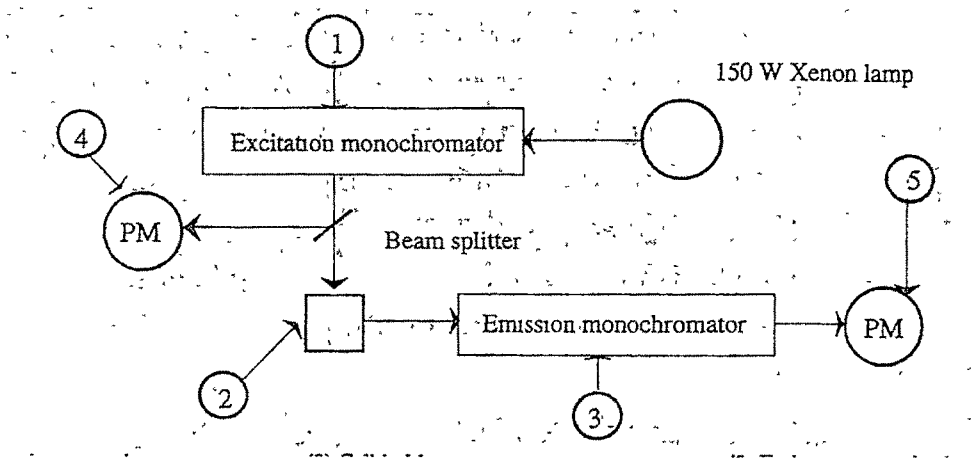
Chapter–III

Instrumentation

Chapter-3
Instrumentation

Optical System of Spectrofluorophotometer:

The spectrofluorophotometer irradiates a sample with excitation light and measures the fluorescence emitted from the irradiated sample to perform a qualitative or quantitative analysis. A typical configuration of the spectrofluorophotometer is schematically described below (see Fig. 3.1taking the RF-530IPC instrument as an example.



1) Excitation monochromator, (2) Cell holder, (3) Emission monochromator,
4) Monitor side photomultiplier tube, (5) Fluorescence side photomultiplier tube

Fig. 3.1Constitution of RF-5301 PC

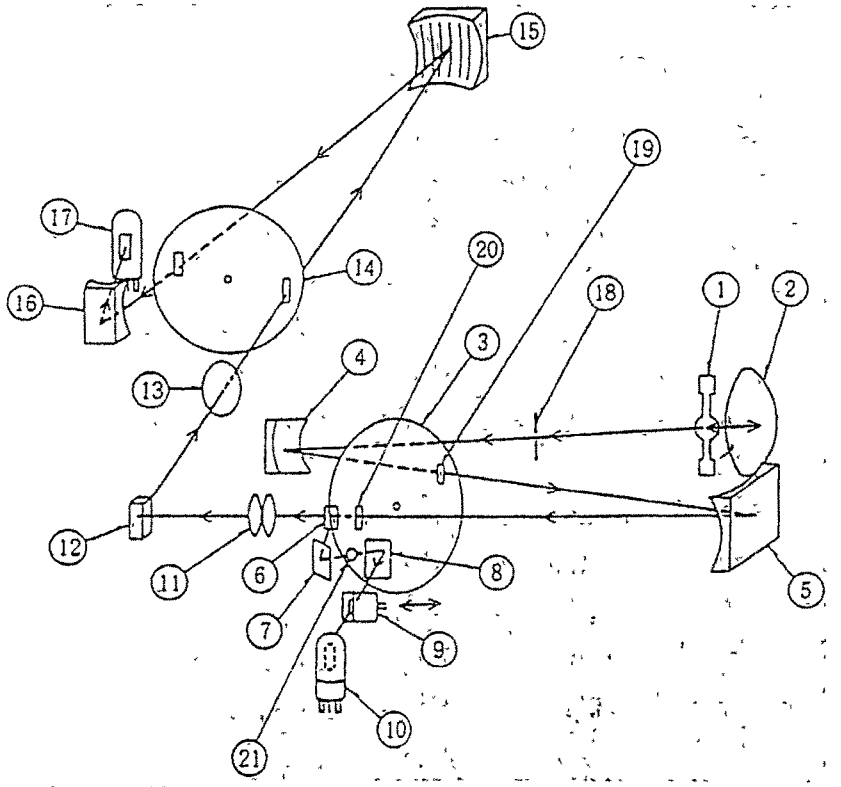
The excitation monochromator (1) isolates a band of a particular wavelength from the Xenon lamp to obtain excitation light. Since brighter excitation light will contribute to higher sensitivity of the spectrofluorophotometer, the excitation monochromator incorporates a diffraction grating with a larger aperture to collect the largest possible amount of light.

The cell holder (2) holds a cell filled with sample. The emission monochromator (3) selectively receives fluorescence emitted from the sample and its photomultiplier tube measures the intensity of the fluorescence. This monochromator has a diffraction grating whose size is the same as that of the excitation monochromator to collect the greatest

possible amount of light. The photomultiplier tube (4) is for monitoring the excitation light. Generally, the Xenon lamps used on spectrofluorophotometer are characterized by very high emission intensity and an uninterrupted radiation spectrum. However, their tendency to unstable light emission will result in greater signal to noise ratio if no counter measure is incorporated. In addition, the non-uniformity in the radiation spectrum of the Xenon lamp and in the spectral sensitivity characteristics of the photomultiplier tube (these criteria are generally called instrument functions) causes distortion in the spectrum. To overcome these factors, the photomultiplier tube (4) monitors a portion of excitation light and feeds the resultant signal back to the photomultiplier tube (5) for fluorescence scanning. (This scheme is called the light-source compensation system.)

The optical system of the RF-5301PC instrument is illustrated in Fig 3 2 A 150 W Xenon lamp (1) serves as the light source. The uniquely designed lamp housing contains generated ozone in it and decomposes the ozone by means of the heat produced by the lamp The bright spot on the Xenon lamp is magnified and converged by the ellipsoidal mirror (2) and then further converged on the inlet slit of the slit Assy (excitation side) (3) by the concave mirror (4). A portion of the light isolated by the concave grating (5) passes through the outlet slit, travels through the condenser lens (11) and illuminates the sample cell. (The concave grating in both the monochromators is a highly-efficient ion-blazed holographic grating) To achieve light -source compensation, a portion of the excitation light is reflected by the beam splitter quartz plate (6) and directed to the Teflon reflector plate 1 (7). The diffusely reflected light from the reflector plate I (7) then passes through the aperture for light quantity balancing (21) and illuminates the Teflon reflector plate 2 (8). Reflected by the reflector plate 2 (8), the diffuse light is attenuated to a specific ratio by the optical attenuator (9) and then reaches the photomultiplier for monitoring (10). The fluorescence occurring on the cell is directed through the lens (13) to the emission monochromator that comprises the slit Assy. (14) and the concave grating (15) Then, the isolated lights introduced through the concave mirror (16) into the photomultiplier for photometry (17) and the resultant electrical signal is fed to the preamplifier.

The spectra recorded using the above instrument displays the spectra along with the peak data the same can be copied to any other format, which is user-friendly software.



1. Xenon lamp, 150 W
2. Ellipsoidal mirror, SiO2-coated
3. Slit Assy., excitation side
4. Concave mirror
5. Concave grating (for excitation)
6. Beam splitter quartz plate
7. Teflon reflector plate I
8. Teflon reflector plate 2
9. Optical attenuator
10. Photomultiplier for monitoring, R212-14
11. Condenser lens (dual-lens)
12. Cell
13. Condenser lens
14. Slit Assy., emission side
15. Concave grating (for emission)
16. Concave mirror
17. Photomultiplier for photometry, R3788-02
18. Focal point
19. Inlet Slit
20. Outlet slit
21. Aperture for light quantity balancing

Fig.3.2 Optical System of RF-5301PC

From routine analysis to research, employing highest level of sensitivity in the world the RF-5301PC is a tool for advanced studies. Compared to absorbance methods, fluorescence sensitivity is tens to thousands times better – this means that one can analyze nano grams to pico gram samples with great results Fluorescence can be used also to identify a specific molecule in a complex background. When the compound of interest does not exhibit natural fluorescence, functional group-specific probes may be used to label the compound & assist our research. The synchronous scanning mode allows mixtures of fluorochromes to be analyzed. The personal computer directly controls the instrument for data acquisition & processing. The windows friendly operating environment allows us to perform measurement, data processing, editing & recording in one continuous operation with a click of the mouse. Using the copy graph function, measurement data or spectra may be easily transferred to word processing or for preparation of documents or additional calculations. The essence of fluorescence analysis is sensitivity The high throughput optical system in the RF-5301PC employs a blazed holographic grating, photomultiplier & digital circuit to provide the highest level S/N ratio attainable. High speed scanning up to 5500 nm/min allows us to measure a spectrum in seconds. And since monochromator slewing is conducted at an ultra-high speed of about 20000nm/min, setting of two or more wavelengths can be performed quickly & easily. High resolution and extended range is possible with R-928 photomultiplier. The band pass on the RF-5301PC may be set as narrow as 1.5nm, which makes is possible to distinguish fluorescent peaks from the background emission. The wave length range of 220 to 750 nm can be extended to 900nm with an optional R-928 photomultiplier. The software performance built in checks. When the instrument is switched on, the operating conditions of the spectrophotometer are automatically verified. Separately, a noise level (S/N ratio) & the light source (xenon lamp) usage are built in features to help maintain the instrument in its optimum condition, providing absolute confidence in the quality of the data.

Versatile sample compartment size:

The sample compartment measuring 140mm,170mm deep & 140mm high, enables use of micro cells ,high sensitivity cells, or low cells ,etc. ,for a wide range of applications. Unique high performance features in the RF-5301PC. Wavelength search functions allow the optimum excitation & emission wavelengths to be found in about two minutes. Vertical optics with dynode feedback, Vertical optics in the RF-5301PC minimizes light loss in measurement with an LC flow cell a micro cell or small test tube. This design assures exceptionally high signal to noise ratio and provides the ability to attain excellent analysis results using very small volumes of precious samples. The dynode feedback enhances RF-5301PC performance by raising or lowering negative high voltage to the detector in response to differences in the excitation energy at wavelengths. Dynode feedback which expands the dynamic range of the signal detecting system is significantly superior to ratio methods.

Automatic shutter protects sample an automatic shutter in the RF-5301PC excitation path closes immediately when measurement ceases, thereby protecting the sample from photodecomposition. See the difference with windows performance working in the windows 3.1 environments makes operation intuitive. The software is driven by pull-down menus displayed at the top of your screen that can be selected with just a click of the mouse. Many convenient and time saving features The RF-5301PC software is the ideal software to meet all our research needs, from teaching to method development and quality assurance. Follow changes in intensity over time for kinetic assays or perform quantitative analysis on several samples. One can save time & effort with features that allow for onscreen data manipulation.

Spectrum measurement mode Perform emission & excitation scans with ease, or overlay the two for interpretation. Obtain & differentiate excitation & emission spectra using color & line Pattern assignments. Zoom in using the mouse or zoom out with the radar function to auto scale all data on-screen. The software picks & tabulates peaks & valleys automatically and if one needs a fast spectral scan in any measurement mode, the pop up scan function displays it on- screen in seconds which is simple but powerful for

extensive data processing. Operations such as first through fourth order derivative, mathematical smoothing functions, log conversions & offsets are easily performed with the RF-5301PC software. Display up to ten spectral curves simultaneously or use mathematical transformations to maximize our results. Select the source & destination channels along with the desired calculation & the results are redisplayed on the screen. The following is the photograph of the 5301R PC along with solid sample holder.

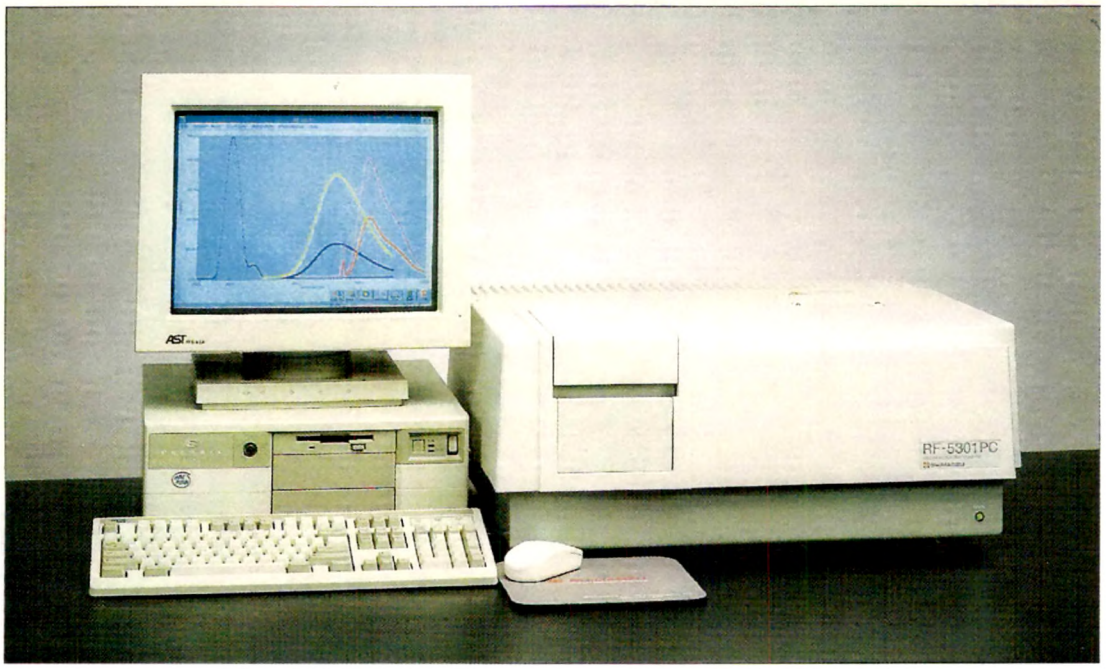


Fig. 3.3 Spectrofluorophotometer, RF-5301PC

Fig.3.4 Spectrofluorophotometer Powder Sample Holder

Hardware specifications

Light source	150W xenon lamp. Ozone resolving type lamp housing
Excitation & emission mono chromators	Concave, blazed holographic grating,f/2.5, 1300 grooves/mm.
Wavelength scale	220-900nm
Measuring wavelength range	220-750nm & 0 order as standard. 220-900nm with the optional R928 photomultiplier.
Spectral bandwidth	6-step selection of 1.5,3,5,10,15 & 20nm.(6nm bandwidth is available for half sample height on the excitation only)
Wavelength accuracy	±1.5nm
Light source compensation	Dynode feedback system with monochromatic light monitoring.
Sensitivity	The S/N ratio is 150 or higher for the Raman line of distilled water (350nm excitation wavelength ,5nm spectral band width ,& 2 second response for 98% of the full scale).
Wavelength scanning	7-step selection of survey(about 5500nm/min), super (about 3000nm/min), very fast ,fast, medium , slow & very slow.
Wavelength slewing speed	About 20000nm/min.
Response	8-step selection of 0.02,0.03,0.1,0.25,0.5,2,4& 8 seconds or 98% of the full scale.
Sensitivity selection	2-steps of high & low. (the sensitivity at high is about 50 times that of low).
Interface	RS-232C interface, interface for the auto sampler , and interface for sipper unit.
Dimensions & weight	667W*530D*270Hmm ;43 kg.
Power requirements	100,120,220,240;50/60 Hz;400VA
Operational temperature range	15-35 C
Operational humidity range	40-80 %(below 70% with temperature higher than 30C)

Software specifications

Measurement	Excitation ,emission & synchronous spectrum measurement ,time-course measurement, quantitation, automatic search of optimal excitation & emission wavelengths ,Popup Scan.
Data processing	Arithmetic calculation between spectra & between a spectrum & a constant, smoothing,1st through 4th derivatives,1/Y,logarithmic conversion, data printout(with or without activity value computation),peak pick, point pick, area calculation, averaging(in quantitation), generation of calibration curves of 1st through 3rd order.
Filing	Save, recall & delete ,of data. Conversion into ASCII & DIF formats.
Data output	Automatic scale adjustment, readout of data at user –specified point, data printout(preview function provided),selection of colors & types of curves
Maintenance	Automatic monitoring of signal-to-noise ratio, monitoring of the run time of light source lamp.
User interface	Speed –box (assigns icons for commonly used menu commands).
Other functions	Data exchange via clipboard, auto response control, and automatic shutter.
PC requirements	IBM-PC/AT or 100% compatible; 486 or higher CPU ; 8 Mbytes or larger main memory. Operates on MS –windows version 3.1 or higher.

Measurement Procedure:

A solid sample holder is provided with the fluorometer. It enables collection of front face fluorescence at an angle of 22.5 °. The powder sample was spread on it. The sample holder was fixed into sample compartment. When analyzing the sample, optical axis runs along the centerline of powder surface. First the excitation spectra were recorded by setting the emission wavelength at the zero order and keeping other parameters as

specified in the manual. The excitation bands were identified from these spectra and the emission spectra were scanned for identified excitation wavelength. This was necessary to know the approximate nature of EX spectrum, so it is necessary to select a particular band in the emission for scanning the excitation. Therefore for proper excitation spectra the emission wavelength was set at the position as identified from the earlier emission spectrum. The excitation and emission spectra were recorded with spectrometer slit fixed at 1.5 mm.

Fig.3.5 Thermoluminescence Setup

Fig. 3.6 Kanthal Strip and TL detection head. Left side is the Sr-90 beta source used in the present investigation.

Thermoluminescence (TL) Glow Curve 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. 3.5. Also Fig.3.6 presents the TL detection head and Sr-90 beta source.

The specimen is spread uniformly (5mg weighed) over a metallic strip of Kanthal (Fe-72 %, Ce- 23 %, Al – 3 %, and Co – 2 %). The strip is narrow and has a circular depression of 15 mm at its center. A chromel-alumel thermocouple is spot welded to record the temperature of the specimen. The uniform heating rate that is controlled by the temperature programmer maintains a linear relationship between the rise in temperature versus time. The photomultiplier tube is housed in a light-tight cylinder and a high voltage is applied to it. When the kanthal strip is loaded with the irradiated specimen which is placed in front of the photomultiplier window, the light emitted by the specimen during heating is recorded through the photomultiplier window. The light emitted by the specimen during heating is detected by a photomultiplier tube and is recorded through auto ranging D.C. amplifier by the output device.

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

PMT housing with drawer assembly, high voltage module, AM576 TL data acquisition module with auto ranging facility, Temperature programmer controller unit, power supply unit, AD-DA card and a personal computer system along with required hardware and software. Block diagram is given in Fig 3.7

The power supply provides four different outputs with a ripple and noise better than 3 mV at full load for all the supplies. The TL data acquisition module AM 576 is a two bit module which converts the PMT current into a proportional voltage signal which is in built auto ranging facility. Due to this facility one can record TL intensity as a digitized signal and can be transferred to the computer

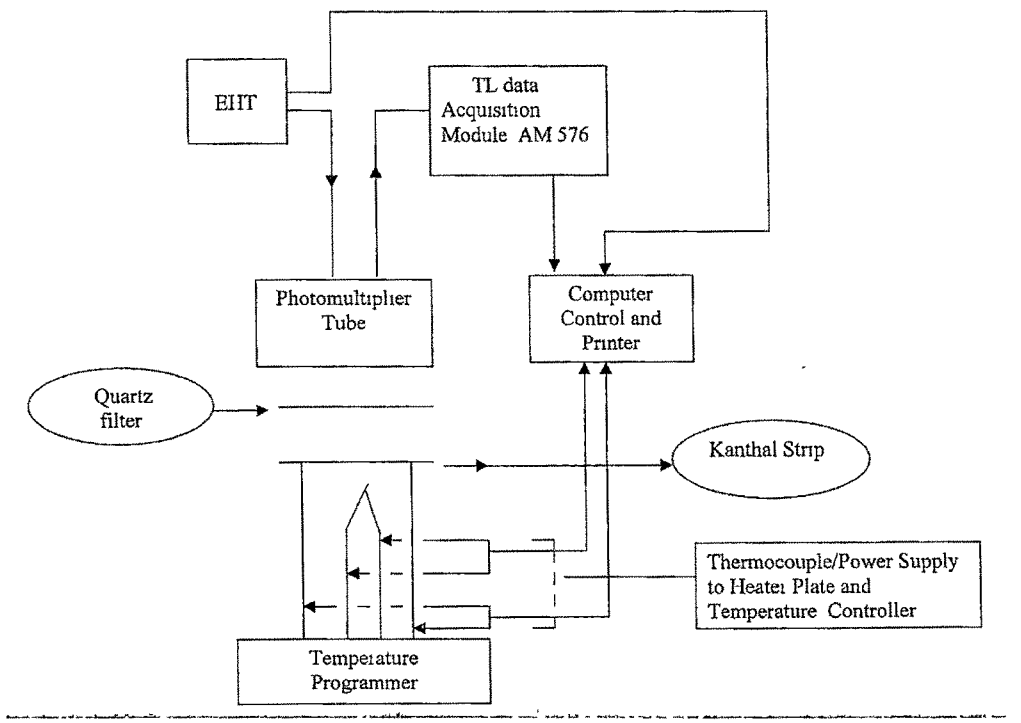


Fig.3.7 Block Diagram of TL Set-up

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 ^{0}C, with an accuracy of $\pm$ 2^{o} C. Temperature is increased by resistive heating and is measured by a thermocouple

sensor. Various type of heating profiles, temperature in different regions, time heating rates, etc. can be set through the windows program specially developed for TL acquisition. The controller accepts DAC output signal from the AD – DA card to make up for the various functions. The high voltage unit, HV 501 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. heat absorbing filter provided just below the PMT window. The housing has a kanthal strip with a circular depression of 15 mm diameter for loading of TL materials.

Among the computer components are, an IBM compatible Pentium-III 750 Mhz or above with 64 MB RAM, 1.44 MB mini FDD, 40 GB Hard disc drive, SVGA color monitor and mouse and A4 size Inkjet printer, with color cartridge. The window-based software is developed in Visual C^{++} 4.0. The following is the procedure for making the TL measurements.

Procedure to Measure TL more accurately using NUCLEONIX PC based TL Reader System:

Precautions to be observed for measurements with TL materials in powder form :

a. It is very important to measure the powder accurately and place it into the kanthal strip.
b. Accuracy depends mainly on the accurate weight measurement.
c. Powder should not be placed on the kanthal strip as a heap but should be
   Should be spread uniformly. This ensures that while heating takes place all the particles in the powder get heated up to the same temperature.
d. While disposing from the kanthal strip, it should be gently brushed aside, so that powder particles falls on to the collection tray.
e. Any particle left out may contribute to the next measurement as a residual TL adding to the next sample, measurement being inaccurate to that extent.

III Choosing appropriate heating profile .

a Depending on the type of TL material ($CaSO_4$, LiF or other material) and the form in which it is used (disc, rod, chip, powder crystals, pellets etc.) the heating profile is to be chosen.

b. The purpose of choosing most appropriate heating profile is primarily to maximize TL output and leave minimum residual TL in it. Also to minimize the contributions due to thermal and IR emissions.

c. Most commonly used heating profiles are

1 Linear

2 Linear with cooling region included into total run time

3 Linear clamped (Single plateau)

4 Linear clamped with cooling region included in run time.

d For Teflon coated disc, it is desirable to choose either linear clamped or linear clamped with cooling region . Longer clamped duration may be required to ensure that TL emission is complete and residual TL is completely removed.

e. Clamping temperature around 300°C is more than is enough in majority of cases for normal TL materials (other than pottery, sand and geological samples)

f. Thermal emission starts above 300 ° C onwards hence it is important that we restrict heating to set temperatures up to maximum of 300 °C Up to 350 °C in some cases provided there is good IR cut-off filtering done.

g. For low-level TL measurements if it is provided it helps in any spurious signal due to oxidation and other effects.

h. For low-level TL measurements it is better to choose a heating profile of " Linear clamped with cooling region included ". Because some TL curve may extend in to this region. Also restrict clamping to 300 °C to restrict thermal contribution.

i. The most recommended heating profiles are "C(2)" & "C(4)" for powders such as $CaSO_4$ & natural discs, micro-rods etc. Typical heating rate may be 5 °C/sec. (I.e. Time to be selected for profile region (0-1) will be approx.: 60 sec) Profile region (1-2) will be "0(zero)" sec and total run time can be selected as 75 sec (this makes the cooling region to be approx 15 sec – enabling glow curve acquisition to be recorded

in this region also.) If user wants to select other heating rate, say 10 °C / sec, then select profile region time between (0-1) as 30 sec , between (1-2) as zero & run time as 45 or 50 sec. This is linear profile with cooling included , but without clamped region.

Some time it may be better to clamp at 300 °C for certain time say 5 to 10 sec or even more to ensure that no residual TL is left. In which choose profile "C(4) " . For powder clamping for 5 to 10 sec may be enough.

After first time TL acquisition, if you rerun the sample, you will get background profile , which will also indicate if there is some residual TL.

For Teflon embedded / coated discs, recommended profile is "C (4)" and it is essential to clamp it for longer duration of the order of 40 to 60 sec. {Profile region {1-2}}. Linear heating region (0-1) may be about 60 sec and total run time can be about 150 sec to include some cooling region.

Typical profiles, glow curves & printouts obtained on the system have been enclosed for ready on formation & reference for user convenience.

j. The best way to require for background is after the TL glow curve acquisition, once again acquire for back ground and save this file as bdg.gtl (by default). This way if it is done it will indicate whether TL has been fully extracted and what extent of residual TL is remaining in the background.

For better accuracy, at least three measurements are to be taken and averaged.

The TL reproducibility of phosphor is found to be ± 2 %

Thermoluminescence (TL) Emission spectra recorder:

The TL- emission spectra have been recorded through rapid heating of the specimen to 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 HM104 monochromator (Central Electronics Ltd. India) ,

where it converges on a short focus grating (1200lines/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 3.8.

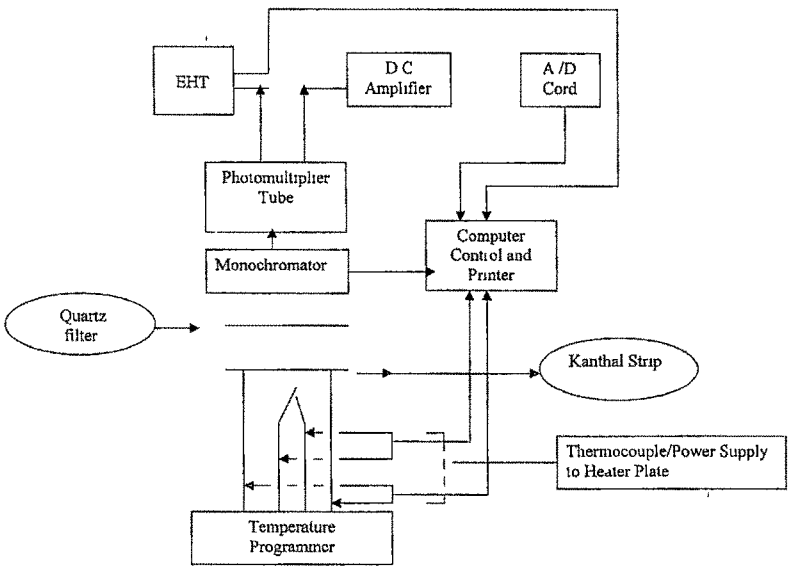


Fig.3.8 TL Emission Equipment Set-up

X-ray diffractometer:

This is an easy technique for the characterization 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 are automatically generated from the computer programme. An important feature of 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 centered on the powder specimen. The essential feature of diffractometer is shown in fig.3.9. 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 θ. 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.

The receiving slits and counter are supported on the carriage E, which may be rotated about the axis θ and whose angular position 2 θ 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 characterization of samples in this study. The supports E and H are mechanically coupled so that a rotation counter through 2 θ degrees is automatically accompanied by rotation of the specimen through θ degrees. This coupling ensures that the angles of incident on, and reflection from, the flat specimen will always be equal to one another and will be equal to half angle of diffraction, an arrangement necessary to preserve focusing conditions.

For recording the diffractogram of a powdered specimen, the counter is set near 2 $\theta = 10^{\circ}$ run up to 100° and collected to a counting rate meter. The output is connected to a PC the d values are calculated automatically. The counter is then driven at a constant angular velocity through increasing values of 2 θ 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 2 θ. This gives a record of counts per second versus diffraction angle 2 θ.

For taking the XRD patterns of samples in the work, a X- ray diffractometer of 'PHILIPS' make was used. The following are the parameters of the set up used in the present study.

Used wavelength: K Alpha 1 : 1.5405600 (AU)

Peak position defined by : Top of smoothed peak.

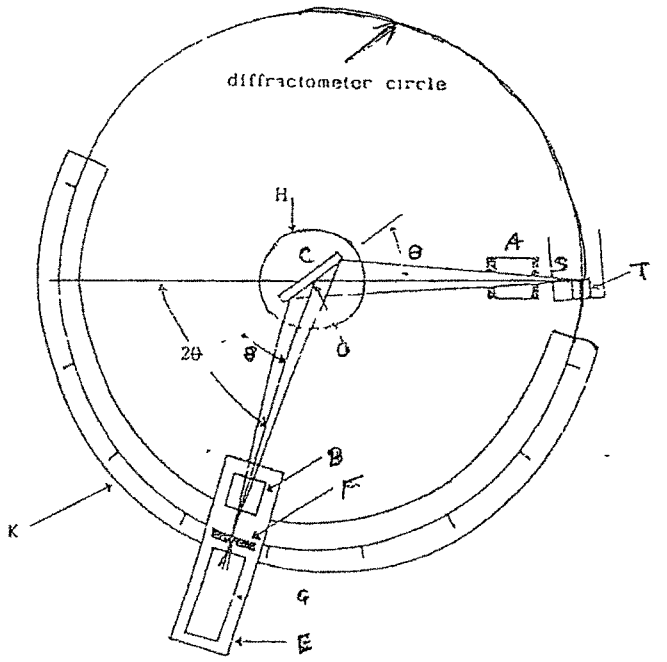
Minimum peak tip width (2 θ) :0.00

Minimum peak tip width (2 θ) : 0.50

Peak base width (2 θ) : 1.00

Minimum significance . 0.60

Fig.3.9 X-ray diffractometer line diagram.



Furnace for Heating the Specimens:

A muffle furnace of muffle sizes 50X50X50 cm is used for preparing the phosphors The sample of synthesized phosphor were heated up to 1200°C for four hours in a furnace made by 'Alfa Furnces, Baroda. The furnace has a very precise temperature controller of 'ADI' make, with a resolution of $\pm 1^{\circ}C$ at 1200°C. However in the present investigation heating required is 1200°C. The detailed process of synthesized phosphor has been discussed in chapter –II.

Radioactive Sources for Irradiation:

The Thermoluminescence of sample was studied after irradiation using a γ-rays as well as β-rays. For γ-irradiation, a Co^{60} gamma ray source is used having a 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. In the present investigation 7Gy γ-irradiation (7000 rads) test dose is given to all 27 synthesized samples of Barium Magnesium Aluminates doped with Eu, Ce, Mn, Nd and Pr phosphor For β- irradiation Sr-90 source is used and a test doses of 7Gy is given to study the dose effect on the phosphor.

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