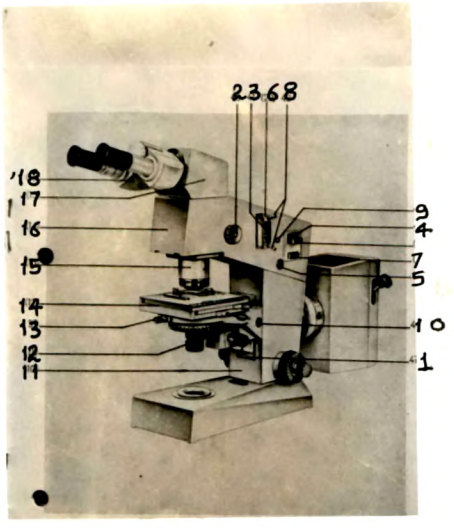


Fig 2.1

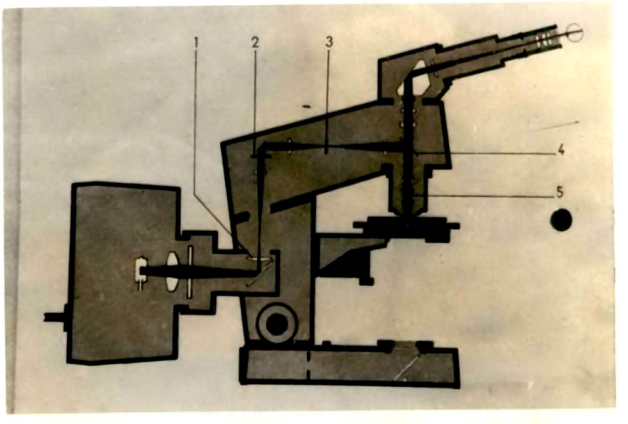


Fig 2.2

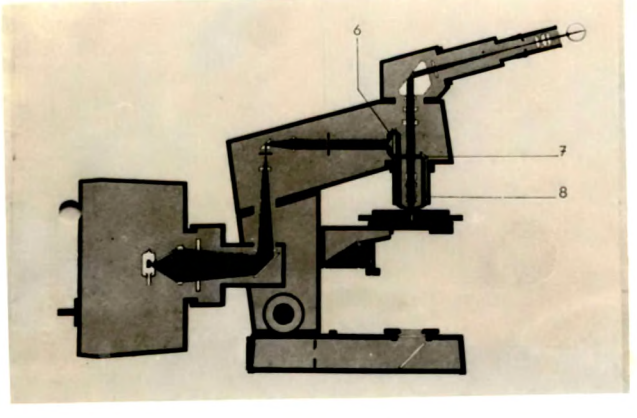


Fig 2.3

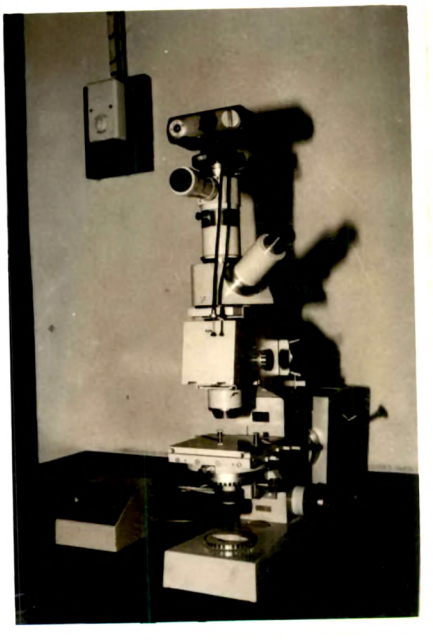

Fig 2.4

Fig 2.5

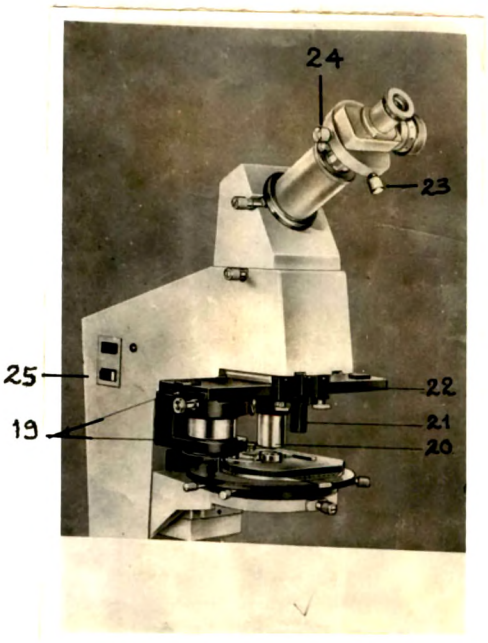


Fig 2.6

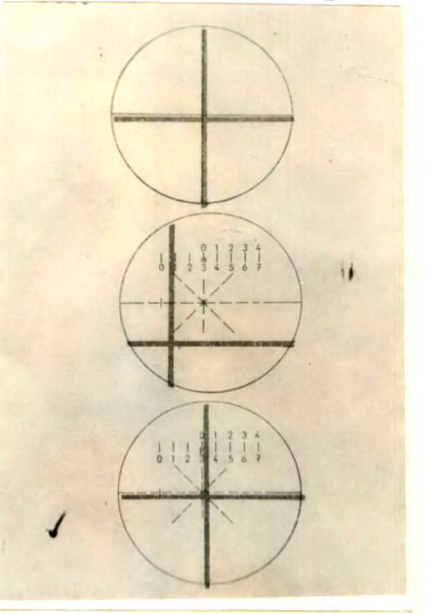

Fig 2.7

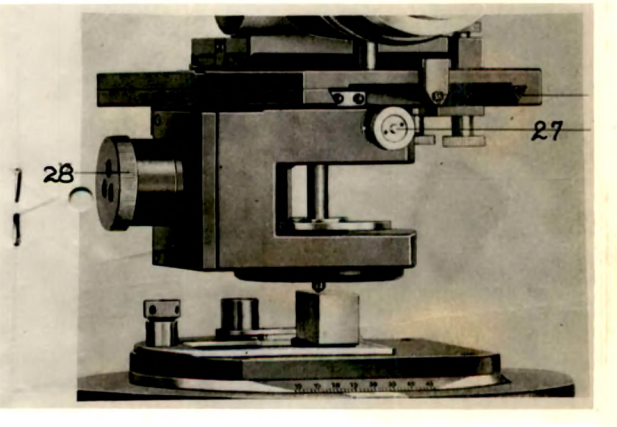


Fig 2.8

# LIST OF TABLES

## CAPTIONS TO FIGURES

2.1 Vertival incident light microscope;

1. Pinion head
2. Switching knob
3,4. Diaphragm
5. Central Screws
6. Diaphragm slide
7. Filter slide
8,9. Centering screws
10. 12/50 lamp adaptor
11. Basic stand for incident light
12. Stage Carrier
13. Tightening screw
14. Specimen table
15. Objective on slide with concave mirror condenser
16. Carrier "VERTIVAL"
17. Angular tube
18. Binocular straight tube

2.2 Ray diagram for bright field;

2.3 Ray diagram for dark field;

2.4 Camera attachment on microscope;

2.5 Vickers Projection Microscope;

2.6 Indentation Technique;

2.7 Zero position of cross wire on graticule of micrometer eyepiece;

2.8 Indentation technique.

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