CHAPTER-2

GENERAL THEORETICAL CONSIDERATION

2.1. X-RAY DIFFRACTION ANALYSIS (XRD)

X-ray diffraction is a basic method for detecting the presence and determining the amount of crystallinity and orientation in a material having crystalline entity[1-2]. It has become an extremely important factor in defining special relationship in polymeric systems. In the field of medicinal plant materials X-ray analysis finds an ever-increasing use for examining their structural behaviors. This method is used for obtaining information about the different parts of medicinal plants structure at the molecular and super molecular levels and helps to evaluate the degree of crystallinity or orientation of crystallites and the size of the plant materials. Because the X-rays are electromagnetic in nature, they must be scattered by the atoms in a crystal. The scattered rays interfere with each other giving strong diffractions in some special directions, if the distance between the crystal planes is comparable to the wave-length of the x-rays used. Crystals consist of a regularly arranged three dimensional lattice order. The rays issuing from different crystal planes interact systematically with one another, leading to discrete reflections. The direction of reflection is related to the shape and size of the unit cell of the lattice and the intensity of reflection depends on the atomic arrangements in the lattice. The position and orientation of a crystal plane is determined by giving the co-ordinates of three non- collinear atoms lying in the plane. If each of the atoms lies on a crystal axis, the plane may be specified by giving the positions of the atoms along the axes in terms of the lattice constants. It turns out to be more useful to specify the orientation of a plane through the crystal by miller Indices hkl

According to Bragg the condition reflection from crystal planes is giving by the relation

$2d_{hkl} Sin\theta = n\lambda$ ------ (1)

d = distance between two parallel crystal planes (interplanner distance)

θ = Angle between incident ray and lattice plane (Bragg angle)

n = order of reflection (=1, 2....)

and λ = wave- length of the incident x-ray beam.

In case of medicinal plant leaves sample, the reflection with the strongest intensity is usually found for n =1 i.e. that is for the first order.

Reflection from crystal planes occurs only when the Bragg's condition is satisfied.

One of the basic techniques used in x-ray diffraction analysis is counter diffractometry. In this technique the pattern of dispersed x-ray diffracted from planes of different spacing of the specimen are scanned by a radiation detector which is moved either continuously or in steps across the pattern. Several detecting devices are available and each in tern can be used with a mide variety of auxiliary electronic circuits. The most commonly used detector is Geiger- Muller counter, the use of which is first described by Geiger and Mullar. The scanning mechanism and the specimen holders are not greatly affected by the type of detector used and the same basic instrument is suitable for a variety of applications.

The diffractometer directly measures the intensity of x-ray diffracted at any particular angle 2θ. The dependence of the diffracted rays on the angle 2θ is continuously recorded in the graphical form with the help of a strip chart recorder.

By measuring the spacing between the corresponding symmetric maximum on the diffraction pattern (difractogram) 2θ values can be determined and hence the interplanner spacing can be evaluated.

2.2. X-RAY FLOURESCENCE (XRF) ANALYSIS

With the help of, x-ray fluorescence technique[3] the element present in a sample can be identify. The analytical method of x-ray fluorescence technique commonly called 'x-ray fluorescence spectroscopy'. It involves the use of Bragg's law given by equation $n\lambda = 2dSin\theta$, excitation of characteristic x-ray lines of element present in a sample, measurement of wavelengths of the characteristic x-ray lines and measurement of intensity of the lines to determine the concentration of the elements present in the samples.

In x-ray fluorescence the source of excitation is a beam of primary x-ray and the specimen need not to be crystalline, it can be liquid, solid or powder. The principal advantages of the x-ray fluorescence method are its speed and non destructive nature. The x-ray fluorescence spectra may be used to analyze composition down to ppm level.

Energy dispersive and wavelength dispersive are the two main types of spectral analyzer used. In x-ray fluorescence analysis. The energy dispersive system consists of the x-ray source, the sample and semi conductor detectors. The fluorescent rays from the sample reaching the detector produced electrical pulse proportional to the energy of the x-rays. The energy level intensities, the element and the number of pulses at a particular energy level give the concentration.

In the wavelength dispersive system, a crystal either flat or curved used as the diffraction grating disperses the fluorescent x-rays at various angles on the basis of the wavelength and the detector set at various angles while moving with the grating identifies the element.

2.2.1. QUALITATIVE ANALYSIS

The method involves measurement of the intensities for qualitative analysis. The information obtained from fluorescent method is in terms of chemical elements. X-ray emission spectroscopy analysis involves use of Bragg's law, where experimental parameter is the angle θ. A crystal monochromator of known spacing 'd' is used to measure the wavelengths of the line emitted.

2.2.2 QUANTITATIVE ANALYSIS

X-ray fluorescence spectrometry is an instrumental method of quantitative analysis for chemical elements based on measurement of the wavelength and intensities of their x-ray spectral lines emitted by secondary excitation. The primary beam from an x-ray tube irradiates the specimen exciting each element to emit secondary spectral lines having wavelength characteristic of that element and intensities related to its concentration.

The net intensity of emitted characteristic x-radiation from an element in a matrix is related to the concentration of the element. figure 2.1 illustrate the theoretical correlation between the peak intensity R_p of an element with its concentration C. the true background R_b is given by intercept of the curve on the ordinate. The slop m of the curve called calibration factor is equal to,

$$\frac{R_p - R_b}{C} \tag{2.34}$$

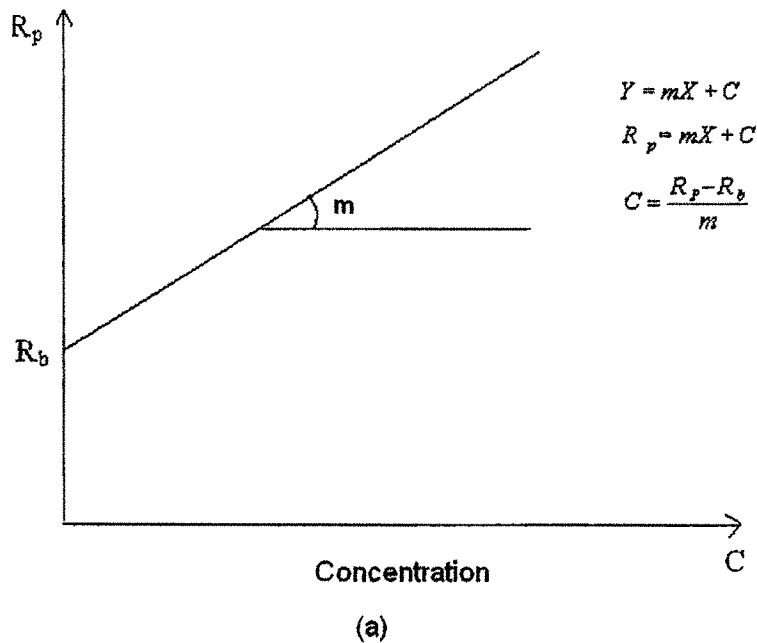and the concentration is given by

$$C = \frac{R_p - R_b}{m} \tag{2.35}$$

Figure 2.1 Basic of quantitative x-ray spectrometry

By use of standard samples, the value of m, for a certain element in a particular type of matrix can be determined by substituting measured values of R_p and R_b equation (2.35)

For quantitative estimation of elements, standard samples are taken. In standard samples, the concentration of major as well as trace elements is known x-ray fluorescence spectrometer is coupled with a scintillation counter detector. When a standard sample is mounted in the x-ray fluorescence, it will give counts with respect to the concentration of the elements present in the standard sample. A graph can be drawn between concentrations of the elements versus count for a number of similar standard samples. In case of an unknown sample, when is mounted in the x-ray fluorescence, counts with respect to the different elements present in the sample will be obtained. By

comparing it with the graph of standard sample, the concentration of different elements can be obtained.

2.3. DIFFERENTIAL THERMAL ANALYSIS (DTA)

A body suffers transformation both physically and chemically under the action of heat. These transformations can be studied by measuring some physical property of the body recorded as a function of temperature. The technique for relating the property of temperature data to possible thermal events in the sample material is called thermal analysis technique. In general differential thermal technique is used where the difference between some property (Temperature) of the sample and that of a stand and material is observed. Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are two main differential thermal analysis techniques[4-5].

In DTA, both the test sample and an inert reference material (usually α-alumina) under a controlled heating or cooling programmed which is usually linear with respect to time. The sample and the reference material are separately heated in identical environments. The reference material undergoes no thermal event in the temperature range under study, and therefore its temperature is the same as the programmed temperature through out the heating. The difference of temperature between the sample and the reference material is zero when the former does not undergo any chemical or physical change. However, if reaction takes place then a temperature difference ΔT will occur between the sample and reference material.

2.3.1 MATHEMATICAL EXPRESSIONS

With change of temperature of the ceramic block of a DTA apparatus temperature of the reference material and the sample also change, and in absence of a thermal anomaly in the sample,

$$\Delta T = T_1 - T_2 = 0 \tag{16}$$

Where T_1 and T_2 are temperature of the sample and the reference material respectively, when an anomaly occurs ΔT would vary and its variation with time or temperature is called the thermogram.

The magnitude $T_2 - T_3$, where T_3 is the temperature of the block, is proportional to the rate of heating H_2; the mass m of the reference material, its heat capacity C and inversely to the thermal conductivity K

i.e.

$$T_2 = T_3 - H_2 \ (mc/k)_2$$

Similarly for the sample

$$T_1 = T_3 - H_1 \ (mc/k)_1$$

Thus $\Delta T = T_1 - T_2 = H_2 \ (mc/k) - H_1 (mc/k)_1$

$$= H \ \{(mc/k)_2 - (mc/k)_1\} \tag{17}$$

Since $H_2 = H_1$

The variation of mc/k with temperate is same for both, then $\Delta T = 0$ at all temperatures and the thermogram is a horizontal straight line. If any one of these quantities varies with temperature, the thermogram will have either endothermic or exothermic peaks depending upon the nature of reaction.

Thus in an endothermic change, e.g. when the sample melts or is dehydrated, the sample temperature is lower than that of the reference material. This condition is only

transitory because on completion of the reaction the sample will again show zero temperature difference compared with the reference.

In DTA, temperature difference ΔT is plotted against furnace temperature. In idealized DTA curve both the shape and size of the peaks can give a large amount of informations about the nature of the sample. Generally phase transitions, dehydration and reduction produce endothermic effects where as crystallization, oxidation and some decomposition reactions produce exothermic effects.

2.3.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The same phenomena may be studied by DSC as by DTA. Differential scanning calorimetry instruments[4-5] measure the energy change in the sample directly not as a temperature change and it is consequently more suitable than DTA instruments for quantitative measurement of heats of reaction and transition, specific heats etc.

The DSC system measures the differential energy required to keep both the sample and reference material at the same temperature through out the analysis when an endothermic transition occurs, the energy absorbed by the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference between the sample and reference. Because this energy input is precisely equivalent in magnitude to the energy absorbed in the transition, the direct calorimetric measurement or energy of the transition is obtained from this balancing energy. DSC measurements may be made isothermally or at very low heating rates without loss of sensitivity. A DSC curve is a plot of differential power (i.e. difference in rate energy supply) against temperature or time. The ordinate signal, the rate of energy absorption by the sample is proportional to the specific heat of the sample. Any transition accompanied by the change in specific

heat produces a discontinuity in the power signal and   endothermic or exothermic enthalpy changes gives peaks whose areas are proportional to the total enthalpy change.

2.3.2(a). THE DSC SIGNAL $\dot{H}$

The heat flow $\dot{H}$ to the sample ($\dot{H}$ in order to express that the heat flow is the change in sample enthalpy) is equal to the difference between the two heat flows $\dot{Q}s$ and $\dot{Q}r$

$$\dot{H} = \dot{Q}s - \dot{Q}r \tag{18}$$

Here $\dot{Q}s$ - heat flows for sample

$\dot{Q}r$ - Heat flows for reference

According to the thermal analogue of Ohm's law it is

$$\dot{Q} = (T_2 - T_1)/R_{th} \tag{19}$$

Where $(T_2 - T_1)$ is the temperature difference

R_{th} is the thermal resistance

When this is applied to the DSC cell, it flows that

$$\dot{H} = \dot{Q}s - \dot{Q}r = \{(Tc - Ts)/R_{th}\} - \{(Tc - Tr)/R_{th}\} \tag{20}$$

Where Tc = furnace temperature

Tr = reference temperature

Ts = sample temperature

For reasons of symmetry, the two Tc and the two R_{th} values are identical.

It follows that $\dot{H} = -(T_s - T_r)/R_{th}$ (21)

In order to avoid problems with signs, an effect is defined as exothermic or endothermic and the sign is omitted. As the temperature difference, $\Delta T = T_s - T_r$, is measured by the gold/Nickel thermopile it follows from the thermo-couple equation,

$\Delta U = \Delta T.S$

From (21) $\dot{H} = \Delta U / (R_{th}.S)$ (22)

Where S is the entropy.

As the two terms in the denominator are functions of the actual temperature, they can be combined as the calorimetric sensitivity $E = R_{th}. S$ which can be divided in to a temperature dependent (relative) term E_{rel} and a temperature independent term Ein, specific to the measuring cell being used $E = E_{rel} .E_{in}$. Thus it follows that the heat flow to the sample is

$\dot{H} = \Delta U / (E_{in}.E_{rel})$ (23)

The temperature dependence of E_{rel} is contained in the TA processor as a hard programmed polynomial $E_{rel} = A + BT + CT^2$

On the other hand E_{in} is determined by calibration using the known heat of fusion of indium.

In general change of enthalpy between two stages is

$\Delta H = \int \dot{H} \, dt$ (24)

The process in which the enthalpy of a body increases is called endothermal as heat is drawn from the surroundings.

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2.3.2(b). BASIC EQUATIONS OF REACTION KINETICS

The kinetic parameters are usually evaluated through expressions derived from the basic equation--

$$\dot{\alpha} = K(1-\alpha)^n \qquad (25)$$

Where $\dot{\alpha}$ = rate of reaction in S^{-1}

K- reaction rate constant in S^{-1}

α = degree of conversion

n = order of reaction

for n = 1,

$$\alpha = 1 - e^{-kt} \qquad (26)a$$

$$\therefore \dot{\alpha} = Ke^{-kt} \qquad (26)b$$

Where t = time of reaction

for n $\neq$ 1, $\alpha = 1 - \{kt(n-1)+1\}^{(1/1-n)} \qquad (27)a$

$$\dot{\alpha} = k\{kt(n-1)+1\}^{(n/1-n)} \qquad (27)b$$

Thus the course of reaction can be calculated with known rate constant and order of reaction for any given temperature

The temperature dependence of rate constant is given by Arrhenius equation,

$$k = k_o e^{(-EA/RT)} \qquad (28)$$

Where k_o = reaction rate constant at infinite temperature (frequency factor or pre-exponential factor in S^{-1})

e = basis of natural logarithm = 2.718

E_A = activation energy in J/mol

T = temperature in Kelvin

R = gas constant = 8.31 J/mol k.

In logarithmic from of the Arrhenius equation-

$$\ln k = \ln k_0 - (E_A/R).(1/T) \qquad (29)$$

The linear curve in k versus $1/T$ gives the slope $-E_A/R$ and ordinate intersection in k_0.

The temperature function of the reaction rate (from equation 25 and 28) is

$$\dot{\alpha} = k_0 e^{(-EA/RT)}.(1-\alpha)^n \qquad (30)$$

2.3.2(c). RELATION BETWEEN DSC SIGNAL AND REACTION KINETICS

Each reacting molecule $d\alpha$ produces a certain enthalpy change dH

$$d\alpha = dH .(1/\Delta H_{tot}) \qquad (31)$$

where ΔH_{tot} = measured enthalpy of reaction in mJ = total peak area

Differentiating equation (31) with respect to time yields

$$\dot{\alpha} = H (1/\Delta H_{tot}) \qquad (32)$$

Thus the rate of reaction is directly proportional to the DSC signal.

From the proportionality of the degree of conversion and the respective enthalpy change (equation 31) it follows.

$$\alpha = (\Delta H_{part}/ \Delta H_{tot}) \qquad (33)$$

and for the term 1-α of the kinetic equation,

$$1-\alpha = (\Delta H_r/ \Delta H_{tot}) \qquad (34)$$

Where ΔH_r is the remaining area of the DSC peak substituting of $\dot{\alpha}$ and $(1-\alpha)$ in equation (30) by equation (32) and (34) and conversion to the logarithmic form gives,

$$\ln (H / \Delta H_{tot}) = \ln k_0 + E_A (1/-RT) + n \ln(\Delta H_r/\Delta H_{tot}) \qquad (35)$$

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The three terms $\ln k_0$, E_A and n are unknown. Choosing three points out of the several points of the DSC curve, the three unknown could be determined.

From the multiple linear regression analysis the accuracy of the results is substantially increased because any number of curve points may be evaluated. The confidence limits are computed for 95% probability. They allow to judge the validity of the equation (25) and (28) for the investigated reaction. They should have a value below 10% of the corresponding kinetic data.

2.3.2(d) PRACTICAL USE OF THE KINETIC PARAMETERS

The computation of the adiabatic course of the reaction is based on numeric integration of the following equation,

$$dT/dt = \alpha \ (\Delta H_{spec}/Cp)$$

$$= K_0 e(-E_A/RT)(1-\alpha)^n(\Delta_{spec}/C_p) \qquad (36)$$

The total adiabatic temperature rise ΔT_{adi} is

$$\Delta T_{adi} = (\Delta H_{spec}/C_p) \qquad (37)$$

Where ΔH_{spec} = Specific reaction enthalpy in J/g

C_p = Mean specific heat during reaction. As an approximation, a C_p value measured before the on set of the reaction is sufficient.

2.3.3. THERMOGRAVIMETRY ANALYSIS (TGA)

Thermogravimetry analysis (TGA) is a technique where by a sample is continuously weighing as it is heated at a constant preferably linear rate. The resulting weight change against temperature curve is known as TG curve and gives information concerning the thermal stability and composition of the original sample.

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The weight of a sample remains constant or decreases on heating unless the sample combines with its immediate atmosphere. Such combinations do occur, e.g. in oxidizing atmospheres and a weight increase is then observed, but they are not often encountered. TG curve is therefore known as weight-loss curve. The change in sample weight may be recorded as the actual weight or weight-loss in grams, milligrams etc. or as the percentage or fractional weight-loss. Unless trapped gas is released or volatiles are desorbed, physical transitions are not accompanied by weight losses and therefore cannot be detected by TG. Thus TGA is a useful technique for differentiating between thermal events arising from physical changes and those arising from chemical changes in sample. The TG curve records a series of weight–loss steps as successive reactions producing volatile materials occur at various temperatures during the programmed heating. Isothermal weight loss measurements, giving weight /time curves, are also used, particularly for kinetic studies of dehydration for hygroscopic materials and decomposition reaction in general. TGA measurements can be made either in the presence or absence of gasses (in Vacuum), air, oxygen, nitrogen etc.

In addition to a thermogravimetric curve (TG), the results of TGA study may also be presented as a Derivative Thermogravimetric (DTG) curve. In DTG, the rate of weight loss of the sample is recorded as a function of the sample temperature. A DTG curve shows better resolution of two or more processes occurring at similar temperature than a TG curve. DTG curve consists of a series of peaks corresponding to the various stages in the decomposition, the peak maximum being equivalent to the point of inflection on the TG curve. Moreover DTG curves often bear a strong resemblance to DTA curves and permit comparison to be made.

The horizontal portions (plateaus) of the TG curve indicate the regions where there is no weight change and the curved portions are indicative of weight losses. If the

rate of change of weight with time, dw/dt is plotted against temperature, a DTG curve is obtained.

2.3.3(a) KINETIC STUDIES FROM TG CURVES

For kinetic measurements[4,6-7] it is essential that the weight loss accurately reflects the reaction rate and the sample temperature should be calibrated. Reactions accompanied by large heat changes often give unreliable values for kinetic parameters since the sample temperature is liable to go away considerably from the programmed temperature as the reactions occur.

The kinetic parameters are usually evaluated through expressions derived from the basic equation-

$$da/dt = K(1-a)^n \qquad (38)$$

Where a=the fraction of sample decomposed

k= a rate constant

n= the order of reaction

t= the time of reaction.

This may also be expressed in terms of the weight of remaining sample 'w'

$$dw/dt = -kw^n \qquad (39)$$

This equation is not applicable to all types of reaction and this is one of the major limitations of the method. An equation of this form should be applied separately to every step in the weight loss curve, and the fractional weight loss during each step referred to the total weight loss for that step. Such a procedure can be applied only to those curves giving a reasonable plateau between each stage.

The rate constant depends, as usual on temperature T, the activation energy E, the pre-exponential factor A and the gas constant R, which is derived as:

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$$K=Ae^{(-E/RT)} \tag{40}$$

These relationships can be manipulated to give equations relating the experimental quantities (weight, temperature, heating rate etc.) to the kinetic parameters and the parameters evaluated graphically. The procedure of Freeman and Carroll [98] eliminates the heating rate giving differential equation as :

$$(-E/2.3R)\ \Delta(T^{-1})/\ \Delta logW_r = -X + \{(\Delta log\ dW/dt)/(\Delta log\ W_r)\} \tag{41}$$

Where $W_r = W_e - W$

$W_r =$ the total weight loss for the particular reaction step.

$W_e =$ weight change at the completion of the reaction.

$W =$ weight of that reactive portion which remains at time t.

$R =$ gas constant in KJ/mol.

Calculation of the activation energy 'E' from the above equation consists of the following steps.

(i) Plot of weight (W) against time (t) and the slope of this curve gives dW/dt.

(ii) Plot of log (dW/dt) , against 'log W_r' at the points corresponding to curve (i) and the slope of this curve gives

$$(\Delta\ log\ dW/dt)/(\ \Delta logW_r)$$

(iii) Plot of T^{-1}, against 'log Wr' at the points corresponding to curve (i) and the slope of this curve gives $\Delta T^{-1}/\ \Delta\ log\ W_r$.

(iv) Finally plot of $(\Delta log\ dW/dt)/(\ \Delta log\ W_r)$ against $\Delta T^{-1}/\Delta logW_r$ and the slope of this straight line gives + or – E/2.3R, where from 'E' can be calculated.

The various slopes (i), (ii), (iii) and (iv) are calculated using the following computed Fortan Programme of second degree polynomial.

Program to calculate activation energy:

Integer n, m, flag

Common d (50.50), a (50, 50), sol (50)

Write (*, *) 'no of observations (n), order of polynomial (m). read (*, *) n, m

Write (*, *) 'Enter (% weight, time, temp)'

read (*, *) (d (i, 1), d (i, 2), d (i, 3), i =1,n)

do 10 i =1,n

d (i,4) = (d(i,1) –d(n,1))

if (d(i,4) .ne.0.0) then

d(i,5) = a log 10 (abs (d(i,7)))

end if

d(i,6) = 1.0/d(i,3)

10 continue

flag = dydx (n,m,1,2,7)

do 44 i = 1,n

if (d (i,7).ne.0.0) then

d (i, 8)= a log 10 (abs (d(i,4)))

end if

44 continue

flag = dydx (n-1,m,8,5,9)

flag = dydx (n-1,m,6,5,10)

flag = dydx (n-1, m,9,10,11)

do 55 i =1 , n-1

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        avr = avr +d(i,11)

55 continue

avr = avr/(n-1)

e= avr*2.3*8.3256

write (*.*)' E = ',e,'kj per mol'

write (*,222)

222 format (1x,//6x,'%wt',8x,'time',4x,'temp',8x,'wr', 8x,* 'log

10wr',3x,'1/T',6x,'dw/dt',5x,'log10dw/dt', 'slope 2', *4x,'slope3',4x,'slope 4'//)

do 66 i =1,n

        write (*,111)(d(i,j),j = 1,11)

111            format (4x,11f10.4)

66 continue

stop

end

integer function dydx (n, m, cy, cx, cr)

integer cy, cx, cr, i, flag, polyreg, gauss

common d (50,50), a (50,50),sol (50)

flag = polyreg (n, m, cx, cy )

flag = gauss (m)

do 88  i =1,n

d (i, cr)= sol (2) + 2*sol(3)*d(i, cx)

88 continue

dydx = 0

return

end
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```
integer function polyreg (n, m, cx, cy)

integer n,m,cx,cy,1

common d (50,50),a(50,50),sol(50)

 do 20  i = 1, m+1

 do 10  j =1, m+1

k = i + j -2

do 10  1 = 1,n

a(i, j) = a(i, j)+ d(1,cx )* * K

10        continue

right hand side vector linear system of equations

do 20 1 = 1,n

      a (i,m+2) = a( i ,m+2) + d (1,cy) * d(1,cx) ** (i-1)

20 continue

polyreg = 0

return

end

integer function gauss (m)

integer m,i,k,j

common d (50,50), a (50,50),sol (50)

n = m+1

do 10  k = 1,n-1

      do 20  i = k+1, n

      qt = a (i,k)/ a(k,k)

      do 30  j = k+1, n+1

      a(i,j) = a(i,j)-qt* a (k,j)
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```
30 continue

20 continue

        do 40 i = k+1 , n

        a (i,k) = 0.0

40 continue

10 continue

    back substitution

    sol (n) = a (n,n+1) /a(n,n)

    do 50 nn = 1,n-1

    sum = 0.0

    i = n-nn

    do 60 j = i + 1,n

    sum = sum + a (i, j)*sol (j)

60 continue

        sol (i) = (a(i, n+1)-sum)/a(i,i)

50 continue

gauss=0

return

end
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