CHAPTER-3

MATERIALS & EXPERIMENTAL ARRANGEMENT

3.1 MATERIALS

The selected medicinal plant leaves A(*Clerodendron colebrookinum*) ,B (*Azadirachta indica*),C.(*Ocimum sanctum*),D(*Vinca rosea*) and two medicinal plant fruits E(*Chisocheton paniculatus*), F(*Cudrania javanensis*) in my present investigation are collected from different localities of the North-Eastern of India mainly in Assam, India. The collected leaves and fruits are first shed dried and grind. The powdered samples are processed for XRD, XRF, TG, DTG and DSC investigations at different thermal condition.

3.2. X-RAY DIFFRACTION (XRD) ANALYSIS

3.2.1. DIFFRACTOMETER

The study of X-ray diffraction of the medicinal plant leaves and fruits powdered sample (unheated, and heated) are carried out in the PW 1710(Automatic powder diffractometer)[1-3]under 40KVvoltage and 20 mA current with Cuk_{α} W.L. 1.544A. A schematic diagram of the instrument is shown in figure 3.1.

3.2.1.1. SAMPLES MOUNTING

The sample holder is of size $3{\cdot}75\times3{\cdot}75\times0{\cdot}10cm^3$ with a rectangular groove $2{\cdot}0\times1{\cdot}5\times0{\cdot}1cm^3$.size.One side of the groove is covered with sealotape. After filling the groove with the leaves powder as well as fruits powder, the other side of the groove is

also covered with the powder leave or fruit samples, the other side of the groove is also covered with sealotape and kept pressed for 24 hours. Then the sample holder is placed at the centre of the goniometer of the APD unit.

3.2.1.2. MEASUREMENT

For taking the reading the automatic powder diffractometer is checked with standard Si samples before inserting the samples inside the gonimeter. Then the PW is set to scan the samples from 5° to 30° using Cu-K_α X-radiation with wavelength 1·5405A. The tube voltage and current being set at 40 KV and 20 mA.The value of 2θ corresponding to the different peaks are measured from the diffractogram records, plotted by the one line recorder.

3.3. X-RAY FLUORESCENCE (XRF) ANALYSIS

XRF studies of the medicinal plant leave and fruit samples are done with the help of Philips PW 1480 X-ray fluorescence spectrometer (XRF). Spectrometer has dual anode. For identification of the elements present in the sample powder Lif 200(2d=0·4077 nm)

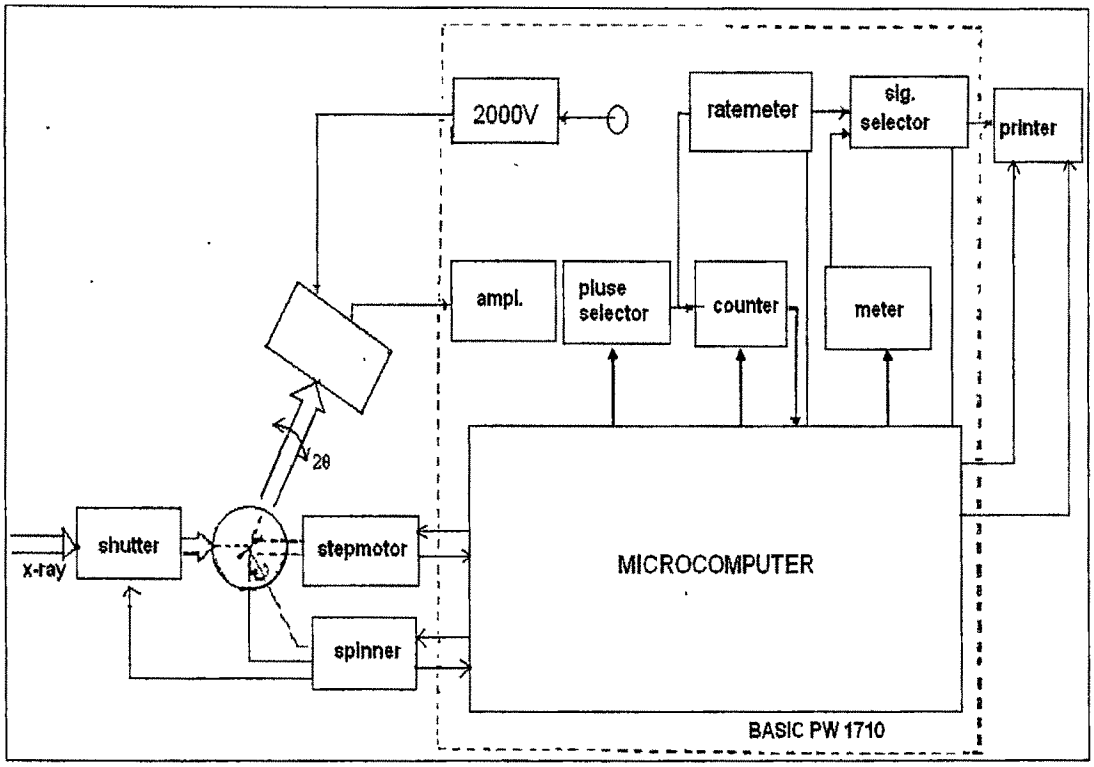

Figure 3.1: Schematic diagram of working principle of the XRD with counter assembly

was used as analyzing crystal. One gram of powdered sample are sieved through 0·5 mm mesh are mixed thoroughly with 0·5 gm of boric acid I.P.The boric acid serves as binder. An alluminium cup with top diameter 3·9 cm and bottom diameter 3·2 cm. is taken. The cup is filled with boric acid I.P.The mixture is placed in the cup on the bed of boric acid I.P.Then the cup is mounted in ahydraulic press.A pressure of (225×2·5)KN is applied for 2 minutes. Under the pressure the sample gets solidified as pellet.

The pellet is mounted in the sample holder of x-ray fluorescence spectrometer. The X-ray path is kept at vacuum. The tube voltage and current being set at 60 KV and 40 mA.The spectrometer is allowed to scan continuously within the scanning range 5° to 147° with scan speed 0·08 deg/S. A graph of relative intensity verses 2θ is generated in the computer interface with X-ray fluorescence spectrometer[4].The peak corresponding to the different elements present in the graph is identified with the help of computer software X-40.

3.4 DIFFERENTIAL THERMAL ANALYSIS (DTA)

It would be extremely valuable to supplement the study of the thermal behavior of the present investigation with the Differential Thermal Analysis data of medicinal plant leave and fruit samples. The small differences in the physical behavior in the sample may cause large differences in the peak area or the peak temperature of the endothermic transition in the DTA thermograms. Hence DTA technique may be used as sensitive calorimetric method for quantitative analysis.

3.4.1 EXPERIMENTAL ARRANGEMENT

The DTA apparatus consisted of a furnace, a sample holder, three thermo couples, a ceramic block for holding the above accessories and temperature measuring and control arrangements. The schematic diagram is shown in Figure 3.2.Thermocouple A is inserted into the experimental sample and B into the reference sample α-alumina, the latter showing no thermal anomaly in the temperature range 673 K used. Any temperature difference between the inert material and the experimental sample arising from possible thermal abnormality of the latter produced a resultant net voltage which is recorded as a function of temperature in the speedomax recorder. The sample and the reference material are placed closed together in the ceramic block D, where temperature could be changed uniformly by means of temperature programmer-controller. The difference in temperature between the sample and the inert material is recorded on a chart in the Micromax. A third thermo-couple C measured the temperature of the block. .

To obtain reliable results, certain precautions had to be taken as follows:

a) The rate of heating had to be kept constant, which is done by the temperature controller in the apparatus.

b) The rate of heating has to be maintained at an optimum value as determined by trial runs.

c) The leaves & fruits sample has to be powdered, sieved and then packed tightly in the cavity of the sample holder.

3.4.2 PREPARATION OF SAMPLES

About 100mg of medicinal plant leaves and fruits powder are taken to pass through 100 mesh sieve and mixed with 200mg of calcinated alumina to make 300mg total weight. This proportion is found to be best for reproducibility of results.

3.4.3 TEMPERATURE MEASUREMENTS AND RECORDING

The hot junctions of the differential chromal-alumal thermocouple are placed centrally in the cavities and well embedded in the material packed inside them. The insulating refractory block, the sample holder and the thermocouples, are placed properly in the furnace. The heating rate is adjusted at 10K/min. Generally, as at this rate, the control is quite sensitive showing sharp peaks. The temperatures are noted from the Micromax chart and also from the reading of a calibrated pyrometer (made by Cambridge Instruments Co. Ltd) with an uncertainty of ±1K

The records of DTA thermograms are made from room temperature to 700K for the leave samples and from room temperature to 730K for fruit samples. Records of each sample are repeated from room temperature to 373K thrice to check the reproducibility of results.

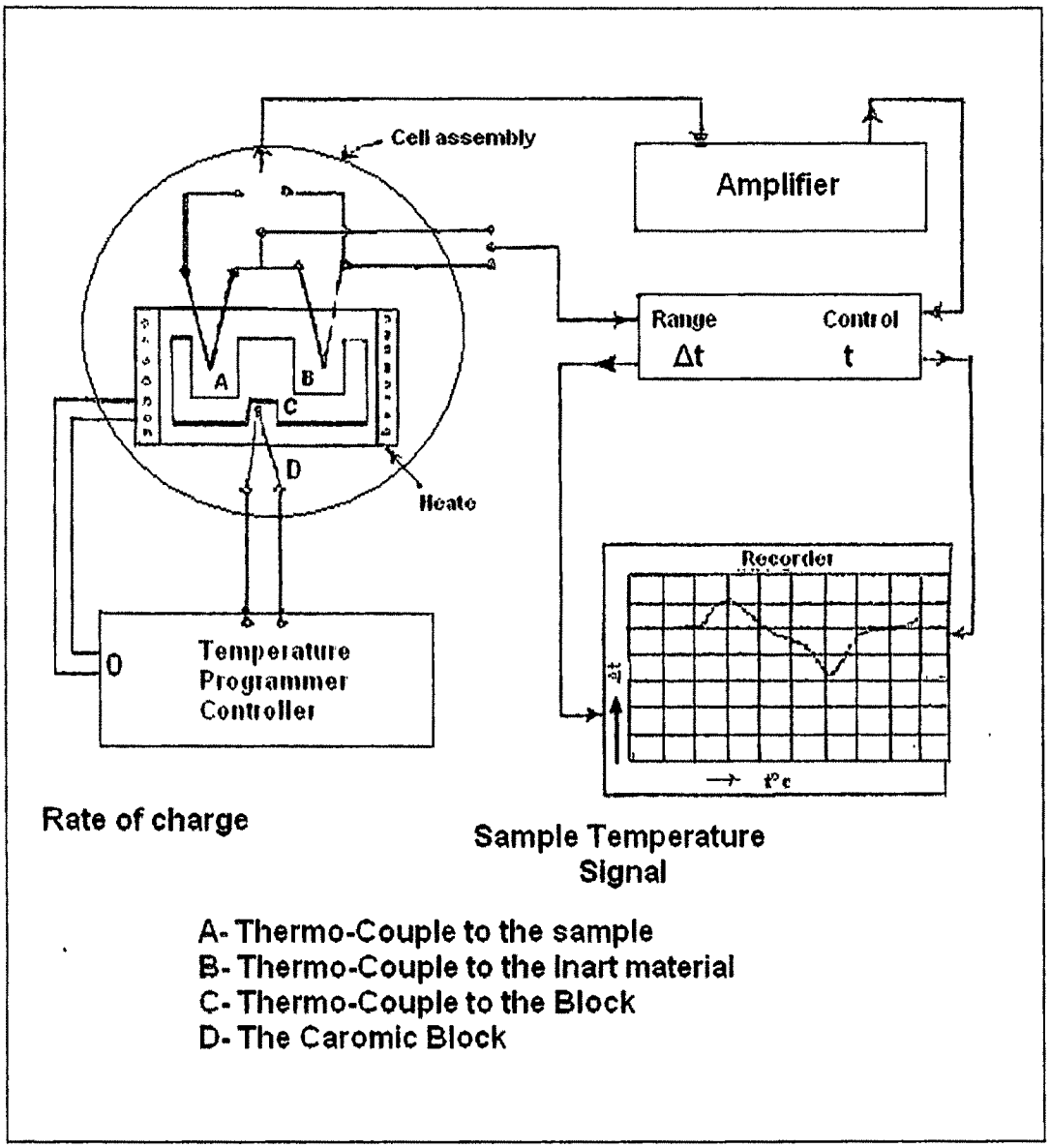

Figure 3.2: Schematic Diagram of Differential Thermal Analyser System.

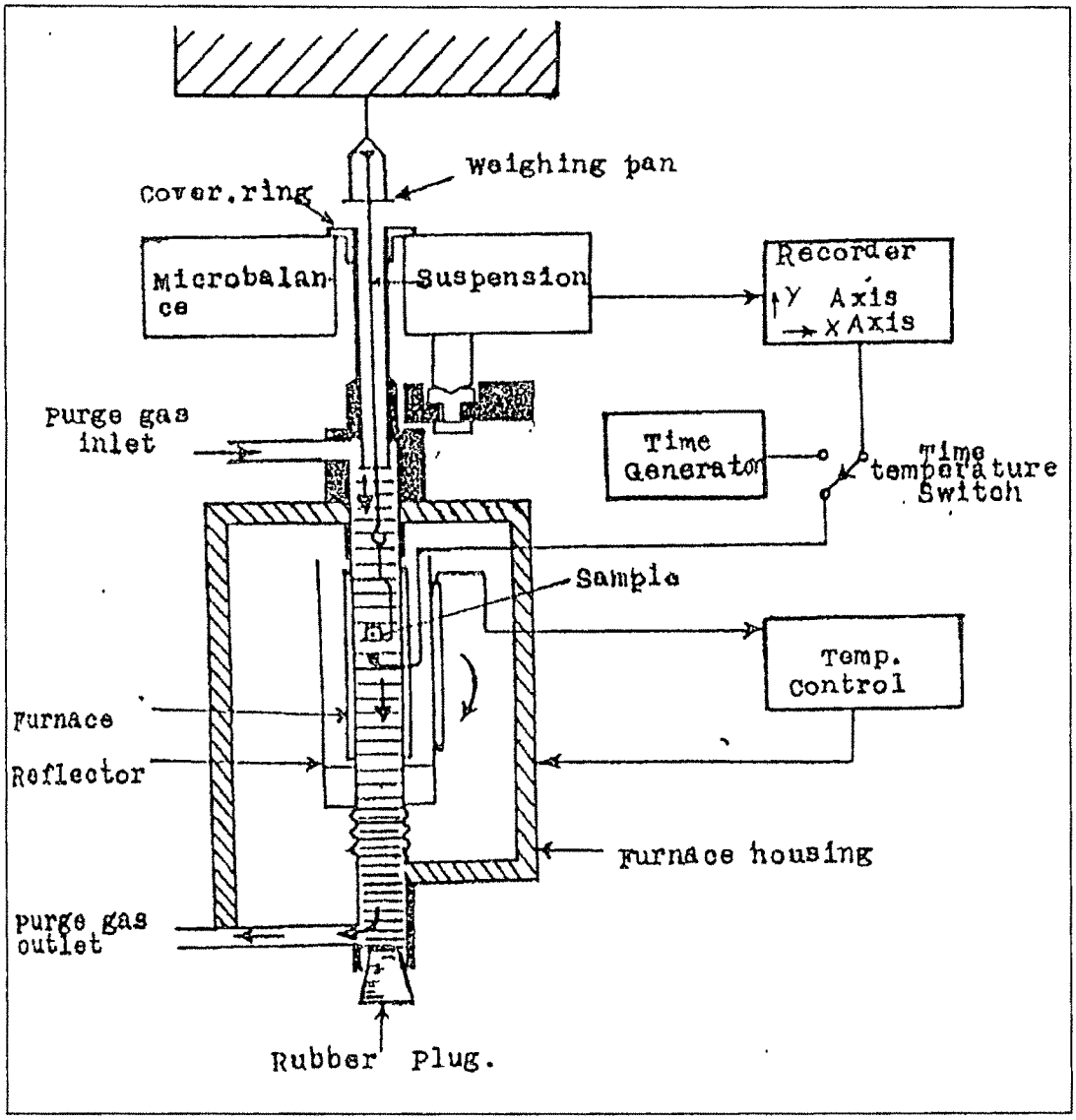

Figure 3.3: Schematic diagram of Thermogravimetric Analyzer

3.5. THERMOGRAVIMETRY (TG) AND DERIVATIVE THERMOGRAVIMETRY (DTG)

3.5.1 EXPERIMENTAL ARRANGEMENT

The TG instrument consist mainly three basic units: such as (i) the microbalance (ii) the temperature control unit and (iii) the recording unit. The arrangement of these components is shown in figure 3.3.

The measuring unit consists of a holder, which fixes the position of the sample in the furnace, a system for controlling the atmosphere around the sample, a thermocouple for sensing the sample temperature, and a property sensor itself. The temperature control unit consists of a furnace and a programmer. The recording unit records the signals from the property sensor and the sample thermocouple, amplifies them and then displays them as the thermal analysis curves.

The DTG, the basic experimental system of thermogravimetry is modified further by technique incorporating a generator to compute the derivative of an input signal. Here, the rate of weight loss of the sample is recorded as a function of the sample temperature. TG and DTG investigations with the techniques described elsewhere[5] (Baruah et.al. 1991) Heat treatment (annealing and quenching) of the samples at different temperature ranges 423-458k were undertaken with the process described elsewhere[6] (Bora et.al. 1997).

Both the thermogravimetry (TG) and Derivative Thermogravimetry (DTG) are carried out with a Perkin-Elmer Thermal Analyzer, operating at a moderate heating rate of 15K $min^{-1}$and 10K min^{-1} in air, oxygen and nitrogen atmospheres with a heat flow rate TG and 30cm min^{-1} in the temperature range 302-730 K.

3.5.2 MEASUREMENTS

5mg of the plant leaves and fruits powder sample are taken on the porcelain crucible specially designed for this purpose. After inserting the sample holder with the crucible into the centre of the furnace carefully, the temperature control unit and other related recording switches are made on so as to heat the sample at the heating rate 15K min^{-1} to 10K min^{-1}. The air is allowed to pass through at constant rate around the operating space of the sample holder inside the furnace.

The TG recorder is allowed to scan the sample continuously from room temperature 305 K up to temperature specified 730K for leaves sample and for fruits sample 310K to 745K. Similar records of TG are made for nitrogen and oxygen atmospheres introducing these gases in steps around the operating space of the sample pan inside the furnace at the same rate controlled for the air atmosphere.

Simultaneously, the DTG recorder is also allowed to scan the sample in the same temperature range and under the same atmospheric conditions at the same heating rate.

The records of temperature (along x-axis) and weight loss (along y-axis) of both TG and DTG thermograms are measured accurately by calibrating them in terms of centimeter with the help of a Norelco traveling microscope having uncertainty of $\pm$ 0.001 cm. Reproducibility of measurements of temperature and weight loss are quite satisfactory on an average of three readings. Both TG and DTG records are initially checked for standard polymer, studied by Deb et.al[7]. Similar TG and DTG records are made for the sample in nitrogen and oxygen atmospheres. TG and DTG thermogram records of each sample in nitrogen and oxygen atmospheres.

TG and DTG thermogram records of each sample are repeated thrice from room temperature to 373 K to check the reproducibility results.

3.5.3 SOURCE OF ERRORS AND THEIR ELIMINATION

Newkirk[8], Lukaszewski[9] and other workers has reviewed the major sources of error in the thermogravimetry and recommended some appropriate methods to eliminate and minimise them. However, in the present investigation, many of the sources of error are checked to minimize with the following precautions:

The optimum size crucible made porcelain is designed. As a result, the errors arised due to air buoyancy of the sample container and the reaction of the sample with container are reduced. The closed furnace housing and controlled furnace-heating rate minimise the furnace convection current and turbulence. The thermo balance is precisely designed, which reduced the errors caused by random fluxuations of recording mechanism, the furnace induction effects etc. The copper-constantan thermo couple is placed vary near to the sample pan to get temperature of the sample. It is calibrated with the standard calibration data for copper constantan thermocouple by the method described elsewhere.

3.6 DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSIS

Differential scanning calorimetry is the most recent reliable technique which may be used as very sensitive calorimetric method for thermal analysis of medicinal plant leave and fruit samples. In this technique, the sample and the reference are both maintained at the temperature predetermined by the programme even during a thermal reaction in the sample. The amount of energy which has to be supplied to or withdrawn from the sample to maintain zero temperature differentials between the sample and the reference material is the experimental parameter displayed as the ordinate of the thermal analysis curve.

3.6.1 EXPERIMENTAL ARRANGEMENT

In DSC instrument, the sample and reference containers are placed on individual bases thermally isolated from each other, each base containing a separately controllable heater and a thermocouple of pt/pt-13% Rh. Both the programmed heating and the balancing heating are performed through the heaters in the sample and the reference bases. These heaters are powered with alternating current and on one half –cycle the power supplied to both heaters is controlled by the temperature programmer. On the other half cycle, however, a different power is supplied to each heater to nullify any temperature differential between the sample and the reference as sensed with the pt/pt-13% Rb thermocouples in the pan bases. Thus, the heating system has two control loops, one responding to the temperature programme and the other responding to the different energy requirements of the sample and reference. The DSC analysis has been carried out using standard cell of Melter DSC 20 instruments with a TA processor of a Mettler TC 10. Air is used as a furnace atmosphere. A schematic diagram of DSC is shown in figure 3.4.

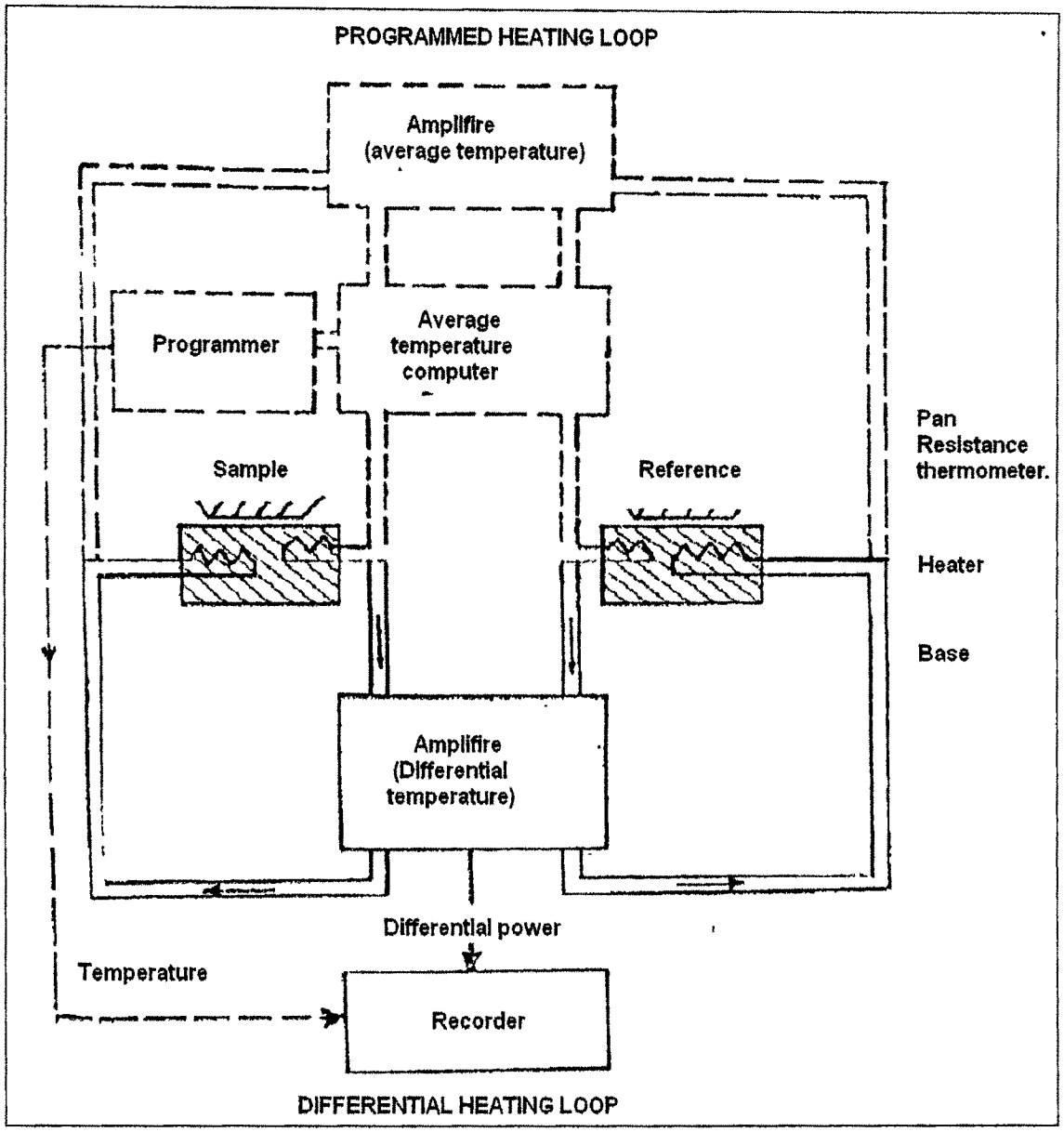

Figure 3.4: Schematic diagram of Differential Scanning Calorimeter Systems.

3.6.2 CALIBRATION OF DSC APPARATUS

The apparatus is calibrated prior to the measurements by using reference material of Al_2O_3. Two pieces of Al_2O_3 samples are placed on the sample side and the reference side, and the calibration constant (the ratio of the thermal resistance of the reference side and the sample side) is determined. This is roughly found to be equal to unity in the temperature, range from (295K to 675K) used in the present investigation.

3.6.3 MEASUREMENT AND RECORDING:

Samples of different medicinal plants leaves and fruits powder (about 2.9mg) are sieved and then are kept in the aluminum sample pan of the DSC cell under air atmosphere purged at a rate of 30 Cm^3/min.

The DSC thermograms are recorded with out most precautions. The maximum scanning rate of 5K/min and 10K/min are maintained to get high temperature accuracy.

At the beginning, the calibration of the DSC sensor is checked using heat of fusion of known quantity of Indium. The experimental uncertainty of this apparatus is found to be within ±1-2%

The thermograms of scanning of heat flow as a function of temperature are recorded in DSC with optimized the base line.

The main limitation of this DSC measurement is ascribed to the fact that radiation heat- loss increases with temperature, and as a result, thermal stability and reproducibility of the isothermal base line signals become poor. This difficulty is overcome by stabilizing the temperature control and establishing the isothermal base line. To check the reproducibility of the results, the DSC thermograms of each sample are recorded thrice from room temperature to 373K.

REFERENCES: 3

1. Sarma I.C, Mukhopadhyay A and Sinha P K, *Indian J Fibre and Textile Research*, vol.24, p.193. sept.1999

2. An Introduction to polymer physics, II Perepechko, Mir publishers, Moscow, p.83.

3. Sterovskii A P and Tarasova L V, Vysocomom Soedi Ser A.20 (5), 1978, p.1116.

4.Bora M N,Baruah G C and Talukdar C, *Thermochimica acta* 218,435,1993.

5. Baruah G.C., Bora M.N., and Talukdar C.1991, *Ind.J.Phys*.56B (6), 641-649.

6. Bora M.N., Saikia D., Saikia R.and Talukdar C.1997 *High Temp High press* 29,683-688.

7. Deb, N.; Gogoi, P.K.and Dass, N.N; *Thermochimica Acta*, 145, 77(1989)

8. Newkirk, A.E; *Anal.Chem.* 32, 1558(1960)

9. Lukaszewski, G.M.; *Nature*, 194,959(1962)

******