Polarimetry and Refractometry

I. General use of Polarimeter

A polarimeter is used to measure the optical rotation per cm or per mm thickness of solution such as cane sugar, invert sugar, egg albumin, nicotine in water and liquids as methanol, turpentine, citron oils, etc. to find out relation between concentration and rotation in polarised light.

These polarimeters available in two different shade systems:

1. Biquartz device polarimeter works on sodium light as well as on daylight source (ordinary bulb light).
2. Half shade device polarimeter works on sodium light source.

On ordinary light the Biquartz gives pink colour at 0° mark on both sides of demarcation line and it will be very sensitive. On other position this gives half portion red and other half green colour. The instrument is workable on both light sources. On sodium light the Biquartz gives semi-dark colour at 0° mark on both sides of demarcation line and will be also very sensitive. On other position, this gives half portion black and other half white.

A polarimeter essentially consists of two Nicol prisms, co-axially placed (Fig. 7.1).

The first Nicol Prism (*P*) called polariser, through which a monochromatic beam from a sodium lamp (*S*) is introduced, is kept fixed. The second Nicol prism (*A*), called analyser, is mounted on a rotating disc. The plane polarised light emerging from the first prism (*P*) falls on the second (*A*). If the second prism be at 90° to the polariser, a complete darkness would occur, when viewed through a telescope (*T*) placed on the other side of the analyser. Initially the instrument is so adjusted that the entire field of view looked through eye-piece (*E*) would have uniform brightness (V_1). The polarimeter is set at this position, which is taken as 'zero position' of the polarimeter, and the reading of the position

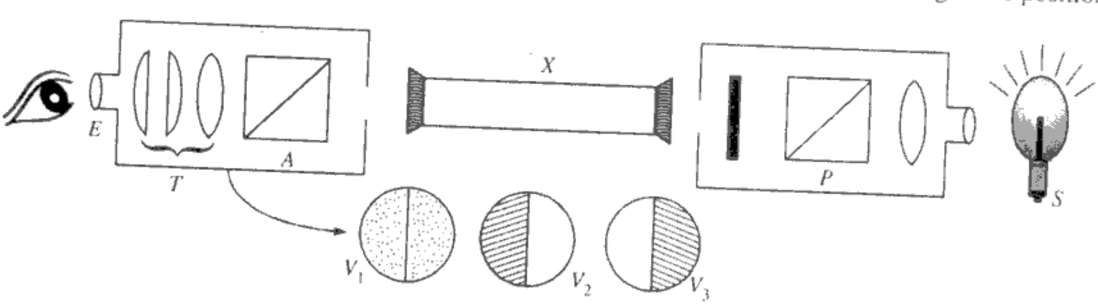
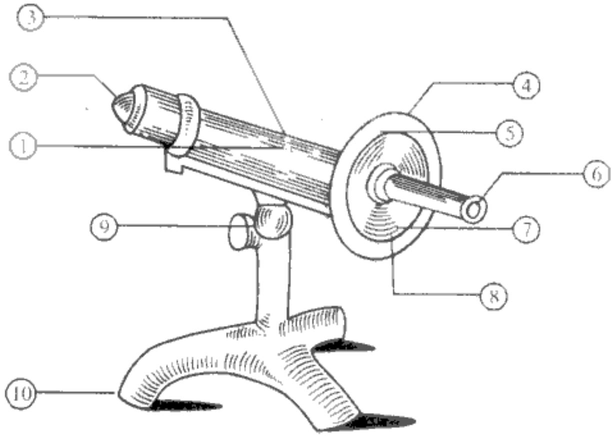


Fig. 7.1: (Schematically) Arrangement of a polarimeter.



Main parts of Polarimeter

1. Space for Pol Tube
2. Input Light
3. Cover Handle
4. Scale 360° Graduated
5. Vernier 1/10° (6 minute)
6. Eyepiece
7. Fine motion Knob
8. Coarse Motion Handle with Lock System
9. Height Adjustment Knob
10. Stand

Fig. 7.2: Biquartz Polarimeter

is taken from the circular disc provided with angular scales. If the scale is moved towards right-hand or left hand from this position, the field view V_2 or V_3 would be seen through the eye-piece (E). X is the polarimeter tube, which is to be filled with the solution, of which the angle of rotation is to be measured. Generally, the polarimeter tube is 2 decimetre in length.

For the measurement of angle of rotation of an optically active substance say sucrose solution, follow the procedure mentioned below:

1. Prepare and keep ready sugar solution before use of polarimeter.
2. Filter the solution twice through filter paper.
3. Clean polarimeter tube with running water and brush and dry it. Place cover glass on one end, then place rubber washer in cap and tighten the cap.
4. Fill the tube with solution and place cover glass in the same way (mentioned above) and tighten the cap. Clean the tube from outside by a cotton cloth or .issue paper, clean both the cover glasses from outside by cloth or tissue paper and look into the tube through cover glass and check clearness.
5. For best transmission of light, solution must be filtered twice.
6. Set the polarimeter in front of light source and adjust the height according to the light gate.
7. Look into the eye-piece and focus the Biquartz device by adjusting eye-piece outside or inside.
8. Set the device illumination, on equally dark (semi-dark) position by rotating (clockwise) Coarse Motion-Handle. During rotation look into the eye-piece and note that semi-dark (equal illumination on both sides) position will come near 0° on the scale. Note also the instrumental error, if any, $\pm$ from 0°.

   One degree of scale = 60 minutes

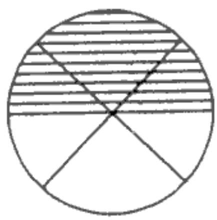
   $$\text{The vernier least count } = \left(\frac{1}{10}\right)^{\circ} = 6 \text{ minutes.}$$

9. Place the solution tube at the space between polariser and analyser in polarimeter and look into the eye-piece. It will be found that semi-dark position is disturbed (one-half is dark and other half bright). Now rotate the vernier handle slowly in clockwise direction and again set the semi-dark position as set earlier and note the angle of rotation from the scale.

II. Measurement of refractive index of a liquid by Abbe-refractometer

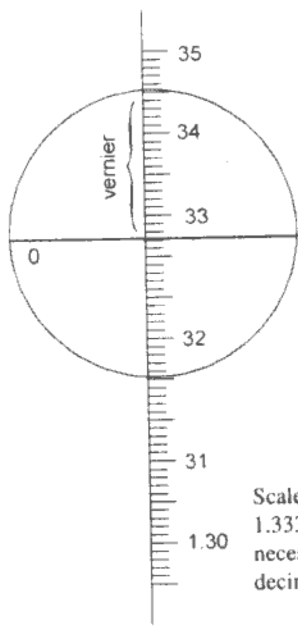
Now-a-days, Abbe-refractometer is most widely used to measure the refractive index of a liquid in the general laboratory. This refractometer has some advantages over the Pulfrich refractometer: (i) refractive index of the liquid can be read directly with an accuracy of about 0.0002; (ii) Only a few drops of liquid are sufficient for examination and (iii) either monochromatic light or ordinary white daylight can be used. The following is the working procedure for measurement of refractive index of a liquid.

1. Open the prism box carefully and clean the surfaces of the prisms (lower and upper) with rectified spirit using cotton and then make it absolutely dry.
2. Place a few drops of distilled water on the ground glass surface of the lower prism and immediately lock the prism box. Semimico-pipette or dropper may be used to place the water on the ground-glass surface of the lower prism.
3. The mirror of the refractometer may be illuminated with the light from sodium lamp (if available) or ordinary bulb. The mirror is so adjusted that a circular light view is observed through the eye-piece. By moving the screw, fitted with the scale, the circular view is adjusted at half shaded position like below:

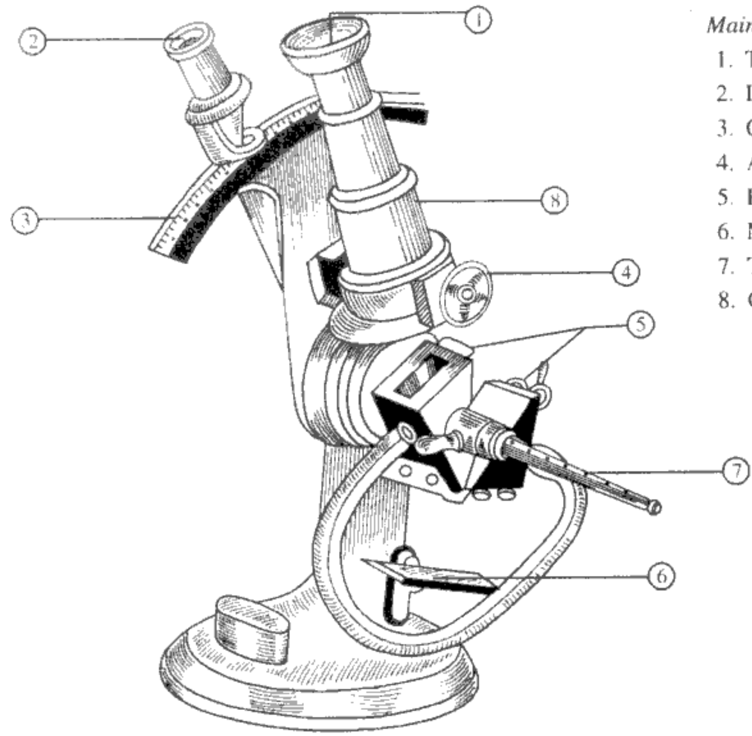


Then note the scale. The scale should give refractive index 1.333. If the above value is not properly observed, adjust it to 1.333 by moving the scale. Then the dark shade is adjusted to exactly mid-position of the circle by moving the fine adjustment screw. This is called zero adjustment.

4. Open the prism box. Clean it with a piece of cotton wool and make it dry. Place a few drops of experimental liquid using a dropper or semimicro-pipette and close the prism box. It will be observed through the telescope that the edge of dark shade is either at lower or at upper position of intersection of the cross-hairs. The edge of the dark band is brought to the intersection of the cross-hairs. The refractive index of the liquid is then read from the scale. Generally, the scale is of the following type. Scale starts from 1.30. Thereafter shown as 31 means 1.31. Between 1.30 and 1.31, there are ten small divisions. There is a diameter line on the circle. The division which coincides with the diameter line is the corresponding scale reading. For water, the diameter line coincides with the third division after 1.33. Thus refractive index of water is 1.333. This corresponds to zero of the vernier scale. So, it is called **zero setting**.



Scale reading is shown as 1.333. Vernier reading is necessary after third decimal of reading.



Main parts of Abbe-Refractometer

1. Telescope
2. Lens
3. Curved scale
4. Adjustable screw
5. Pair of prism
6. Mirror
7. Thermometer
8. Compensator

Fig. 7.3: Abbe-Refractometer

Experiment 1

Determination of (a) specific rotation of sucrose and (b) composition of sucrose solution by polarimeter.

Theory: The magnitude of angle of rotation of an optically active substance depends upon several factors: (i) the density or concentration of the substance, (ii) the temperature (iii) the wavelength of light and (iv) the length of the substance through which the beam has to pass, i.e., the length of the polarimeter tube.

The rotatory power of the substance is expressed in terms of specific rotation, $[\alpha]_\lambda^t$ such that

$$[\alpha]_\lambda^t = \frac{100\alpha}{l \times c}, \qquad (1)$$

where α is the observed angle of rotation,

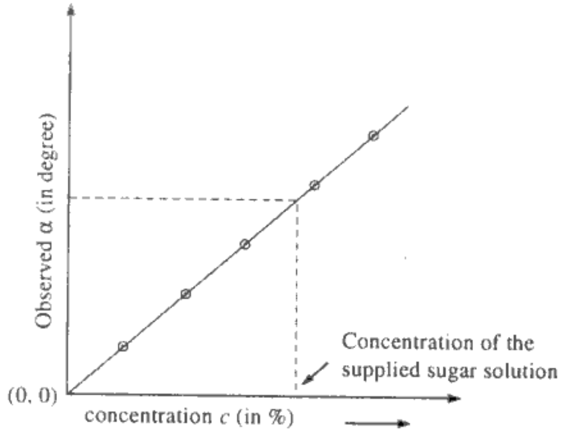
l is the length of the polarimeter tube in decimeters, and

c is the concentration of the solution in percentage $\left(\frac{W}{V}\right)$

Thus, temperature, wavelength of light and length (l) of the tube remaining constant, the angle of rotation (α) of an optically active substance is directly proportional to the concentration of that substance, as specific rotation, $[\alpha]_\lambda^t$, is a characteristic constant of an optically active substance.

If we plot the observed angles of rotation (α) against concentration (c), a straight line passing through the origin with a positive slope will be obtained and the concentration of the supplied solution of the same substance can be determined from the graph.

Again, from equation (1) $[\alpha]_\lambda^t$ can be calculated as c, l are known and α is to be measured by a polarimeter. For most of the cases l is generally 2 dm.



Materials required: (i) Polarimeter with sodium lamp and polarimeter tube, (ii) Sucrose, (iii) Beakers (100 ml capacity, 6 pcs), (iv) Burette or 25 ml graduated pipette, (v) Volumetric flask (250 ml capacity, 1 pc), (vi) Cotton or tissue paper, etc.

Procedure

1. Prepare 250 ml 20% sucrose solution by accurate weighing. The solution should be **colourless and homogeneous**. Filter the solution, if necessary. Then prepare 40 ml each of 15%, 10%, 7.5%, 5% and 2.5% solutions from the original 20% solution by quantitative dilution in 100 ml clean and dry beakers.
2. Measure the angle of rotation of six sugar solutions starting from lower concentration (2.5% to 20%). The detailed procedure for the measurement of angle of rotation has already been described in the general use of polarimeter of this chapter.
3. Wash the polarimeter tube with distilled water and then rinse with the supplied sugar solution of unknown concentration and measure the angle of rotation of this solution using similar procedure.
4. Plot angle of rotation (α) against the known concentrations and find the concentration of the unknown (supplied) solution from the graph.
5. Calculate the specific rotations at each concentration and make conclusion from the result.

Results and Calculations

Table 1: Recording of room temperature

	Before experiment	After experiment	Mean
Temperature →	... °C	... °C	... °C

Table 2: Preparation of sucrose solutions of different compositions

Set Nos. (100 ml beakers)	Vol. of 20% sucrose solution (ml)	Vol. of distilled water (ml)	Total Vol. (ml)	Concentration of sucrose solution
1	40	0	40	20.0%
2	30	10	40	15.0%
3	20	20	40	10.0%
4	15	25	40	7.5%
5	10	30	40	5.0%
6	5	35	40	2.5%

Table 3: Observed angle of rotation (α) and calculated specific rotation $[\alpha]_\lambda^t$ from equation (1)

Concentration of soluction (c)	Observed α (degree)	Length of the polarimeter tube	$[\alpha]_\lambda^t$	Mean $[\alpha]_\lambda^t$
2.5%	...		...	
5.0%	...		...	
7.5%	...		...	
10.0%	...	... dm	...	...
15.0%	...		...	
20.0%	...		...	

4. **Graph plotting and determination of concentration of supplied sucrose solution**
   From the data of the above table, a plot of α against c, gives a straight line passing through the origin.
   Now, the observed angle of supplied sugar solution = ··· degree.
   Hence from the graph, concentration of the supplied sucrose solution = ··· %.
5. *Conclusion:* The angle of rotation increases with increase in concentration of sucrose solution, but specific rotations $[\alpha]_\lambda^t$ are practically constant and the mean value of specific rotation of source $[\alpha]_\lambda^t = \cdots$

[**N.B.** : 1. Expected value of specific rotation of sucrose $[\alpha]_D^t = +66.67 - 0.0247\,(t - 20)$ (t = 14 °C to 30 °C); D means sodium D-line.

2. *Suggestions of similar experiment*: Other optically active substances, such as tartaric acid or camphor may be studied in the same way as sucrose. Nonaqueous solvent may also be used (e.g., camphor in benzene or carbontetrachloride).

Experiment 2

Determination of rate constant of acid catalysed inversion of sucrose and also determination of catalytic co-efficient—polarimetrically.

Theory: The experiment is given in the chapter 'Reaction Kinetics'.

Experiment 3

Determination of concentration of a given solution of aqueous ethanol by refractivity measurements.

Theory: When a ray of light (preferably monochromatic) passes from one medium to another (obviously the medium should be transparent), it suffers a change of direction, which is known as refraction. According to Snell's law, the degree of refraction is such that the ratio (n) of the sine of the angle of incidence (i) to the sine of the angle of refraction (r) is constant. This ratio is equal to the ratio of the velocities of the light in the two media. Hence,

$$n = \frac{\sin i}{\sin r} = \frac{V_1}{V_2},$$

where the constant n is called the refractive index or index of refraction, V_1 is the velocity of light in vacuum and V_2 is that in the other medium. The velocity of light in a material body is less than that in