CHAPTER II

EXPERIMENTAL TECHNIQUE

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2.1 INTRODUCTION

In the electromagnetic spectrum of radiations, the X-ray region falls in the range about 0.01 A^{o} to a few tens of Angstroms. The experimental technique adopted in the X-ray spectroscopy depends on the wavelength region to be employed, considering which the X-ray spectrograph is chosen and fabricated. The general requirements for a spectrograph are i) X-ray source, ii) dispersing agency and iii) a detector. For X-ray spectrographic work a variety of sources such as filament tubes (e.g. Coolidge tube, demountable gas tube), synchrotron radiation, Van-de-Graff generator can be used. Different dispersing agencies such as plane crystal, plane reflection gratings, bent crystals and concave gratings are used. The detection of the radiations can be made either by photographic method or with electronically operated detectors such as Geiger Muller counter, proportional counter and scintillation counter. The details regarding these have appeared elsewhere (1-4).

In the following sections, the experimental set-up and the technique used in the present work are described.

2.2 X-RAY SOURCE

The X-ray generator used in the present work was originally supplied by M/s. Radon House Company, Calcutta, India.

Its principal components are power supply unit, X-ray tube and the cooling system. These are described below.

2.2(a) Power Supply Unit

It supplies power to the X-ray tube. It consists of (i) input transformer, (ii) variac or the dimmerstat, (iii) H.T. transformer and rectifiers, (iv) L.T. transformer.

i) Input transformer : This is a heavy duty, multitapped, auto-transformer. It provides different voltages, 0 - 6 volts for the indicator bulb, 0 - 220 volts for the L.T. transformer and the variac etc. Since it is essential that the potential across the X-ray tube and the current through it be constant, the output of the single phase stabilized power supply unit was fed to the input transformer.

ii) Variac or Dimmerstat : This is a continuous variable auto-transformer which can stand upto 15 amps. of current at 260 volts. Input to this is given from the input transformer and the continuous variable output is fed to the H.T. transformer through appropriate circuitary.

iii) H.T. transformer : Input supply to the primary winding is given from variac. The circuit is so designed that the input can be given in steps or in a continuous variable manner; and hence the H.T. available is in steps or the same can be varied as per requirement from 0 to 48 kv, at 0 - 30 mA.

The H.T. (a.c.) made so available is rectified by rectifier circuit and is applied to the X-ray tube at cathode, the anode being earthed. The H.T. transformer alongwith the rectifiers is immersed in an oil-tank.

In order to avoid the damage to the X-ray unit due to drastic variations in supply voltages occasionally, a miniature type circuit breaker is used in series with the stabilizer.

iv) L.T. transformer : L.T. transformer is used for heating the filament of the X-ray tube. The voltage and current specifications for the filament of the X-ray tube used for the present work were 7 volts and 4 amps., as specified by the manufacturer. It has a potentiometric arrangement to control filament current which decides the tube current and hence the intensities of the X-rays.

2.2(b) X-Ray Tube

X-ray tube used for the present work is a sealed type Chirana X-ray tube with copper target. Copper tube gives fairly intense white radiation alongwith the emission lines of copper.

2.2(c) Cooling System

The anode and metallic body get heated due to the tremendous amount of heat energy developed in the process of production of X-rays. They are therefore cooled by circulating

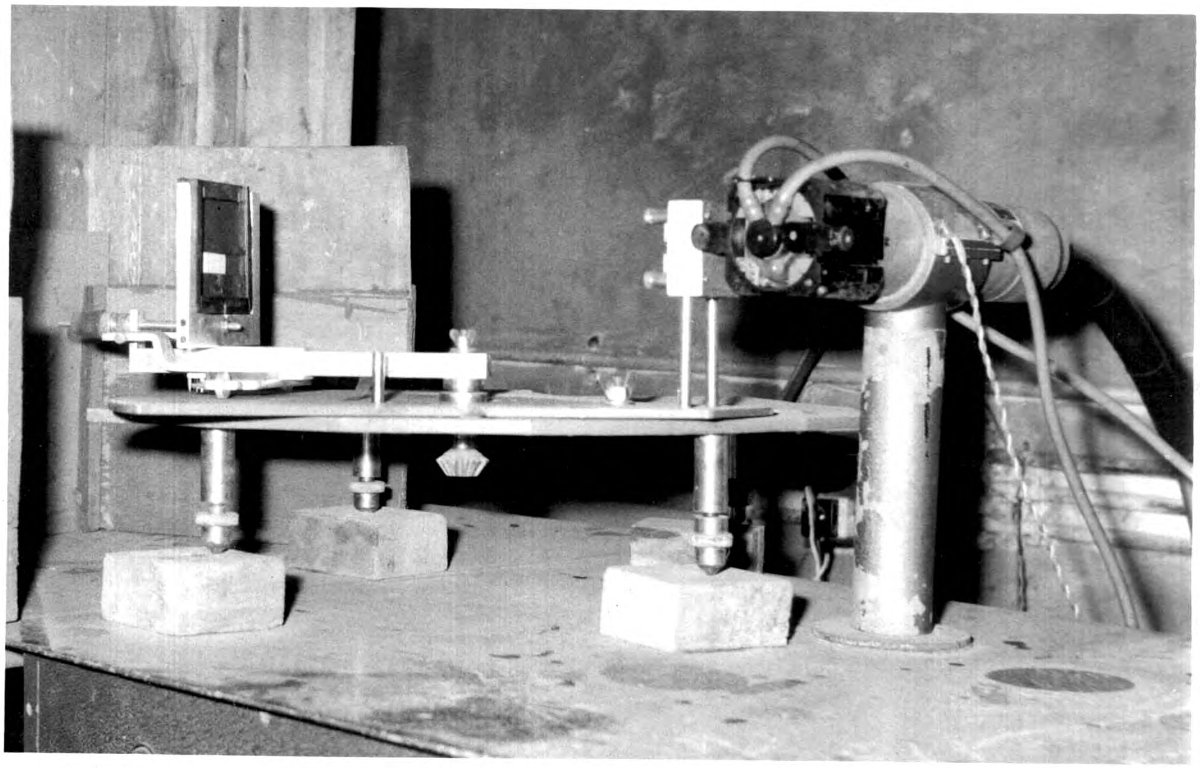

PLATE 2·I

a flow of demineralised water by a water pump connected to a pressure tank. Water is circulated at a specific pressure by adjusting relay in the water-pump circuit.

2.3 SPECTRAL REGION

The wavelength of K-absorption discontinuity of cobalt (5) is λ = 1604.80 XU. Cobalt is the only element by interest in the present study. The X-radiations in this region are fairly penetrating and hence spectra can be recorded in air. The most suitable instrument in this region is Cauchois type bent crystal spectrograph. This type of spectrograph with radius 400 mm is fabricated in the departmental work-shop. The details about it are described in the following section. A general view of the experimental set-up used is shown in Plate 2.I.

2.4 SPECTROGRAPH

The schematic diagram of the spectrograph used is given in Fig. 2.1. The metal plate P_1 which forms the base for the whole spectrograph is supported by four levelling screws L_1- L_4. The plate is cut in such a way that it forms a sector of a circle with center at O and radius equal to 400 mm. The plate P_2 which rests on P_1 can be rotated about a vertical axis passing through O. This plate acts as a Rowland circle of radius 200 mm with center at C. A circular scale S_1 graduated on P_1 whose center is at O, reads the angular position of P_2

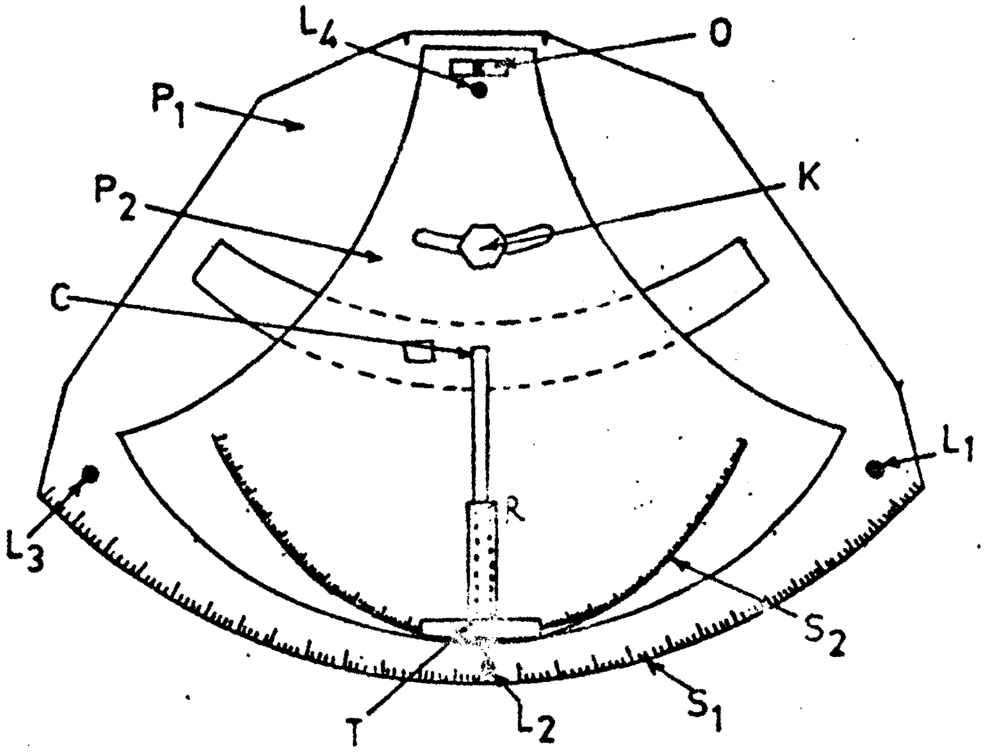

Fig. 2·1: Spectrograph

with respect to P_1. The knob K can be used to clamp the plates P_1 and P_2 for any desired setting.

2.4(a) Crystal Holder

This is the most important part of the spectrograph. It consists of two perfectly matching pieces A and B as shown in Fig. 2.2. One of them (A) is concave cylindrical and the other (B) is convex cylindrical. They are perfectly machined, lapped and polished carefully such that both of them have the same radius of curvature equal to 400 mm. The four screws binding the two pieces are spring loaded so as to provide an adjustable pressure on the crystal (mica sheet) placed between the two pieces. The crystal holder has an opening of 2 cms x 1 cm at the center. The useful aperture could be controlled by using two lead shutters which can slide in a groove cut on the back-side of the holder. The holder is so mounted on P_2 that the center of the aperture is located vertically above O with the convex side of the crystal facing the X-ray window.

2.4(b) Film Holder

The film holder is a rectangular wooden frame in which a quarter size plate or a film can be loaded. The film used in the present work was Kodak Dental X-ray film of size 41 mm x 31 mm. The film was to be fixed on the film holder coincident with the focussing plane. The advantage of the film is that it is light-leak-proof and hence dark-room loading is not required.

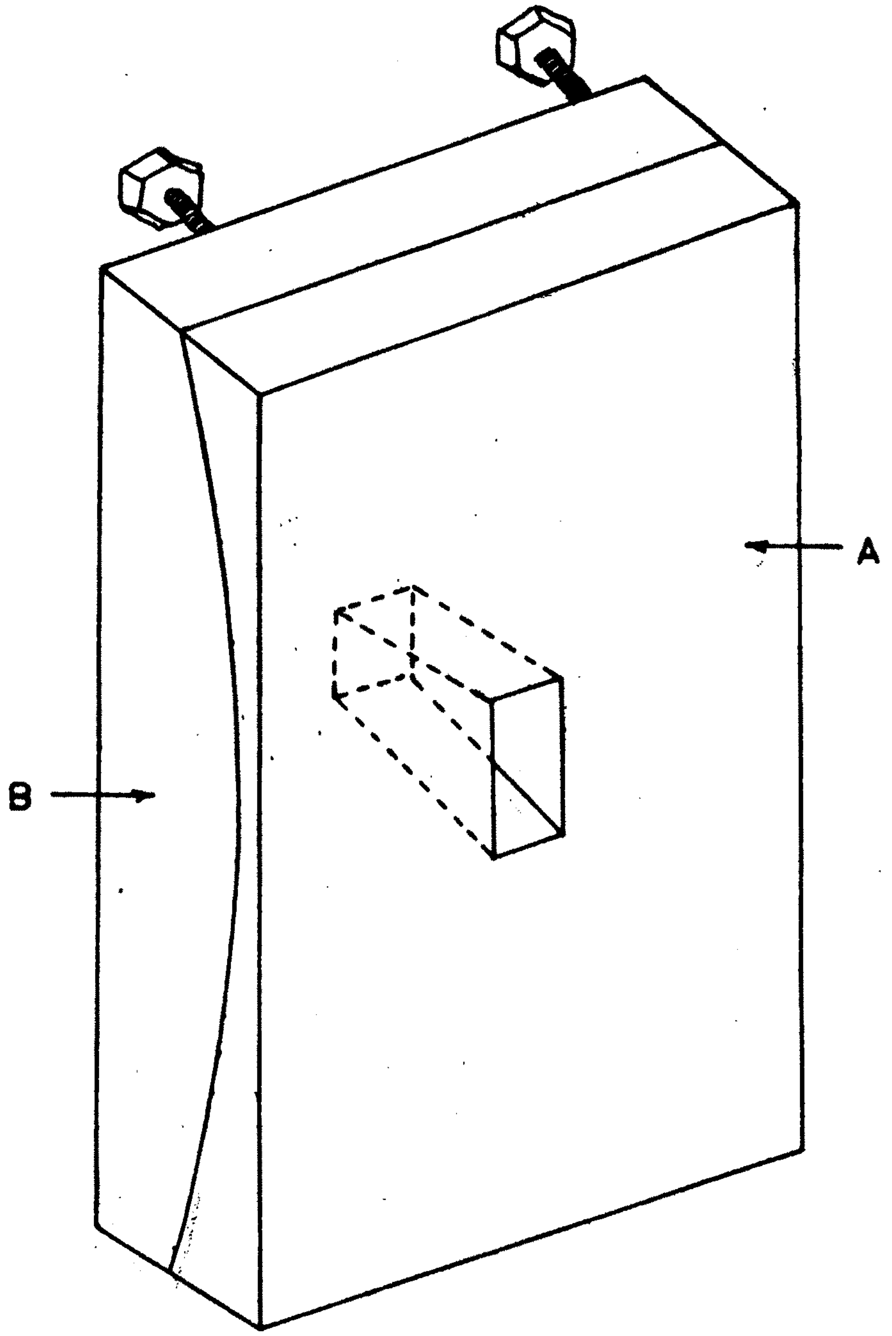

Fig.2·2: **Crystal holder**

2.4(c) Arm and Film Holder Carriage

The arm R carries the plate-holder carriage. It is vertically pivoted at point C upon the plate P_2. The distance OC is equal to 200 mm and OC is normal to the crystal surface. The plate holder is mounted in the grooves on the carriage in such a way that the photographic plate is always tangential to the focussing circle whose center is at C. An arrangement is provided on the arm to vary the distance between the plate and the point C by a spring and screw, This facilitates the setting of the film exactly on the Rowland circle. The movement of the arm R gives the required angle to the film with respect to the plate P_2, which can be read by means of the pointer on the scale S_2.

2.5 DISPERSING MEDIUM

2.5(a) Selection of the Crystal

Quartz, calcite, gypsum and mica crystals are in use as dispersive media in X-ray spectroscopy. Brogren (6) claimed that quartz is the best suitable crystal for spectroscopic work and then the calcite. However, equally good results have been obtained in many laboratories using mica as dispersing and focussing agency. Moreover, mica can be cleaved easily, can be bent easily to the desired curvature and is easily available. Mica was therefore selected as a dispersing medium in the present investigation.

2.5(b) Mounting of the Crystal

The quality of the crystal and its mounting are very important as they greatly influence the results of the X-ray spectroscopic work. A clean sheet of mica was cleaved to get thin pieces and Laue patterns for these were obtained. One of them giving symmetrical and sharp Laue pattern was selected and sandwiched between the two metal pieces A and B of the crystal-holder. The assembly was mounted on an optical bench for the optical testing. The concave face of the crystal holder was illuminated by an intense narrow beam of light obtained with the help of a slit. The image of the slit was observed on a screen placed 40 cm in front of the crystal. The pressure on the crystal was adjusted using the spring-loaded screws till a sharp image was obtained. The real quality of the crystal was judged however only by its performance on the spectrograph. The crystal so tested was mounted properly in its position on the spectrograph. After levelling the spectrograph and aligning it with the X-ray beam target, X-ray emission spectrum was obtained at the pre-determined position of the film-holder (ref. to sec. 2.6). The crystal giving sharp intense undisturbed emission line spectrum was finally selected for the work.

2.6 PRINCIPLE AND SETTING OF THE SPECTROGRAPH

Fig. 2.3 illustrates the principle of the focussing action of the spectrograph. X-rays are reflected from the

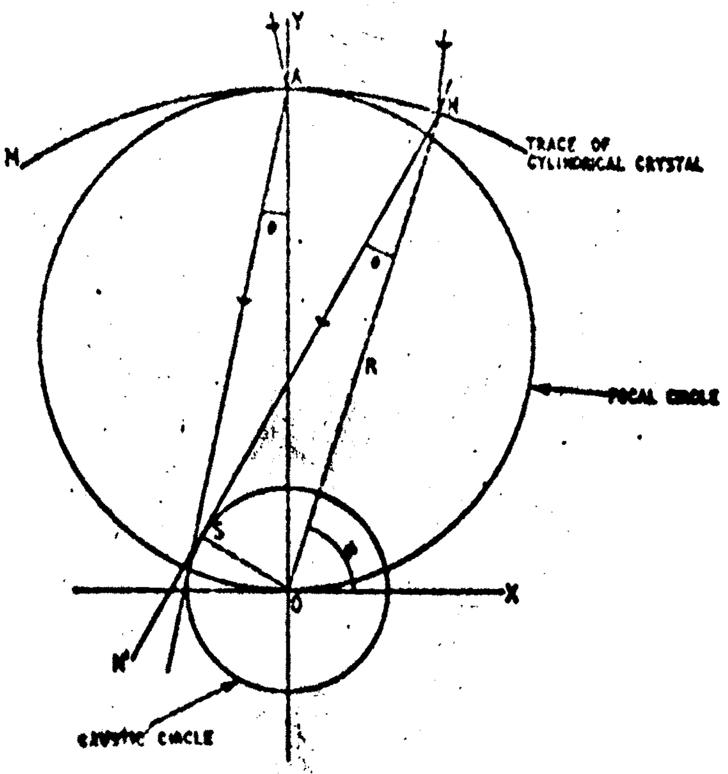

Fig. 2·3: Principle of focussing action of Cauchois type spectrograph.

family of lattice planes which are perpendicular to the plane of the cylindrically bent sheet of mica crystal M. And, X-rays of wavelength λ incident at the Bragg angle θ on the crystal at N get reflected along N'. It can be mathematically shown that all the rays of the wavelength λ incident at the Bragg angle θ, on the crystal will be brought to focus approximately at N' (or more accurately on the caustic circle) provided the aperture is small. A typical photograph of well focussed Cu K_{α} lines and the corresponding microphotometer record obtained in the laboratory are shown in Fig. 2.4. The locus of the point N' is the Rowland circle or the focal circle. Therefore, if the film is bent and placed along the circle various wavelengths will be well focussed upon it.

The Bragg angle for the K-absorption discontinuity of cobalt in the first order can be calculated from the Bragg equation -

$$\lambda = 2\, d_{(h\ k\ l)} \cdot \operatorname{Sin}\theta \qquad \ldots\ 2.1$$

For the (1 0 0) and ($\bar{2}$ 0 1) planes of mica $d_{(1\ 0\ 0)} = 2.61$ A° and $d_{(\bar{2}\ 0\ 1)} = 2.65$ A° and the corresponding Bragg angles θ are 17°-56' and 17°-39' respectively. But, the (1 0 0) and ($\bar{2}$ 0 1) planes make angles α = 10°-10' and α = 4°-56' with the normal to the cleavage plane. Therefore, to set the crystal for Bragg angle, the crystal should be rotated through an angle $(\theta + \alpha)$ about the vertical axis through O. For the (1 0 0) plane, this is achieved by setting the plate P_2 at the angle $(\theta + \alpha)$ = 28°-6' with respect to the plate P_1. In order to

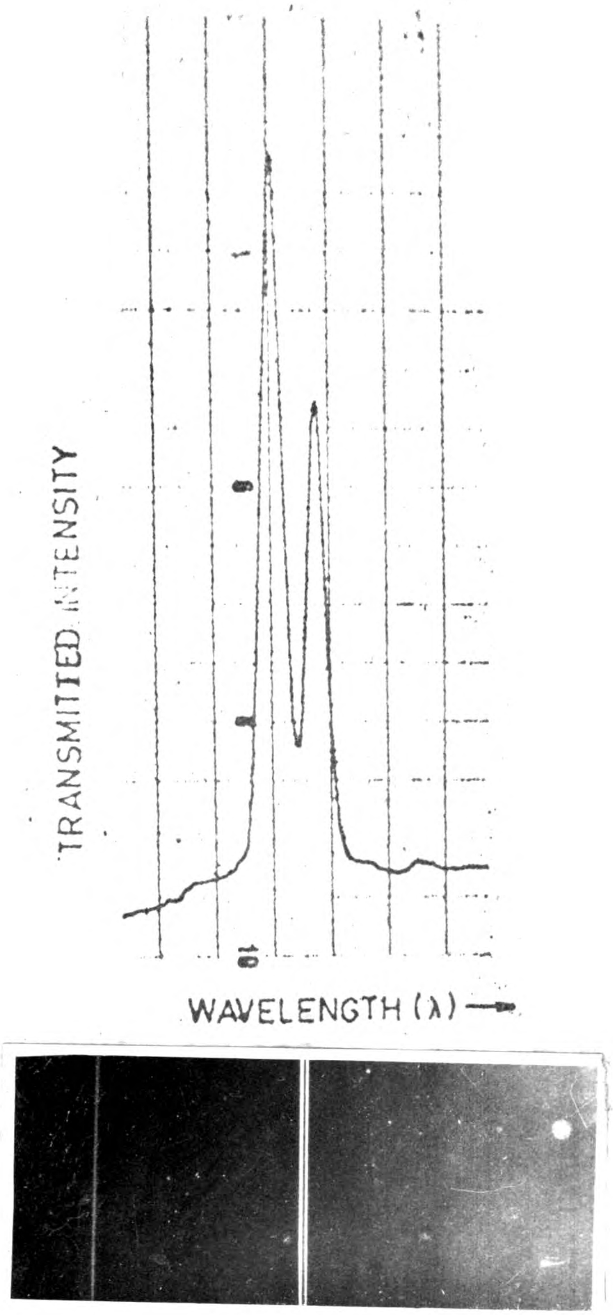

Fig. 2·4 : K_{α_1,α_2} EMISSION LINES OF COPPER receive the diffracted rays the photographic film is set at an angle $2(\theta - \alpha) = 15^{o}$-32' with respect to the plate P_1.

The position of the plate P_2 and that of the film holder are adjusted so as to get emission lines as well as absorption edge well focussed on the film.

2.7 OPTIMUM CONDITIONS FOR OBTAINING GOOD SPECTRA

The optimum conditions required for obtaining good absorption spectra from the view point of both the contrast and the microphotometric work are as follows.

2.7(a) High Tension

If the unnecessary high values of voltage be applied across the X-ray tube, the details of the absorption spectrum are invariably obscured. Sandstrom (1) has shown that good spectrum of an absorption edge can be obtained if the voltage applied across the tube does not exceed 1.5 times, the excitation potential of the energy level from which the electron is ejected. The energy of K-level of cobalt according to Bearden (5) is 7.709 Kev. Therefore, in the present work the value of the H.T. across the X-ray tube was about 11.5 Kev, for studying cobalt K-absorption spectrum. Because of the facility of continuously variable power supply the optimum voltage could be applied. The tube current during the course of these investigations, ranged between 8 to 12 mA.

2.7(b) Thickness of the Absorber

Thickness of the absorber should be optimum to obtain good absorption spectra. There are two different criteria existing for the optimum thickness depending on whether the structure at the edge itself or the extended fine structure is to be examined (1, 7). Sandstrom (1) has given the following formula for the optimum thickness for the absorbing screen.

$$x = 2.3 \frac{\log (\mu_2/\mu_1)}{\mu_2 - \mu_1} \qquad \ldots 2.2$$

where x is the mass of the absorbing element in grams per square centimeter and μ_1 and μ_2 are the linear absoption coefficients on the low and high energy sides of the absorption edge. For recording the fine structure, Kurylenko (8) has given the following formula for optimum thickness of the absober.

$$x = 1/\mu_2 \qquad \ldots 2.3$$

It is clear from equations 2.2 and 2.3 that the absorbing screen should be thinner to record extended fine structure. Krishnan and Nigam (9) and K. Tsutsumi et al. (10) have also studied the thickness effect on the recording of fine structure.

The uniformity of the absorber and the grain size also play an important role in obtaining good absorption spectrum. The grain size should be less than five times the optimum thickness of the absorber (11). Fine powder of cobalt complexes was prepared by grinding. About 12 mgms of the powder was spread uniformly on the cellophane tape and sandwiched without leaving any holes in-between. This was judged by naked eye. A number of trial screens were prepared and number of spectra were recorded. It was found that in order to obtain good extended fine structure, the screens had to be prepared with special care wherein the screens were rubbed between hard and smooth surfaces to improve their quality.

2.7(c) Placement of the Absorber

The absorber should be kept ahead of the crystal (12) so that any fluorescent radiation emitted by the absorber does not reach the detector.

2.7(d) Exposure and Photographic Processing

The trial spectra of each sample were first obtained on the Kodak fast dental films so as to determine the necessary exposing conditions. The usefulness of these dental films, has already been established (13, 14). The final spectra were recorded on Kodak Dental X-ray film. Due to fine grain emulsion of the film the resolution was increased. It was observed that slow developing (about seven minutes) at lower temperature gives better contrast and transparency of the film. At each time, freshly prepared ice-cooled developer was used. The developer supplied by May and Beckers Ltd. Company, was used.

2.8 MICROPHOTOMETRY AND MEASUREMENTS

The microphotometric records were obtained with magnifications 25 X and 50 X with corresponding chart speed of 300 mm/min and 120 mm/min on Carl Zeiss Jena type rapid microphotometer (Plate 2.II). The height and the width of the slit of the photometer was adjusted to get good line profile. Several records were obtained for each film at different positions. The film was placed on the scanning platform so that image of the line was exactly parallel to the slit and the spectrum moved parallel to the slit. The said chart speed reveals the minute details of the X-ray spectrum without hindering the synchronization of wrapping and unwrapping of the chart paper. The accurate location of the inflection point on the edge and the maxima and the minima of the extended fine structure was done with great care, inspecting a number of similar records.

Generally, to measure the wavelength of the edge, reference lines are taken on both sides of the edge. The cobalt edge was recorded copper target. As cobalt K-edge position lies on the low energy side of the copper K spectrum, it was not possible to bracket it and hence the measurement on the edge had to be done with extrapolation method. However, this would not cause any appreciable error in the measurements as dispersion is linear in this region. In case of extended fine structure measurements no question of such reference lines arises as the inflection point on the absorption edge itself is taken as reference point.

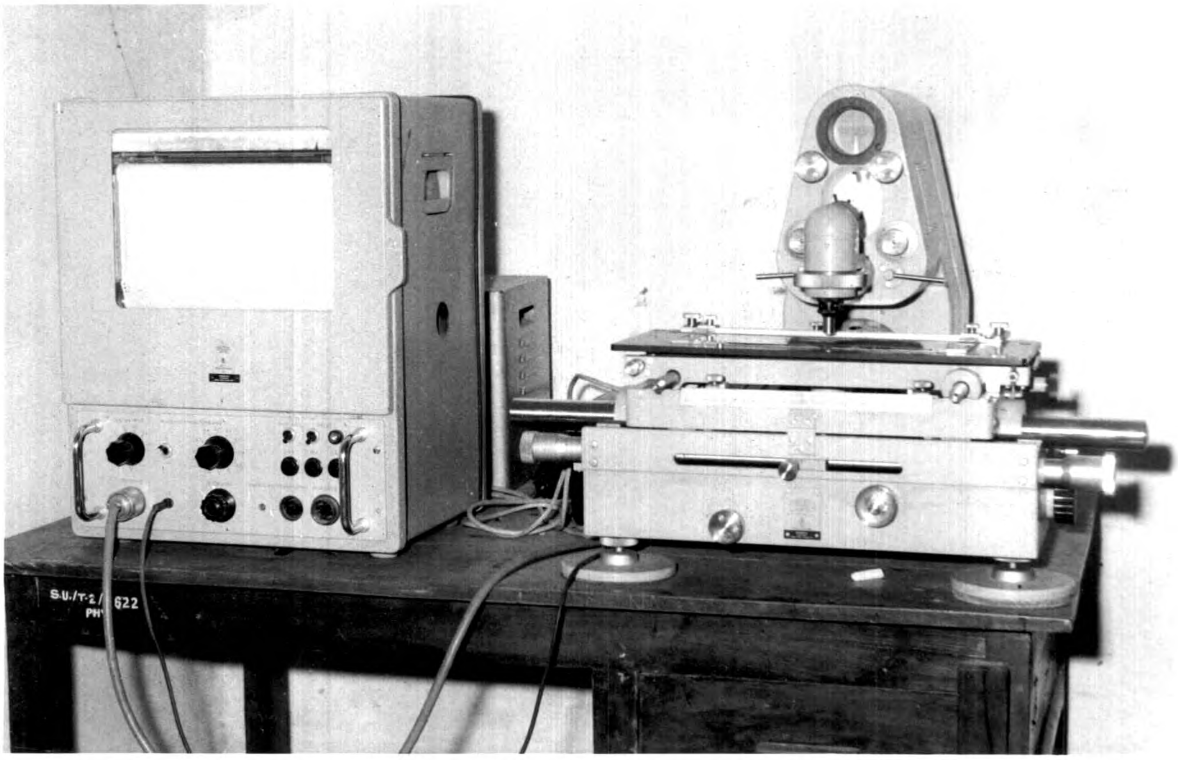

PLATE 2·II

2.9 DISPERSION AND ACCURACY OF RESULTS

The linear dispersion obtained on a bent crystal spectrograph is given by

$$\frac{\delta\lambda}{\delta L} = \frac{\lambda}{R \tan\theta} \qquad \ldots\ 2.4$$

where R is the radius of curvature of the crystal and θ is the Bragg angle for a particular λ. The linear dispersion calculated with this formula for CuK_α lines is 12.60 XU/mm, which agrees fairly well with the dispersion accurately obtained on the film which is 12.62 XU/mm.

There are a number of sources of errors in the determination of wavelength/energy of an absorption edge. They are as follows.

i) Non-uniform development of the film.

ii) Non-uniform motion of the microphotometer due to line fluctuations.

iii) Errors in measurements.

Precautions were taken to minimise these errors. The average error in the measurement of the edge position was estimated from a number of readings taken and by using the well-known formula,

$$\sigma = \sum_{i=1}^{n} \frac{|R_i - R|}{n} \qquad \ldots\ 2.5$$

with usual notations. The average errors in the measurements are indicated alongwith results.

2.10 PREPARATION OF COMPLEXES

The general formula of the complexes prepared in the laboratory is cis and trans form of $[Co(AA)_2\ X_2]^{+1}$, where (AA) can be ethylenediamine (en), propylene-diamine (pn), trimethylenediamine (tn) and X can be monodentate ligand $(NO_2)^-$ and Cl^-. Following methods were used to prepare the complexes.

2.10(a) Preparation of trans-dinitro-bis-ethylenediamine cobalt(III) nitrate : $trans[Co(en)_2(NO_2)_2]NO_3$

A mixture of 6.85 gms of 70 % ethylenediamine (0.08 mol) and 10 ml of water was partially neutralized by the addition of 3 ml concentrated nitric acid (0.048 mol). The resulting solution was added to a solution of 11.5 gms of cobalt(II) nitrate 6-hydrate (0.040 mol) and 6.0 gms of sodium nitrite (0.087 mol) in 20 ml of water. A vigorous stream of air was passed through the solution, the yellow trans-dinitro-bis-ethylenediamine cobalt(III) nitrate began to precipitate after a few minutes and the reaction took twenty minutes for its completion. The mixture was cooled in an ice-salt bath and filtered. The yellow crystalline solid was recrystallized from boiling water, washed with alcohol and ether and air dried.

In the similar way the complexes namely trans$[Co(tn)_2(NO_2)_2]NO_3$ and trans$[Co(pn)_2(NO_2)_2]NO_3$ were prepared by using trimethylenediamine and propylenediamine.

2.10(b) Preparation of cis-dinitro-bis-ethylenediamine cobalt(III) nitrate : cis$[Co(en)_2(NO_2)_2]NO_3$

4.8 gms of a 10 % ethylenediamine solution (0.080 mol) was added to 2 gms of potassium hexanitro-cobaltate(III) (0.044 mol). The mixture was stirred constantly while it was heated slowly on a steam bath to about 70°C, whereupon the reaction occurred as evidenced by the dissolving of the yellow hexanitro-cobaltate to form a dark brown solution. While it was still hot, the reaction mixture was filtered to remove any traces of unreacted hexanitro-cobaltate, and the filtrate was cooled in an ice-salt bath to precipitate the brown cis-dinitro-bis-ethylenediamine cobalt(III) nitrate. The crystals were removed by filtration. Distinction between cis and trans isomers was done chemically (15).

In the similar way the complexes cis$[Co(tn)_2(NO_2)_2]Cl$ and cis$[Co(pn)_2(NO_2)_2]Cl$ were prepared by using trimethylenediamine and propylenediamine solutions.

2.10(c) Preparation of transdichlorobis (ethylenediamine) cobalt(III) chloride : trans$[Co(en)_2Cl_2]Cl$

Sixty grams of 10 % solution of ethylenediamine was added with stirring to a solution of sixteen grams of cobalt chloride 6-hydrate in 50 ml of water in a beaker. A vigorous stream of air was passed through the solution for 10 or 12 hours. 35 ml of concentrated hydrochloric acid was added and the solution was evaporated on the steam bath until a crust formed over the surface. The solution was allowed to cool and stand overnight before the bright green square plates of the hydrochloride of the trans form were filtered. These were washed with alcohol and ether and dried at 110° C so as to obtain a dull-green powder.

In the similar way trans$[Co(tn)_2Cl_2]NO_3$ was prepared using trimethylenediamine solution.

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