THE CHARACTERISATION OF MANGANESE(IV) COMPOUNDS AND THE STUDY OF THE THERMAL DECOMPOSITION OF POTASSIUM CHLORATE ALONE AND WITH Mn(IV) AND OTHER OXIDES AND SALTS

A Thesis submitted for the Degree of Doctor of Philosophy

by

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ABSTRACT

Manganese dioxide compounds are preferred curing agents for Polysulphide resins used a sealants in industry. These are required to have consistent setting characteristics and th investigation was initiated to characterise a number of proffered compounds of this type an to establish criteria by which an informed choice could be made of an optimum curing agen for a specific set of conditions.

Several different chemical and physical properties were examined and critical parameter were established.

A compound - sodium birnessite- was identified as a significant agent in the determination o curing properties.It was synthesised and its curing properties alone and in combination wit other manganese dioxide compounds was evaluated.

In an effort to find a specific reaction which might be used to characterise manganes dioxide curing agents it was decided to examine the classical reaction between thes compounds and potassium chlorate. A literature search revealed major contradictions in th reported conditions under which potassium chlorate undergoes thermal decomposition as result of which it was decided to study the decomposition of potassium chlorate alone and i the presence of manganese dioxide and other catalysts.

During this investigation a hitherto unreported high temperature structural change i potassium chlorate at 341° C was identified. The existence of this reversible change wa confirmed by Powder Diffraction X-Ray analysis and an orthorhombic (near tetragonal) more open structure was assigned to it.

It is suggested that the rapid decomposition of potassium chlorate in the solid state presence of catalysts is related to this change to a more open structure.

CONTENTS

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CHAPTER 1

INTRODUCTION

Polysuide sealants are widely used in the Building, Engineering, Double Glazing and Aeronautical and Space Industries. The sealant is required to have stable setting time characteristics i.e. pot life, work life, tack-free time and cure time controlled within narrow limits which will vary with the particular application.

Complex " recipes" have been developed in which curing agents are mixed with the basic Polysulphide resin in the presence of plasticisers, accelerators and retarders to achieve the desired result for a particular application. There is also a division between "one-part" and " two- part"products the reaction in the latter only commencing on mixing the components prior to application. According to the nature of the polysulphide, curing agents are oxygen-donating materials and the overall pH of the system is the controlling factor. Acidic materials retard, and alkalies accelerate the curing reaction.

Manganese (IV) dioxide is the preferred curing agent for a number of two-part sealing agents which are required to have a working life of 1 to 3 hours followed by a tack-free time of several days after which contact may be made with the sealant without damage.

This investigation was undertaken in order to characterise a range of so-called Manganese Dioxide samples, many of which are offered as curing agents in the formulation of Polysulphide Sealants. These samples possess widely differing curing properties and often the same offered material behaves differently under what seem to be identical conditions. It has been reported that curing agent success rate can be as low as 50% in apparently situations . In some cases users make their own empirical additions to achieve a desired result[1] .

The aims of the present research were to find a rationale for the behaviour of manganese dioxides, to characterise the differences between commercial curing agent grades and the electrolytic and oxidising grades and to establish criteria by which an informed choice could be made of an optimum curing agent for a specific purpose. To achieve this, twenty-eight samples of " Manganese Dioxide" were obtained from various sources. These included natural ore, Battery grades, Oxidising grades and a number of activated products specifically offered as curing agents for polysulphide sealants. Chemically pure (99.999%) MnO_2 was included in the range to establish a datum. The compounds were submitted to a comprehensive range of tests including chemical analysis, particle size analysis, rate of curing of a standard polysulphide, and thermographic analysis. The detailed description of these tests is given in Chapter 2.

What became clear was that few of the so-called manganese dioxide curing agents were in fact manganese dioxide. The majority of these samples consisted of MnO_2 in combination with the alkali oxides` Na_2O, K_2O or Li_2O and water in various proportions. A compound - Synthetic Sodium Birnessite - was identified as a possible significant agent in the determination of curing properties and was synthesised and evaluated during this research. The results of this evaluation are recorded in Chapter 5.

In an effort to find an additional parameter by which to characterise these samples, it was decided to used the classical catalytic effect of manganese dioxide on the thermal decomposition of potassium chlorate to identify any differences between the samples. The thermal decomposition of potassium chlorate involves the evolution of oxygen and has been extensively reported in the literature*. The results reported however contained contradictions of such magnitude that it became necessary to study the temperature

* bibliography Chapter 3

products and rate of decomposition of potassium chlorate alone and in the presence of manganese dioxide and other catalysts. The experimental results which include the report of the discovery of a structural change in potassium chlorate are recorded in Chapters 3 & 4 respectively.

The significance of the structural change on the thermal decomposition of pure potassium chlorate is discussed in Chapter 3 and its effect on the reactions of potassium chlorate with transition metal species including manganese dioxide and other metal salts and oxides is discussed in Chapter 4.

CHAPTER 2

CHARACTERISATION CATALYTIC & CURING PROPERTIES OF MANGANESE DIOXIDE

2.0 GENERAL OUTLINE OF OBJECTIVES

Although manganese dioxide is used extensively as a curing agent for polysulphide sealants it is known[1] that not all commercial or laboratory samples function effectively as curing agents. This field is dominated in Europe by one particular manganese dioxide product which itself is often modified by some users to achieve satisfactory results. In general there seems to be no good reason why a particular product produces a good curing result on one occasion and an indifferent result in an apparently identical mix at another time.

The first task in the present study was therefore to characterise a range of manganese dioxide products by submitting them to a number of chemical and physical tests to determine which test result in a set of test results would provide the best assessment of potential curing ability. These experiments included comparative curing tests under standard empirical conditions to define those characteristics which give "good" curing properties.

2.1 CHEMISTRY OF MANGANESE & MANGANESE DIOXIDE

Manganese (Mn) is a metallic element and is one of the first row transition transition metals of Group VIII of the Periodic Table. Its Atomic Number is 25 and its Atomic Weight is 54.938. TheElectronic Configuration is $3d^5$ $4s^2$ beyond the Argon core. Manganese forms compounds in a number of different oxidation states viz:- 0 2+ 3+ 4+ 6+ 7+ . The stability of the different states is shown in Fig. 2 - 1.

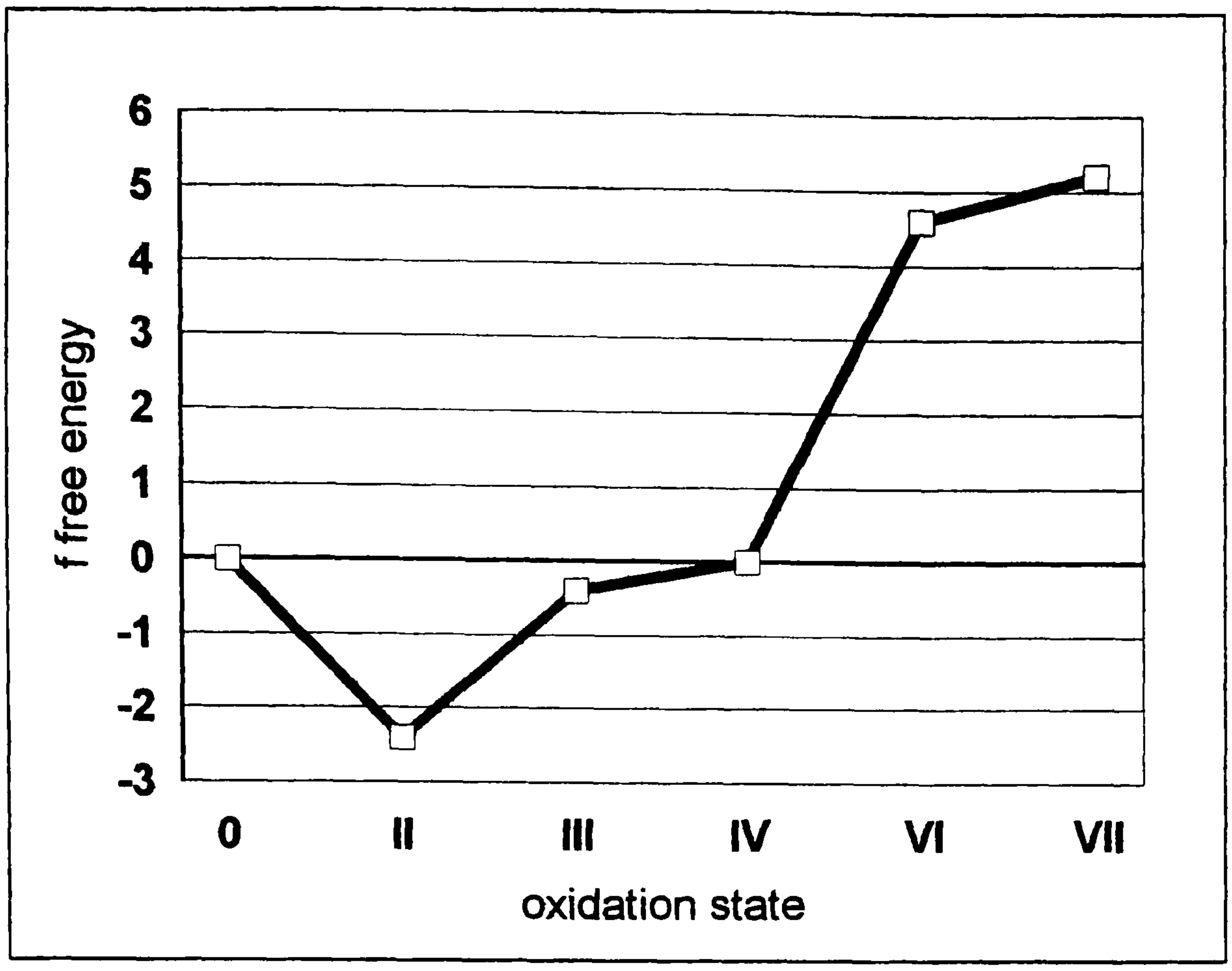


Fig. 2-1 Oxidation state/free energy (- ΔG/F = ηE, V) diagram for manganese after Mackay and Mackay(8)

The most obvious features of Mn chemistry in Fig. 2-1 are (1) the high stability of the high-spin Mn^{2+} cation which arises from the stability of the d^5 electronic configuration and (2) the strong oxidising properties that must be associated with Manganese VII+ VI+ compounds.

Manganese is known to form oxides in the II+ (MnO) III+ (Mn_2O_3) IV+ ($(MnO)_2$) and V(Mn_2O_7) oxidation states .The oxide of particular interest in the present work is the MnIV oxide (MnO_2). Although not the most stable oxide of manganese, it is by far the most important commercially. It decomposes to Mn_2O_3 at high temperatures and is reduced to Mn^{2+} in hot concentrated sulphuric and hydrochloric acid. The structural history of manganese dioxide is complicated and confused due to the fact that non-stochiometry is prevalent and that it is easily hydrated to give a material which acts as a cation exchanger. The only stochiometric form is that named β -MnO_2 which has the rutile structure and which is the mineral Pyrolusite. Even in the rutile form,however, a range of stochiometries from $MnO_{1.93}$ to $MnO_{2.00}$ has been reported. Manganese Dioxide is known to exist in several different forms and Gattow & Glemser (3) have tabulated the principal modifications as follows:-

Type	Lattice Structure	Mineral
α- MnO_2	Tetragonal-monoclinic	Cryptomelane
β-MnO_2	Tetragonal	Pyrolusite Polianite
γ- MnO_2	Hexagonal Tetragonal	Nsutite and other minerals
δ- MnO_2	Hexagonal Tetragonal	Birnessite
ϵ- MnO_2	-	-
Ramsdellite MnO_2	Rhombic	Ramsdellite

They also report the existence of η-MnO_2 and ρ-MnO_2 and describe two β- , three -γ- , two δ- , three η- , and two ϵ- sub groups. All of these modifications of MnO_2 convert into α-Mn_2O_3 at temperatures above 450° C . Fig. 2-2 is reproduced from their paper (p142) and illustrates diagrammatically the X-Ray patterns of the types of manganese dioxide that they described.

Details of the properties reported for the principal modifications are as follows:-

α-MnO_2 The material called α- manganese dioxide is a naturally occurring mineral -Cryptomelane and can be synthesised (6) by the action of manganese (II) sulphate dissolved in acetic acid on potassium permanganate. It is clear that this material is not a pure manganese dioxide and that it always contains potassium or ammonium ions and that it is better described as a potassium or ammonium manganate(IV). Gattow and Glemser (3) for example reported in 1961 that " *with confidence there has as yet been no*

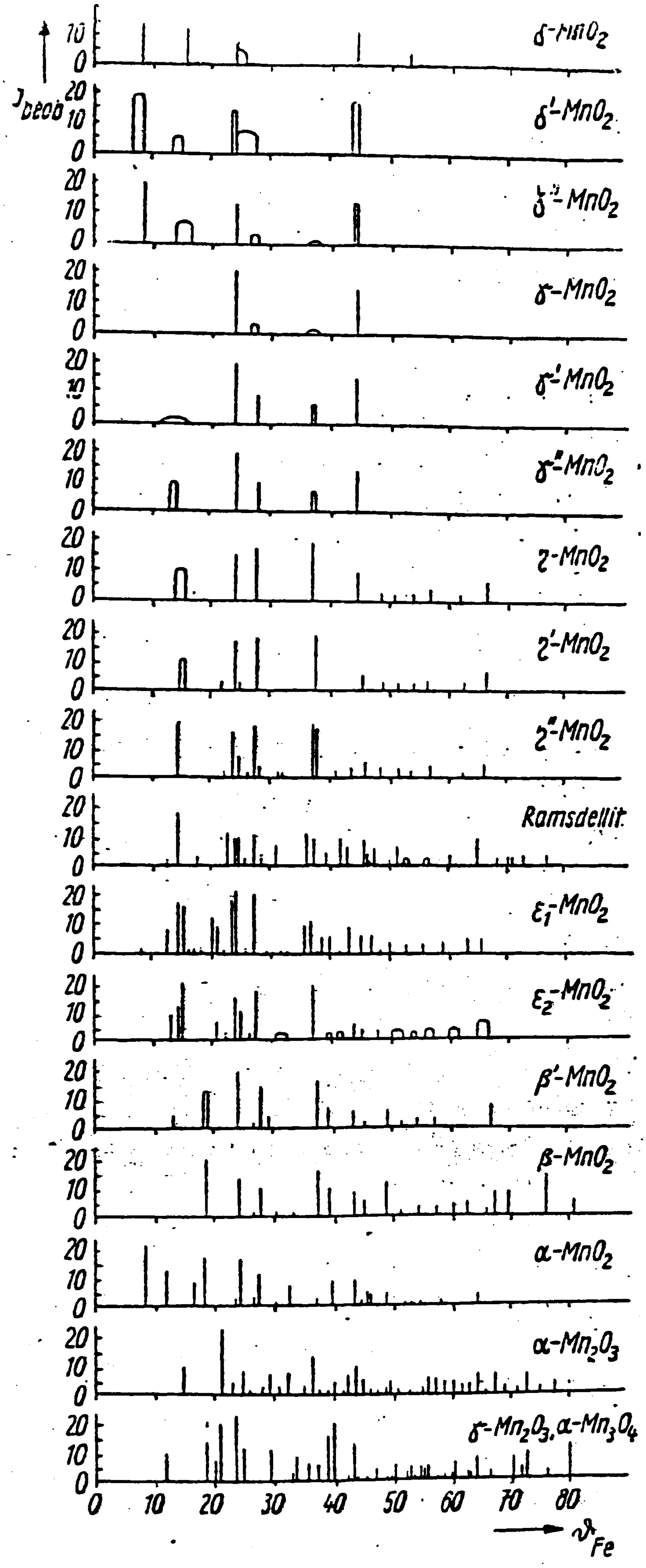


FIG. 2 - 2

X-RAY PATTERNS OF THE VARIOUS MODIFICATIONS OF MANGANESE DIOXIDE

(reproduced from the paper by Gattow & Glemser. ref. 3) *preparation of pure alpha-manganese dioxide. It must always contain either K^+ or NH_4^+ ions* " In the reaction described above McKenzie(6) for example obtained a product containing 2.2% K. According to this author there is an upper limit to the K content of about 7% above which the product is γ-MnO_2 and a lower limit of between 0.25% and 2.2% K . The same author quotes a general formula - $K_{2-y}Mn_{8-z}\,O_{16}$ suggested by Bystrom & Bystrom[9] in which O may be replaced by OH and Mn by lower valence ions; y is always approximately unity and z is always small so that this formula gives a K content of about 5.3%. A tetragonal compound $K_2\,Mn_8\,O_{16}$ has been reported(14) which has an identical calculated X-Ray pattern to that of alpha- manganese dioxide and which is presumably at the upper range of the general formula given above. There is no information on the extent to which O^{2-} may be replaced by OH- in either the natural or the synthethised products and therefore the extent to which the water content (if any) is combined or physisorbed. This mineral exists in both Tetragonal and Monoclinic forms and there are at least five different sets of X-Ray data recorded for this Cryptomelane and its analogue Hollandite in which potassium is partially replaced by barium. These data are shown in Table 2F and serve to show the complications that exist in the so-called α-manganese dioxide phase.

β- MnO_2 The natural form of β-manganese dioxide is Pyrolusite (and the probably identical Polianite)(7) . The synthetic material is prepared[6] by gentle heating of manganese(II) nitrate. It has been produced to a high degree of purity with consistent and reproducible analyses and X-Ray Diffraction patterns. β-MnO_2 is tetragonal and crystallises in the Rutile phase.(see Fig. 2-3) Nothing has been found in the literature to suggest that β-manganese dioxide contains any combined water. The synthetic product has a Mn/O ratio between $MnO_{1.90}$ and $MnO_{1.99}$ and samples of natural Pyrolusite have been reported with ratios between $MnO_{1.91}$ and $MnO_{2.00}$ (3)

β-MnO_2 is also reported(4) to result from heating γ- δ- η- and ϵ- manganese dioxides to 350/400°C

γ- MnO₂ This comprises a range of non-stochiometric dioxides the naturally occurring varieties of which have been named "nsutite" after the abundant deposits at Nsuta, Ghana. The synthesis of the material was reported by Bricker(9) who also quoted Dubois ((10) ,Glemser(11) ,and Gattow and Glemser(3) .The latter proposes the treatment of a solution of $Mn(NO_3)_2 .4H_2O$ in Nitric acid with a solution of $KMnO_4$ at 20 - 40° C . The precipitate is dried at 60° C. Other methods are described. Even though their composition varied from $MnO_{1.76}$ to $MnO_{1.93}$ the products all gave identical X-ray Diffraction patterns with a monoclinic structure. Bricker prepared two γ-MnO_2 products which had oxidation grades of $MnO_{1.91}$, and $MnO_{1.99}$ respectively .No differences were observed in the X-Ray structures of the two products. He suggested the following general formula for γ - manganese dioxide:- $Mn_{1-x}\ Mn_x\ O_{2-2x}\ (OH)_{2x}$ indicating a range of combined water content.

This modification appears to be the principal constituent of battery grade manganese dioxide, in which an average water content of 4.7% has been found in an analysis of 22 samples(13)

δ- MnO_2 This comprises the range of non-stochiometric compounds under the generic name "Birnessite". In general they are associated with water and they have a layered structure. These compounds are dealt with in detail in Chapter 6.

ϵ - MnO_2 This phase is described by Gattow & Glemser (3) and was prepared by them by heating a solution of $Mn(NO_3)_2$ in a sealed vessel at 150° C for 12 hours. The X-Ray Diffraction pattern is significantly different from the other MnO_2 phases. It is converted to β-MnO_2 (3) when it is heated to 350/400°C and to α-Mn_2O_3 at 500° C. ε-manganese dioxide contains 4.4% water which is evolved at 120° C. No structure has been reported and there is also no report of any natural occurrence of this phase.

Ramsdellite This is a naturally-occurring mineral first reported(15) from New Mexico by Ramsdell. It has an Orthorhombic structure and an Mn/O ratio of 1.973(3) . It evolves water on heating to about 120° C but no quantitative data could be found. Earlier papers report the failure of efforts to produce this modification synthetically. However, a recent report(16) by Roussouw et al gives detailed X-Ray Powder diffraction data for synthetic ramsdellite which they prepared by the reaction of $LiMn_2O_4$ or $Li_2Mn_4O_9$ with sulphuric acid at 95° C for 24 hours.

Table 2E sets out the X-Ray Powder diffraction data on the phases of MnO_2 listed above.

2.2 MANGANESE DIOXIDE AS A CURING AGENT FOR POLYSULPHIDE RESINS

According to the manufacturers of the synthetic resin, the mechanism of curing is expressed by the following reaction:-

$$2 \quad \text{-RSH} + O_2 \text{ ------> } \text{R-S-S-R} + H_2O$$

where -SH is a mercaptan terminal and R is a long chain bis-(ethylene oxy) methane polymer. The oxidation thus converts the mercaptan terminals to disulphide bonds forming a high molecular weight polymer. When manganese dioxide is the source of oxygen the reaction is expressed as:-

$$2 \quad \text{-RSH} + MnO_2 \text{ ------> } \text{R-S-S-R} + H_2O + MnO$$

However, in view of the observation that different samples of manganese dioxide behave differently in the curing process the above reaction must be oversimplified.

2.2.1. MANGANESE DIOXIDE AS A CATALYST IN THE DECOMPOSITION OF $KClO_3$

This subject is dealt with in detail in Chapter 4. Early reports(12) refer to the fact that manganese dioxide , although chemically the same after it has taken part in the decomposition of potassium chlorate, has apparently undergone physical transformation and the residue is much finer than the original . This may indicate that in catalysing the decomposition of the potassium chlorate it has itself undergone a series of changes culminating in the restoration of the original compound. What is not clear is whether the various forms of manganese dioxide behave in the same way in the reaction and whether the end product exists in the same allotropic form as the starting material.

2.3 CHARACTERISATION OF MANGANESE DIOXIDE-CONTAINING PHASES AS CURING AGENTS AND CATALYSTS

As part of the present work, a study was carried out on the characterisation of material loosely described as manganese dioxide. The samples used in the study are listed in section 2.3.1 and the methods of characterisation in section 2.3.2.

2.3.1 SAMPLES INVESTIGATED

The following samples were characterised in the early stages of the investigation:-

SAMPLE	SUPPLIER	SUPPLIER'S DESCRIPTION
1	SEDEMA	Battery Grade
2	SEDEMA	Battery Grade
3	SEDEMA	New product for Lithium-Manganese rechargeable battery systems said to contain Li
4	SHEPHERD	Samples 1 or 2 modified to activate curing properties
5	SHEPHERD	Duplicate of 4
6	SHEPHERD	Similar to 4 & 5 but with high moisture to minimise effect of exothermic curing reaction
7	SHEPHERD	Samples 1 & 2 modified
8	SEDEMA	Oxidation Grade for Organics
9	SEDEMA	Batteries and Oxidation Grade
10	TWINSTAR	Natural Ore
11	RIEDEL-HAHN	Principal Catalytic Curing Agent (HOECHST) used throughout Europe.
12	RIEDEL-HAHN	As for 11
13	unnamed	Good quality electrolytic grade used as a dry cell polariser.
14	TWINSTAR	Sample 10 ground to -8μ
15	CARUS	Activated MnO_2 Curing Agent
16	JOHNSON-MATTHEY	Reagent Grade 99.999% pure MnO_2
17	SHEPHERD	Sample 4/5 sized - oversize
18	SHEPHERD	Sample 4/5 sized - undersize
19	EAGLE PICHER	Type I Active MnO_2 Curing Agent for the Aerospace Industry

20	EAGLE PICHER	Type II Active MnO_2 Curing Agent- Building& Double-Glazing
21	EAGLE PICHER	Type III Synthetic MnO_2 Oxidising Agent
22	CHINESE	Electrolytic MnO_2
24	SEDEMA	Experimental Curing Agent
25	SEDEMA/TWINSTAR	Sample 24 sized - fines
26	SEDEMA/TWINSTAR	Sample 24 sized - middlings
27	SEDEMA/TWINSTAR	Sample 24 sized - oversize
28	INDIAN SAMPLE OF CURING AGENT	
29	CHEMATALS U.S.A.	Experimental curing agent

The purpose of the first stage of the characterisation was to seek common factors and common properties which determine the effectiveness of a particular sample or group of samples as a curing agent and establish whether a relationship exists between these characteristics and the effectiveness of a sample or group of samples as a catalyst. For this purpose the catalytic decomposition of potassium chlorate when it is heated with manganese dioxide was considered to be a suitable characterisation reaction for study.

2.3.2 METHODS OF CHARACTERISATION OF MANGANESE DIOXIDE

The following test methods were used in the first stage of the study of manganese dioxides-containing phases:-

1 Particle size analysis

2 Residue on 45u test sieve

3 Specific Surface Area

4 pH of water suspension

5 Moisture content at 120 deg C

6 Mn(IV) content

7 Thermographic analysis to derive total weight loss to 600 deg

8 Cation impurities by XRF

9 Metal impurities by ICP - AES

10 Structure characterisation of selected samples by powder XRD

11 Electron microscopy

12 Aggregation levels by ultrasonic treatment

13 Curing of Polysulphide Resin

14 Catalytic performance with Potassium Chlorate using thermographic analysis. This work is described in Chapters 3 and 4.

Details of the test methodology are given in section 2.3.3 Methods 1 to 12 were applied to the first 9 samples tested. Those methods which did not contribute significantly to the characterisation were not used on subsequent samples.

2.3.3 CHARACTERISATION TESTS - METHODOLOGIES

a. Particle Size Analysis Samples were sized on a Malvern Instrument Zetasizer 3 particle size analyser after dispersion with a surfactant solution. Results are tabulated in Table 2A

b. Residue on 45u Test Sieve Weighed samples were washed through a 45u standard test sieve and the residue was dried at 120 deg.C weighed and examined visually at 66x magnification. Except for the natural ore the residue of which consisted of discrete mineral particles, the residues consisted almost entirely of aggregates which broke up on further attrition. Results tabulated in Table 2A, were therefore inconclusive.

c. Specific Surface Area (SSA) These results were obtained using Single Point BET surface area by nitrogen absorption. Results are tabulated in Table 2A.

d. Alkalinity. pH was measured on a dispersion of a 1g sample in 10ml of freshly prepared de-ionised water. Results are shown in Table 2A.

e. Water content . This was determined in the course of Thermographic analysis (see par. 2.3.3 g and 3.3.2) for total weight loss. (By itself this method does not distinguish between physisorbed water and combined water and, if required, differentiation must be achieved by other means.) Total weight loss is reported in Table 2A and the weight loss profile over the temperature range is detailed in Table 2D.

f. Mn(IV) content. This was determined by a volumetric back titration method using a $KMnO_4$ solution on samples dissolved in standard sodium oxalate solution. The results are shown in Table 2A.

g. Total Weight Loss including loss of water from all sources and oxygen arising from the change of state of the manganese dioxide was determined thermographically (see 2.3.5). Samples were heated to a maximum of about 640 deg. C and the results are reported in Tables 2A and 2D. The method is described fully in Chapter 3.

h. Cation impurities were determined by XRF standard procedures using a Link XR300 Spectrometer. The data were judged to be of little value and the test was discontinued after 9 samples were examined. The results are shown in Table 2B.

i. Cation impurities were also determined by standard atomic spectroscopy methods using a Perkins-Elmer Plasma 40 Emission Spectrometer for Li, Na, K, Ca,Mg, Ti, Pb, and Cu. Atomic Absorption Spectroscopy was used to determine Cobalt. The results are shown in Table 2C.

j. Speciation Standard XRD procedures were adopted using a Philips Diffractometer with CuK alpha radiation available in the department. An internal Silicon standard was used . In view of the importance of this test selected samples were then sent to an outside laboratory and these results are shown in Table 2G.

k. Electron Microscopy. Electron micrographs were obtained on selected samples on a JEOL 840A Electron Microscope at magnifications of 300x and 3000x . No material deductions could be made and no further work was done.

l. Aggregation Samples were sonicated for 5 minutes in a 0.1% detergent solution prior to microscopic examination. No significant information was obtained.

m. Curing of Polysulphide Resin. In commercial practice when manganese dioxide is used as a curing agent in two-part systems it is mixed with accelerators, retarders and fillers. The mixture is processed mechanically in three roll dispersion mills or similar equipment to achieve maximum uniformity, fineness of grind and reduction of occluded air. The number of variables inherent in such a procedure,the time required for each test and the need for equipment which was not immediately available all contributed to the desirability of developing a simple empirical standardised test to make comparative assessments of curing efficacy. By restricting the test to the reaction between the oxiding agent and the polymer the complicating effects of accelerators, retarders etc.

would be avoided and the test would show the actual curing effect of the particular manganese oxide sample being assessed. It was further decided to limit the test to representative samples of the various manganese dioxide product groups.

After numerous trials the following standard procedure was adopted:-

150/180g of the polysulphide is weighed into a disposable plastic cup. The cup is placed in a temperature-controlled water bath at 23/25° C located in a fume cupboard for safety and to maintain reasonably constant ambient conditions.The contents are stirred with a speed controlled glass spatulate bladed electric stirrer at constant speed for 5/10 minutes. 7.5% by weight of the candidate curing agent is added to the polymer and stirring is continued for precisely 10 minutes. A sample of about 20g is withdrawn into a suitable plastic boat for subsequent hardness determination. The stirrer is replaced by the HA7 spindle of a Brookfield Dial Reading Viscometer and the viscosity of the blend is monitored with respect to time until a practical limit of 12000/14000 poise is reached. The hardness of the retained 20g sample is monitored over a period of 2/4 weeks using a hand held Shore A hardness meter. Discussions with users and reference to trade literature indicated that a satisfactorily cured two-part sealant should have the following viscosity and hardness attributes:

<u>Pot life</u>: during which the mixture is capable of being transferred to the site - 20 to 40 minutes by which time the viscosity will be 100/1200 poises.

<u>Work Life</u>: the period during which the curing mixture is capable of being re-worked on site after being applied to a substrate - minimum 1 to 2 hours and maximum 4/5 hours by which time viscosity will have reached a value of 12000/ 14000 poises.

<u>Tack-free time</u>: at which the applied sealant is sufficiently robust to withstand damage by contact or handling. - 1 to 2 days.

Cure Time: empirically defined as the end point at which the desired hardness and tensile strength is achieved - 1/2 weeks and Shore A hardness of 30 to 40.

Using this test and the criteria set out above a number of samples were evaluated and thereafter mixtures of different proportions of commercially promising samples were examined. It became clear that a prime objective was to secure by blending with slower agents a "slowing down" of the very effective but rapid curing agents to comply with the criteria . The results are shown in Tables 2H 2J 2K and illustrated in Figs. 2-3 & 2-4.

n. Catalytic Performance. Preliminary results obtained when using the manganese dioxide/potassium chlorate reaction as a means of characterising the catalytic properties of MnO_2 were sufficiently encouraging to suggest that a more detailed study was required both of potassium chlorate decomposition and of the effect of manganese dioxide catalysis on that reaction. The results of these studies are given in Chaps 3 & 4.

2.4 RESULTS

The results of all the characterisation tests are given in Tables 2A through to 2K.

2.5 DISCUSSION OF RESULTS

The results of the following tests either showed no discernible relationship between test parameters and curing properties or were incapable of interpretation at this stage:-

Particle size

Residue on 45u

Specific Surface Area

Electron Microscopy

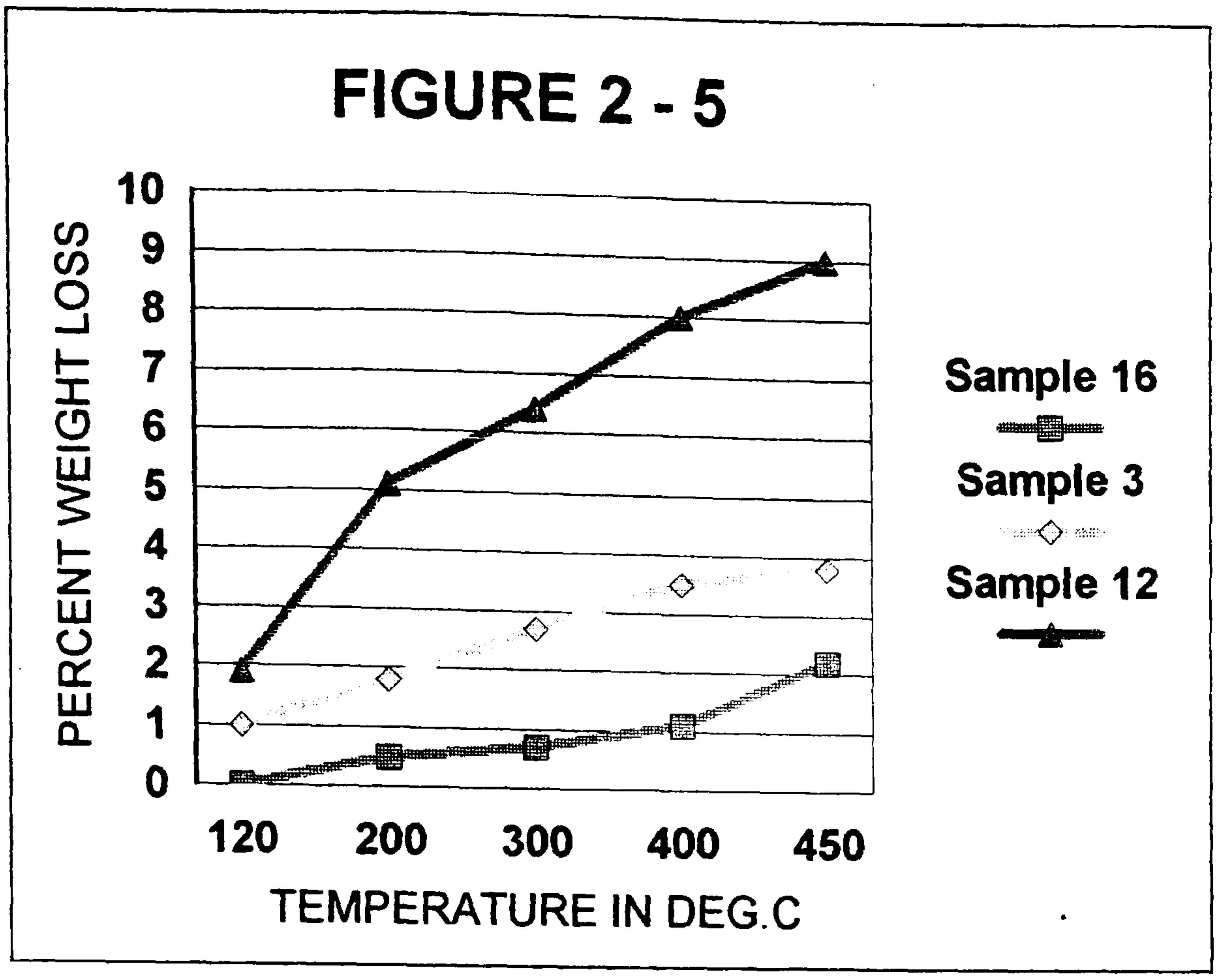
Aggregation Levels

The remaining tests were carried out on all samples except where there was duplication of samples or suppliers data were made available.

Inspection of the data in Tables 2A 2C and 2D showed differences in properties between samples with relatively low alkali content (< 1% total alkali oxides) and those with higher alkali content. The former group includes the natural ore, pure manganese dioxide, and most of the oxides manufactured for battery electrolytic and oxidising agent applications; the "high" alkali group were all supplied as curing agents (with the exception of sample 3 described as a component of a rechargeable battery system and sample 21 said to be an oxidising agent).

The thermal decomposition profiles in Table 2D show water and total weight loss of the low alkali group as distinctly different from those of the high alkali group there being substantial weight loss at temperatures below 400° C for the high alkali group. This weight loss combined with the relatively lower MnO_2 content of this group suggests a high content of combined water. Fig. 2-5 illustrates the comparative weight loss during heating in three samples with nil ,low and high alkali contents .

The groups are also differentiated by pH. The high alkali samples have pH values between 9 and 12 (again with the exception of samples 3 and 21 with values of 4.7 and 4.6 respectively) and the low alkali group having pH values between 4.4 and 6.3. The high pH samples are, without exception, curing agents.



Sample 16	nil total alkalies
Sample 3	3.1% total alkalies
Sample 12	7.5% total alkalies

When the curing properties of selected samples are examined (see Table 2H) the distinction between the low and high alkali types becomes clearer. Samples 12 20 and 24 all achieve tackfree endpoints within an acceptable, albeit different, time frame whereas the low alkali samples 14 and 16 are still not tack-free after 3 months. Sample 14 does not even achieve a satisfactory work life endpoint until some 160 hours have elapsed while the pure β-MnO_2 - Sample 16 - achieves a viscosity of 12000 poises (the endpoint of its work life) after 160 minutes but remains tacky even after 3 months indicating that full curing has not been effected. This lack of complete curing when pure manganese dioxide is used confirms the comment made in par. 2.2 that the provision of oxygen to convert mercaptans to disulphides is probably an oversimplification of the explanation of the total curing process.This complexity is confirmed in a paper[17] by Coates et al and in a private discussion with Dr.Coates (who is on the staff of one of the manufacturers of the polysulphide resins).

X-Ray Powder Diffraction analyses of a number of selected samples. (Table 2G) provides further evidence of the differences between curing agents and the other samples studied. Identification of the phases present in all the samples studied is ,as yet, incomplete but the patttern is clear. Sample 12 - the most effective curing agent - shows the presence of Sodium and Potassium Birnessite in addition to manganese dioxide in the Rutile β-MnO_2 phase (pyrolusite); Samples 20 and 24 also show the presence of Sodium Birnessite with, in the case of 20 , Potassium Birnessite and possibly Lithium Birnessite.Both contain pyrolusite. On the other hand samples with poor curing properties e.g. Sample 16 which is chemically pure Manganese Dioxide -is shown to consist entirely of β-manganese dioxide and Sample 14 - the natural ore - contains Pyrolusite as well as a small quantity of Sodium Birnessite. The Sodium Birnessite in the ore is a natural product and in contrast to the freshly prepared precipitated synthetic product must have its cation exchange capacity fully saturated. In samples 11 12 and 20 the Sodium Birnessite is synthetic and differs from the Sodium Birnessite in the ore in that it has a high cation exchange capacity.This ion exchange capacity may be a significant factor in curing ability.The general type difference between the curing agents and, in particular, samples 14 and 16 is clearly shown by the X-Ray Powder Diffraction diagrams attached as Appendix 2.

The results of the characterisation of the manganese dioxide-containing phases suggest that the active curing agent (s) are the hydrated alkali compounds of $\Delta -$ Manganese Dioxide and, in particular, Synthetic Sodium or Potassium Birnessite with high active cation exchange capacity and high pH values .The final cure i.e. the disappearance of tackiness and the development of an acceptable level of hardness appears to be related to the pH and total alkali content. In contrast those phases with indifferent curing properties consist substantially of β- or other phases of manganese dioxides with or without combined water, with lower or nil alkali content but, in all cases studied, with acid pH values. This interpretation is supported by the assertion of the manufacturers of the polysulphide that " the overall pH of the system is a controlling factor (in the curing process) in that acid materials retard the cure and alkali materials accelerate the cure"

The question that then arises is whether mixtures of the inactive sample 14 with the active sample 12 or 24 and more specifically with synthetic Sodium Birnessite should be satisfactory curing agents with moderated curing times. This has been confirmed with a series of experiments (Tables 2H 2J 2K and 5D) the results of which confirm the hypothesis and demonstrate that rapid reaction curing agents such as 12 or Sodium Birnessite itself can be modulated in a controlled way by the addition of natural ore.

The synthesis of the Sodium Birnessite used in these experiments and further discussion of its curing properties and their modulation with natural ore is described in Chapter 5.

It is concluded that effective manganese dioxide curing agents may be characterised as layered hydrated alkali manganese dioxides with high pH of the birnessite type (delta-manganese dioxide) with unsatisfied cation exchange capacity and that their curing rate may be modified by the inclusion of less active or inactive manganese dioxides with acid pH either with satisfied cation exchange capacity (e.g.natural birnessite) or with no cation exchange capacity (e.g.pyrolusite).

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TABLE 2A

MANGANESE DIOXIDE SAMPLES - PHYSICAL AND PRINCIPAL CHEMICAL RESULTS

SAMPLE NUMBER	PARTICLE SIZE nm	RESIDUE +45u %	SSA	pH	Mn(IV) %	MnO2 %	THEOR. LOSS OF WEIGHT (O2)	EXPTL TOTAL LOSS OF WEIGHT	L.O.W. MOISTURE +LOW TEMP COMBINED WATER @ 120deg C	L.O.W. HIGH TEMP WATER + EXPTL LOSS	L.O.W. TOTAL WATER + EXPTL LOSS
1	243	5.6	79.5	4.4	57.1	90.4	8.3	12.0	1.8	1.9	3.7
2	195	18.3	77.5	4.4	59.8	94.6	8.7	12.0	2.2	1.1	3.3
3	210	6.3	31.0	4.7	58.4	92.4	8.5	11.4	1.0	1.9	2.9
4	295	0.1	67.8	9.3	54.7	86.6	8.0	14.0	1.9	4.1	6.0
5	253	0.1	78.8	9.4	55.1	87.2	8.0	12.0	2.0	2.0	4.0
6	224	0.0	81.5	9.2	55.5	87.8	8.1	12.3	2.2	2.0	4.2
7	204	0.1	79.9	8.8	55.8	88.3	8.1	12.1	2.4	1.6	4.0
8	156	13.9	91.5	4.3	57.3	90.7	8.3	12.0	1.1	2.6	3.7
9	180	17.6	81.6	4.0	56.7	89.7	8.3	12.6	2.3	2.0	4.3
10	820	0.8	2.9	5.1	57.9	91.6	8.4	8.5	0.0	0.1	0.1
11	460	0.0	18.9	8.5	49.4	78.2	7.2	11.5	0.8	3.5	4.3
12	755	0.1	20.5	9.2	49.2	77.9	7.2	12.9	1.9	3.8	5.7
13	268	32.5	30.0	5.8	57.6	91.2	8.4	12.2	0.8	3.0	3.8
14	ND	ND	3.7	6.3	55.1	87.2	8.0	9.2	0.0	1.2	1.2
15	491	ND	104.5	4.6	43.7	69.2	6.4	13.0	2.7	3.9	6.6
16	ND	ND	35.9	4.3	63.2	100.0	9.2	10.0	0.3	0.5	0.8
17	331	ND	72.3	ND	ND	ND		13.9	1.7	ND	ND
18	267	ND	69.4	ND	ND	ND		17.0	1.5	ND	ND
19	592	ND	117.7	10/12	46.9	74.2	6.8	10.7	3.5	0.4	3.9
20	524	ND	30.9	9/11	45.0	71.2	6.6	10.3	1.0	2.7	3.7
21	287	ND	143.6	4/6	46.3	73.3	6.7	18.0	6.0	5.3	11.3
22	ND	ND	31.6	5.7	ND	ND		12.7	1.6	ND	1.6
24	292	ND	27.7	11.2	51.2	81.0	7.5	14.0	1.6	4.9	6.5
25	<24u	ND	24.5	10.3	50.0	79.1	7.3	18.5	6.4	4.8	11.2
26	<39u	ND	25.9	10.5	49.8	78.8	7.3	17.6	6.4	3.9	10.3
27	<77u	ND	24.6	10.3	50.0	79.1	7.3	16.2	4.5	4.4	8.9
28	ND	ND			43.9	69.5	6.4	18.2	4.6	7.2	11.8
29	ND	ND			50.1	79.3	7.3	15.1	0.1	7.7	7.8

TABLE 2B

XRF DETERMINATION OF CATIONS PRESENT

Note: Values shown are relative heights of major peaks and have no other quantitative significance.

SAMPLE	Al	P	K	Ca	Ti	Cu
1	0	2.2	0	3.5	2.9	1.0
2	0.4	0.7	2.1	1.9	3.2	0.5
3	0.6	1.4	3.8	2.3	2.4	0.4
4	0.2	0.6	1.7	3.8	2.6	1.8
5	0.3	1.2	1.8	5.5	2.7	0.9
6	0.5	1.5	1.7	3.0	2.7	0.8
7	0.7	2.2	2.2	4.0	10.8	2.1
8	0.8	2.2	2.5	3.6	2.4	0.5
9	0.6	1.8	2.9	4.2	3.4	0.7

The test was of very limited value and no further samples were submitted to it.

TABLE 2C

MANGANESE DIOXIDE SAMPLES - ANIONS PRESENT

SAMPLE	Li2O %	Na2O %	K2O %	CaO %	MgO %	Ti ppm	Cu ppm	Co ppm	Pb ppm
1*	nd	0.1	0.05	0.06	0.07	nd	1	6	1
2*	nd	0.16	nd	nd	nd	nd	1	5	2
3	tr	1.19	1.92	nd	nd	5	15	5	50
4	nd	1.71	nd	nd	nd	nd	nd	nd	nd
5	tr	2.52	0.10	0.21	0.03	5	17	nd	nd
6	nd	1.93	nd	nd	nd	nd	nd	nd	nd
7	nd	1.25	nd	nd	nd	nd	nd	nd	nd
8*	nd	0.13	0.06	0.04	0.01	nd	nd	7	7
9*	nd	0.16	nd	nd	nd	nd	nd	nd	nd
10	0.01	0.03	0.17	0.54	0.39	97	1600	98	674
11*	nd	7.46	0.11	0.95	0.58	164	1422	64	1241
12*	nd	7.38	0.13	0.10	0.58	172	1276	60	1544
13	0.01	0.28	0.05	0.22	0.02	84	20	nd	nd
14	0.03	0.11	0.69	nd	nd	80	1450	110	1662
15	tr	0.36	4.29	nd	nd	nd	tr	nd	nd
16*	nd	tr	nd	tr	tr	nil	nil	nil	nil
17	tr	1.81	0.10	nd	nd	1	25	12	25
18	tr	1.98	0.12	nd	nd	12	25	12	12
19	0.42	3.65	3.65	nd	nd	124	12	12	12
20	1.53	4.10	0.58	nd	nd	644	25	62	12
21	0.09	0.58	2.32	nd	nd	50	12	12	50
22	tr	0.04	0.04	nd	nd	114	<25	<5	<50
24*	nd	8.56	0.04	0.09	0.03	nd	1	12	1
25				not determined					
26						do			
27							do		

TABLE 2D

THERMAL ANALYTICAL DATA FOR ALL SAMPLES

PROFILE OF CUMULATIVE PERCENTAGE LOSS OF WEIGHT AGAINST TEMPERATURE

SAMPLE NUMBER	ONSET OF LOSS OF WT. deg.C	TEMPERATURE in deg. C 120	200	300	400	500	550	600	625	650	ACTUAL END PT OF LOSS OF WT.
		PERCENTAGE LOSS OF WEIGHT									
1	37	1.8	3.0	3.6	4.6	6.2	9.0	12.0			575
2	35	2.0	3.4	4.4	5.3	6.9	12.7				546
2	49	2.5	3.5	4.5	5.7	9.4	11.3				527
3	51	1.0	2.0	3.2	4.2	7.2	11.8				525
3	66	0.7	1.4	2.0	3.0	3.4	4.5	11.0			584
3	r.t.	1.2	2.1	2.8	3.4	4.1	5.0	11.5			557
4	32	1.9	2.9	3.8	5.2	9.0	11.2	14.0			614
5	58	2.0	3.3	4.1	5.1	6.7	9.0	12.0			641
6	r.t.	2.2	3.2	4.3	5.5	6.8	9.0	12.3			637
7	28	2.4	3.8	4.5	5.6	7.0	9.2	12.1			611
8	61	1.1	2.1	3.2	4.3	5.8	8.6	12.0			591
9	32	2.3	3.5	4.6	5.6	7.6	9.8	12.6			573
10	456	0.0	0.0	0.0	0.0	0.2	0.5	1.1	7.2	8.5	650
10	584	0.0	0.0	0.0	0.0	0.0	0.0	0.6	3.4	8.0	657
10	293	0.0	0.0	0.1	0.9	1.1	1.9	4.0	7.3	9.0	645
11	110	0.4	2.0	4.1	5.9	8.0	8.6	9.3		12.0	654
11	95	1.2	2.0	3.9	5.2	7.9	8.2	9.3		11.0	653
12	80	1.4	2.8	4.0	6.0	8.0	8.3	9.4		11.0	654
12	83	2.4	7.5	8.8	10.0	12.2	12.9	13.9		14.8	637
12	91	1.8	5.0	6.4	8.0	9.9	10.2	11.2		12.8	645
13	51	0.8	1.7	3.2	5.0	7.2	11.0	12.2			652
14	428	0.0	0.0	0.0	0.0	0.4	1.0	2.7	6.7	9.2	634
15	30	2.9	5.4	9.0	9.9	10.5	13.0				550
15	64	2.5	4.2	8.6	10.0	11.0	14.0				550
16	143	0.0	0.5	0.7	1.1	3.7	10.0				550
16	70	0.5	0.8	1.1	1.6	3.9	10.6				540
16	80	0.4	0.7	1.0	1.5	3.0	10.0				560
17	37	1.7	2.5	3.6	5.0	8.3	10.8			13.9	632
18	45	1.5	2.8	4.0	6.2	10.0	13.0			17.0	616
19	r.t.	4.5	6.5	7.7	8.4	9.2	9.7	10.0		10.7	630
20	97	1.0	3.5	4.5	5.4	6.6	7.4	8.7		10.0	628
20	90	1.1	3.5	4.7	5.7	7.2	8.1	9.6		10.5	630
21	35	6.0	9.9	12.2	13.7	15.3	17.5	18.0			600
22	r.t.	1.6	2.5	4.3	5.6	8.8	11.5			12.7	580
24	75	1.6	7.0	8.6	10.2	11.7	12.5	13.0		14.0	647
25	35	8.4	11.5	13.3	15.0	16.4	17.1	18.0		18.5	632
26	r.t	6.4	10.6	12.1	14.0	15.3	15.9	16.9		17.6	642
27	r.t.	4.5	8.7	10.2	12.2	13.7	14.4	15.4		16.2	645
28	51	4.6	10.9	13.3	14.8	16.3	17.1	17.9	18.0	18.2	621
29	63	0.1	5.0	6.3	8.0	9.8	12.1	14.6	15.0	15.1	637

TABLE 2E

POWDER DIFFRACTION X-RAY DATA ON THE DIFFERENT FORMS OF MANGANESE DIOXIDE(excluding values of I/Io <5)

alpha-MnO2		beta-MnO2		gamma-MnO2		delta-MnO2		eta-MnO2			
CRYPTOMELANE		PYROLUSITE		NSUTITE						RANSDELLITE	
SYNTHETIC		SYNTHETIC		MINERAL SAMPLE		SYNTHETIC		SYNTHETIC		SYNTHETIC	
42-1348		24-0735		17-0510		18-802		12-141		44-0142	
MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io
6.94	14					7.20	80				
4.89	14										
						4.75	90				
								4.49	70		
				4.00	39b					4.04	100
								3.89	80		
								3.71	100		
3.09	61	3.34	95								
								2.83	55		
								2.69	70		
				2.59	13b						
2.44	25									2.56	46
						2.44	100	2.43	80	2.44	49
2.38	100	2.41	67	2.42	44						
								2.37	80		
										2.35	18
										2.33	30
				2.28	49b			2.26	10		
2.19	19									2.23	6
2.14	81	2.20	11	2.21	7						
				2.13	35	2.12	40b	2.12	90	2.14	34
		2.11	22								
				2.07	5			2.05	20	2.08	11
1.92	19	1.97	7								
								1.94	10		
1.82	90			1.90	12b					1.91	13
								1.80	10		
						1.67	10b	1.67	55		
1.63	33			1.64	100					1.65	57
		1.62	100					1.63	70	1.62	31
				1.60	46b						
		1.56	27								
				1.48	28b					1.47	22
		1.44	16	1.43	16	1.42	80b			1.43	20
		1.39	17								
				1.37	48b						
				1.34	15b						
		1.31	45								
		1.31	45	1.30	25b						
				1.26	8	1.27	10b				
		1.20	7	1.21	16						
				1.17	8						
		1.06	6								
		1.00	11								

TABLE 2F

POWDER DIFFRACTION X-RAY DATA ON DIFFERENT SAMPLES OF alpha-MnO2

CRYPTOMELANE SYNTHETIC		CRYPTOMELANE MINERAL SPECIMEN		CRYPTOMELANE MINERAL SPECIMEN		K2Mn8O16 CALCULATED PATTERN		HOLLANDITE MINERAL SPECIMEN	
42-1348		34-0168		20-908		29-1020		34-174	
MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io	MAIN dA	I/Io
		7.01	27						
6.94	14	6.90	29	6.90	90	6.94	26		
		4.98	35						
4.89	22	4.86	46	4.90	80	4.91	32		
		3.51	10					3.52	35
		3.45	11	3.45	10	3.47	11	3.46	35
		3.16	33					3.18	58
		3.13	77					3.14	100
3.09	61	3.10	79	3.10	80	3.10	68	3.10	98
		3.07	35					3.07	58
		2.46	24					2.76	11
2.44	25	2.43	22					2.41	73
		2.42	54						
		2.41	100						
2.38	100	2.40	78	2.39	100	2.39	100		
		2.34	10					2.24	11
2.19	19	2.20	22	2.19	20			2.20	25
								2.18	32
		2.17	36					2.17	24
2.14	81			2.15	60	2.15	18	2.15	29
1.92	19							1.97	14
								1.86	18
1.82	90			1.83	60	1.83	12	1.82	24
								1.67	21
1.63	33			1.64	30	1.64	12	1.62	20
								1.61	13
								1.55	23
				1.54	60			1.54	20
				1.42	40				
				1.35	50				
				1.29	20				

TABLE 2G

XRD ANALYSIS OF SELECTED SAMPLES

SAMPLE NUMBER	PHASES IDENTIFIED
1	PYROLUSITE OTHER PHASES NOT YET IDENTIFIED
3	NSUTITE OTHER PHASES NOT YET IDENTIFIED
4	NOT YET IDENTIFIED
8	NOT YET IDENTIFIED
9	BIRNESSITE OTHER PHASES NOT YET IDENTIFIED
12	PYROLUSITE,SODIUM BIRNESSITE,POTASSIUM BIRNESSITE,KMnO2,
13	NOT YET IDENTIFIED
14	PYROLUSITE,SODIUM BIRNESSITE,K3(MnO4)2 ,QUARTZ
16	PYROLUSITE
19	BIRNESSITE OTHER PHASES NOT YET IDENTIFIED
20	PYROLUSITE,KMn8O16,probably SODIUM BIRNESSITE,Na2Mn8O16
21	NOT YET IDENTIFIED
22	NOT YET IDENTIFIED
24	PYROLUSITE Mn7O13.5H2O possibly K2Mn4O8
28	SODIUM BIRNESSITE Mn7O13.5H2O small amounts (Na,K)Mn8O16.xH2O
SODIUM BIRNESSITE	SODIUM BIRNESSITE,trace phase MnO3
NAB2	SODIUM BIRNESSITE, small amounts Mn3O4 and/or Mn2O3

TABLE 2H

VISCOSITY & CURING DATA ON SELECTED MANGANESE DIOXIDE SAMPLES

CURING DATA

SAMPLE NUMBER	pH	CURING ABILITY	POT LIFE mins	WORK LIFE mins	TACK-FREE TIME days	CURE TIME
1	4.4	NIL	-	-	-	-
3	4.7	NIL	-	-	-	-
4	9.3	VERY RAPID	20	20/25	50	>50
7	8.8	VERY RAPID	35	nd	>7	nd
9	4.0	NIL	-	-	-	-
12	9.2	RAPID	80/180	80/200	1/14	14/30
14	6.3	POOR. NO FINAL CURE	>8000	>9000	>90	-
15	4.6	NIL	-	-	-	-
16	4.1	POOR. NO FINAL CURE	20	170	>90	-
19	10/12	VERY RAPID	<10	<10	nd	nd
20	9/11	VERY RAPID	<20	25	<14	<14
21	4/6	POOR	160	-	-	nd
24	11.2	RAPID INITIAL.V.SLOW FINAL	50	65	42	49
29	nd	POOR. NO FINAL CURE	120	-	-	-
SYN. Na BIRNESSITE	10.0	VERY RAPID	<10	<10	7	-

TABLE 2J

VISCOSITY OF MIXTURES OF SAMPLE 12 (RIEDEL-HAHN) AND 14 (NATURAL CRE)

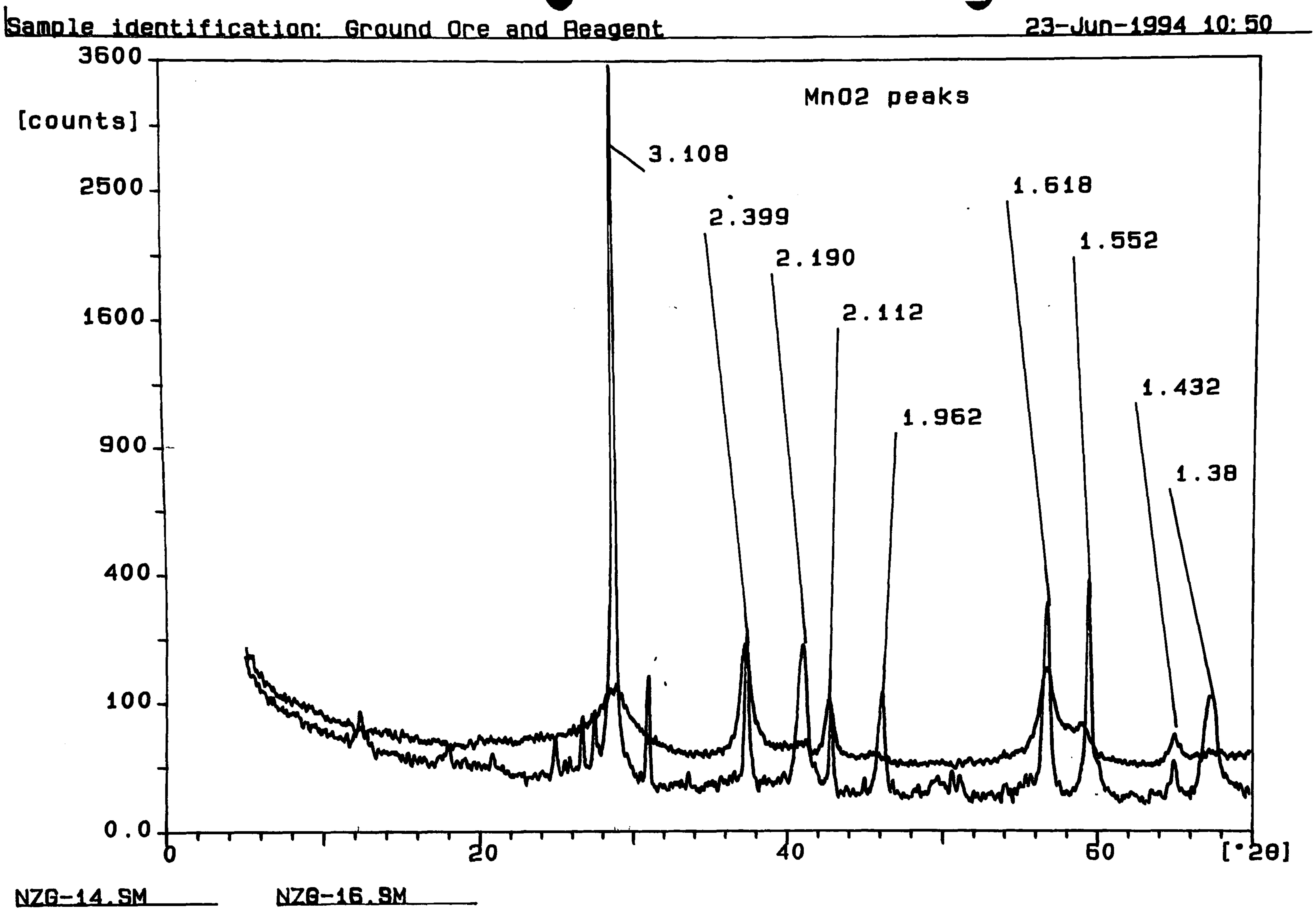
SAMPLE NUMBER	12	1205	1210	1220	1275	1280	1285	1290	1295	14	SAMPLE NUMBER
%12	100	95	90	80	25	20	15	10	5	0	%12
%14	0	5	10	20	75	80	85	90	95	100	%14
ELAPSED TIME											ELAPSED TIME
		VISCOSITY IN POISES									
10 mins					1512						10 mins
20		507	659	696	5560	1035	1012	894	688	270	20
30		579	672	4000	14240	2582	1830	1360	738	266	30
40	601	669	766	12320		7215	3034	1900	862	269	40
50	664	744	838	31000		16792	4992	2568	998	275	50
60	720	821	792				7408	3154	1072	278	60
70	761	872	890				10016	4182	1320	279	70
80	807	9509	3000				13256	4618	1272	281	80
90	1415	18560	21504					5674	1428	284	90
100	1603		30400					6338	1480	284	100
110	1965							7200	1560	281	110
120	2190							8198	1680	280	120
130	2671							9466	1752	281	130
140	3271							10970	1880	281	140
150	4211							12372	1960	280	150
160	5753								2060	552	160
170	7490								2088	614	170
180	9490								2212	630	180
3h 10	12088								2280	600	3h 10
3h 20	16648								2344	570	3h 20
3h 30									2420		3h 30
3h 40									2504		3h 40
5h									2944	560	5h
6 days										1480	6 days
1 week										3168	1 week
POT LIFE	105	70	70	25	15	20	20	32	150	>8600	1 week
WORK LIFE	210	85	85	40	<30	50	90	165	n.d.	>9000	
TACK FREE											minutes
TIME	<2WKS	<1WK	<1WK	<1WK	<1 DAY	<4DAYS	<6DAYS	1 DAY	>4DAYS	>9WKS	minutes
'URE TIME	<2WKS	<1WK	<1WK	<1WK	<3 DAYS	4DAYS	6DAYS	1 DAY	>4DAYS	>9WKS	
HARDNESS SHORE A	36	32	40	40	35	42	43	38	38		HARDNESS SHORE A

TABLE 2K

VISCOSITY OF MIXTURES OF SAMPLE 24 (SEDEMA EXPERIMENTAL) WITH NATURAL ORE

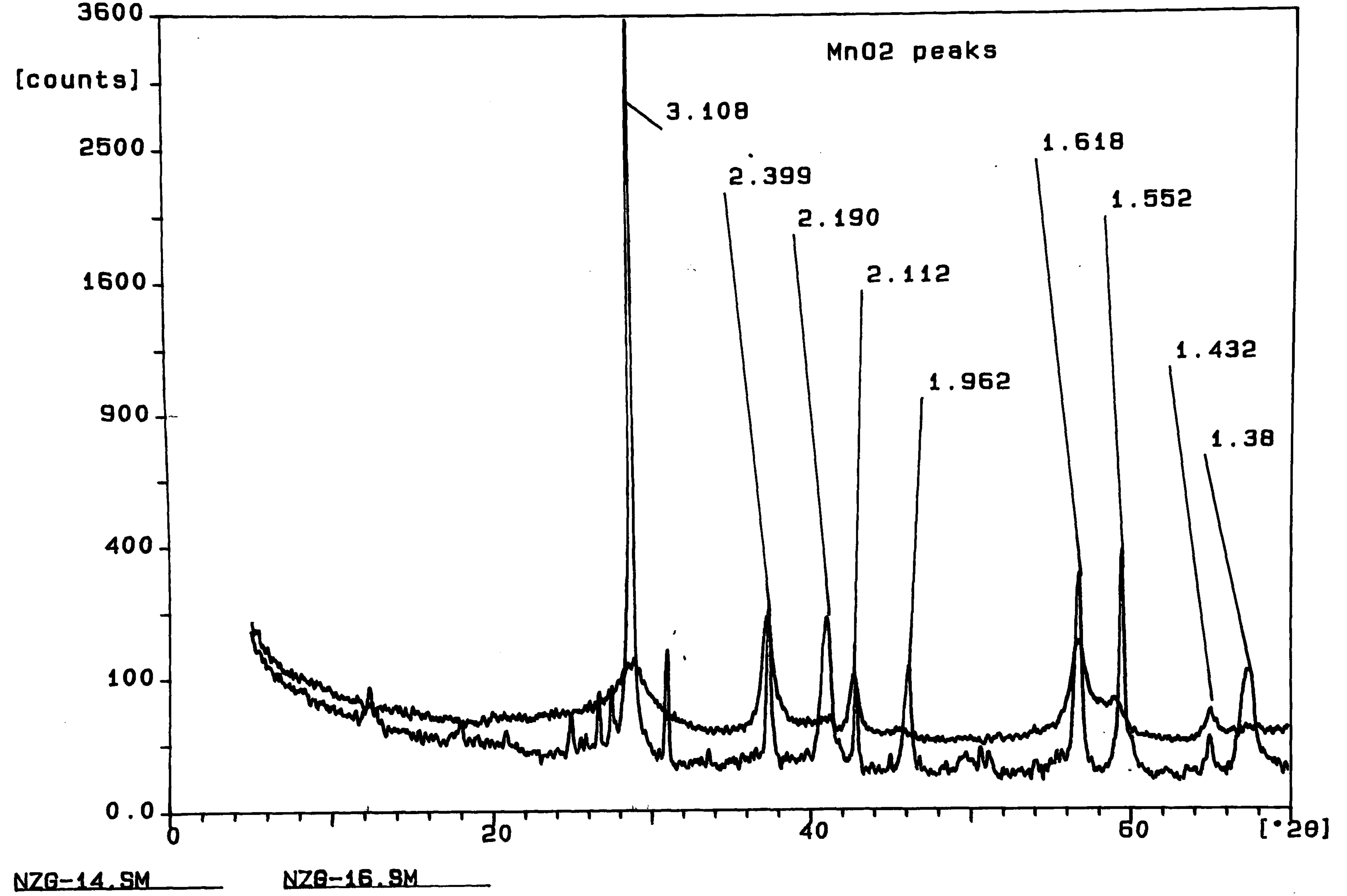
SAMPLE NUMBER	24	2420	2440	2440(2)	2450	2450(2)	2460	2480	2490	14	SAMPLE NUMBER
%24	100	80	60	60	50	50	40	20	10	0	%24
%14	0	20	40	40	50	50	60	80	90	100	%14
ELAPSED TIME	VISCOSITY in POISES										ELAPSED TIME
20	1253	1046	792	539	762	766	627	547	456	270	20
30	2952	1832	1344	864	1144	1166	909	691	526	266	30
40	6880	3208	2212	1600	1716	1772	1227	792	594	269	40
50	15384	5296	3380	4008	2400	2564	1672	939	632	275	50
60	22048	8400	5024	8880	3460	3620	1960	1059	656	278	60
70		12432	6960	19552	4480	5112	2384	1174	675	279	70
80		18400	9600		6040	6928	2864	1278	699	281	80
90			12912		8000	9280	3760	1480	723	284	90
100			17120		10432	12080	4376	1628	752	284	100
110					13600	16160	5192	1748	779	281	110
120					16032		6000	1800	808	280	120
130							7200	1908	838	281	130
140							8640	1964	864	281	140
150							10480	2060	872	280	150
160							12370		910	552	160
170							14688			614	170
180										630	180
3h 10										600	3h 10
3h 20										570	3h 20
5h										560	5h
6 days										1480	6 days
1 week										3168	1 week
POT LIFE	25	30	35	35	30	30	60	120	>160	860	POT LIFE
WORK LIFE	50	75	95	65	110	105	170	>150	>160	>9000	WORK LIFE
TACK FREE TIME	3WKS	>1WK	2WKS	>2 WKS	>5 DAYS	3 DAYS	>2WKS	>2WKS	>2WKS	>3 MTHS	TACK FREE TIME
CURE TIME	3WKS	>1WK	>2WKS	>2 WKS	8 DAYS	6 DAYS	>2WKS	>2WKS	>2WKS	>3 MTHS	CURE TIME
HARDNESS SHORE A	36	38	33	n.d.	38	39	n.d.	n.d.	n.d.	n.d.	HARDNESS SHORE A

APPENDIX 2


Sample identification: Ground Ore and Reagent
23-Jun-1994 10:50
MnO2 peaks
3600
[counts]
2500
1600
900
400
100
0.0
0
20
40
60
[°2θ]
3.108
2.399
2.190
2.112
1.962
1.618
1.552
1.432
1.38
NZG-14.SM
NZG-16.SM

APPENDIX 2 Page 2

Sample identification: Ground Ore and Reagent 23-Jun-1994 10:50



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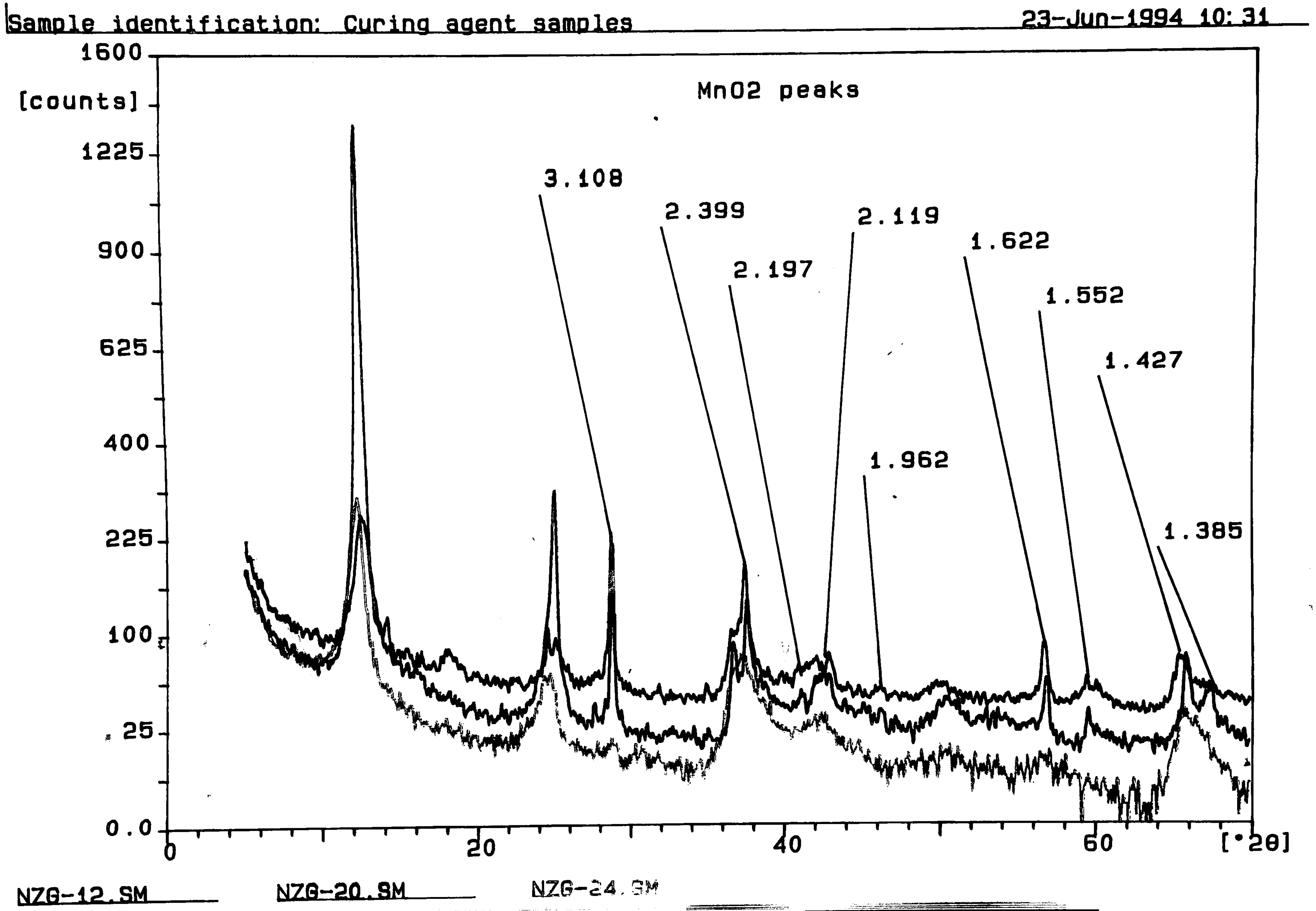


CHAPTER 3

THERMAL DECOMPOSITION OF POTASSIUM CHLORATE

3.1 In order to use the catalytic decomposition of potassium chlorate as a test for manganese dioxide activity it was necessary to understand fully the nature of the decomposition of potassium chlorate. This chapter describes the work carried out in the present study on the decomposition of potassium chlorate.

Potassium Chlorate, $KClO_3$, has a molecular mass of 122.55 and a density of 2.33g/cc. The room temperature crystals are monoclinic and a transformation to an orthorhombic phase at 250°C has been reported. (15) The material melts at 357°C and decomposes at temperatures above this (1) . There is, however,no general agreement on the exact nature of the decomposition reactions. In the presence of manganese dioxide this decomposition occurs at a much lower temperature.

Potassium Chlorate is used in the manufacture of safety matches, weedkillers and fireworks and generally as an oxidising agent.

3.2 Literature Survey

There are a number of reports on the study of the thermal decomposition of potassium chlorate in the literature.Brown et al (3 & 4) found that there was practically no decomposition of pure $KClO_3$ at temperatures up to 400°C using what they describe as "the best $KClO_3$ commercially available".

Farmer & Firth(5) reported 85/90% decomposition between 480 and 540°C the percentage varying with the composition of the reaction vessel.

Otto & Fry(6) described the thermal decomposition in terms of three reactions:-

$$4KClO_3 \longrightarrow 3KClO_4 + KCl \qquad \text{(i)}$$

$$2KClO_3 \longrightarrow 2KCl + 3O_2 \qquad \text{(ii)}$$

$$KClO_4 \longrightarrow KCl + 2O_2 \qquad \text{(iii)}$$

They suggested that (iii) takes place at higher temperatures and that KCl is a catalyst for reaction (i). For $KClO_3$ to which no KCl is added they obtained the following data:-

25% $KClO_3$ is decomposed after 24 hours at 409° C

52% $KClO_3$ is decomposed after 6 hours at 460° C

76% $KClO_3$ is decomposed after 1.75 hours at 492° C

78% $KClO_3$ is decomposed after 1.5 hours at 506° C

Details of their results in the presence of KCl are given in par.4.0 of Chapter 4.

Glasner & Weidenfeld(7) measured the decomposition of $KClO_3$ in terms of the oxygen evolved as a function of time at various temperatures and found:-

2.9% decomposition after 200 minutes at 455° C

29% after 200 minutes at 506° C

59% after 200 minutes at 527° C

65% after 70 minutes at 552° C

95% after 40 minutes at 575° C

They concluded that :-

(1) the reactions were :- $2KClO_3 \longrightarrow 2KCl + 3O_2$ (iv)

$4KClO_3 \longrightarrow 3KClO_4 + KCl$ (v)

and (2) they occurred consecutively rather than simultaneously.

Markowitz et al(8) studied reagent grade $KClO_3$ dried at 110° C by following its decomposition thermographically under dry Argon with temperature increasing at 4° per min. They found the melting point of the pure chlorate to be 357° C; the onset of decomposition to be 472° C and the decomposition to take place in two exothermic steps at about 560 and 600° C.

When they heated the chlorate isothermally at 370° C for 2 days under dry Argon they obtained only 0.44% decomposition.

Rudloff & Freeman(9) used 99.5% reagent grade $KClO_3$ and found no significant differences in their results when the material had been recrystallised or between crushed and uncrushed material. They reported results of investigations carried out under air, unpurified oxygen, oxygen purified over a molecular sieve, oxygen purified over a molecular sieve and then moistened, unpurified nitrogen, and nitrogen purified over a molecular sieve. Although DTA peak heights varied under the different conditions their positions did not change significantly. They found that with uniform heating at 10 deg/min pure $KClO_3$ starts to decompose at 500° C in a two step decomposition with the first step completed at 565° C and giving 15% decomposition measured by weight loss and the second step completed at 650° C

The results they obtained with isothermal heating were:-

33% decomposition	after 90 minutes at 480° C
50%	after 35 minutes at 560° C

65% decomposition after 50 minutes at 560° C

50% after 10 minutes at 590° C

90% after 30 minutes at 590° C

Their conclusions were :-

1. that the decomposition reactions are irreversible with respect to O_2

2. that $KClO_3$ decomposes in at least two steps, the first involving disproportionation with an oxygen transfer from one ClO_3^- anion to a neighbouring anion. They suggested that the products of this transfer will be $KClO_4$. which is relatively stable and a hypothetical intermediate $KClO_2$ which is very unstable and decomposes to form KCl and O_2 thus:-

$2KClO_3$ --------> slow $KClO_4$ + $KClO_2$ (vi)

$KClO_2$ --------> fast KCl + O_2 (vii)

giving

$2KClO_3$ --------> $KClO_4$ + KCl + O_2 (viii)

They reported that at higher temperatures the intermediate $KClO_4$ seemed to decompose in two ways:-

$2KClO_4$ -------> $2KClO_3$ + O_2 (ix)

$2KClO_3$ -------> 2KCl + $3O_2$ (x) giving

$KClO_4$ -------> KCl + $2O_2$ (xi)

Rudloff and Freeman(10) give the following thermal data obtained from studies with pure $KClO_3$:-

Melting Point	360° C
Initial decomposition	515° C
25% decomposition	580° C

50% decomposition	595° C
Final decomposition	622° C

Solymosi(11) studied the decomposition of chlorates generally and stated that *"a characteristic of alkali metal chlorates is the great temperature difference between their Melting Points and the initial temperature of their decomposition"* . He quoted from Markowitz et al(8) that a sample taken just before the first exotherm at 566° C gave $KClO_3$ 0.9% ; KCl 33.9% and $KClO_4$ 65.5% from which he deduced that 12.1% of the sample is KCl and 87.9% is $KClO_4$. He assumed from this that the first exotherm found on a DTA trace is due to two simultaneously occurring reactions:-

$$2KClO_3 \longrightarrow 2KCl + 3O_2 \qquad \text{(xii)}$$

$$4KClO_3 \longrightarrow 3KClO_4 + KCl \qquad \text{(xiii)}$$

and he asserted that the second exotherm represents the decomposition of the perchlorate formed in reaction (xiii).

In 1994 Cannon and Zhang(13) claimed that the onset temperature of the decomposition of $KClO_3$ is difficult to determine unambigously; they therefore used the 50% decomposition temperature for comparing sets of experimental results and they reported that the 50% decomposition temperature for $KClO_3$ was 600° C.

In 1995 Shimada[14] investigated the thermal decomposition of potassium chlorate by simultaneous Thermosonimetric- Differential Thermal Analytical(TS-DTA) measurements and high temperature microscopic observations. "Thermo- sonimetry" is the analysis of acoustic emissions resulting from chemical reactions. Shimada used a system that permitted the simultaneous measurement of thermosonic emissions and DTA while heating $KClO_3$ through its melting and decomposition stages. At the same time changes in the sample were observed using a high temperature optical microscope. Although Shimada reported that melting was seen to commence "around 340° C " the peak of the DTA curve in his paper occurs at about 368° C. He concluded that TS evidence points to the onset of decomposition at about 380° C in contrast to his own DTA value of 530° C and 500° C from TG data.

3.2.1 RESUME OF PUBLISHED WORK

Although a number of studies have been carried out on the thermal decomposition of $KClO_3$ there is no general agreement on the specifics of the decomposition parameters. The temperatures at which 25% decomposition occurs have been reported to have various values in the range 409 - 606° C with the reported values for 50% decomposition in the range 460 - 622° C. There is also no consistency in the data reported for isothermal decomposition studies. It was therefore clear that, if the thermal decomposition of $KClO_3$ was to have any value in assessing the effectiveness of catalysts such MnO_2, a better understanding of its thermal behaviour was required.

3.3 OUTLINE OF THE WORK ON THE THERMAL DECOMPOSITION OF $KClO_3$

3.3.1 RAW MATERIAL

Three grades of potassium chlorate were used in the present study viz:- (1) a 98% minimum grade supplied by ALDRICH; (2) a 99.5% grade supplied by FLUKA; and (3) a 99%

product supplied by ALFA (Johnson & Matthey). Three sources were chosen to reduce the possibility that any experimental results were sample specific. Analytical data for the samples provided by the suppliers were as follows:-

	ALDRICH	FLUKA	ALFA	
DESIGNATED AS:-	98%	PURE	JM	
& SPECIFIED AS:-				
not less than	98%	99.5%	99%	$KClO_3$
and containing:-				
Total N		< 0.0005%		
Bromate		< 0.010%		
Chloride		< 0.001%	< 0.05%	
Sulphate		< 0.02%		
As		< 0.00005%		
Ca		< 0.002%		
Cd		< 0.0005%		
Co		< 0.0005%		
Cu		< 0.0005%		
Fe		< 0.005%	< 0.005%	
Mg		< 0.001%		
Na		< 0.01%		
Ni		< 0.0005%		
Pb		< 0.0005%	< 0.005%	
Zn		< 0.0005%		

3.3.2 TECHNIQUES USED

All the initial investigations were carried out using the technique of Dynamic Thermogravimetry (TG and DTG) and Differential Thermal Analysis (DTA) described below. However when a thus far unrecorded structural change was identified the investigation was extended to include Differential Scanning Calorimetry and High Temperature X-Ray Powder Diffraction .

Thermal Analysis

This term is used to describe the analysis of the dynamic behaviour of a material submitted to controlled heating or cooling during which chemical and physical changes in the material resulting from such heating (or cooling) are examined. The changes may include loss of physisorbed or combined water, phase changes and chemical decomposition. The procedure allows for the measurement of parameters such as weight loss, rate of weight loss and enthalpy changes which are constantly measured and recorded as functions of temperature and time.

The techniques of measuring weight loss and rate of weight loss are known as Thermogravimetry (TG) and Differential Thermogravimetry (DTG) respectively and are usefully employed to assess the progress of decomposition of a material during heating. This includes loss of physisorbed water, water of hydration, breakdown of hydroxides, and decomposition of the substance with evolution of gaseous products. A typical TG - DTG trace is shown in Fig 3.1

The assessment of enthalpy changes is achieved by measurement of the temperature of the sample being investigated and a reference sample of a material which is inert at the temperature of the experiment and recording of the difference between these two measurements. This technique is known as Differential Thermal Analysis (DTA). Thus during constant rate heating, if the sample undergoes a phase change involving an energy change it's temperature will rise or fall differentially in comparison with the reference material depending on whether energy is absorbed or evolved as a result of the change. If the phase change involves an endothermic reaction the sample will absorb heat during the phase change and its temperature will either not rise or rise at a lower rate than the reference material; conversely if the phase change is exothermic the sample temperature will rise more rapidly than that of the reference. The recorded trace in the endothermic case will thus show a dip and in the exothermic case, a rise. The area under the dip or rise provides a measure of the energy absorbed or emitted by the phase change.If there is no loss of weight involved in this phase change the DTA trace will provide the only thermo-analytical evidence of the change. Fig. 3 - 2 shows an idealised DTA trace of an endotherm and exotherm.If there is a concurrent loss of weight then both the TG -DTG and the DTA traces will record the event. In addition to these sharply defined phenomena,differences between the Heat Capacities of the sample and reference material will result in differences in the temperatures of the two materials developing and these will show as gradual changes in the slope of the DTA curve. The combination of TG and DTA measurements in one instrument eliminates the need to transpose the TG -DTG data on to a DTA trace or vice-versa.(Fig. 3-2a)

DTA-TG studies in the present work were carried out on a Stanton Redcroft 780 combined Differential Thermal Analyser and Thermogravimeter which simultaneously records changes in mass (TG), rate of change of mass (DTG), temperature and differential temperature (DTA).The instrument consists of a microbalance one arm of which is suspended in an electric furnace. Two platforms are fitted to this arm and each accommodates a crucible

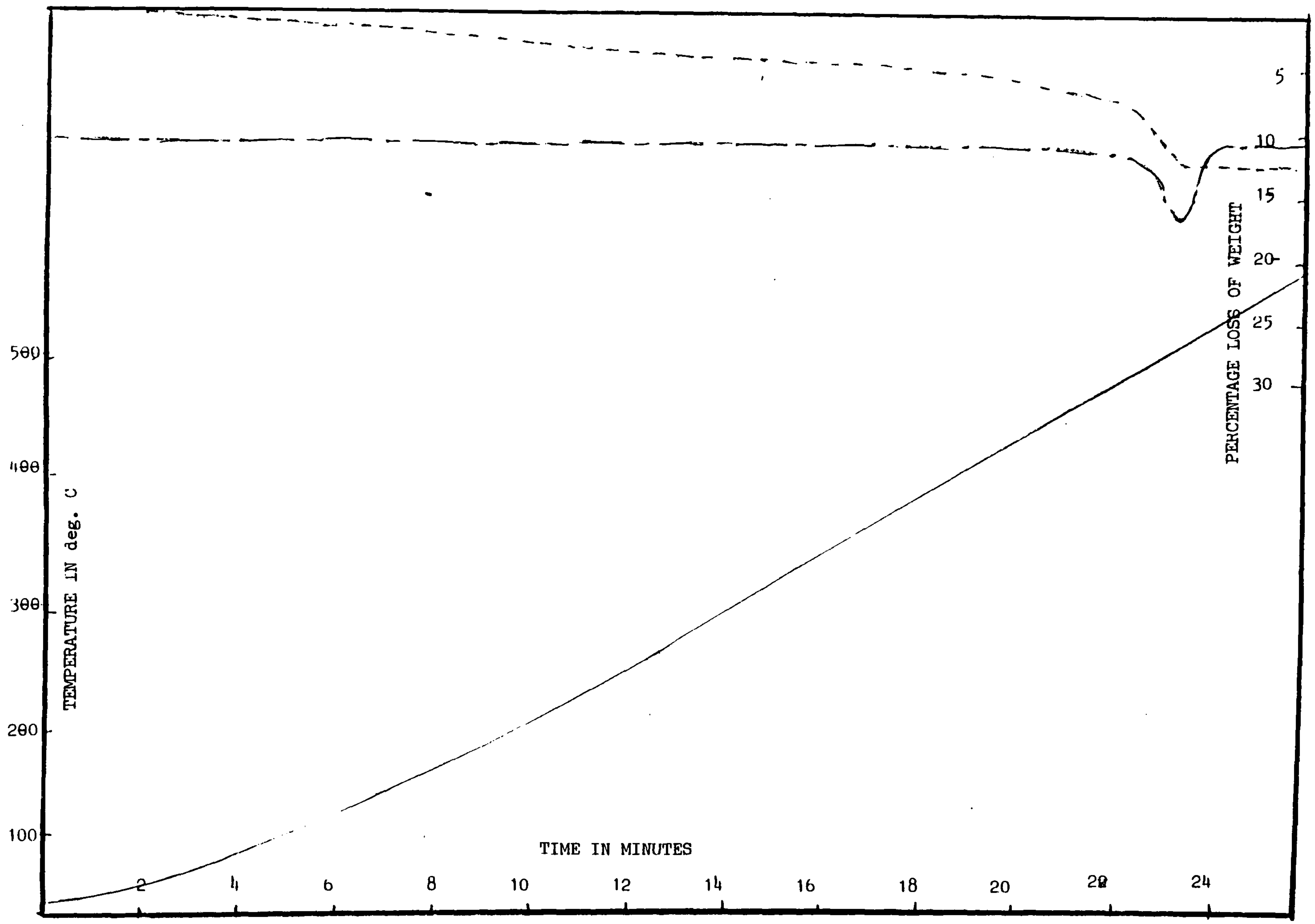


Fig. 3-1

Typical TG - dTG

Thermogram showing

TEMPERATURE _____

LOSS OF WEIGHT ------

RATE OF L. O.W.____ _

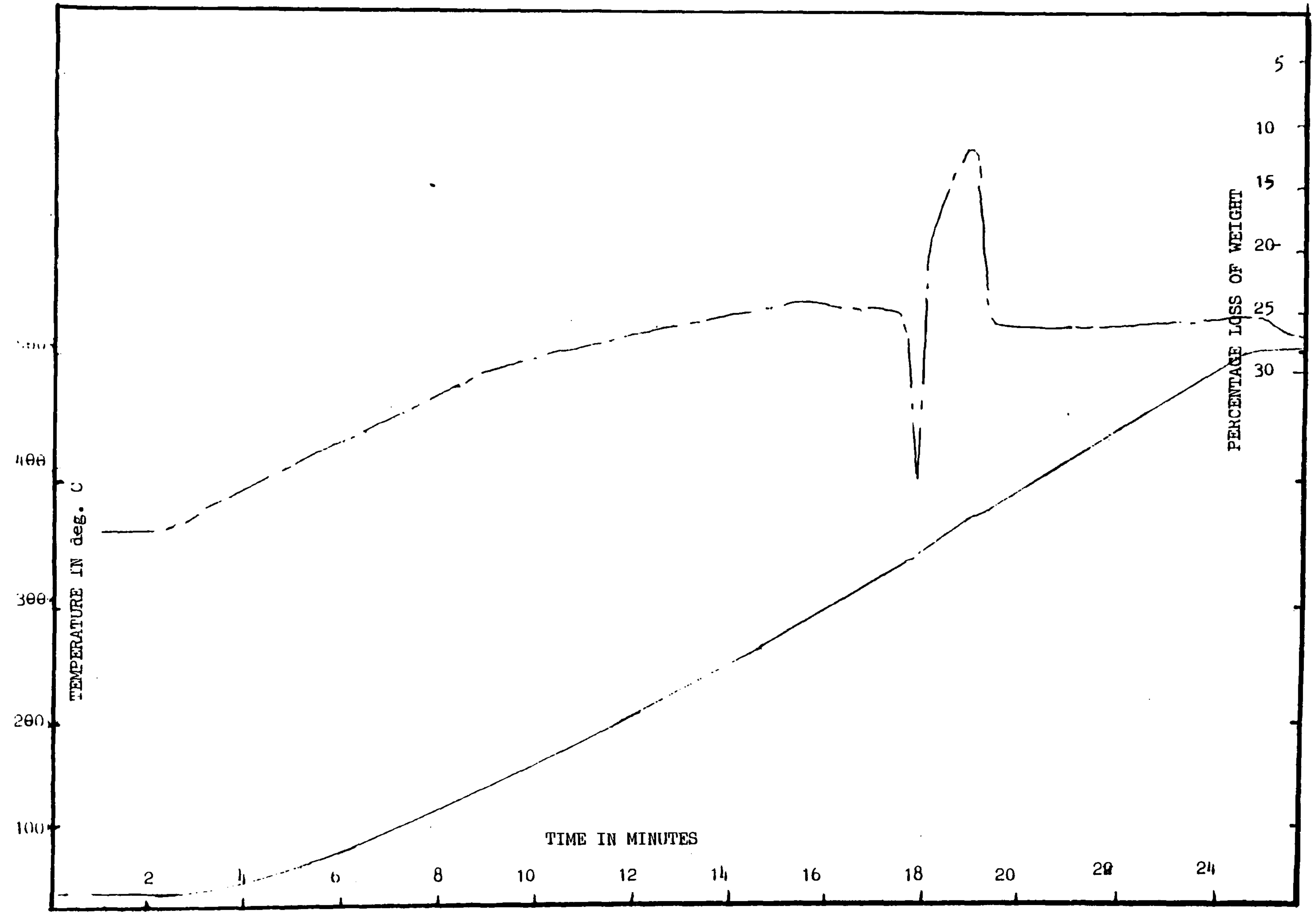
Fig. 3-2

Typical TEMP - D.T.A.

Thermogram showing

TEMPERATURE _____

D.T.A. — — — — — —



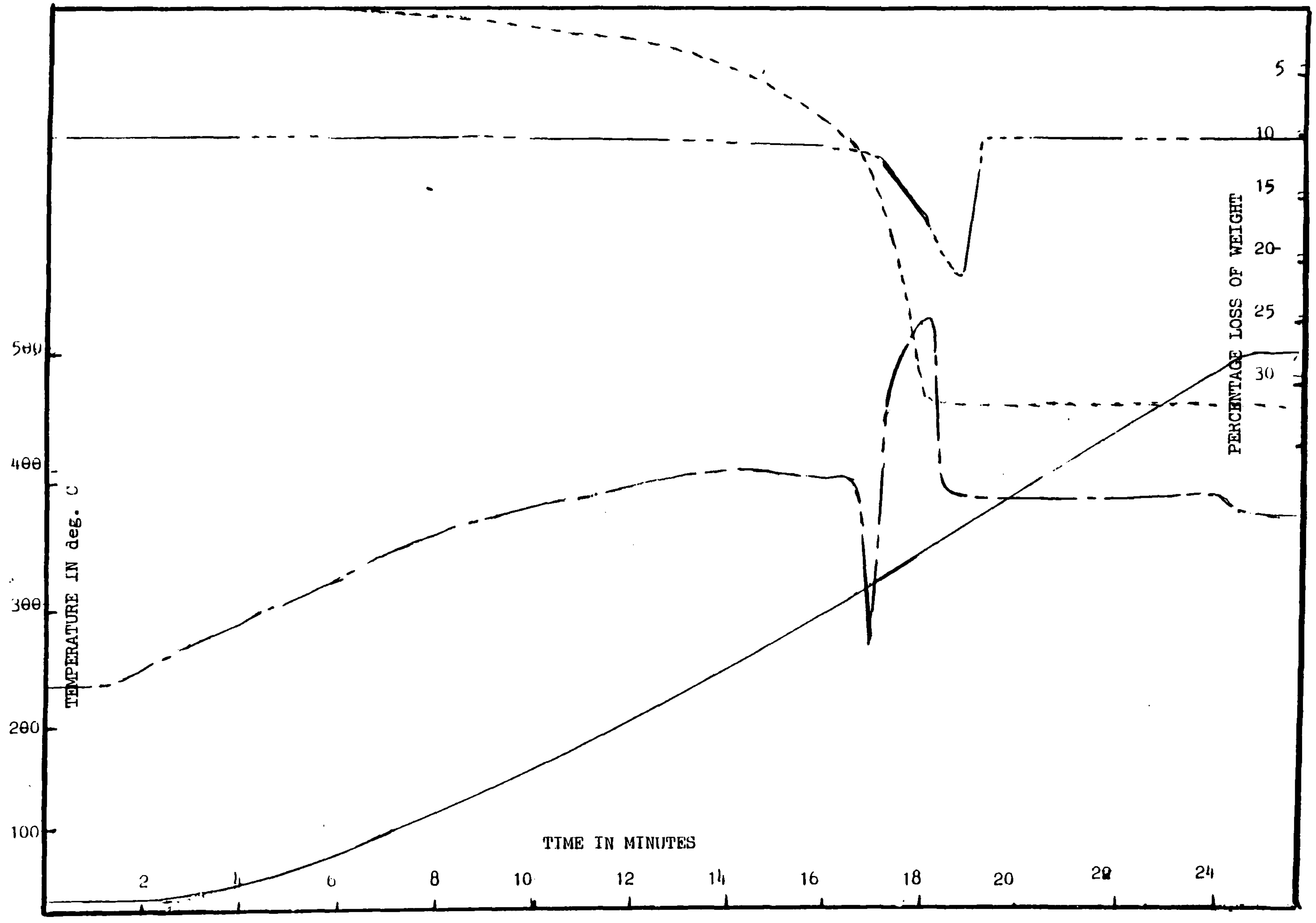


Fig. 3-2a

Typical Combined

TG.dW/dT - D.T.A.

Thermogram showing

TEMPERATURE ____

D.T.A. ____ _ _ ____ _ _

L.O.W.----------------------

dW/dT____ _ _ _ ____

fitted with a thermocouple. The furnace can be lowered to expose the crucibles for loading and raised to heat the crucibles and contained samples. A separate thermocouple records the furnace temperature.A facility is provided for purging the furnace atmosphere with a selected gas such as oxygen,nitrogen,argon etc. One crucible is loaded with the sample under investigation; the other with a material which is inert under the temperature conditions of the experiment such as ,in this case, aluminium oxide.

The furnace is fitted with a controller which permits it to be heated at a specified rate or, if required, to be held at a pre-determined temperature to investigate reactions under isothermal conditions. All measured parameters are recorded on a chart-recorder the X axis of which is time based.

The facilities available enable the measurements described above to be made as the sample is heated (or cooled) . However there are limitations to the interpretation of the data obtained. The information yielded by this technique alone is total weight loss and where the loss of weight may be due to the combined evolution of water, oxygen and/or other gases the method cannot differentiate between the weight losses due to each of the individual gases being evolved in a single stage. To identify evolved gases recourse must be had to more sophisticated DTG - DTA equipment which has a facility for handling and identifying evolved gases. It is also possible for phase changes to occur that are not readily identifiable and which will require substantiation by other methods such as Differential Scanning Calorimetry and XRD.

All the thermal analysis experiments were carried out in a stream of nitrogen. Most were carried out in aluminium crucibles; to eliminate the possibility that the aluminium was taking part in the reaction a platinum crucible was used for a number of runs: no differences were found between the results for Aluminium and Platinum crucibles. There was frequently a loss due to spattering. To avoid this the use of crucibles with lids was adopted.

In general, samples were heated at a constant rate of 10° C per minute to a maximum of about 630° C. Some experiments were conducted with isotherms interposed at specific temperatures. In these cases the isotherm temperature was held until reasonably constant weight was reached; thereafter the temperature was raised at a uniform rate of 10° per minute to the next isotherm or to the maximum temperature.

Cyclical experiments were conducted in a platinum crucible with heating and cooling cycles at or near the melting point of the $KClO_3$ to probe the occurrence of a reversible change at about 340° C.

Differential Scanning Calorimetry. This method also uses the concept of controlled heating and weighing of a test sample and an inert reference sample but in this case energy input is the controlling parameter .Data are derived by controlling measuring and recording the electrical energy input required to maintain constant temperature between the sample and the reference material while both are heated (or cooled) either at a controlled constant rate or isothermally .Thus, if there is an endothermic change in the sample a higher energy input into the sample is required in order to maintain parity of temperature and that energy input is monitored and recorded as a peak on the chart. An exothermic change will result in a need for a reduced energy input to the sample and this is shown as a trough in the DSC trace. The area under the peak (or trough) provides a measure of the heat input (or output) of the recorded reaction.

The DSC equipment used in this work was a Perkins-Elmer Thermal Analyser TAC7/DX . The instrument consists of two separate self-contained calorimeters one of which contains the sample and the other the reference material. The aluminium sample pot is fitted with a crimped lid with a hole to allow escape of evolved gases. The system is computer controlled and a heating , cooling or combined heating/cooling program is set up. When an endo- or exothermic change occurs in the sample, power is applied to (or removed from) one or both calorimeters to compensate for the energy change. The system is maintained in a thermally "null" condition throughout. The power supplied is of course directly proportional to the energy change and is monitored and recorded. Peaks showing endotherms and troughs showing exotherms are plotted on a chart recorder and a computer interface is programmed to calculate the energy input/output within the area of each peak or trough. Weight and changes in weight are monitored and recorded and from these data the computer program calculates Heats of Reaction and Heats of Formation.

High Temperature X-Ray powder Diffraction

In order to confirm a structural change which , it is suspected, occurs on heating a material and reverses on cooling it is necessary to carry out X-Ray Powder Diffraction measurements on the material during the heating cycle and at the temperature at which the change is expected to occur.

In order to achieve this a conventional X-Ray Diffractometer equipped to investigate the crystal structure of powdered materials is fitted with a High-Temperature Camera in which the sample is accommodated in a heating block fitted with a thermocouple. The heating block is attached to the goniometer within which it rotates. The whole assembly is enclosed and tests can be carried out under vacuum, in air or in an inert gas atmosphere at precisely controlled temperatures.

The data reported in this work was obtained in the Karlsruhe Laboratories of the associated company of Siemens plc. The equipment was a Siemens D5000 Powder Diffractometer with the following general configuration:-

Goniometer	D5000 Theta/Theta
Measurement circle	435 mm
Tube	2.2 kW Cu long fine focus
Divergence slit	0.27°
Soller slit	2°
K-alpha 2 filter	Nickel
Detector	OED Braun Scan Modus
Canal	0.019°
Generator	K760-80, 40kV, 30mA
Measurement time	15secs/1° = 7500 secs/scan

The Diffractometer is linked to a computer which records all relevant data. A Siemens software program DIFFRAC AT operates the system.

For the high temperature measurements the D5000 was fitted with a HTK10 High Temperature camera manufactured by Anton Paar. This is fitted to the goniometer and enables X-ray studies to be carried out up to 1600° C at incident angles from 4 to 164° values of 2θ. The sample is supported on a platinum matrix.

3.3.3 EXPERIMENTAL RESULTS

3.3.3.1 THERMAL ANALYSIS

CONSTANT RATE HEATING

Table 3A contains details of the temperatures at which thermal events occurred in the 18 constant rate heating experiments, 9 of these using the Aldrich grade; 8 the Fluka grade and 1 the Alfa grade. Data on the decomposition (measured by loss of weight) and reaction rates of the three well defined reactions which occur during decomposition are given in Table 3B. These three reactions are shown at points A ,A1, and B in Figs. 3-3 and 3-4. The reaction rates are expressed in moles O_2 produced per minute x 10^3 it being assumed that any loss of weight after initial drying is entirely due to the evolution of O_2.

ISOTHERMAL HEATING

Details of the experiments in which the potassium chlorate was heated to a specific isotherm and held there until reasonable constancy of weight was achieved are shown in Table 3C and Fig. 3-5. It was noted that upwards of 75% decomposition occurs at 370° C.

3.3.3.2 DISCOVERY OF A NEW PHASE

When the samples were heated at a uniform rate in a stream of nitrogen a small endothermic "blip" showed almost invariably at about 340° C. No mention of this was found anywhere in the literature although the occurrence is visible in one diagram in the Rudloff paper (9). At first this was thought to be an instrument aberration. However its regular appearance and, in some cases, greater signal strength justified further investigation. It was found to occur in samples of all three commercially available grades of $KClO_3$ and to be independent of the material of construction of the crucible used in the thermal analysis. This newly observed thermal phenomenon occurred at an average temperature of 341° C.(i.e. below the Melting Point of the potassium chlorate) in 14 of the 18 experiments carried out. There was no weight loss associated with this thermal feature.The endothermic "blip" is clearly shown in Figs.3-3 and 3-4. The existence of the endotherm at about 340° C was also noted in the isothermal heating experiments recorded in Table 3C.(Fig. 3-5)

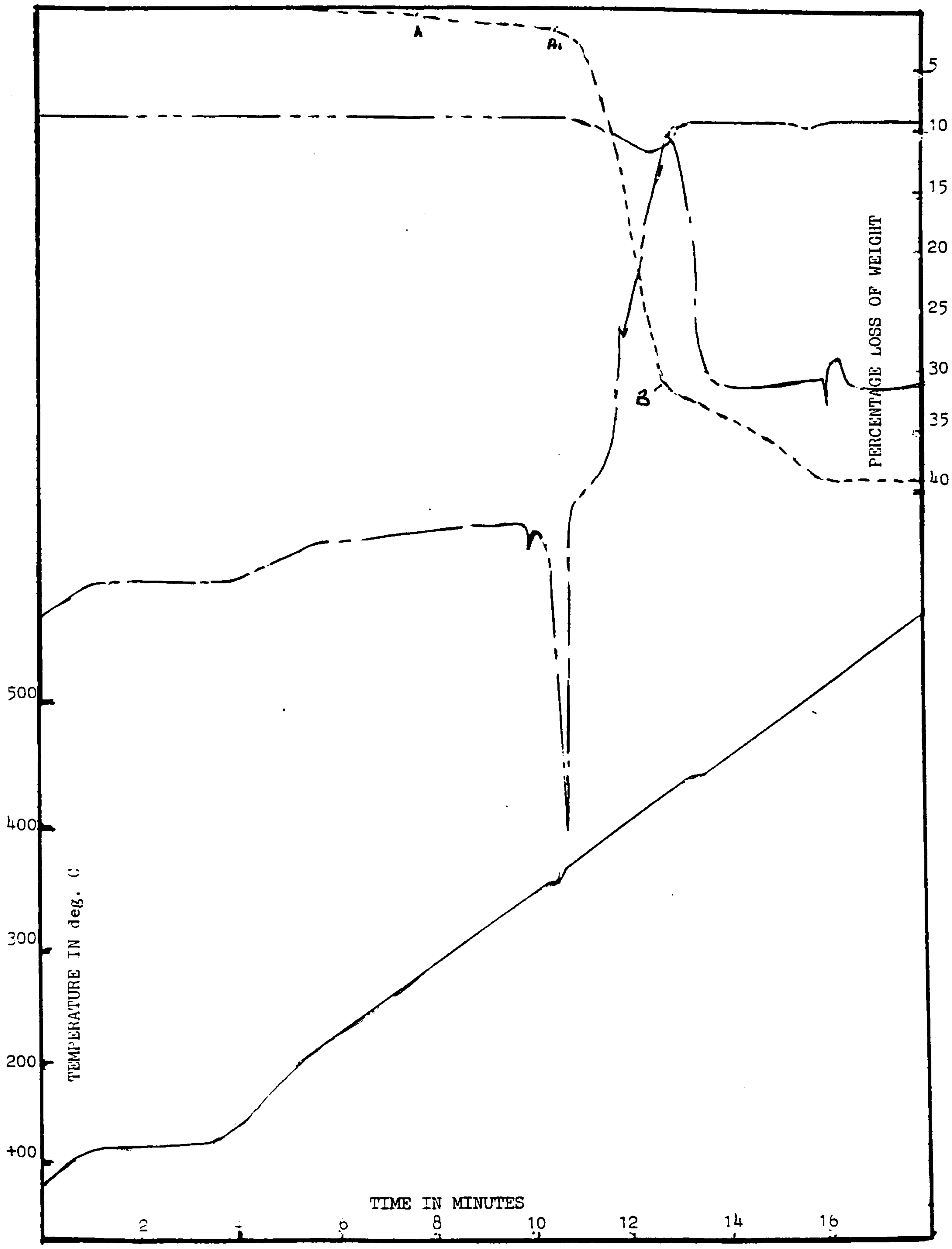


Fig. 3-3 Thermal decomposition of 98% potassium chlorate TEMPERATURE _____

D.T.A. ___ __ ___ __ __

L.O.W.-----------------------

dW/dT_____ __ __ _____

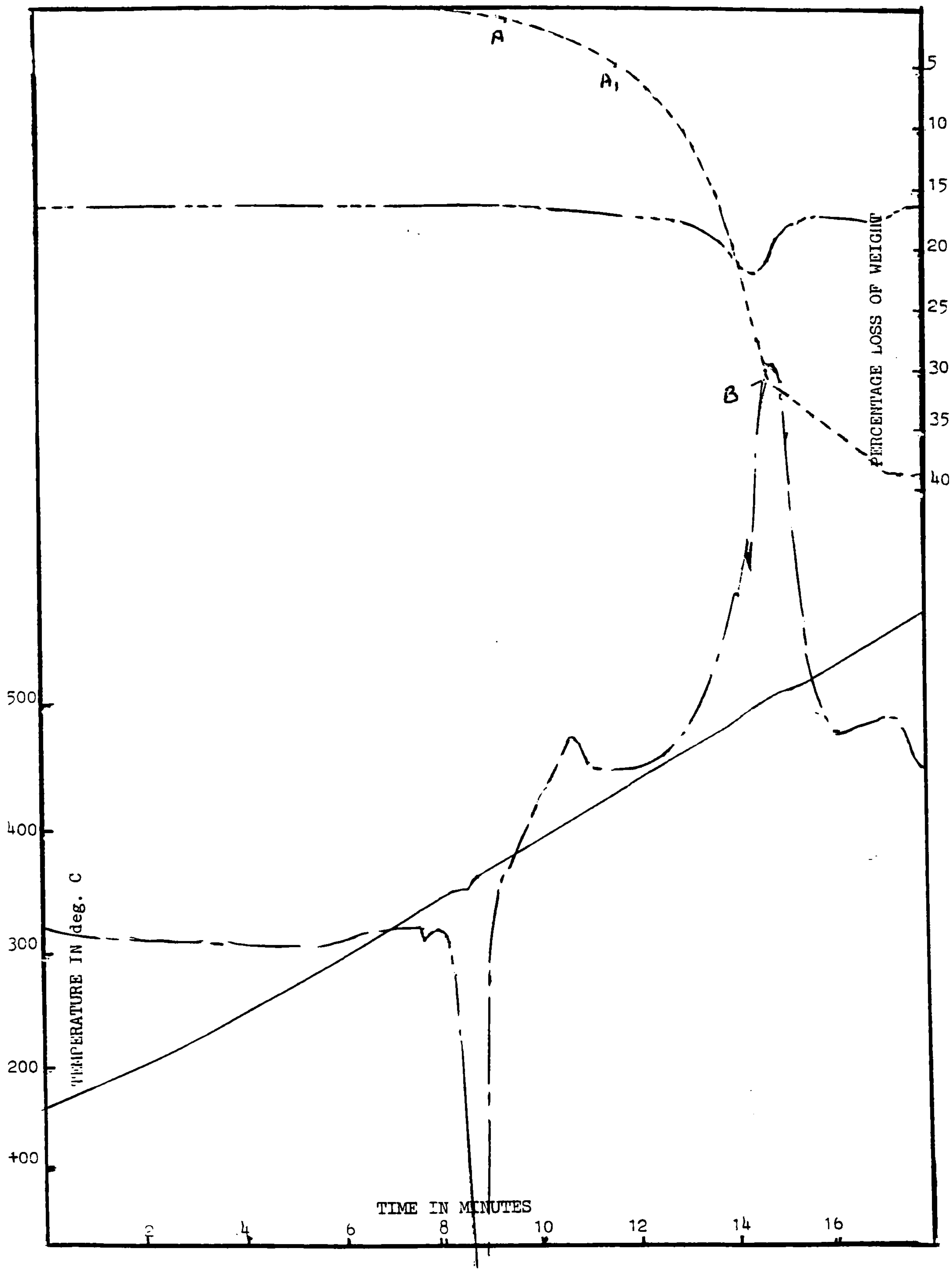


Fig.3-4 Thermal decomposition of pure potassium chlorate TEMPERATURE ____

D.T.A. __ __ ____ __ __

L.O.W.------------------------

dW/dT____ __ __ ______

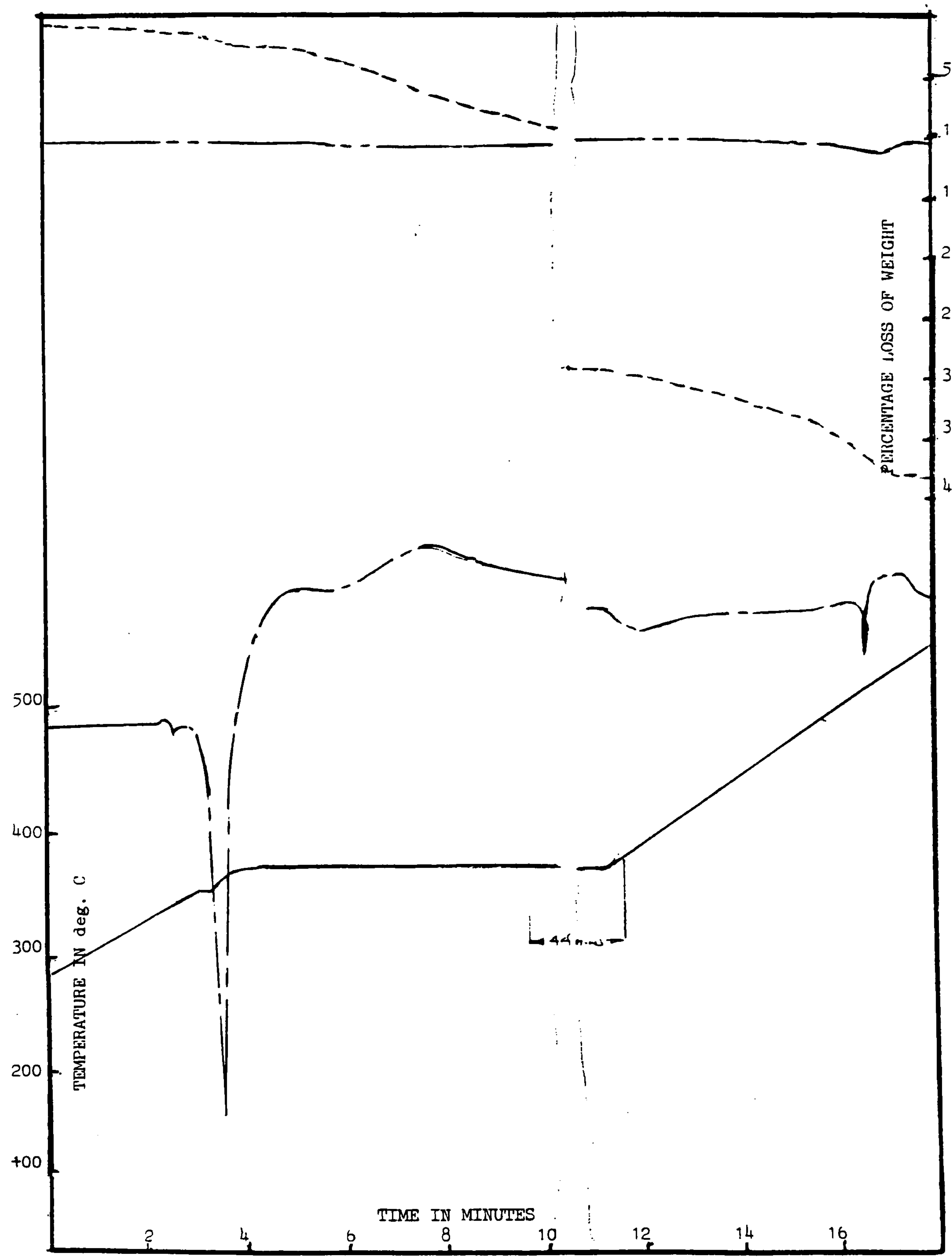


Fig.3-5 Isothermal decomposition of pure potassium chlorate TEMPERATURE _____

D.T.A. ___ _ _____ _ __

L.O.W.----------------------

dW/dT___ _ _ _ ____

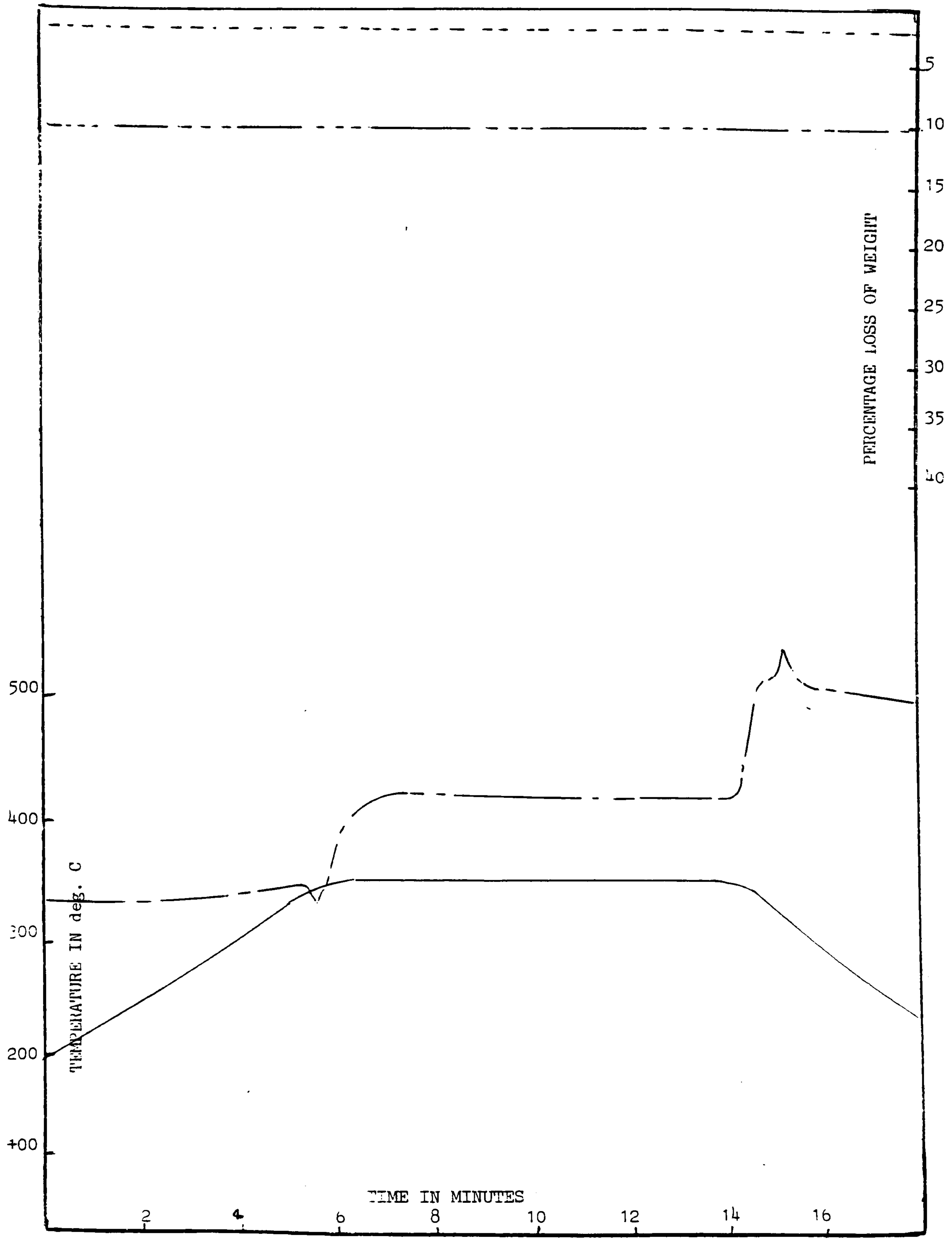


Fig. 3-6 showing one heating and cooling cycle to and from 355° C for pure potassium chlorate.

TEMPERATURE ________ D.T.A. ____ _ ____ L.O.W. --------- dW/dT____ _ _ _ ____

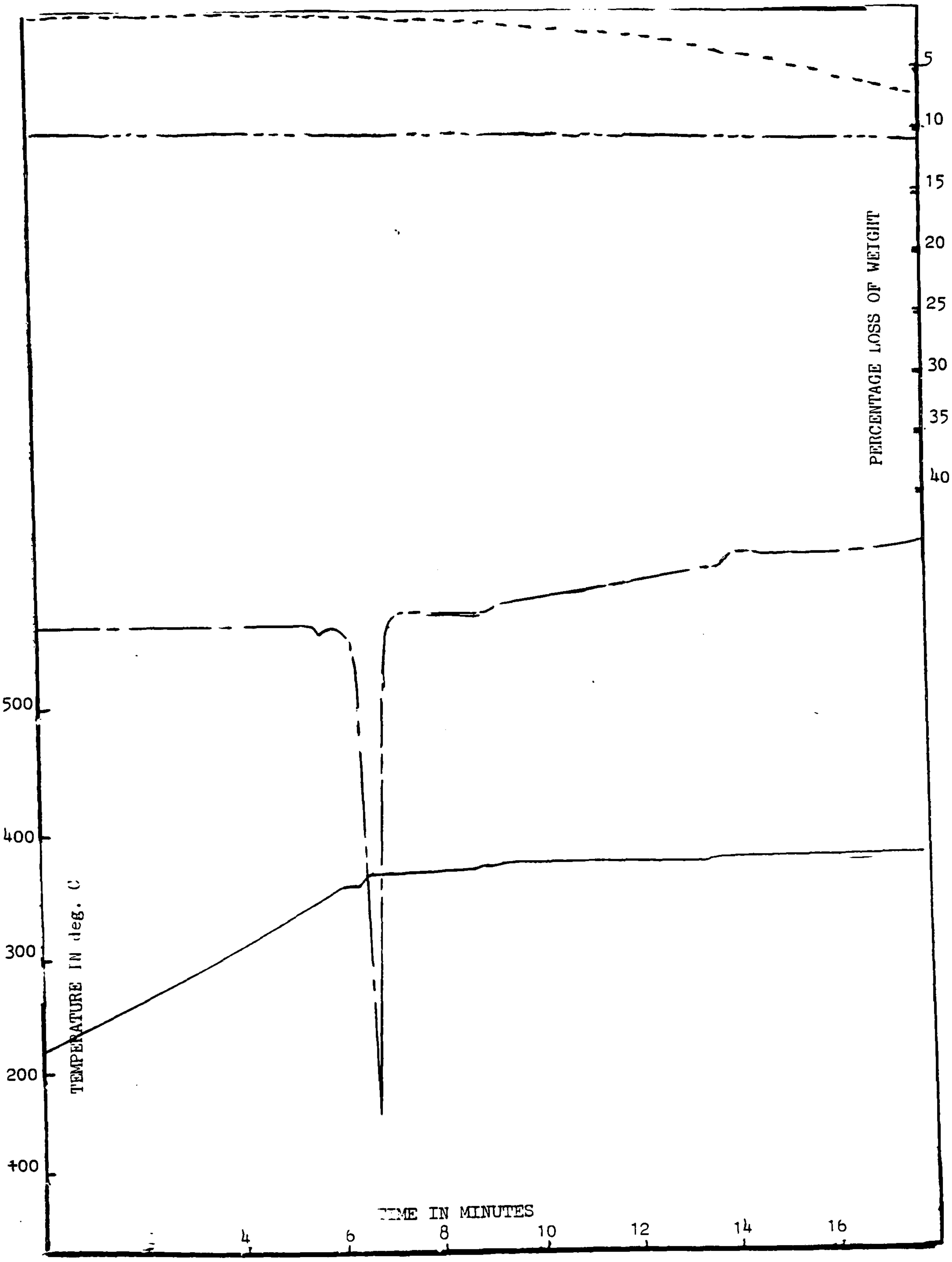


Fig.3-6a Heating of JM grade potassium chlorate to the melting point showing endotherm at 341° followed by much larger melting endotherm at 360° C

TEMPERATURE______

D.T.A. ___ _ _____ _ _

L.O.W.-----------------------

dW/dT_____ _ _ _ ______

CYCLICAL HEATING

To probe the existence of the phase change at about 340° C and to establish whether it is reversible, two experiments were carried out in which ground Fluka grade potassium chlorate was heated in a platinum crucible to the melting point and just below the melting point respectively and allowed to cool. The cycle of heating and cooling was repeated several times. Each time there was an endothermic peak on heating and an exothermic trough at 334/336°C on cooling (Fig.3-6); both were independent of the much larger melting and solidifying endo- and exotherms.(Fig.3-6a) These data are set out in Table 3D .

DIFFERENTIAL SCANNING CALORIMETRY

To obtain verification of this thermal event which was independent of the TG-DTA experiments the same ground sample of Fluka potassium chlorate was investigated in a Differential Scanning Calorimeter. The sample was heated to 350° C at 10° per minute, held there for 5 minutes, cooled to 300° C at a cooling rate of 10° per minute and then heated to 400° C (above the M.P.) at the same rate.The results are shown in Figs.3-7 3-8 and 3-9.

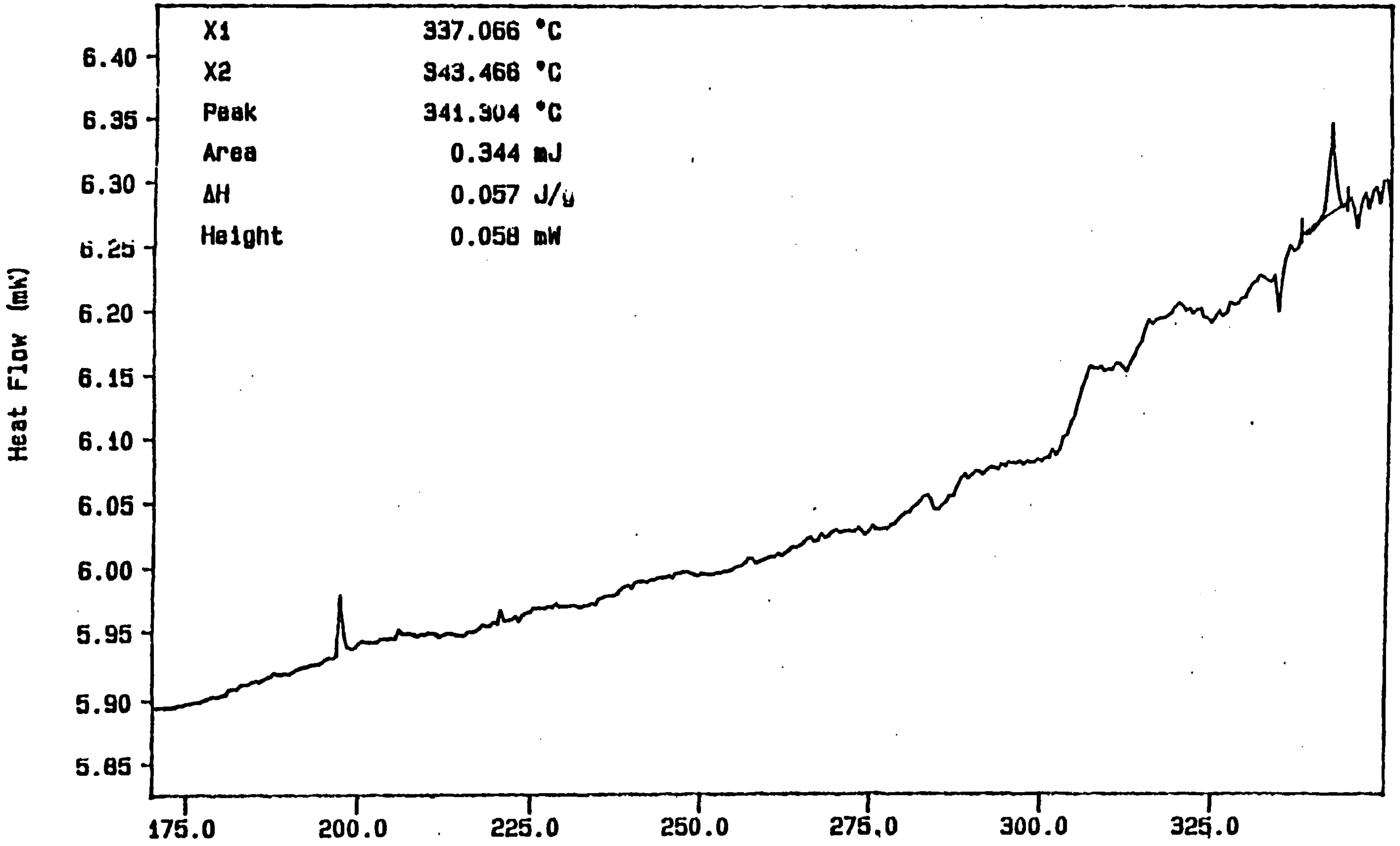
During the heating cycle a peak (endotherm) was identified at 341.3° C and during cooling a trough (exotherm) showed at 335.7° C These are shown in Figs.3-7 and 3-8. The large melting endotherm is clearly visible in Fig.3-9 peaking at 361.8° C.

The results of the Cyclical Heating and Differential Scanning Calorimetry experiments can only be consistent with a phase change or a major change in structure ordering.

X-RAY POWDER DIFFRACTION

The existence of a reversible phase change or structural disorder at 341° C having been suggested by thermal measurements, there was a need to determine whether that feature

Curve 1: DSC
File info: NZ6KC Mon Aug 21 13:54:26 1995
Sample Weight: 6.020 mg
KCLO3



X1	337.066	°C
X2	343.466	°C
Peak	341.304	°C
Area	0.344	mJ
ΔH	0.057	J/g
Height	0.058	mW

NITROGEN ATMOS
TEMP1: 40.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C TIME2: 5.0 min

NZG
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Aug 21 14:04:02 1995

FIG. 3 - 7

DIFFERENTIAL

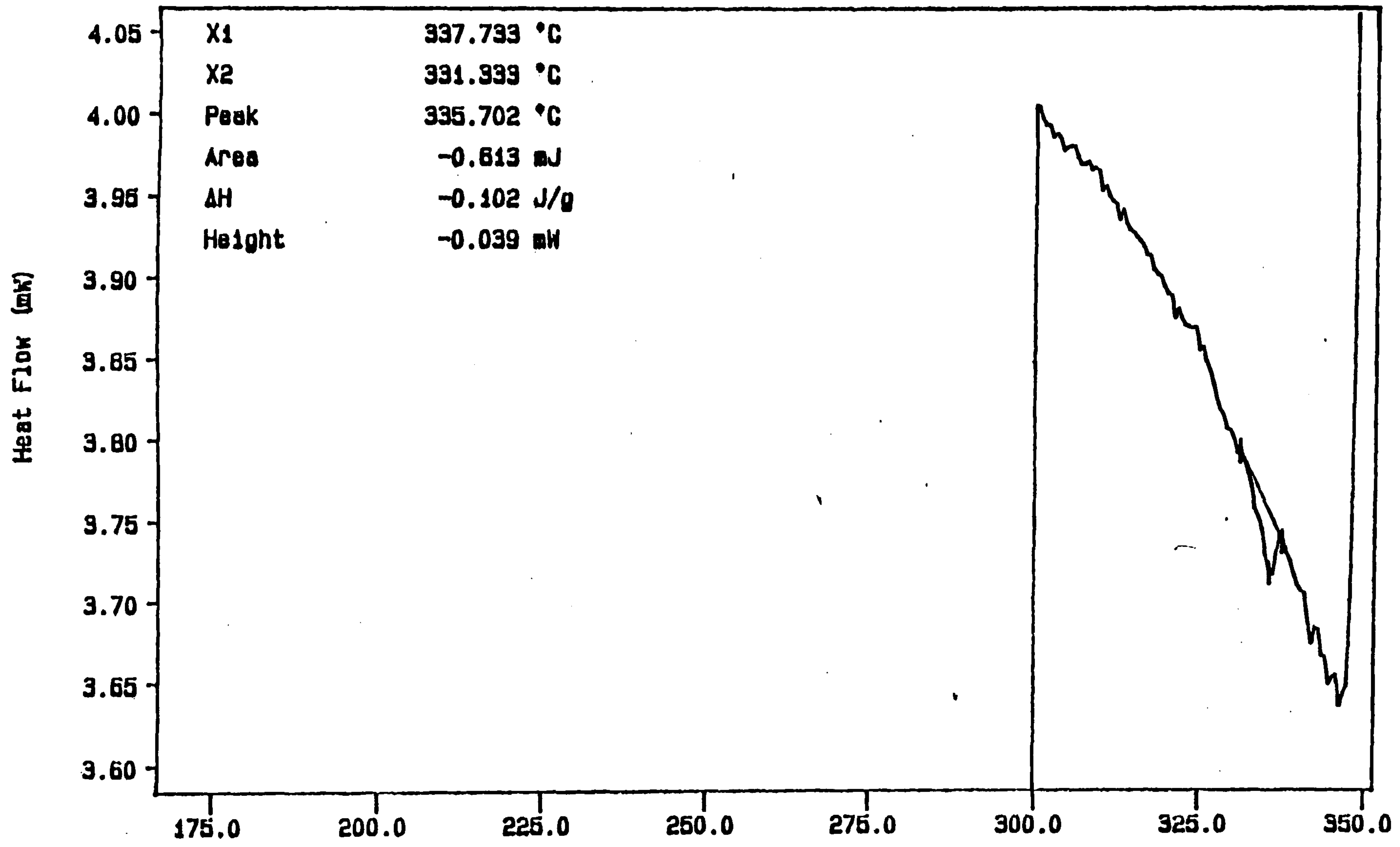
SCANNING

CALORIMETER

$KClO_3$ HEATING

CURVE

Curve 1: DSC
File info: NZ6KC   Mon Aug 21 13:54:28 1995
Sample Weight: 6.020   mg
KCLO3



X1	337.733 °C
X2	331.339 °C
Peak	335.702 °C
Area	-0.613 mJ
ΔH	-0.102 J/g
Height	-0.039 mW

NITROGEN ATMOS
TEMP1: 350.0 C TIME1: 5.0 min RATE1: 10.0 C/min
TEMP2: 300.0 C TIME2: 1.0 min

NZG
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Aug 21 15:00:21 1995

FIG. 3 - 8

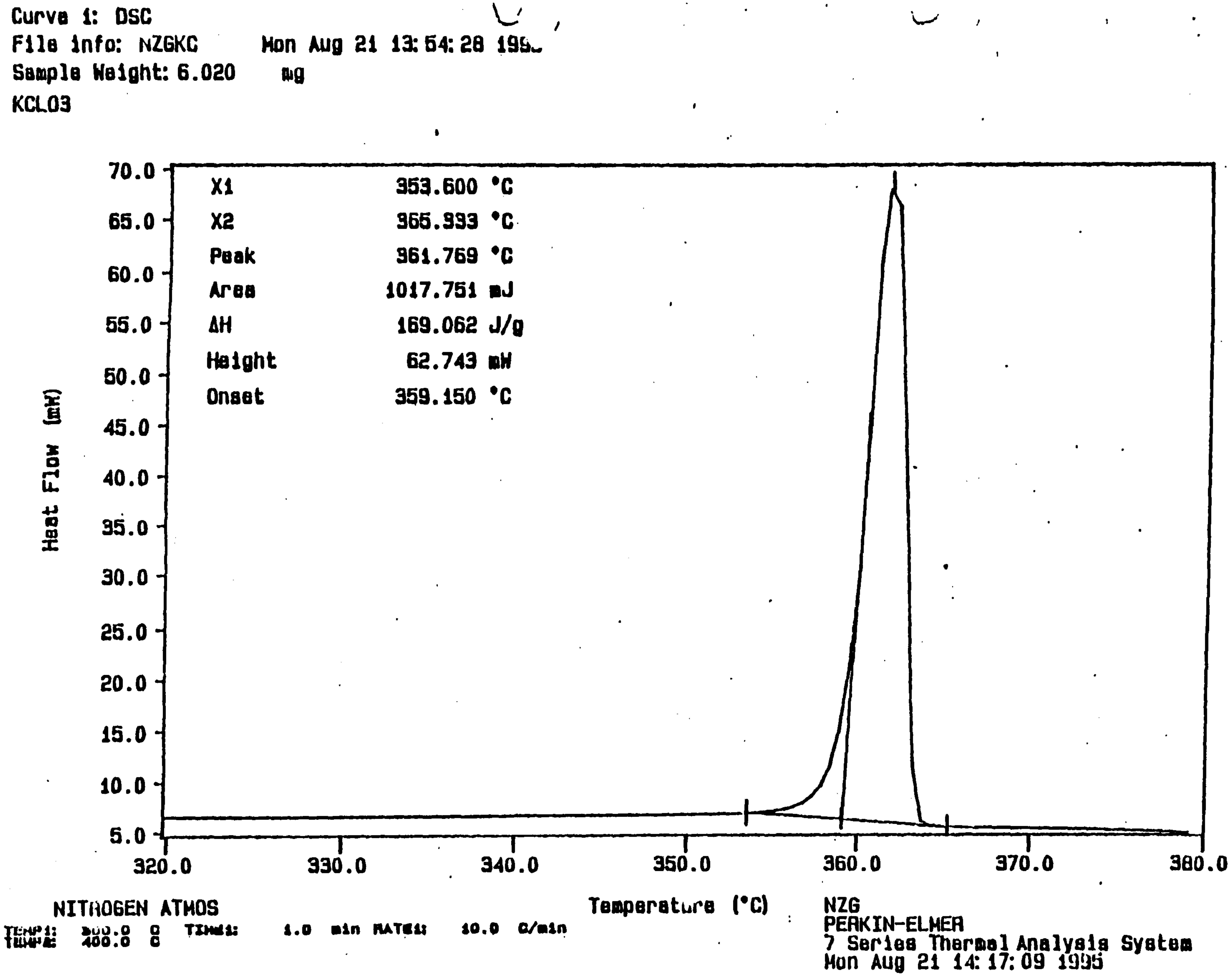
DIFFERENTIAL

SCANNING

CALORIMETER

KClO$_3$ COOLING

CURVE



Curve 1: DSC
File info: NZGKC Mon Aug 21 13:54:28 1995
Sample Weight: 6.020 mg
KCLO3

X1	353.600 °C
X2	365.933 °C
Peak	361.769 °C
Area	1017.751 mJ
ΔH	169.062 J/g
Height	62.743 mW
Onset	359.150 °C

NITROGEN ATMOS
TEMP1: 300.0 C TIME1: 1.0 min RATE1: 10.0 C/min
TEMP2: 400.0 C

NZG
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Aug 21 14:17:09 1995

FIG. 3 - 9

DIFFERENTIAL

SCANNING

CALORIMETER

$KClO_3$ MELTING

CURVE

was in fact a phase change or was a structural disorder . The sample was therefore examined by High Temperature X-Ray Diffraction in the Siemens D5000 Diffractometer to which was attached a High Temperature HTK10 Camera. Readings were taken at 10° C intervals from 245° C to 365° C and over a 2-theta range from 23 to 65° at intervals of 0.0187/0.0188 values of 2-θ.The detailed X-Ray data are contained in Appendix 3 and the critical data are extracted in Fig 3-10 which shows the changes with temperature over the entire temperature range. This is supplemented by printouts of Count/2-θ diagrams at 335 and 345° C (Figs. 3-11 and 3-12) showing the changes which have occurred between these two temperatures. These changes are tabulated in Table 3E from which the following data highlighting the changes,are extracted:-

335° C			345° C		
2-θ	counts	d-spacing	2-θ	counts	d-spacing
24.51	640	3.63	24.51	463	3.63
			25.13	1485	3.54 *
25.37	2978	3.51	25.37	1827	3.51
			25.54	2863	3.49**
25.63	7492	3.47			
30.00	407	2.98	29.96	409	2.98
30.09	435	2.97	30.08	516	2.97
31.11	923	2.87	31.07	962	2.88
			31.14	774	2.87
31.20	800	2.87			

* Major new line **significant shift of most intense line with reduction of intensity.

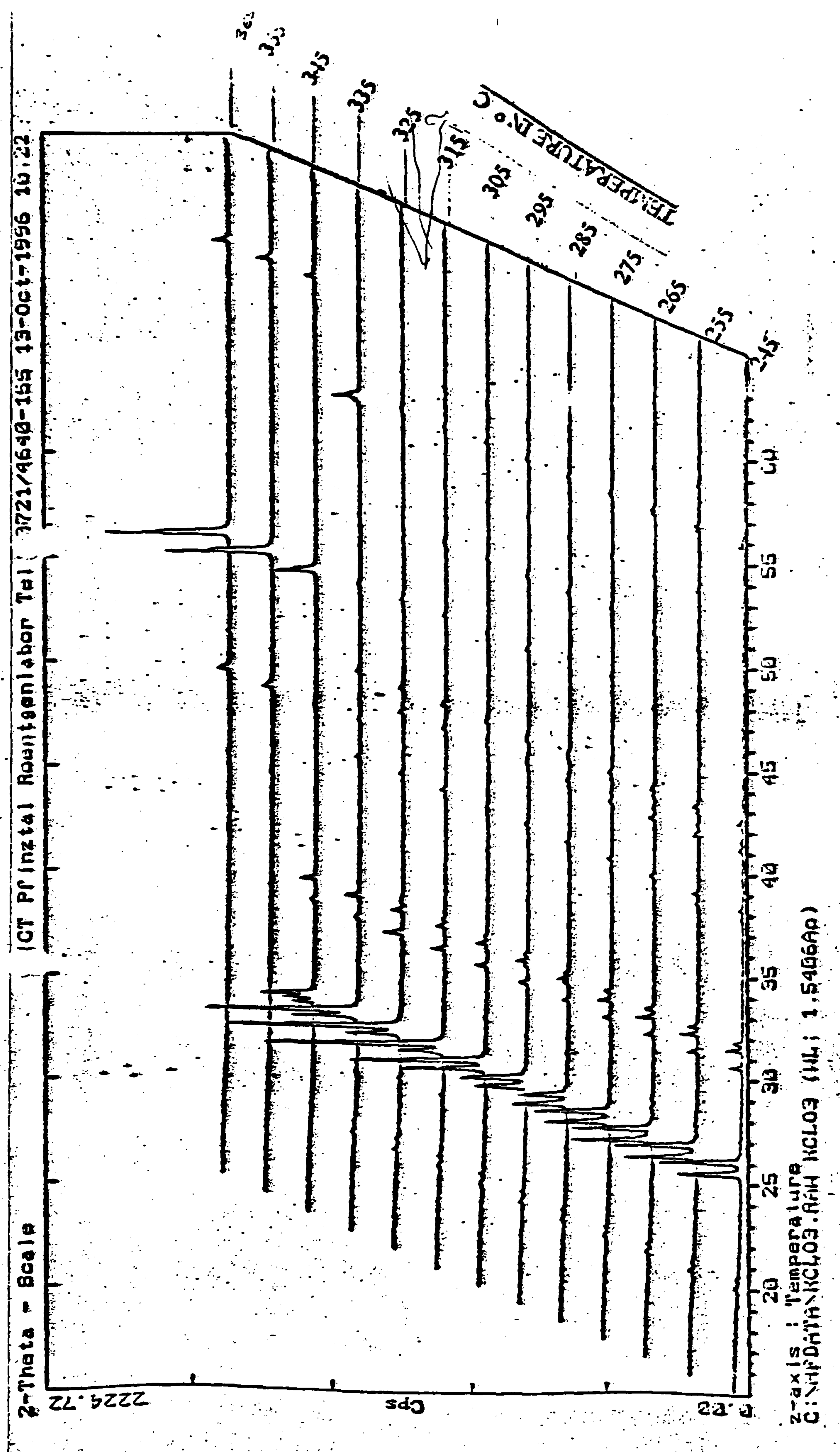

2-Theta - Scale
ICT Pfinztal Roentgenlabor Tel: 3721/4640-155 13-Oct-1996 10:22
2224.72
Cps
0.00
20
25
30
35
40
45
50
55
60
z-axis : Temperature
C:\NHFDATA\KCLO3.RAW KCLO3 (WL: 1.5406Ao)
TEMPERATURE IN °C
365
355
345
335
325
315
305
295
285
275
265
255
245

FIG. 3-10

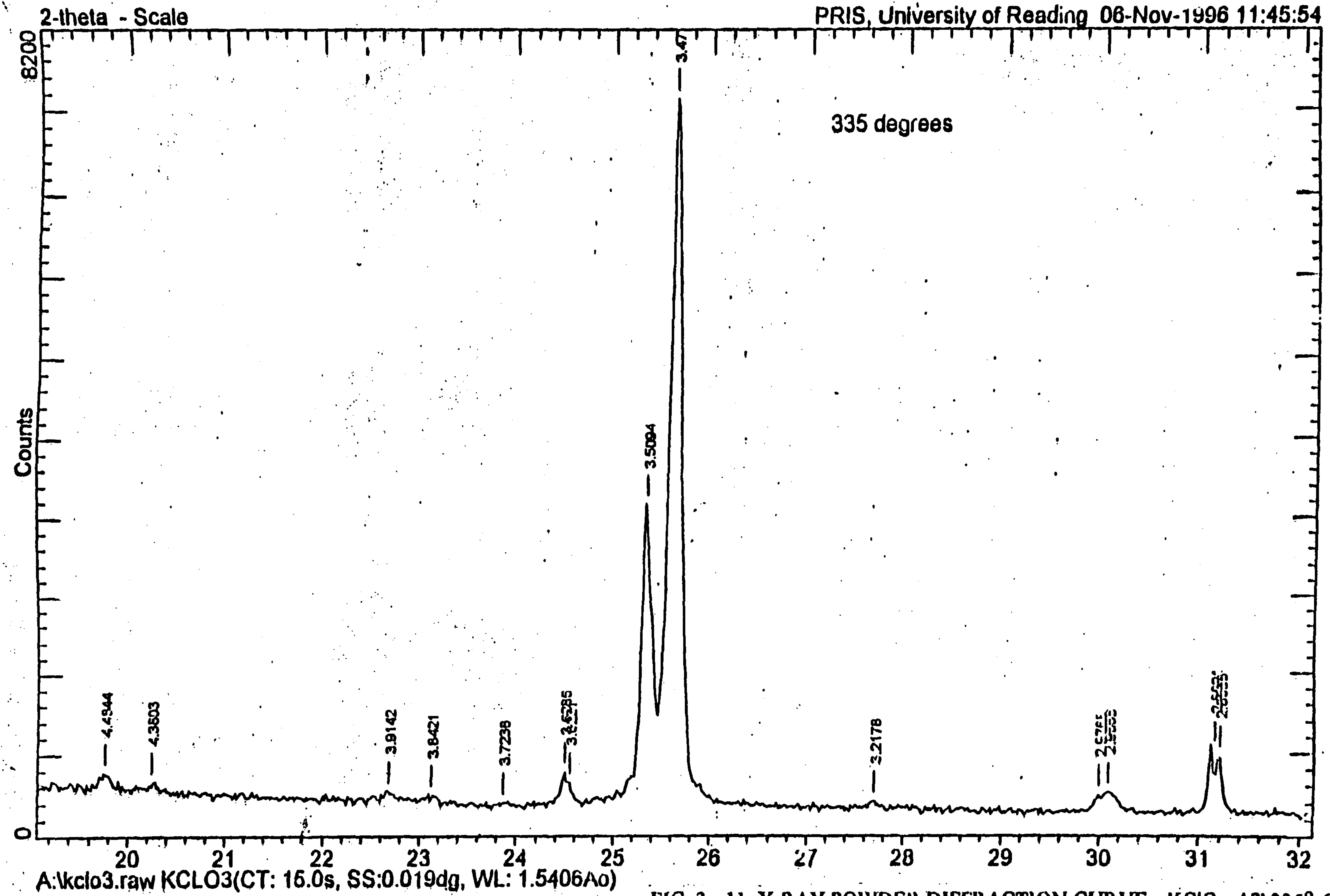


FIG. 3 - 11 X-RAY POWDER DIFFRACTION CURVE - $KClO_3$ AT 335° C

TWO-THETA RANGE 19 - 32°

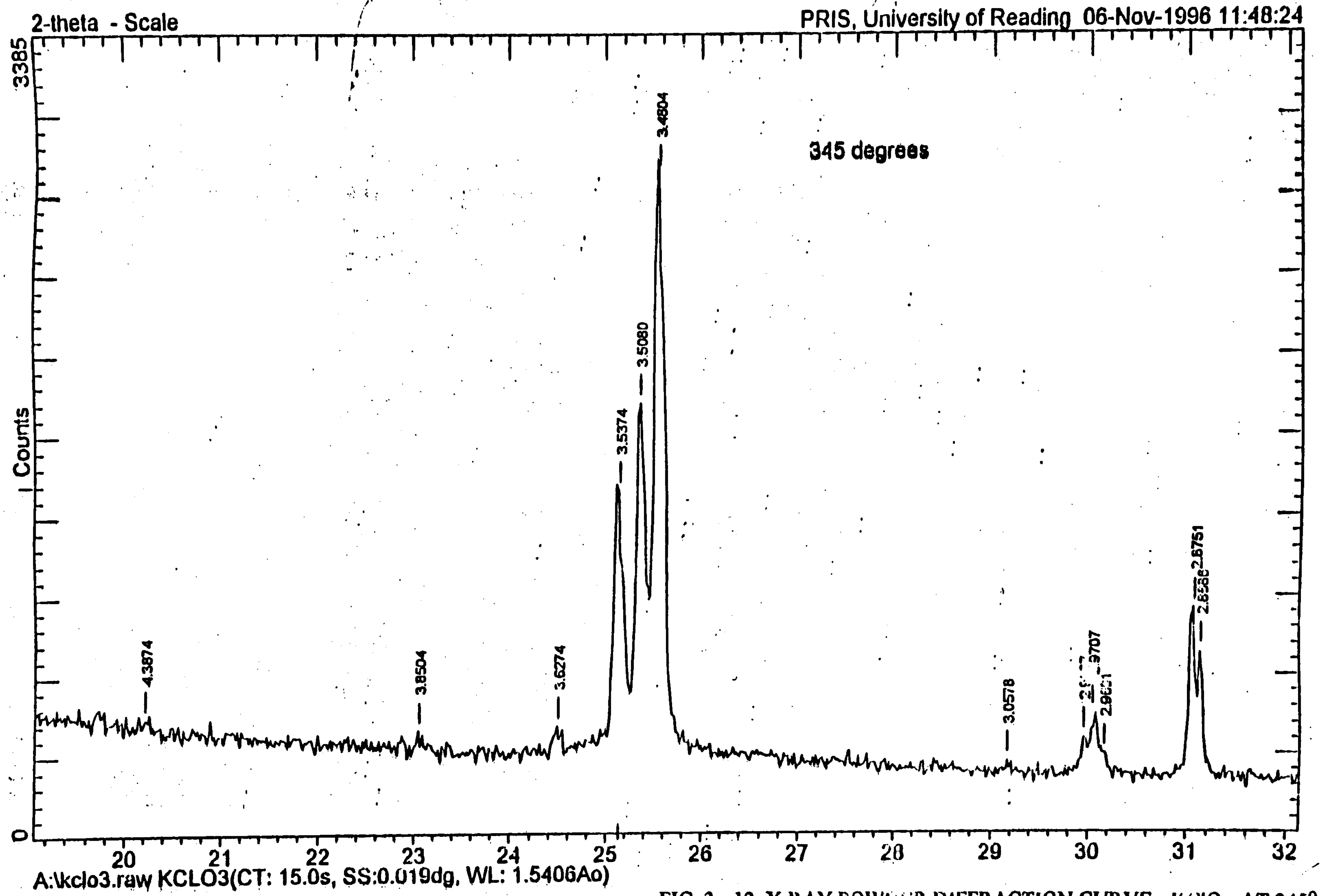


FIG. 3 - 12 X-RAY POWDER DIFFRACTION CURVE - $KClO_3$ AT 345° C

TWO THETA RANGE 19 - 32°

3.3.4 DISCUSSION OF RESULTS

Thermal Events

Uniform Heating

Referring to Table 3A the Melting Point T3 occurs at a mean temperature of 358.7° C and there is no significant difference between the melting points of the three types of potassium chlorate used. There is however a wide spread of results for the temperatures at which subsequent thermal events occur.

	Temperature ° C	
	Range	Mean
T1 Endotherm - structural change	332 - 343	339
T2 Exotherm - first decomposition	368 - 438	394
T3 Melting Point	355 - 363	359
T4 Exotherm - second decomposition	397 - 535	443
T5 Endotherm	399 - 539	483
T6 Exotherm - third decomposition	433 - 564	509
T7 Endotherm	503 - 597	542
T10 10% of theoretical decomposition	315 - 484	404
T50 50% of theoretical decomposition	415 - 555	479
T75 75% of theoretical decomposition	438 - 590	506

Table 3B details the Loss of Weight, Reaction Time, and Reaction Rate for each of the three decomposition stages which appear to have taken place In summary the data in Table 3B are:-

		1st Reaction	2nd Reaction	3rd Reaction
Onset Temp.°C	Range	283 - 436	388 - 572	438 - 604
Elapsed Time mins	Mean	6.0	5.0	6.7
	Range	2.1 - 12.5	2.0 - 11.4	2.0 - 16.0
	Std. Deviation	3	2	2
Percent decomp.	Mean	23.0	73.0	98.0%
	Range	12.8 - 60.6	54.8 - 87.0	92.7 - 100%
	Std. deviation	5	8	2
Reaction Rate Mols.O_2 /min x 10^3				
	Mean	4.7	12.4	5.3
	Range	2.0 - 9.4	6.3 - 21.3	0.9 - 10.7
	Std. deviation	2	4.5	2.8

From the data in Tables 3A and 3B a"typical" decomposition profile of potassium chlorate can be extrapolated and compared with published results as follows:

	This	References			
	Work	(8)	(9)	(13)	(14)
T1 Temp. of Structural Change	341° C	not reported			
T3 Melting Point ° C	359	357	360	360	340-380
First decomposition starts ° C	380	525	565	520	380
peaks ° C	394	551	567	580	360-480
ends ° C	440	557	585	570	480
% decomposition	23%	36%	23%	25%	not stated
Reaction Rate mols/min x 10^3	4.7	not stated			

	This Work	(8)	(9)	(13)	(14)
Second decomposition starts ° C	440	557	585	570	530
peaks ° C	443	566	603	630	530-570
ends ° C	501	587	620	635	570
% decomposition	73%	87%	100%	100%	not stated
Reaction Rate mols/min x 10^3	12.7	not stated			
Third decomposition starts ° C	501	587	-	-	570
peaks ° C	509	-	-	-	570-620
ends °	620	-	-	-	620
% decomposition	98%	97%			
Reaction Rate mols/min x 10^3	5.3	not stated			
and from Table 3A					
50% decomposition temp. ° C	479	575	590	605	not stated
75% decomposition temp. ° C	506	580	606	625	not stated

Isothermal heating At isothermal temperatures below 370° C the percentage decomposition was low ; however when the isotherm temperature was raised to 370/375° C decomposition proceeded steadily at that temperature to approximately the end of the second reaction i.e. to the same point as was achieved under uniform heating conditions at 440° C - 73 to 82% (Fig.3-5) . When the isotherm temperature was raised to 413° C decomposition equivalent to the end of the third reaction -about 97% -was achieved within 12 minutes.Published results for isothermal heating of potassium chlorate are:

-90% decomposed after 60 mins.(Quartz vessel) at 480° C

85.4% 90 mins.(Unglazed porcelain) at 510° C

90% 45 mins.(Glass vessel) at 540° C (5)

25% decomposed after 24 hours at 409° C

51.8% 6 hours at 460° C

75.5% 1.75 hours at 492° C

78.1% 1.5 hours at 506° C (6)

19.3% decomposed after 200 min. at 455° C

94.2% 200 mins. at 506° C

95.4% 62 mins. at 510° C

96.3% 66 mins. at 552° C

95.5% 10 mins. at 575° C (7)

0.44% decomposed after 48 hours at 370° C (8)

This Work

14% decomposed after 30 minutes at 281° C

8% decomposed after 14 minutes at 364° C

21% decomposed after 4 minutes at 370° C

73% decomposed after 30 minutes at 370° C

82% after 64 minutes at 370° C

66% after 43 minutes at 390° C

75% after 35 minutes at 403° C

97% after 16 minutes at 413° C

Thermal Decomposition parameters

There are no obvious reasons for the differences between the results reported in the literature and those from the present work. It is possible that the differences in decomposition temperatures at constant heating rates are due to differences in experimental technique or the presence or absence of trace elements which may have an accelerating or retarding effect. The difference in behaviour under isothermal conditions - confirmed by several experiments - seems to be of greater significance ; it was thought that the catalytic effect of KCl suggested by Glasner & Weidenfeld (6) resulted from the formation of KCl soon after melting and that this effect caused continuous decomposition during isothermal heating. An experiment with added KCl (Run 6028 Table 4B) produced no such effect.

Structural Change

The most significant outcome of this investigation is the observation that a small but distinct thermal feature consistent with a change in the structure of potassium chlorate occurs on heating at or near 341°C and that this change is reversible on cooling at or near 336°C . The change was identified in High Temperature X-Ray studies and in the DTA traces from variable temperature, uniform heating; isothermal heating; and Differential Scanning Calometric studies. In addition the cyclical heating experiment highlights the independence of the change from the melting porcess which is clearly shown by a large endotherm on heating and exotherm on cooling. The feature in the thermal analysis curves that is consistent with this change is shown in the following Tables and Figures.

Differential Thermal Analysis:	uniform heating	Table 3A and Figs. 3-3 & 3-4
	isothermal heating	Table 3C and Fig.3-5
	cyclical heating	Table 3D and Fig.3-6

Differential Scanning Calorimetry (DSC) Figs. 3-7 , 3-8 and 3-9

The DSC experiment confirmed the presence of the feature associated with the phase change and defined more accurately the temperatures at which this change occurred, namely:- 341.3° C on heating and 335.7° on cooling. The DSC data also permitted calculation of the heats absorbed and evolved by the change. The calculated values of ΔH are 0.057J/g (7.0J/mole)on heating and 0.102J/g (12.5J/mole) on cooling.

The detailed data from the high temperature X-Ray diffraction studies are contained in Appendix 3. The data clearly shows changes that are consistent with the formation of a new phase with the following features:-

1. There is still a strong line at about 3.48Å which is the position of the 004 line in the orthorhombic cell that is known to exist at temperatures above 250° C.

2. Some of the lines in the new pattern are narrowly split. This suggests that two of the new cell dimensions are of similar length.

3. The new pattern has a line at about 2.88Å close to the value of the 020 reflection in the orthorhombic cell but no line attributable to the 200 (2.37Å) reflection of the existing orthorhombic cell.

4. These observations suggest that the new phase is also orthorhombic with approximate cell dimensions of :-

$\underline{a} = 5.74$ $\underline{b} = 5.76$ $\underline{c} = 13\ 90$

5. refinement of this cell to fit the observed diffraction data (see indexing data in Table 3F) for the new phase gives a cell of:-

$\underline{a} = 5.737$ $\underline{b} = 5.758$ $\underline{c} = 13.924$

The phase changes from monoclinic to the orthorhombic cell existing at 250° C and thence to the new phase found in this work which , although orthorhombic, is near to tetragonal are consistent with changes in packing arising from the expansion of the $KClO_3$ lattice.

Incipient melting is shown by the disappearance of an X-Ray pattern due to solid forms of

$KClO_3$. It is probable that the incipient melting noted by Shimada(14) to occur at "around 340° C actually occurred between 345 and 355° C.

The crystal structure of the monoclinic form is known and there are two $KClO_3$ formula units per cell (i.e. $z = 2$).

The cell dimensions for this cell at 20° C are:-

$$\underline{a} = 4.647 \quad \underline{b} = 5.585 \quad \underline{c} = 7.085 \quad \beta = 109.63°$$

giving a cell volume of 173.20 Å^3 and a calculated X-Ray density of 2.33 g/cc.

At 250° C the cell dimensions are:-

$$\underline{a} = 4.706 \quad \underline{b} = 5.632 \quad \underline{c} = 7.209 \quad \beta = 108.29°$$

giving a cell volume of 181.40 Å^3 and an X-Ray density of 2.24 g/cc.

When the monoclinic form changes to an orthorhombic structure at 250°C it doubles in volume because of a doubling of one cell dimension.The cell dimensions of the orthorhombic cell at 280° C are:-

$$\underline{a} = 4.74 \quad \underline{b} = 5.64 \quad \underline{c} = 13.8$$

giving a cell volume of 368.9 Å^3 and, with four $KClO_3$ formula units per cell ($z = 4$) an X-Ray density of 2.21g/cc.

At 335° C the cell dimensions of this orthorhombic modification are:-

$$\underline{a} = 4.7534 \quad \underline{b} = 5.7382 \quad \underline{c} = 13.88$$

giving a cell volume of 378.59Å^3 and an X-Ray density of 2.14g/cc.

The formation of the new orthorhombic (near tetragonal) phase at 345° C results from an increase in only one of the cell dimensions and this expansion cannot be associated with an increase in z (the number of $KClO_3$ formula units in the cell) but must be due to the formation of a more open structure perhaps because of the relaxation on the constraints on ClO_3^- packing giving rise to free rotation of this ion. The new cell dimensions of the new orthorhombic (near tetragonal) form at 345° C are :-

$\underline{a} = 5.737 \quad \underline{b} = 5.758 \quad \underline{c} = 13.924$

giving a cell volume of 459.96$Å^3$ and a calculated X-Ray density of 1.77g/cc. consistent with a more open structure.

The work on the thermal decomposition of potassium chlorate described in this chapter has been extended to studies on the effect of catalytic decomposition by metal oxides and salts (Chapter 4) and the rotation of the ClO_3^- suggested would be consistent with triggering the thermal decomposition described therein.

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TABLE 3A

DECOMPOSITION OF POTASSIUM CHLORATE HEATED UNIFORMLY

TEMPERATURES OF THERMAL EVENTS IN ORDER OF DESCENDING VALUES OF THE MELTING ENDOTHERM

T1 - TEMPERATURE OF ENDOTHERMIC CHANGE
T2 - EXOTHERM OF FIRST DECOMPOSITION REACTION
T3 - TEMPERATURE OF MELTING ENDOTHERM
T4 - TEMPERATURE EXOTHERM DECOMPOSITION
T5 - TEMPERATURE ENDOTHERM
T6 - TEMPERATURE EXOTHERM
T7 - TEMPERATURE ENDOTHERM

T10 - TEMPERATURE AT WHICH 10% OF THEORETICAL DECOMPOSITION OCCURS
T50 - TEMPERATURE 50%
T75 - TEMPERATURE >75%

RUN,TYPE OF KClO3 CRUCIBLE MATERIAL	T1	T2	T3	T4	T5	T6	T7	T10	T50	T75
5949 , pure , Al	0	438	365	0	0	552	574	475	555	590
5950 , pure , Al	0	414	363	459	514	0	0	430	495	540
5611 , pure , Al	343	375	360	414	474	539	572	315	461	507
239 , 98%grd, Al	343	435	360	508	510	519	537	472	515	525
5333 , 98% , Al	0	368	360	438	510	522	0	367	424	438
244 , 98% , Al	343	399	360	535	539	548	566	484	539	564
5612 , 98% , Al	341	407	359	449	517	564	584	339	464	510
5666 , 98% , Al	336	409	359	409	439	480	503	324	466	491
6068A, JM , Al	343	414	358	496	498	508	539	412	491	509
5770 , pure , Al	332	375	358	409	512	526	597	454	523	540
5663 , 98% , Al	339	380	358	459	500	513	563	336	451	475
5761 , pure , Pt	344	385	358	424	472	512	557	452	520	560
5771 , pure , Pt	0	380	357	0	423	475	507	408	469	498
5773 , 98%grd, Pt	336	378	357	404	448	472	506	415	468	491
5759 , pure , Pt	340	370	357	397	399	433	509	370	415	440
5668 , 98% , Al	338	395	357	428	508	517	531	396	429	440
5772 , pure , Pt	337	379	356	443	459	466	506	379	438	477
5743 , pure , Al	337	396	355	409	494	503	528	438	498	516

TABLE 3B

DECOMPOSITION OF POTASSIUM CHLORATE HEATED UNIFORMLY

REACTION RATES TABULATED IN THE SAME ORDER AS IN TABLE 3A

A - ONSET OF DECOMPOSITION deg.C
A1 - ONSET OF RAPID REACTION deg.C
B - ONSET OF FINAL REACTION deg.C

	RUN,TYPE OF KC1O3 CRUCIBLE MATERIAL	SAMPLE WEIGHT mgm	THEOR 100% L.O.W. mgm	ONSET TEMP A deg.C	ONSET TEMP A1 deg.C	ELAPSED TIME A - A1 mins.	PERCENT DECOMP @A1	REACTION RATE MOLS/MIN x 1000	ONSET TEMP B deg.C	ELAPSED TIME A1 - B mins.	PERCENT DECOMP @B	REACTION RATE MOLS/MIN x 1000	ELAPSED TIME B/END mins.	PERCENT DECOMP AT END	REACTION RATE MOLS/MIN x 1000
1	5949 , pure , Al	15.97	6.25	436	572	12.5	60.6	9.48	604	2.7	87.0	19.11	2.0	98.0	8.76
2	5950 , pure , Al	8.31	2.47	394	436	4.0	16.2	3.13	491	5.0	57.1	6.32	6.6	92.7	4.17
3	5611 , pure , Al	13.15	5.15	360	409	4.7	14.4	4.93	486	6.8	63.9	11.71	7.7	100.0	7.54
4	239 , 98%grd, Al	10.37	4.06	409	487	6.1	18.2	3.79	527	3.6	72.7	19.21	3.7	100.0	9.36
5	5333 , 98% , Al	3.70	1.45	366	395	3.0	13.0	1.96	438	3.0	75.0	9.36	10.0	94.0	0.86
6	244 , 98% , Al	10.06	3.94	411	503	6.0	17.1	3.51	553	3.6	67.1	17.10	4.3	86.4	8.39
7	5612 , 98% , Al	7.84	3.07	283	424	10.1	25.1	2.38	486	5.6	65.5	6.92	7.9	100.0	4.19
8	5666 , 98% , Al	11.13	4.36	370	420	5.0	12.8	3.49	501	7.5	85.6	13.22	6.0	100.0	3.27
9	6068A, JM , Al	8.62	3.38	404	491	7.7	42.3	5.79	512	2.0	75.5	17.51	4.2	97.5	5.53
10	5770 , pure , Al	10.17	3.98	405	498	8.4	25.1	3.72	526	3.3	54.8	11.20	4.9	97.0	10.72
11	5663 , 98% , Al	7.75	3.03	370	418	4.0	26.4	6.26	481	5.6	80.2	9.11	7.4	100.0	2.54
12	5761 , pure , Pt	10.17	3.98	415	477	5.3	21.1	4.95	544	6.2	65.3	8.87	5.4	99.7	7.93
13	5771 , pure , Pt	9.65	3.78	372	435	5.0	23.0	5.43	501	5.8	75.9	10.77	5.5	98.4	4.83
14	5773 , 98%grd, Pt	7.49	2.93	389	424	3.1	13.3	3.93	496	6.8	77.5	8.65	5.8	98.0	3.24
15	5759 , pure , Pt	9.17	3.59	360	388	2.1	17.5	9.35	446	5.0	83.0	14.70	6.0	100.0	3.18
16	5668 , 98% , Al	10.22	4.00	370	404	6.0	16.3	3.40	443	7.0	79.3	11.26	16.0	99.3	1.56
17	5772 , pure , Pt	12.65	4.95	360	408	8.0	21.4	4.14	471	11.4	76.0	7.41	12.7	99.0	2.80
18	5743 , pure , Al	13.23	5.18	370	475	9.1	27.6	4.91	517	4.0	80.3	21.33	5.3	98.5	5.56

TABLE 3C

ISOTHERMAL DECOMPOSITION OF POTASSIUM CHLORATE

RUN No.	TYPE OF KClO3 AND CRUCIBLE MATERIAL	ISOTHERM TEMP deg.C	T1 deg.C	T3 deg.C	SAMPLE WEIGHT mgm.	THEOR 100% L.O.W. mgm.	PERCENT DECOMP BEFORE ISOTHER	PERCENT DECOMP AT ISOTHERM	TIME TO CONSTANT WT.AT ISOTHERM mins.	REACTION RATE MOLS/MIN x 1000
5655	98% Al	369	341	360	9.02	3.53	14	21	4mins	1.93
	two isotherms	413				3.53	29	97	12	6.25
5748	pure Al	375	341	358	7.47	2.92	4	74	42	1.52
5762	pure Pt	370	340	357	7.13	2.79	3	82	64	1.08
5656	98% Al	370	340	358	7.51	2.94	14	73	30	1.81
5665	98% Al	281	342	360	7.68	3.01	0	14	30	0.44
5704	98% Al	364	339	360	9.24	3.61	2	8	14	0.48
6070	JM Al	390	341	360	8.73	3.42	1	66	43	1.62
6071	JM Al	403	342	360	7.23	2.83	0	75	35	1.90

TABLE 3D

HEATING & COOLING POTASSIUM CHLORATE WITHOUT DECOMPOSITION

T1 - ENDOTHERM ON HEATING
T1A - EXOTHERM ON COOLING
T3 - ENDOTHERM ON MELTING

RUN.No.	TYPE OF KClO3 AND CRUCIBLE MATERIAL		T1	T1A	T3
5901	pure ground	Pt	342	336	
5903	pure ground	Pt	342	336	
6070	JM	Al	341	334	360

TABLE 3E

POTASSIUM CHLORATE - POWDER DIFFRACTION X-RAY DATA

(excluding lines with intensity below 3)

POTASSIUM CHLORATE ROOM TEMPERATURE 14-544 ZACHARIASEN Ref.2			POTASSIUM CHLORATE 250 - 270 deg. C RAMACHANDRAN Ref. 15			POTASSIUM CHLORATE 345 deg. C THIS WORK		
d- SPACING	2-THETA	INTENSITY	d-SPACING	2 - THETA	INTENSITY	d-SPACING	2-THETA	INTENSITY
			6.9	12.83	20			
6.69	13.26	4						
			4.48	19.8	12			
4.41	20.15	10						
						4.39	20.26	6
			4.37	20.34	3			
4.29	20.73	6						
						3.85	23.08	7
			3.63	24.53	4	3.63	24.51	7
						3.54	25.13	47
			3.51	25.38	100	3.51	25.37	60
						3.49	25.54	100
3.45	25.75	100	3.45	25.82	71			
3.34	26.7	60						
3.23	27.6	4						
			3.21	27.78	4			
3.20	27.86	4						
						2.98	29.96	5
						2.97	30.08	9
			2.94	30.37	36			
						2.88	31.07	27
2.87	31.21	35				2.87	31.14	19
			2.84	31.5	63			
			2.82	31.74	20			
2.79	32.06	35						
2.78	32.23	25						
			2.61	34.34	8			
2.58	34.83	4						
			2.39	37.7	7			
			2.38	37.74	38			
			2.37	38	3			
2.36	38.16							
2.33	38.7							
2.15	42.07							
2.145	42.08							
2.135	42.33							
2.115	42.80							
1.92	47.41							
1.90	47.86							
1.678	54.7							
1.60	57.6							
1.457	63.9							

TABLE 3F

INDEXING DATA FOR NEW HIGH TEMPERATURE POTASSIUM CHLORATE PHASE BASED ON THE ORTHORHOMBIC CELL a=5.737 ; b=5.758 ; c=13.924

hkl	CALCULATED VALUE d	OBSERVED VALUE d
002	6.962	
100	5.758	
010	5.736	
101	5.321	
011	5.304	
003	4.641	
102	4.437	
012	4.427	
110	4.064	
111	3.901	
103	3.614	3.627
013	3.608	3.537
112	3.51	3.508
004	3.481	3.480
113	3.058	
104	2.979	2.980
014	2.976	2.970
200	2.879	2.875
002	2.869	2.868
201	2.819	
021	2.81	
005	2.785	
202	2.66	
022	2.652	
114	2.644	

For an orthorhombic crystal of dimensions (a; b; c;) the "d" spacings of the planes represented by the Miller indices (hkl) are calculated using the formula:-

$$d_{hkl} = \frac{abc}{\sqrt{h^2b^2c^2 + k^2c^2a^2 + l^2a^2b^2}}$$

SIEMENS

APPENDIX 3

Application Note X-ray Analysis

Applikationsbericht Röntgenanalyse

axs
Analytical X-Ray Systems GmbH
Product Support
Dr. Götz Menges
76181 Karlsruhe
Germany

Karlsruhe, 28. Oktober 1996
phone: 0049-(0)721-595-4503
FAX: 0049-(0)721-595-4503
Email: Menges@KHE.SCN.de

BARNET
Mr. N. Z. Goldblatt
38 Grimsdyke Crescent
HERTS EN5 4AG

One sample was send to the application lab for measurements under different temperature conditions. The measurements were executed on a D5000 system attached with a HTK 10 from Anton Paar. The measurement was executed by heating the sample in 10°C steps between 245° C and 445°C. Figure 7 shows a 3D plot of all measured ranges.

The following table describes the general configuration of the D5000:

Goniometer	D5000 Theta/Theta
measurement circle	435 mm
Tube	2,2 kW Cu long fine focus
Divergence slit	0,27°
Soller slit	2° slit
sample holder	Paar HTK 10
K-alpha 2 filter	Nickel
Detector	OED, Braun, Scan-Modus
Canal	0,019°
Generator	K760-80, 40 kV, 30 mA
measurement time	15 sec./1° = 7500 sec/scan

The measurement was executed using the DIFFRAC AT Software. The evaluation was made with DIFFRAC AT Software and with the new DIFFRAC^{plus} 32bit software for the WINDOWS NT 3.51, WINDOWS NT 4.0 or WINDOWS95 Platform.

results

Figure 1 shows a scan of the material at 245°C. At 345° C (Figure 2) the first small lines of the sample are gone, the peak doublet at ca. 25° 2 Theta splits to a triplet and the peaks at 30° 2 Theta changed, too. After melting (Figure 3) only Pt-peaks of the heating band are visible. Figure 4, 5 and 6 are comparisons between the measurement at 245° C, 345°C and 365° C. As described above, Figure 7 shows 3D prints of all measured ranges. It is clearly visible in the pattern that there is a phase transformation. The phase transformation from monoclinic $KClO_3$ to orthorhombic (?) $KClO_3$ starts at 275° C.
Figure 8 to 18 are different print outs of the measurement. In the diagrams there are markers which point on interesting changing in the sample during the heating procedure.

Attached to the report is a floppy disc with the DIFFRAC AT file of the measurement.

We hope, that these results help to solve your analytical requirements. If you have further questions about this application or about the capability of the D5000 system, please feel free to contact us.

best regards

Götz Menges

ANALYTICAL X-RAY SYSTEMS

Application Lab Karlsruhe

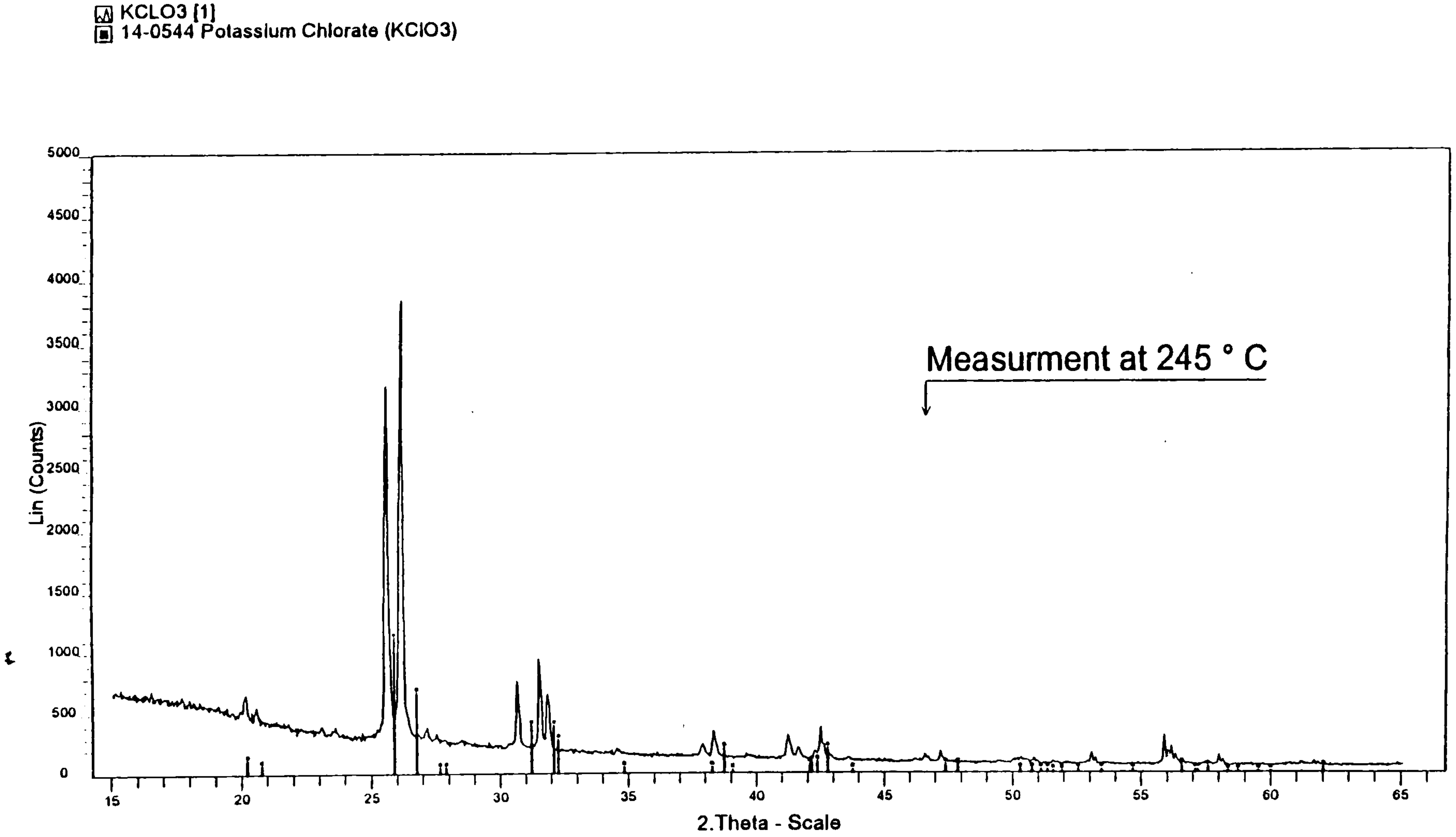


Figure 1

ANALYTICAL X-RAY SYSTEMS

Application Lab Karlsruhe

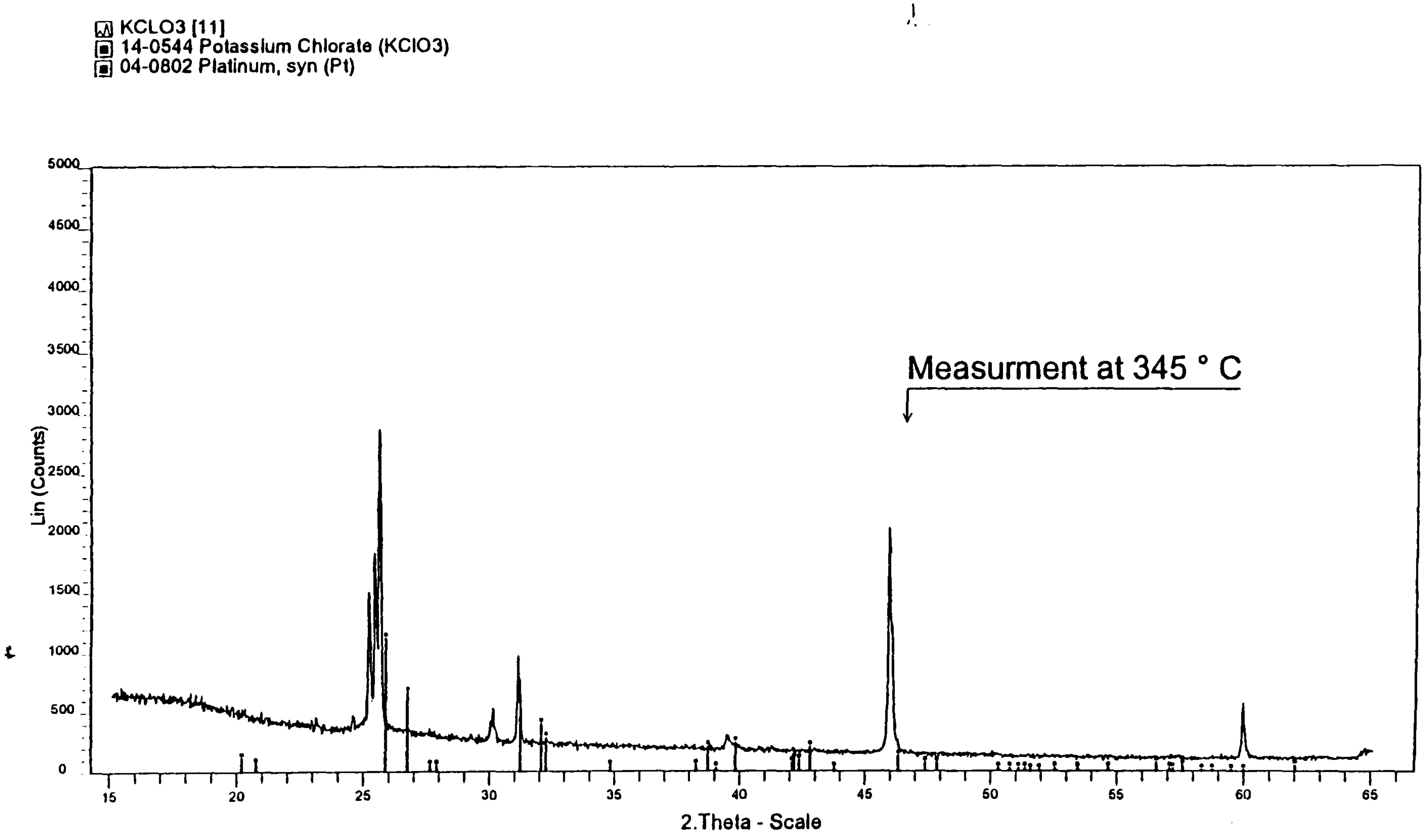


Figure 2

axs
ANALYTICAL X-RAY SYSTEMS

Application Lab Karlsruhe

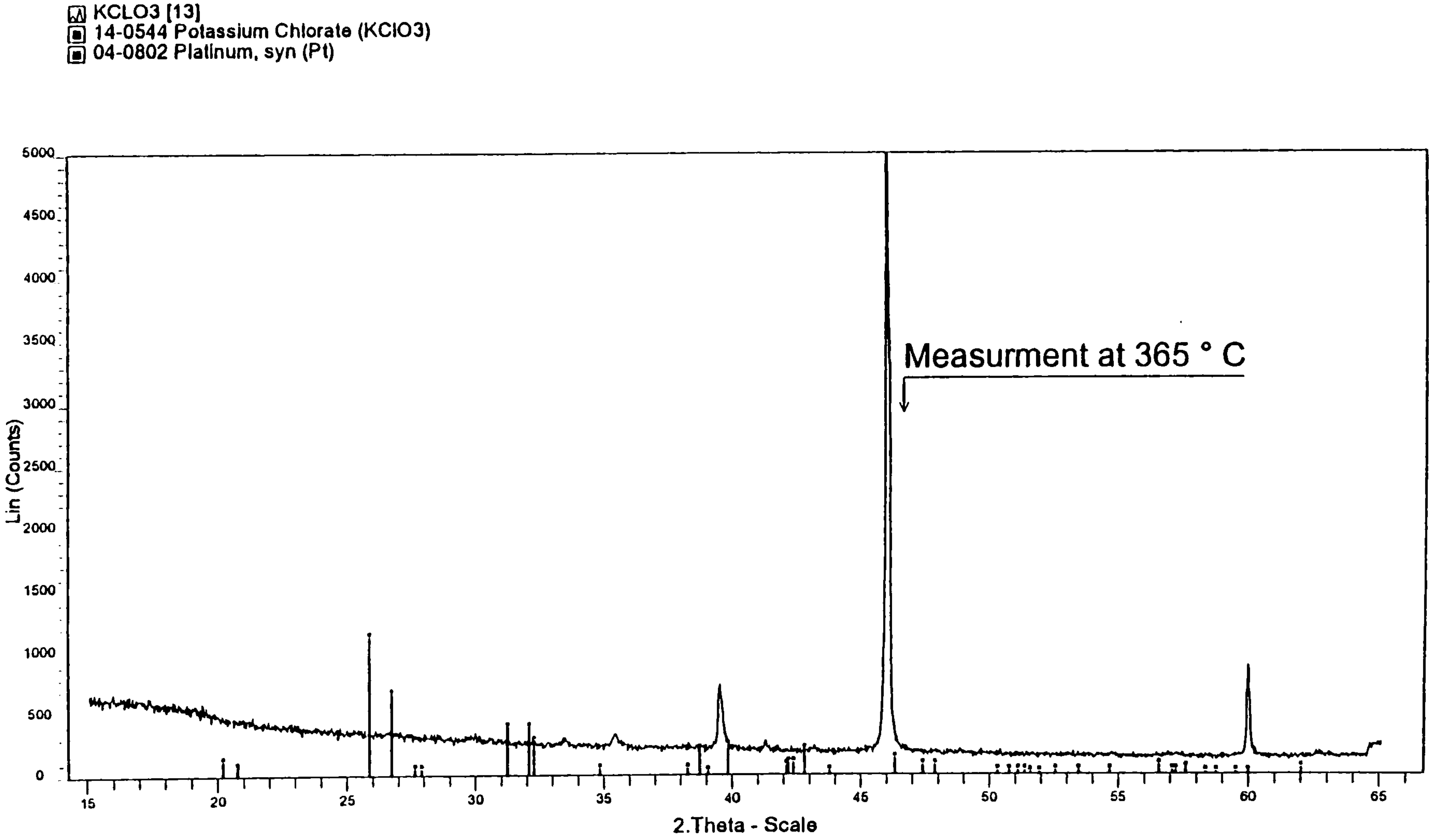


Figure 3

ANALYTICAL X-RAY SYSTEMS

Application Lab Karlsruhe

APPENDIX 3

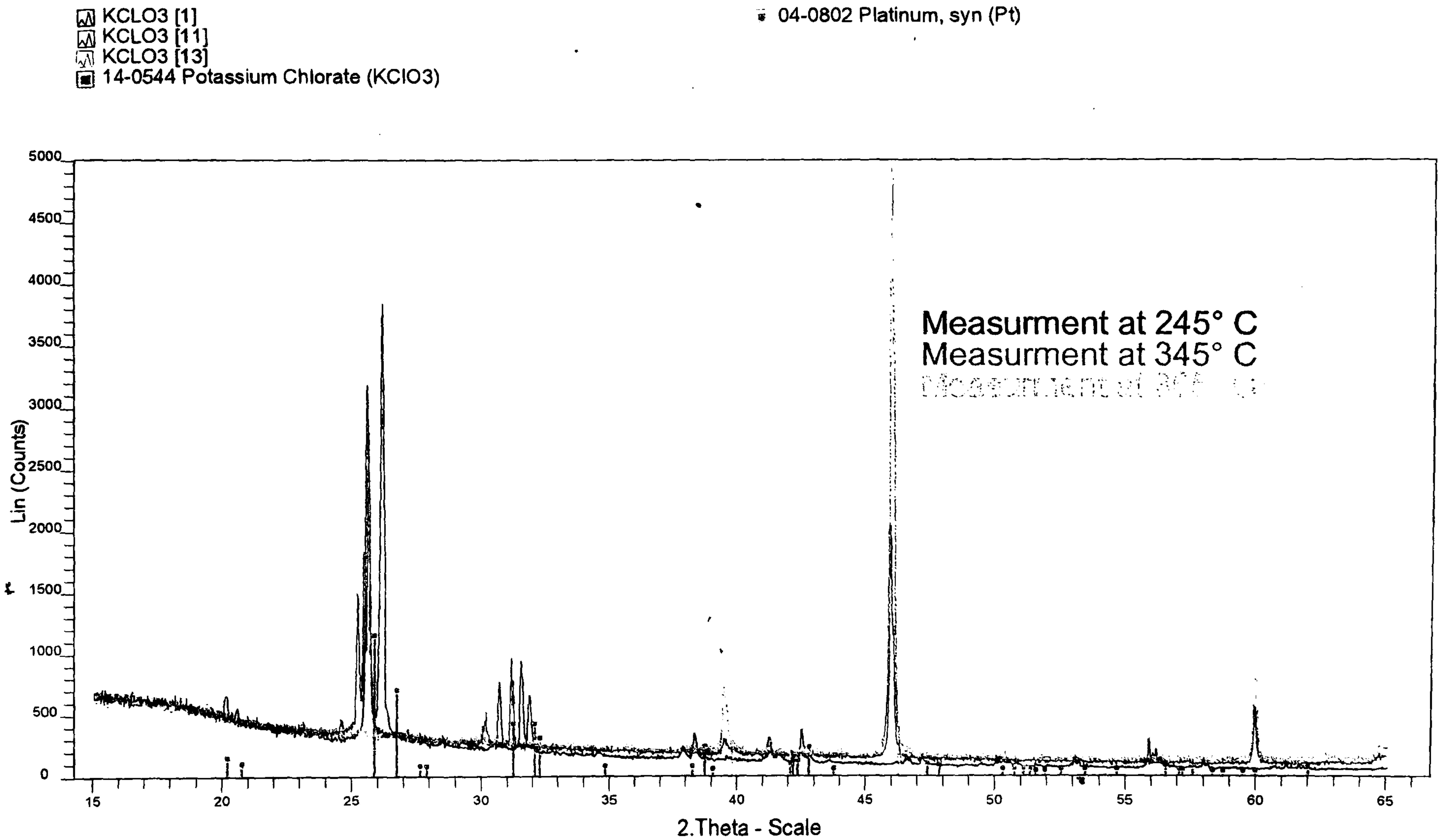


Figure 4

ANALYTICAL X-RAY SYSTEMS

Application Lab Karlsruhe

APPENDIX 3

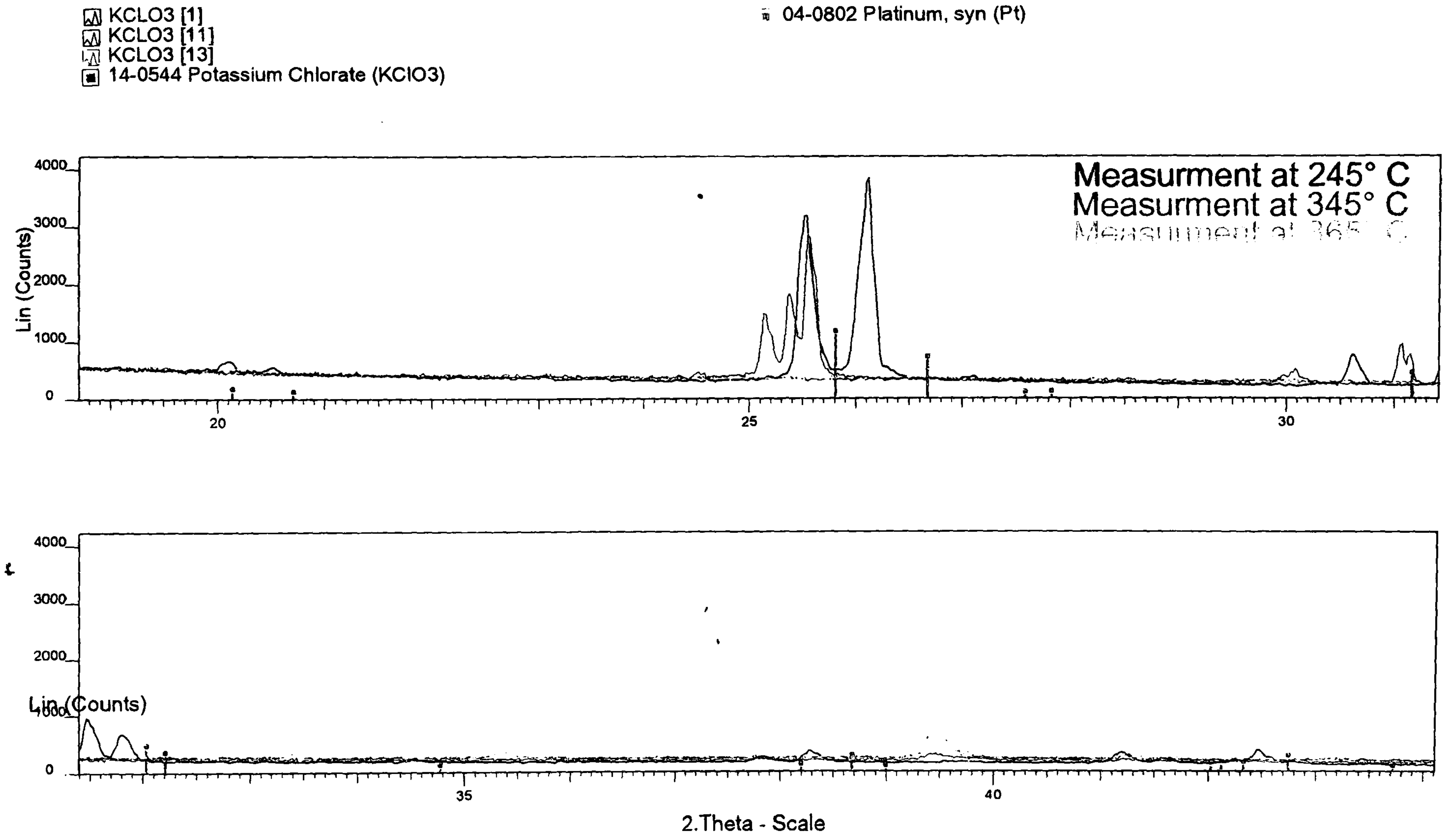


Figure 5

ANALYTICAL X-RAY SYSTEMS

Application Lab Karlsruhe

APPENDIX 3

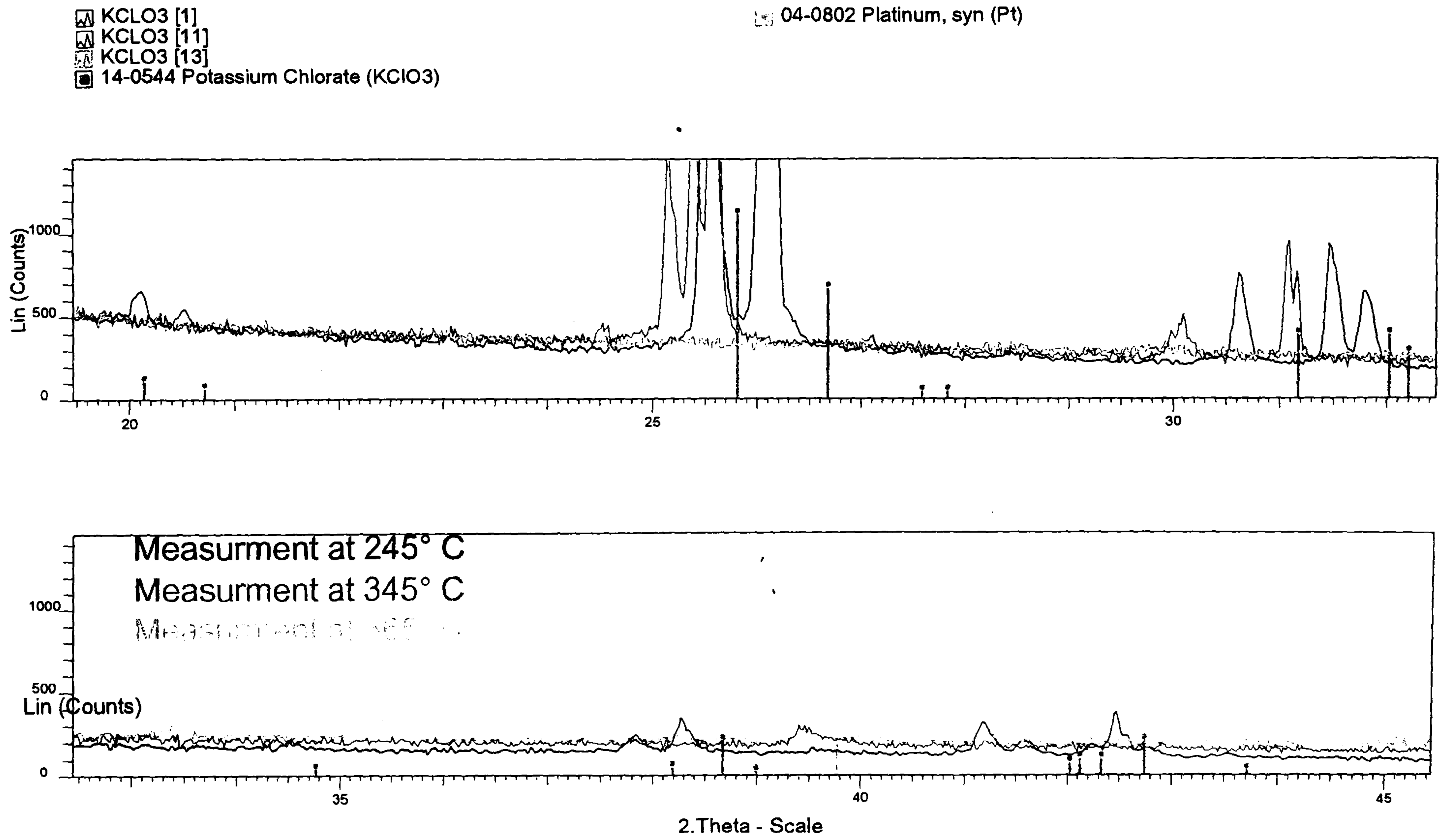


Figure 6

X : [17.600-63.734]° 2.Theta
Y : [8948.250-0.000] Counts (Lin scale)
Z : by increasing scan order

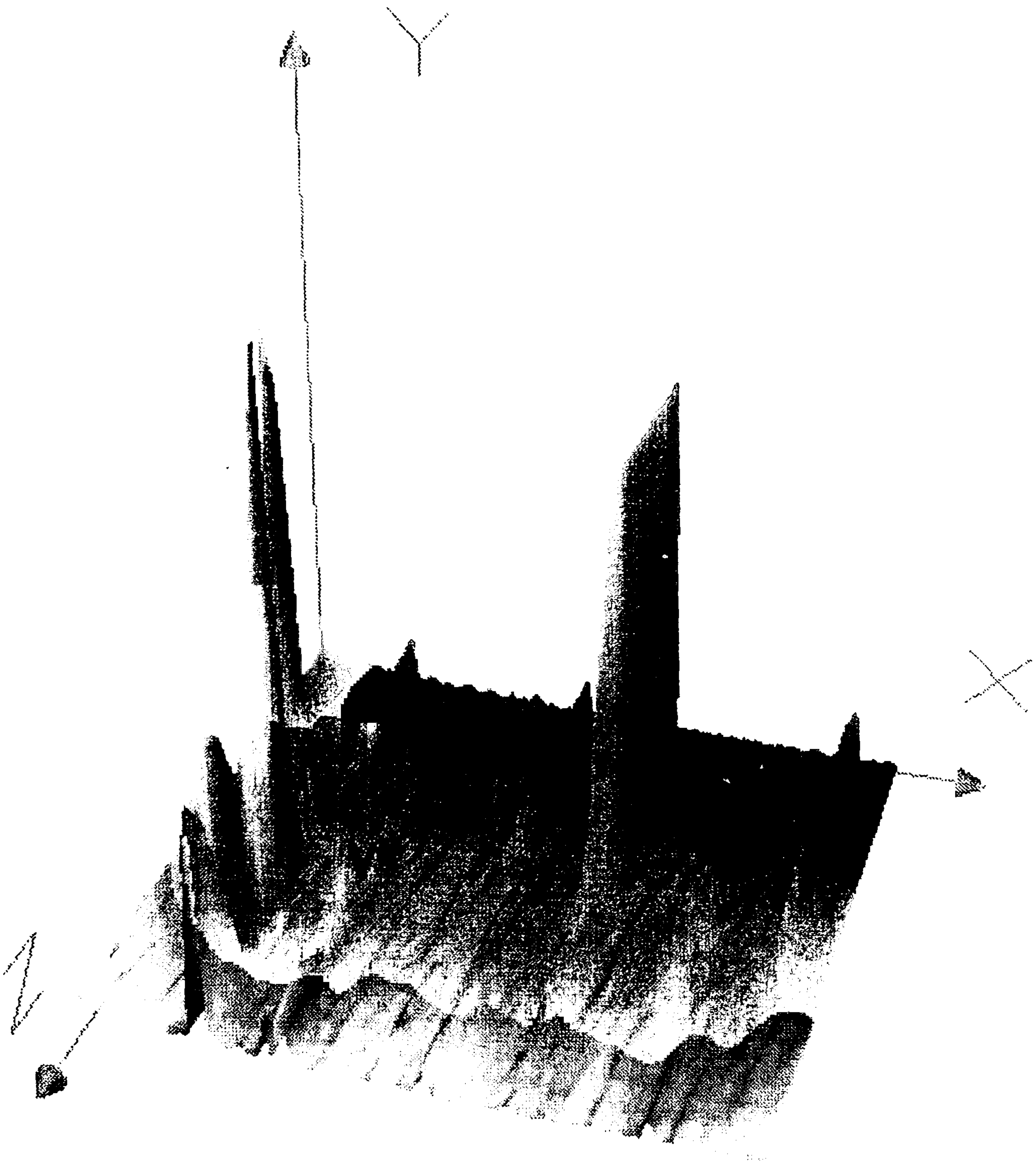


Figure 7

APPENDIX 3

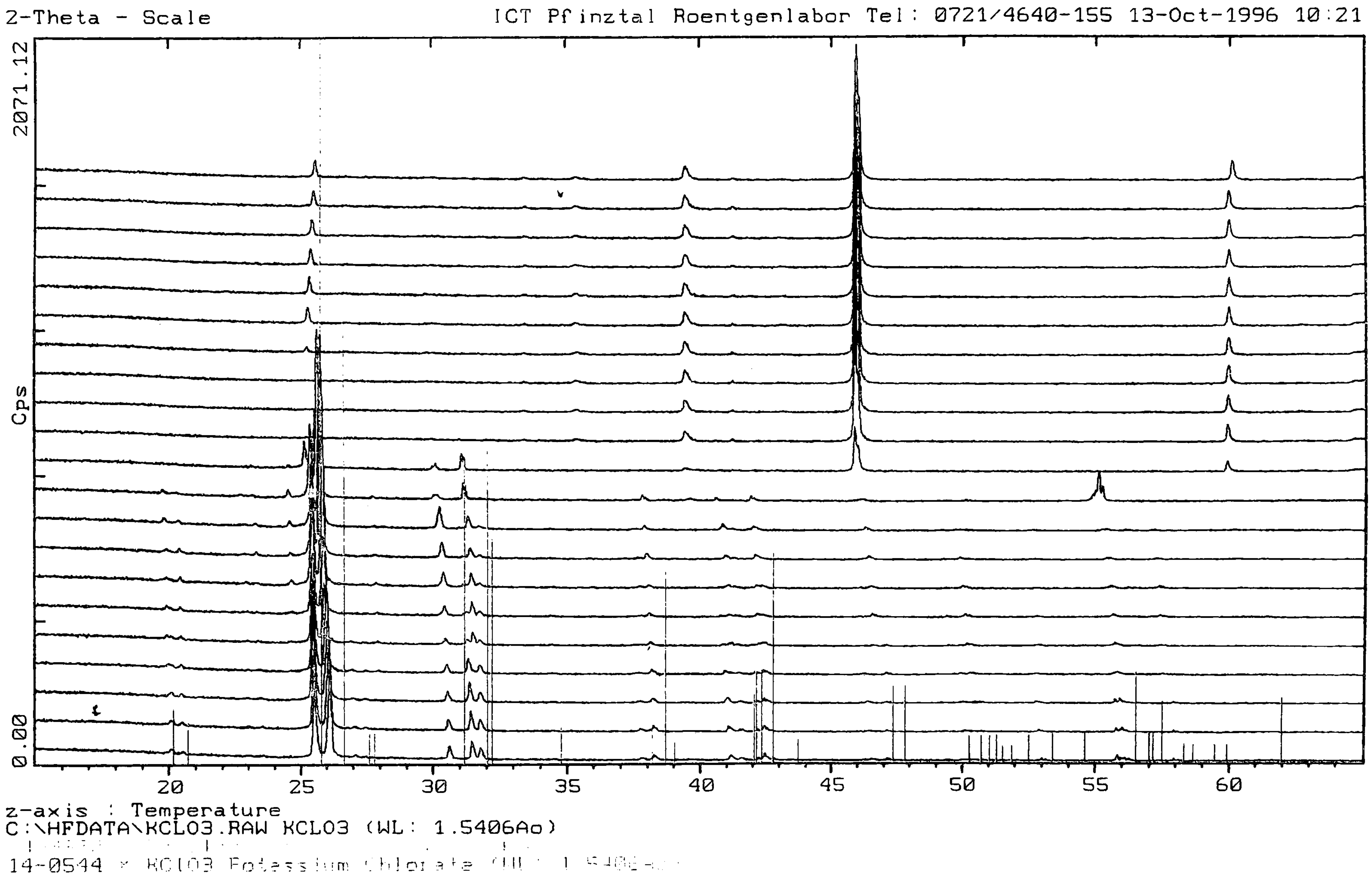


Figure 8

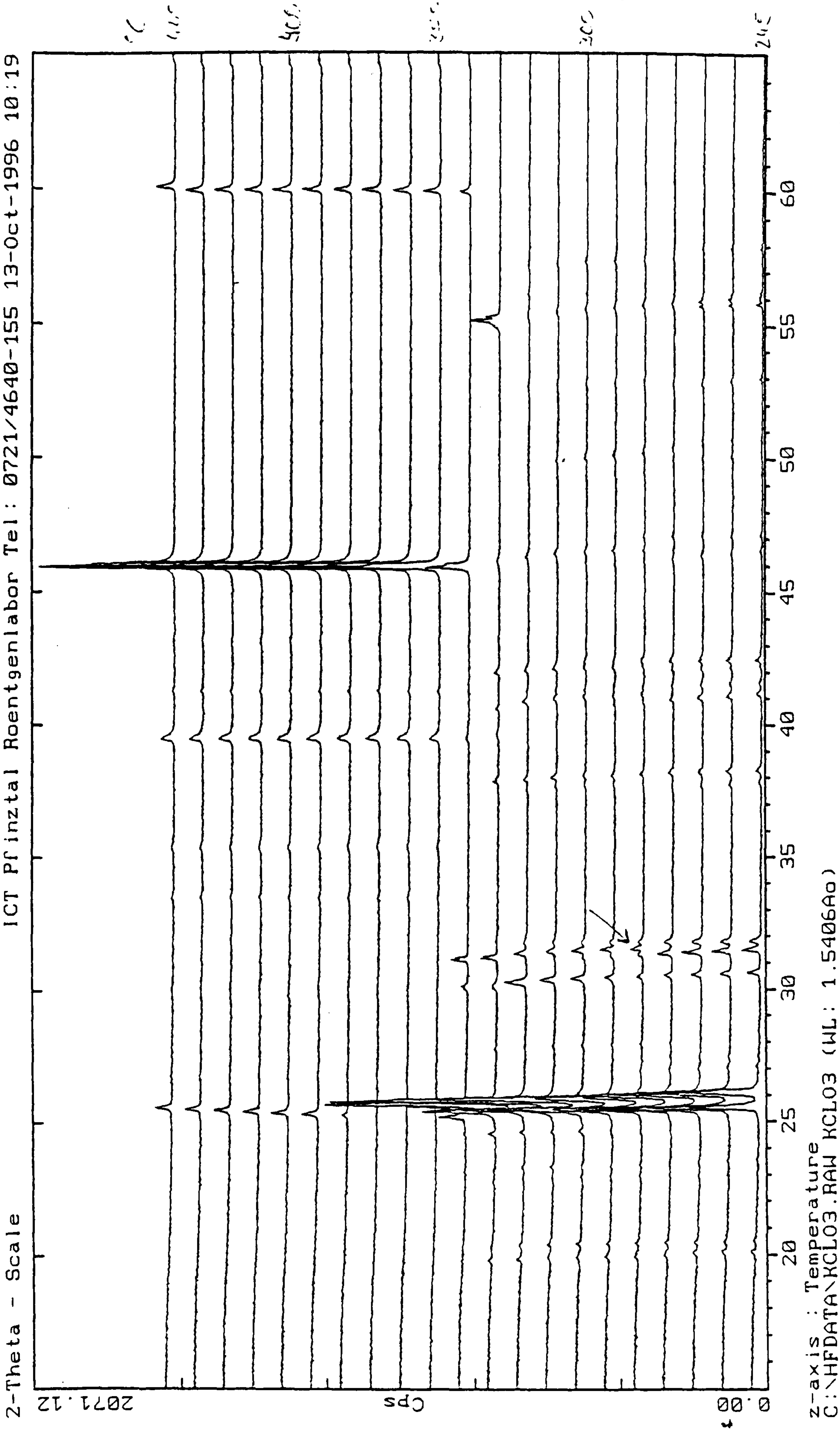

2-Theta - Scale
ICT Pfinztal Roentgenlabor Tel: 0721/4640-155 13-Oct-1996 10:19
2071.12
Cps
0.00
20
25
30
35
40
45
50
55
60
z-axis : Temperature
C:\HFDATA\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

Figure 9

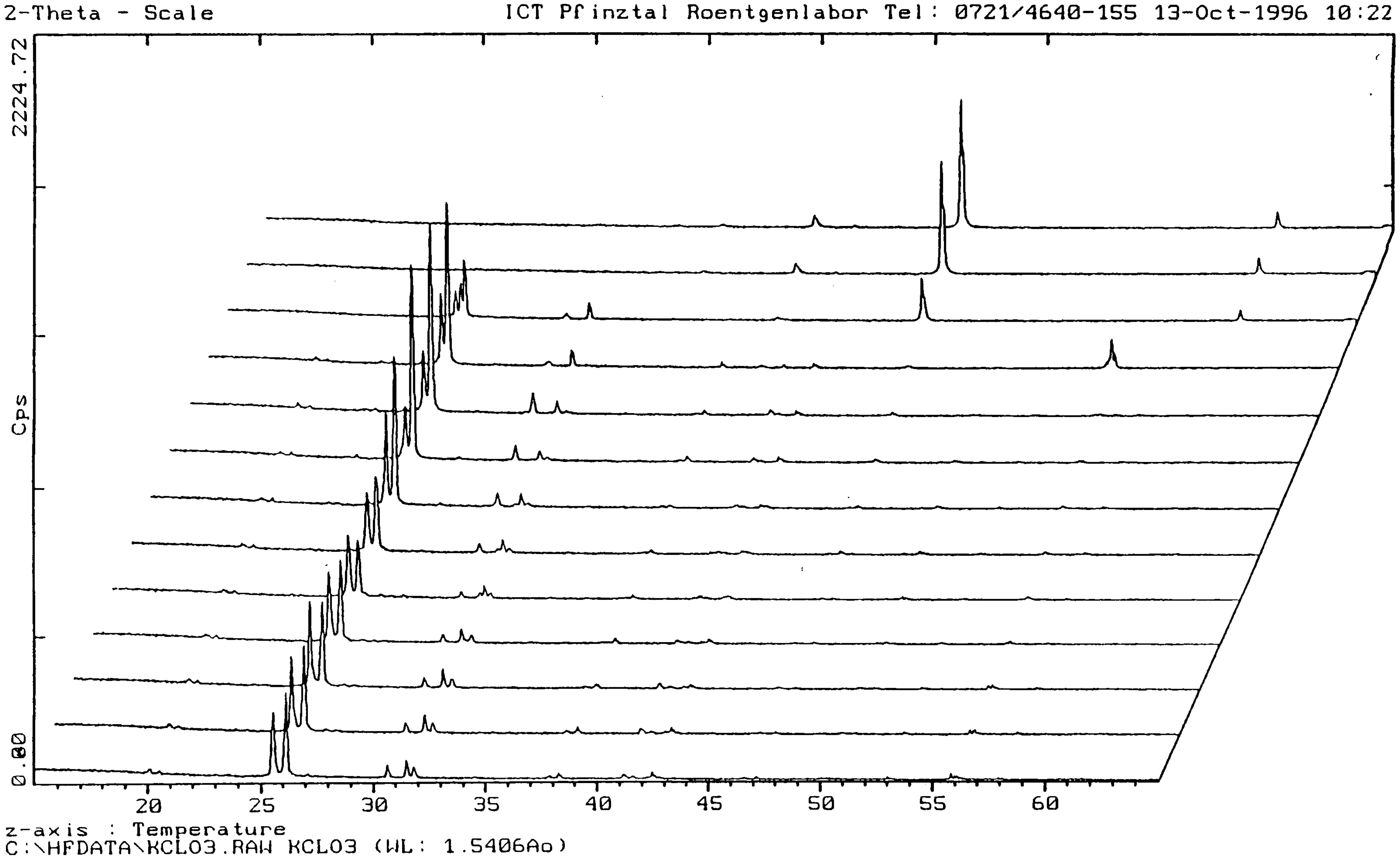
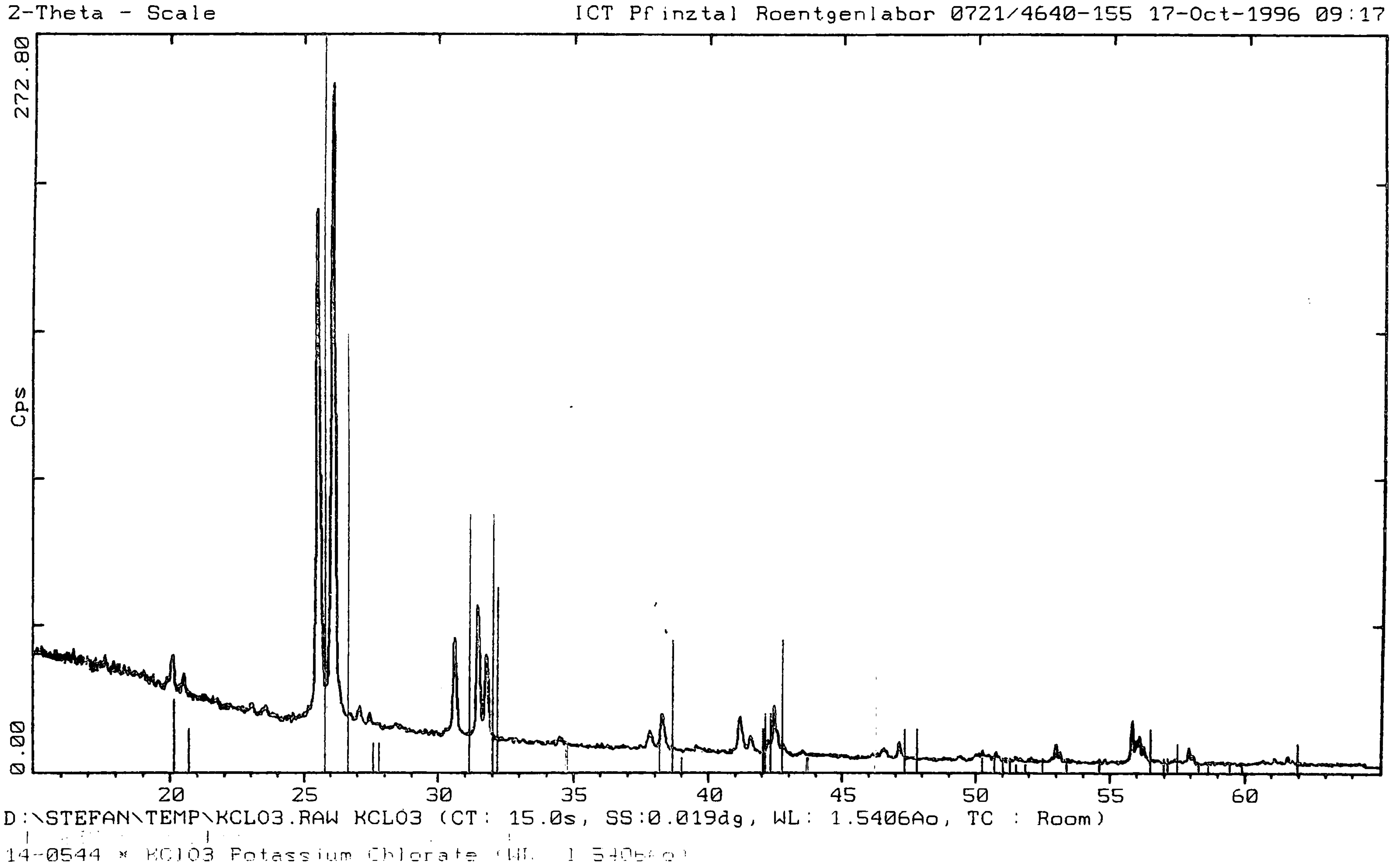

2-Theta - Scale
ICT Pfinztal Roentgenlabor Tel: 0721/4640-155 13-Oct-1996 10:22
2224.72
Cps
0.00
20
25
30
35
40
45
50
55
60
z-axis : Temperature
C:\HFDATA\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

Figure 10

Range: 1   240°C



D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (CT: 15.0s, SS:0.019dg, WL: 1.5406Ao, TC : Room)

14-0544 * KClO3 Potassium Chlorate (WL: 1.5406Ao)

Figure 11

APPENDIX 3

Sample : 35°C

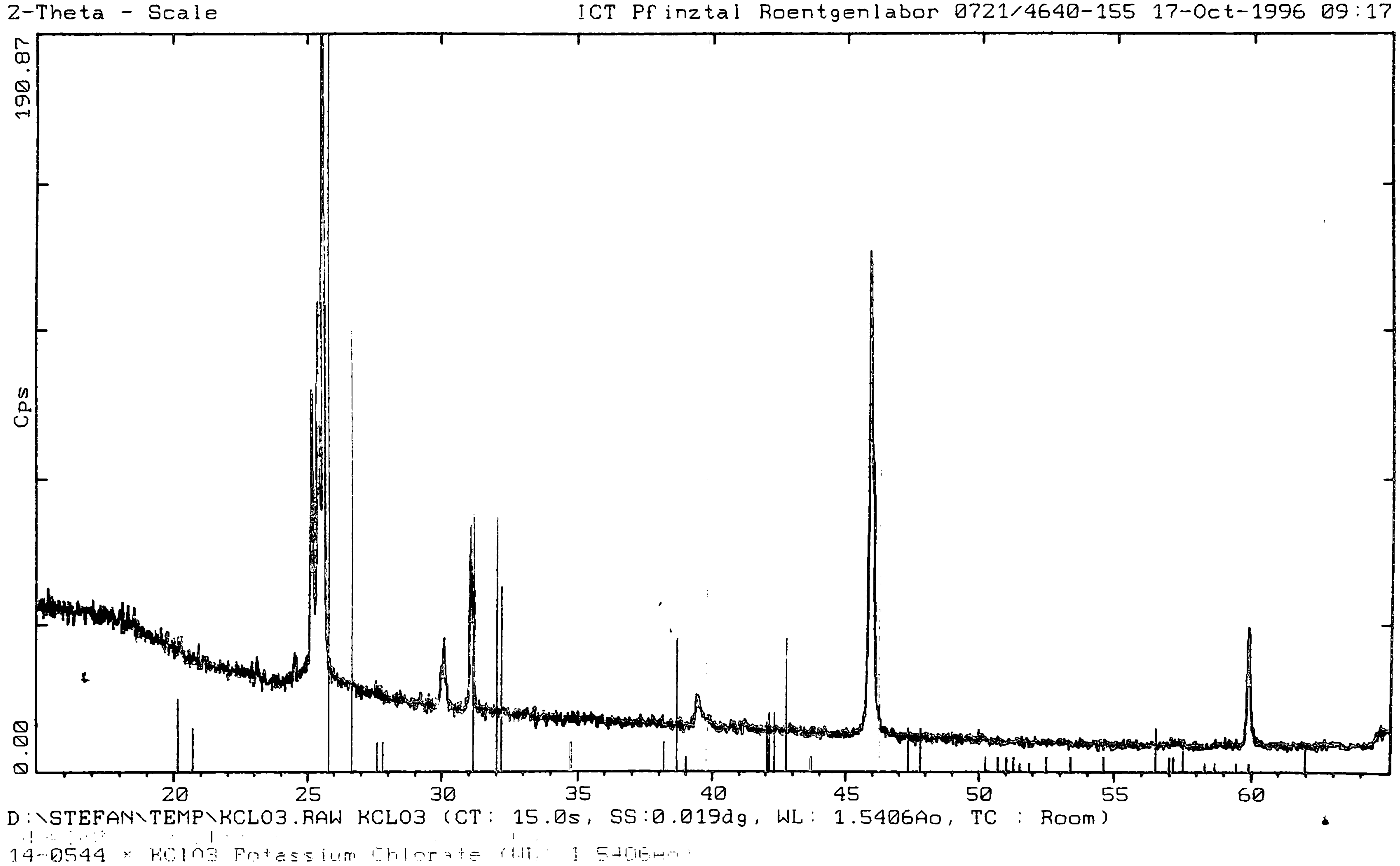


Figure 12

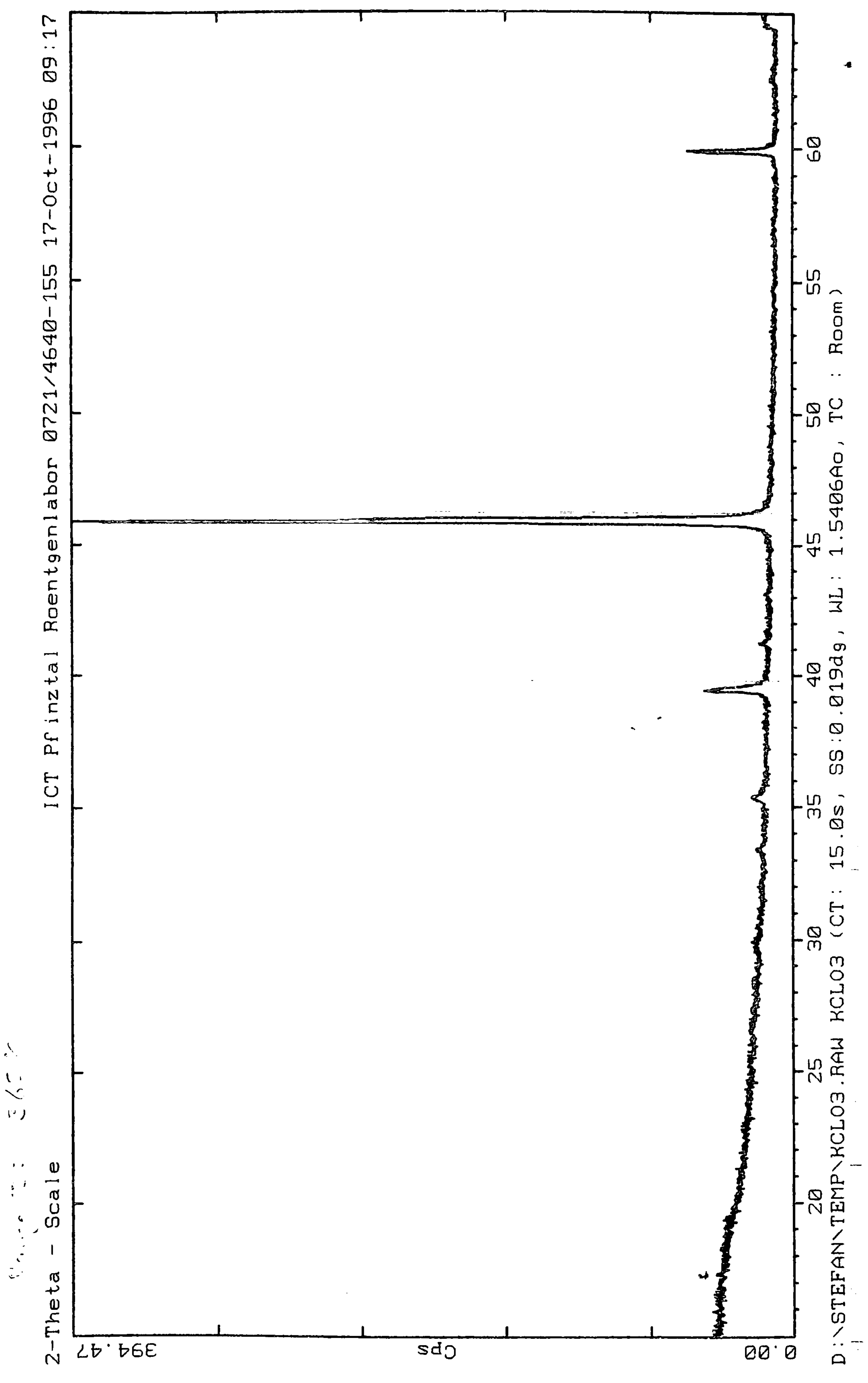

ICT Pfinztal Roentgenlabor 0721/4640-155 17-Oct-1996 09:17
2-Theta - Scale
394.47
Cps
0.00
20
25
30
35
40
45
50
55
60
D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (CT: 15.0s, SS:0.019dg, WL: 1.5406Ao, TC : Room)

Figure 13

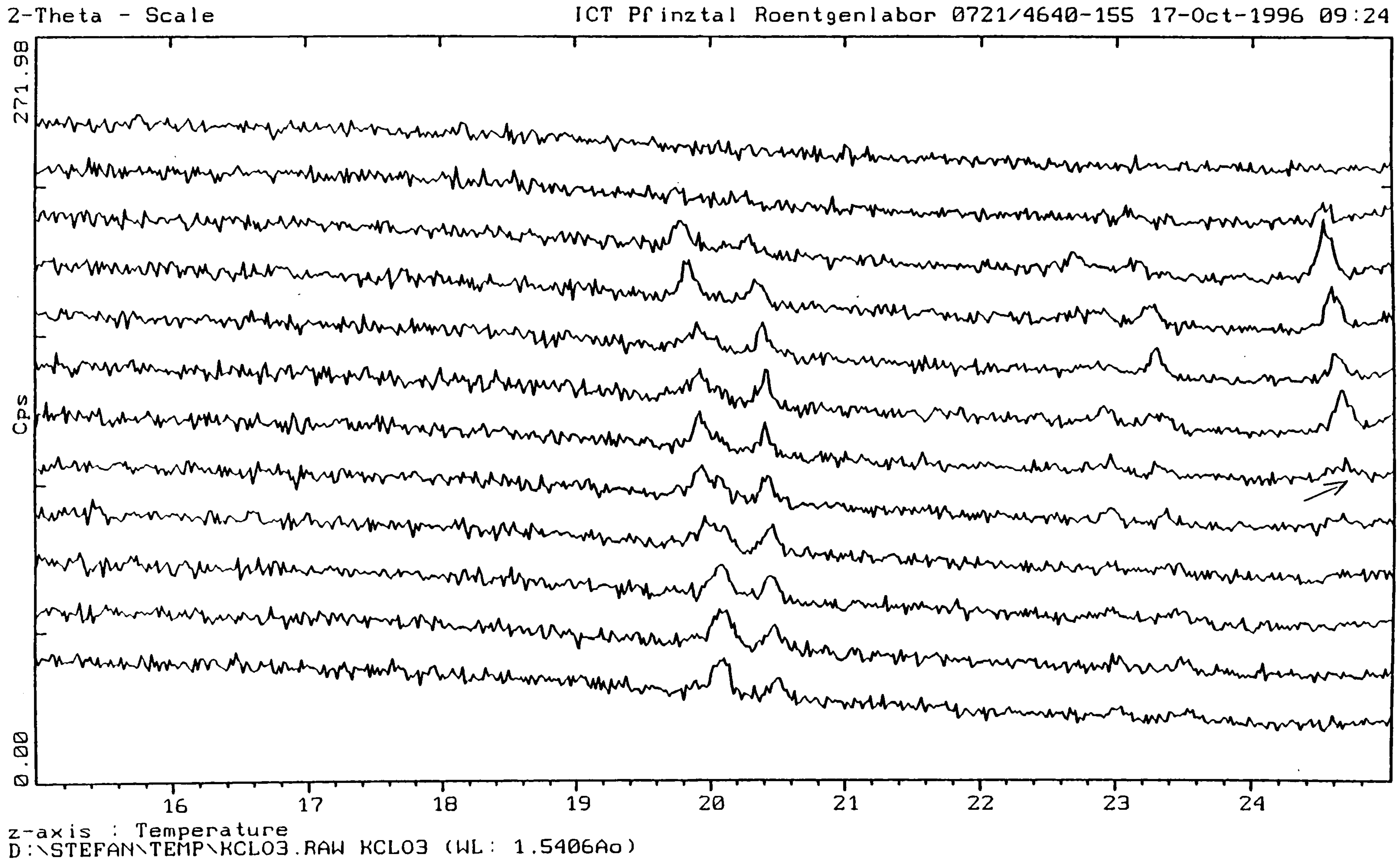

2-Theta - Scale
ICT Pfinztal Roentgenlabor 0721/4640-155 17-Oct-1996 09:24
271.98
Cps
0.00
16
17
18
19
20
21
22
23
24
z-axis : Temperature
D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

Figure 14

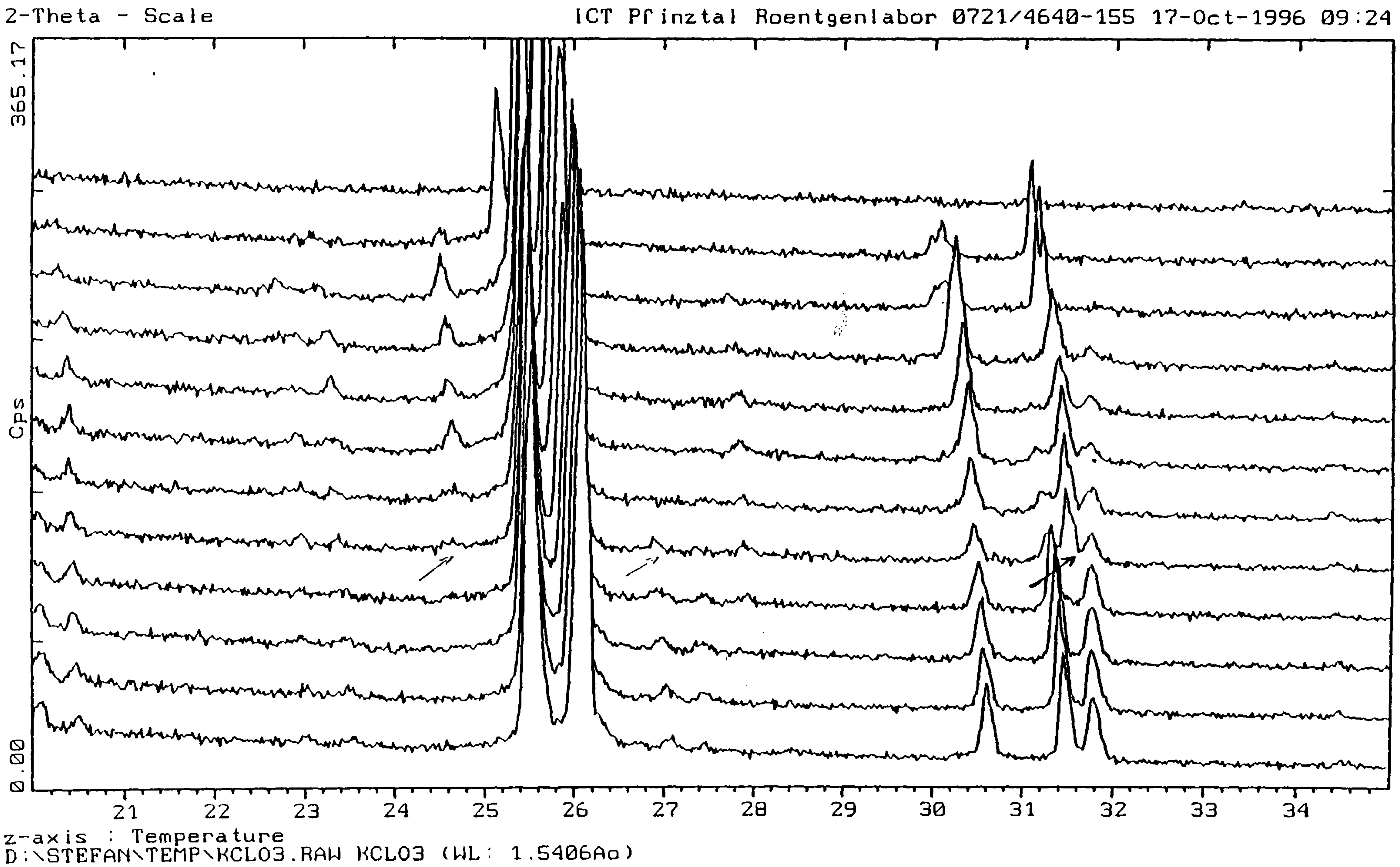

2-Theta - Scale
ICT Pfinztal Roentgenlabor 0721/4640-155 17-Oct-1996 09:24
365.17
Cps
0.00
21
22
23
24
25
26
27
28
29
30
31
32
33
34
z-axis : Temperature
D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

Figure 15

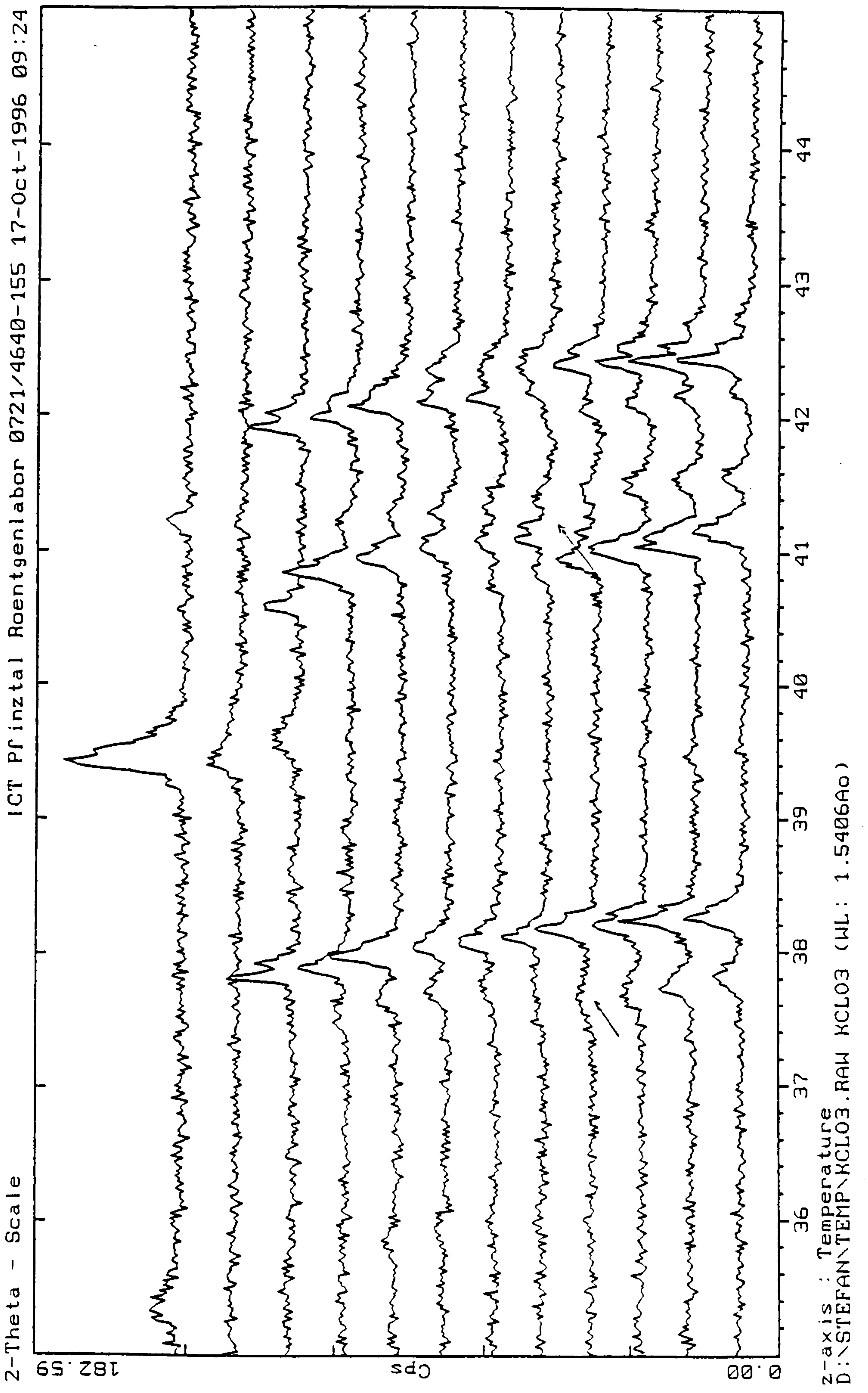

ICT Pfinztal Roentgenlabor 0721/4640-155 17-Oct-1996 09:24
2-Theta - Scale
182.59
Cps
0.00
36
37
38
39
40
41
42
43
44
z-axis : Temperature
D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

Figure 16

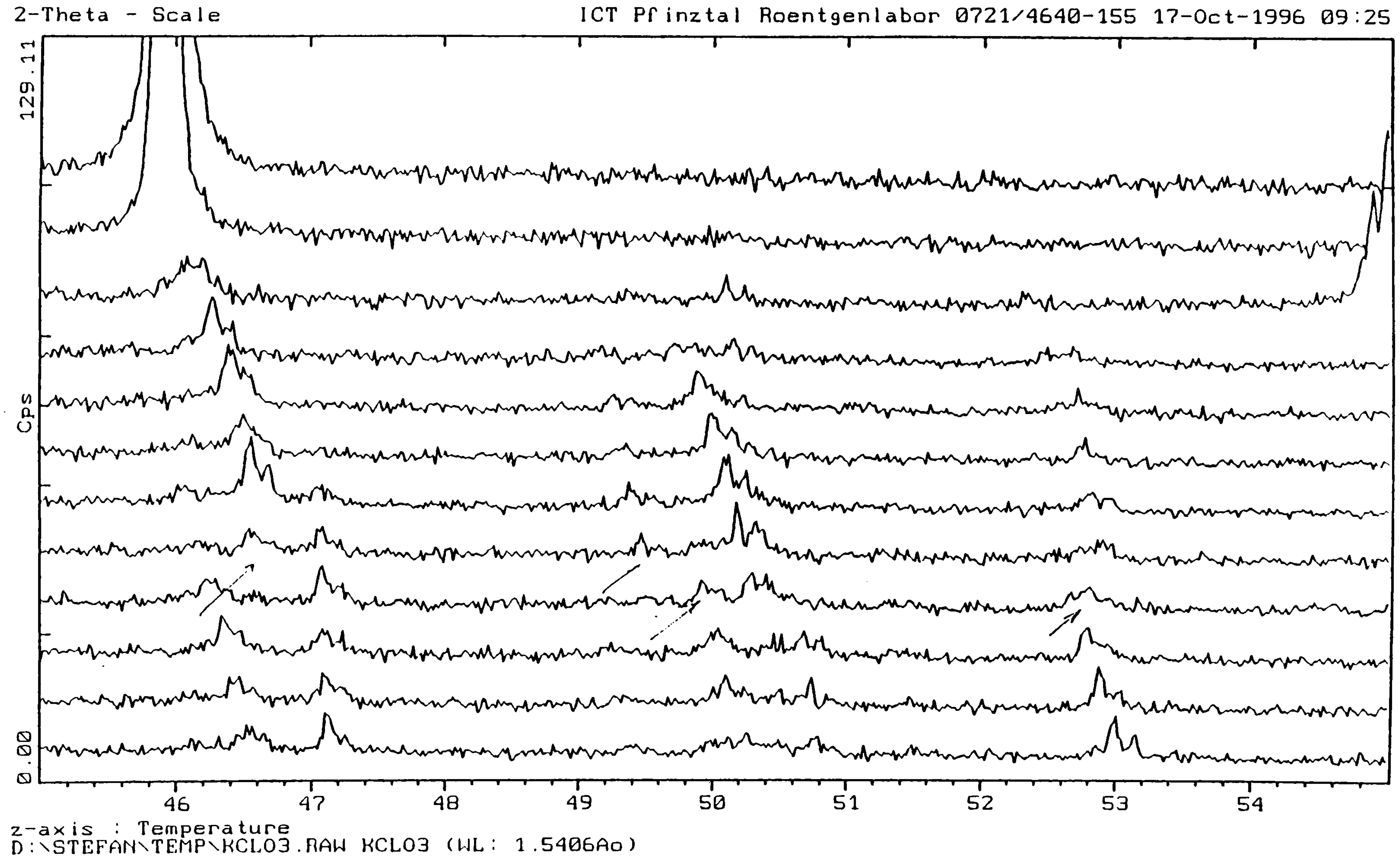

2-Theta - Scale
ICT Pfinztal Roentgenlabor 0721/4640-155 17-Oct-1996 09:25
129.11
Cps
0.00
46
47
48
49
50
51
52
53
54
z-axis : Temperature
D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

Figure 17

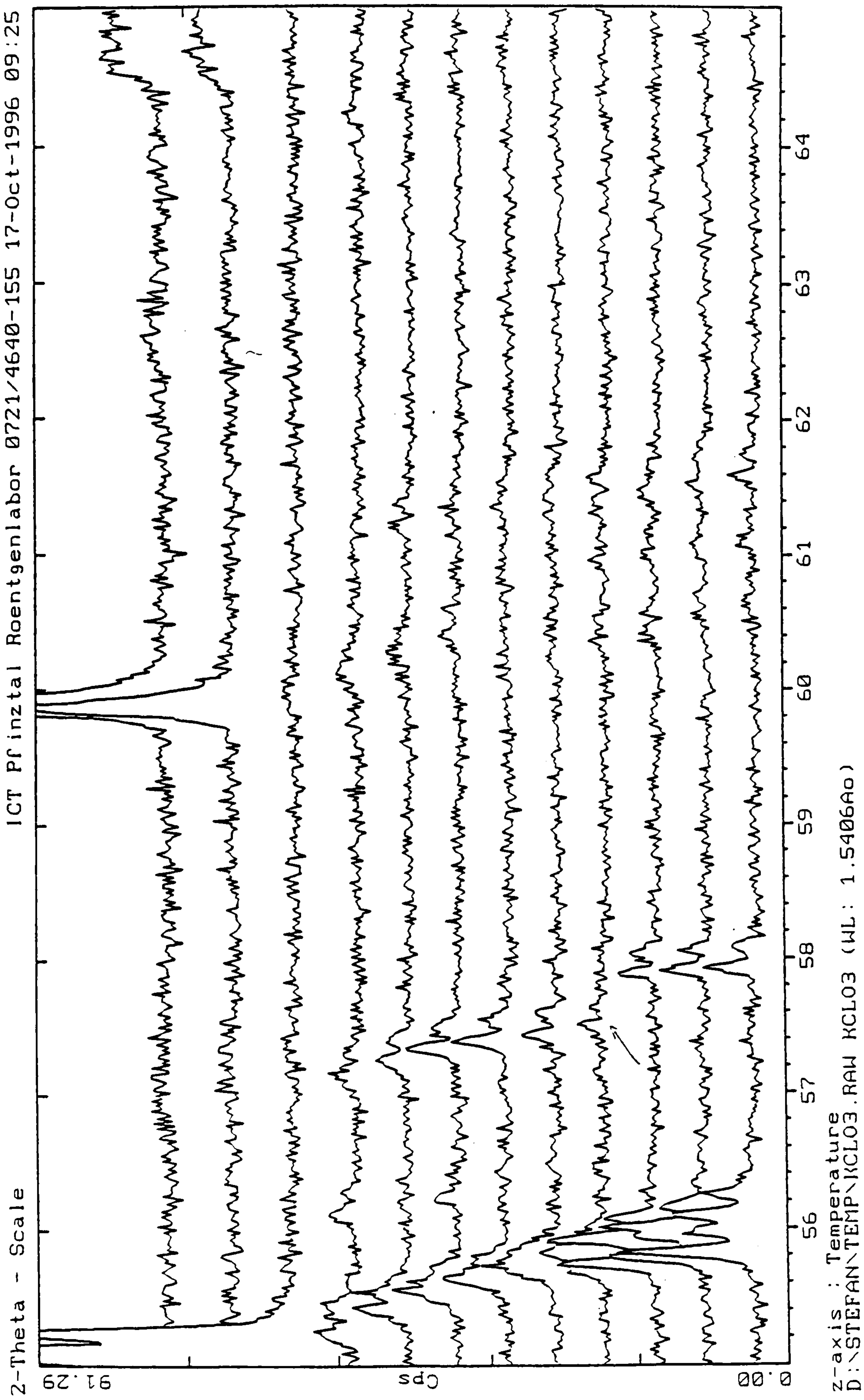
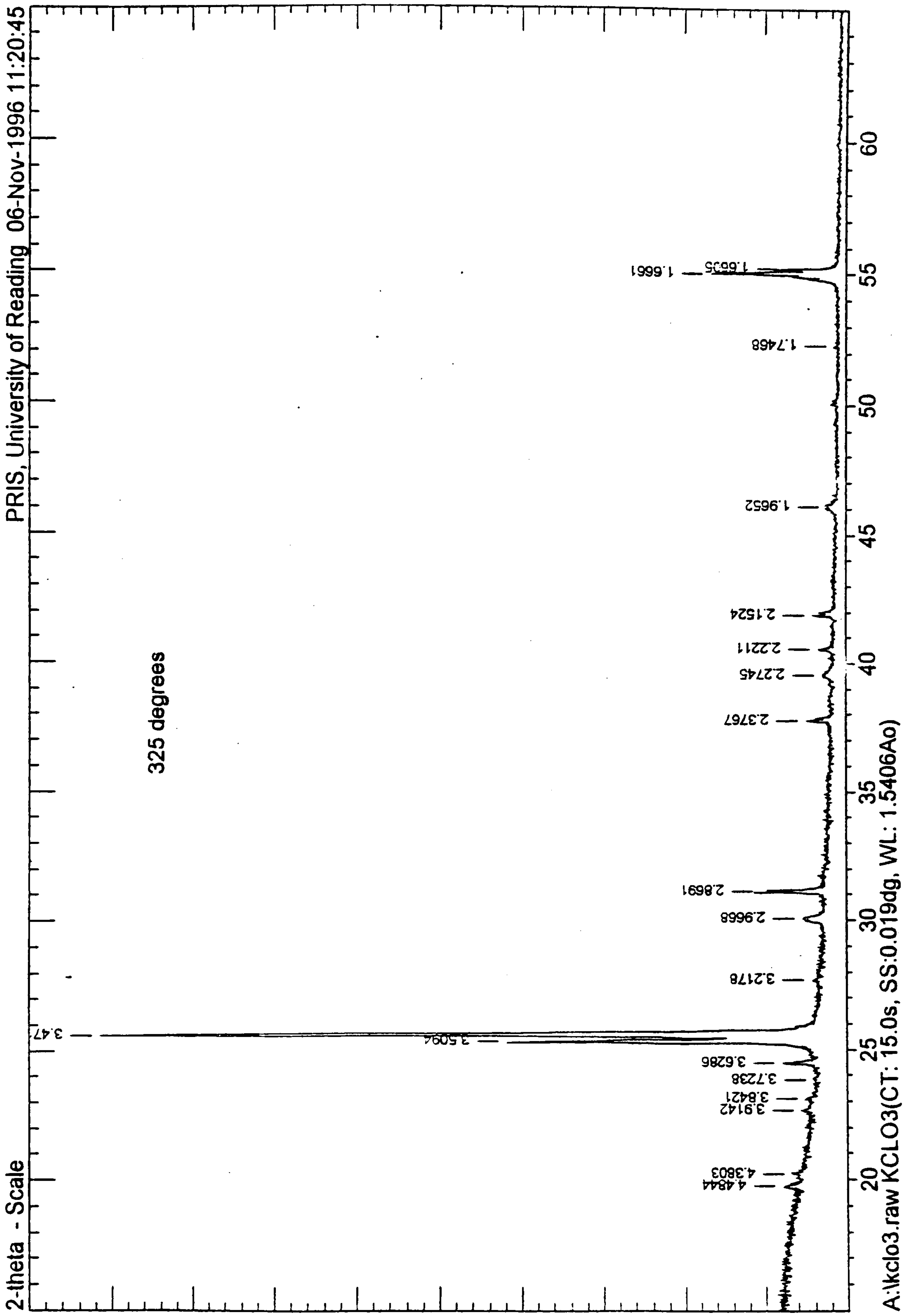
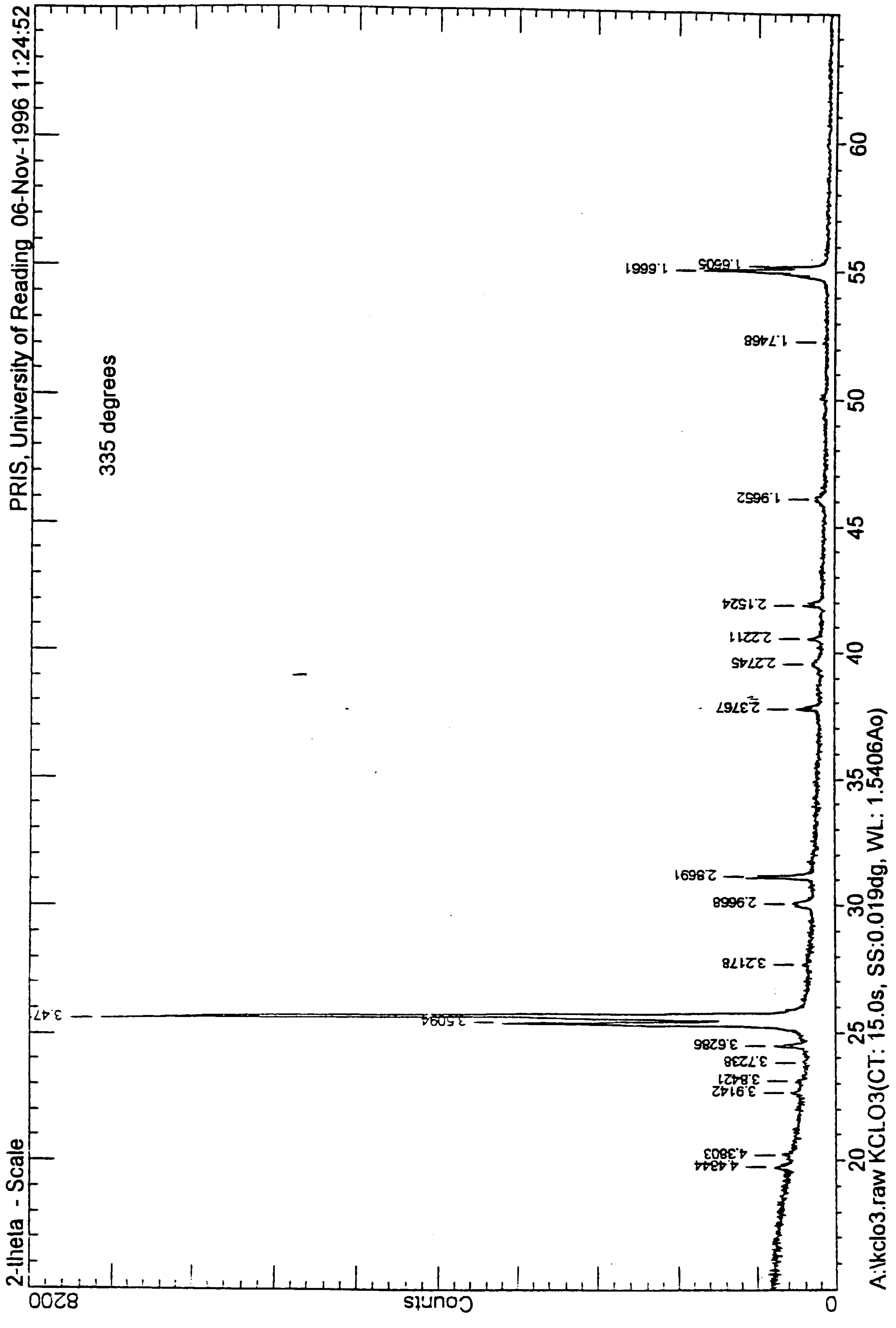
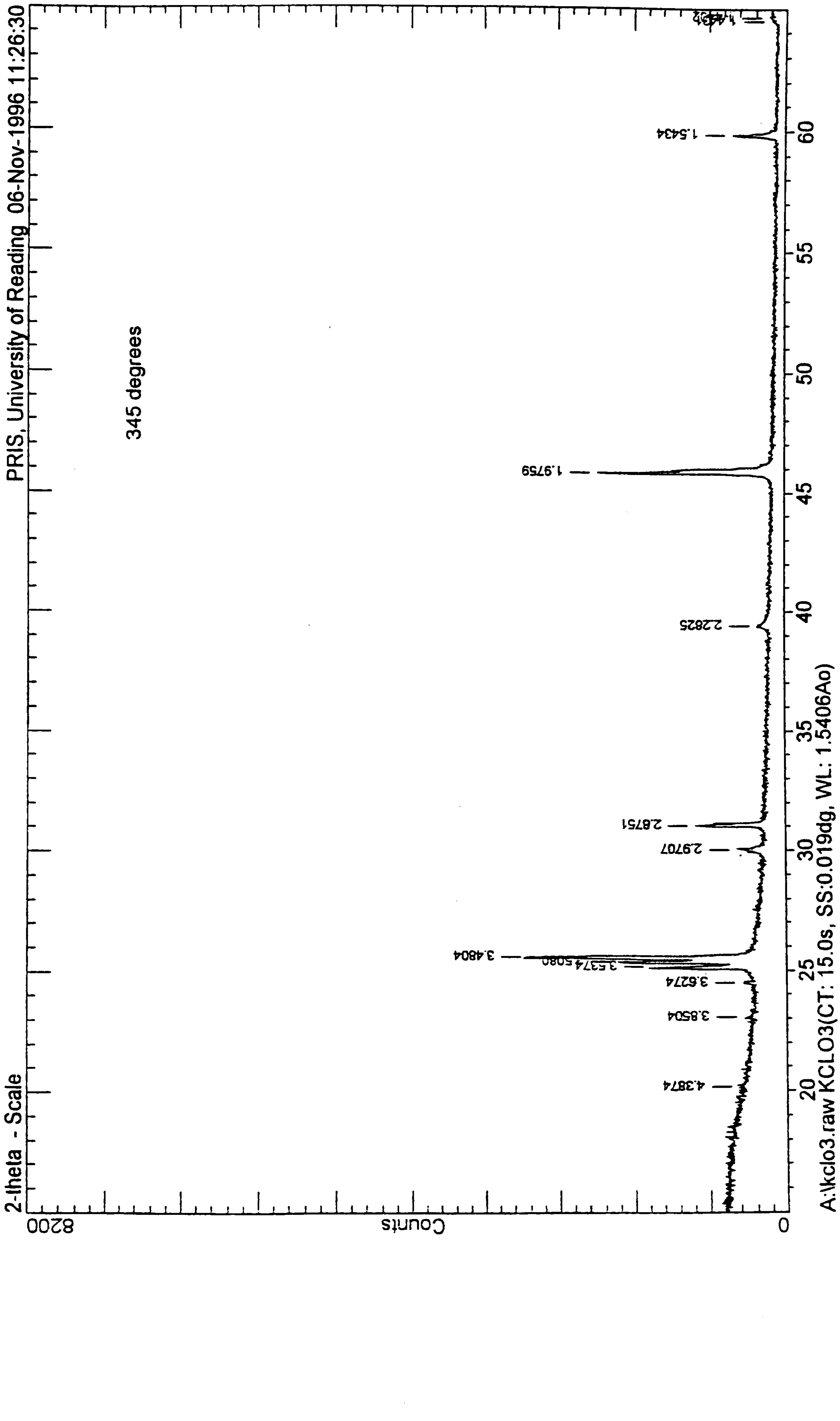
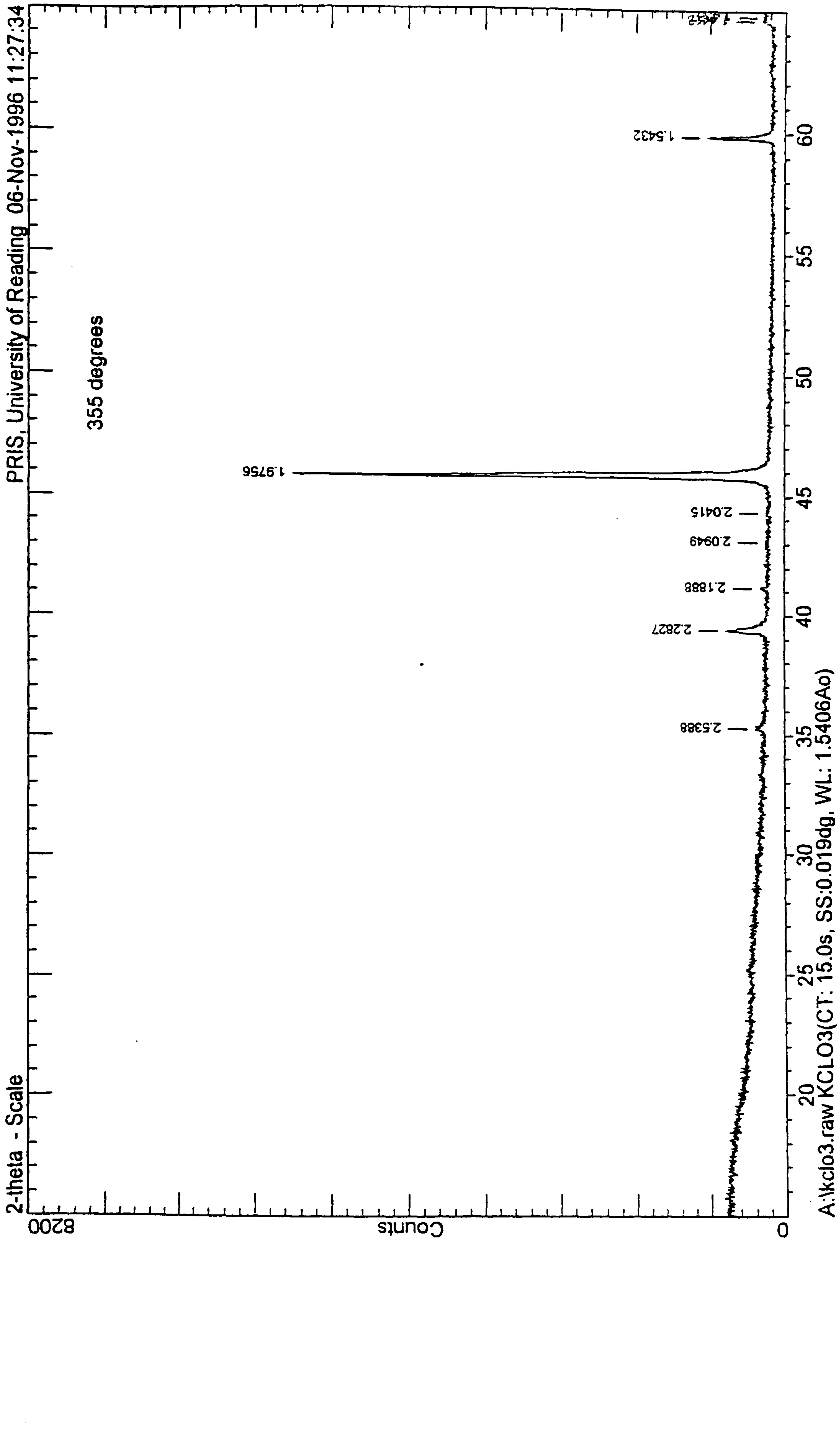

2-Theta - Scale
ICT Pfinztal Roentgenlabor 0721/4640-155 17-Oct-1996 09:25
91.29
Cps
0.00
56
57
58
59
60
61
62
63
64
z-axis : Temperature
D:\STEFAN\TEMP\KCLO3.RAW KCLO3 (WL: 1.5406Ao)

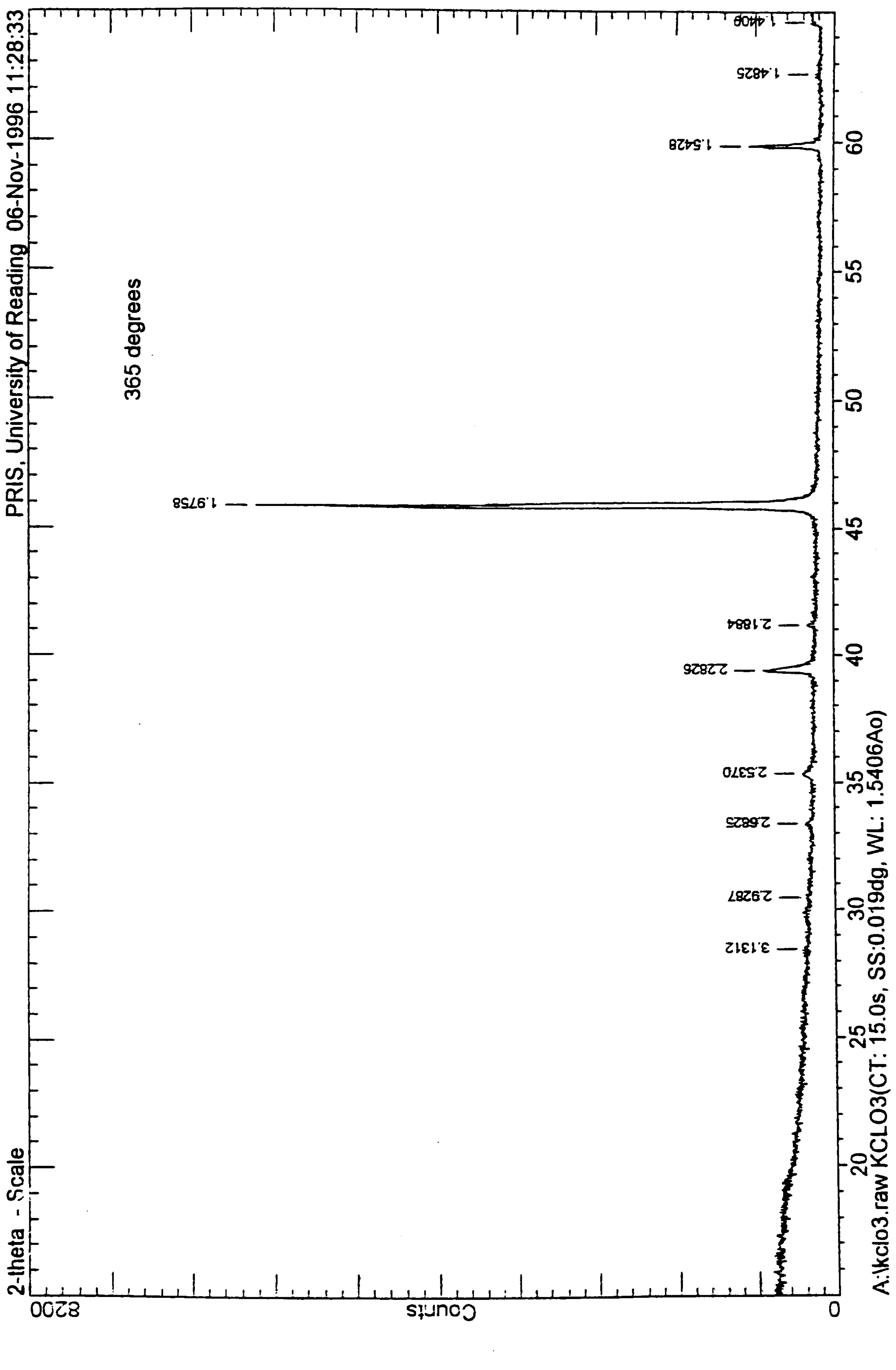
Figure 18


PRIS, University of Reading 06-Nov-1996 11:20:45
2-theta - Scale
325 degrees
A:\kclo3.raw KCLO3(CT: 15.0s, SS:0.019dg, WL: 1.5406Ao)
Counts
8200
0
20
25
30
35
40
45
50
55
60
4.4844
4.3803
3.9142
3.8421
3.7238
3.6286
3.5094
3.47
3.2178
2.9668
2.8691
2.3767
2.2745
2.2211
2.1524
1.9652
1.7468
1.6661
1.6535


PRIS, University of Reading 06-Nov-1996 11:24:52
335 degrees
2-theta - Scale
Counts
8200
0
20
25
30
35
40
45
50
55
60
4.4344
4.3803
3.9142
3.8421
3.7238
3.6286
3.5094
3.47
3.2178
2.9668
2.8691
2.3767
2.2745
2.2211
2.1524
1.9652
1.7468
1.6661
1.6505
A:\kclo3.raw KCLO3(CT: 15.0s, SS:0.019dg, WL: 1.5406Ao)


PRIS, University of Reading 06-Nov-1996 11:26:30
345 degrees
2-theta - Scale
Counts
8200
0
20
25
30
35
40
45
50
55
60
4.3874
3.8504
3.6274
3.5374
5080
3.4804
2.9707
2.8751
2.2825
1.9759
1.5434
A:\kclo3.raw KCLO3(CT: 15.0s, SS:0.019dg, WL: 1.5406Ao)


PRIS, University of Reading 06-Nov-1996 11:27:34
355 degrees
2-theta - Scale
Counts
8200
0
20
25
30
35
40
45
50
55
60
2.5388
2.2827
2.1888
2.0949
2.0415
1.9756
1.5432
A:\kclo3.raw KCLO3(CT: 15.0s, SS:0.019dg, WL: 1.5406Ao)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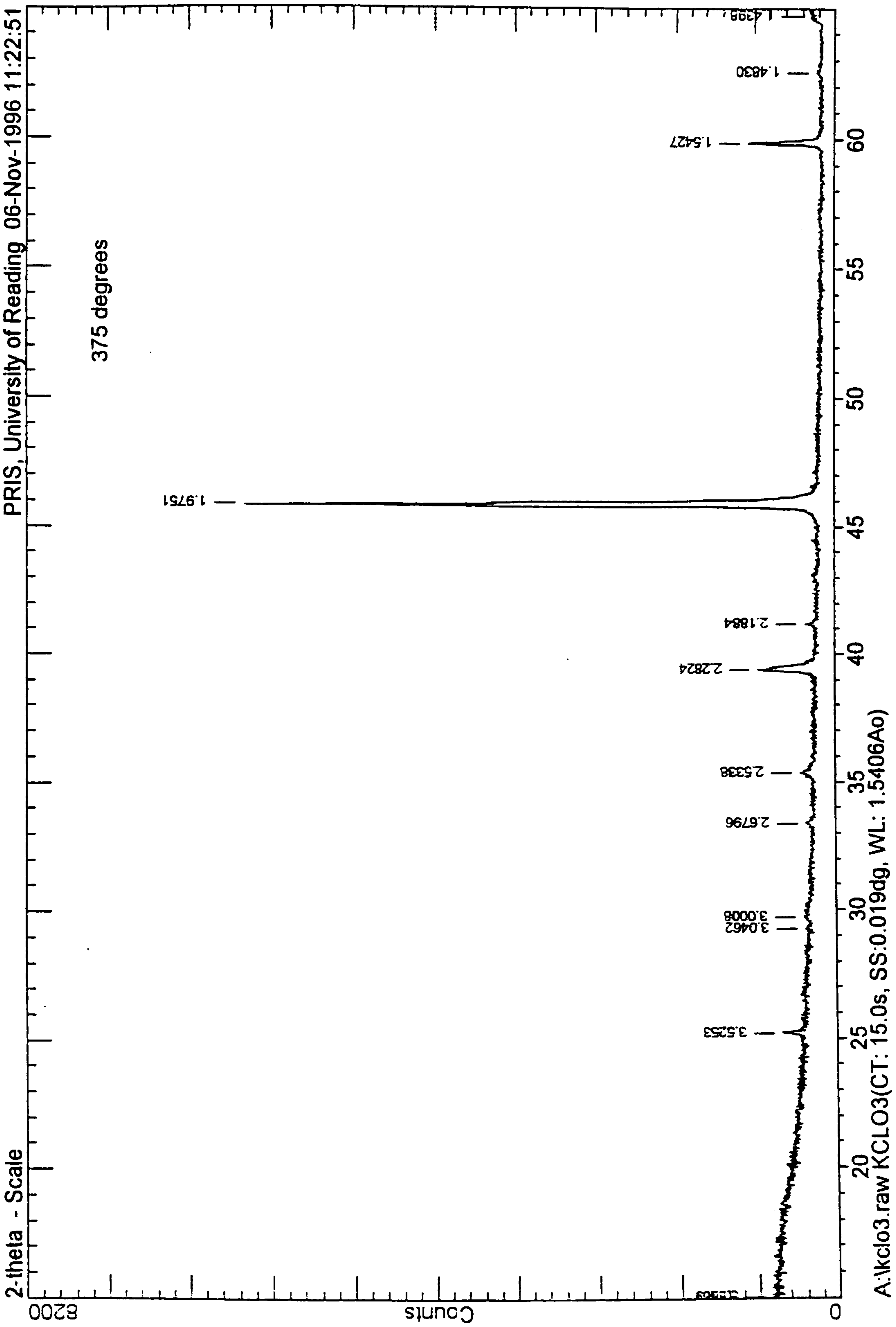
2-theta - Scale
8200
Counts
0
20
25
30
35
40
45
50
55
60
3.1312
2.9287
2.6825
2.5370
2.2826
2.1884
1.9758
1.5428
1.4825
1.4408
A:\kclo3.raw KCLO3(CT: 15.0s, SS:0.019dg, WL: 1.5406Ao)


PRIS, University of Reading 06-Nov-1996 11:22:51
375 degrees
2-theta - Scale
A:\kclo3.raw KCLO3(CT: 15.0s, SS:0.019dg, WL: 1.5406Ao)
Counts
8200
0
20
25
30
35
40
45
50
55
60
3.5253
3.0462
3.0008
2.6796
2.5338
2.2824
2.1884
1.9751
1.5427
1.4830
1.4208

EXTRACT FROM COMPUTER PRINTOUT OF TWO-THETA COUNT DATA FOR THE TEMPERATURES SHOWN

_1A=30	325	335	345	355	365
_TIMESTAR	19727	TEST 10	TEST 11	TEST 12	TEST 13
_2THETACOUNTS					
23.0063	346	360	373	364	370
23.025	319	369	382	397	421
23.0438	384	381	390	392	366
23.0625	338	375	444	388	402
23.0813	367	381	382	383	362
23.1	337	424	428	349	347
23.1187	359	357	382	392	393
23.1375	369	411	368	450	387
23.1563	372	397	389	373	374
23.175	388	401	384	374	348
23.1938	430	375	378	383	321
23.2125	417	376	365	386	357
23.2313	437	306	355	408	398
23.25	422	332	344	390	397
23.2688	444	339	370	398	374
23.2875	404	344	312	405	368
23.3062	389	314	381	377	366
23.325	359	352	364	386	347
23.3438	357	330	344	395	388
23.3625	312	349	396	384	390
23.3813	346	343	378	372	365
23.4	329	316	382	371	376
23.4188	345	306	338	373	353
23.4375	277	321	337	375	381
23.4563	298	316	339	364	360
23.475	342	308	347	410	384
23.4937	345	303	334	399	365
23.5125	315	318	347	417	364
23.5313	318	330	350	365	374
23.55	353	332	341	373	345
23.5688	314	325	352	363	361
23.5875	326	318	344	364	359
23.6063	323	299	361	386	383
23.625	306	293	362	398	359
23.6438	325	330	345	378	377
23.6625	319	298	314	421	358
23.6812	301	304	379	365	375
23.7	298	340	357	377	396
23.7188	325	290	361	369	354
23.7375	314	303	374	369	378
23.7563	323	279	358	395	345
23.775	304	317	324	389	393
23.7938	276	321	371	389	380
23.8125	300	320	358	389	387
23.8313	327	335	351	377	382
23.85	299	307	327	404	371
23.8687	313	331	380	397	352
23.8875	323	325	365	363	380
23.9063	292	323	338	413	338
23.925	319	344	340	364	377
23.9438	299	320	359	369	331
23.9625	328	309	327	365	343
23.9813	301	313	324	410	367
24	325	300	349	359	378
24.0188	289	289	332	350	352
24.0375	300	301	345	362	350

24.0562	312	305	370	387	388
24.075	309	292	349	394	348
24.0938	306	282	353	348	361
24.1125	307	309	353	355	346
24.1313	315	332	311	379	362
24.15	286	314	360	361	336
24.1688	305	308	363	350	382
24.1875	337	345	377	370	335
24.2063	289	307	345	357	372
24.225	310	314	343	358	336
24.2437	277	326	357	375	355
24.2625	310	317	371	338	384
24.2813	300	310	366	424	370
24.3	292	323	340	376	361
24.3188	289	292	388	370	398
24.3375	318	326	348	406	362
24.3563	301	345	342	390	355
24.375	313	338	367	367	370
24.3938	322	327	348	365	348
24.4125	336	379	327	385	326
24.4312	331	384	368	390	352
24.45	332	426	402	369	348
24.4688	335	480	420	372	370
24.4875	340	545	425	402	338
24.5063	437	640 →	463 →	375	374
24.525	451	548	408	357	350
24.5438	505	527	430	369	382
24.5625	541 →	534 →	448 →	367	294
24.5813	455	457	348	365	351
24.6	488	409	350	348	373
24.6187	448	364	368	376	323
24.6375	433	362	370	376	337
24.6563	356	338	380	387	390
24.675	339	326	371	373	337
24.6938	329	308	393	363	333
24.7125	318	336	361	393	346
24.7313	357	372	397	369	335
24.75	320	333	388	398	360
24.7688	331	336	373	365	352
24.7875	348	341	375	375	331
24.8062	337	372	404	379	316
24.825	330	365	399	388	333
24.8438	342	379	392	377	339
24.8625	343	366	393	367	342
24.8813	341	359	422	372	342
24.9	357	368	394	359	373
24.9188	350	339	381	354	353
24.9375	405 →	382	390	372	364
24.9563	345	379	444	410	324
24.975	398	396	421	383	323
24.9937	360	371	429	410	355
25.0125	379	371	451	372	327
25.0313	403	396	418	370	317
25.05	398	447	501	388	319
25.0688	415	431	655	405	355
25.0875	372	398	564	364	339
25.1063	357	429	1163	361	350
25.125	429	428	1488 →	349	331
25.1438	425	500	1462	366	350

25.1625	432	555	1206	395	329
25.1812	463	565	1144	378	376
25.2	490	597	1085	422	365
25.2188	550	601	834	426	342
25.2375	584	762	710	393	367
25.2563	712	990	641	391	359
25.275	743	1252	609	420	354
25.2938	817	1847	693	381	348
25.3125	1052	2563	918	381	336
25.3313	1501	3266	1275	392	358
25.35	2008	3435	1773	384	344
25.3687	2728	2978	1827	353	377
25.3875	2933	2498	1651	360	328
25.4063	2997	2225	1446	414	343
25.425	2505	1826	1290	409	337
25.4438	2178	1460	1082	386	369
25.4625	1848	1222	1053	397	354
25.4813	1468	1355	1020	385	326
25.5	1207	1629	1535	361	367
25.5188	1030	1917	2393	344	318
25.5375	1011	2378	2863	372	303
25.5562	1022	3260	2798	391	342
25.575	1125	4342	2414	391	330
25.5938	1349	5671	2259	365	345
25.6125	1779	6966	2084	350	372
25.6313	2338	7492	1568	351	310
25.65	3294	7355	1042	331	316
25.6688	4567	6334	709	379	317
25.6875	6148	4948	584	393	325
25.7063	7489	3756	514	393	318
25.725	8513	2825	503	365	318
25.7437	8550	1885	438	343	318
25.7625	7578	1150	428	379	367
25.7813	6390	875	392	363	316
25.8	5280	681	406	367	320
25.8188	3993	587	439	361	331
25.8375	2702	541	389	358	328
25.8563	1962	532	385	345	329
25.875	1377	484	404	386	313
25.8938	997	498	342	371	323
25.9125	697	514	387	344	332
25.9312	671	457	371	359	334
25.95	587	420	369	343	291
25.9688	579	393	402	374	323
25.9875	526	386	356	378	335
26.0063	491	408	373	378	339
26.025	466	372	350	363	370
26.0438	432	361	369	381	348
26.0625	421	328	360	352	333
26.0813	419	367	372	403	311
26.1	418	326	381	342	337
26.1187	393	347	330	340	341
26.1375	395	335	349	365	341
26.1563	352	335	347	376	315
26.175	378	317	332	379	347
26.1938	350	333	361	382	345
26.2125	358	330	331	368	338
26.2313	325	319	354	357	350
26.25	360	311	322	379	302

26.2688	345	330	359	374	316
26.2875	347	312	323	329	308
26.3062	342	346	338	350	337
26.325	340	314	342	336	317
26.3438	322	307	364	351	322
26.3625	326	360	338	373	333
26.3813	321	311	340	384	317
26.4	299	326	328	335	329
26.4188	310	319	349	337	345
26.4375	335	299	349	333	339
26.4563	307	298	340	352	353
26.475	337	308	339	332	342
26.4937	332	328	320	340	328
26.5125	298	316	313	337	351
26.5313	336	307	348	336	357
26.55	294	320	348	353	331
26.5688	278	322	337	374	360
26.5875	294	295	350	372	328
26.6063	337	295	336	393	345
26.625	287	308	339	367	325
26.6438	318	284	334	348	351
26.6625	285	298	337	359	333
26.6812	293	293	332	373	348
26.7	294	331	330	345	312
26.7188	301	269	328	362	343
26.7375	316	308	350	335	353
26.7563	314	282	338	379	341
26.775	303	308	326	365	314
26.7938	282	296	337	360	354
26.8125	299	271	320	351	334
26.8313	308	295	284	353	314
26.85	319	293	316	332	355
26.8687	318	285	343	313	318
26.8875	285	277	322	350	332
26.9063	299	298	330	376	336
26.925	310	314	290	372	339
26.9438	304	282	330	383	298
26.9625	332	257	293	364	315
26.9813	314	286	334	327	357
27	278	279	279	340	356
27.0188	305	300	285	323	317
27.0375	302	294	299	315	307
27.0562	271	264	329	393	306
27.075	293	330	300	352	315
27.0938	313	283	297	319	327
27.1125	302	296	302	380	299
27.1313	266	280	305	328	312
27.15	293	242	294	325	273
27.1688	275	302	322	360	318
27.1875	305	289	291	299	332
27.2063	274	276	332	337	312
27.225	288	297	289	319	322
27.2437	283	283	315	331	306
27.2625	335	275	317	370	344
27.2813	318	281	301	327	320
27.3	266	281	283	340	305
27.3188	269	273	315	354	301
27.3375	293	284	291	341	343
27.3563	298	294	300	318	308

27.375	280	273	317	354	333
27.3938	279	287	319	329	323
27.4125	323	246	306	342	307
27.4312	297	281	313	350	344
27.45	273	251	303	343	310
27.4688	268	302	304	323	272
27.4875	260	271	302	320	319
27.5063	315	300	256	360	305
27.525	277	304	326	385	295
27.5438	290	269	351	336	323
27.5625	267	295	299	354	303
27.5813	277	273	288	342	288
27.6	283	291	304	319	325
27.6187	282	308	280	325	310
27.6375	288	270	330	362	307
27.6563	285	313	284	371	312
27.675	284	335	284	304	290
27.6938	330	345	291	335	277
27.7125	325	343	316	320	303
27.7313	303	309	333	356	321
27.75	294	313	274	328	294
27.7688	338	288	302	341	271
27.7875	348	299	299	323	309
27.8062	310	290	303	325	297
27.825	269	262	288	352	299
27.8438	311	253	260	323	307
27.8625	272	265	271	320	290
27.8813	284	303	299	339	300
27.9	257	265	302	331	280
27.9188	254	272	312	334	336
27.9375	274	275	267	304	276
27.9563	265	297	301	327	302
27.975	288	286	267	303	292
27.9937	298	275	290	330	320
28.0125	299	286	283	309	291
28.0313	258	282	276	345	305
28.05	311	302	266	346	300
28.0688	283	268	287	327	293
28.0875	262	265	271	304	293
28.1063	278	298	277	323	300
28.125	257	275	277	338	291
28.1438	247	285	282	322	288
28.1625	308	262	272	323	308
28.1812	274	267	295	308	332
28.2	252	222	276	327	332
28.2188	252	241	273	331	282
28.2375	277	289	273	335	296
28.2563	267	245	263	343	311
28.275	247	275	256	339	302
28.2938	263	249	297	321	281
28.3125	256	279	304	327	337
28.3313	256	300	248	290	289
28.35	268	232	262	320	256
28.3687	255	274	278	309	298
28.3875	247	274	286	326	301
28.4063	240	253	263	306	279
28.425	237	227	315	321	338
28.4438	285	261	292	335	325
28.4625	273	268	301	295	310

28.4813	257	291	267	333	290
28.5	247	233	285	362	310
28.5188	266	234	260	304	331
28.5375	259	253	290	328	324
28.5562	266	259	269	329	297
28.575	241	266	272	308	321
28.5938	225	275	279	334	281
28.6125	234	282	297	363	284
28.6313	245	282	268	295	291
28.65	274	244	277	282	283
28.6688	246	279	267	320	298
28.6875	235	243	276	317	280
28.7063	237	241	265	298	262
28.725	246	249	259	287	288
28.7437	238	255	259	345	284
28.7625	240	237	261	300	289
28.7813	245	227	270	316	278
28.8	249	237	256	300	297
28.8188	254	271	244	336	300
28.8375	275	258	262	321	280
28.8563	241	244	264	351	297
28.875	253	240	283	298	291
28.8938	228	279	264	334	303
28.9125	242	228	260	316	275
28.9312	220	242	258	316	286
28.95	250	263	281	298	315
28.9688	247	250	237	313	299
28.9875	230	284	273	292	286
29.0063	233	247	263	321	274
29.025	249	225	248	312	286
29.0438	245	253	241	330	272
29.0625	243	227	274	298	243
29.0813	255	248	248	306	253
29.1	230	260	270	299	264
29.1187	218	262	277	315	279
29.1375	213	233	262	288	311
29.1563	266	229	270	312	290
29.175	233	237	306	333	282
29.1938	263	267	276	324	275
29.2125	247	243	301	282	256
29.2313	192	243	255	308	291
29.25	219	213	265	297	295
29.2688	231	231	276	306	295
29.2875	239	252	263	290	284
29.3062	236	239	255	311	268
29.325	221	247	263	266	285
29.3438	226	243	251	322	273
29.3625	209	262	230	303	271
29.3813	260	263	255	280	277
29.4	232	222	281	317	290
29.4188	234	275	260	293	301
29.4375	250	228	269	305	285
29.4563	236	217	221	327	266
29.475	249	255	270	289	284
29.4938	229	253	300	290	265
29.5125	235	246	242	319	290
29.5313	242	235	249	297	320
29.55	228	222	242	326	277
29.5688	217	241	275	263	277

29.5875	221	237	228	312	298
29.6063	229	229	257	310	310
29.625	251	252	274	295	285
29.6438	255	246	280	282	287
29.6625	247	240	239	305	300
29.6813	213	265	237	280	312
29.7	223	232	242	331	301
29.7188	195	230	241	293	278
29.7375	239	250	257	292	324
29.7563	207	256	242	311	299
29.775	207	241	283	298	305
29.7938	258	243	242	298	300
29.8125	253	241	272	336	308
29.8313	261	261	265	313	297
29.85	254	248	256	312	278
29.8688	261	250	280	290	292
29.8875	258	253	269	301	313
29.9063	257	263	302	328	341
29.925	255	286	316	318	322
29.9438	261	301	365	319	299
29.9625	255	338	409	293	308
29.9813	276	370	390	284	262
30	244	407	360	328	301
30.0188	245	370	385	288	276
30.0375	274	380	455	265	315
30.0563	273	412	440	325	300
30.075	297	418	516	294	318
30.0938	353	435	475	254	266
30.1125	436	430	359	269	280
30.1313	557	420	368	295	292
30.15	700	393	343	250	259
30.1688	846	379	333	259	255
30.1875	879	353	334	273	248
30.2063	1005	327	276	271	287
30.225	1127	294	272	307	281
30.2438	1092	278	251	301	290
30.2625	873	277	231	248	292
30.2813	807	242	274	271	253
30.3	700	256	268	267	276
30.3188	603	264	254	307	265
30.3375	480	270	265	286	259
30.3563	364	251	238	254	250
30.375	297	240	251	299	283
30.3938	292	227	252	267	283
30.4125	242	230	254	295	265
30.4313	243	229	248	282	269
30.45	240	235	254	273	308
30.4688	237	222	209	276	282
30.4875	263	241	259	264	295
30.5063	233	229	242	297	294
30.525	198	235	247	272	283
30.5438	221	238	240	284	280
30.5625	195	218	224	283	293
30.5813	190	230	255	282	300
30.6	210	232	267	272	246
30.6188	212	249	235	278	277
30.6375	218	254	241	283	249
30.6563	219	231	226	278	262
30.675	254	203	270	279	257

30.6938	214	237	236	276	259
30.7125	214	239	236	289	271
30.7313	205	226	241	282	242
30.75	209	244	221	276	262
30.7688	208	271	240	239	257
30.7875	205	223	248	257	293
30.8063	233	245	247	277	274
30.825	235	259	247	284	280
30.8438	202	208	232	263	259
30.8625	210	223	241	282	277
30.8813	237	236	248	310	267
30.9	202	251	264	260	288
30.9188	247	233	266	262	288
30.9375	252	258	263	298	249
30.9563	260	279	284	288	241
30.975	274	234	279	316	242
30.9938	233	240	364	311	268
31.0125	214	244	503	284	270
31.0313	214	256	769	303	251
31.05	252	280	924	236	260
31.0688	222	369	962	244	283
31.0875	215	530	704	280	272
31.1063	235	923	573	270	233
31.125	267	853	699	295	272
31.1438	245	641	774	255	266
31.1625	300	618	647	283	294
31.1813	268	756	411	269	279
31.2	285	800	290	276	263
31.2188	424	647	316	295	248
31.2375	470	451	276	229	271
31.2563	528	382	257	267	241
31.275	629	326	246	261	254
31.2938	747	285	248	249	232
31.3125	688	278	223	263	245
31.3313	646	239	250	271	245
31.35	546	252	226	258	262
31.3688	481	274	244	283	250
31.3875	492	217	275	266	235
31.4063	399	226	228	300	258
31.425	317	240	251	245	235
31.4438	320	262	254	261	265
31.4625	245	226	253	271	261
31.4813	250	242	213	278	259
31.5	256	216	228	250	213
31.5188	276	247	230	268	246
31.5375	215	239	254	270	262
31.5563	233	218	214	235	255
31.575	266	242	250	286	266
31.5938	246	236	247	249	263
31.6125	251	238	193	254	280
31.6313	247	234	256	272	239
31.65	249	218	264	265	249
31.6688	309	236	242	250	262
31.6875	309	256	249	260	255
31.7063	333	213	232	263	250
31.725	306	220	229	259	235
31.7438	294	233	226	222	232
31.7625	279	284	243	247	253
31.7813	277	227	221	253	245

31.8	249	255	225	249	252
31.8188	241	241	223	264	277
31.8375	248	255	241	241	247
31.8563	220	232	231	273	237
31.875	255	224	207	247	268
31.8938	237	238	218	251	255
31.9125	220	228	216	259	235
31.9313	270	235	258	269	275
31.95	229	247	221	249	240
31.9688	209	216	231	286	287
31.9875	212	220	222	245	236
32.0063	223	213	232	282	292

CHAPTER 4

THERMAL DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF METALLIC OXIDES AND SALTS

The literature on the pyrolysis of potassium chlorate alone and in the presence of other compounds is characterised by contradictory evidence on the detail of the decomposition. A study of the thermal decomposition of potassium chlorate alone is described in Chapter 3 and the work described in this chapter deals with its decomposition in the presence of other compounds that could act as catalysts. Particular attention is paid to the effect of manganese dioxide on the decomposition of potassium chlorate because of the potential relevance to its curing properties.

4.0 LITERATURE SURVEY

Brown and co-workers(1&2) report that "a violent evolution of Oxygen abruptly commenced" in reactions between $KClO_3$ and MnO_2 and they defined the temperature at which this occurred as the "spontaneous decomposition temperature" which varied with the proportion of MnO_2 in the mix within the range 300/380° C.They reported practically no decomposition of pure $KClO_3$ at temperatures up to 400° C. Farmer & Firth(3) discuss several catalysts excluding MnO_2

Otto and Fry[4] suggested that potassium Chloride acts as a catalyst for the conversion to perchlorate but not for the direct decomposition to KCl.They suggested that the three stages in the decomposition were:-

$$4KClO_3 \text{ --------> } 3KClO_4 + KCl \quad \text{(i)}$$

$$2KClO_3 \text{ --------> } 2KCl + 3O_2 \quad \text{(ii)}$$

$$KClO_4 \text{ --------> } KCl + 2O_2 \quad \text{(iii)}$$

and that KCl acts as a catalyst for reaction (i)

The comparative data with and without KCl are as follows:-

TEMP	408° C		463° C		487° C	
TIME	4 hours		1 hour		0.25 hours	
	%KCl	%Decomp.	%KCl	%Decomp.	%KCl	%Decomp.
	0	2.3	0	2.0	0	9.0
	3.9	0.3	5	15.0	2.5	7.6
	6.0	0.7	7.5	23.0	3.9	9.6
	9.2	2.0	12.0	31.0	9.3	17.0
	11.6	2.9			14.0	21.8

Glasner & Weidenfeld(5) re-examined the decomposition of $KClO_3$ with and without the addition of KCl. They concluded that there are differences in the catalytic effect produced by different samples of potassium chloride with some samples catalysing reaction (ii) above and others having virtually no effect.

Gaidis & Rochow(6) suggested that the effectiveness of MnO_2 as a catalyst depends on the amount and the proportion present in the mixture.

Markowitz and co-workers(7) carried out an in-depth Differential Thermal Analysis into the pyrolysis of Alkali Metal Chlorates including Potassium Chlorate with and without the addition of Manganese Dioxide.They confirm that the M.P. of pure $KClO_3$ is 357° C ; that the onset of decomposition is 472° C and that the decomposition region consists of a pair of exotherms at approximately 560 and 600° C. When they heated the material isothermally at 370°C for 2 days under dry Argon they obtained 0.44% decomposition.When the $KClO_3$ was mixed with MnO_2 in the proportion of 90 mole % $KClO_3$ to 10 % MnO_2 decomposition was said to become rapid soon after the M.P. although it started slowly around 300°. They suggested that the primary catalytic effect of the MnO_2 was to increase the rate of the reaction

$2KClO_3$ ---> $2KCl + 3O_2$ with a resulting dimunition in the extent to which the reaction

$4KClO_3$ -----> $3KClO_4$ + KCl occurs.

Rudloff & Freeman(8&9) investigated the decomposition of potassium chlorate alone and in mixtures with potassium chloride and potassium perchlorate and the catalytic effect of metal oxides including 99.5%pure manganese dioxide on the thermal decomposition of potassium chlorate and perchlorate.With uniform heating at 10°/min they found that:-

pure $KClO_3$ starts to decompose at 500° C with a two step decomposition the first stage ending at 565° C and 15% weight loss and the second complete decomposition stage ending at 650° C ;

pure $KClO_3$ is more reactive at lower temperatures whereas a mixture of 1:1 :: $KCl:KClO_3$ is more reactive at intermediate temperatures and evidence of a two-stage reaction disappears;

with isothermal heating of pure $KClO_3$ at 480° C the reaction seems to stop at 33% decomposition after 90 minutes; at 560° C there was 50% decomposition after 35 minutes and 65% after 50 minutes; at 590° C there was 50% decomposition after 10 minutes and over 90% after 30 minutes.

In general they found that that the oxides of the transitional metals were the most reactive.For example with 99.5% MnO_2 in a molar ratio corresponding to 1 oxide cation to 5 potassium cations they found:-

the melting point was depressed from 360 to 338° C; the onset of initial decomposition was reduced from 515 to 320° C; 25% decomposition was reduced from 580 to 395° C; 50% from 595 to 420° C and final decomposition was reduced from 622° to 500° C.

In a later paper(11) the same authors reported data on $KClO_3$ doped with 1 molar % of a number of salts (excluding Mn salts) and they gave the following data:-

Dopant	Average Peak endotherm temp.°C	Average 25% decomp.temp.°C	Average 50% decomp.temp.°C
None	368	606	620
LiCl	363	589	607
KCl	360	582	607
CsCl	368	602	608
$CuCl_2$	353	398	?
$CdCl_2$	355	562	586
$FeCl_3$	358	354	375
$Pb(NO_3)_2$	342.5	442	544
$LiNO_3$	349	549	585

In a study of the thermal stability of metal chlorates Solymosi(10) concludes that a characteristic of alkali metal chlorates is the " great temperature difference between the melting point and onset of decomposition".

Cannon(12) found the 50% decomposition temperature of a 4% molar mixture of $KClO_3$ and $MnCl_2.4H_2O$ to be 339° C and final decomposition to occur close to this temperature.

4.1 OUTLINE OF THE WORK

The Potassium Chlorate used was that described in Chapter 3 the "98%"Aldrich grade being used for the initial mixtures and the purer Fluka grade and the Johnson & Matthey ALFA product being progressively introduced at later stages.

The Manganese Dioxide (Sample 16 - Chapter 2) used was supplied by Johnson & Matthey with the following Certificate of Analysis:-

Manganese(IV) Oxide 99.999% (Metals basis)

Batch No. 20931A Elements detected by d.c.arc emission sprectroscopy in parts per million:

Al <1 Ca <1 Fe <1 Mg 2 Si 7

Its structure was identified by XRD as Pyrolusite.(see Chapter 2)

The other Manganese Dioxide samples were those tabulated in Chapter 2. (par. 2.2.1)

The oxides and salts used were standard Laboratory Reagents many of which had absorbed atmospheric moisture which showed up in the thermographic tests. They included zinc, vanadium, tin and titanium oxides; the chlorides of the alkali metals rubidium, sodium and potassium, natural manganese ore, manganese dioxide, manganese compounds principally comprising hydrated sodium and potassium manganese oxides , and chloride and sulphate of manganese.

The thermal decomposition experiments were carried out in the present work on accurately weighed mixtures of $KClO_3$ and the metal compound ground together in a mortar . In general weight percentages were based on the proportion of 80% $KClO_3$ and 20% MnO_2 . To establish a datum the purest available Manganese Dioxide (sample 16) was reacted with the purest available Potassium Chlorate (Fluka) , with the standard Aldrich grade (98%) and with the Johnson & Matthey ALFA grade. The first two were reacted in Platinum as well as Aluminium crucibles.

To determine the effect of a reduction in the proportion of manganese dioxide in the mix experiments were carried out with reducing proportions of MnO_2 down to 0.1% .

The other manganese dioxide samples specified in par.2.2.1 of Chapter 2 were all weighed out in the same 80:20 proportions although the true proportion of MnO_2 varied in accordance with the particular Mn(IV) content. The other metal salts were generally mixed in quantities such that molar percentage of each dry salt was approximately equal to the molar percentage of MnO_2 in the pure 80:20 manganese dioxide-potassium chlorate mixture. Since the salts used were drawn from laboratory stocks without preliminary drying the true proportions varied.

4.2 EXPERIMENTAL RESULTS

The thermographic experiments were similar to those carried out on the $KClO_3$ alone (see Chapter 3). The results of all the experiments are set out in the following Tables:-

REACTIONS BETWEEN PURE $KClO_3$ AND PURE MnO_2

TABLE 4A Thermal events

TABLE 4B Reaction Rates with uniform heating

TABLE 4C Reaction Rates under isothermal conditions

REACTIONS BETWEEN $KClO_3$ AND OXIDES & SALTS (SIMPLE REACTIONS)

TABLE 4D Thermal events

TABLE 4E Reaction Rates with uniform heating

TABLE 4F Reaction Rates under isothermal conditions

REACTIONS BETWEEN $KClO_3$ & OXIDES & SALTS (COMPLEX REACTIONS)

TABLE 4G Thermal events

Symbols used for the measurements made and in the above tabulated results are:-

T1	Endotherm at point of structural change
T2	Exotherm at point of first decomposition reaction
T3	Melting point endotherm
T10	Temperature at which 10% decomposition has occurred
T50	Temperature at which 50% decomposition has occurred
T75	Temperature at which 75% decomposition has occurred
A	Onset temperature at start of decomposition
A1	Onset temperature of rapid decomposition reaction
B	Onset temperature of final decomposition reaction

4.3 DISCUSSION OF RESULTS

4.3.1 Reactions with pure Manganese Dioxide.

Tables 4A & 4B and Figures 4 -1 & 4 -2 ,the data for which are extracted from Tables 3B and 4B, clearly show the effect on the thermal decomposition of $KClO_3$ of increasing the proportion of MnO_2 in the mixture. For mixtures containing from 0.14 to 6.18 molar % MnO_2 there is a gradual decrease in the onset temperature A1 ,the reaction rate is relatively constant and slow and the melting endotherm is clearly defined. For mixtures containing between 6.18 and 8.46% MnO_2 there is a sharp change in the type of reaction , the second stage reaction rate and the temperature effects . There is no sign of the melting endotherm and there is a violent - frequently explosive - exothermic reaction which occurs at 341 to 332°C i.e. at or below the temperature of the structural change found in the present work (Chap 3) in pure $KClO_3$ and below its melting point .In all of these cases the reaction appears to have taken place in the solid state.

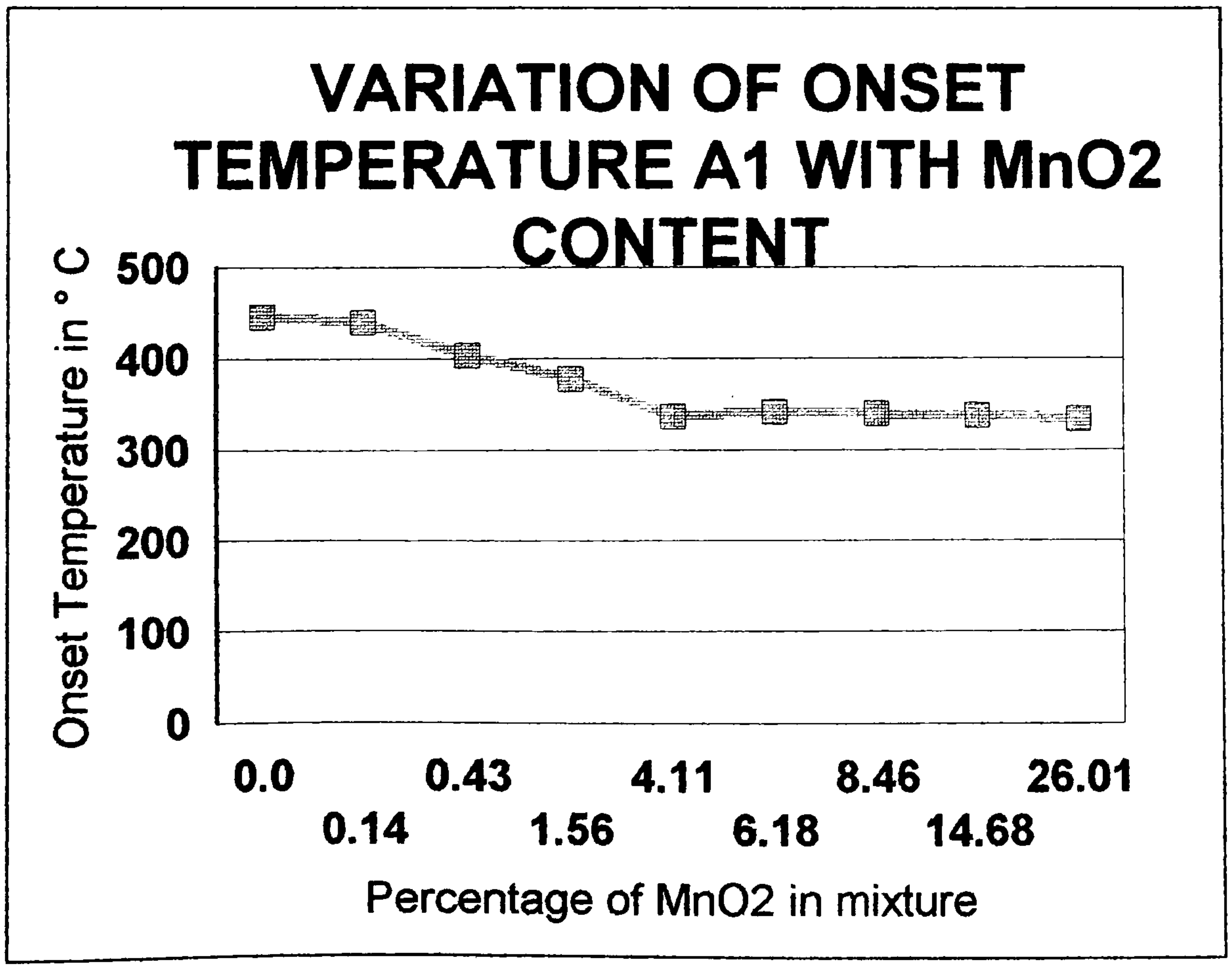


Fig.4-1

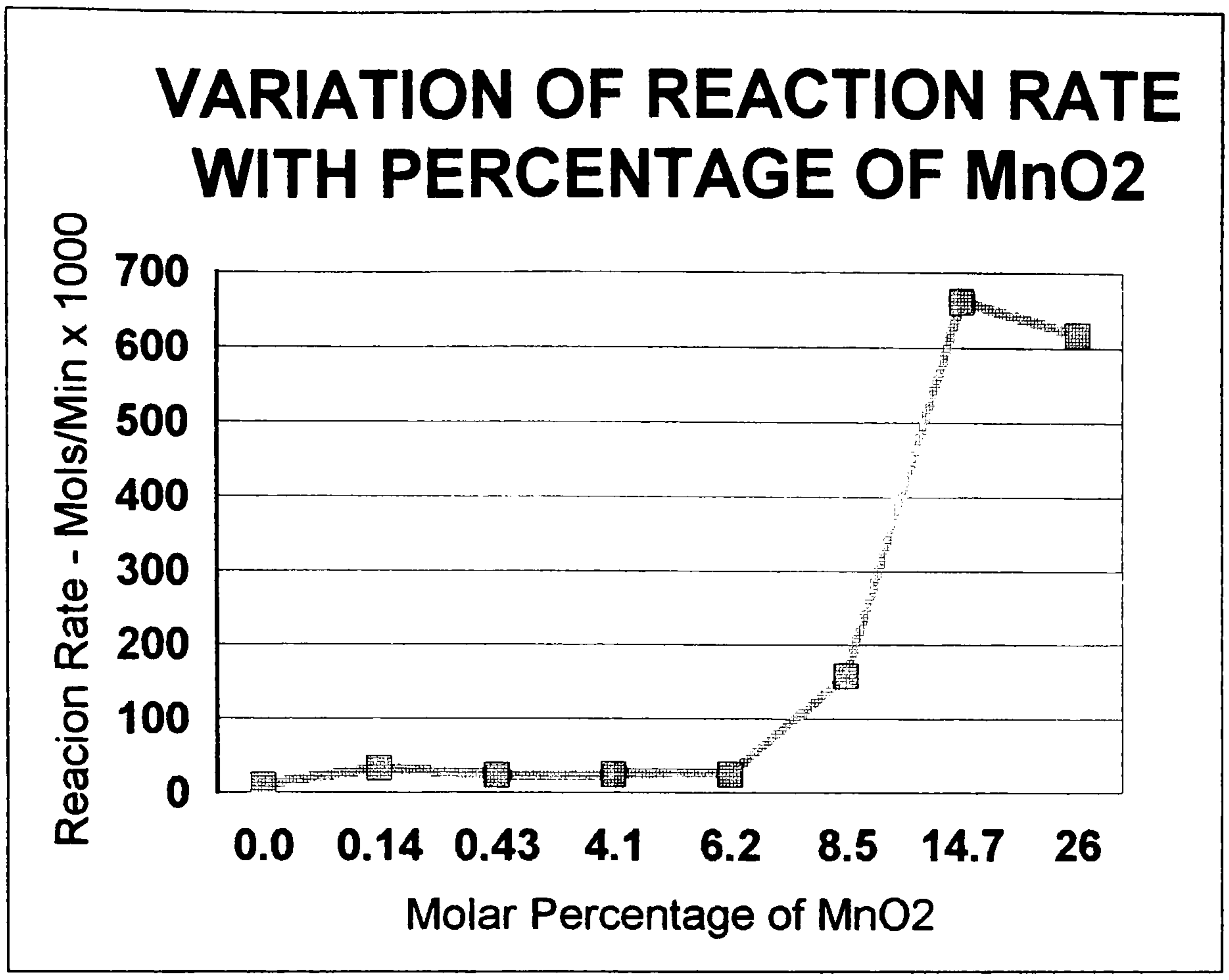


Figure 4 - 2

The temperature at which 50% decomposition has occurred indicates that decomposition starts in some cases well below the instantaneous reaction temperature. The results show good consistency and there is no significant difference as the proportion of MnO_2 in the mix is increased from 8.5 to 26 molar %.

Table 4B shows the reaction times for the three identifiable stages of the decomposition reaction for the "slow" and explosive reactions respectively. The slow reaction occurs at values of T2 above 350°C and MnO_2 contents below 6.2% . The explosive reaction occurs values of T2 below 350°C and is associated with MnO_2 above 6.2% molar.In the explosive situation the time shown for second stage reactions below 350°C is notional; the reaction is so rapid - almost instantaneous in most cases - that its true measurement on the chart scale of 0.5cms/minute is impossible. Despite this limitation the calculated reaction rate for this stage is ,on average 20 times that of the slow reaction, whilst the rate for the first stage is almost identical in both the "slow" and "rapid" cases. The addition of small quantities (0.1 -0.3%) MnO_2 appears to increase the temperature T2 of the exotherm of the first reaction i.e.actually to retard the reaction over that for $KClO_3$

alone; the addition of MnO_2 from 0.4% to 6.2% while not affecting reaction rate progressively reduces T2 and reaction temperature and melting point to just above the structural change point detected in this work . In general the reactions are consistent with those reported by Brown(1) (2) and by Cannon(12) except for any effect of the new phase change.Comparing these results with those of Brown :-

Molar Composition %		Spontaneous Decomposition	
MnO_2	$KClO_3$	Temperature ° C	Temperature(2) ° C
3	97	380	380
3.9	96.1	330	350
11.1	88.9		322
14.3	85.7	330	317
20	80	318	304
33.3	66.7		292
50	50	298	294
66.7	33.3	295	309
80	20	307	326

This Work			T2
0.0	100	(range 368-438)	394
0.1	99.9		456
0.4	99.6		432
1.6	98.4		401
4	96		376
6	94		357
8.5	91.5		339
15	85		340

Cannon(12) found the 50% decomposition temperature of a 4% molar mixture to be 339° C and final decomposition to occur close to this temperature. The 50% decomposition temperature of the same mixture in this work is 352° C whilst that for a 6% mixture is 341° C (Table 4A)

Table 4C shows the effect of isothermal heating on the 26% molar mixture of MnO_2 and $KClO_3$ There is a considerable reduction in the isotherm temperature at which decomposition occurs compared with that for pure $KClO_3$. An isotherm temperature of 329° C results in 96% decomposition compared with 413° C for decomposition of the same percentage of the pure material.

4.3.2 Reactions with Metal Oxides and Salts other than pure MnO_2

4.3.2.1 Uniform Heating Rate

Tables 4D and 4E summarise the thermal events and reaction rates and show the sharp split between reaction mixtures with values T2 above (Fig.4-3)and below (Fig.4-4)350° C. As with reactions with pure MnO_2 the reactions above 350° C are generally slow; those below are invariably rapid to explosive. (A small set of anomolous results in which secondary compounds appear to have been formed is shown in Table 4G. Fig. 4 - 5 shows the trace of such a reaction between $KClO_3$ and LiCl . Endotherms at 87 and 181°C without any accompanying weight loss would appear to indicate atypical formation of secondary compounds or new phases.)

Inspection of the charts and tabulated data for the two main groups shows that the decomposition follows distinctly different patterns in the two groups. Where decomposition takes place above 350° C it is preceded by a well defined melting endotherm i.e. decomposition takes place in the liquid phase and all the reactions occur slowly and over a considerable temperature range. When decomposition occurs below 350° C it generally takes place with explosive rapidity and there is

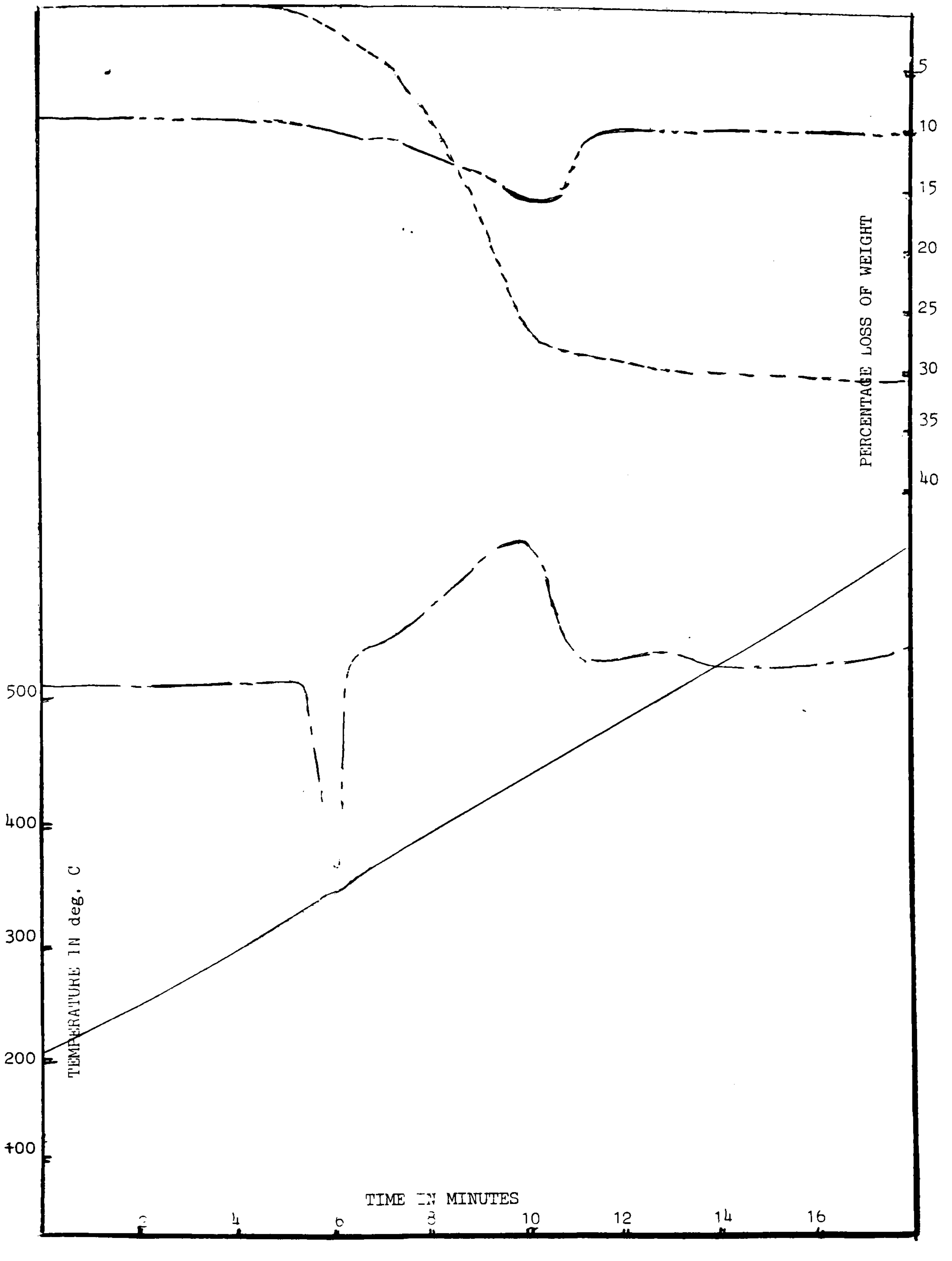


Fig.4-3 Thermal decomposition of 98% potassium chlorate in the presence of manganese dioxide (sample 14)

TEMPERATURE_______

D.T.A. ___ _ _____ _ __

L.O.W.-----------------------

dW/dT____ _ _ _ ____

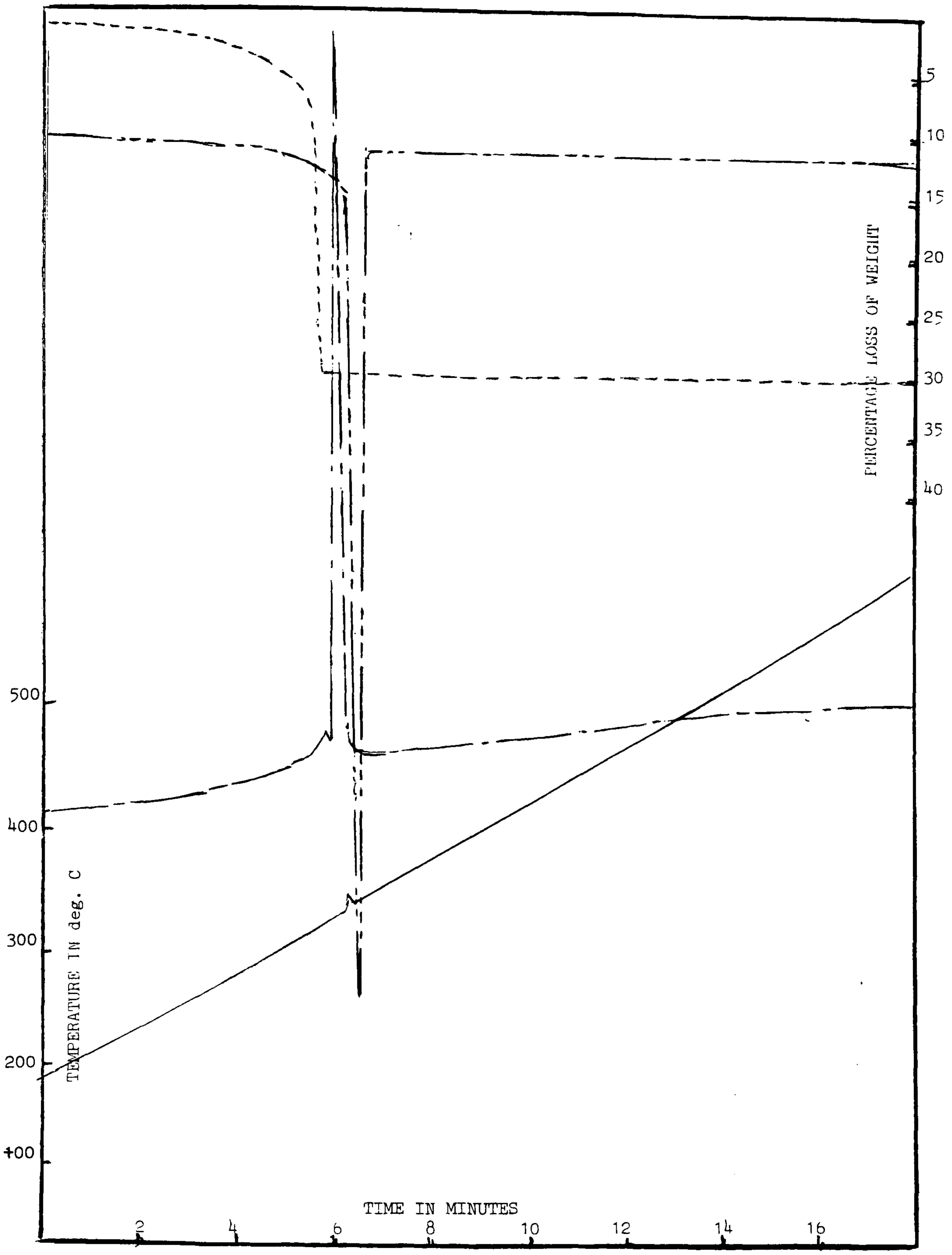


Fig.4-4 Thermal decomposition of 98% potassium chlorate in the presence of manganese

dioxide (sample 27)

TEMPERATURE________

D.T.A. ___ _ ___ _ _

L.O.W.-----------------------

dW/dT______ _ _ _ _____

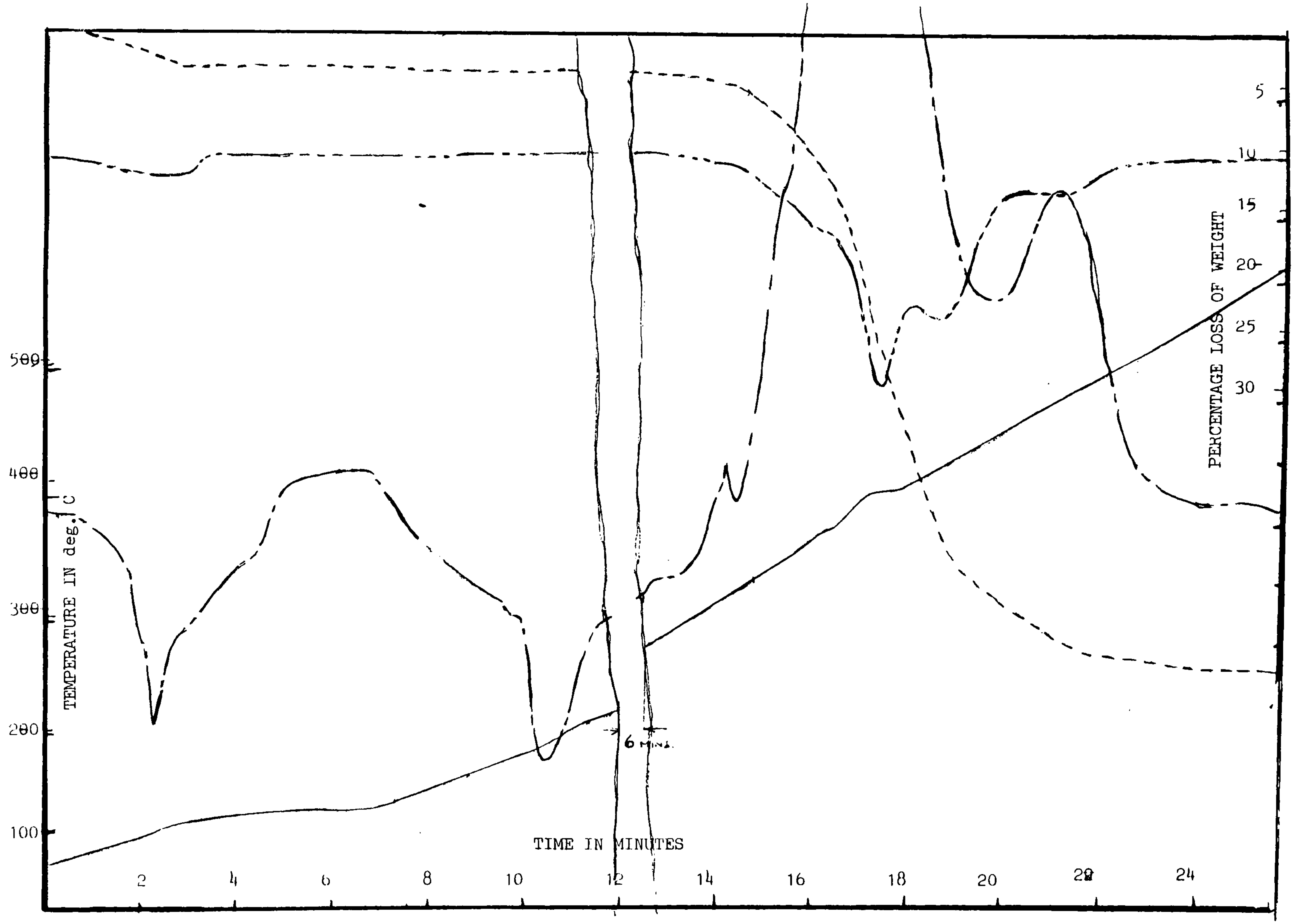


Fig. 4-5

Thermal decomposition of

pure potassium chlorate

mixed with lithium chloride

TEMPERATURE _____

D.T.A. ___ _ ____ _ ___

L.O.W.-----------------------

dW/dT___ _ _ _ _____

no melting endotherm leading to the conclusion that decomposition has occurred in the solid state.(Fig.4-4)

It is observed that, as with small additions of MnO_2 (par.4.3.1), the presence of the Alkali metal Chlorides, Titanium and Zinc oxides and the natural Manganese Dioxide Ore actually increase the temperature of the first reaction exotherm T2 above that of pure $KClO_3$.

The Ore used in this work assayed 87 - 92% MnO_2 and XRD showed it to comprise two principal phases - Pyrolusite (β - manganese dioxide) and δ - manganese dioxide . With this material , as with that used by Rudlow(9) and ,separately by Markowitz(7) , the DTA curves show the melting point of the $KClO_3$ to have been depressed to about 340° C and the principal decomposition to have occurred non-violently in the range 400 - 450° C.(Fig.4-3) Both these authors refer to the use of "Reagent Grade Manganese Dioxide of 99.5% purity"; there is no record of its structure. A similar reaction pattern was exhibited by Sodium Birnessite synthesised in the course of this work (Chapter 6) and by a manganese dioxide compound (sample 11 & 12) produced specifically as a curing agent for Polysulphide resins and shown by XRD analysis to contain Pyrolusite and Sodium Birnessite.

The thermal events and reaction rates of the second group - broadly those in which the first reaction exotherm T2 occurs below 350° C -are dramatically different.(Fig.4-4) All of these decomposition reactions occur rapidly or with explosive violence. In all cases T2 is well below the normal melting point of $KClO_3$ and is generally remarkably close to T1 , the temperature of the new structural change in pure $KClO_3$ detected in this work . In only three cases is there any sign of the melting endotherm indicating that in the majority of experiments the decomposition reaction has taken place in the solid state. This is confirmed by the powdery or partly sintered appearance of the residue .

The 50% decomposition temperature is generally equal to or even below T2 the exotherm reaction temperature and in most cases the reaction is virtually complete at or near that temperature. Reaction rates are exceedingly high.

4.3.2.2 Isothermal Heating

Table 4F details the results of isothermal experiments on mixtures selected from the slow and rapid reaction groups shown in Table 4D. It is significant that even in the slow reaction group decompositions are almost complete at isotherm temperatures of 325 to 342° C . This accords with the isotherm temperature of 327° C (Table 4C) for $KClO_3$ + pure MnO_2 and is well below the isotherm temperature of 413° C required for the complete decomposition of pure $KClO_3$

In summary:

In the uniform heating experiments two groups were identified:-

(i) those in which decomposition occurs in the molten state above 350° C , reactions are slow and, in some cases, retarded rather than catalysed by the additive;

(ii) those in which decomposition occurs in the solid state below 350° C ,reactions are fast or explosive and are catalysed by the additive. Decomposition in the solid state in most cases occurs and is virtually complete at or slightly below T1 the temperature at which the newly-identified structural change occurs. It is observed that Cu, Co and Fe salts reduce the decomposition temperature significantly more than the other salts and oxides examined.

In the isothermal experiments all of those additives studied acted as catalysts ,generally reducing the 50% decomposition temperature below that resulting from the decomposition temperature of pure potassium chlorate.

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TABLE 4A

DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF PURE MANGANESE DIOXIDE

TEMPERATURES OF THERMAL EVENTS IN ORDER OF
DESCENDING VALUES OF FIRST REACTION ENDOTHERM T2

T1 - TEMPERATURE OF ENDOTHERMIC CHANGE
T2 - EXOTHERM OF FIRST DECOMPOSITION REACTION
T3 - TEMPERATURE OF MELTING ENDOTHERM
T10 - TEMPERATURE AT WHICH 10% DECOMPOSITION HAS OCCURRED
T50 - TEMPERATURE AT WHICH 50% DECOMPOSITION HAS OCCURRED
T75 - TEMPERATURE AT WHICH 75% DECOMPOSITION HAS OCCURRED
RATE - SLOW, MODERATE, RAPID OR EXPLOSIVE REACTION RATE

RUN No.,	TYPE OF $KClO_3$ PERCENT MnO_2 (SAMPLE 16)	CRUCIBLE MATERIAL	MOLAR PERCENT SAMPLE 16	T1	T2	T3	RATE	T10	T50	T75
6080	pure + 0.1%	Al	0.14	344	456	360	SLOW	411	450	462
6078	pure + 0.3%	Al	0.42	341	432	354	SLOW	391	419	428
6072	pure + 1%	Al	1.55	0	401	344	MOD	344	388	396
6073	pure + 2.9%	Al	4.05	328	377	343	MOD	302	352	370
6075	pure + 2.9%	Al	4.05	0	374	342	MOD	310	352	375
6076	pure + 4.5%	Al	6.24	0	355	341	RAP	284	338	345
6085	pure + 4.5%	Al	6.24	0	359	346	RAP	291	345	360
6074	pure + 5.74%	Al	7.91	341	341	0	EXP	270	338	341
5934	pure + 10.85%	Pt	14.65	0	341	0	EXP	278	336	339
5937	pure + 10.85%	Pt	14.65	0	339	0	EXP	263	337	339
205	98% + 19.89%	Al	25.92	0	338	0	EXP	280	335	337
6077	JM + 11.7%	Al	14.76	0	338	0	EXP	244	317	337
6006	pure + 6.15%	Al	8.45	0	338	0	EXP	273	338	338
5943	pure + 19.97%	Pt	26.01	0	337	0	EXP	250	333	337
245	98% + 19.89%	Al	25.92	0	336	0	EXP	276	336	343
5660	98% + 19.89%	Al	25.92	0	335	0	EXP	163	317	335
5661	98% + 19.89%	Al	25.92	0	335	0	EXP	215	321	335
5755	pure + 19.97%	Al	26.01	0	335	0	EXP	254	330	333
5752	pure + 19.97%	Al	26.01	0	335	0	EXP	259	335	335
5763	pure + 19.97%	Pt	26.01	0	335	0	EXP	248	328	337
5389	98% + 19.89%	Al	25.92	0	334	0	EXP	163	325	334
5391	98% + 19.89%	Al	25.92	0	332	0	EXP	240	333	333

TABLE 4B

DECOMPOSITION OF POTASSIUM CHLORATE IN PRESENCE OF PURE MANGANESE DIOXIDE

REACTION RATES TABULATED IN THE SAME ORDER AS IN TABLE 4A

RUN No.	REACTANTS TYPE OF KC1O3 + % MnO2	CRUCIBLE MATERIAL	MOLAR % SAMPLE 16	SAMPLE WEIGHT mgm	THEOR. 100% L.O.W.	T2	ONSET TEMP A	ONSET TEMP A1	ELAPSED TIME A - A1	PERCENT DECOMP @A1	REACTION RATE MOLS/MI x 1000	ONSET TEMP B	ELAPSED TIME A1 - B	PERCENT DECOMP @ B	REACTION RATE MOLS/MIN x 1000	ELAPSED TIME B/END	PERCENT DECOMP AT END	REACTION RATE MOLS/MIN x 1000
6080	pure + 0.1%	Al	0.14	10.69	4.18	456	358	441	7.3	23.2	4.15	463	2.0	74.6	33.57	7.4	85.4	1.91
6078	pure + 0.3%	Al	0.42	7.46	2.91	432	356	404	3.8	22.0	5.26	433	2.6	91.0	24.13	9.6	94.5	0.33
6072	pure + 1%	Al	1.55	7.13	2.76	401	331	378	3.8	33.3	7.56	400	2.1	100.0	27.39	partial loss of sample		
6073	pure + 2.9%	Al	4.05	9.80	3.73	377	246	334	7.3	23.0	3.67	378	3.2	87.9	23.64	3.5	90.0	0.70
6075	pure + 2.9%	Al	4.05	7.30	2.78	374	287	340	4.4	29.9	5.90	373	2.9	83.8	16.15	3.7	88.0	0.99
6076	pure + 4.5%	Al	6.24	7.32	2.74	355	244	341	7.9	54.4	5.90	359	1.3	102.6	31.75	partial loss of sample		
6085	pure + 4.5%	Al	6.24	9.23	3.45	359	240	343	8.9	51.6	6.25	363	1.8	84.6	19.80	1.0	85.5	0.94
6074	pure + 5.74%	Al	7.91	11.06	4.08	341	234	341	8.8	50.0	7.24	350	0.3	87.5	159.38	2.5	89.2	0.87
5934	pure + 10.85%	Pt	14.65	8.24	2.88	341	232	339	9.4	36.8	3.52	350	0.1	85.4	437.40	3.0	86.5	0.33
5937	pure + 10.85%	Pt	14.65	14.83	5.18	339	218	338	8.8	40.9	7.52	360	0.1	95.8	888.69	5.2	86.5	0.22
205	98% + 19.89%	Al	25.92	10.08	3.16	338	212	339	7.8	40.2	5.09	350	0.1	98.4	574.73	4.0	100.0	0.39
6077	JM + 11.7%	Al	14.76	6.98	2.43	338	217	338	10.5	63.4	4.59	344	0.1	94.7	237.68	4.1	96.7	0.37
6006	pure + 6.15%	Al	8.45	13.65	5.02	338	239	338	8.5	36.5	6.74	350	0.2	73.3	288.65	2.0	74.3	0.78
5943	pure + 19.97%	Pt	26.01	13.09	4.10	337	210	338	10.8	46.8	5.55	350	0.1	98.8	666.25	4.0	99.0	0.06
245	98% + 19.89%	Al	25.92	11.14	3.49	336	240	335	7.0	44.1	6.87	346	0.1	97.4	581.30	1.2	100.0	2.36
5660	98% + 19.89%	Al	25.92	7.40	2.32	335	198	334	11.7	50.9	3.15	343	0.1	-	-	partial loss of sample		
5661	98% + 19.89%	Al	25.92	6.95	2.18	335	192	335	12.4	50.0	2.75	345	0.1	91.3	281.36		do	
5755	pure + 19.97%	Al	26.01	12.50	3.92	335	211	333	9.7	54.8	6.92	350	0.1	100.0	553.70	1.0	100.0	0.00
5752	pure + 19.97%	Al	26.01	13.62	4.27	335	223	334	9.6	49.4	6.87	349	0.1	97.0	635.16	1.8	100.0	2.22
5763	pure + 19.97%	Pt	26.01	5.68	1.78	335	216	334	10.1	57.9	3.19	341	0.1	100.0	234.18	2.0	100.0	0.00
5389	98% + 19.89%	Al	25.92	7.23	2.27	334	184	334	12.9	41.9	2.30	344	0.1	-	-	partial loss of sample		
5391	98% + 19.89%	Al	25.92	11.55	3.62	332	221	332	9.8	45.3	5.23	350	0.1	-	-		do	

TABLE 4C

ISOTHERMAL DECOMPOSITION OF POTASSIUM CHLORATE WITH PURE MANGANESE DIOXIDE

RUN No., TYPE OF KClO3, PERCENT MnO2 (SAMPLE 16) CRUCIBLE MATERIAL	MOLAR PERCENT SAMPLE 16	ISOTHERM TEMP	T1	T2	% DECOMP BEFORE ISOTHERM	% DECOMP AT ISOTHERM	TIME IN MINS AT ISOTHERM
208 98% + 19.6% Al	25.92	265			9	26	24
two isotherms		331	340	340	37	79	24
5672 98% + 19.6% Al	25.92	262			24	50	43
two isotherms		329	340	340	61	96	23
5693 98% + 19.6% Al	25.92	316	339	339	28	88	77
5753 pure + 19.97% Al	26.01	261			9	42	40
two isotherms		327	339	339	44	86	26
5766 pure + 19.97% Pt	26.01	260			7	27	28
two isotherms		339	338	338	38	68	22

TABLE 4D

DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF MnO2 & METALLIC SALTS THERMAL EVENTS TABULATED IN DESCENDING ORDER OF T2 & EXCLUDING SAMPLE 16

T1 - TEMPERATURE OF ENDOTHERMIC CHANGE
T2 - EXOTHERM OF FIRST DECOMPOSITION REACTION
T3 - TEMPERATURE OF MELTING ENDOTHERM
T10 - TEMPERATURE AT WHICH 10% DECOMPOSITION HAS OCCURRED
T50 - TEMPERATURE AT WHICH 50% DECOMPOSITION HAS OCCURRED
T75 - TEMPERATURE AT WHICH 75% DECOMPOSITION HAS OCCURRED
RATE - SLOW, MODERATE, RAPID OR EXPLOSIVE REACTION RATE

RUN NO	TYPE OF KC1O3 +	CRUCIBLE MATERIAL	WEIGHT % REACTANT	T1	T2	T3	RATE	T10	T50	T75
6027	pure + TiO2	Al	17.4	341	597	358	SLOW	472	586	580
6036	pure + RbCl	Al	15.2	320	543	337	SLOW	475	530	556
6034	pure + NaCl	Al	24.3	0	466	318	SLOW	426	466	482
6028	pure + KCl	Al	19.6	0	466	343	SLOW	441	469	495
5959	pure + ZnO	Al	13.7	0	464	360	SLOW	385	436	447
5590	98% + MnO2 10	Al	19.9	346	456	346	SLOW	357	429	455
5589	98% + MnO2 14	Al	19.0	350	452	350	SLOW	370	429	447
6079	pure + TiO2	Al	17.4	343	431	360	SLOW	443	523	-
5764	pure + MnO2 14	Pt	19.2	338	426	338	SLOW	350	402	421
5339	98% + MnO2 10	Al	19.9	342	419	348	SLOW	388	413	428
5754	pure + MnO2 14	Al	19.2	341	417	341	SLOW	344	390	406
243	98% + MnO2 10	Al	19.9	342	404	343	SLOW	368	398	440
5933	pure + NAB1	Pt	19.9	344	390	344	SLOW	336	388	388
5927	pure + NAB1	Pt	19.9	341	384	341	SLOW	331	380	380
6068	pure + SnO2	Al	14.7	342	380	359	SLOW	320	460	518
5342	98% + MnO2 11	Al	19.9	339	375	339	SLOW	221	339	350
5768	pure + NAB	Pt	19.9	343	372	343	SLOW	336	367	367
5341	98% + MnO2 11	Al	19.9	338	370	338	SLOW	254	351	362
5335	98% + MnO2 12	Al	20.4	339	365	339	SLOW	254	339	354
6054	pure + V2O5	Al	18.1	331	358	346	RAP	323	353	353
5588	98% + MnO2 12	Al	20.4	340	350	340	MOD	107	337	353
5417	98% + MnO2 20	Al	18.8	334	350	336	SLOW	295	345	349
6005	pure + NiSO4.7H2O	Al	37.7	336	349	340	RAP	118	340	347
6004	pure +CuCl	Al	26.1	301	349	334	EXP	283	333	335
5492	98% + MnO2 24	Al	19.9	350	349	0	EXP	257	350	350
5703	98% + MnO2 26	Al	18.9	346	346	0	EXP	270	315	320
6009	pure + CuSO4	Al	24.1	336	346	0	EXP	276	329	336
6007	pure + CoCl2.6H2O	Al	33.7	0	343	0	EXP	218	334	-
5421	98% + MnO2 21	Al	18.4	0	342	0	EXP	303	341	341
5521	98% + MnO2 22	Al	19.0	341	341	0	EXP	177	340	341
5958	pure + FeCl3.6H2O	Al	37.8	0	341	0	EXP	111	187	325
5951	pure + MnSO4.4H2O	Pt	33.8	0	340	0	RAP	338	339	
5907	pure + MnCl2.4H2O	Pt	35.8	0	340	0	EXP	186	336	338
5938	pure + MnCl2.4H2O	Pt	35.8	0	340	0	EXP	166	336	339
5345	98% + MnO2 3	Al	19.9	340	340	0	RAP	310	340	340
5908	pure +MnCl2.4H2O	Pt	35.8	0	340	0	EXP	290	338	338
5332	98% + MnO2 2	Al	19.5	0	339	0	EXP	264	339	339
5953	pure + NiSO4.7H2O	Pt	37.7	339	339	0	EXP	318	339	339
5906	pure + MnCl2.4H2O	Pt	35.8	0	339	0	EXP	247	336	336
5347	98% + MnO2 2	Al	19.5	0	339	0	EXP	287	339	339
6087	98% + MnO2 21	Al	18.4	0	339	0	EXP	294	339	349
5336	98% + MnO2 13	Al	19.8	339	339	0	RAP	325	339	339
5960	pure + FeCl2.4H2O	Pt	30.9	0	339	0	EXP	188	337	338

TABLE 4D

continued

DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF MnO2 & METALLIC SALTS
THERMAL EVENTS TABULATED IN DESCENDING ORDER OF T2 & EXCLUDING SAMPLE 16

RUN NO	TYPE OF KC1O3 +	CRUCIBLE MATERIAL	WEIGHT % REACTANT	T1	T2	T3	RATE	T10	T50	T75
5940	pure + MnO2 29	Pt	20.0	0	339	0	EXP	250	337	339
6086	pure + CuCl	Al	28.1	338	338	338	EXP	284	334	338
5397	98% + MnO2 17	Al	20.6	0	338	0	EXP	250	338	338
5346	98% + MnO2 8	Al	20.1	0	337	0	EXP	303	337	337
5331	98% + MnO2 1	Al	20.2	0	337	0	EXP	283	337	337
5554	98% + MnO2 27	Al	19.7	337	337	0	EXP	295	337	337
5955	pure + CuCl	Pt	28.1	337	337	0	EXP	270	331	337
5954	pure + CuSO4	Pt	24.1	337	337	0	EXP	279	315	337
5956	pure + CoCl2.6H2O	Pt	33.7	0	337	0	RAP	211	293	326
5436	98% + MnO2 2	Al	19.5	0	336	0	EXP	272	336	336
5348	38% + MnO2 5	Al	20.1	0	336	0	EXP	316	337	337
5601	98% + MnO2 24	Al	19.9	336	336	0	EXP	272	336	336
5344	98% + MnO2 7	Al	19.4	0	336	0	EXP	275	336	336
5435	98% + MnO2 2	Al	19.5	0	336	0	EXP	269	336	336
5544	98% + MnO2 26	Al	19.9	0	336	0	RAP	107	321	336
6018	pure + MnSO4.4H2O	Al	33.8	0	336	0	EXP	291	337	337
5338	98% + MnO2 9	Al	20.1	0	336	0	EXP	290	336	336
5545	98% + MnO2 27	Al	19.7	335	335	0	EXP	243	335	335
5399	98% + MnO2 18	Al	19.4	0	335	0	EXP	271	333	335
5910	pure + MnO2 28	Al	20.0	335	335	0	EXP	194	333	336
5349	98% + MnO2 6	Al	19.9	0	335	0	EXP	310	335	335
5334	98% + MnO2 4	Al	20.3	0	335	0	EXP	312	335	335
5418	98% + MnO2 21	Al	18.4	0	335	0	EXP	83	315	335
5543	98% + MnO2 25	Al	19.9	0	335	0	EXP	229	335	335
5392	98% + MnO2 15	Al	19.9	0	333	0	EXP	221	333	333
5390	98% + MnO2 15	Al	19.9	0	333	0	EXP	255	332	332
5416	98% + MnO2 19	Al	19.2	0	331	0	EXP	295	331	331

TABLE 4E

TABLE 4E

DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF MnO2 & METALLIC SALTS
THERMAL EVENTS TABULATED IN THE SAME ORDER AS IN TABLE ^4D (EXCLUDING SAMPLE 16)

RUN NO.	TYPE OF KClO3 +	CRUCIBLE MATERIAL	SAMPLE WEIGHT	THEOR 100% L.O.W.	T2	ONSET TEMP A	ONSET TEMP A1	ELAPSED TIME A - A1	PERCENT DECOMP @ A1	REACTION RATE MOLS/MIN < 1000	ONSET TEMP B	ELAPSED TIME A1 - B	PERCENT DECOMP AT B	REACTION RATE MOLS/MIN x 1000	ELAPSED TIME B/END	PERCENT DECOMP AT END	REACTION RATE MOLS/MIN x 1000
6027	pure + TiO2	Al	7.91	2.56	597	455	561	9.9	41.4	3.35	584	2.0	82.4	16.40	1.1	93.4	7.96
6036	pure + RbCl	Al	11.85	3.84	543	447	512	5.8	14.7	3.12	551	3.4	72.1	20.77	4.0	87.6	4.78
6034	pure + NaCl	Al	10.24	3.04	466	403	443	3.2	13.2	3.91	474	2.9	64.5	18.81	7.2	94.7	3.99
6028	pure + KCl	Al	13.15	4.14	466	428	447	1.7	13.3	10.11	480	3.1	87.6	22.68	6.2	87.7	4.18
5959	pure + ZnO	Al	8.40	2.84	464	370	411	3.6	28.9	7.12	455	3.8	80.6	12.09	6.6	94.4	1.85
5590	98% + MnO2 10	Al	6.12	1.92	456	335	412	7.0	38.0	3.26	464	4.7	84.9	5.98	5.7	94.8	1.04
5589	98% + MnO2 14	Al	8.53	2.70	452	346	398	4.3	22.6	4.43	448	4.7	78.5	10.04	8.0	96.7	1.91
6079	pure + TiO2	Al	10.90	3.53	431	402	490	8.0	29.2	4.02	562	6.7	89.0	9.84	1.3	93.5	3.84
5764	pure + MnO2 14	Pt	9.93	3.14	426	341	380	3.1	31.9	10.08	432	4.6	87.9	11.86	7.3	97.1	1.24
5339	98% + MnO2 10	Al	3.62	1.13	419	377	390	1.2	13.0	3.83	428	3.3	81.4	7.32	2.2	83.4	0.31
5754	pure + MnO2 14	Al	16.37	5.18	417	331	380	4.1	40.2	15.85	414	3.0	92.3	28.13	3.2	95.0	1.37
243	98% + MnO2 10	Al	9.22	2.89	404	355	388	2.8	29.4	9.49	413	2.2	77.5	18.75	6.7	82.0	1.96
5933	pure + NAB1	Pt	10.39	3.25	390	286	372	7.1	26.5	3.78	395	1.4	97.8	51.79	2.5	99.1	0.50
5927	pure +NAB1	Pt	11.90	3.73	384	261	361	6.7	15.6	2.71	391	1.9	97.1	50.00	1.3	97.3	0.22
6068	pure + SnO2	Al	12.30	4.11	380	398	431	3.0	21.9	9.38	473	4.0	63.5	13.38	7.7	85.4	3.65
5342	98% + MnO2 11	Al	4.25	1.33	375	-	339	-	-	-	370	-	-	-	partial loss of sample		
5768	pure + NAB	Pt	10.81	3.39	372	279	365	7.0	46.3	7.01	377	0.8	95.1	64.82	2.2	100.0	1.40
5341	98% + MnO2 11	Al	5.88	1.84	370	305	328	1.9	16.1	4.87	368	3.0	93.5	14.84	2.0	100.0	1.87
5335	98% + MnO2 12	Al	3.17	0.99	365	213	336	11.0	33.0	0.93	367	2.5	99.0	8.17	1.5	100.0	0.21
6054	pure + V2O5	Al	8.43	2.70	358	300	346	3.3	34.1	8.71	358	0.7	74.1	48.21	4.4	79.3	1.00
5586	98% + MnO2 12	Al	7.29	2.28	350	222	331	9.6	29.0	2.15	360	2.3	100.0	22.01	2.2	100.0	0.00
5417	98% + MnO2 20	Al	7.02	2.23	350	290	331	4	8.1	1.56	355	2.2	98.9	26.13	2.2	100.0	0.89
6005	pure + NiSO4.7H2O	Al	18.17	7.51	349	296	334	2.6	28.3	24.55	349	1.3	76.0	84.36	stopped @ isotherm 341 deg		
6004	pure + CuCl	Al	14.53	4.09	349	279	334	4.8	40.3	10.74	350	0.2	86.1	389.57	stopped @ isotherm 341 deg		
5492	98% + MnO2 24	Al	5.76	1.81	349	210	350	12.4	36.1	1.74	363	0.2	100.0	175.00	0.4	100.0	0.00
5703	98% + MnO2 26	Al	6.03	-	346	-	-	-	-	-	-	-	-	-	abandoned instrument fault		
6009	pure + CuSO4	Al	12.03	3.58	346	303	335	2.6	55 3	23.80	346	0.3	88.6	123.96	stopped @ isotherm 341 deg		
6007	pure + CoCl2.6H2O	Al	10.02	4.01	343	277	336	5.0	43.1	10.81	343	0.1	58.6	387.47	stopped @ isotherm 341 deg		
5421	98% + MnO2 21	Al	4.61	1.44	342	300	341	3.6	36.1	4.51	350	0.1	117.0	-	partial loss of sample		
5521	98% + MnO2 22	Al	5.89	1.87	341	245	342	7.9	53.5	3.96	352	0.2	113.0	-	partial loss of sample		
5958	pure + FeCl3.6H2O	Al	12.65	4.23	341	237	341	9.1	86.2	12.52	353	0.1	100.0	365.63	0.1	100.0	0.00
5951	pure + MnSO4.4H2O	Pt	10.05	4.60	340	266	340	6.0	28.3	6.77	350	0.1	100.0	1031.26	0.2	100.0	0.00
5907	pure + MnCl2.4H2O	Pt	10.36	3.63	340	195	338	12.4	47.4	4.33	357	0.1	100.0	596.81	3.0	100.0	0.00
5938	pure + MnCl2.4H2O	Pt	20.18	7.26	340	192	338	11.1	60.7	12.41	367	0.1	100.0	691.62	0.1	100.0	0.00
5345	98% + MnO2 3	Al	3.96	1.24	340	249	337	7.4	26.8	1.40	349	0.6	92.3	42.27	6.2	99.0	0.42
5908	pure + MnCl2.4H2O	Pt	11.30	4.31	340	194	338	12.3	36.4	3.99	355	0.1	99.0	842.74	1.5	100.0	0.80
5332	98% + MnO2 2	Al	3.92	1.23	339	-	339	-	-	-	346	0.1	115.0	-	partial loss of sample		
5953	pure + NiSO4.7H2O	Pt	7.55	3.09	339	107	339	20.1	50.8	2.44	350	0.5	100.0	95.00	5.2	102.0	0.37
5906	pure + MnCl2.4H2O	Pt	21.54	8.23	339	192	336	11.7	65.6	14.42	365	0.1	100.0	864.47	severe TG & DTG interferenc		
5347	98% + MnO2 2	Al	4.26	1.35	339	235	339	8.6	38.3	1.88	346	0.1	100.0	260.25	1.0	100.0	0.00
6087	98% + MnO2 21	Al	16.69	5.34	339	263	339	6.1	41.0	11.22	365	0.1	92.8	1731.16	0.6	93.5	1.59
5336	98% + MnO2 13	Al	3.56	1.12	339	298	340	3.6	19.4	1.69	349	0.6	92.6	42.70	5.3	99.0	0.42
5960	pure + FeCl2.4H2O	Pt	22.00	7.20	339	210	336	10.5	40.6	9.69	360	0.1	93.2	2366.35	0.5	94.0	3.76

TABLE 4E continued

DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF MnO2 & METALLIC SALTS
THERMAL EVENTS TABULATED IN THE SAME ORDER AS IN TABLE ^4D (EXCLUDING SAMPLE 16)

RUN NO.	TYPE OF KC103 +	CRUCIBLE MATERIAL	SAMPLE WEIGHT	THEOR 100% L.O.W.	T2	ONSET TEMP A	ONSET TEMP A1	ELAPSED TIME A - A1	PERCENT DECOMP @ A1	REACTION RATE MOLS/MIN x 1000	ONSET TEMP B	ELAPSED TIME A1 - B	PERCENT DECOMP AT B	REACTION RATE MOLS/MIN x 1000	ELAPSED TIME B/END	PERCENT DECOMP AT END	REACTION RATE MOLS/MIN x 1000
6027	pure + TiO2	Al	7.91	2.56	597	455	561	9.9	41.4	3.35	584	2.0	82.4	16.40	1.1	93.4	7.96
6036	pure + RbCl	Al	11.65	3.94	543	447	512	5.8	14.7	3.12	551	3.4	72.1	20.77	4.0	87.6	4.76
6034	pure + NaCl	Al	10.24	3.04	466	403	443	3.2	13.2	3.91	474	2.9	64.5	16.81	7.2	94.7	3.99
6028	pure + KCl	Al	13.15	4.14	466	428	447	1.7	13.3	10.11	480	3.1	67.6	22.68	6.2	87.7	4.18
5959	pure + ZnO	Al	8.40	2.84	464	370	411	3.6	28.9	7.12	455	3.8	80.6	12.09	6.6	94.4	1.85
5590	98% + MnO2 10	Al	6.12	1.92	456	335	412	7.0	38.0	3.26	464	4.7	84.9	5.98	5.7	94.8	1.04
5589	98% + MnO2 14	Al	8.53	2.70	452	346	398	4.3	22.6	4.43	448	4.7	78.5	10.04	8.0	96.7	1.91
6079	pure + TiO2	Al	10.90	3.53	431	402	490	8.0	29.2	4.02	562	6.7	89.0	9.84	1.3	93.5	3.84
5764	pure + MnO2 14	Pt	9.93	3.14	426	341	380	3.1	31.9	10.08	432	4.6	87.9	11.96	7.3	97.1	1.24
5339	98% + MnO2 10	Al	3.62	1.13	419	377	390	1.2	13.0	3.83	428	3.3	81.4	7.32	2.2	83.4	0.31
5754	pure + MnO2 14	Al	16.37	5.18	417	331	380	4.1	40.2	15.85	414	3.0	92.3	28.13	3.2	95.0	1.37
243	98% + MnO2 10	Al	9.22	2.89	404	355	388	2.8	29.4	9.49	413	2.2	77.5	19.75	6.7	92.0	1.96
5933	pure + NAB1	Pt	10.39	3.25	390	266	372	7.1	26.5	3.78	395	1.4	97.9	51.79	2.5	99.1	0.50
5927	pure +NAB1	Pt	11.90	3.73	384	281	361	6.7	15.6	2.71	391	1.9	97.1	50.00	1.3	97.3	0.22
6068	pure + SnO2	Al	12.30	4.11	380	398	431	3.0	21.9	9.38	473	4.0	63.5	13.36	7.7	85.4	3.65
5342	98% + MnO2 11	Al	4.25	1.33	375	-	339	-	-	-	370	-	-	-	partial loss of sample		
5768	pure + NAB	Pt	10.81	3.39	372	279	365	7.0	46.3	7.01	377	0.8	95.1	64.62	2.2	100.0	1.40
5341	98% + MnO2 11	Al	5.88	1.84	370	305	328	1.9	16.1	4.87	368	3.0	93.5	14.84	2.0	100.0	1.87
5335	98% + MnO2 12	Al	3.17	0.99	365	213	336	11.0	33.0	0.93	367	2.5	99.0	8.17	1.5	100.0	0.21
6054	pure + V2O5	Al	8.43	2.70	358	300	346	3.3	34.1	8.71	358	0.7	74.1	46.21	4.4	79.3	1.00
5588	98% + MnO2 12	Al	7.29	2.28	350	222	331	9.6	29.0	2.15	360	2.3	100.0	22.01	2.2	100.0	0.00
5417	98% + MnO2 20	Al	7.02	2.23	350	290	331	4	8.1	1.56	355	2.2	96.9	28.13	2.2	100.0	0.99
6005	pure + NiSO4.7H2O	Al	18.17	7.51	349	298	334	2.8	29.3	24.55	349	1.3	76.0	84.38	stopped @ isotherm 341 deg		
6004	pure + CuCl	Al	14.53	4.09	349	279	334	4.8	40.3	10.74	350	0.2	86.1	389.57	stopped @ isotherm 341 deg		
5492	98% + MnO2 24	Al	5.76	1.81	349	210	350	12.4	38.1	1.74	363	0.2	100.0	175.00	0.4	100.0	0.00
5703	98% + MnO2 26	Al	6.03	-	346	-	-	-	-	-	-	-	-	-	abandoned instrument fault		
6009	pure + CuSO4	Al	12.03	3.58	346	303	335	2.6	55.3	23.80	346	0.3	88.6	123.96	stopped @ isotherm 341 deg		
6007	pure + CoCl2.6H2O	Al	10.02	4.01	343	277	336	5.0	43.1	10.81	343	0.1	58.6	387.47	stopped @ isotherm 341 deg		
5421	98% + MnO2 21	Al	4.61	1.44	342	300	341	3.6	36.1	4.51	350	0.1	117.0	-	partial loss of sample		
5521	98% + MnO2 22	Al	5.89	1.87	341	245	342	7.9	53.5	3.86	352	0.2	113.0	-	partial loss of sample		
5958	pure + FeCl3.6H2O	Al	12.65	4.23	341	237	341	9.1	86.2	12.52	353	0.1	100.0	365.63	0.1	100.0	0.00
5951	pure + MnSO4.4H2O	Pt	10.05	4.60	340	266	340	6.0	28.3	6.77	350	0.1	100.0	1031.26	0.2	100.0	0.00
5907	pure + MnCl2.4H2O	Pt	10.36	3.63	340	195	338	12.4	47.4	4.33	357	0.1	100.0	596.91	3.0	100.0	0.00
5938	pure + MnCl2.4H2O	Pt	20.18	7.26	340	192	338	11.1	60.7	12.41	367	0.1	100.0	891.62	0.1	100.0	0.00
5345	98% + MnO2 3	Al	3.96	1.24	340	249	337	7.4	26.8	1.40	349	0.6	92.3	42.27	6.2	99.0	0.42
5908	pure + MnCl2.4H2O	Pt	11.30	4.31	340	194	338	12.3	36.4	3.99	355	0.1	99.0	842.74	1.5	100.0	0.90
5332	98% + MnO2 2	Al	3.92	1.23	339	-	339	-	-	-	346	0.1	115.0	-	partial loss of sample		
5953	pure + NiSO4.7H2O	Pt	7.55	3.09	339	107	339	20.1	50.8	2.44	350	0.5	100.0	95.00	5.2	102.0	0.37
5906	pure + MnCl2.4H2O	Pt	21.54	8.23	339	192	336	11.7	65.6	14.42	365	0.1	100.0	884.47	severe TG & DTG interferenc		
5347	98% + MnO2 2	Al	4.28	1.35	339	235	339	8.6	38.3	1.88	348	0.1	100.0	260.25	1.0	100.0	0.00
6087	98% + MnO2 21	Al	16.69	5.34	339	263	339	6.1	41.0	11.22	365	0.1	92.9	1731.16	0.6	93.5	1.59
5336	98% + MnO2 13	Al	3.56	1.12	339	298	340	3.6	19.4	1.89	349	0.6	92.6	42.70	5.3	99.0	0.42
5960	pure + FeCl2.4H2O	Pt	22.00	7.20	339	210	338	10.5	40.6	8.69	360	0.1	93.2	2368.35	0.5	94.0	3.78

TABLE 4F

ISOTHERMAL DECOMPOSITION OF KC103 WITH METAL OXIDES & SALTS AS SHOWN

RUN NO.	TYPE OF KC103 +	CRUCIBLE MATERIAL	WEIGHT % REACTANT	ISOTHERM TEMP	T1	T2	T3	% DECOMP. BEFORE ISOTHERM	% DECOMP. AT ISOTHERM	TIME IN MINS AT ISOTHERM
SLOW REACTIONS										
211a	pure + 14	Al	19.2	331	338	340		8	39	54
211a	two isotherms			341			340	43	98	49
5679	98% + 12	Al	20.4	327	340	346	340	26	88	41
5694	98% + 14	Al	19.0	339	340	0	0	3	98	132
5698	98% + 20	Al	18.8	325	337	346	337	19	88	91
5767	pure + 14	Pt	19.2	342	339	0	339	0	89	68
5990	pure + NAB	Al	19.9	341	337	341	337	12	99	25
5992	pure + ZnO	Al	13.7	341	0	0	0	0	26	28
6010	pure + 14	Al	19.2	342	0	0	0	2	79	78
RAPID TO EXPLOSIVE REACTIONS										
5680	98% + 24	Al	19.9	325	0	338	338	12	92	77
5703	98% + 26	Al	19.9	320	0	346	346	11	75	21
6004	pure + CuCl	Al	28.1	341	300	335	335	22	88	2
6005	pure + NiSO4.7H2O	Al	37.7	341	336	339	339	25	77	5
6007	pure + CoCl2.6H2O	Al	33.7	341	0	337	0	61	76	5
6009	pure + CuSO4	Al	24.1	341	336	336	0	50	89	5

TABLE 4G

DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF METALLIC SALTS & OXIDES SHOWN
COMPLEX REACTIONS PROBABLY INVOLVING SECONDARY REACTION PRODUCTS

RUN NO	TYPE OF KC103 +	CRUCIBLE MATERIAL	WEIGHT% REACTANT	T1	T2	T3	RATE	T10	T50	T75
6035	pure + LiOH.H2O	Al	43.0	0	490	360	EXP	456	476	487
6038	pure + LiCl	Al	43.8	0	415	0	EXP	148	413	628
6037	pure + LiCl	Al	43.8	319	408	0	EXP	334	380	400
5962	pure + CrO3	Pt	19.9	0	380	309	SLOW	196	308	355
5961	pure + CrO3	Pt	19.9	0	380	304	SLOW	196	308	370
6026	pure +VOSO4.3H2O	Al	34.4	310	350	344	EXP	stopped @380deg C		
6081	pure + LiCl	Al	43.8	0	361	166	SLOW	300	395	_
6082	pure + CaO	Al		substantial loss of sample.CaO may be defective. abandoned.						

CHAPTER 5

SYNTHESIS CURING PROPERTIES & CHARACTERISATION OF SODIUM BIRNESSITE

5.1 OBJECTIVE

As a result of the X-Ray studies and experiments on curing of polysulphides by selected samples of so-called manganese dioxides(see Chap. 2.5) including the commercially successful Sample 12 it was suspected that the active compound in manganese dioxide curing agents might be synthetic sodium birnessite the composition of which is said to be $Na_4Mn_{14}O_{26}.9H_2O$ (17 18 19)

This compound was identified in Sample 12 during an XRD examination and it and its potassium (and probably lithium) derivatives were identified in Sample 20 which is the American counterpart of Sample 12.

The work described in this chapter deals with the development of a reproducible method of synthesising sodium birnessite and the comparison of its curing properties with those of Samples 12 and 20.

5.2 THE CHEMISTRY OF SODIUM BIRNESSITE

In 1956 Jones and Milne(1) described a new mineral found near Birness, Scotland. It gave a X-Ray pattern identical to delta- Manganese dioxide and analysis of an impure sample gave a formula close to $(Na_{0.7}Ca_{0.3})Mn_7O_{14}.2.8\ H_2O$. They named the mineral "Birnessite" and it was subsequently reported in several other localities. Bricker(2) assigned the name

"Birnessite" to delta-manganese dioxide. Feitknecht and Marti(3) proposed a double -layer structure for δ-MnO_2 and Bricker suggested that this type of structure lends itself to accommodating large amounts of other cations accounting for the complexity of the composition of natural birnessites .

Although the range of compounds is complex and not fully resolved δ-MnO_2 may be regarded as the starting member of a series:-

δ-MnO_2	δ-Manganese Oxide (to which Bricker assigned the name " Birnessite")
$Mn_7O_{13}.5H_2O$	Birnessite (hydrated)
$Na_4Mn_{14}O_{26}.9H_2O$	Sodium Birnessite
$(Na_{0.7}Ca_{0.3})Mn_7O_{14}.2.8H_2O$	mineral Birnessite
$(Na,Ca,K)(Mg,Mn)Mn_6O_{14}.5H_2O$ (11)	generalised formula for mineral birnessite

The first three compounds have been synthesised (2) to (10) and X-Ray studies have confirmed their similarity to the natural materials. (Table 5-A)

δ-manganese dioxide is synthesised by treating boiling $KMnO_4$ with HCl, washing the precipitate formed with water and treating it with H_2O_2. (12)(13)

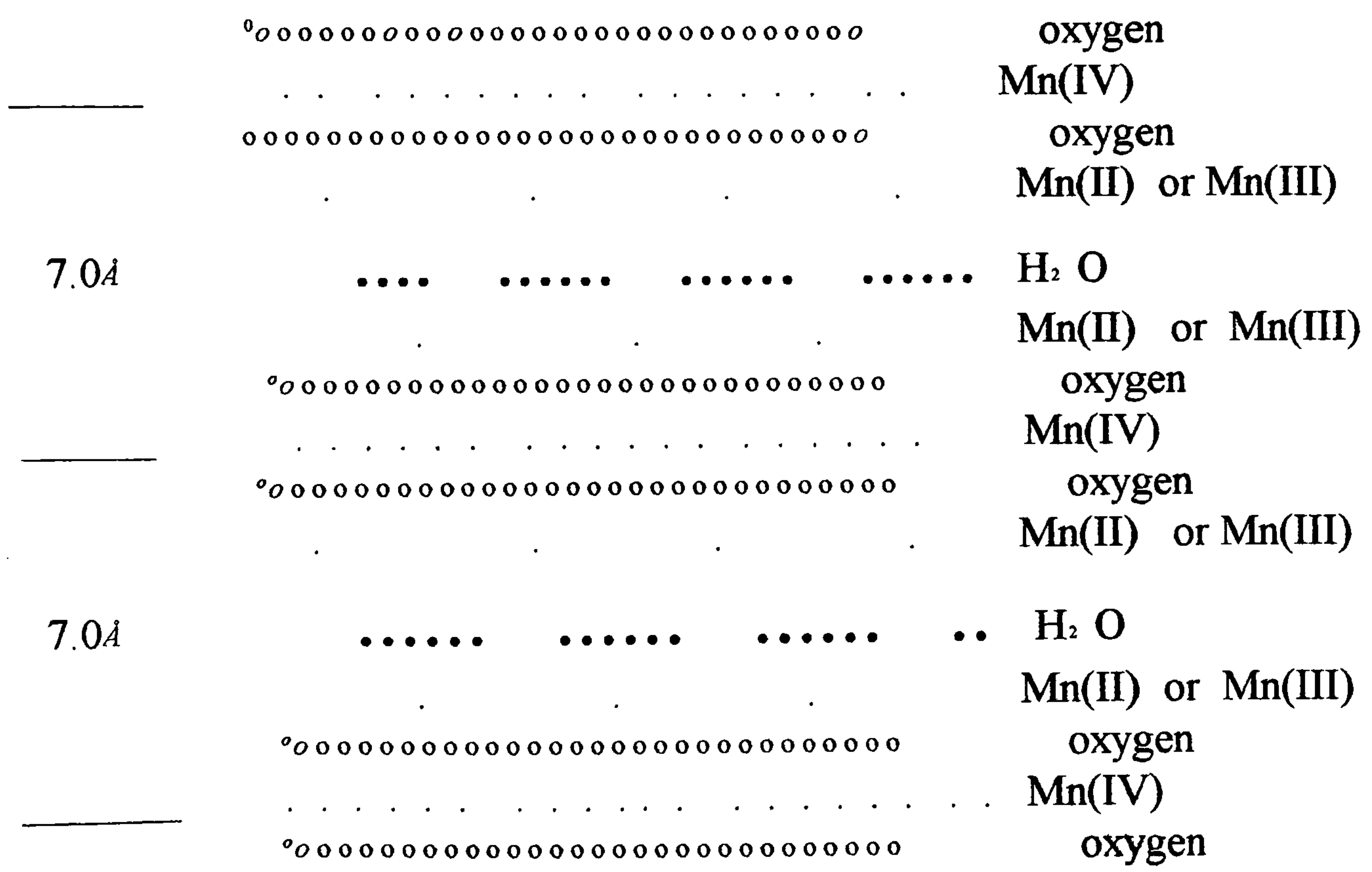
$Mn_7O_{13}.5H_2O$ is synthesised by reacting sodium birnessite with dilute nitric acid. (9)

According to Giovanoli(18) and Golden(21) synthetic sodium birnessite is obtained by dehydrating synthetic Sodium Buserite.($Na_4Mn_{14}O_{27}21H_2O$). Buserite and Birnessite are said to have "layered" structures with sheets of water molecules between sheets of edge-sharing MnO_6 octahedra the arrangement being repeated about every 7.2 Å in the case of birnessite (Fig.5-1) and 10 Å in buserite.(9,10,14,15)

Golden #(10) suggested that one of the octahedral sites in the MnO_6 octahedra is unoccupied, and Mn^{2+} and Mn^{3+} lie above and below each octahedral vacancy. These lower-valence Mn ions are coordinated to oxygens in both the octahedral MnO_6 sheet and the water sheet.

Fig. 5-1 after Burns[24] shows the layered arrangement in the Birnessite structure and Fig.5-2 after Le Goff et al (18) shows the layered structure of sodium birnessite . According to Le Goff the interlayer distance, d = 7.1Å corresponds to two consecutive superimposed MnO_6 layers and the trigonal prismatic sites within the interlayer are occupied by sodium ions and water molecules. He describes the structure of Na-birnessite as a lamellar phase of monoclinic symmetry (space group C2/m) with the following unit cell parameters:- a = 5.17Å , b = 2.85Å, c = 7.31Å and β = 103.2°. The interlayer distance = c x sinβ = 7.11Å.The structure is compatible with a strong cation exchange capability which is satisfied in the natural product by the reaction with naturally occurring metal ions. The synthetic product has been shown to exhibit this exchange capability.

Fig. 5 - 1 Structure of Birnessite after Burns



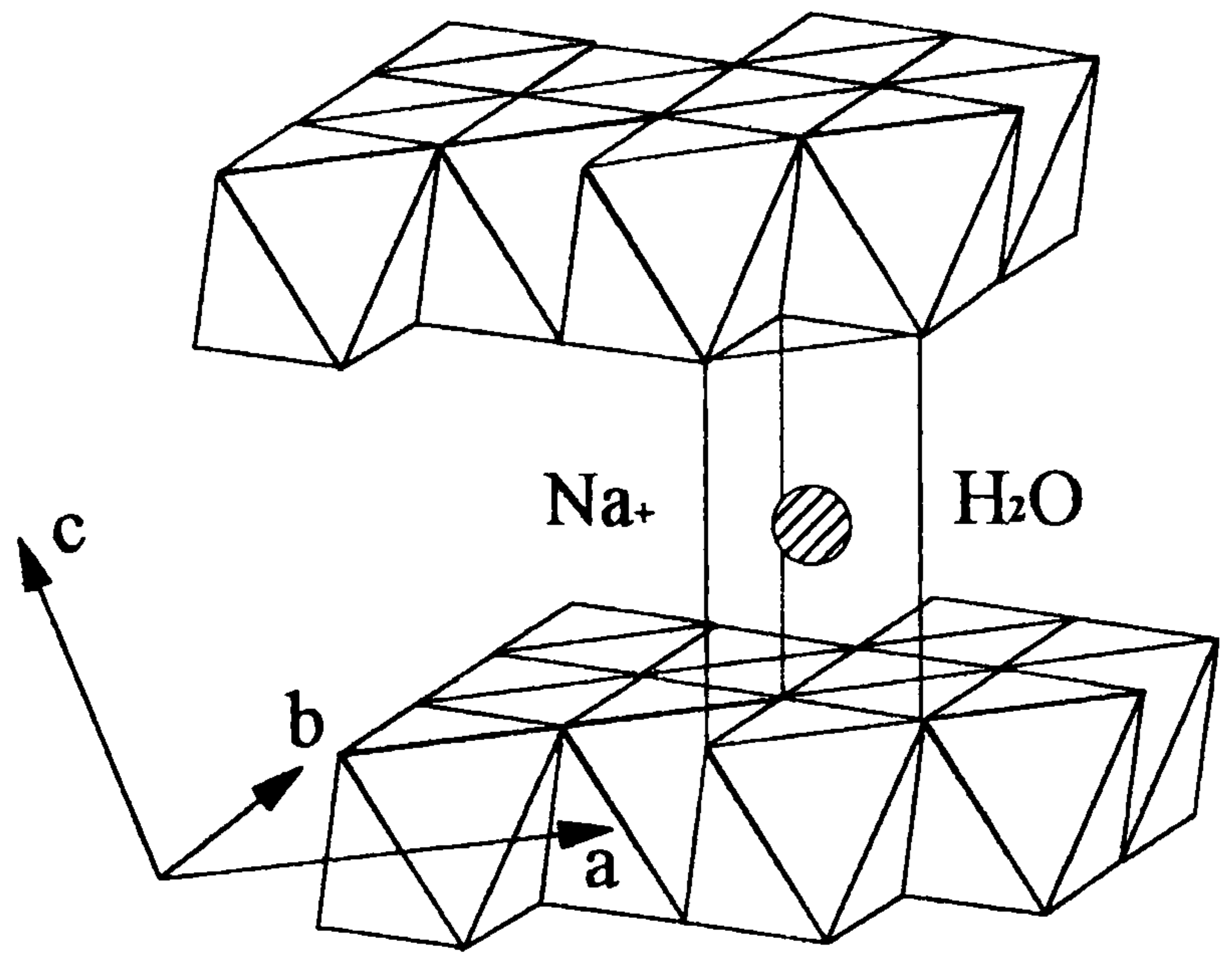


Fig. 5-2 Structure of Sodium Birnessite after Le Goff

5.3 SYNTHESIS OF SODIUM BIRNESSITE

The aim of this part of the work is to develop a reproducible method of synthesising sodium birnessite which has been defined as follows:-

Formula: $Na_4Mn_{14}O_{26}.9H_2O$

Formula weight :- 1439.16 giving :

Sodium	6.39%
Manganese	53.44
Oxygen	28.91
Water	11.26%
	100.00%

The preparation methods described by Giovanoli (9) and Golden(10) involve the reaction of a solution of a manganese salt with sodium hydroxide in the presence of oxygen to produce the black precipitate sodium buserite $Na_4 Mn_{14} O_{27} . 21H_2 O$ which is dehydrated at low temperature to produce sodium birnessite.

Fig. 5-3 after the paper by Le Goff et al(18) shows the suggested course of the reaction.

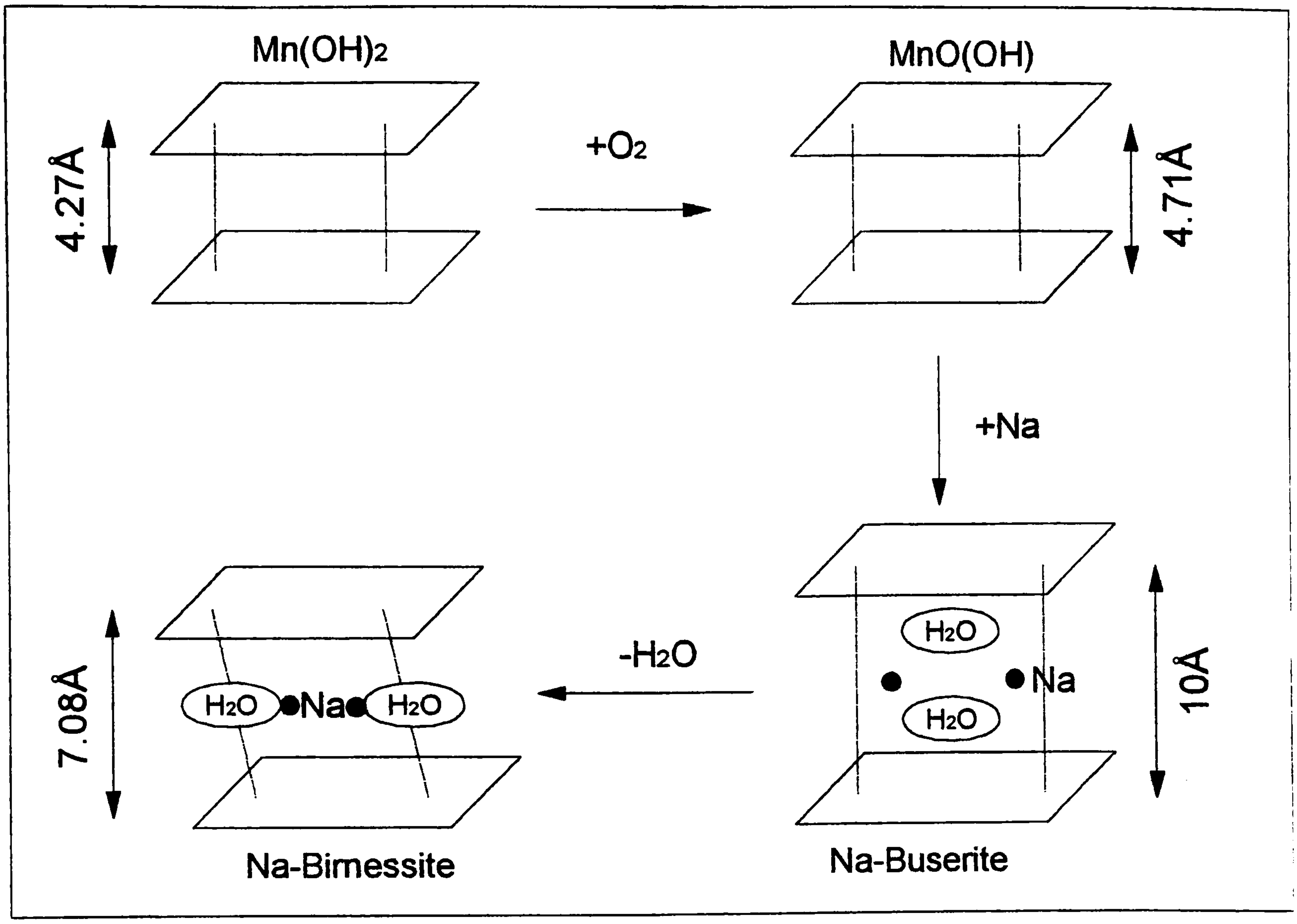


Fig. 5-3 Synthesis of Sodium Birnessite showing diagrammatically the removal by drying of water layers from Na-buserite and linking of the remaining water to Na ions in Na-birnessite.

The literature cites the use of a solution of $Mn(NO_3)_2$ $MnCl_2$ or $MnSO_4$ as starting materials for treatment with NaOH in the presence of a rapid flow of oxygen or air. If air is used quantities of Hausmannite $Mn_3 O_4$ are also said to be produced(16) : $Mn_3 O_4$ is also obtained if insufficient time is allowed for oxidation or if the flow rate of oxygen is too low.

The literature describes situations in which the resulting precipitate is washed thoroughly according to some authors; and in which,according to others, it is partially washed or not washed at all (9,10,14,16) . In the synthesis Buserite is converted to Birnessite in a drying process.Various drying processes have been reported including freeze-drying , vacuum drying at ambient temperature and oven drying at 100° C although the latter suggestion can probably be disregarded since sodium birnessite starts to decompose at around 50° C .

5.3.1 EXPERIMENTAL SYNTHESIS OF SODIUM BIRNESSITE

The first step in this study was to use a literature-based synthesis to determine whether this did result in the formation of sodium birnessite. The practice recommended by Giovanoli(9) and by Golden(10) was followed. Thus:-

A solution of 55g NaOH in 250ml water was added to 200ml of a 0.5% molar solution of $MnCl_2$ in water at room temperature in a plastic one- litre measuring cylinder. Oxygen was bubbled through a G-I glass frit into the suspension at a rate of 2.5 - 3.0 l/min for 4-5 hours. The precipitate obtained was washed and centrifuged several times and the moist cake was freeze-dried . The resulting product (Sample No. NAB) was examined by X-Ray Diffraction (Fig.5-4 and accompanying Certificate of Analysis No.94LTS0001) which confirmed that the product was predominantly sodium birnessite with trace phases of Mn_2O_3 and $Na_2Mn_8O_{16}$.

A second sample (Sample NAB2) was produced under the same nominal conditions but difficulty was experienced with control of the oxygen flow rate and the X-Ray Diffraction result on this sample reflected this showing the presence of Mn_3O_4 and MnO_2 product. (Certificate of Analysis No. 95TSC0038). Fig. 5-6 shows the principal X-Ray Diffraction differences between Samples NAB and NAB2.

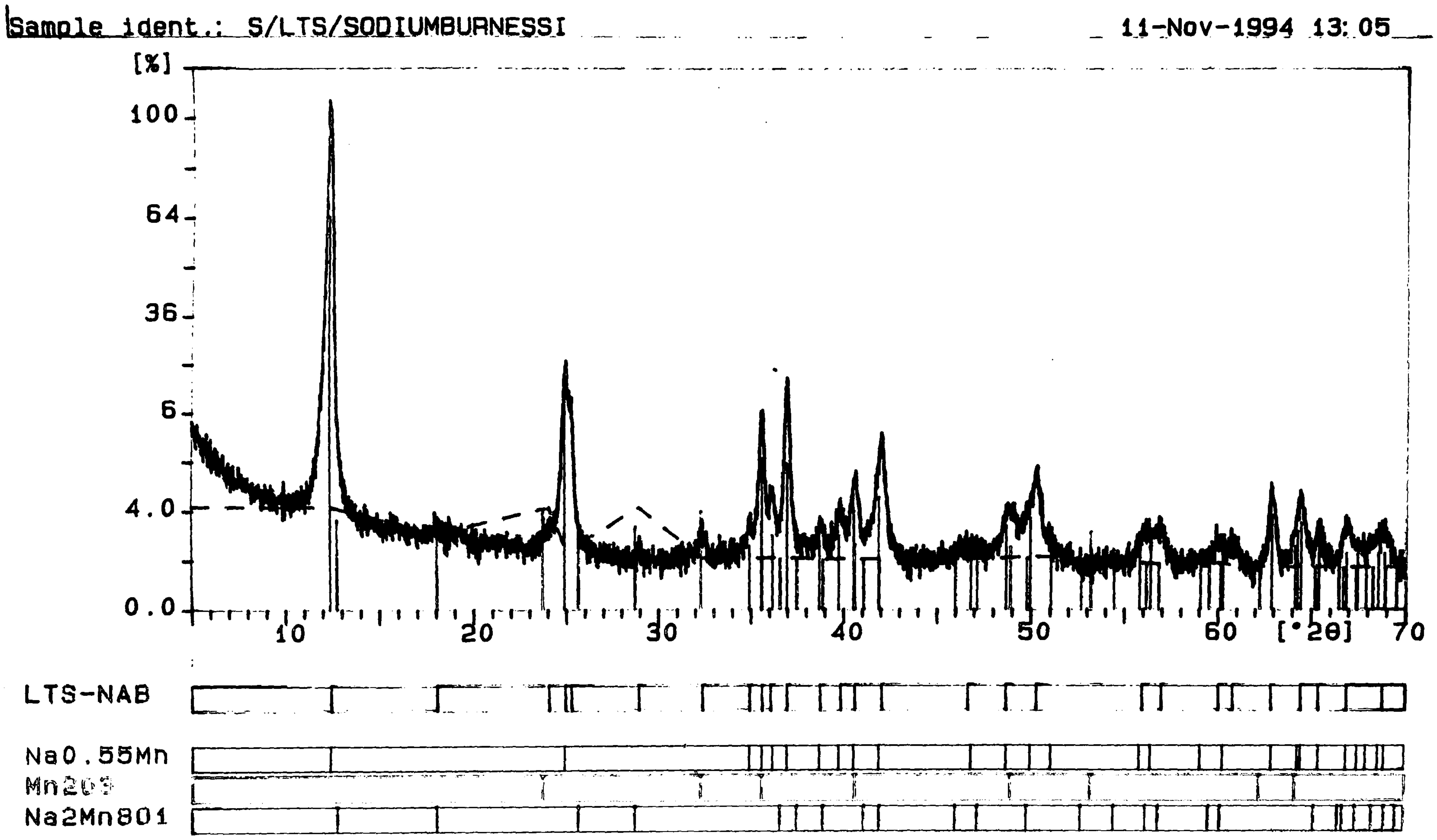

Sample ident.: S/LTS/SODIUMBURNESSI
11-Nov-1994 13:05
[%]
100
64
36
6
4.0
0.0
10
20
30
40
50
60
[°2θ]
70
LTS-NAB
Na0.55Mn
Mn2O3
Na2Mn8O1

FIG. 5-4

LONDON & SCANDINAVIAN METALLURGICAL CO LIMITED

Fullerton Road, Rotherham, South Yorkshire S60 1DL, England

Tel. 0709-828500
Fax. 0709-830391
Telex. 54531

ANALYTICAL SERVICES

CERTIFICATE OF ANALYSIS

TO
Laminor Technical Services Limited
38 Grimsdyke Crescent
Barnet
Herts
EN5 4AG

FAO
M Z Goldblatt

Certificate Date
17 Nov 94

Certificate No.
94LTS0001

Date of Receipt
10 Nov 94

Your Ref./Order No.

Sample Details
Sodium Birnessite

Analysis Results

SODIUM BIRNESSITE

PHASES IDENTIFIED :

Major Phase:

$Na_{0.55}Mn_{2}O_{4}.1.5H_{2}O$

Trace Phases:
MnO_{3}
Plus possibly $Na_{2}Mn_{8}O_{16}$

Charts enclosed.

*** END OF REPORT ***

Comments/Remarks

Analysed using in-house documented procedures for XRD.

Signed M. E. J. Birch

M.E.J.BIRCH
LABORATORY MANAGER

This analysis is subject to our conditions of assay which appear on the reverse of this document.

Registered Office: 45 Wimbledon Hill Road London SW19 7LZ. Registered No. 345279. V.A.T. No. GB 172 7580 46

LONDON & SCANDINAVIAN METALLURGICAL CO LIMITED

Tel. 01709-828500
Fax. 01709-830391

ANALYTICAL SERVICES

NAMAS
TESTING
No 1091

CERTIFICATE OF ANALYSIS 1 OF 2

TO
Laminor Technical Services Limited
38 Grimsdyke Crescent
Barnet
Herts
EN5 4AG

Certificate Date
21 Sep 95

Certificate No.
95TSC0038

Date of Receipt
1 Sep 95

Your Ref./Order No.

Sample Details
Two samples submitted.

FAO
N Z Goldblatt

Analysis Results

NAB2

Phases identified:

$Na_{0.55} Mn_2O_4. 1.5H_2O$ - Birnessite

and small amounts
Mn_3O_4 and/or Mn_2O_3
and possibly MnO_2.

Comments/Remarks

Analysed using in-house documented procedures for XRD.
Please find attached XRD reports pages 1 to 6.

Signed
pp M.E.J.BIRCH
LABORATORY MANAGER

This analysis is subject to our conditions of assay which appear on the reverse of this document.

95TSC0038
Attachment Page 1 of 6

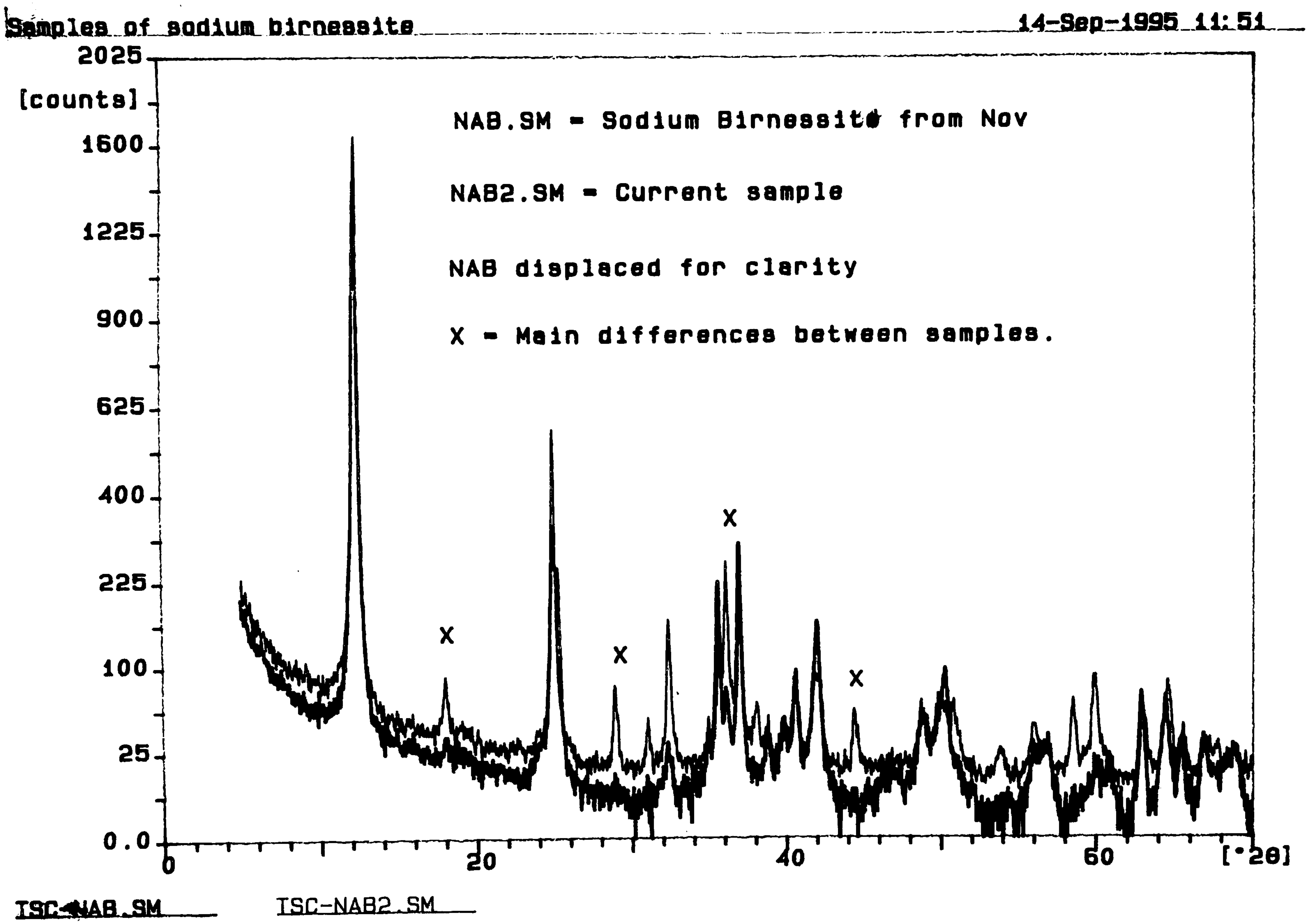


FIG. 5 - 6

It is clear that the methods described in the literature do result in the production of sodium birnessite but variations in procedure can lead to the introduction of impurities. For this reason work was carried out to determine the effect of the following variables on the preparation method and on the quality of the product using X-Ray Diffraction and Thermogravimetry as convenient and cost-effective means of monitoring product quality:-(except where otherwise indicated the oxygen flow rate hereafter was controlled at 2.75l/min.)

1. Drying

Freeze drying was found to be a laborious and, if this material were ever to be exploited commercially, an expensive process. Accordingly, a vacuum drying method was developed in this work in which the wet buserite cake was contained in a polypropylene beaker in a modified desiccator connected to a vacuum pump. The beaker was surrounded by a metal coil connected to a source of continuous hot water.A Wolff bottle surrounded by a container filled with dry ice was interposed between the desiccator and the vacuum pump to condense and freeze the extracted water and prevent it from reaching the pump. A thermocouple was fitted within a glass probe which penetrated the wet cake to enable the cake temperature to be monitored continuously and a pressure gauge was mounted in the vacuum pump circuit to monitor and control the vacuum. Fig. 5-7 shows this layout schematically . In the drying system it was possible to expose the wet cake to a pressure of about 10^{-1} Torr and to compensate for the drop in temperature due to evaporative cooling by providing heat through the heating coil when the cake temperature dropped to about 5° C. The temperature could be held within the range 2 to 15° C by controlling the rate of flow and temperature of the hot water supply.

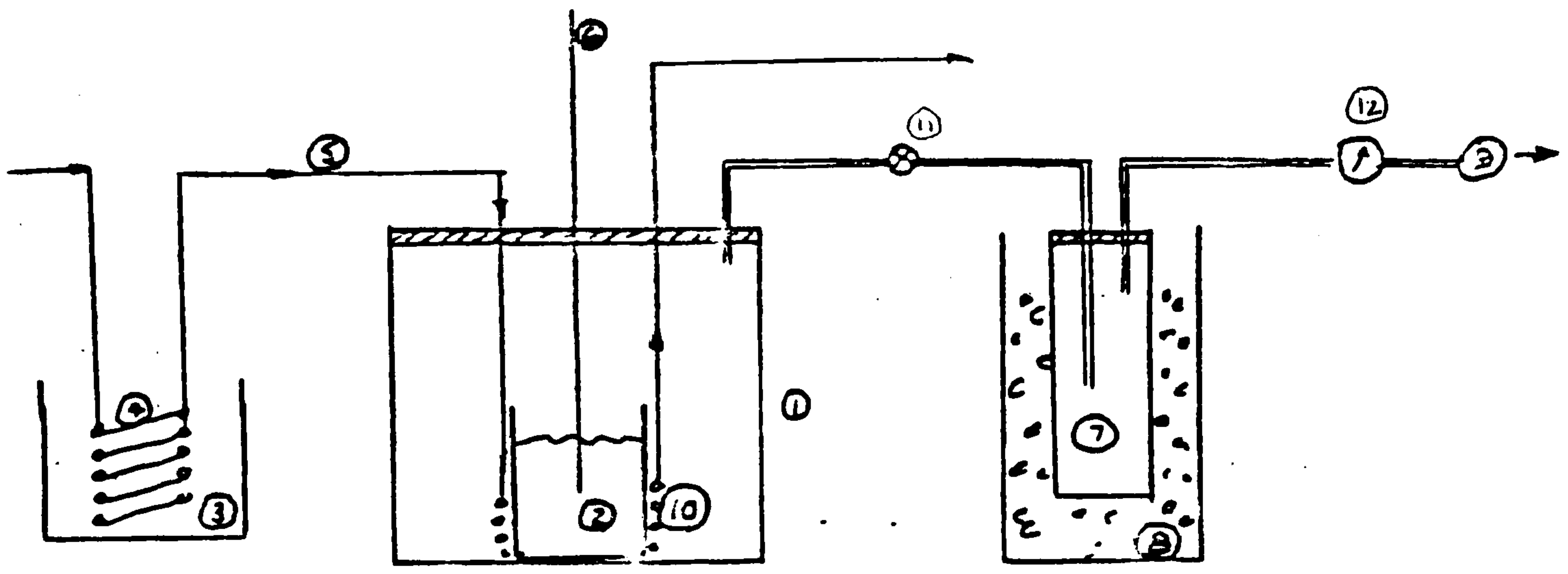


FIG.5-7

DIAGRAMMATIC LAYOUT OF APPARATUS FOR DEHYDRATING
SODIUM BUSERITE TO PRODUCE SODIUM BIRNESSITE

1. GLASS VACUUM VESSEL WITH REMOVABLE TOP
2. POLYETHYLENE REACTION VESSEL CONTAINING SODIUM BUSERITE
3. THERMOSTATICALLY CONTROLLED WATER BATH
4. HEATING COIL DRAWING MAINS WATER SUPPLY
5. HOT WATER SUPPLY
6. THERMOCOUPLE
7. WASH BOTTLE TO TRAP DISTILLATE
8. DRY ICE IN CONTAINER SURROUNDING WASH BOTTLE
9. VACUUM PUMP
10. HEAT EXCHANGE COILS
11. STOPCOCK
12. VACUUM GAUGE

2.Reaction Time:- The reaction times used in this study were:-

10 8 7 6 4 3 and 2 hours

giving Samples No.NAB 20 21 22 23 24 25 and 26

X-Ray Diffraction results: Traces of MnO and MnO_2 were found in all samples and Mn_3O_4 and Mn_2O_3 were found in samples with reaction times below 4 hours.

Using a reaction time of 4 hours and holding all other variables as above three experiments were carried out to determine the consistency of the reaction giving

samples No. NAB21A 21B and 21C

The characterisation using X-Ray Diffraction showed that consistent results were obtained.

3.Oxygen Flow Rate:- With a reaction time of 4 hours two other oxygen rates were studied.viz:-

Litres/min. 2.0 1.5

giving samples nos. NAB 27 28

Again X-Ray Diffraction data showed that the products were the same in both cases.

4.Manganese salt:- In the preparation procedure Manganese Chloride was replaced with commercial grade Manganese Sulphate in the same molar proportions using a flow rate of 2.75 l/min O_2 and a reaction time of 4 hours to give replicate samples nos. 29 and 30.

X-Ray Diffraction data showed that the duplicates agreed well and that the products were the same as those produced with manganous chloride.

The X-Ray Diffraction results on all the samples obtained in the above study are recorded in Table 5B. It is concluded that with a reaction time of 4 hours or more the procedure is capable of consistently producing a satisfactory grade of sodium birnessite typified by theX-Ray pattern shown in Fig. 5-8 .

Composite sample

Having established that a satisfactory grade of sodium birnessite can be made with commercial manganese sulphate with a reaction time of 4 hours and an oxygen flow rate of 2.75l/min. a number of batches were produced under these conditions; each batch was subjected to X-Ray Diffraction examination to ensure that quality was maintained; and the batches were combined, ground gently with a pestle and mortar, screened and stored as " Composite Sample of Sodium Birnessite" to be used for characterisation and tests of efficacy as a curing agent for polysulphide resin. The composite was analysed in duplicate by Inductively Coupled Plasma Atomic Emission Spectroscopy after digestion with HNO_3 and H_2O_2 with the following results:-

	(1)	(2)	Mean	Theoretical
Sodium	6.1	6.0	6.05	6.39%
Manganese	54.7	54.6	54.65	53.44%

Thermographic Analysis

The cumulative loss of weight data for a number of samples including the composite sample were obtained by thermal analysis .These are shown in Table 5-C which records the profile of the cumulative Loss of Weight as temperature is increased. Figs.5- 9 shows a typical thermographic trace of temperature plotted against loss of weight and rate of loss of weight and also the Differential Thermal Analysis of partly dehydrated buserite,sodium birnessite and sodium birnessite with what appears to be absorbed moisture.

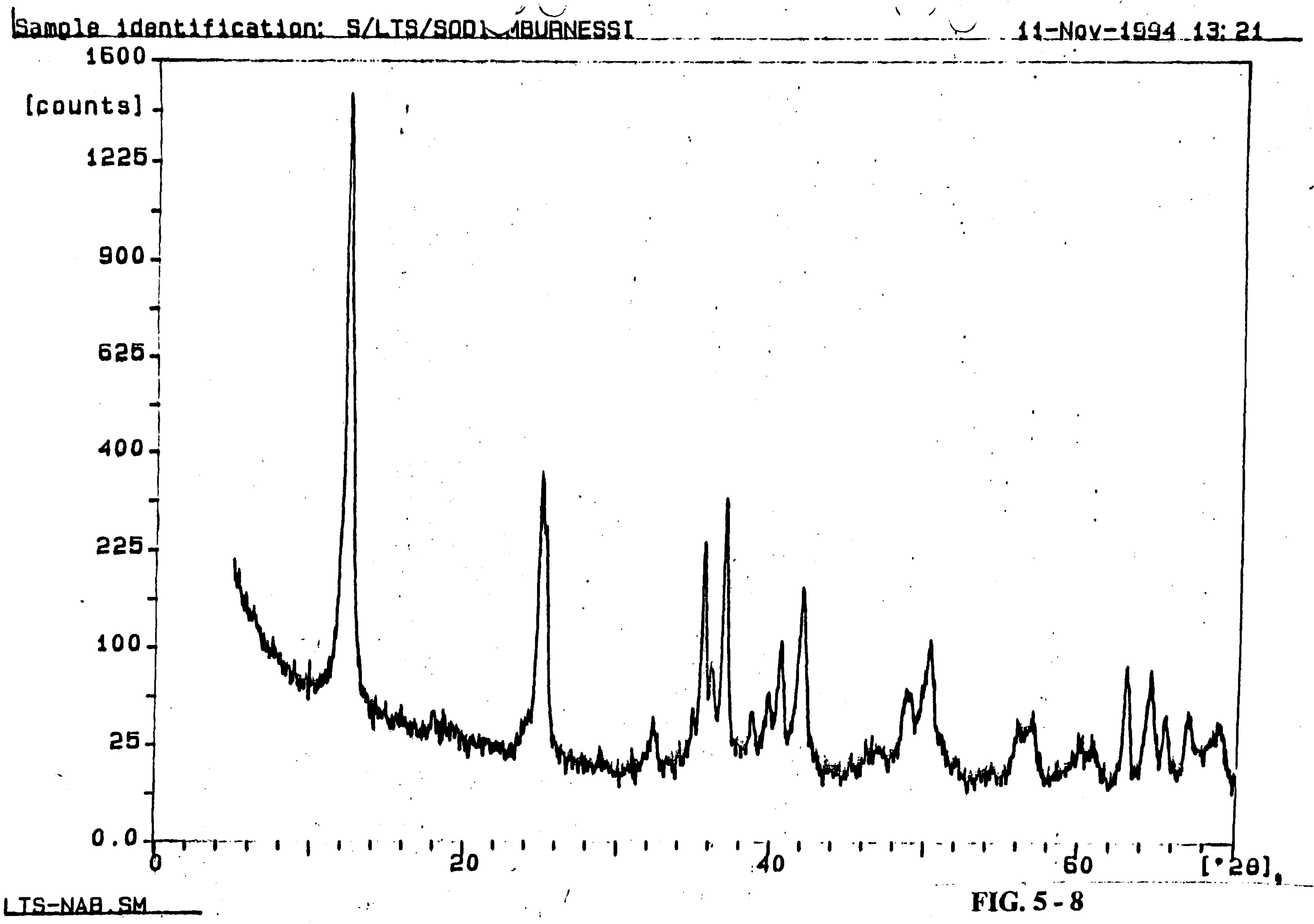


FIG. 5 - 8

X-RAY POWDER DIFFRACTION DIAGRAM
FOR SODIUM BIRNESSITE

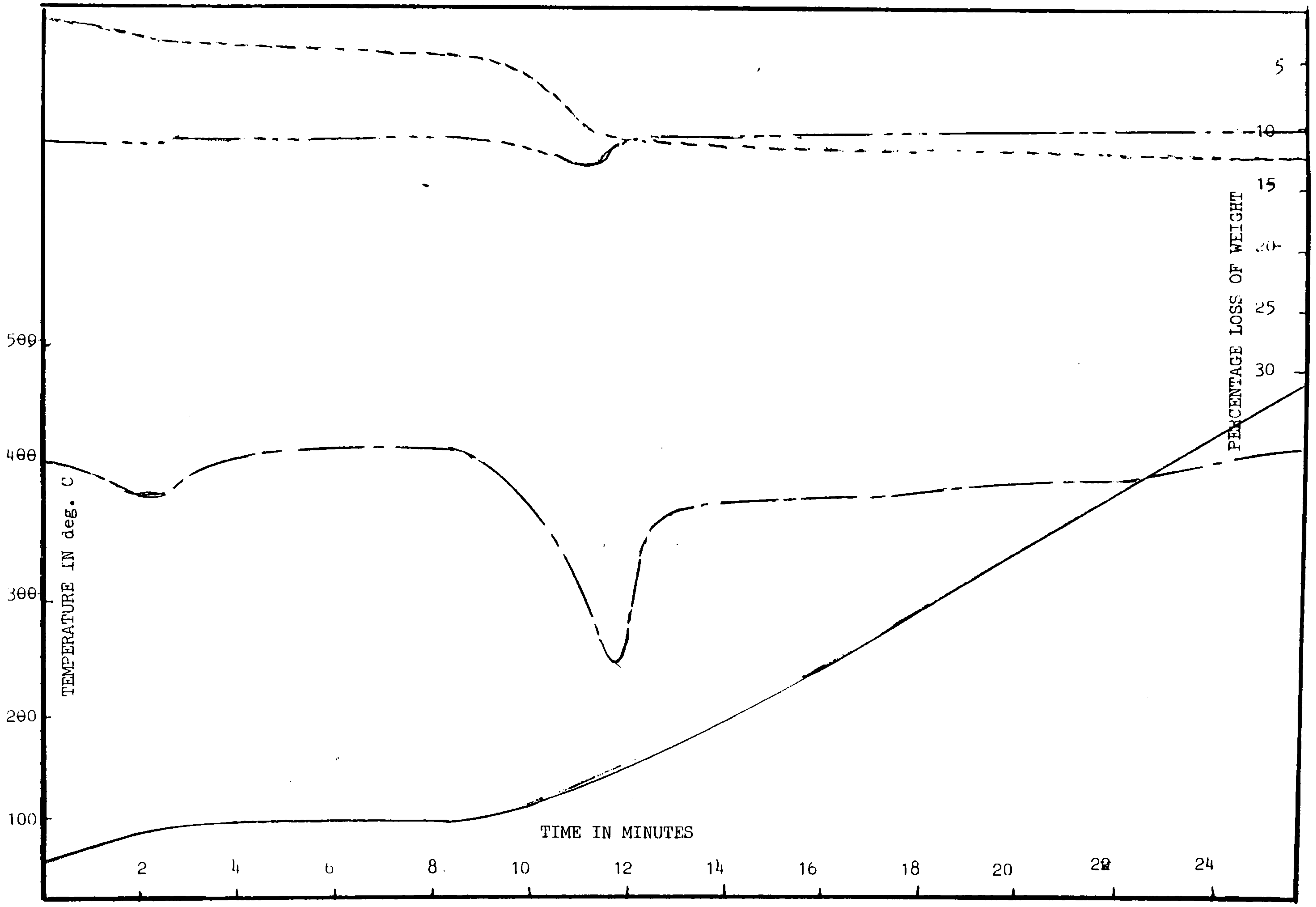


Fig. 5-9

Thermal decomposition of

sodium birnessite

TEMPERATURE _____

D.T.A. ____ _ _____ _ _

L.O.W.------------------------

dW/dT____ _ _ _ _____

Curing Properties

In a Patent Specification Cookson(16) claims that Sodium Birnessite is a rapid curing agent for polysulphide resins. Using the "standard" procedure developed in the present work (see Chapter 2 ,par.2.3.13) viz:- 7.5% of the Composite Sample was added to a weighed quantity of polysulphide and mixed in a temperature-controlled water bath at 23/25° C for 10 minutes.Curing was so rapid that it proved impossible to measure the viscosity, the resin having set during the mixing period. The curing was then studied by measuring the viscosity when blends of sodium birnessite with natural ore were used to cure the polysulphide resin using the same procedure as that set out in par.2.3.13 of Chapter 2.The results are shown in Table 5-D.

5.4 DISCUSSION OF RESULTS AND CONCLUSION

A method for the consistent synthesis of sodium birnessite has been developed and used to synthesise a composite sample made up of a number of batches. The method produces a satisfactory grade of sodium birnessite consistently and is reasonably robust in that it can tolerate the use of a commercial quality of manganese sulphate, a lower flow rate of oxygen and a lower reaction time than is suggested by the literature.

The X-Ray Diffraction pattern of the composite sample (Fig. 5-8 and Table 5 -B) of the composite sample conforms well with the Powder Data File 43-1456 for synthetic sodium birnessite while the analytical results on the duplicate composite sample conform reasonably well with the theoretical composition for the material suggested by various authors and listed below.

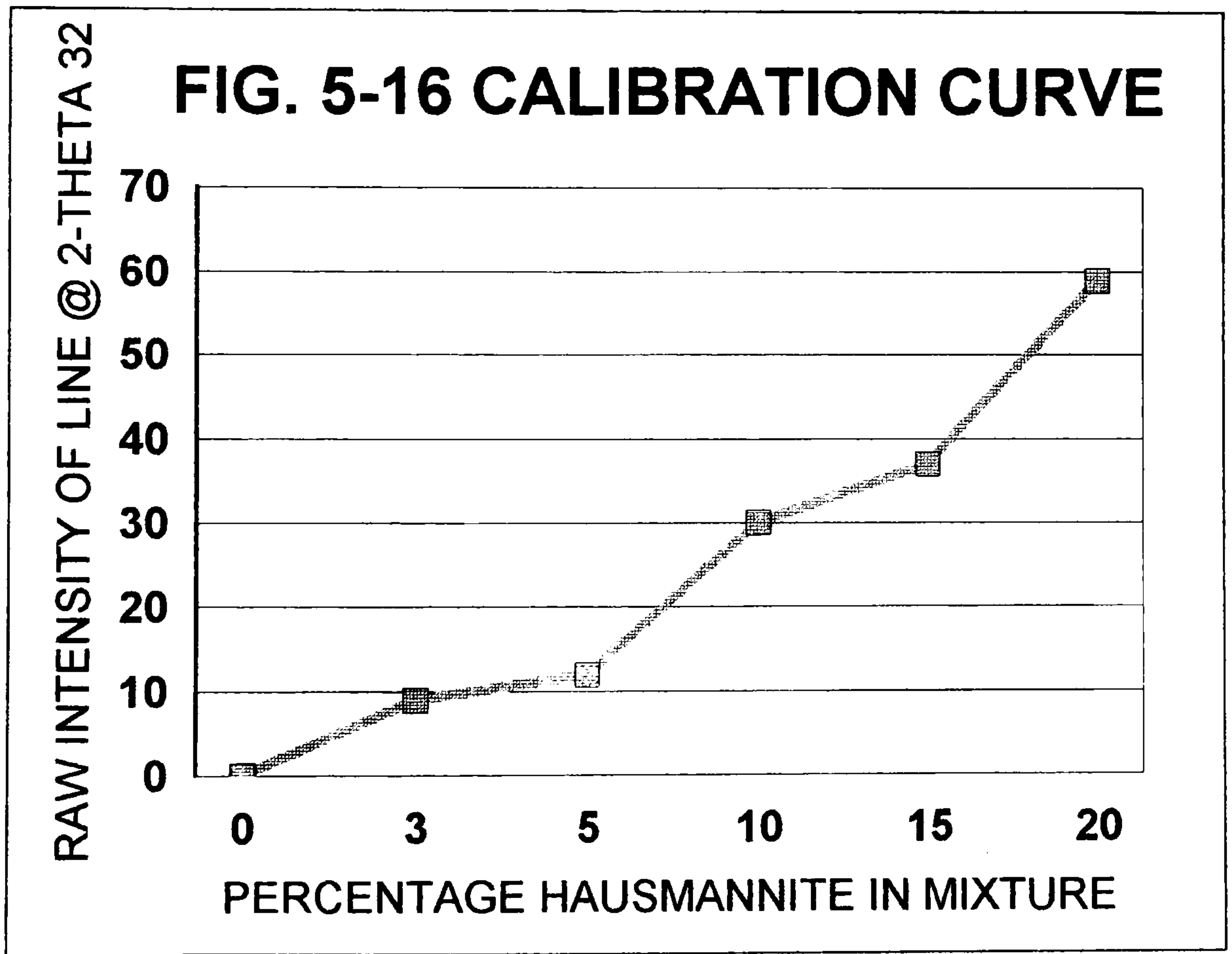
Ref.	Formula	F,W.	%Na	%Mn	%H2 O
This work: Composite Sample					
	$Na_{3.78} Mn_{13.4} O_{25} 9H_2 O$	**1429.64**	**6.08**	**54.6**	**11.33**
(9)	$Na_4 Mn_{14} O_{27} 9H_2 O$	1455.16	6.32	52.9	11.13
(25)	$Na_4 Mn_{14} O_{25} 9H_2 O$	1439.16	6.38	53.4	12.5
(15)	$Na_{3.47} Mn_{12} O_{25.7} 9H_2 O$	1313.39	6.08	50.3	12.33
(15)	$Na3.48 Mn_{12} O_{24} 9H_2 O$	1285.32	6.22	51.3	12.69
(18)	$Na_{4.3} Mn_{13.4} O_{26.9} 9H_2 O$	1428.66	6.92	51.7	11.3

The curing rate experiments demonstrate (Table 5-D) that blends of the composite sodium birnessite sample with Twinstar natural ore produce , under the test conditions used, results comparable with those produced by blends of commercial curing agent (samples 11 & 12) with the natural ore. This commercial material has been shown to contain a significant proportion of sodium birnessite. It seems reasonable to conclude that sodium birnessite is the active and rapid curing agent in this material and that,in this particular product, its activity is partly modulated by the other ingredients (note that in Table 2-J 100% sample 12 does not cure as rapidly as 100% sodium birnessite in Table 5-D) .In both the commercial product and pure sodium birnessite the curing activity is modulated by natural ore.

The work described herein highlights the importance of sodium birnessite in the curing of polysulphide resin by manganese dioxide phases.

During the production of sodium birnessite it has been demonstrated that,when insufficient reaction time is allowed or the flow rate of oxygen is too low,Hausmannite is produced. Cookson(16) records that when air is used in place of oxygen Hausmannite is produced. It was thought possible that the controlled production of a percentage of Hausmannite may have had a similar modulating effect on the curing rate of synthetic sodium birnessite .If this were so it could have provided an economic and commercial method of producing a range of Sodium Birnessite curing agents "custom built" to achieve specific curing rate.However no such relationship could be established between percentage Hausmannite (using reagent grade Mn_3O_4) in the birnessite and curing rate . In the course of this investigation a calibration curve was developed using X-Ray Diffraction measurements of the change in intensity of a specific hausmannite line with increasing percentages of Mn_3O_4 in mixtures with sodium birnessite. The line selected occurs at a 2-theta value of 32.39° and the calibration curve is shown in Fig. 5-16 which is based on data recorded in Table 5-E.

FIG. 5-16 CALIBRATION CURVE



Conclusion

It has been established that sodium birnessite is a rapid and effective curing agent for polysulphide resin; that its curing action can be modulated by the use of natural manganese dioxide ore to give practical pot and working life parameters in a controlled fashion; that it is probably the principal active ingredient in so-called manganese dioxide curing agents for this resin and that it can be synthesised consistently on a small scale by modifying the methods outlined by Golden(10) and Giovanoli

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TABLE 5A

PUBLISHED XRD DATA ON DELTA-MANGANESE DIOXIDE & BIRNESSITE

SYNTHETIC delta-MnO2		SYNTHETIC delta-MnO2		Mn7 O13.5H2O		SYNTHETIC Na-BIRNESSITE Abridged		MINERAL BIRNESSITE from Birness		MINERAL BIRNESSITE from Todoroki	
(2)		18-803		23-1239		43-1456		Ref:(1) & (2)		(2)	
d	I	d	I	d	I	d	I	d	I	d	I
7.2	8	7.2	80	7.21	100	7.21	100	7.27	s	7.37	37
3.6-3.7	2	4.75	90	3.61	80	3.57	27	3.6	w	4.69	11
2.42	7	2.44	100	2.46	100	2.57	1	2.44	m	3.69	9
2.12	2	2.12	40b	2.33	100	2.52	14	1.41	m	3.32	5
1.62	2	1.67	10b	2.04	80	2.48	2			3.27	4
1.39-1.4	6	1.42	80b	1.72	80	2.43	13			2.45	5
		1.27	1	1.45	20	2.32	2			2.37	7
				1.42	60	2.27	2			2.09	5
				1.39	40	2.22	5				
				1.32	20	2.15	5				
				1.23	20	1.87	3				
				1.21	20	1.82	4				
				1.16	10	1.65	2				
				1.09	10	1.63	2				
				1.02	10	1.53	2				
				0.93	10	1.48	5				
				0.87	10	1.45	3				
				0.82	10	1.44	4				
						1.43	3				
						1.40	1				

TABLE 5B

XRD DATA ON SAMPLES OF SODIUM BIRNESSITE PRODUCED DURING TRIALS

POWDER DATA FILE		Sample NAB20		Sample NAB21		Sample NAB22		Sample NAB23		Sample NAB24	
Ref. 43-1456		Reaction Time		Reaction Time		Reaction Time		Reaction Time		Reaction Time	
Abridged		10 Hours		8 Hours		7 Hours		6 Hours		4 Hours	
d	I	d	I	d	I	d	I	d	I	d	I
7.144	100	7.167	100	7.19	100	7.178	100	7.178	100	7.202	100
3.572	27	3.576	37	3.581	35	3.579	35	3.581	45	3.584	41
2.567	1	2.524	10	2.527	10	2.525	8	2.574	6**	2.527	13
2.519	14	2.494	2*	2.436	11	2.483	2	2.525	17	2.491	6*
2.480	2	2.483	2	2.331	1	2.431	9	2.487	8	2.435	14
2.429	13	2.434	11	2.224	3	2.222	3	2.434	20	2.327	3
2.324	2	2.162	3	2.156	5	2.159	5	2.329	5	2.263	4
2.265	2	2.149	5	1.867	3	1.867	2	2.271	6	2.227	6
2.222	5	1.868	4	1.823	3	1.825	3	2.229	8	2.155	11
2.154	5	1.827	4	1.814	3	1.477	3	2.157	14	1.871	5
1.868	3	1.475	3	1.791	1	1.446	3	1.87	7	1.827	6
1.823	4	1.445	3	1.64	1			1.826	8	1.64	3
1 645	2	1.425	2	1.478	4			1.785	5	1.478	5
[illegible]29	2			1.448	2			1.477	7	1.444	5
1.533	2							1.446	6	1.425	4
1.476	5							1.425	5		
1.447	3							1.402	5		
1.443	4										
1.425	3										
1.397	1										
1.367	1										

POWDER DATA FILE		Sample NAB25		Sample NAB26		Sample NAB21A		Sample NAB21B		Sample NAB21C	
Ref. 43-1456		Reaction Time		Reaction Time		Reaction Time		Reaction Time		Reaction Time	
Abridged		3 Hours		2 Hours		4 Hours		4 Hours		4 Hours	
d	I	d	I	d	I	d	I	d	I	d	I
7.144	100	7.88	8#	10.179	100**	7.146	100	7.170	100	7.134	100
3.572	27	7.19	100	7.19	72	3.571	65	3.574	46	3.565	37
2.567	1	3.587	35	5.092	64**	3.022	2*	2.567	5	2.568	3
2.519	14	2.524	11	3.579	26	2.573	2	2.521	18	2.518	15
2.480	2	2.49	4*	3.388	23**	2.540	2***	2.484	8	2.477	6
2 429	13	2.434	13	2.584	10**	2.520	6	2.431	22	2.427	15
[illegible]24	2	2.229	5	2.525	21	2.480	3	2.324	5	2.220	6
2.265	2	2.156	8	2.487	16	2.431	7	2.261	5	2.156	9
2.222	5	1.874	5	2.435	20	2.380	2***	2.225	7	1.864	6
2.154	5	1.829	5	2.3	14	2.328	2	2.215	6#	1.825	6
1.868	3	1.478	5	2.149	15	2.262	3	2.164	10#	1.781	3
1.823	4	1.426	2	1.842	9**	2.220	3	2.155	12	1.635	3
1.645	2	1.4	3	1.642	6	2.152	6	2.144	10#	1.474	5
1.629	2			1.475	9	1.869	3	1.869	7	1.444	6
1.533	2			1.446	8	1.825	4	1.835	6	1.424	4
1.476	5			1.428	8	1.783	4	1.826	9**		
1.447	3					1.631	3	1.816	8***		
1.443	4					1.475	3	1.642	5		
1.425	3					1.444	3	1.561	2***		
1.397	1					1.425	2	1.477	8		
1.367	1							1.446	6		
								1.425	5		
								1.397	4		
								1.364	4***		

TABLE 5B (continued)

XRD DATA ON SAMPLES OF SODIUM BIRNESSITE PRODUCED DURING TRIALS

POWDER DATA FILE Ref. 43-1456 Abridged		Sample NAB27 O_2 Flow Rate 2.0 L/min		Sample NAB28 O_2 Flow Rate 1.5 L/min		Sample NAB29 Manganese Sulphate		Sample NAB30 Manganese Sulphate		Composite Bulk Sample	
d	I	d	I	d	I	d	I	d	I	d	I
7.144	100	7.122	100	7.167	100	7.167	100	7.132	100	7.146	100
3.572	27	3.565	39	3.57	39	3.57	46	3.564	40	3.571	41
2.567	1	2.517	14	2.523	14	2.523	23	2.516	17	2.520	16
2.519	14	2.475	5	2.434	15	2.431	25	2.481	11	2.430	17
2.480	2	2.427	14	2.327	3	2.225	10	2.426	21	2.225	10
2.429	13	2.325	4	2.225	6	2.154	16	2.333	7	2.210	10****
2.324	2	2.219	6	2.156	8	1.971	4**	2.256	6	2.163	12#
2.265	2	2.148	8	1.867	5	1.947	5	2.221	10	2.148	11
2.222	5	1.861	5	1.824	6	1.867	8	2.172	9#	1.868	10
2.154	5	1.820	5	1.794	3	1.838	9**	2.152	13	1.820	11
1.868	3	1.638	3	1.631	2	1.823	11	2.143	12#	1.475	10
1.823	4	1.475	5	1.478	6	1.639	6	1.865	8	1.445	10
1.645	2	1.443	4	1.446	5	1.533	4	1.821	10	1.425	9
29	2	1.423	3	1.426	4	1.476	9	1.638	5		
1.533	2					1.444	9	1.475	8		
1.476	5					1.425	7	1.442	7		
1.447	3					1.401	6	1.424	7		
1.443	4					1.395	7	1.399	5		
1.425	3					1.369	5	1.367	4		
1.397	1					1.362	5				
1.367	1										

POSSIBLE IMPURITIES

*	Mn_2O_3 or Mn_3O_4
**	Buserite
***	MnO_2 or $MnO_{1.48} \cdot (H_2O)_{.15}$
****	MnO
#	Unidentified

TABLE 5C

THERMAL ANALYTICAL DATA FOR SODIUM BIRNESSITE

PROFILE OF CUMULATIVE LOSS OF WEIGHT AGAINST TEMPERATURE

SAMPLE		TEMPERATURE in deg C							
NUMBER	ONSET	120	200	300	400	500	550	600	625
Mean of Nos 20/25	80 deg	6.5	10.1	10.9	11.3	11.5	12.2	13.3	14.6
Original NAB	75	8.6	9.2	10.3	10.5	10.5	10.5	13.0	13.5
Composite 23.1.97	57	4.9	10.6	12.0	12.5	13.2	14.3	15.5	16.0
Composite 28.5.97	63	5.9	13.0	14.6	15.8	16.5	17.0	18.6	19.4

TABLE 5D

VISCOSITY OF MIXTURES OF SODIUM BIRNESSITE WITH NATURAL ORE (SAMPLE 14)

SAMPLE NUMBER	NAB	30NAB	20NAB	10NAB	10NAB	10NAB	5NAB	14	SAMPLE NUMBER
%NAB	100	30	20	10	10	10	5	0	%NAB
%14	0	70	80	90	90	90	95	100	%14
				(1)	(2)	(3)			
TIME	VISCOSITY IN POISES								TIME
20 mins	40000	4000	2080	872		1392	896	549	20
30		11760	3480	1352	1280	2220	1008	546	30
40			4920	2172	2320	3580	1232	528	40
50			6720	3280	2800	4120	1460	567	50
60			9280	4696	3760	4550	1680	557	60
70			11440	6160	4320	5600	1840	551	70
80			13760	7560	5120	6600	2060	586	80
90				9760	6240	7680	2180	564	90
100				11856	7000	8560	2360	565	100
110				14416	8000	10160	2600	558	110
120					9440	11520	2780	584	120
130					10240	12800	3000	579	130
140					10880		3160	580	140
150					11760		3320	598	150
160							3480	552	160
170							3640	614	170
180							4000	630	180
3h 10								600	3h 10
3h 20								570	3h 20
4h							6400		4h
5h								560	5h
6 days								1480	6 days
1 week								3168	1 week
POT LIFE mins	nil	nil	20	30	30	20	40	>8600	minutes
WORK LIFE mins	nil	30	70	100	150	120	>8600	>9000	minutes
TACK FREE TIME				2days				>9WKS	
CURE TIME								>9WKS	
HARDNESS		40	38	42	42	40	40	nil	HARDNESS

TABLE 5E

POWDER DIFFRACTION DATA FOR CALIBRATION
CURVE FIG. 5 - 16
PERCENTAGE HAUSMANNITE v RAW INTENSITY
OF LINE AT 2-THETA = 32.39 deg.

PERCENTAGE HAUSMANNITE IN MIXTURE WITH Na-BIRNESSITE	RAW INTENSITY OF LINE AT 2-THETA = 32.39deg
0	0
3	9
5	12
10	30
15	37
20	59
100 (not shown on curve)	352

CHAPTER 6

COORDINATION OF RESULTS

The aims of the present research were to find a rationale for the behaviour of manganese dioxide phases as curing agents for polysulphide resins. The need for such a rationale stems from the large variation found in curing properties with the source and preparative history of the manganese dioxides. A series of twenty-eight manganese dioxide samples were characterised in the early stages of the project to determine which of the properties of the material were important indicators of curing activity. A relatively simple standard procedure for assessing comparative curing activity was devised. The critical indicators were found to be pH, alkali metal content, combined water content and crystal phase. All of the good curing agents for polysulphide resins were found to contain varying amounts of hydrated alkali metal based on the delta- manganese dioxide lattice. In particular this early work suggested that synthetic Sodium Birnessite was likely to be particularly active.

A laboratory method was developed from the procedures reported in the literature for the laboratory preparation of Sodium Birnessite avoiding the recommended costly and laborious freeze-drying of the intermediate sodium buserite. The composition of the product was confirmed by X-Ray powder diffraction. The effect of a number of variables on the consistency and quality of the product was examined and a "standard " preparation method was adopted. The scale of production was necessarily small and a large number of batches was produced and combined into a composite sample which was used to characterise the material and to carry out curing tests on polysulphide resin. It was found that curing was extremely rapid and complete.

During the initial work on the twenty-eight samples it had been found that that the curing rate of the good curing agents could be modulated in a controlled fashion by the admixture of pre-determined quantities of the natural ore. This particular ore consists substantially of pyrolusite with small quantities of natural birnessite. This ore is ,by itself, a poor curing agent achieving only an incomplete cure even after over 3 months. The mixtures which produced results comparable with industry definitions of "acceptable" curing properties were those in which the major constituent was the natural ore (85/90% by weight) A similar modulating effect was found when the natural ore was mixed with the composite sample of synthetic sodium birnessite in similar proportions. Although the manufacturers of the polysulphide resin describe the mechanism of the curing reaction as the oxidation of mercaptan terminals to disulphide, complete curing is not obtained even by very pure MnO_2 after three months whereas rapid curing is achieved by MnO_2 in the form of synthetic sodium birnessite containing an alkali metal and hydroxyl ions and possessing high cation exchange capacity . This strongly suggests that satisfactory and complete curing is considerably more complex with an initial oxidation reaction followed by a second stage of polymerisation in which the additional characteristics of synthetic sodium birnessite function.

As part of the early work on the characterisation of the manganese dioxide phases their ability to catalyse the thermal decomposition of potassium chlorate was investigated. A literature search showed a considerable divergence in the reported results on the decomposition of pure potassium chlorate as well as potassium chlorate to which manganese dioxide (and other catalysts) has been added. It was deemed advisable investigate the decomposition of potassium chlorate itself. A frequently occurring anomaly in the heating curve just below the melting point was noted. A hitherto unknown reversible high temperature structural modification of solid Potassium Chlorate was found and its existence confirmed.by Differential Scanning Calorimetry and by high temperature X-Ray Powder Diffraction analysis. Three modifications of potassium chlorate had been reported prior to this work *viz:* a monoclinic room temperature phase; an orthorhombic phase phase which is said to exist from 250° C ; and a rhombohedral high pressure phase. The new phase found in this work has been shown to occur at a temperature of 341° C (between 335 and 345° *C* in High Temperature X-Ray Powder Diffraction experiments ; between 339 and 341° C in Thermographic experiments ; and at 341° C in the Differential Scanning Calorimetric experiment) The cell dimensions of the new phase have been deduced from the X-Ray powder data and its structure is orthorhombic (pseudo-tetragonal) Its density is calculated at 1.76g/ml. at 345° C compared with the density of 2.33g/ml at 20° C for the monoclinic phase and 2.14g/ml at 325° C for the lower temperature orthorhombic phase.

The nature of the thermal decomposition of potassium chlorate in relation to its response to the metal oxides and salts investigated as catalysts for the decomposition appears to be connected to the behaviour of the phases near to the melting point:

orthorhombic phase <<<>>> new phase <<<>>> molten $KClO_3$

Potassium chlorate shows two distinct types of decomposition on heating depending on the nature of the catalyst present. These are:-

type 1 - a rapid often explosive reaction in the solid state below the melting point of potassium chlorate and

type 2 - a slow decomposition in molten potassium chlorate.

It is however significant that the type 2 catalysts can be made to trigger decomposition in the solid state if the system is subjected to isothermal treatment by holding the temperature below the melting point for sufficient time.The rapid decompositions in the solid state occur at temperatures close to the phase transition to the new phase found in this work and there is evidence that some catalysts lower this phase transition temperature. The fact that type 2 catalysts can be made to trigger the decomposition in the solid state under isothermal conditions where the temperature is held at near to the phase transition for sufficient time is also indicative of the importance of this change in the catalytic thermal decomposition.

Although all of the good polysulphide curing agents are of type 2 the reaction with potassium chlorate is not a good indicator of curing ability because some manganese dioxides triggering type 2 decomposition are not good curing agents.

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The catalytic action of pure beta- Manganese dioxide (Pyrolusite) on potassium chlorate was examined in detail. Pyrolusite is not a good curing agent and when present in less than 5.74% by weight it behaves as a type 2 catalyst. Above that minimum it catalyses the reaction violently in the solid state at a temperature at or below that reported for the structural modification. This rapid catalytic action is similarly exhibited by all the other listed manganese dioxide samples with the exception of the natural ore, synthetic Sodium Birnessite, and those of the high alkali manganese dioxide samples which contain sodium ,potassium or lithium birnessite. Similar rapid catalytic behaviour is shown by salts of nickel Copper (I) and (II) Manganese (II) Cobalt (II) Iron (II) & (III) but not with rubidium potassium and sodium chlorides and the oxides of titanium tin vanadium & zinc. Complex reactions were noted when the chlorate was mixed with lithium chloride and lithium hydroxide, vanadium sulphate and chromium (III)oxide.

The work described in this thesis has opened up new areas of research on the catalytic decomposition of potassium chlorate , on its high temperature crystal structure and on polysulphide curing that will be developed by other workers.