DIFFERENTIAL THERMAL ANALYSIS INSTRUMENT DESIGN

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in

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By

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Approval of the Graduate School of Natural and Applied Science

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ABSTRACT

DIFFERENTIAL THERMAL ANALYSIS

INSTRUMENT DESIGN

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M.S. in Engineering of Physics
Supervisor: Assoc. Prof.Dr.Ata SELÇUK
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In this work, thermal analysis methods are introduced and differential thermal analysis (DTA) is briefly investigated, designed and constructed.

The instrument then checked with native sulphates which are $CaSO_4.2H_2O$, $MgSO_4.7H_2O$, $MgSO_4.H_2O$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $NiSO_4.7H_2O$ and $ZnSO_4.7H_2O$. Analysis have been carried out in the temperature range of (room temperature - 350 ^oC) and the exponential heating rate is used. The obtained DTA curves are compared with literature. As seen that, the resultant curves which are obtained as same as the available documents.

The minimum detectable sample is found as 20 mg.

Keywords: Thermal analysis, DTA,

ÖZET

DİFERANSİYEL TERMAL ANALİZ CİHAZININ TASARIMI

ÖZKAN R.Güler
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Tez Yöneticisi: Doç.Dr.Ata SELÇUK
Şubat 1991, 42 sahife

Bu çalışma, Diferansiyel Termal Analiz (DTA) cihazının tasarımı ve yapımı ile ilgilidir.

Yapılan bu cihazla doğal (native) sülfatlar [$CaSO_4.2H_2O$, $MgSO_4.7H_2O$, $MgSO_4.H_2O$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $NiSO_4.7H_2O$ ve $ZnSO_4.7H_2O$] oda sıcaklığından, 350 ^oC sıcaklık aralığında exponensiyel (üssel) ısıtma hızı ile analiz edildiklerinde, elde edilen DTA eğrileri literatürlerle karşılaştırıldıklarında aynı sonuçlar elde edildi.

Cihazın duyarlı olduğu en düşük madde miktarı 20 mg olarak bulundu.

Anahtar kelimeler: Termal analiz, DTA.

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CHAPTER 1

THERMAL ANALYSIS

1.1 THERMAL ANALYSIS

Thermal analysis may be considered to be an analytical technique in which some physico-chemical parameter is measured as a function of temperature, or as a function of time at constant temperature or heating rate. Thus measuring the change in heat capacity of a speciman at constant heating rate, the change in mass with respect to time at constant temperature, or the change in mass with respect to time at constant heating rate are all thermal analysis methods.

Every system has a tendency to attain a state in which the free energy is at a minimum at a given temperature. The formation of a more stable crystalline structure, or of another state with a lower free energy (minimum free energy) may take place on heating the sample, or via intermediary steps. For example, melting, boiling, sublimation, change of crystalline structure, chemical reaction, etc. may represent such a transformation. The transformation is characterized by the temperature at which it occurs and by a change in heat content, manifested by an increase or decrease in the temperature, depending on whether the reaction is exothermic or endothermic. This is the basis of differential thermal analysis (DTA).

The change in weight can also be influence the change in heat content, that is, during a chemical degradation,dehydration, sublimation or oxidation. The method is concerned with the change in weight named as thermogravimetry (TG).

When a substance is heated or cooled, some changing occurs in its dimensions. They are depending on initial dimensions of substance and on the temperature. The observation of the change in dimensions during

heating is the basis of dilatometry and has great importance in metallurgy, physics and in glass and ceramic technology [1]. Some thermal analysis methods are given in Table 1.

1.2 CLASSIFICATION OF THERMAL ANALYSIS METHODS

Thermal analysis covers a group of mutually related instrumental techniques for measuring the parameters of any physical property or chemical stability depending on temperature [2].

Thermal analysis methods can be classify into four groups:

a) Methods associated with a change in mass
b) Methods associted with change of energy
c) Methods associted with the evolution of volatile products
d) Methods associted with dimensional changes

Methods associated with a change in mass can be divided into two methods which are static and dynamic methods.

i) Static methods

Isobaric weight-change determination: A technique which the mass of the substance is recorded as a function of the temperature T, at a constant partial pressure of the volatile products. The record is the isobaric weight change curve, it is normal to plot weight as the ordinate with weight decreasing downwards and temperature T, on the abcissa increasing from left to right.

Isothermal weight-change determination: A technique in which the mass of the substance is recorded at the time t,at a constant temperature. The record is the isothermal weight change curve, it is normal to plot weight on the ordinate, with weight decreasing downwards and t on the abscissa increasing from left to right.

TABLE 1 Thermal Analysis Methods [1]

Technique	Quantity Determined	Apparatus
1.Thermogravimetry (TG)	Weight change	Thermobalance
2.Derivative thermogravimetry (DTG)	Rate of change of weight	Thermobalance or derivative thermobalance
3.Differential thermal analysis (DTA)	Temperature difference between the sample and thermally inert substance	DTA apparatus
4.Derivative DTA	Derivative of the temperature difference	DTA apparatus
5.Differential scanning calorimetry (DSC)	Amount of heat transmitted to the sample	Differential Calorimeter
6.Measurement of specific heat	Specific heat	Calorimeter
7.Evolved gas analysis	Amount of gas liberated	Gas analyser
8.Pyrolysis	Product of pyrolysis	Gas chromatograph, mass spectrometer, IR spectrometer,etc
9.Thermal luminescence analysis	Light emission	Photomultiplier thermoluminescence apparatus
10.Dilatometry	Change in volume	Dilatometer
11.Electric conductivity analysis	Change in electric resistance	Resistance bridge
12.High-temperature x-ray diffraction	Change in lattice dimensions	X-ray diffractometer
13.Thermometry	Temperature change as a function of time or volume of the titration reagent	Thermometric titrator

TABLE 1 Thermal Analysis Methods

Technique	Quantity Determined	Apparatus
14.Enthalpimetry	Enthalpy change as a function of amount of reagent added	Thermometric titrator
15.Classical calorimetry	Temperature as a function of time. Heat content as a function of temperature	Calorimeter

ii) Dynamic methods

Thermogravimetry (TG): A technique where the mass of a substance in given surroundings, heated or cooled under controlled conditions at a constant rate, is recorded as a function of time or of temperature $m = f(t \text{ or } T)$.

Derivative thermogravimetry (DTG): This techniques indicate the first derivative of TG curve with respect to either time or temperature $dm/dT = f(t \text{ or } T)$.

Methods associated with change of energy includes two type instrumental techniques which are differential thermal analysis (DTA) and differential enthalpic analysis (DEA).

Diffrential thermal analysis: DTA is a technique of recording the difference in temperature between substances and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an enviroment heated or cooled at a controlled rate. The record is DTA curve, the temperature difference (ΔT) should be plotted on the ordinate with endothermal processes downward and exothermal ones upward and time (t) or temperature (T) on

the absicsca increasing from left to right. Some applications of DTA is given in Table 2.

Differential enthalpic analysis: DEA is a techniques for recording the energy required to study difference of temperature between a substance and a material releated either to time or to temperature as the two substances are subject to identical amounts of temperature in surroundings heated or cooled at controlled rates.

Methods associated with the evolution of volatile products include instrumental techniques for determining the nature of the source of volatile products formed during the thermal process.

Methods associated with dimensional changes include dilatometry and differential dilatometry. These methods include instrumental techniques for measuring the changes in size of a substance depending on temperature.

TABLE 2 Some Application of DTA and TG [1]

Methods	Process investigated	Substances
TG, DTA	Dehydration-determination of free and bound water	Organic and inorganic compounds (precipitates, minerals,combustibles, coordination compound, etc.)
TG, DTA	Thermal decomposition	Organic and inorgonic substances (precipitates, catalysts,minerals, polymers etc.)
TG, DTA	Roasting and calcination	Minerals
TG, DTA	Distillation and evaporation	Inorganic and organic substances
TG, DTA	Thermal oxidation-corrision	Inorganic and organic substances (metals etc.)
TG, DTA	Solid phase reaction	Inorganic and organic substances
TG, DTA	Gas, solid reactions (oxidation,reduction, corriosion)	Inorganic and organic substances
TG, DTA	Study of new chemical	Inorganic and organic substances
TG, DTA	Catalysis	Inorganic and organic substances
TG, DTA	Study of reaction kinetics and reaction mechanism	Inorganic and organic substances
Calorimetry,DTA	Study of heats of reaction	Inorganic and organic substances
TG, DTA	Thermal stability and purity	Analytical reagents
DTA	Phase changes	Organic and inorganic compounds (glasses, liquid crystals,ceramics, minerals, etc.)

CHAPTER 2

DIFFERENTIAL THERMAL ANALYSIS

2.1 INTRODUCTION

Differential thermal analysis (DTA) is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material, is recorded as a function of the, inert material, or furnace temperature as the sample is heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase changes, fusion, boiling, sublimation, crystalline structure inversions and vaporization, dehydration reactions, dissociation or decomposition reactions, oxidation and reduction reactions, destruction of crystalline lattice structure, and other chemical reaction [3]. Endothermic effects are produced by phase transitions, dehydration, reduction and some decomposition whereas exothermic effects are produced by cyrstallization, oxidation,and some decomposition reactions. The technique although comparable with dynamic thermogravimetry is complementary to it.However it yields no information directly about the chemistry of any reactions [4].

A typical DTA curve is shown in Figure 2.1. Four types of transitions are illustrated as follow.,

a) Second-order transition in which a change in the horizantal base line is detected,
b) An endothermic curve peak, due to a fusion or melting transition,
c) An endothermic curve peak which is due to a decomposition or dissociation reaction,
d) An exothermic curve peak caused by a crystalline phase change.

The number, shape, and position of the various endothermic and

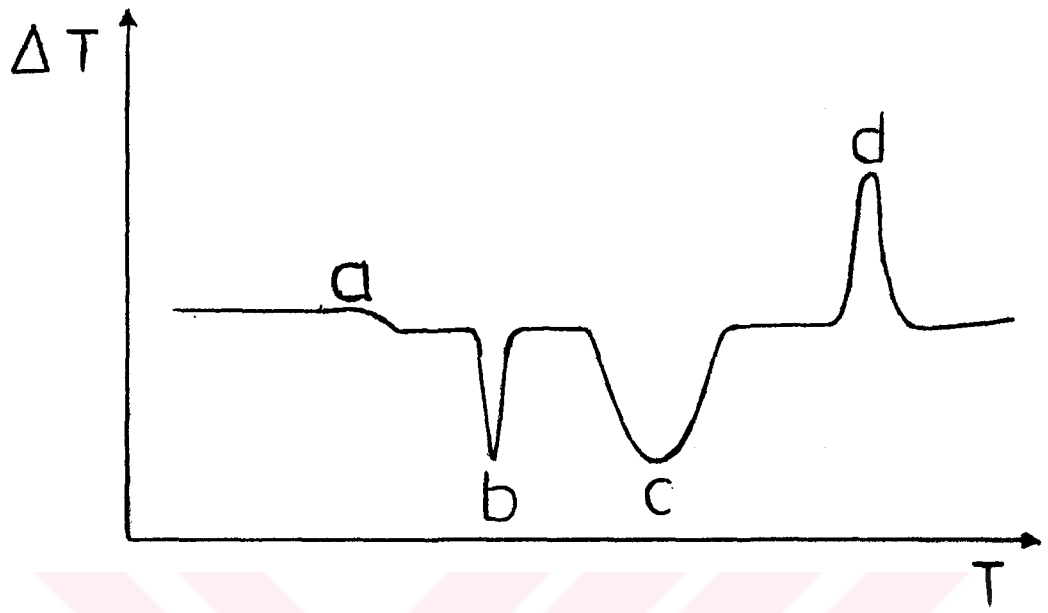

Figure 2.1 Typical DTA curve.

exothermic peaks may be used as a means of qualitalive analysis and because the area under the curve is proportional to the enthalpy change, the technique is useful as semiquantitalively if the heat of reaction is known [2] . The block diagram of DTA is given in Figure 2.2.

2.2 HISTORICAL ASPECTS

The differential thermal analysis methods may be begining with same period with thermogravimetric method. In 1887 Le Châteller used this method for the first time for the study of calcite and later for the study of clay materials. At its beginings, this method consisted of a direct determination of the rate of change in temperature of the sample during regular heating. The reactions followed in this way gave a series of plateaux on temperature versus time plots, and their determination was rather inaccurate [1] .

Le Châtelier and other investigators, Ashley, Wholin, Rieke, Wallach and Mellar and Holdcroft studied the thermal changes which took place in a substance as it was heated by recording its temperature as

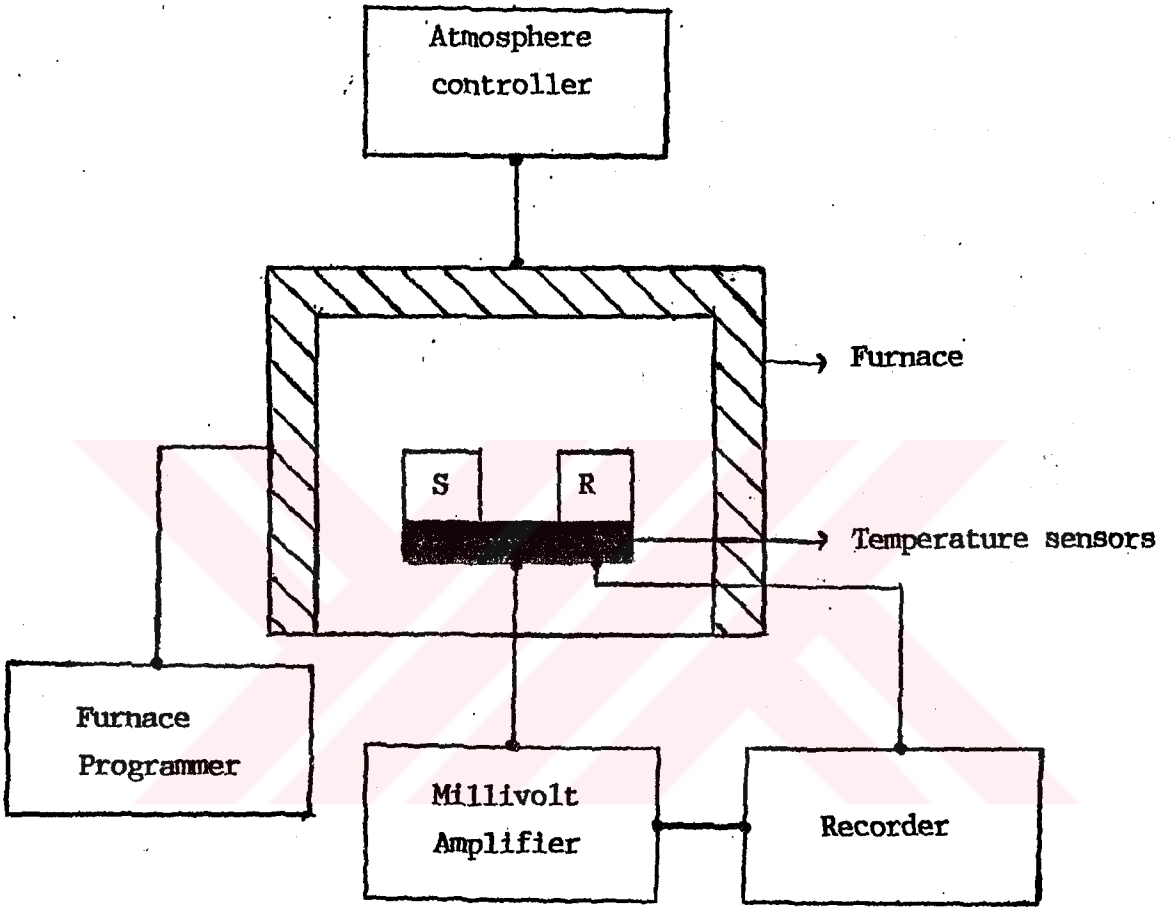

Figure 2.2 Block diagram of DTA [3]

S: Sample

R: Thermally inert reference material

measured with a thermocouple, as a function of time. This heating curve method was not very sensitive to small heat effects and was adversely affected by changes in heating rate, recording equipment, and other factors [3] .

In 1899, Robert-Austen who improved Le Châtelier's method. They suggested that a two-thermocouple system be employed. One of the thermocouples was placed in the sample and the other one in a reference block in a furnace [3,1,2]. The differential temperature reading which was more sensitive to small temperature changes in the sample than the single-thermocouple method, was recorded or plotted as a function of time or temperature [3]. Wallach (1913) and Fenner (1913) were the first to use DTA in investigation of argillaceous minerals and silicates. De Keyser (1938-1939), Norton (1939),Hendriks and Alexander's (1939) papers have resulted in rapid development and generalization of these methods for the study of minerals. Since 1940 the technique has been improved appreciably and the fields of use have been extended[2].

2.3 THE COMPONENTS OF DTA INSTRUMENT

A differential thermal analyzer includes seven basic components a) a furnace or heating device, b) a sample holder, c) a low-level dc amplifier, d) a differential temperature detector, e) a furnace temperature programmer, f) a recorder, and, g) control equipment for maintaining a suitable atmosphere in the furnace and sample holder.

2.3.1 SAMLE HOLDER

Sample holder is one of the most important parts of the DTA apparatus. The type of sample holder used depends on the nature and quantity of the sample and also on the maximum temperature to be investigated [5] .

The materials used in the construction of the sample holders are

of two kinds; metals or ceramics. Metal materials used in the construction of sample holders include nickel, high temperature stainless stell, aluminum, platinum or platinum alloys, silver, copper; tungsten, noble and half-noble (plain or alloyed) metals. Ceramic materials used in the construction of sample holder include alumina with silica admixtures, burnt clays, high temperature resistant glass and graphite.

Advantage of metallic sample holders can much more easily be processed, they are not porous and give only small deviations of the heat flux and hence of the basic line of DTA curve. Their disadvantage, however, is that the intensity of the thermal effects tends to be small because the heat transfer takes place rapidly through their walls and between these walls and the sample mass.

On the other hand, ceramic sample holders, yield thermal effects large intensities for the same amount of reacting material as in metallic one, because the heat transfer proceeds slowly through their walls [5] . The ceramic holders also have certain disadvantages, they have porous structures, they may affect the shape of the thermal effects or they may get contaminated in the case when the sample contains a compound which melts. Generally, in such sample holders the base line of the DTA curve is very difficult to obtain, because of the low and nonuniform heat transfer rate from the exterior towards the interior of the groove.

Two type sample holders are used. One of block-shaped holders, the other one is crucible-shaped holders. Block-shaped holder are provided with two or more than two orifices, one of them is used for the substance to be analysed, one of them is used for the thermally inert substance, and if there are third one is used for measuring the temperature of furnace. Block-shaped holder are most indicated for investigating the heat exchange that is, for differential thermal analysis. The crucible-shaped holders are made of metals. These holders use in complex thermal analysis, satisfying the requirements imposed

both upon heat exchange and mass exchange measurements. [1,3,2] . Figure 2.3

Wendlandt [7] compares the relative performance of the two types of sample holder, block and isolated container types and quotes the work of Sarasohn, and reproduces the table also reproduced as Table 3 below.

TABLE 3

Advantages	Disadvantages
Block type	
1. Good temperature uniformity	1. Poor exchange with atmosphere
2. Good thermal equilibration	2. Poor calorimetric precision
3. Good resolution	3. Difficult sample manipulation
4. Good for b.p. determination	4. Sensitive to sample density change
Isolated container type	
1. Good exchange with atmosphere	1. Poor resolution
2. Good calorimetric precision	
3. Good for high temperature use	

2.3.2 FURNACES AND FURNACE TEMPERATURE PROGRAMMERS

The choice of furnace heating element and type of furnace depends on the temperature range under investigation. The operating range of DTA furnaces have been described from -190 to 2800°C. The furnace may be located vertically or horizontaly, it may be heated by resistance element, by a coil of tubing through, which a heated or cooled liquid or gas is circulated [6] .

Resistance elements are used in construction of furnace. The temperature limits of these resistance elements depend upon the furnace desing and insulation. Some resistance element and their approximation temperature limits are given Table 4 [3] .

TABLE 4 Maximum Temperature Limits For Furnace Resistance Elements [3] .

Element	Approximate Temperature ^{o}C
Nichrome	1000
Kanthal	1350
Platinum	1400
Platinum -10 % Rhodium	1500
Rhodium	1800
Tantalum	1330
Globar	1500
Kanthal Super	1600
Molybdenum	2200
Platinum - 20 % Rhodium	1500
Chromel A	1100
Tungsten	2800

The requirements for a good DTA furnace must have a symmetry in heating and the ability of the heater elements to heat uniformly. The furnace temperature distribution must be uniform in the area of the sample holder for good results.

For the operation at low temperature, the furnace may be surrounded by a Dewar flask and precooled with liquid nitrogen. The furnace is then heated by the furnace element using a heating - mode program.

The rate of temperature increase of the furnace is controlled by

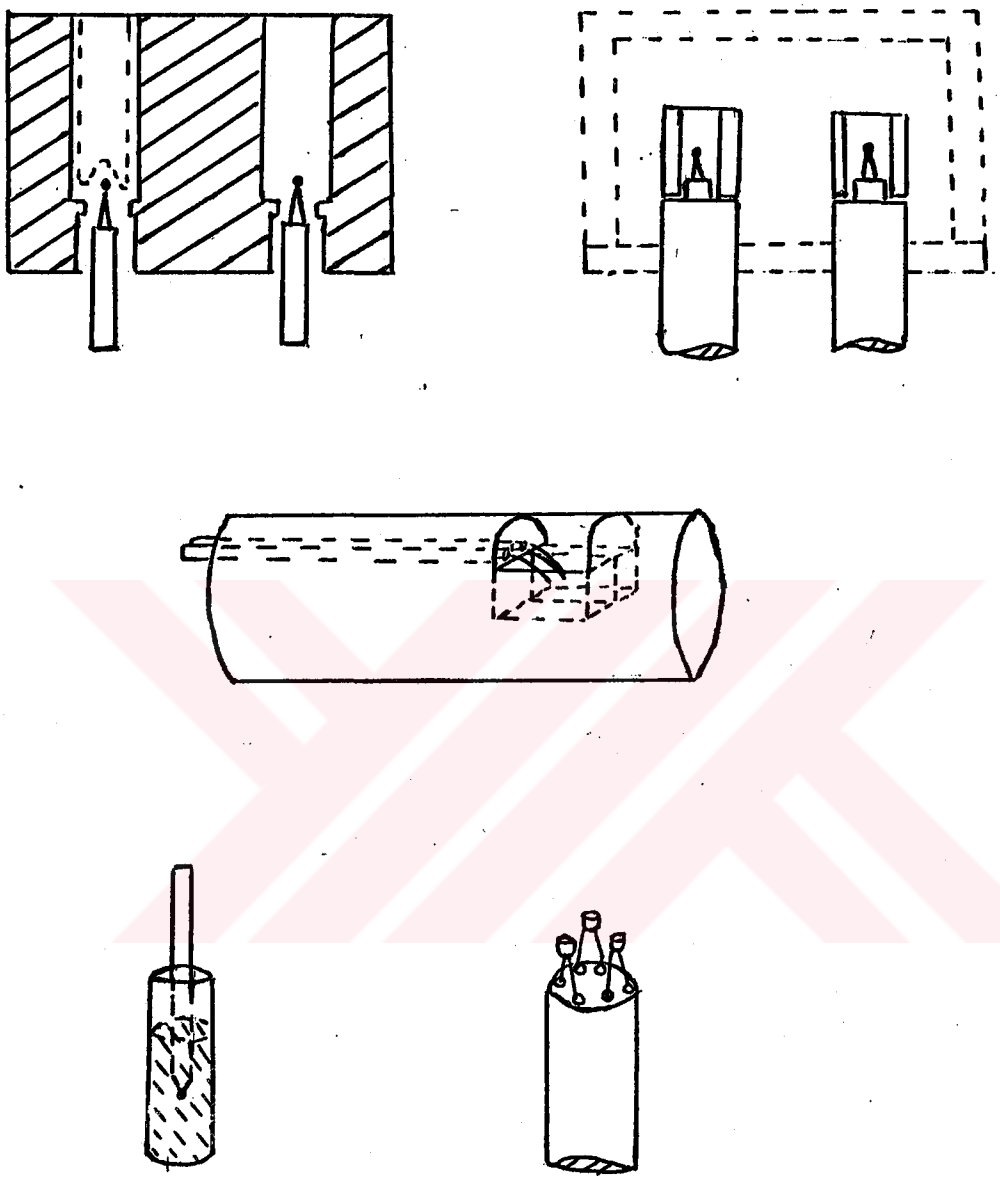

Figure 2.3. Some Sample Holders For DTA 1

a temperature programmer. This programmer should be capable of linear temperature programming over a number of different temperature ranges and also must be compatible with several different thermocouple types.

The type of temperature programmers [3] are the simple variable-voltage transformer coupled, a synchronous motor, the more sophisticated feedback and proportional-type programmer. On - off - type programmers can not be used because of the fluctuating power outputs which give rise to severe thermal gradients in the furnace and sample holder system.

The heating rates of most DTA furnaces can be varied from 0,5 to 200°C/min. But most DTA curves are recorded at heating rates of 10 to 20°C/min.

In conclusion, the heating rate affects the height and width of thermal effects recorded by DTA and DTG curves while the TG curve is substantially changed at various heating rates. High heating rates produce narrow peaks with sharp points whilst low heating rates produce broad superficial peaks. The optimum heating rate must be a compromise depend upon the nature of sample under investigation, upon the technical potentialities of the analytical instrumental device, upon the reference inert material and also upon the furnace.

2.3.3 AMPLIFIER AND RECORDING SYSTEM

The output of the thermocouple is the order of 0.1 to 100 μV, depending on the type of thermocouples used and the temperature difference between them. Some typical thermocouples characteristics are given Table 5.

The differential temperature (ΔT) signal must be amplified by a low-level microvolt dc amplifier which must have low noise, low drift, and high stability to be useful for DTA instrumentation.

TABLE 5 Some Typical Thermocouples Characteristics at 25°C

Metal No.1 (Positive)	Metal No.2 (Negative)	Maximum temp.°C	E.M.F at maximum temp. mV
Platinum	Platium- 10 % Rhodium	+20 to 1700	17.96
Copper	Constantan	-200 to 600	32.04
Iron	Constantan	+20 to 800	45.0
Chromel	Constantan	+20 to 800	60.0
Platinum	Platinum- 8 % Rhenium	+20 to 1300	60.38
Tungsten	Tungsten - 25 % Molybdenum	+ 2700	6.0

A two - channel recorder is using to record both the differential temperature and reference material temperature as a function of time. The modern X-Y recorder in which the differential temperature is plotted directly as a function of reference material temperature.

2.4 TEMPERATURE MEASUREMENTS

It is now generally agreed that temperature may be considered to be basic parameter in the same way as mass, length and time, and it is quite interesting to view the steady development of the liquid in glass thermometer and the scales of temperature. However, expanding liquid thermometers are not useful for measuring furnace temperature. WEDGWOOD in 1782 attempted to use a pyrometer based upon the shrinkage an firing of standart clay pieces, unfortunately this had a non - linear scale. It was the discovery by SEEBECK in 1822 of the thermoelectric effect which paved the way for the development of the thermocouple as a temperature measuring device. Although BEQUEREL employed platinum and palladium thermocouples for the measurement of high temperatures, it

was not until metals and alloys of high purity were developed. It was LE CHÂTELIER who finally developed the thermocouple into an accurate temperature measuring device. The optical pyrometer and resistance thermometer were both developed in later half nineteenth century, but for most thermal analysis work the thermocouple is the first choice temperature probe.

2.5 THERMOCOUPLE

In thermal analysis the most commonly used the method of temperature measurement is the thermocouple. Materials used for thermocouples should display as large a thermal electromotive force (emf) as possible with increasing temperature and these emf's should be constant even on prolonged heating. The materials should also be very resistant to physical and chemical influences and they must be available in wire from. The thermoelectric potential depends on their degree of purity. The thermocouple wires should be as thin as possible to minimize loss of heat. In the case of precious metals the diameters are usually 0.35 - 0,5 mm, in other cases 0.5 - 3.0 mm. To obtain a constant thermoelectric potential the wires should be artificially aged by annealing. The welding is usually done with an electric arc or or an oxygen-hydrogen flame. In arc welding a mercury or graphite arc is suitable. For thermocouples made from platinum metals, the most common in thermal analysis, graphite arc welding is suitable. The graphite rod is connected one electrode (pole) and thermocouple is connected another electrode of current source for welding of thermocouples. Thermocouples are useful in thermal analysis because they are small and avoid heat loss for the rate of temperature change used. The size of weld and diameter of the thermocouple wire are important for response to temperature changing.

There are a lot of thermocouples but its range are different due to its making materials. Some of these are,
Copper - Constantan [(Cu 100 %)-(Cu 55%, Ni 45 %)] which can be used

from -200 to + 600 ^{o}C.

Chromel - Nickel [(Ni 87,5 , Cr 12,5 %) - Ni 100 %)] which can be used from + 200 to 1200 ^{o}C.

Nickel Iron -Nickel [(Ni 66 %, Fe 34 %), (Ni 100 %)] At temperatures over 800^{o}C it should be protected against air oxidation. It becomes brittle between 600 and 800^{o}C and it can be used from +200 to +1000 ^{o}C .

Platinum - Platinum Rhenium [(Pt 100 %)-(Pt 92 %,Re 8 %)] is very sensitive to reducing gases and gases containing S, CO,Si and P. In an oxidative atmosphere it is stable up to 1200 ^{o}C. It displays a high emf value (apporox.60.0 mv at 1300 ^{o}C) as does the AuPd-PtRh (Gold palladium - Platinum rhodium) thermocouples.

Platinum - Platinum Rhodium [(Pt 100 %)-(Pt 90 %, Rh 10 %)] is called Le Châtelier's thermocouple. It is employed for measurements + 20 to 1700 ^{o}C. It is sensitive to a reducing atmosphere in the presence of Si.

Tungsten - Tungsten Molybdenum (W-WMo) and special combinations of graphite and carbides are used higher temperatures as a thermocouples.

A special thermocouples which are not made by a simple welding of wires but by direct welding between crucible and its carrier. Yamamoto et al. used a dumbbell-shaped piece of chromel which consisted of two circular discs connected by a narrow strip. Alumel wire, welded to the center of each disc, served as the other thermocouple junction.

2.6 THE POSITION OF THE THERMOCOUPLE

The position of the thermocouple with respect to the sample is most important for DTA curve. The importance has been investigated by

SMYTH [8] who show that considerable differences in the differential temperature occured according to where the thermocouple was located within the sample. In particular he demostrated that the placing of the sample and reference thermocouples asymmetrically within their respective chambers resulted in distinct distortion of the peak maxima. Assymetric location was also shown to give rise to significant base line drift particularly if the reference and sample materials are not uniformly packed.

When thermocouples immersed in the sample, getting a very sensitive emf, because there is no doubt, thermocouples are placed bottom of crucibles or not.

CHAPTER 3

DESIGN OF DTA INSTRUMENT

3.1 INTRODUCTION

DTA is a useful technique, that able to detect changes in enthalpy of the sample under study. In this work, low temperature DTA, ranged from room temperature to 350 ^{o}C is designed. For the enviromental conditions as atmosphere inert gas or air also provided. A cylindrical graphite block are used as a furnace body with conjuction with 150 watts heater in the center, Figure3.1. Then the furnace is fixed on a

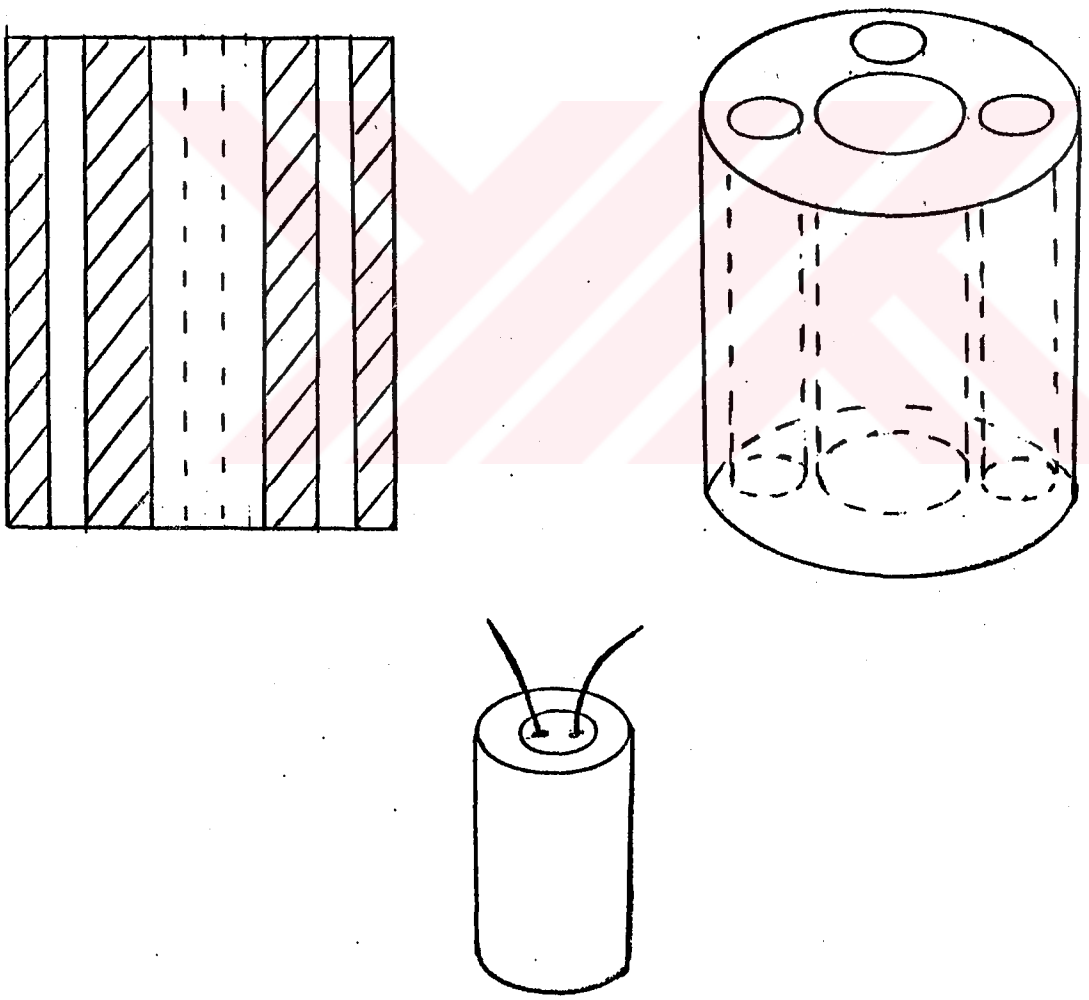

Figure 3.1 Graphite block and heater

box as a support is made of steel all the connections are fixed inside the box.

3.2 SUPPORT

The dimensions of the box which is used as support for the furnace and for the external supplies is 7,5 x 15 x 19,8 cm. A glass flask is used to protect the furnace and sample system from the air contact in case when the inert gas is used. Two metallic pipes with adjustable taps are in contact with flask volume, one provides controlled gas while the other used as gas exit. All the connections sealed by the vacuum adhessive to protect air pass into the flask, Figure 3.2.

3.3 FURNACE

Commercial DTA instruments have furnaces operating in ($-190^{o}C$ to $2800^{o}C$) temperature range depending on the purpose of experiment.

The instrument designed in this work uses room temperature to 350 ^{o}C range. For uniform heating block-type of furnace is preferred. The block has symmetrical holes, first three holes for thermocouples and in the centre the fourth hole for heater which is insulated from the block which is made of graphite. Dimensions of this cylindrical graphite block are r = 2,5 cm and h = 7 cm. This block mounted in vertical position and supported by the metallic box.

3.4 HEATER

220 Volt, 150 Watt heater is used for the furnace. When this voltage is supplied, the furnace temperature increases depending on the furnace body and conditions. This temperature increase shown in Figure 3.3. As seen from the Figure 3.3, Temperature - Time curve is exponential.

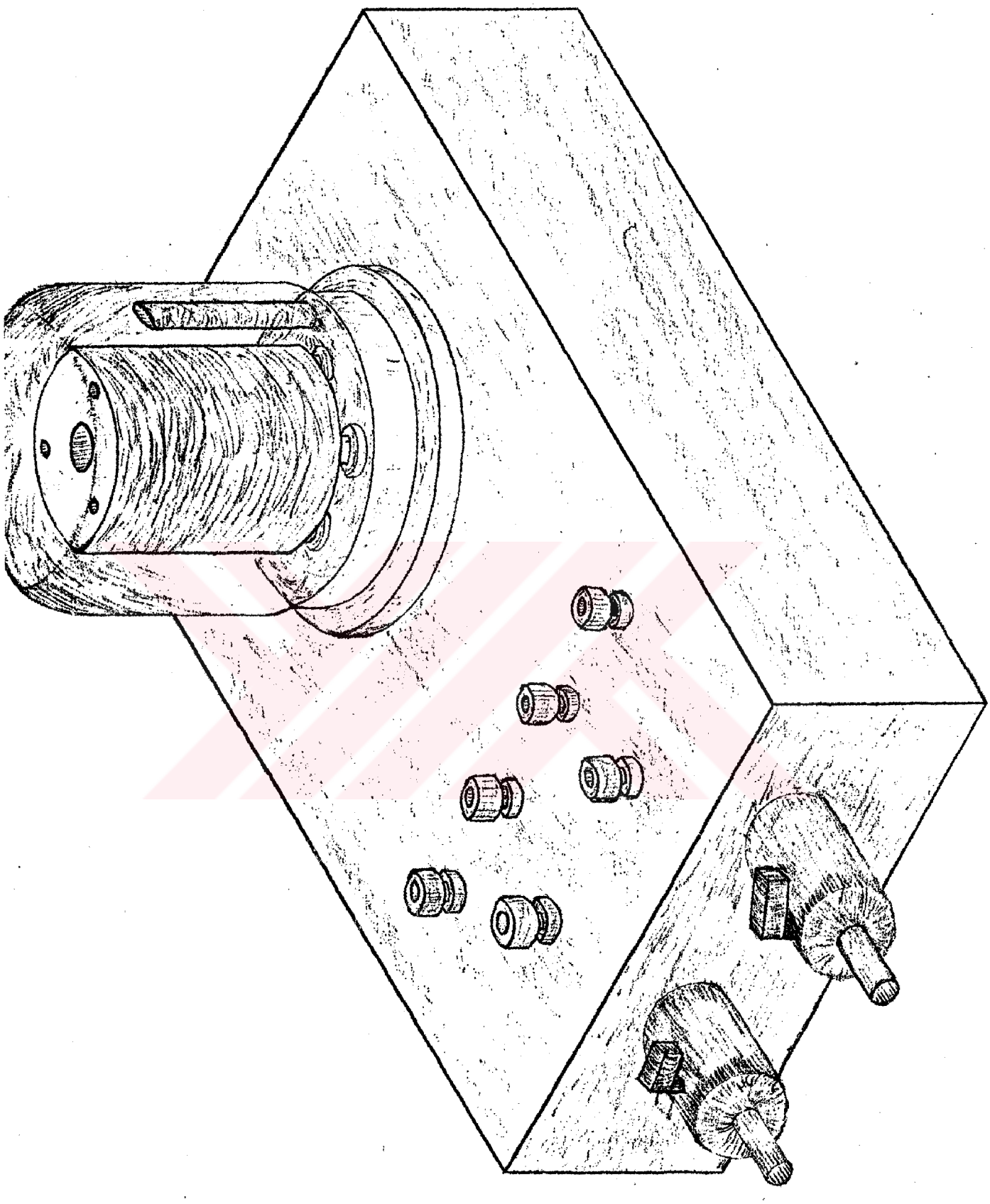

Figure 3.2 The support and glass flask

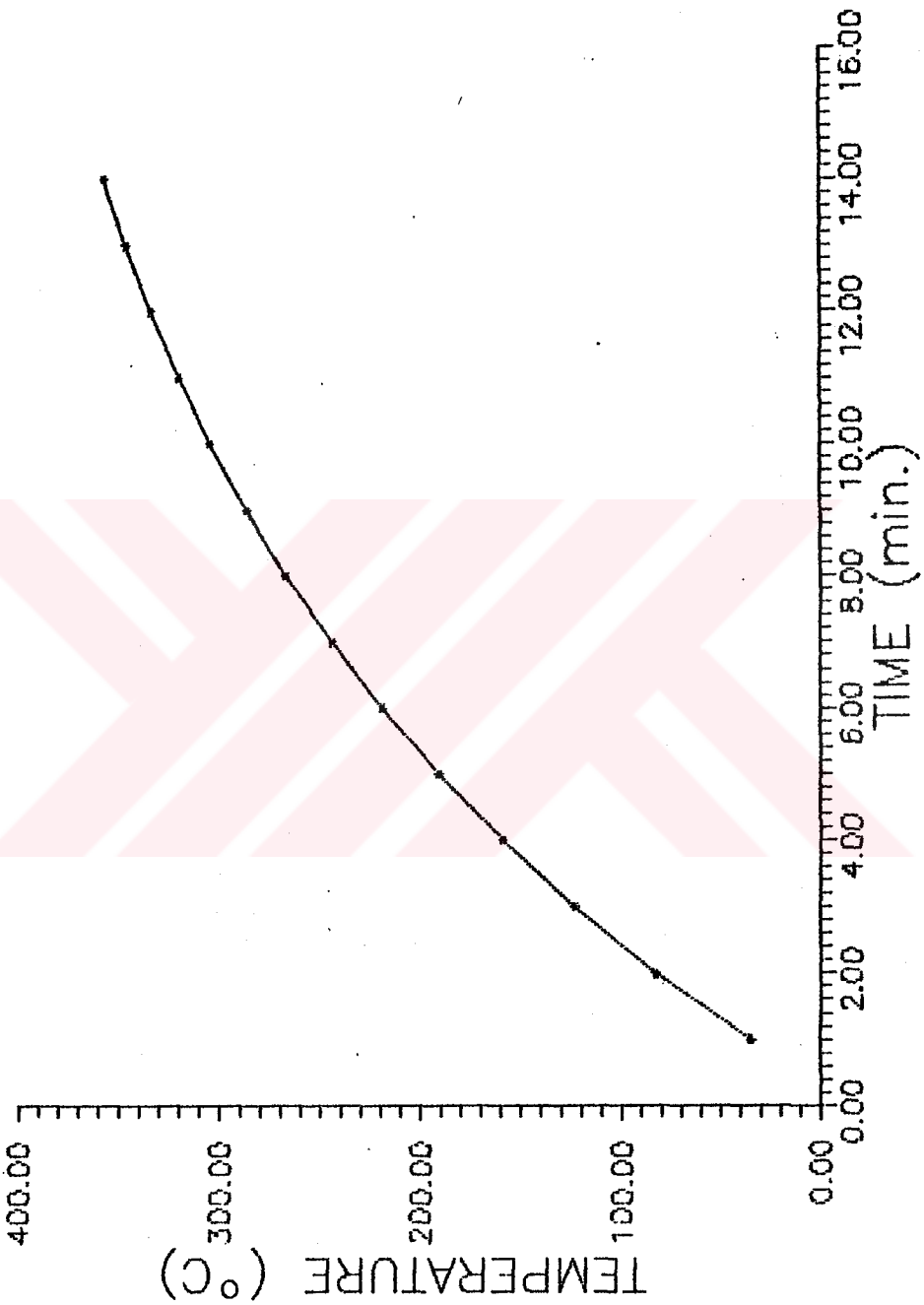

Figure 3.3 Temperature - Time curve.

3.5 SAMPLE HOLDER

0,4 cm diameter pyrex glass tube is used for sample holder, sealed from one end and placed on thermocouple as the open end up. The sample and reference materials placed in these glass cups that their positions are symmetrical to the heater while the third cup placed on the third equivalent position to measure the furnace temperature during the experiment. To prepare these cups a mould of metal is used Figure 3.4, after sealing one end of the glass which is pushed into the mould to give the convenient shape to the sample holder to be able to fit the thermocouple head.

3.6 THERMOCOUPLES

In this work, the copper - constantan thermocouple which can usually operates at (-200 ^{o}C to 600 ^{o}C) range is used. Thermocouple is produced by using electrical welding method improved in laboratory. Before welding copper and constantan wires are separated from each other by the using of capillary glass tubes in convenient length and then welded from one end. The two equal thermocouples are connected by their constantan ends, leaving the copper ends to measure the temperature difference of the sample and the reference. Figure 3.5 shows the system used in the experiment.

For sensitivity the thermocouple tips are immersed in the materials are tested, instead touching to the sample holder. So two thermocouple systems can be used in the same time to compare the results. The emf's of Cu-constantan thermocouple is given in Appendix I.

3.7 MILLIVOLTMETER AMPLIFIER

In this work, the measuring microamplifier (Unilab) is used. A versatile measuring amplifier, mains driven, to convert any 1 mA meter to the following ranges:

Millivolts : 0,1,1, 10, 100, 1000
Microampers: 0,1, 1, 10, 100, 1000
Microcoulombs: 1 (only)

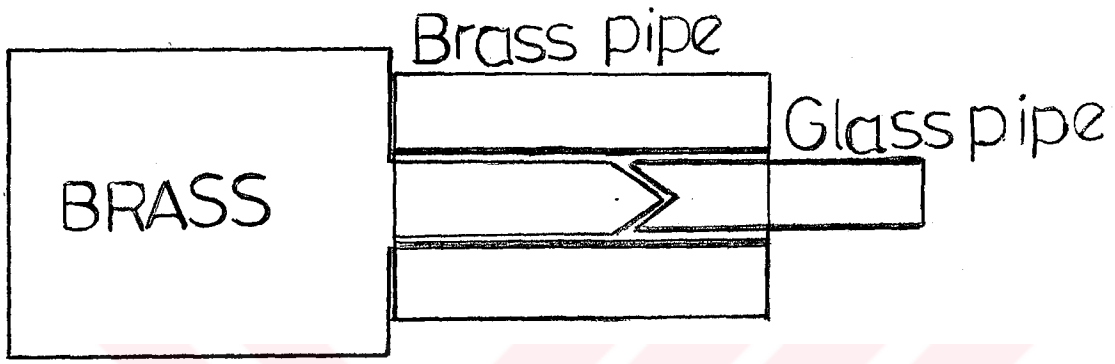

Figure 3.4 Brass Mould

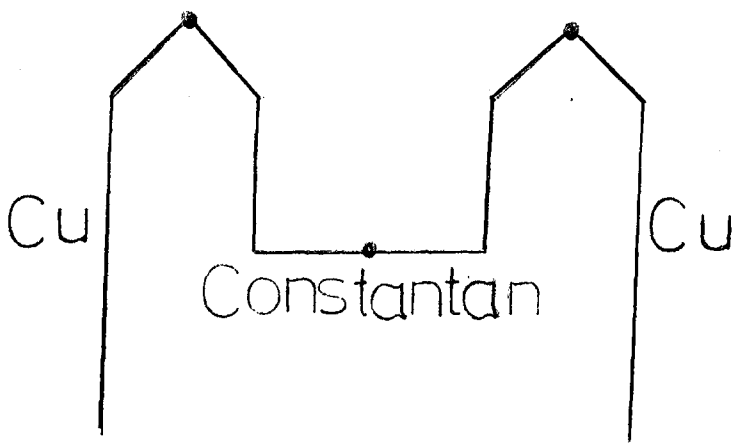

Figure 3.5 Thermocouple connections

The function is selected by plug-in modules, available separately. This instrument can also used as an oscilloscope preamplifier, having accurate gains of 1000, 100, 10, 1, and 0.1.

Millivolts dc module is used and provides full-scale deflection (on 1 mA meter) of 0.1, 1, 10, 100 or 1000 mV at 10 M Ω V^{-1}.

3.8 X-Y RECORDER

X-Y recorder used in this experiment which is fed by ΔT from its Y- probe and T from X- probe and it draws ΔT versus T curve. Where ΔT is the temperature difference between the sample and reference material and T is the furnace temperature which fixes the reaction temperatures.

The ranges of the recorder are 0,25 mV/cm 1 mV/cm, 2,5 mV/cm, 10 mV/cm, 25 mV/cm, 100 mV/cm, 0,25 V/cm, 1 V/cm, 2,5 V/cm, 10 V/cm, and the time ranges of the recorder are 0,1 sec/cm, 0,2 sec/cm, 0,5 sec/cm, 1 sec/cm, 2 sec/cm, 5 sec/cm, 10 sec/cm, 20 sec/cm, 50 sec/cm.

CHAPTER 4

PERFORMANCE OF THE DESIGNED INSTRUMENT

4.1 INTRODUCTION

The samples are already investigated are used to show the performance of the instrument designed. The samples are compared with Alumina (Al_2O_3) as a reference material. The native sulphates are choosed as testing materials. Their specifications and DTA curves are already investigated using commercial instruments.

These materials are gypsum ($CaSO_4.2H_2O$), epsomite ($MgSO_4 . 7H_2O$), kieserite ($MgSO_4 . H_2O$), chalcantite ($CuSO_4 . 5H_2O$) melantherite ($FeSO_4 . 7H_2O$), morenosite ($NiSO_4 . 7H_2O$), goslarite ($ZnSO_4 . 7H_2O$) are analyzed with designed DTA instrument.

4.2 GYPSUM ($CaSO_4.2H_2O$)

Native was studied by Mitsuki (1952) Yamanchi and Togai (1953) West and Sutton (1954) and Sudhir (1958) using DTA methods, Duval (1963) made a comparative study by thermal gravity between data obtained an artifical and native samples.

Thermal curves of gypsum show only two effects determined by the removal of the water of crystallization, Figure 4.1 comparatively by the results given by TODOR [2] , Figure 4.2.

4.3 EPSOMITE ($MgSO_4.7H_2O$)

Lorant (1966) [9] , showing the way in which water of crystallization is removed at two heating rates, namely at 5^oC/min and 10^oC/min. In both cases, epsomite expels water of crystallization in two clearly distinct stages. In the first stage six molecule are expelled up to a temperature of 290^oC when the heating rate was 5^oC/min or 305^oC when

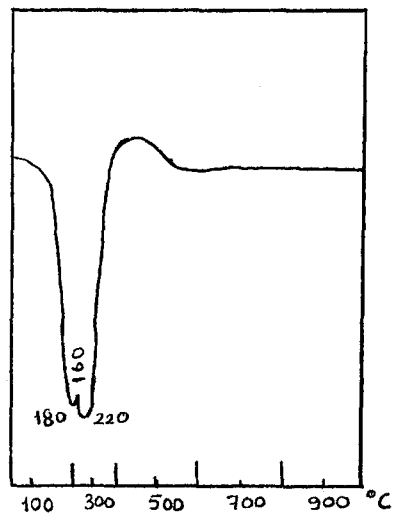

Fig. 4.2

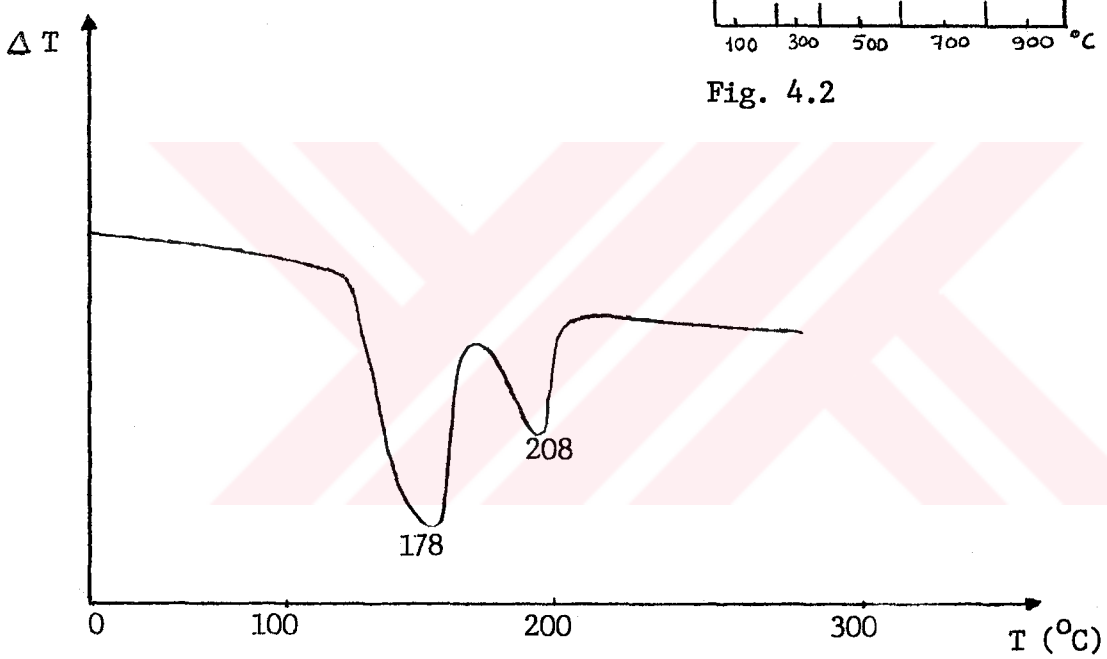

Figure 4.1 DTA curve of $CaSO_4.2H_2O$ is obtained from designed instrument.

Figure 4.2 DTA curve of $CaSO_4.2H_2O$ is taken from reference.

the heating rate was 10 ^{o}C/min. The removal of the last molecule of water crystallization requires high temperatures namely 400 ^{o}C Figure 4.3.

The DTA curve is obtained from designed instrument, is shown in Figure 4.4.

4.4 KIESERITE ($MgSO_4.H_2O$)

Cocco (1952) [10] employing the method of DTA. Popa and Todor (1969) show that the kieserite expels its water molucele crystallization in the temperature range 300-400 ^{o}C.

The curve which is obtained from designed instrument is shown in Figure 4.5 and the another curve which is taken from reference [2] , in Figure 4.6.

4.5 CHALCANTITE ($CuSO_4.5H_2O$)

Todor, examine the behaviour on heating of crystallized copper sulphate. The first four water molecules are removed quite readily in two clearly distinct stage, two molecules at a time. The last of water molecule is expelled at higher temperature.

Vanhellemont [11] , shows the various phase transitions taking place on heating $CuSO_4.5H_2O$.

$$CuSO_4.5H_2O \xrightarrow{90^{o}C} CuSO_4.3H_2O \xrightarrow{110^{o}C} CuSO_4.1H_2O \xrightarrow{240^{o}C} CuSO_4$$

The curve which obtained from designed DTA instrument is given Figure 4.7 and the reference curve is shown in Figure 4.8.

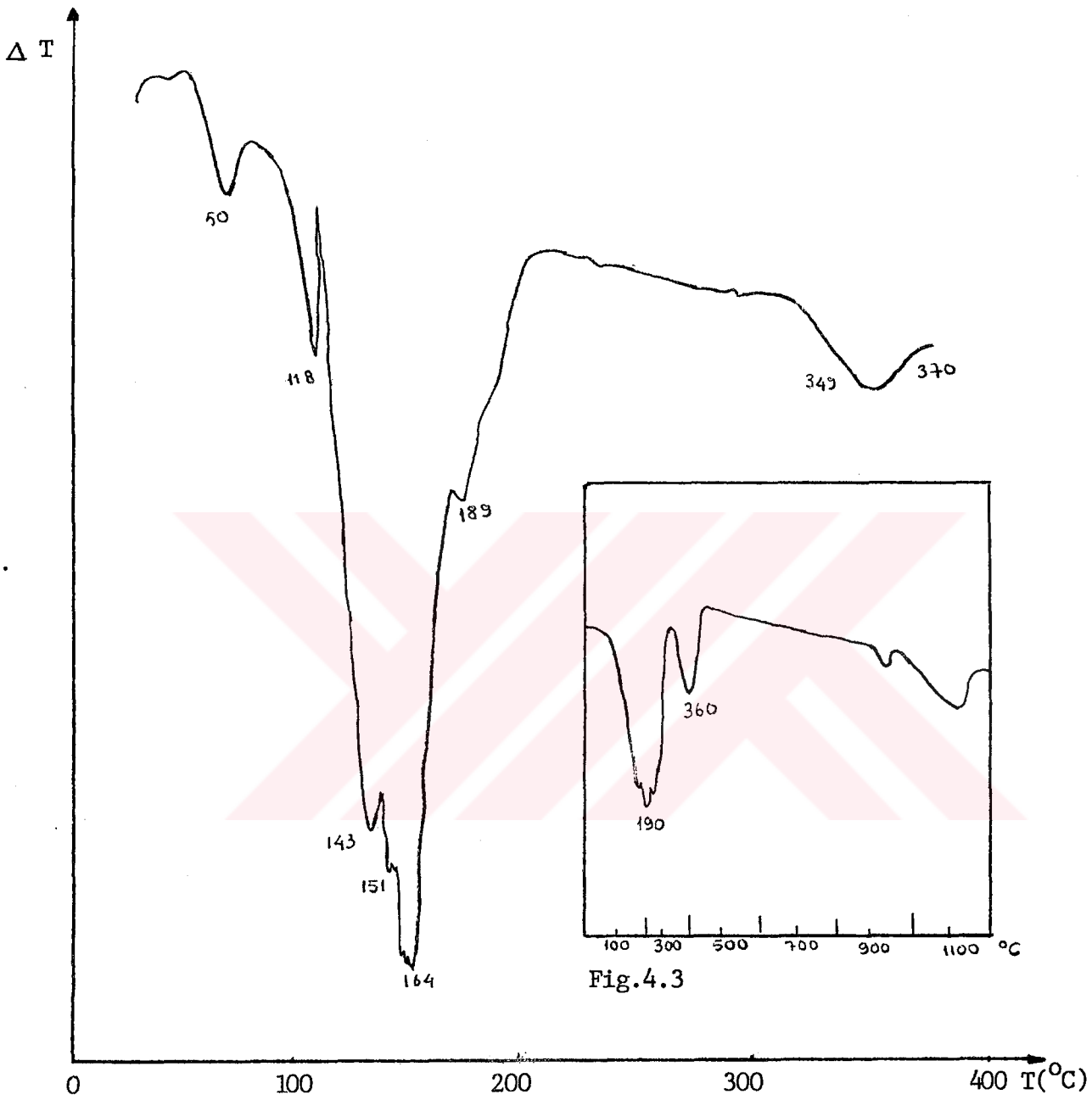

Fig.4.3

Figure 4.3 DTA curve of $MgSO_4.7H_2O$ is taken from reference.

Figure 4.4 DTA curve of $MgSO_4.7H_2O$ is obtained from the designed instrument.

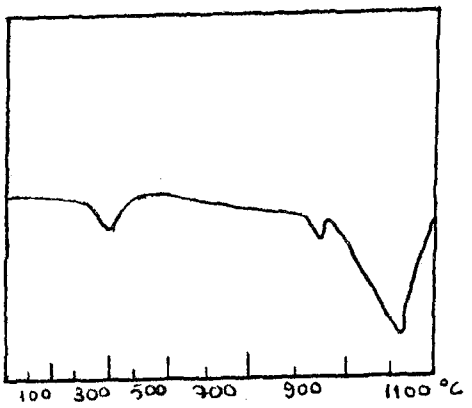

Fig.4.6

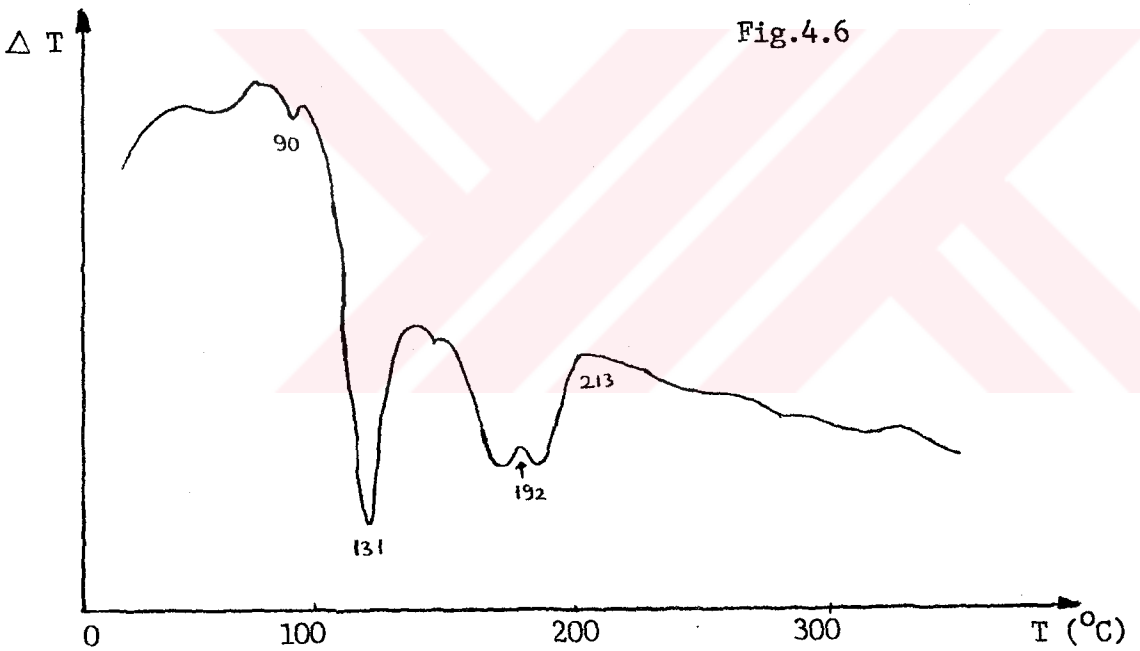

Figure 4.5 DTA curve of $MgSO_4.H_2O$ is obtained from the designed instrument.

Figure 4.6 DTA curve of $MgSO_4.H_2O$ is taken from the reference.

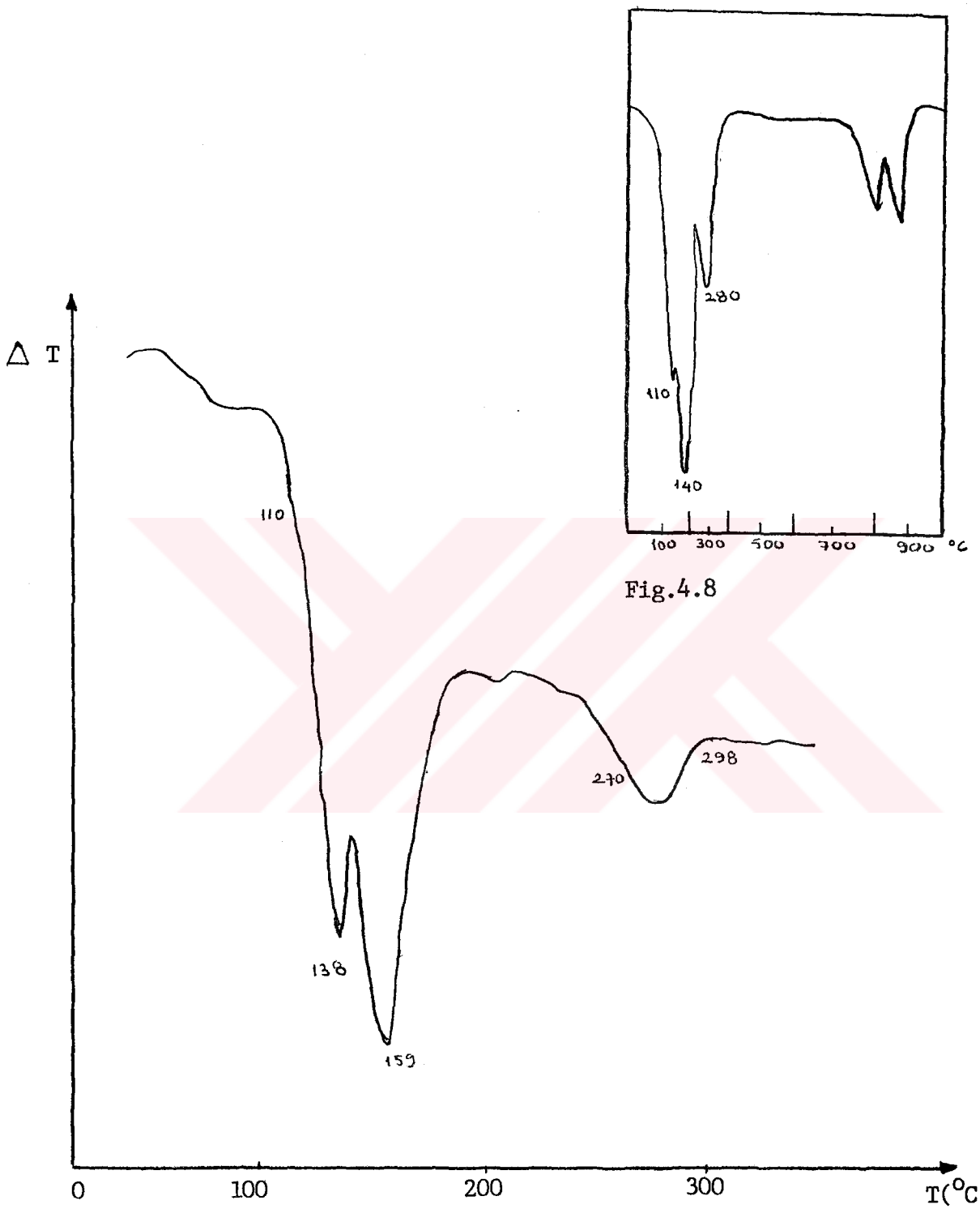

Fig.4.8

Figure 4.7 DTA curve of $CuSO_4.5H_2O$ is obtained from designed instrument.

Figure 4.8 DTA curve of $CuSO_4.5H_2O$ is taken from reference.

4.6 MELANTHERITE ($FeSO_4.7H_2O$)

Tvetkon and Voliashikina (1953) and Ivanova (1961) study on the ferrous sulphate crystallized with seven water molecules [12] . Todor (1971), more conclusive analytical results are obtained when the analysis of this compound is performed at a heating rate of 5 ^{o}C/min. In this case oxidation is completed in the temperature range at which dehydration occurs, the endothermic effect caused by the expulsion of the last molecule of water is completely missing, its place begin taken by the exothermic effect due to oxidation.

The DTA curve of melantherite which is obtained from the designed instrument as shown in Figure 4.9 and the reference one is shown in Figure 4.10.

4.7 MORENOSITE ($NiSO_4.7H_2O$)

A study employing DTA is mentioned in a paper signed by Berg and co-workers (1944) [13].

The water of crystallization of morenosite is removed in five stages when heating rate is 5^{o}C/min. The first six water molecules are expelled in a narrow temperature range, and the last molecule is driven off at high temperature when the heating rate is 10^{o}C/min, dehydration occurs in only three steps, Figure 4.11. The DTA curve of morenosite is obtained from designed instrument, Figure 4.12.

4.8 GOSLARITE ($ZnSO_4.7H_2O$)

The goslarite behaves similarly to epsomite when heated and it is in fact, isomorphous with this sulphate. The DTA curve of goslarite is obtained from designed instrument is shown in Figure 4.13 and the another one which is taken from reference is shown in Figure 4.14.

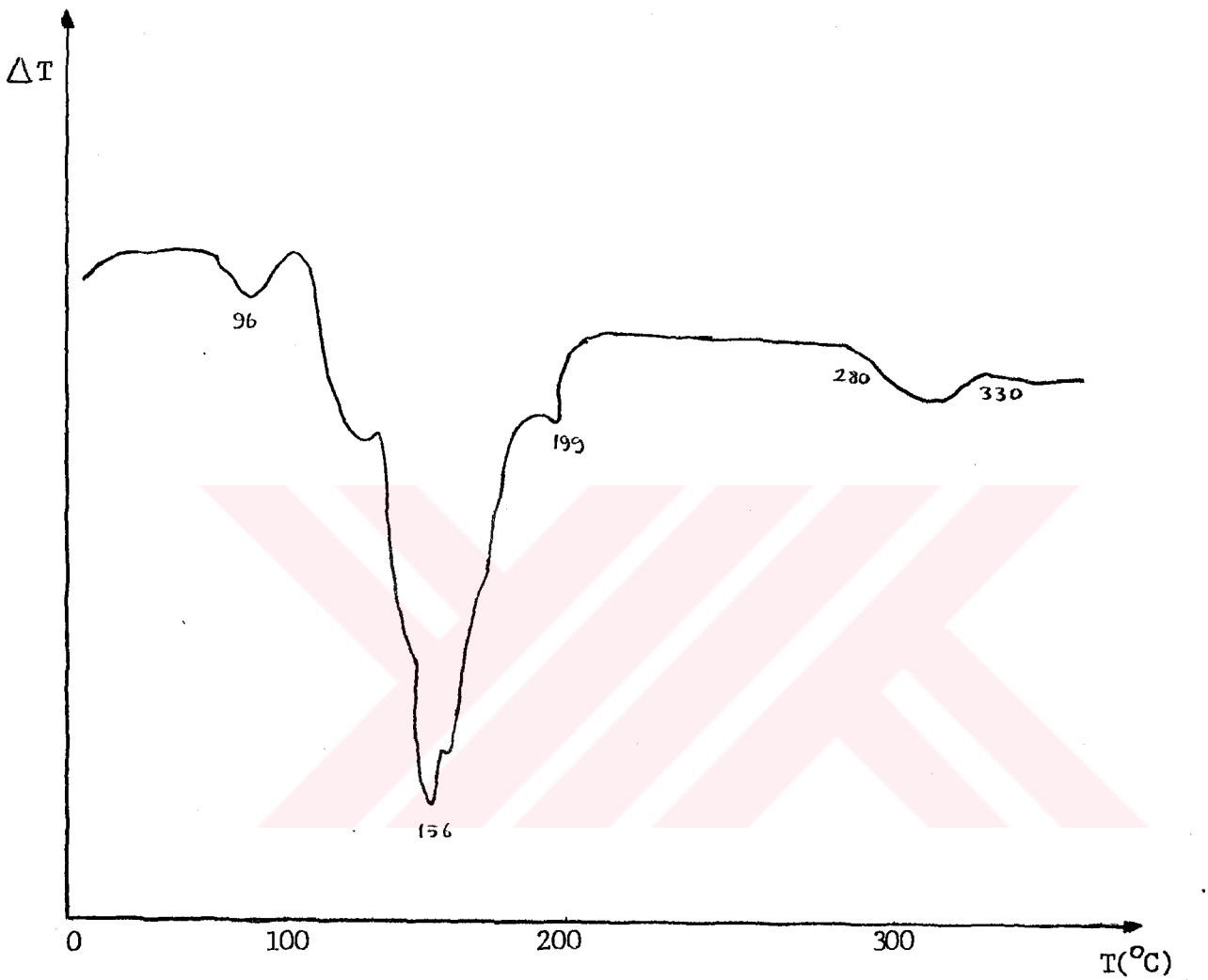

Figure 4.9 DTA curve of $FeSO_4.7H_2O$ is obtained by using of designed instrument.

Figure 4.10 a) DTA curve of $FeSO_4.7H_2O$ is taken from reference with heating rate is 5^oC/min.

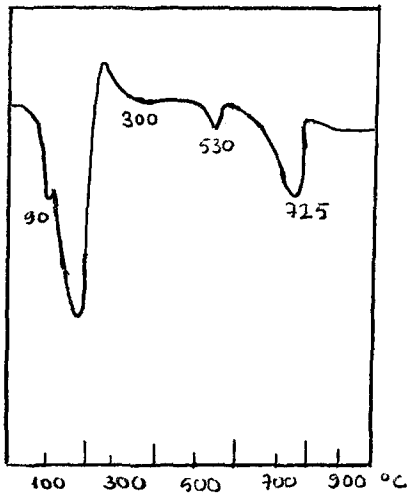

Figure 4.10 b) DTA curve of $FeSO_47H_2O$ is taken from reference with heating rate is 10 ^oC/min.

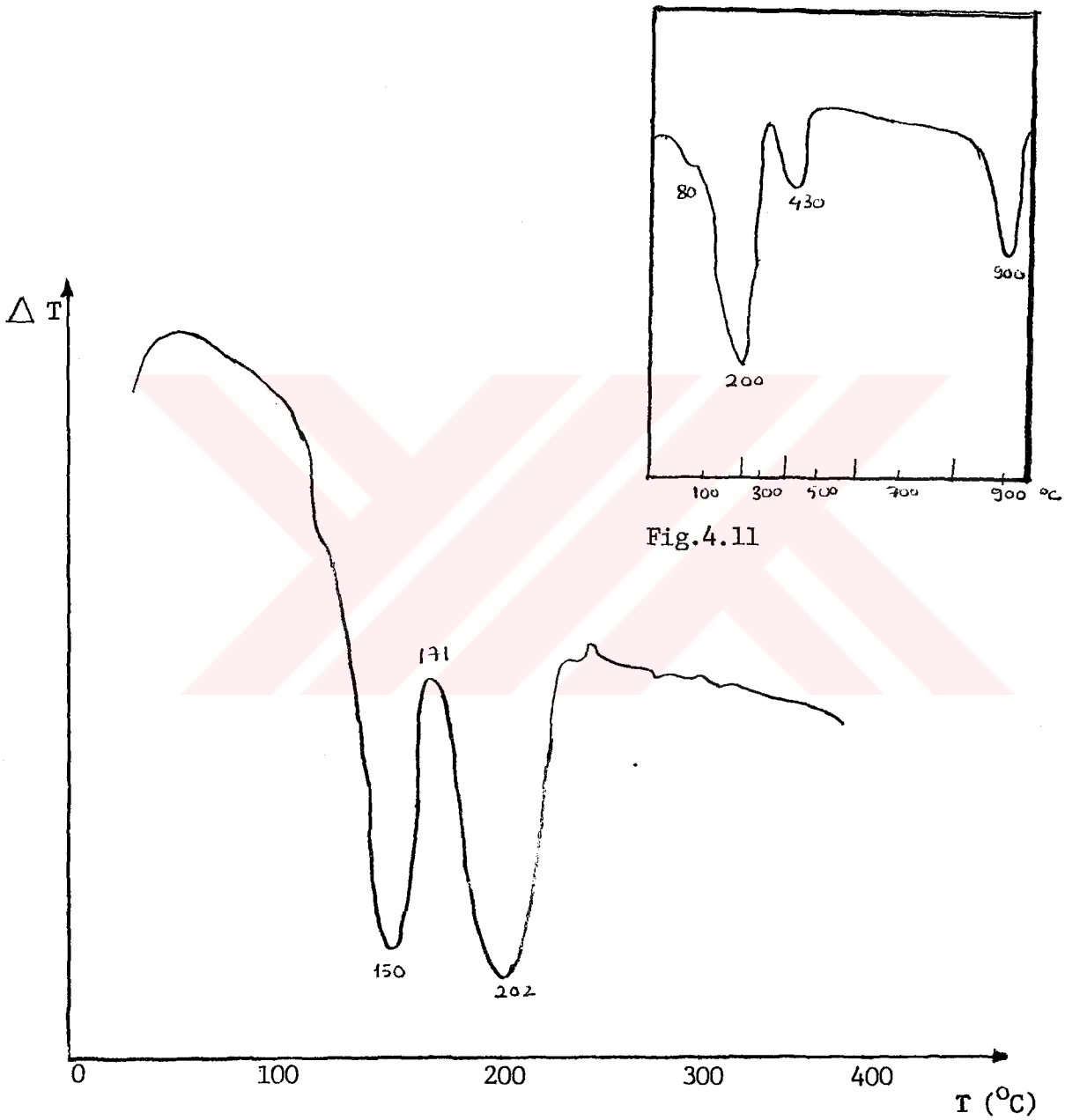

Fig.4.11

Figure 4.11 DTA curve of $NiSO_4 \cdot 7H_2O$ is taken from reference.

Figure 4.12 DTA curve of $NiSO_4 \cdot 7H_2O$ is obtained from designed instrument.

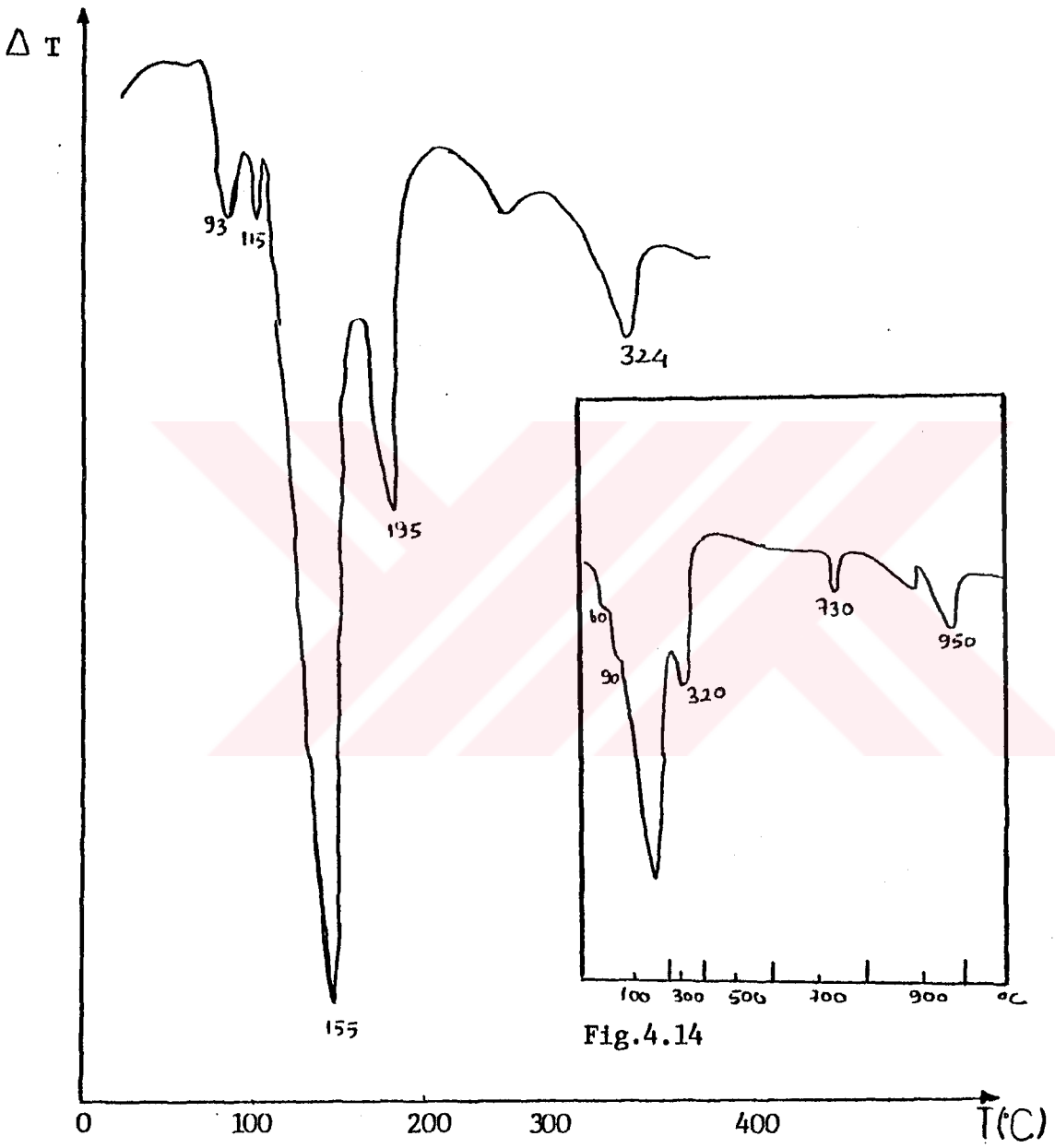

Fig.4.14

Figure 4.13 DTA curve of $ZnSO_4.7H_2O$ is obtained from designed instrument.

Figure 4.14 DTA curve of $ZnSO_4.7H_2O$ is taken from reference.

CHAPTER 5

RESULTS

As seen from the previous chapter that the obtained DTA curves were very acceptable, because of the curves were obtained without using linear heating temperature controller-programmer. The exponential temperature-time heating rate was used. In this experiment, 220 ac voltage was applied to the heater of furnace which has 150 watts.

In order to detect the temperature-time curve, the third thermocouple was used to indicate the oven temperature. The output of the third thermocouple was connected to Y-probe of X-Y recorder while the X- probe was used to sweep axis.

It is known that, the reaction temperature and the shape of the analyzed curve affected by the heating rate, the amount of sample, the grain size of sample, the surrounding atmosphere, the geometry of sample holder and the system parameters in thermal analysis techniques. The reaction temperature which is represented by the maximum peak varies with the heating rate. When the heating rates were supplied by furnace, the reaction temperature will increase. The reaction temperature obtained from our measurements are found to be slightly different from these reported by TODOR [2] . This difference is appearantly due to the different heating rates used in the two studies.

Copper-Constantan type thermocouple was used throughout the measurements. The thermocouple was inserted into the sample holder in order to measure the sample temperature more accurately.

In order to find the sensitivity of the instrument, the minimum amount of detectable sample was investigated. As a result, the sensitivity of the instrument was found to be about 20 mg. This was considered to be a significant result when compared to the instruments

commercially available.

In this study, temperature range of 20^{o}C to 350 ^{o}C was used with the heating rate of 25 ^{o}C/min. When the DTA method was applied to the seven native sulphates sample, the removal of water of crystallization peaks were observed. These peaks also reported by other authors [2,9,10, 11,12,13] and they found to be in reasonably good agreement.

The design and the construction of the instrument for the measurement of DTA was found to be highly satisfactory for the required study. This instrument can be succesifully used in future work, providing that the, temperature range is extended to higher temperatures.

REFERENCES

1. Atonin BLAZEK
Thermal Analysis, Van Nostrand Reinhold Company London,1973

2. Dumitru N. TODOR
Thermal Analysis Of Minerals, Abacus Press,1976

3. W.W. WENDLANDT
Thermal Methods Of Analysis, 2nd Ed. Wiley-Interscience publication, 1974

4. Ata SELÇUK
Development Of Various Mass Spectrometric Thermal Analysis Techniques And Their Application To Lead Oxalate Decomposition, Ph.D.Thesis,1985

5. W.W. WENDLANDT
Differential Thermal Analysis In Technique Of Inorganic Chemistry, H.B. Jonassen And A Weissberger Eds. Interscience, NewYork 1963 Vol 1. Chap.6.

6. W.W. WENDLANDT (Ref. B.H. CLAMPITT)
Anal. Chem. 35, 577 (1963)

7. W.W. WENDLANDT (Ref.SARASOHN)
Thermal Methods Of Analysis, P.163,1974 (Am. Chem.Soc. Washington D.C.)

8. H.T. SMYTH
J.Am.Cera.Soc. 34. 221 (1981)

9. Dumitru N. TODOR (Ref B. LORANT)
Z. Analyst Chem. 3. 1968 No: 219, 256

10.Dumitru N. TODOR (Ref C.COCCO)
Period Mineral, Roma 21, 1952 No:1

11.G.VANHELLEMONT
Studiecentrum Voor Kernenergie, Mol

12.Dumitru N.TODOR (Ref V.P. IVANOVA)
Zapiskj, Vsesoiuz Mineral Obshcestva, 90, 1961, 50

13.Dumitru N.TODOR (Ref. L.G.BERG and V.P.EGUNOV)
J.Thermal Analysis 1, 1969 5

APPENDIX I

COPPER-CONSTANTAN

°C Ref.0°C

THERMOELECTRIC VOLTAGE IN ABSOLUTE MILLIVOLTS

DEG C	0	1	2	3	4	5	6	7	8	9	10	DEG C
-270	-6.258											-270
-260	-6.232	-6.236	-6.239	-6.242	-6.245	-6.248	-6.251	-6.253	-6.255	-6.256	-6.258	-260
-250	-6.181	-6.187	-6.193	-6.198	-6.204	-6.209	-6.214	-6.219	-6.224	-6.228	-6.232	-250
-240	-6.105	-6.114	-6.122	-6.130	-6.138	-6.146	-6.153	-6.160	-6.167	-6.174	-6.181	-240
-230	-6.007	-6.018	-6.028	-6.039	-6.049	-6.059	-6.068	-6.078	-6.087	-6.096	-6.105	-230
-220	-5.889	-5.901	-5.914	-5.926	-5.938	-5.950	-5.962	-5.973	-5.985	-5.996	-6.007	-220
-210	-5.753	-5.767	-5.782	-5.795	-5.809	-5.823	-5.836	-5.850	-5.863	-5.876	-5.889	-210
-200	-5.603	-5.619	-5.634	-5.650	-5.665	-5.680	-5.695	-5.710	-5.724	-5.739	-5.753	-200
-190	-5.439	-5.456	-5.473	-5.489	-5.506	-5.522	-5.539	-5.555	-5.571	-5.587	-5.603	-190
-180	-5.261	-5.279	-5.297	-5.315	-5.333	-5.351	-5.369	-5.387	-5.404	-5.421	-5.439	-180
-170	-5.069	-5.089	-5.109	-5.128	-5.147	-5.167	-5.186	-5.205	-5.223	-5.242	-5.261	-170
-160	-4.865	-4.886	-4.907	-4.928	-4.948	-4.969	-4.989	-5.010	-5.030	-5.050	-5.069	-160
-150	-4.648	-4.670	-4.693	-4.715	-4.737	-4.758	-4.780	-4.801	-4.823	-4.844	-4.865	-150
-140	-4.419	-4.442	-4.466	-4.489	-4.512	-4.535	-4.558	-4.581	-4.603	-4.626	-4.648	-140
-130	-4.177	-4.202	-4.226	-4.251	-4.275	-4.299	-4.323	-4.347	-4.371	-4.395	-4.419	-130
-120	-3.923	-3.949	-3.974	-4.000	-4.026	-4.051	-4.077	-4.102	-4.127	-4.152	-4.177	-120
-110	-3.656	-3.684	-3.711	-3.737	-3.764	-3.791	-3.818	-3.844	-3.870	-3.897	-3.923	-110
-100	-3.378	-3.407	-3.435	-3.463	-3.491	-3.519	-3.547	-3.574	-3.602	-3.629	-3.656	-100
-90	-3.089	-3.118	-3.147	-3.177	-3.206	-3.235	-3.264	-3.293	-3.321	-3.350	-3.378	-90
-80	-2.788	-2.818	-2.849	-2.879	-2.909	-2.939	-2.970	-2.999	-3.029	-3.059	-3.089	-80
-70	-2.475	-2.507	-2.539	-2.570	-2.602	-2.633	-2.664	-2.695	-2.726	-2.757	-2.788	-70
-60	-2.152	-2.185	-2.218	-2.250	-2.283	-2.315	-2.348	-2.380	-2.412	-2.444	-2.475	-60
-50	-1.819	-1.853	-1.886	-1.920	-1.953	-1.987	-2.020	-2.053	-2.087	-2.120	-2.152	-50
-40	-1.475	-1.510	-1.544	-1.579	-1.614	-1.648	-1.682	-1.717	-1.751	-1.785	-1.819	-40
-30	-1.121	-1.157	-1.192	-1.228	-1.263	-1.299	-1.334	-1.370	-1.405	-1.440	-1.475	-30
-20	-0.757	-0.794	-0.830	-0.867	-0.903	-0.940	-0.976	-1.013	-1.049	-1.085	-1.121	-20
-10	-0.383	-0.421	-0.458	-0.496	-0.534	-0.571	-0.608	-0.646	-0.683	-0.720	-0.757	-10
0	0.000	-0.039	-0.077	-0.116	-0.154	-0.193	-0.231	-0.269	-0.307	-0.345	-0.383	0

DEG C	0	1	2	3	4	5	6	7	8	9	10	DEG C
0	0.000	0.039	0.078	0.117	0.156	0.195	0.234	0.273	0.312	0.351	0.391	0
10	0.391	0.430	0.470	0.510	0.549	0.589	0.629	0.669	0.709	0.749	0.789	10
20	0.789	0.830	0.870	0.911	0.951	0.992	1.032	1.073	1.114	1.155	1.196	20
30	1.196	1.237	1.279	1.320	1.361	1.403	1.444	1.486	1.528	1.569	1.611	30
40	1.611	1.653	1.695	1.738	1.780	1.822	1.865	1.907	1.950	1.992	2.035	40
50	2.035	2.078	2.121	2.164	2.207	2.250	2.294	2.337	2.380	2.424	2.467	50
60	2.467	2.511	2.555	2.599	2.643	2.687	2.731	2.775	2.819	2.864	2.908	60
70	2.908	2.953	2.997	3.042	3.087	3.131	3.176	3.221	3.266	3.312	3.357	70
80	3.357	3.402	3.447	3.493	3.538	3.584	3.630	3.676	3.721	3.767	3.813	80
90	3.813	3.859	3.906	3.952	3.998	4.044	4.091	4.137	4.184	4.231	4.277	90
100	4.277	4.324	4.371	4.418	4.465	4.512	4.559	4.607	4.654	4.701	4.749	100
110	4.749	4.796	4.844	4.891	4.939	4.987	5.035	5.083	5.131	5.179	5.227	110
120	5.227	5.275	5.324	5.372	5.420	5.469	5.517	5.566	5.615	5.663	5.712	120
130	5.712	5.761	5.810	5.859	5.908	5.957	6.007	6.056	6.105	6.155	6.204	130
140	6.204	6.254	6.303	6.353	6.403	6.452	6.502	6.552	6.602	6.652	6.702	140
150	6.702	6.753	6.803	6.853	6.903	6.954	7.004	7.055	7.106	7.156	7.207	150
160	7.207	7.258	7.309	7.360	7.411	7.462	7.513	7.564	7.615	7.666	7.718	160
170	7.718	7.769	7.821	7.872	7.924	7.975	8.027	8.079	8.131	8.183	8.235	170
180	8.235	8.287	8.339	8.391	8.443	8.495	8.548	8.600	8.652	8.705	8.757	180
190	8.757	8.810	8.863	8.915	8.968	9.021	9.074	9.127	9.180	9.233	9.286	190
200	9.286	9.339	9.392	9.446	9.499	9.553	9.606	9.659	9.713	9.767	9.820	200
210	9.820	9.874	9.928	9.982	10.036	10.090	10.144	10.198	10.252	10.306	10.360	210
220	10.360	10.414	10.469	10.523	10.578	10.632	10.687	10.741	10.796	10.851	10.905	220
230	10.905	10.960	11.015	11.070	11.125	11.180	11.235	11.290	11.345	11.401	11.456	230
240	11.456	11.511	11.566	11.622	11.677	11.733	11.788	11.844	11.900	11.956	12.011	240
250	12.011	12.067	12.123	12.179	12.235	12.291	12.347	12.403	12.459	12.515	12.572	250
260	12.572	12.628	12.684	12.741	12.797	12.854	12.910	12.967	13.024	13.080	13.137	260
270	13.137	13.194	13.251	13.307	13.364	13.421	13.478	13.535	13.592	13.650	13.707	270
280	13.707	13.764	13.821	13.879	13.936	13.993	14.051	14.108	14.166	14.223	14.281	280
290	14.281	14.339	14.396	14.454	14.512	14.570	14.628	14.686	14.744	14.802	14.860	290
300	14.860	14.918	14.976	15.034	15.092	15.151	15.209	15.267	15.326	15.384	15.443	300
310	15.443	15.501	15.560	15.619	15.677	15.736	15.795	15.853	15.912	15.971	16.030	310
320	16.030	16.089	16.148	16.207	16.266	16.325	16.384	16.444	16.503	16.562	16.621	320
330	16.621	16.681	16.740	16.800	16.859	16.919	16.978	17.038	17.097	17.157	17.217	330
340	17.217	17.277	17.336	17.396	17.456	17.516	17.576	17.636	17.696	17.756	17.816	340
350	17.816	17.877	17.937	17.997	18.057	18.118	18.178	18.238	18.299	18.359	18.420	350
360	18.420	18.480	18.541	18.602	18.662	18.723	18.784	18.845	18.905	18.966	19.027	360
370	19.027	19.088	19.149	19.210	19.271	19.332	19.393	19.455	19.516	19.577	19.638	370
380	19.638	19.699	19.761	19.822	19.883	19.945	20.006	20.068	20.129	20.191	20.252	380
390	20.252	20.314	20.376	20.437	20.499	20.560	20.622	20.684	20.746	20.807	20.869	390
400	20.869											400

DEG C	0	1	2	3	4	5	6	7	8	9	10	DEG C