Instrumental Techniques

Chapter 2

Several experimental techniques have been used for characterisation of the collected and developed lamp phosphors which are undertaken in this thesis The instruments involved are X-ray diffractometer, Spectrophotofluorometer, Quantum efficiency measurement apparatus, Thermoluminescence glow curve and emission spectra recorder, Electron Paramagnetic Resonance Spectrometer, Integrator, Colorimeter, Particle size analyser, etc. This chapter deals with these instrumentation techniques in a brief manner.

X - ray Diffractometer

This is an easy technique for the characterisation of known as well as unknown samples. The simplicity of this technique is due to the specific value of d spacing for a compound. These d values can be calculated from the observed diffraction angles. An important feature of the diffractometer is its ability to focus into a sharp line, the radiation that is Bragg reflected from an extended specimen area.

In this instrument, essentially monochromatic radiation is used and the X - ray detector is placed on the circumference of a circle centred on the powder specimen The essential features of a diffractometer are shown in **Fig. 2A.** A powder specimen C, in the form of a flat plate, is supported on a table H, which can be rotated about an axis O, perpendicular to the plane of the paper. The X - ray source is S, the line focal point on the target T of the X - ray tube, S is also normal to the plane of the drawing and therefore parallel to the diffractometer axis O X - rays diverge from this source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit F and then enters the counter G A and B are special slits which define and collimate the incident and diffracted beams.

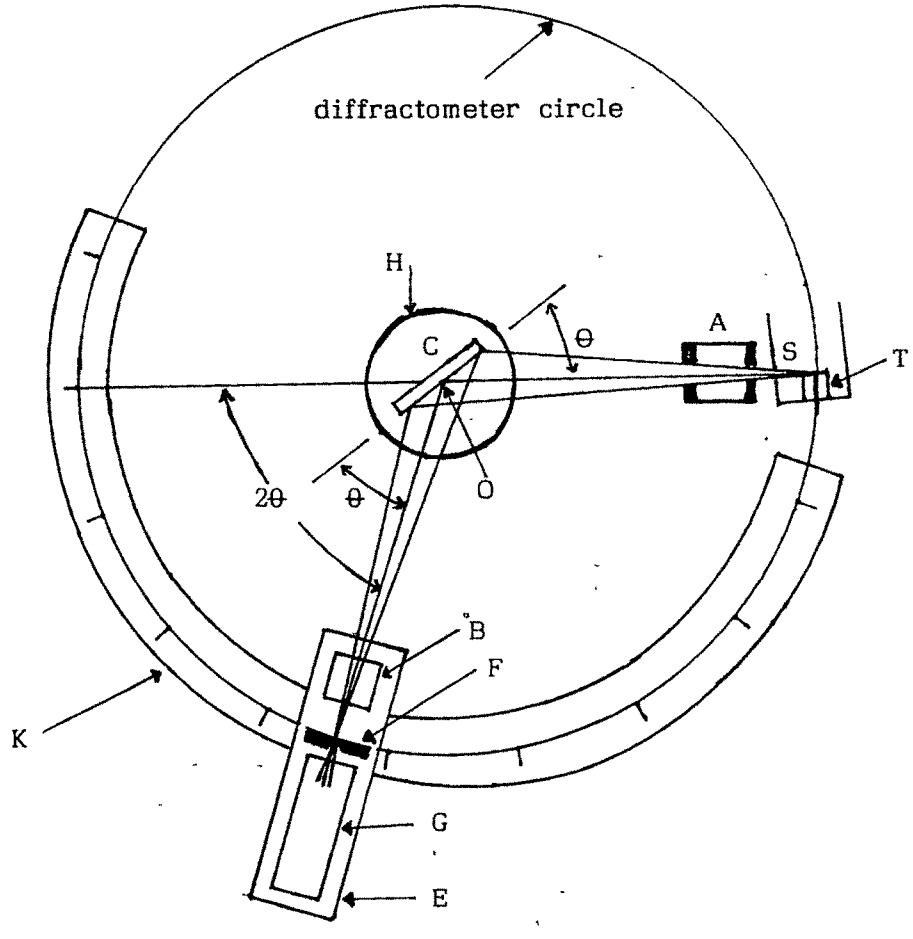

Fig. 2A : Schematic diagram of X-ray diffractormeter.

The receiving slits and counter are supported on the carriage E, which may be rotated about the axis O and whose angular position 2θ may be read on the graduated scale K or directly on a X - ray recorder as is the situation with the 'PHILIPS' diffractometer, which was used for the characterisation of samples in this study. The supports E and H are mechanically coupled so that a rotation of the counter through 2θ degrees is automatically accompanied by rotation of the specimen through θ degrees This coupling ensures that the angles of incidence on, and reflection from, the flat specimen will always be equal to one another and will be equal to half the total angle of diffraction, an arrangement necessary to preserve focusing conditions.

For recording the diffractogram of a powdered specimen, the counter is set near 2θ = 0 and connected to a counting rate meter. This output is connected to a strip chart recorder The counter is then driven at a constant angular velocity through increasing values of 2θ until the whole angular range is scanned. At the same time, the paper chart on the recorder moves at a constant speed, so that the distances along the length of the chart are proportional to 2θ. This gives a record of counts per second versus diffraction angle 2θ.

For taking the XRD patterns of samples in this work, a X - ray diffractometer of 'Philips' make was used. The system has a PW - 1729 X - ray generator, a PW - 1840 diffractometer control and a PM - 8203 A model one line recorder.

Spectrophotofluorometer

The three principal components of this instrument are; the source of excitation, the sample cell and the detector. The source is either a mercury or a xenon arc. The mercury arc gives very high intensities at its emission lines. The advantage with the xenon arc is that the lines are uniformly distributed over the range of frequencies most commonly used, although the intensity is low compared to the mercury lines The xenon lamps are used extensively.

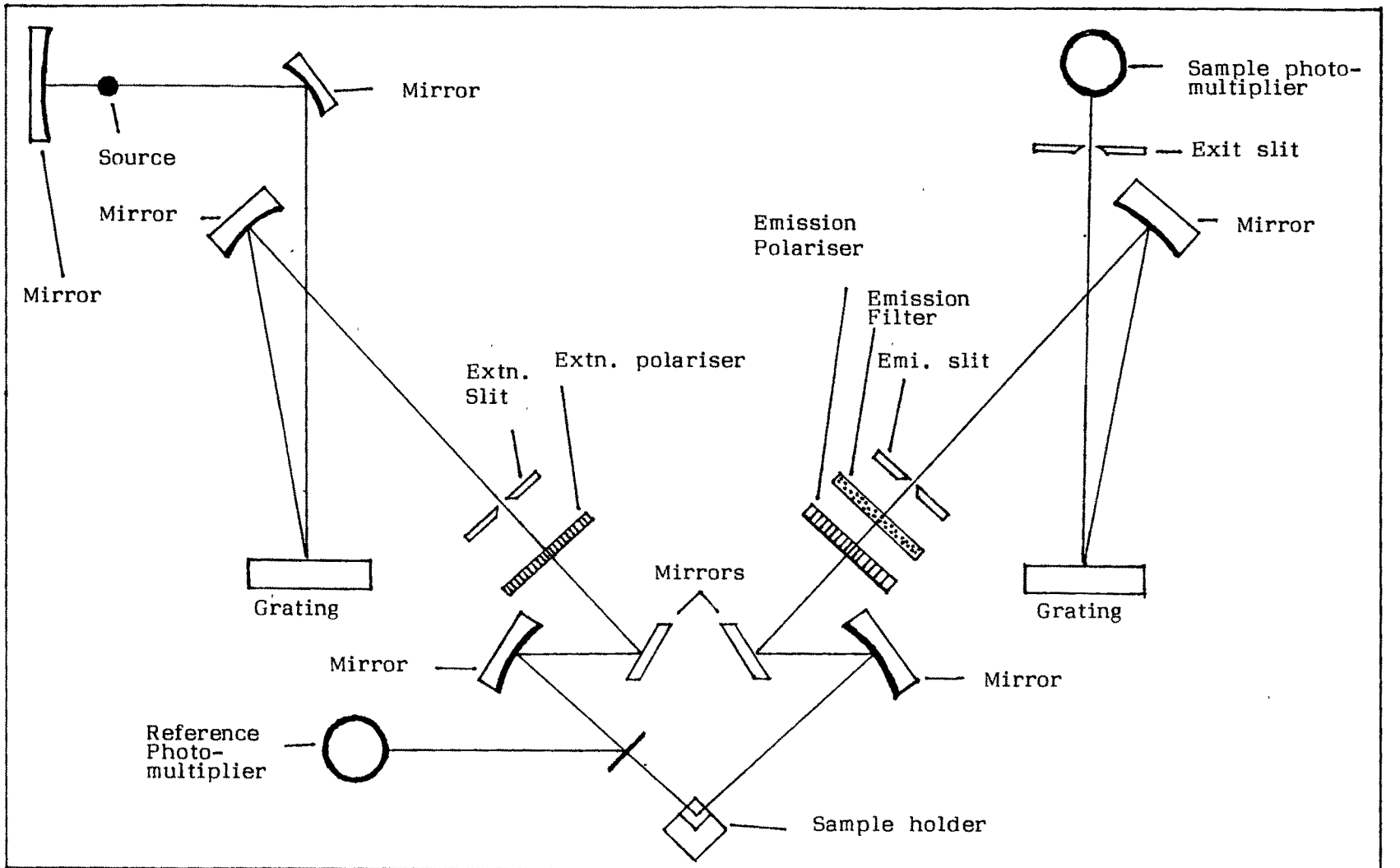

Fig. 2B : Block diagram of Spectrophotofluorometer.

Going to the working of the instrument, the light from the source passes through the device used to select the excitation radiation, often being focused in order to obtain increased intensity. This device may either be a filter or a monochromator. Filters give a greater quantity of light but the selectivity is poor Interference filter can provide much better selectivity. In case of monochromators, the one having a prism has the advantage of greater intensity in the ultraviolet region, which is usually needed for excitation However quartz prisms, which are needed for dispersion in this region are quite expensive. The light loss with grating monochromators is often less than that with a prism one but the problem of overlapping spectra due to the passage of different orders can be serious. Commercial instruments are found with either prism or grating monochromators, in general.

The sample cell should be made of material which does not absorb appreciably the wavelength of interest In most cases, a good grade of glass is suitable, however, for region below 250 nm, quartz cell should be used A right angle arrangement is generally used for placing the cell with respect to the excitation and detection components

The fluorescence leaving the sample cell usually passes directly into a filter, which is used to eliminate any scattered light of the excitation frequency, or into a monochromator. In some cases, both, a filter and a monochromator are used. This monochromator, called fluorescence or emission monochromator, is usually of grating type, since it normally will provide better dispersion and less light loss than a prism system When using monochromators for both the excitation and emission components, the problem of slit width becomes particularly important. Even when using high intensity sources, the amount of excitation light hitting a sample is small, and the fluorescent light leaving the sample is even smaller This small fluorescence is then passed through another monochromator, i.e. the emission monochromator, before being detected. Fortunately, it is seldom necessary to have small slit width on both monochromators simultaneously When measuring emission spectra, the slit of the excitation monochromator can be large,

and when recording excitation spectra, the slit on the emission monochromator can be large.

The instrument needs a highly sensitive detection system In most instruments, high gain photomultiplier tubes with their requisite high voltage power supplies are necessary. Some systems measure under DC condition, while others use a chopped light beam and incorporated tuned AC amplifiers. The DC system, although less complicated, are inconvenient for differentiating fluorescence and phosphorescence. The output of the detection system can be displayed in several ways. Simply a meter, an oscilloscope or a recorder can be used For particularly low level signals, where the signal to noise ratio is the limiting factor, integrator with large time constant circuits can be advantageous.

The excitation and emission spectra of the commercial lamp phosphors as well as lab system have been recorded on a 'Hitachi' system The Hitachi, model F - 4010 is a high resolution fluorescence spectrophotometer, in which the excitation beam is automatically corrected for intensity variations of the source with wavelength The detector used is the Hamamatsu make photomultiplier (type no R 955 of multialkali photocathode), which has a flat spectral response over the entire range of wavelength of measurement i e from 200 to 900 nm For spectral measurements, the phosphor powder is loaded in a metallic plaque having a quartz window and placed in the sample compartment using a solid sample holder.

A collimated monochormatic beam of UV rays from the excitation monochromator falls on the phosphor surface at an angle of 45 and the luminescent light emitted enters through the entrance slit to the emission monochromator. From the emitted light, one of the prominent emission line is selected by the emission monochromator and held fixed for signal detection by the PMT. The excitation monochromator is now continuously scanned from as low as 200 nm upwards upto the lower limit of the emission region, until spectrum is recorded by the recorder

The instrument has a emission monochromator of high resolving power with a range upward of 800 nm, which covers the entire visible range From the previously recorded excitation spectrum, any wavelength of interest in the UV range can be selected for exciting the phosphor. The emitted light from the phosphor plaque window, enters the entrance slit of the emission monochromator, which is being continuously scanned over the entire visible region of interest, and recorded. Several filters of the Corning series are provided to prevent the excitation wavelength and its higher orders from getting recorded erroneously as emission peaks.

A 150 W xenon lamp is used as a source. Concave gratings of 900 lines per mm are used on both the excitation and emission sides for monochromators

Block diagram of a Spectrophotofluorometer is given in **Fig. 2B.**

Quantum efficiency apparatus

The apparatus for the measurement of quantum efficiency is shown in **Fig. 2C** It consists of a demountable stainless steel assembly of two chambers - one upper and the other lower. The upper chamber consists of a stainless steel tube of internal diameter 50 mm and length 25 cm. A HPMV lamp of 125 W without its outer shell, is located vertically in this chamber. The lamp provides the UV radiation of wavelengths 254, 312 and 365 nm in sufficient intensities The UV rays from the HPMV lamp is collimated with the help of two aluminium rings of 20 mm internal diameter fitted inside the stainless steel tube A thin metal plate introduced through a side cutting in the tube acts as a shutter

The lower chamber of 10 cm internal diameter stainless steel tube and 10 cm height, holds the interference filter and quartz lens on suitable supports, the aluminium sample holder and silicon photodiode The base of the apparatus is a graphite disc (2 cm thick and 10 cm diameter). A channel of width exactly equal to the diameter of the sample holder is an aluminium plaque of outer diameter 20 mm, inner diameter 15 mm and

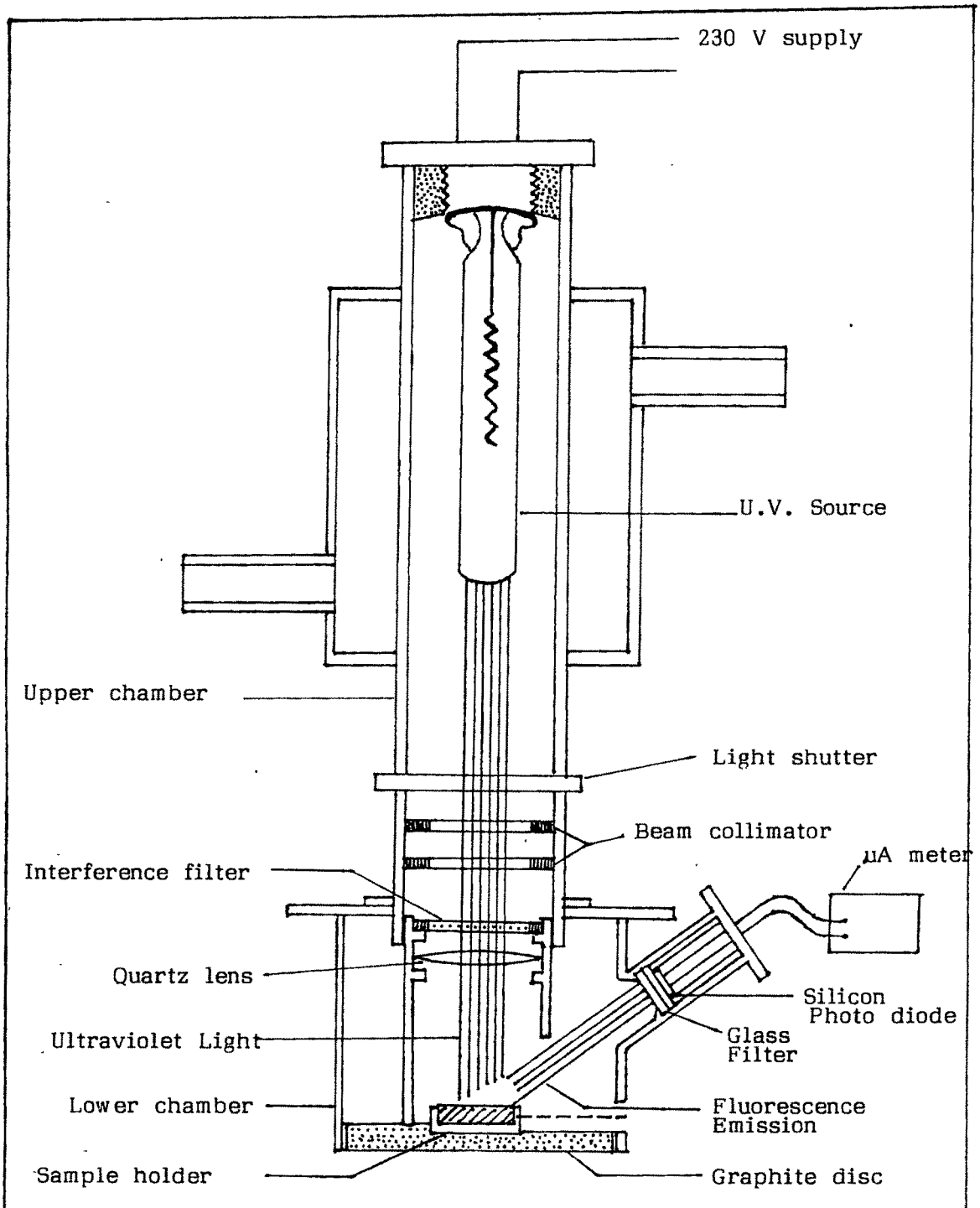

Fig. 2C : Block diagram of apparatus for Quantum Efficiency Measurement.

depth 3 mm. When placed in the apparatus, the sample holder sits exactly at the centre of the graphite disc. Since geometry remains unchanged for the sample holder, phosphor efficiencies of number of samples can be compared with. The plaque is loaded with 3 mm phosphor layer of uniform thickness. The Silicon Photodiode, mounted on a cylindrical beckalite frame placed at the viewing port will view the light coming out of the phosphor surface at an angle of 45. The mercury line interference filter can select the suitable wavelengths for UV excitation The quartz lens of focal length 5 cm focuses UV light onto the phosphor surface The light falling on the photodiode surface of one square cm surface area produces a photocurrent which is measured by the electrometer amplifier The pyrex filter is introduced through the viewing port. The beam of UV strikes the phosphor surface and the fluorescent emission falls on the photodiode

Thermoluminescence glow curve and emission spectra recorder

The thermoluminescence glow curve reader consists of a specimen holder along with heater, a temperature programmer, a photomultiplier tube as detector, a high voltage unit, a D.C. amplifier and a suitable displaying or recording device, as shown in **Fig. 2D**

The specimen is spread uniformly over a metallic strip of Kanthal (Fe - 72%, Cr - 23%, Al - 3%, and Co - 2%). The strip is narrow and has a circular depression at its centre. A chromel-alumel thermocouple is generally used to record the temperature of the specimen. A linear relationship between the rise in temperature and time is maintained by the uniform heating rate that is controlled by the temperature programmer The photomultiplier tube is housed in a light - tight cylinder and a high voltage is applied to it When the kanthal strip with the irradiated specimen is placed in front of the photomultiplier window, the light emitted by the specimen during heating is recorded through the photomultiplier tube and a D C amplifier by the output device

In the present study, the thermoluminescence glow curves of the samples were taken on a Nucleonix make PC based thermoluminescence reader. The system consists of

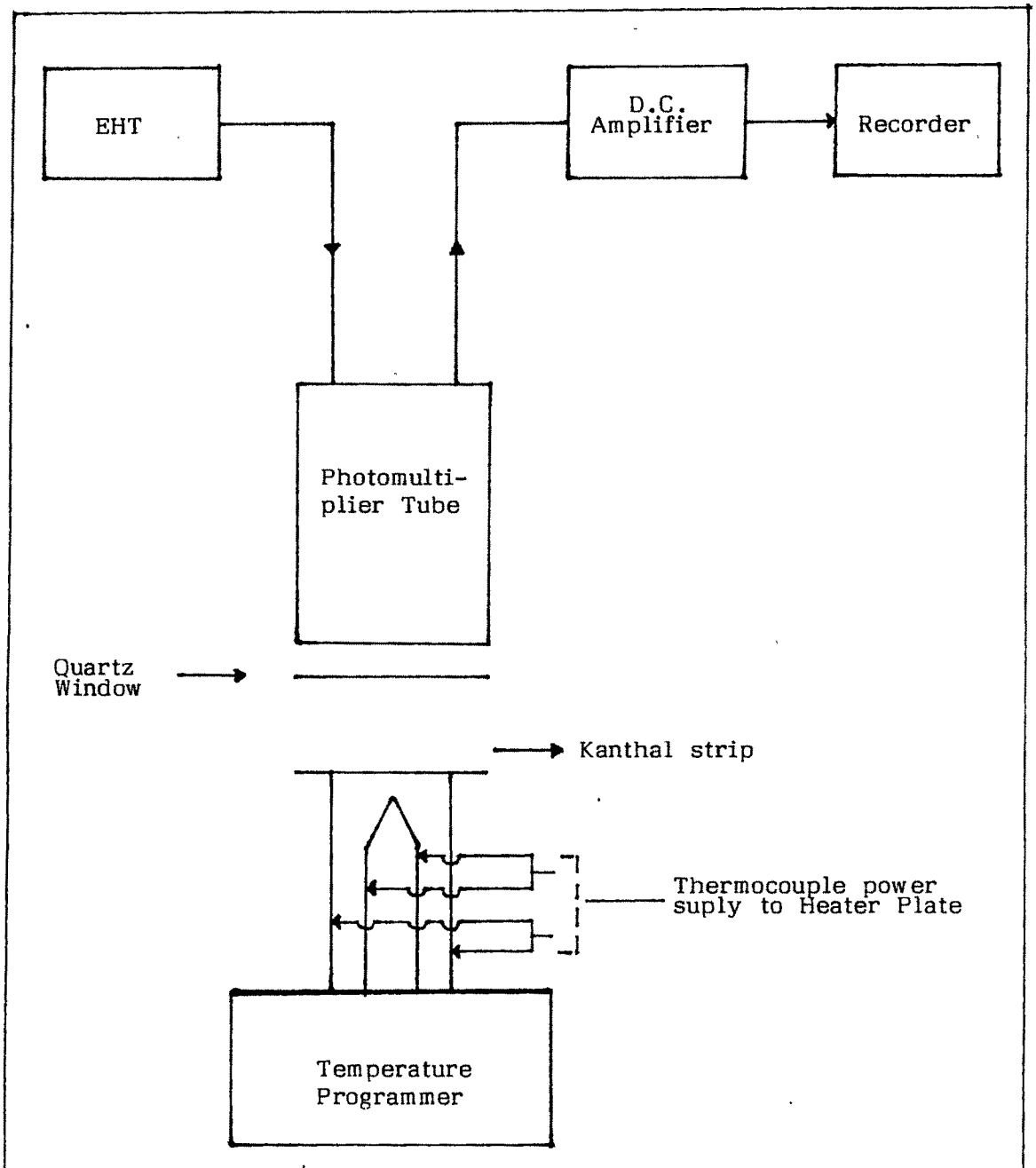

Fig. 2D : Block Diagram of TL Set-up.

a PMT housing with drawer assembly, high voltage module, D.C amplifier module, Temperature controller unit, power supply unit, AD - DA card and a personal computer system along with software. Block diagram is given in **Fig. 2E.**

The power supply provides four different outputs with a ripple and noise better than 3 mV at full load for all the supplies The D C amplifier/ integrator of model No D A 552 is a two bit module which converts the PMT current into a proportional voltage signal. This unit has eight overlapped current ranges from (0 - 10 μA) to (0 - 800 pA) In each of the ranges, one can record TL intensity as a digitized signal on the Y - axis. The PMT current signal received at the D. C. amplifier is converted into voltage signal which inturn is presented to the AD - DA card for digitization. A read/zero switch is also provided In the read position, the PMT current is taken to the D C. amplifier and in zero position, it is disabled. A.D C off-set is provided to normalize the D. C level against dark current signal This is a ten turn helipot. Provision is made for the direct indication of the TL intensity.

The temperature controller T C 575 works in PC programmable mode as well as ISO mode. The temperature range is from room temperature to 500° C, with an accuracy of +/- 2°C. Temperature is increased by resistive heating and is measured by a thermocouple sensor. Various types of heating profiles, temperatures in different regions, time heating rates, etc. can be set through the PC. The controller accepts DAC output signal from the AD - DA card to make up for the various functions.

The high voltage unit, HV 502 generates EHT in the range of 0 - 1500 V, @ 1 mA, which is used for biasing the PMT The ripple and noise is better than 15 mV The PMT (type EMI 9924 B) and heater drawer assembly is a compact, light leakage free housing with PMT mounted inside There is a IR cut-off, i.e. a heat absorbing filter provided just below the PMT window The housing has a kanthal strip with a circular depression of 14 mm diameter for loading of TL materials

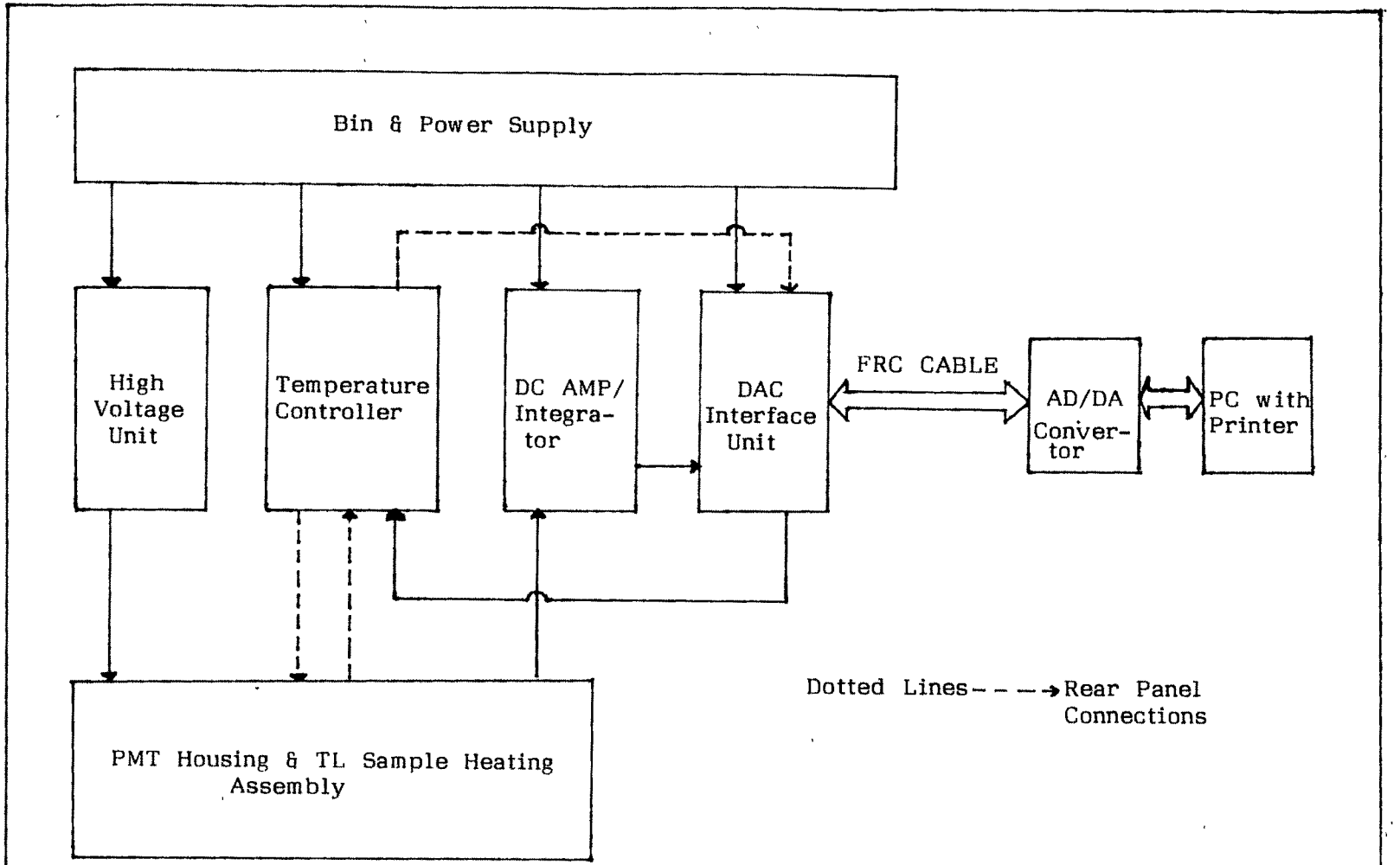

Fig. 2E : Block Diagram of PC based Thermoluminescence Analyser.

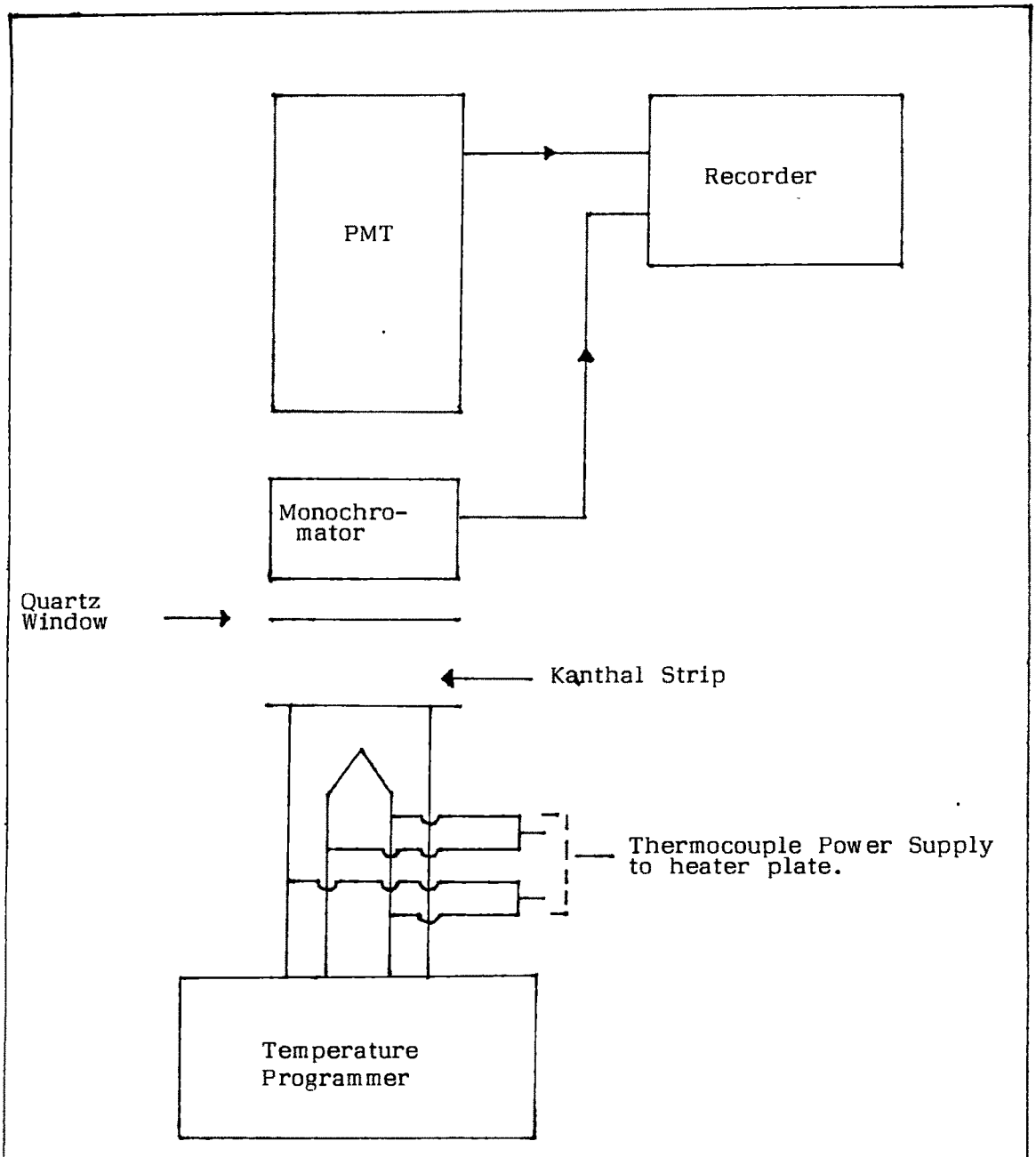

Fig. 2F : Block Diagram of TL Spectrum Set-up.

Among the computer components are, an IBM compatible Pentium - 133 Mhz or above with 24 MB RAM, 1.44 MB mini FDD, 1.2 GB Hard disc drive, SVGA colour monitor and mouse and A4 size Inkjet printer, with colour cartridge. The windows based software is developed in Visual C^{++} 4.0.

For recording the Thermoluminescence emission spectra, the samples were rapidly heated to the desired temperature. The temperature was held constant by using a Variac, which is also used for heating by increasing the current supply to the resistive element. The TL emission is then fed to the monochromator, where it converges on a short focused grating (1200 lines/cm). The grating can be rotated with the help of a small stepper motor, at the desired rate The light emerging from the exit slit of the monochromator is fed to the PMT, which has a flat spectral response over the region of interest. The PMT output signal is amplified and then coupled to the PC, where the spectra can be displayed or recorded. The block diagram of TL emission recorder is given in **Fig. 2F.**

Electron paramagnetic resonance spectrometer

The EPR investigations of the samples were carried out using a Varian V-4502 EPR spectrometer operating in the X - band range of frequencies (8.8 - 9 5 Ghz) **Fig. 2G** gives the block diagram of the EPR spectrometer. The system consists of a precision electromagnet unit with a low impedance magnet and matching power supply equipped with a feildial magnetic field regulator and automatic sweep, a control console with 100 KHz and audio frequency modulation and detection, a microwave bridge, resonance cavity, oscilloscope and a strip chart recorder.

Absorption of microwave power in the sample as a result of resonance imbalances the bridge. The 100 KHz modulated microwave power output containing the EPR signal is detected by a phase sensitive detector and recorded graphically with the strip chart recorder or displayed on an oscilloscope having audio frequency sweep The magnetic field between the pole pieces is varied linearly with time by applying a constant voltage to

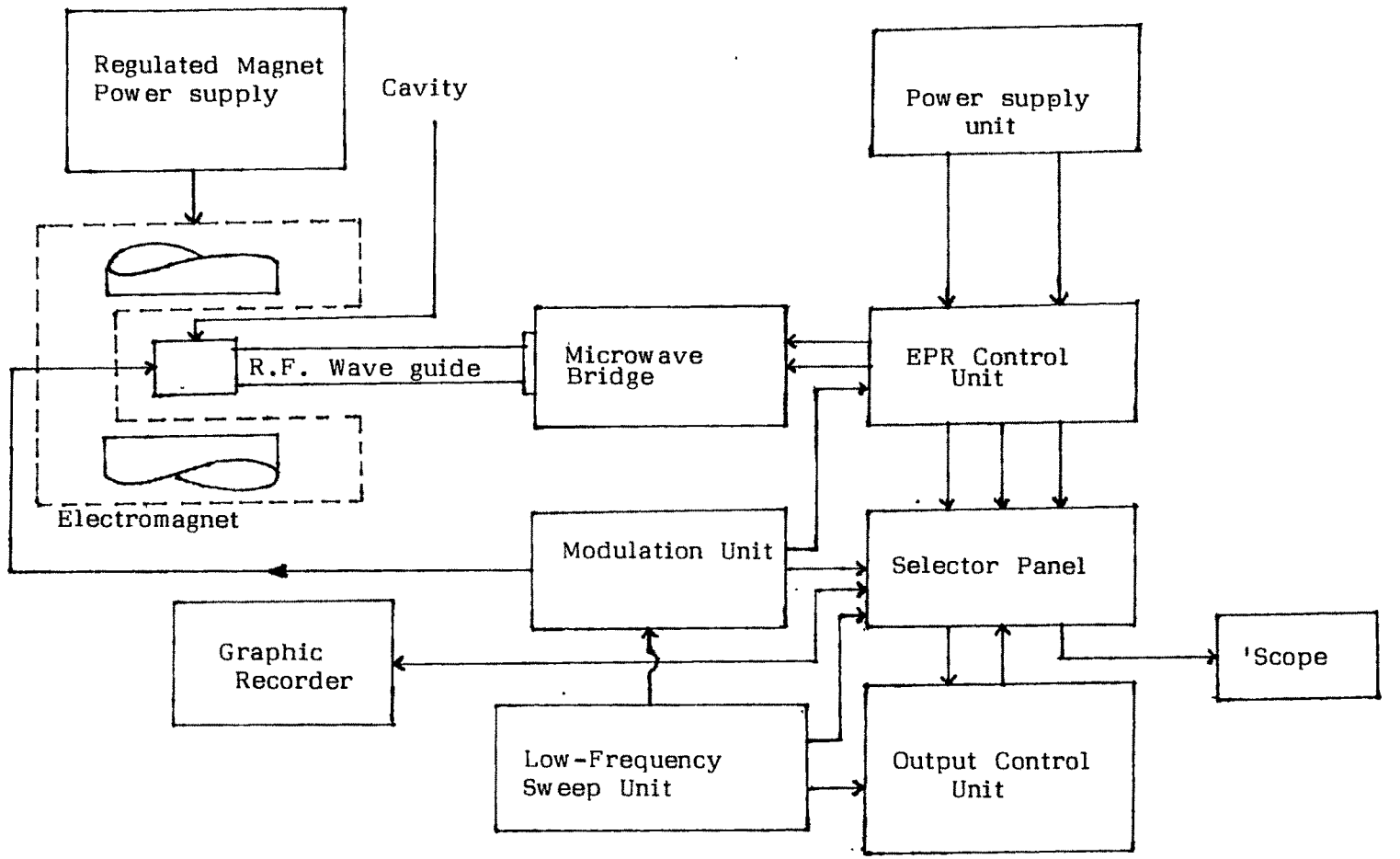

Fig. 2G : Block Diagram of EPR Spectrometer.

the input of the current regulated magnet power supply. Field measurements were done using a NMR flux monitor. A rectangular dual reflection cavity (V - 4532) was used to record the EPR spectra The spectra of the sample and the reference material were recorded simultaneously using a dual pen strip chart recorder DPPH (α, α - diphenyl picryl hydrazyl) is the reference used in the experiments. The g values of the samples were determined by calibrating the observed spectra with signal from DPPH (with a g value of 2.0036) placed in the other cavity. The samples were sealed in thin (dia - 3 mm) suprasil tubes and then kept in another quartz tube and kept in the EPR cavity.The Varian variable temperature controller (V - 4557) is used to study the temperature dependence of the EPR spectra in the range - 185 to 300° C. In this system, the temperature of the system is controlled by passing a regulated current through an electric heater which is placed in a nitrogen stream that is directed towards the sample cavity. The temperature at the sample is monitored by a resistance type of temperature sensor. For studies at room temperature and above, gas flows directly into the cavity, where it is heated to desired temperature. The sample temperature is controlled to an accuracy of + 2° C with the help of a sensor and temperature setting potentiometer.

Integrator

The lumen output of the lamps was measured with the help of an integrator of LMT, Germany make. The model UL 1500 consists of a metallic hollow sphere with a diameter of 2000 mm As shown in **Fig. 2H** , the sphere opens up into its two halves. The tubular fluorescent lamp is fitted into the socket provided inside the sphere. The societ is mounted to a vertical pipe which passes through the top of the sphere. The wiring required for the lamp holding socket passes through this pipe The sphere is coated from inside with a LMT photometer point PHP - 80. The finishing coat, composed of highly purified barium sulphate, binder and selected pigments is characterised by diffuse and aselectic reflection.

A flange is provided to mount the light sensing device i.e the photometer head to the sphere The LMT photometer head P 30 SCT is suitable for an integrating sphere for

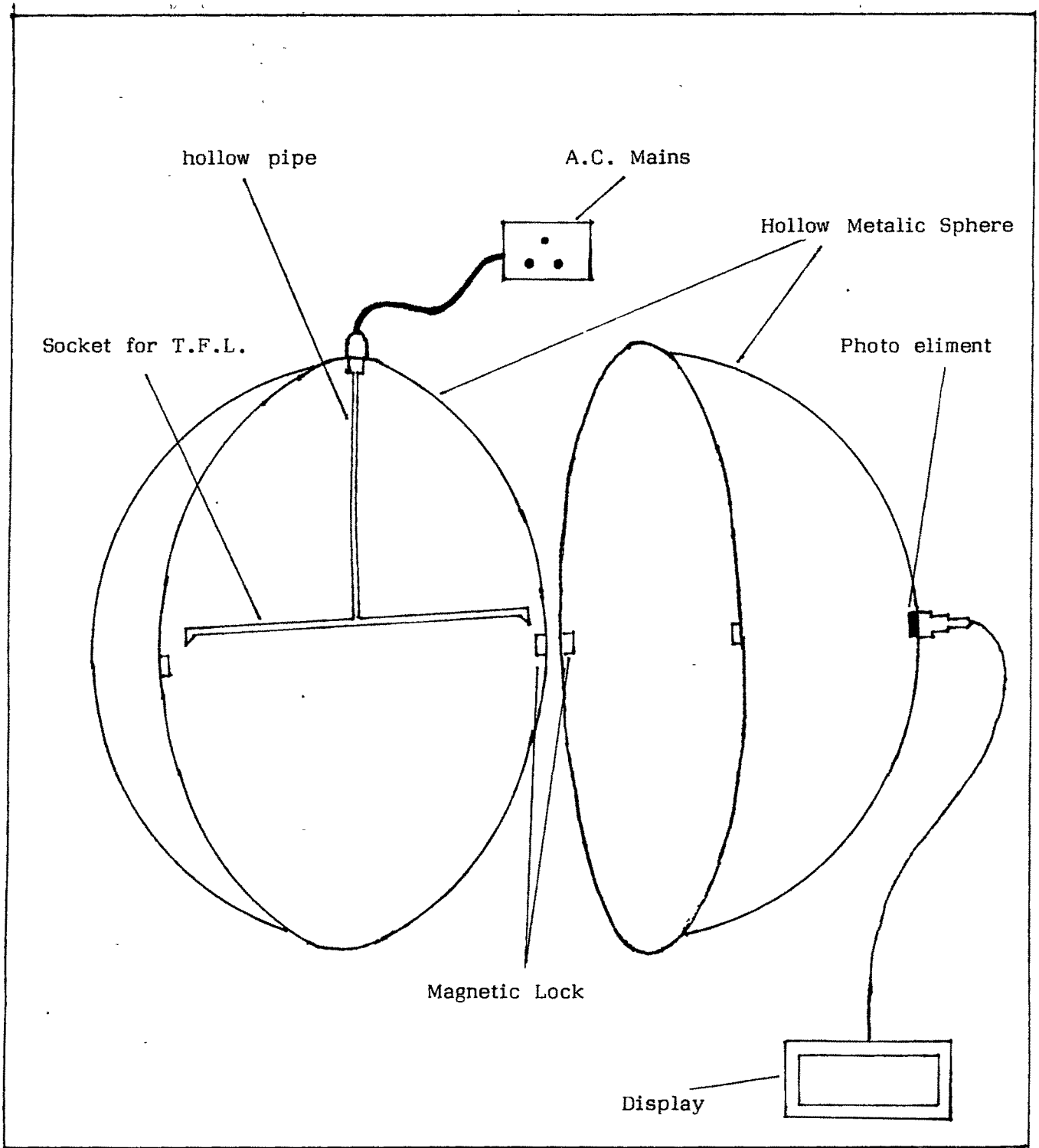

Fig. 2H : Schematic diagram of Integrator.

luminous flux measurements. It has silicon photoelements having sensitivity 18-28 mA/lux with a 30 mm diameter of the light sensitive area. It has a fine V (λ) approximation and is provided with thermostatic stabilization.

The lumen output can be read on an electronic display unit U - 2000 with 5 digit display. Facility for auto, manual or remote programmable range setting is provided The display range has a minimum of 10^{-3} lumen and a maximum of 10^{6} lumens. The instrument has a built in precise temperature sensor for measurement of inside temperature of the sphere The temperature can be read on a digital display with 0.1° C resolution A magnetic locking system is provided to ensure that the sphere is tight fitted.

Colorimeter

The colour co-ordinates of the lamps were recorded using LMT colorimeter type C 1210. The colorimeter head CH 60 consists of selected silicon photoelements which are carefully adjusted to the CIE colour matching functions X (λ), Y (λ) and Z (λ) for a 2° standard observer The photoelements are housed in a cylinder which is insulated with foam plastic. At the receiving end, there is a translucent glass plane and right behind it are two filters, one IR and one UV, which effectively limit the wavellengths reaching the photoelements. Behind the mounting pane of the photoelements, a metal block with heating resistors is placed which, together with an integral electronic circuit, maintain a constant temperature of 35° C $\pm$ 0.1° C. At the rear side of the CH 60 are located, the connection for the cable to the evolution and display unit and the LED that indicates that the thermostat is working. Depending on the ambient temperature and the state of heating, this diode will e illuminated more or less

By means of partial filtering using coloured glass filters, the relative spectral sensitivity of the photoelements can be made to coincide, with the CIE colour matching functions. The very sensitive photoelements ensure that the absolute sensitivity is a few μA/L for each of the tristimulus values.

The evaluation and display unit is a 19 inch case, which can be used as a rack or desktop housing. The unit contains 3-channel high quality amplifiers which are coupled to the silicon photoelements of the colorimeter head. These amplifiers are used to make the current to voltage conversion of the signals Three precise analogue to digital converters convert the voltages of the amplifier outputs to digital signals. The digital measurement signals are further evaluated by microprocessor - controlled circuits.

Particle size Analyser

The particle size analysis of the commercial lamp phosphor samples was carried out on a ' Microsizer E ' analyser, made in U.K Such analysers employ laser based techniques to measure the particle size A He-Ne laser beam is scanned circularly by a rotating wedge prism and focussed down to a small spot around a micron, which scans the sample measurement volume. As the particles within that sample volume are individually bisected by the laser spot, interaction signals are generated. These signals are then detected by the photodiode. Since the beam rotates at a constant speed, the durations of interaction provide a direct measurement of each particle size The interaction signals are collected by a dedicated data aquisition card and analysed in discrete size intervals Sophisticated pulse analysis algorithms are employed to reject out of focus and off - center interactions

This technique is based on the Time of Transition theory, which relates solely and directly to particle size rather than to secondary properties from which size can be inferred. Problems of coincidence and orifice clogging are avoided by using interaction pulse analysis to provide an optically defined measurement zone rather than a mechanically defined orifice. Simultaneously, it offers high resolution and wide dynamic range. This technique generates the most accurate sizing of

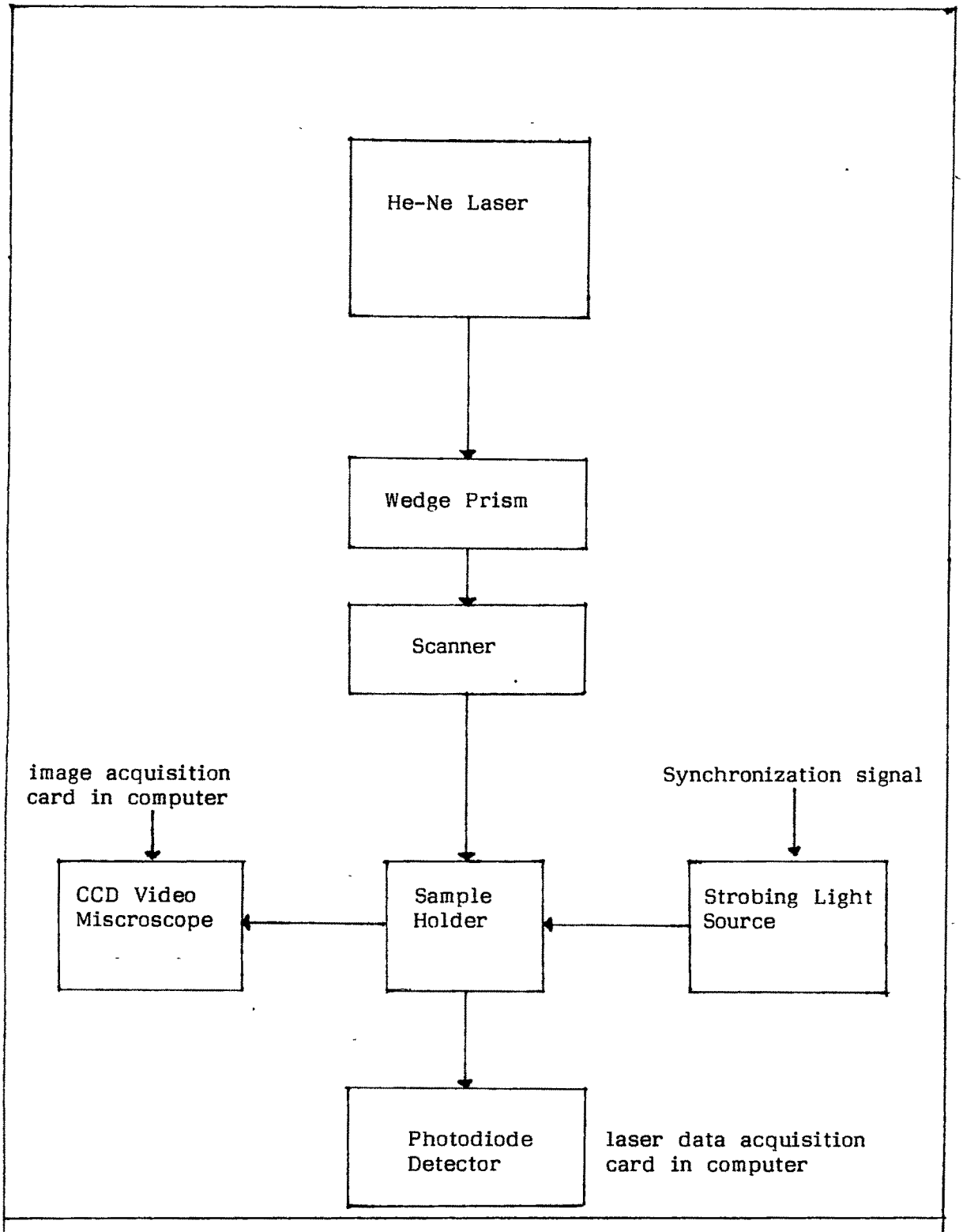

Fig. 2I : Block diagram of particle size analyser.

particles having range with a minimum below 1 microns and a maximum of few hundred microns, with very high resolution.

The block diagram of à Particle size analyser is given in **Fig. 2I**.

Furnace

The samples of synthesised phosphor were prepared in a furnace made by 'Precision Control', having Molybdenum heating elements. The furnace has a very precise temperature controller of 'Eurotherm' make, with a resolution of 1° C. It can go upto a maximum of 1700° C. A mechanical protection system is provided so that the input to the heating elements would be cut-off, once the temperature reaches 1650° C.

Sources for irradiation

The samples were irradiated by γ - rays as well as ultraviolet rays For γ - irradiation, a Co^{60} gamma ray source was used, its strength was calculated at about 15 Gy/min. The set-up consists of a radiation source, biological shield, central drawer incorporating the sample chamber, driving system, control panel and external cabinet The central drawer can be moved up and down as required and this movement is controlled by the front control panel through an electrical circuit. For ultraviolet irradiation, a low pressure mercury vapour UV source was used. This lamp is of 'Insiotech' make and operates on 6 watt. The radiation has a wavelength of 253.7 nm

References :

-- B. D. Cullity, Elements of X- ray diffraction, Addison - Wesley Inc., 1978.

-- B. P. Straughan & S. Walker, Spectroscopy, Vol. 1 & 3, Chapman and Hall Ltd., 1976.

-- G. Alexander et. al., Proceedings of National Conference on Luminescence and its Applications, 1994.

-- S. W. S. Mckeever, Thermoluminescence of solids, Cambridge University Press, 1985.

-- W. Elenbass, Fluorescent Lamps and Lighting , Philips Technical Library, 1959.

-- R W. G Hunt, Measuring Colour, Ellis - Horwood Ltd., 1987.