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The Monitoring and Control of Specialist Ceramic Kiln Atmospheres and Emissions

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ABSTRACT

The ceramic glazing techniques of vapour glazing, reduction lustre, Raku and fuming all require specialised firing conditions with the use of potentially hazardous kiln atmospheres and specialist kiln designs for their successful execution. The technique of reduction lustre is an ancient, highly decorative technique in which pigments or glazes containing reducible metal oxides such as copper, silver and bismuth are subjected to a reducing atmosphere which results in the formation of stable iridescent lustrous colour effects. Conventionally hydrocarbons are used to produce a reducing atmosphere, the combustion of which can lead to potentially high levels of CO. This research has concentrated on the technique of reduction lustre with the aim of producing a safe, environmentally friendly firing system.

Reduction lustre effects were reproduced using a 100 litre down draft gas kiln designed and constructed for the purpose. A 40 litre electric kiln was modified for use with reducing atmospheres and a laboratory muffle kiln was also adapted to provide closely controlled firing conditions. Alternative reducing atmospheres were assessed, consisting of either 5% H_2 in N_2 or hydrocarbon vapour in N_2 The former is reliable, safe, environmentally friendly and is recommended for studio pottery use. A theoretical design for a reduction lustre kiln incorporating a gas control system based on the use of a 5% H_2 in N_2 gas mixture and a gas tight outer casing was developed.

Thermoanalytical methods were used to investigate the reduction behaviour of raw materials, glazes and frits under different atmospheric conditions. Diffusional and topochemical models of reduction reactions occurring in a typical lustre glaze have been evaluated. In-glaze lustres reduce with thecharacteristics of diffusion processes. Water diffusion out of the glaze may be rate determining. Studies carried out using energy dispersive x-ray analysis and photo electron spectroscopy show that lustres are associated with the presence of metallic copper, the actual colour being dependent on the surface concentration of the metal.

The aesthetic results of the various firing methods developed were assessed using a perceptual study based on the use of a semantic differential test developed from a multiple sorting survey carried out using lustred tiles. The survey used both lustred tiles to represent a 2-dimensional surface and lustred vases which represented a 3-dimensional lustre glazed surface. The survey showed that statistically significant differences were observed between lustred ceramics fired in different systems, allowing comparisons to be made in an objective manner.

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CHAPTER ONE

1 General Introduction, Literature Review, Aims and Research Methodology

1. 1 Introduction

Craft potters exploit a number of esoteric firing methods designed to produce ceramics which are highly individual in nature. Among these techniques are salt firing, reduction lustre, Raku and fuming. All of these techniques have their associated problems. They all require specialised kiln designs and firing atmospheres.

Reduction lustre, vapour glazing, Raku and fuming are techniques almost completely confined to studio or craft potteries. On an industrial scale, those techniques that were once used, have long since been abandoned due to the development of more reliable alternatives, for example resinate (liquid gold) lustres are used in preference to reduction lustres. Gempper et al (1989) describe the wide variety of commercial lustres available and their use in the tile industry. Clean air legislation and changing fashions in public taste have also contributed to this division between the industrially produced product and the work produced by studio potters. Perhaps because the techniques of salt firing, reduction lustre, Raku and fuming are confined to the craft sector, very little scientific research has been devoted to these firing methods. The knowledge that does exist is mainly of an anecdotal nature, acquired through the experience of an individual potter by a process of trial and error. Experiments which are referred to are mainly empirical in nature, once a successful procedure is established no further inquiry is made. This may be due to commercial restraints.

Before improvements to individual firing procedures can be made, an understanding of the process is required. For this reason, a large number of experiments have been carried out which investigate the properties of the glazes and raw materials involved, and the control of kiln atmospheres. Kiln atmospheres are often referred to by ceramicists, as being either 'neutral', meaning the combustion system being used is operating stoichiometrically and complete combustion of the fuel, to carbon dioxide and water, is being achieved, 'oxidising' , meaning an excess of oxygen is present during combustion, or as 'reducing', meaning insufficient oxygen is present for complete combustion of the fuel, in which case, carbon monoxide is present in the kiln atmosphere. The behaviour of glazes and clay bodies under reducing conditions depends on the fuel to air ratio and the type of fuel being used, or on materials introduced into the kiln during the firing, such as salt or fuming agents. This research programme is mainly concerned with the monitoring and control of specific kiln atmospheres designed to produce a particular decorative effect. The results which have been obtained may be of greatest interest to potters working in the craft sector, however the general principles may be equally applicable to industrial processes.

The following sections in this chapter describe the esoteric techniques investigated during this study, their associated problems relating to safety and emissions into the environment.

1.1.1 Esoteric Firing Methods

Esoteric firing methods refer to specialised firing techniques adopted by craft potters. These techniques offer a particular quality or means of expression, that gives a potential for a highly individualised art object. A large degree of participation or control on behalf of the ceramic artist is required when carrying out the firing. The firing techniques which are included in this category are reduction lustre, vapour glazing, Raku and fuming. They all require particular conditions of kiln atmosphere and temperature for their successful execution. Reduction lustre requires a strongly reducing atmosphere in the temperature range between 600°C and 750°C. Vapour glazing may require an oxidising or reducing atmosphere high in alkaline fluxes, for example sodium oxide. Raku requires very localised atmospheric and temperature control during the smoking or fuming stage after the ware has been removed from the kiln.

There are a number of different terms used to describe the various types of lustre, these are defined in the following section.

1.1.1.1 Definition of Terms

Reduced clay paste lustre or reduced pigment lustre. This term applies to all Islamic, Italian and Spanish lustre ware made before 1800. It also applies to the work of William De Morgan, among other nineteenth century ceramicists. The technique involves the preparation of a mixture of copper and silver oxides with clay in a ratio of approximately 3:7 metal to clay. This mixture is ground and applied to a suitable underglaze.

Underglaze. This term refers to the glazes used under reduced clay paste lustres, this may include reduced lustre glaze.

Reduced lustre glaze or in-glaze lustre. This is a glaze in which the reducible metal compounds are incorporated into the glaze batch before it is fired. Silver, copper and bismuth oxides are the main lustre ingredients used. The glazed ware is fired to earthenware temperatures. It is then subjected to a period of reduction, either on the cooling cycle of the glost firing or in a separate third firing.

Resinate lustres. This technique was developed in the eighteenth century and makes use of gold, platinum and bismuth metals. The metals are dissolved into a solution using acids and mixed with fluxes in a resin balsam. Once applied to any glazed ceramic ware they are fired under oxidizing conditions, the burning resinous carrier produces a localised reduction effect. The technique is widely used in industry where it is also referred to as liquid lustre.

1.1.2 Reduction Lustre

Examples of lustred glass exist which date back to the Roman empire. (Frank, 1983). The earliest examples of lustred ceramics make use of a white clay slip applied to the ware under a soft alkaline transparent glaze. The lustre materials were applied as a clay paste onto the fired glaze surface after which, the ware was refired to red heat and then smoked using brush wood.

There are two types of reduction lustre. Clay paste lustre, sometimes referred to as reduced pigment lustre, consists of silver and copper oxides in a clay carrier medium which is often applied to an alkaline glaze, opacified with tin oxide and fired to red heat (approximately 600°C to 700°C) whereupon it is subjected to a strongly reducing atmosphere. The silver and copper oxides are reduced to their metal form and combine with the glaze surface to form a finely divided metallic film bound to the surface of the glaze. Figure 1.1 shows two examples of clay past lustre by William De Morgan, figure 1.2 shows an example of a contemporary piece of clay paste lustre. The other type of reduction lustre was developed in the 17th century and involves the incorporation of reducible metal oxides into the glaze (figure 1.3). These oxides include silver, copper and bismuth. The firing procedure is similar to that used for clay paste lustres except a shorter reduction time is required. Reduced clay paste lustres may require between 20 and 60 minutes of reduction, lustre glazes may require between 10 and 20. The precise conditions required for the reduction of the lustre depend on the temperature, the reducing gases used, the glaze or pigment recipe and the particle sizes of the materials used. The melting behaviour of glazes is affected by the particle sizes of the constituent ingredients and whether or not the glaze has been fritted (pre-fired and ground to a fine powder). The reducing behaviour of clay paste lustres is affected by the degree of grinding the clay paste receives during preparation, or whether it is calcined (fired to 700°C to remove molecular bound water and other combustible matter, such as carbon). All of these factors are addressed in detail in later sections.

Figure 1.1 Two examples of clay paste reduction lustre by William De Morgan. (Victoria and Albert Museum collection)

Figure 1.2 An example of a clay paste lustre used over a transparent glaze (#6, table 2.1). A black engobe has been used under the glaze. The clay paste was applied by brush and the bowl was fired in the down draft gas kiln described in section 5.2.1.

Figure 1.3 In-glazed lustre dish made by Margery Clinton.

Commercial lustres of the type used in industry today first appeared around 1780, following the discovery of platinum in 1750. The technique requires dissolving gold and platinum using a mixture of hydrochloric acid and nitric acid in the ratio 3:1 (sometimes referred to as Aqua Regia (John and Baker, 1951). The discovery of the technique of using dissolved precious metals is ascribed to John Hancock of Hanley, Stoke-on-Trent. John and Baker quotes a recipe for the manufacture of this type of lustre which became known as liquid gold, or resinate lustre. The recipes are those of Thomas Larkin and were published by his widow in 1824. Modern liquid resonate lustre preparations are still basically the same, except a much greater range of colours is now available owing to the inclusion of bismuth and other colouring oxides (Guller ,1987; Chornewy, 1986).

Liquid lustres can be fired onto ware under oxidizing conditions. This is an important consideration when white ware is being produced (Brahmbhatt, 1990). Gold and platinum are not tarnished by acids or alkalis and do not re-oxidise. For these reasons development of resonate lustres led to the decline of reduction lustre as an industrial process.

Resinate lustres have a different appearance from reduction lustres and as such, a different aesthetic appeal which is why they are still regarded as a technique worth pursuing by ceramic artists. The main difference is in the degree of iridescence produced by the different techniques. The reduction process tends to produce fine films of lustre over the glazed surface which produce a large degree of iridescence. Resinate lustres are highly lustrous but tend to be more like an opaque metal coating. The iridescence of the clay paste reduced lustres is a consequence of the semi transparency of the lustre layer. The cost of the precious metals makes resinate lustres very much more expensive than reduced lustres. However a direct comparison is not valid since the aesthetic result is qualitatively different. This topic is discussed further in chapters seven and eight.

Gilding is sometimes confused with fired lustre techniques. Gilding makes use of gold leaf or powdered gold metal which is applied to the surface of ceramics by either adhesives or fired on using sodium silicate under oxidising conditions (Caiger-Smith, 1985). An historical review of the technique is given by Hunt (1979). Table 1.1 gives a brief historical summary of lustre processes.

Table 1.1: A Brief History of the Lustre Process.

Century	Place and Technique
Late 9th Early 10th c. 840 - 920 A.D.	Mesopotamia (Sumarra & Baghdad) clear lead alkaline glaze with all over copper/silver lustre.
10th -11th	Egypt (Fostat, Ciro) coarse clay, relatively roughly made.
10th - 11th	Mesopotamia, tin used to opacify the glaze, poly-chrome decoration with silver/copper lustre.
11th - 12th	Hispano Moresque (Valencia, Maiolica) coppery lustres with heraldic designs.
c. 1020 -1170 12th - 14th	Italy (Deruta, Gubbio) golden and ruby red colours with designs from Renaissance painting.
c. 1556- 1559	Piccolpasso:- The Three Books of the Potters Art.
18th	Platinum was discovered, dissolved gold and platinum lustres were developed in English Potteries and bismuth was also used to obtain a wide variety of colours.
Late 19th &	William De Morgan (Chelsea, Fulham) and William Burton (Stoke on Trent) carried out many experiments into lustre.
Early 20th Late 20th	Reduction lustre largely confined to studio potters except for Royal Doulton Rouge Flambé (Ruby Red lustre) otherwise resinate lustres are used.

1.1.3 Vapour Glazing

Vapour glazing, or salt firing is a stoneware glazing technique which involves introducing sodium into the kiln chamber, usually in the form of sodium chloride (common salt). The salt decomposes and volatilizes. The sodium component combines with the alumina and silica, present in the clay bodies and glaze materials, to produce a sodium-alumina silicate glaze. This glaze has a unity formula of:

$$1.0\ Na_2O : 0.5 - 1.0\ Al_2O_3 : 2.8 - 5.5\ SiO_2$$

The chlorine component of the salt combines with water vapour, given off during the combustion of the fuel, to produce gaseous hydrogen chloride, a toxic gas. See section 1.4.3 for details of exposure limits.

The technique of vapour glazing was first used in the Rhineland. The Rhenish stoneware consisted largely of wine bottles known as bellarmines, beer mugs and storage jars. The use of stoneware was developed in this area in the 12th to 14th centuries and salt glazing was part of this development (Hamer and Hamer, 1986). In Britain this type of ware was produced in the 17th century, most notably by John Dwight of Fulham. At the end of the 19th century, the Martin Brothers of Salford used the technique to produce a range of art wares. However on an industrial scale it was mainly used to glaze sewer pipes.

Traditionally vapour glazing was a 'once fire' process, this was one of its main advantages as a glazing process. Contemporary potters tend not to once fire since they are using the technique for its decorative surface qualities rather than economy. Colouring oxides, cobalt, copper, iron and manganese for example, clay slips and glazes are often applied at the bisque stage to form variegated, decorative surfaces (Troy, 1977; Starkey, 1978; Mansfield, 1991).

1.1.3.1 Vapour Glazing Firing Methods

Preparation for firing ware in a vapour kiln involves placing the ware on pads of alumina and china clay mixed, with plain flour as a temporary binder, this mixture is known as 'wadding'. The wadding prevents the ware from becoming glazed to the kiln furniture during the firing. The kiln furniture is also given a coat of alumina to prevent it becoming glazed together. The inside of hollow ware has to be given a conventional glaze since the salt vapour cannot reach these areas. The salt kiln is fired as for a normal stoneware firing, up to a temperature above 1200°C at which point, the salt is introduced into the fire box, this being the hottest part of the kiln. The chimney damper is normally partially closed at this stage in the firing to slow the gases and keep them in the chamber for as long as possible. The progress of the firing is monitored using draw trials taken from the hot chamber. Pyrometric cones are used to give an indication of the progress of the firing but are not reliable guides since they are affected by the sodium atmosphere and bend prematurely. Clay bodies which have an alumina to silica ratio of 1:5 or higher, are considered most suitable for salt glaze (Hamer and Hamer, 1986).

1.1.4 Raku

Raku is a low temperature firing technique in which pots, made from a coarse refractory clay, are put into and taken out of, a hot kiln using tongs. When the pots are withdrawn from the kiln they are put into sawdust or straw. This produces strongly reducing conditions which turn exposed areas of clay black with carbon. Because of the rapid cooling as the pots are taken from the hot kiln, the glazes craze. The carbon stains the cracks formed by the crazing and produces the characteristic Raku appearance. Copper, silver and lithium are often used on the surface of the ware to produce lustrous finishes. These lustres tend to re-oxidise unless they are successfully trapped in the glaze lattice. Because of the need to handle the ware while it is at red heat the technique is normally carried out out-of-doors. The fumes from the burning sawdust can be excessive. It was this aspect of the technique which was originally considered as a problem which could be eliminated by examining the kiln design, so that the reduction could be carried out inside the kiln rather than in a separate container. Firing Raku is a very interactive process in which the potter has to make rapid judgements while handling the red hot pots from the kiln. Decisions as to whether or not to cover the pot with sawdust, or whether to spray water on to areas of the glaze to produce oxidised patches, are all judgements which have to be made by the potter. Although it might be possible to design a kiln capable of containing the fumes from the burning sawdust material, this would inevitably result in less immediate control of the final result. So long as firings are undertaken out-of-doors, the degree of hazard is very low. A respirator gas mask can be worn while transferring pots to the sawdust container. Taking these considerations into account further research was not undertaken into this process.

1.1.5 Fuming

The fuming process involves the use of metallic chlorides and nitrates, which react with heated glaze surfaces, to produce an iridescent sheen. The technique can be used in fuel burning or electric kilns and on any glaze surfaces. Stanous chloride, ferric chloride, silver nitrate, zinc chloride, titanium chloride, vanadium tetrachloride and strontium nitrate have been used for this process.

The fuming procedure is carried out at the end of glost firing as the kiln is cooling down, between 600°C and 700°C . If the fuming agent is introduced at too high a temperature it volatilises too quickly. If the temperature is too low, the chlorides form a scum-like surface rather than an iridescent surface. A scummy appearance can also be caused by excessive fuming. The fumes have a detrimental effect on electric kiln elements. The vapour from the chlorides and nitrides are toxic.

The fuming procedure is carried out in the following manner; the materials are introduced directly into the firing chamber through the spy hole or into the flame path via burner ports, using a pre-heated spoon attached to a length of metal tubing. The damper is left open to create a draft. Traditionally, the potter would blow down the tube to disperse the vapour through the kiln. This practice is clearly hazardous and should not be attempted. The use of a hair drier for this purpose has been suggested as a way of creating the necessary current of air (Acero, 1975). Fuming is often seen as an extension of the Raku process (Byers, 1990). When used as part of the Raku technique, ware is placed in a container while at a temperature of approximately 700°C and then sprayed with an aqueous solution containing the fuming agents. This procedure is carried out out-of-doors and a respirator mask should be worn. The technique is not used on an industrial scale and is restricted to very few craft potters. The technique can also be applied as part of the reduction lustre technique. In this case the fuming agents are introduced into the chamber, after the reduction is complete, while the kiln is still at red heat. Watkin (1922), investigated the degree to which different glaze compositions would become lustrous when exposed to various fuming agents. The fuming agents used by Watkin were first used by Weiskoft (date not known)(Jahresbericht and Stohman Kerl's Dictionary), the mixture used by Weiskoft consisted of barium carbonate 1 part, strontium carbonate 0.5 parts, stanous chloride 2 parts. This mixture when placed in a muffle kiln at red heat produced mother-of-pearl effects when coming into contact with the ware, strontium giving a red colour, barium blue and stannous chloride a variety of colours. Watkin used a muffle kiln held at a temperature of 700°C and the following fuming mixture for his investigation:

Barium nitrate	2 parts
Strontium nitrate	1 part
Stanous chloride	3 parts
Bismuth nitrate	0.5 parts
Sulphur	1 part

Watkin states that glazes having an oxygen component ratio of approximately 3:1, medium or low acid content, a $B_2O_3 : SiO_2$ ratio of approximately 1:2.5 and which were high in lead and low in calcia, produced the best vapour lustre effects, based on an arbitrary scale which ranged from ‘poor’ to ‘excellent’.

Kilns used to carry out the fuming technique are permanently contaminated, as the fuming materials are absorbed into the kiln lining. As a result of this consideration, the technique was not included as part of the research carried out to investigate lustres.

1.2 Problems Identified

The problems tackled during this research project fall into several categories. There are technical problems, requiring a technical solution, such as finding a suitable alternative to a hazardous kiln atmosphere. There are design problems which may be evident at the start of the project, or which may emerge as new possibilities are presented when technical problems are solved. The approaches to tackling these problems are somewhat similar. The process of concern is reduced to its basic principles, after which new solutions can be tried and tested.

The purposes of the various firing techniques referred to in this study are to enhance the appearance of ceramics, including both functional and non-functional ceramics. Ceramic designers and makers should be able to use the techniques to enrich their work. Any improvements to safety, or reduction in harmful emissions to the environment, must also not cause any detrimental effects to the aesthetic qualities being striven for, rather, technical and design improvements should work to extend the existing limits of the technique.

Although the techniques of vapour glazing, reduction lustre, fuming and Raku are confined largely to the craft sector of ceramics, it should not be concluded that the problems encountered are of a trivial nature. Many livelihoods depend on the success of such techniques in addition to the fact that many individual practitioners are at risk, individuals who are not covered by health and safety legislation.

1.2.1 Problems Associated With Reduction Lustre Glazing

The success of reduction lustre relies on the ability to maintain a particular temperature for as long as necessary, while controlling the degree of reduction. Some clay paste lustres require that a temperature of 665°C, plus or minus ten degrees, be maintained for as long as an hour while a strongly reducing atmosphere is present within the kiln. This requires a high level of skill, on behalf of the potter, or a sophisticated control system capable of monitoring and controlling temperature and atmosphere simultaneously.

Temperature control is most easily achieved using an electric kiln, and in this case, a hydrocarbon gas, usually methane (north sea gas), or propane is used as the reducing agent. Both gases are potentially explosive in admixture with air. The normal procedure when adopting this technique is to use an inert gas, such as nitrogen, to purge the kiln of oxygen before the combustible gases are introduced into the kiln chamber (Clinton, 1991). Potters familiar with their own kiln and firing method may operate a potentially unsafe system without mishap. A similar system used by someone less competent may be less fortunate. If kiln atmosphere monitoring equipment is not being used, oxygen may still be present in the kiln if the purge has been incomplete. Gases can escape from the kiln if it is not gas tight, as is the case with most craft kilns. Gases leaving the kiln are normally flared off at the top of the kiln and a pilot light is used to ensure the flame does not go out. However, this pilot light can also be a source of ignition for other gases escaping from leaks in the kiln (other than from the gas out-let hole beneath the pilot light). William de Morgan in his lecture to the Society of Arts, in 1892, refers to a delay in developing the technique, brought about by setting fire to the roof of his workshop. Further to the possible danger of explosion, reduction atmospheres can produce large quantities of carbon monoxide, which is a toxic gas.

1.2.2 The Problems of Vapour Glazing

Perhaps the most serious problem associated with vapour glaze firing using salt as the glazing medium is the toxic nature of the emissions from the kiln (Stanbridge, 1991). The other consequence of using salt as the glazing medium is the alkaline atmosphere created within the kiln chamber. The alkaline fluxes react with the kiln refractories and cause them to deform and eventually fail.

All ceramic kilns give off noxious fumes to some degree. Typical pollutants include dust, soot, sulphur dioxide, sulphur trioxide, nitric oxide, hydrogen fluoride, carbon monoxide, hydrogen chloride and traces of heavy metals from the glaze materials. Fortunately the concentrations of these emissions in craft kilns does not require preventative measures to be taken other than good ventilation (Schlandt, 1986)

In addition to the problems surrounding the toxic nature of the emissions from a salt kiln, there are major problems associated with the destruction of the kiln lining refractories, caused by the fluxing of the alumina silicates in the bricks by the alkalis in the kiln atmosphere. A conventional salt kiln, built from heavy duty fire bricks may require substantial maintenance after twenty to thirty firings. Some kilns are on the point of collapse after as little a fifty firings. Figure 1.4 shows a catenary arch, oil fired salt kiln built from heavy duty fire bricks. The kiln is in a state of collapse. The precise number of firings achieved varies according to how heavily the kiln is salted and how well the kiln was built originally. The kiln furniture is also affected and generally lasts for a smaller number of firings. Kordurite-type shelves are usually unusable after ten firings. Silicon carbide shelves can be used, however these have two substantial drawbacks; they have a tendency to crack when used in salt kilns and salt glaze accumulates in droplets on the surface which can drop on to the ware during the firing. Figure 1.5 is a photograph of the inside of a kiln built from a high alumina insulating refractory brick (MPK 135 Hepworth Refractories PLC), the brick work has been badly effected and has lost much of its insulation value (Malins, 1992).

Salt kilns are generally built from heavy duty high density fire bricks, which become glazed after several firings. The build-up of salt glaze and traces of colouring oxides, which re-volatilise during subsequent firings, help to produce a rich variegated, ceramic glaze. This aesthetic consideration may over-ride attempts to find a refractory material capable of resisting the effects of the alkali attack. Attempts have been made to find viable alternatives to heavy-duty fire bricks as a lining material. Brodie (1982) describes the use

Figure 1.4 Conventional catenary arch salt kiln. The interior brick work has been badly affected by alkaline attack.

Figure 1.5 Conventional fire bricks showing damage due to alkaline attack.

of a ceramic fibre product called Safil, manufactured by ICI. Safil is 90% alumina and 10% silica. When used as a roof lining material by Michael Casson, in his gas fired 40 cu ft salt kiln at his pottery near Ross on Wye. (Casson Pers. Comm.) Casson found that the material became powdery and disintegrated after only three firings. Low density refractories have open porous or fibrous structures which trap air and slow down thermal energy transfer. The open structure provides a large surface area for the alkalis to come into contact with the silica in the refractories. As a result, these type of structures are badly affected by the salting process. Alumina is relatively unaffected by alkalis, but most refractories contain silica which forms a eutectic mixture with alumina and sodium. A eutectic mixture is one in which two or more substances when mixed together in a particular ratio, will melt at the lowest temperature possible for the given components, and lower than any of the individual melting points of the separate materials. As a result even refractories containing 90% alumina soon become glazed and start to loose their thermal efficiency. Zirconia has also been suggested as a possible alternative (Detric Limited and Hepworths Limited, Pers. Comm.). Zirconia fibre products have been developed with working temperatures of over 1700°C. However these products are currently priced at over £3000 per square metre. In this form zirconia fibre products are unlikely to provide a cost effective alternative to heavy duty fire brick. Zirconia used as a kiln wash has to be used in combination with silica and alumina. This is because of the high thermal expansion of zirconia which tends to spall from surfaces when not combined with other materials. Murray and Myers (1988), Casson (Pers. Comm.) and Hendricks and Piltcher (1977) suggest the use of high alumina castable cements. The method of construction of the kiln described by Murray and Myers involves casting sections of wall or arch, to a thickness of approximately 50 mm. The former is covered with plastic sheeting so that a smooth surface is formed on the cast sections, thus reducing the surface area, on which the alkalis can impinge, to a minimum. Conventional ceramic fibre blanket up to 225 mm provides insulation. Brodie recommends that pre-cast shapes are cured in a conventional kiln before assembly, this is to pre-shrink the sections and helps to avoid cracking.

1.3 Literature Review

This thesis covers a very broad range of subject areas, from the history of reduction lustre to the control of furnace atmospheres. In some subject areas of interest to industry, there is an abundance of material, in others however, very few relevant studies have been carried out.

In the search for relevant material, two main approaches were adopted. Ceramic text books and specific books covering the subject were consulted and their bibliographies investigated. Contemporary practitioners of the reduction lustre technique were visited and interviewed. The practitioners visited included John Calderwood of Glasgow School of Art, Margery Clinton, Haddington Pottery near Edinburgh and Alan Caiger-Smith at Aldermaston Pottery, Berkshire. The second approach was to use computer based searches using the science citation index and an art index stored on optical disk. Remote data bases via computer links were also searched. World Ceramic abstracts were consulted in this manner.

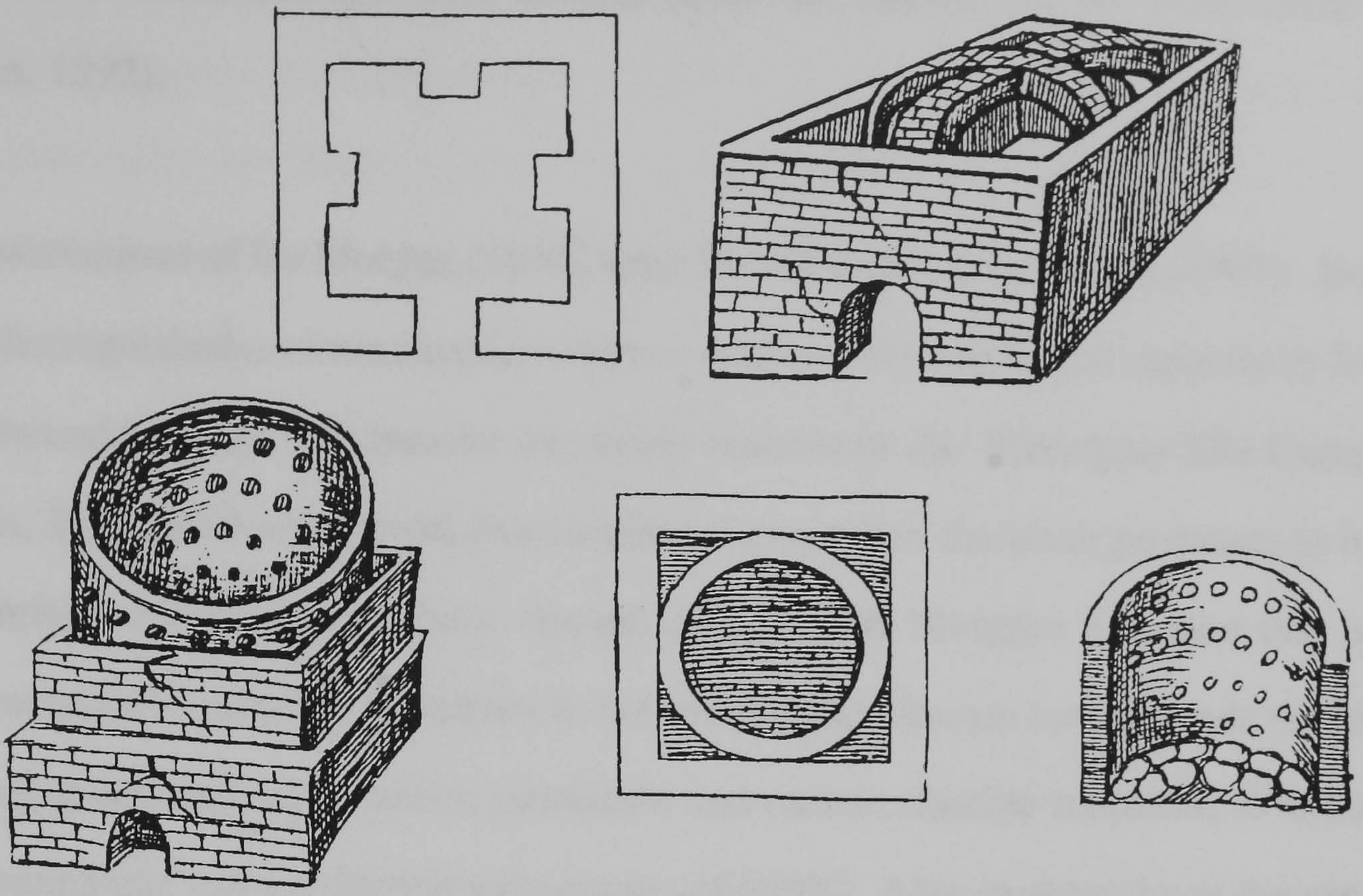
1.3.1 Lustres, Historical and Contemporary Methods

The technique of reduction lustre is thought to have originated around the ninth century, centering around Baghdad (Caiger-Smith, 1985;, John and Baker, 1951; Davis, 1954; Clinton, 1991). Over the centuries, the technique has had periods of high demand and excellence in technical quality. For example, the 15th century Italian potters of Deruta and Gubbio (Rackham and Van de Put, 1934,; Mallet, 1979) who were particularly renowned for their ruby lustres. Also the lustre wares of Spain around the same period, often referred to as Hispano Moresque ware, were also considered to be of particular merit (Randell, 1956; Van de Put, 1909; Lane, 1946; Caiger-Smith, 1985).

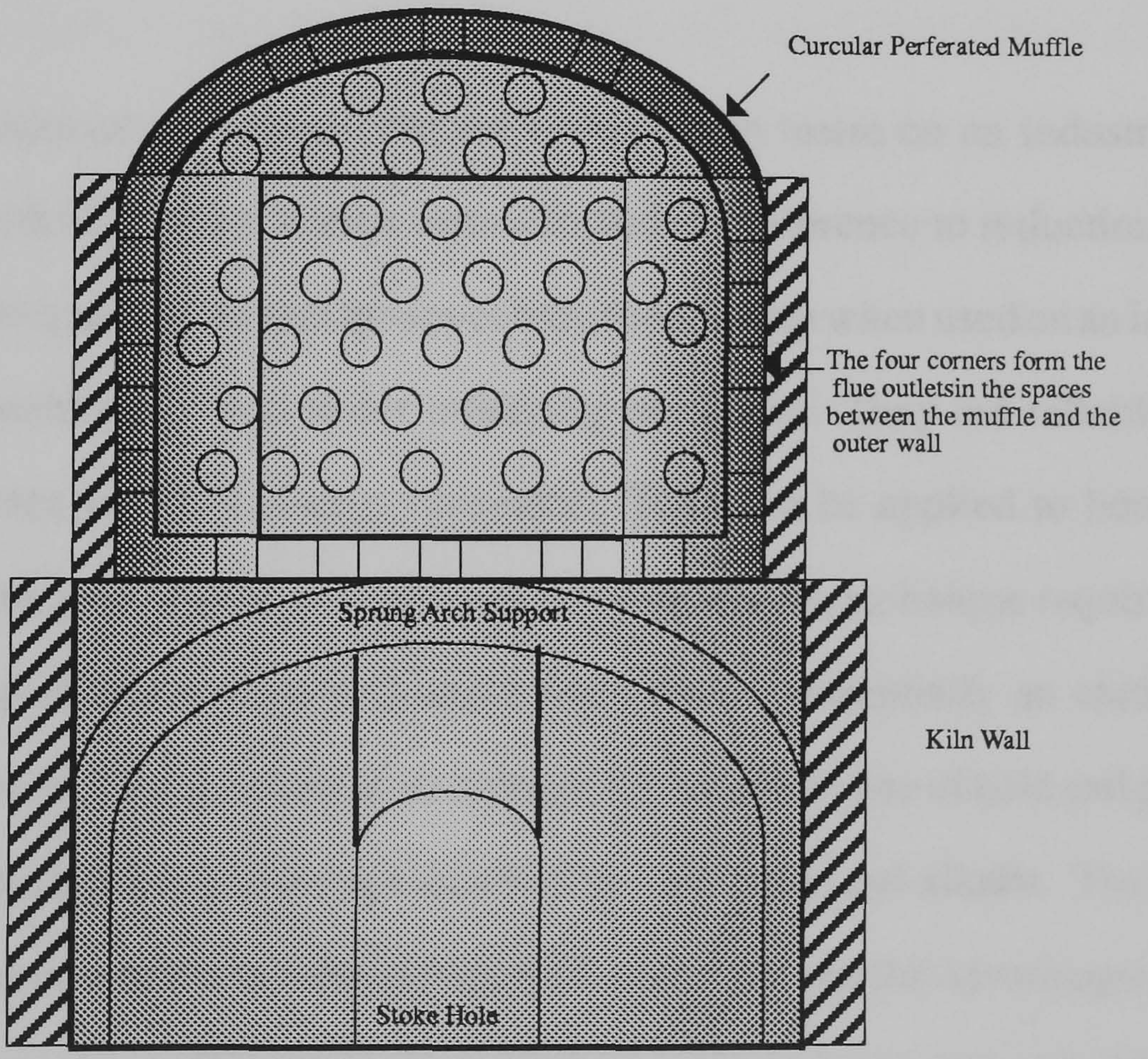
Following a gradual decline of the Spanish lustre ware around the end of the sixteenth century, the technique appears to have almost disappeared from the potters repertoire until its revival by the English potter William De Morgan, (1892) who claimed to have rediscovered the technique in 1874.

Historical documentation of reduction lustre is fragmentary. One of the earliest descriptions of the technique is given by the Persian potter and court historian Abu'l Qasim in his "Treatise on Ceramics", written in 1301 (Alan, 1973). Quasim lists all the materials needed for the manufacture of glazed, coloured decorated vessels, including lustre and describes their preparation and interactive effects .

A more detailed account of the lustre process has been given by Rackham and Van de Put (1934) in a translation of Cavaliere Cipriano Piccolpasso's second volume of his "Three Books of the Potters Art" . Piccolpasso was in fact a military architect from Castel Durantee whose brother was a potter of that town. The description given by Piccolpasso includes drawings of the kiln used in the process (figure 1.6). The account given by Piccolpasso was referred to by William De Morgan in a lecture given to the Society of Arts in 1892 and again, fifteen years later by William Burton in another lecture to the same society. De Morgan presented the following conclusions based on his personal experience. On the subject of reducing agents, De Morgan reports using carbonaceous smoke (not specified), ammonia, steam in contact with reducing fuel (not specified), coal gas, water vapour and glycerine, and spirit (not specified). He observed "no new results". On the subject of using chlorides, ammonium chlorides, or iodides vapours of copper and silver, combined with the use of a resist (not specified), De Morgan suggests these experiments "might be repeated with advantage". In a similar experiment, De Morgan suggests painting a pattern using a susceptible glaze on top of a refractory glaze and then exposing the ceramics to a vapour containing copper or silver. De Morgan generally used a coal fired muffle kiln and wood as the reducing agent. The coal itself would not have been a suitable reductant because of its sulphur content. De Morgan reports using a variety



Drawings originally made by Piccolpasso of a medieval lustre Kiln



Drawings made by Piccolpasso of a medieval lustre kiln

Figure 1.6 Medieval lustre kiln

of different woods and saw-dust without observing changes in the fired results (De Morgan, 1892).

The observations of De Morgan (1892) were later confirmed by Burton (1907). Burton was a distinguished ceramic chemist who was employed in a technical capacity by Josiah Wedgewood Limited. He became managing director of the Pilkington Tile Company (Burton, 1992).Burton confirms Pioccolpasso's account of the lustre processes as being substantially an accurate account. Burton confirms De Morgans assertion that using different woods makes no difference to the fired results. Burton recommends the use of reducing gases such as a carbon monoxide and carbon dioxide mixtures, or ordinary illuminating gas and a reduction temperature of 650°C. Also suggested was the use of a "muffle constructed of iron with tapped pipes passing into and out of the kiln to allow for the slow passage of a current of the particular gas to be used."

Shortly after the turn of the century the use of reduction lustre on an industrial scale declined, the effects of resinate lustres were adopted in preference to reduction effects. Resinate lustres have several advantages over reduction lustres when used on an industrial scale. Resinate lustres are fired under oxidising conditions. They are reliable in that lustrous surfaces are virtually always successful. They can be applied to bone china, porcelain or earthenware. Reduction lustre is often an elusive technique requiring very precise conditions of temperature and atmosphere and is essentially an earthenware technique. A further advantage of resinate types of lustre is in the use of gold and platinum metals. They do not oxidise and are not attacked by most acids and alkalis. The obvious disadvantage of the cost of the metals was not sufficient to off-set the advantages for their industrial use. From the craft potters' point of view, resinate lustre and reduction lustre are not comparable. The two techniques are aesthetically different.

There is one exception to the use of a reduced copper earthenware glaze on a industrial scale. Royal Doulton's 'Rouge Flambé' range consists of a reduced copper red earthenware. The company has been careful not to publish details of any research which has been undertaken into the technique. It is known however that following difficulties experienced after the change from coal gas to north sea gas, propane was found to be a reliable alternative.

The most comprehensive study of reduction lustre among contemporary literature is Alan Caiger-Smith's book on lustre pottery. (Caiger-Smith, 1985). The book gives a historical account and details Caiger-Smiths own methods of reproducing reduction lustre. The final chapter of Caiger-Smiths book consists of a series of questions and answers dealing with aspects of the technique. The answers have been provided by Frank Hamer[1]. Caiger-Smith makes use of a wood fired kiln, using wood smoke as the reducing agent. Caiger-Smith's lustred ceramics are all of the clay paste type.

Several articles written by contemporary ceramic artist potters appear in the literature, (Peascod, 1981; Taylor, 1983; Caiger-Smith, 1984; Clinton, 1987). These articles are generally anecdotal in nature. Glaze and pigment recipes are given and Taylor includes drawings of his downdraft wood kiln. Peascod details efforts to develop a stoneware glaze that will be receptive to clay paste lustre. His reduction temperature is 640°C. Peascod also mentions the use of carbon monoxide gas but states that this was prohibitively expensive and that best results were obtained from LPG (Liquid Propane Gas). Clinton refers to the use of an electric kiln using natural gas as the reducing agent and nitrogen to purge the kiln of oxygen . In a more recent publication by Clinton (1991), a fuller description of this kiln is given. Clinton refers to the possible use of an oxygen probe as a way of monitoring kiln atmospheres, as well as timing the purging stage using nitrogen before allowing natural gas into the kiln chamber. The natural gas is ignited by a pilot light as it leaves the kiln at the top of the chamber.

In a paper published in the Journal of the American Ceramics Society (Burnham and Harder, 1944), details are given of experiments carried out in a down draft gas fired, semi muffle kiln. Two types of lustre are identified, termed "superficial" and "hard" lustre.

The superficial lustre is of the resinate type and the hard lustre is in-glaze reduced lustre as defined in section 1.2.1. The paper reports on the relative importance of the following factors: strength of colorant dispersion and stability, method and thickness of application, glaze composition, firing rate, kiln atmosphere and temperature, control over transparency, wear and acid resistance. The authors state that the best results were obtained when reduction temperature coincided with the softening point of the glaze. Reduction effects were obtained over a wide range of temperatures provided re-oxidation was prevented. Volatalisation effects were an important factor in colour development, and led to variations in the results. A control was used in the form of a conventionally glazed sample, containing no reducible metal oxides, the control sample was placed in the kiln adjacent to the lustre glazed ware. The control sample became lustred by the volatile oxides present in the kiln atmosphere during the reduction process. The authors also suggest the use of colouring oxides and commercial stains to extend the colour range of the technique. Their conclusion stated that: "exact duplication of lustre colours would be possible if a specially designed kiln were constructed or if the problem of re-oxidation could be minimised by the introduction of carbon dioxide gas at the conclusion of the reduction period".

Five tested in-glaze recipes were given, fired and subjected to the following acid resistance tests:

4% acetic acid at room temperature, immersed for 24 hours.
3% hydrochloric acid solution at room temperature, immersed for 5 hours.
1% sodium carbonate at boiling temperature, immersed for 30 minutes.

No changes in the quality of the lustre or in the texture of the glaze were observed. The glaze formulas are reproduced as Appendix I. These experiments were not repeated in the studies reported here, but other chemical resistance tests were undertaken and are referred to in Chapter Eight.

Both in-glaze and clay paste lustres are described by Davis (1954). For clay paste pigment lustres, the author recommended ground flour tiles (equivalent to calcined red clay) passed through a 60 mesh lawn. Copper and silver salts were ground and added to form an aqueous solution the consistency of paint. Improvements of this mixture were not achieved. The use of a tunnel kiln for commercial production of reduced lustre using coal gas as fuel and reducing agent was also referred to. A variety of reducing agents; wood, resin, coal gas, calor gas (assumed to be propane or butane) and acetylene gas were used. Davis reported that the use of coal gas vapour could lead to blackish results if ware became over-reduced, but all reductants tried produced similar results.

A paper by Wakamasu *et al.* (1985), describes the influence of kiln atmosphere on the colour of copper glaze under constant glaze composition and firing schedules. Samples were heated in a tube furnace at the rate of 4°C per minute up to a temperature of 1300°C. This temperature was maintained for 20 minutes, the sample was then cooled at 5°C per minute. Details of various controlled atmospheres used with both oxidising and reducing conditions are given. The "controlled atmospheres were generally introduced when the kiln temperatures were above 1000°C."

For examination and analysis of lustre techniques including Energy Dispersive X-ray (EDX) analysis, were used. The use of lustre glazing whilst producing a range of colours, requires the supply and accurate mixing of a number of gases, adding to the complexity and overall cost. In addition, the high temperatures used requires the maintenance of a controlled atmosphere, down to the point where the glaze has hardened, to prevent changes in the lustre on cooling.

Wakamatsu *et al.* (1986 and 1989) demonstrated by the use of EDX that (1) the dominant copper species in the red glaze (R_O) was Cu_2O and an isolated Cu^+ and (2), metallic copper was almost undetectable in the glaze. Tichane (1985) found that the red colour was not Cu_2O but metallic copper. Coloured particles visible in red glazes were caused by the aggregation of metallic copper. Reflectance spectroscopy has been used to demonstrate the presence of certain elements in glazes, for example Wakamatsu *et al.* (1989) used the technique to identify the presence of copper oxide in reduction stoneware copper glazes. The use of this technique for the examination of lustre glazes was found to be unsuccessful due to the highly reflective nature of the glaze surfaces.

Warterberg (1984), describes a new process for developing a lustrous surface layer on ceramics. A glazed ceramic substrate is coated with a specially adapted chemical vapour deposition (CVD) process. The process involves the deposition and formation of a thin layer on the surface of the substrate as a result of chemical reactions occurring in the gas phase. The volatile reaction compound is vaporised and is thermolytically deposited onto the surface of the heated substrate, precipitating a thin coating. The process may be thermolytically or hydrolytically induced. Metallic halides, carbonyls and hydrides are used as the volatile compounds. Some of the compounds decompose through thermolysis alone and others require one or more reaction partners, for example hydrogen. Water is also required for hydrolytic reactions. The CVD process requires a gas generator, a gas handling system and a reaction chamber in which the substrate is placed for coating. The process makes use of the Leidenfrost phenomenon. The substrate is heated to 600°C and submersed in an inert, low-boiling point organic liquid which is held at its boiling point. A uniform gas envelope forms around the substrate and is sustained by the emission of radiant heat from the substrate. The gradual cooling of the substrate causes the heat transmission coefficient to drop to the point at which the surrounding insulating gas envelope breaks down. At that point the film-boiling phenomenon (Leidenfrost phenomenon) changes into nucleate boiling, the substrate cools to the boiling point of the liquid. A solid volatile reactive substance is added to the volatile inert liquid which comprises the gas envelope. The soluble substance and the inert liquid act together as a common gas envelope around the hot substrate. The resulting chemical reaction forms a thin adherent coating on the surface of the substrate. Butyl alcohol may be used as the inert liquid and iron pentacarbonyl used to form the metallic coating. When heat is selectively applied to the surface a coloured pattern can be made to form caused by light refraction. Wartenberg describes the decorative effects which can be produced with this technique and details the apparatus required. The method has not yet been exploited on a commercial basis. The process may be likened to the fuming process except it is carried out under very controlled conditions.

1.3.2 Kiln Monitoring and Control Systems

The requirements and instruments necessary for temperature control of ceramic kilns has been reviewed by Soames (1986). Emphasis was made on the need for multiple heating and cooling ramps, and set-points in the range 20-1350°C. In addition, soak periods and programme storage requirements are discussed. The author also describes future developments in instrument design "As equipment becomes more sophisticated, the need for simplicity of operation is increasingly important. Ideally a 'no-handbook' design is required, so that the operator very easily understands the instrument operation and becomes confident in using it. This requires more information in the form of visual displays, to be presented on the instrument front panel." The author then goes on to say, "The need for interfacing to small personal computers is also becoming apparent, so that some remote monitoring or control can be carried out. With such a system, a printed record of each firing can be obtained."

The advantages of process control using personal computers has been recognised by Graham (1989), who stated that, "process control, like most computer application areas, has been migrating to the use of personal computers... in many cases providing more effective control at less cost." The author describes the use of a Macintosh II computer with Labview software to control a small scale distillation plant for laboratory studies; "The use of a microcomputer as opposed to conventional PID (Proportional Integrated Differential) controllers, allows the inputs and outputs to be semi-permanently wired to the Computer, and virtually all of the necessary revisions can be made through programming changes." The author further states, "The software programming power also allows for more complex algorithms than can be achieved with conventional PID controllers."

Clarke and Pellerin (1988) describe the conversion of electrically heated curing ovens to Microcomputer control. Various designs of computer screen information are given, for example combination group, the computer monitor displays the measured temperatures from the two different thermocouples in each oven. Software enhancement of the display system providing actual time-temperature profiles of oven curing cycles are also described and comparisons made with desired profiles in the recipes.

1.3.3 Pollution Control and Safety Hazards

During the use of ceramic kilns noxious fumes may often be emitted, particularly with the use of salt kilns which produce hydrogen chloride in significant quantities. This gas is an environmental concern. A review from the American Conference of Governmental Industrial Hygienists (1985), agreed on a 'ceiling limit' for the concentration of hydrochloric acid fumes in long-term exposure of humans. A maximum concentration of 5 ppm was set as the limit, based on a number of reports published throughout the fifties, sixties and seventies, most of which reported concentrations between 4 and 5 ppm to be immediately irritating to the respiratory tract, e.g. (Elkins, 1959; Patty, 1963; Fairhall, 1957; Smyth, 1956). Some authors reported much higher concentrations, greater than 34 ppm, which caused similar effects in both animals and humans (Michle and Associates, 1942; Henderson, 1943).

Brodie (1982), suggests a safe level of exposure to hydrogen chloride for the average adult to be 5 ppm. People suffering from respiratory ailments may be affected at lower levels. Some of the toxic effects have been reported to include irritation of the skin, eyes, throat and mucous membranes. Measurements of gaseous chlorine emissions were made by Brodie in the vicinity of a salt kiln. No chlorine gas was detected. Concentrations of hydrogen chloride of 20 ppm were detected 30.5 cm above the kiln door and salt ports while the kiln was being salted. A white mist was visible. The kiln was located out of doors where ventilation was good.

Hendricks and Piltcher (1977) estimate the effluents produced by a 0.85 m^3 (30 cu ft) salt kiln in the final two hours of firing, to consist of: 27.3 kg water vapour, 38.2 kg carbon dioxide, 207.3 kg nitrogen, 0.5 kg sodium compounds, 6.1 kg chlorine in the form of hydrochloric acid and other chlorine compounds. With the exception of the sodium and chlorine compounds, these emissions were calculated to be equivalent, in terms of fuel combustion, to the effluents produced by a car running at 70 mph for one hour or a 707 aeroplane at cruising speed for three seconds. By using sodium carbonate as a glazing agent, the chlorine compounds can be eliminated from the effluents. Using this comparison the authors express the opinion that this kiln should not be regarded as a significant source of air pollution.

The most recent legislation which refers specifically to vapour glazing is the 1990 Environmental Protection Act which came into force on 1st April 1991 (Tromans, 1991). The implications of the act were reviewed by Stanbridge (1991). The Act describes a wide range of processes for which specific authorisation, from either HM inspector of Pollution or from the local authority, will be required. The aim of the act is to reduce the number of processes which could be described as causing environmental pollution. This will be achieved by setting strict conditions which will have to be complied with in order to gain authorisation. Previously the responsibility for taking action against sources of pollution has rested with the Local Environmental Health Officer. The onus of responsibility has now shifted to the operator who is now required to apply for permission prior to use of equipment. Failure to obtain the necessary authorisation, or operating in breach of one of the conditions laid down, will be an offence which carries a possible fine of £20,000. Within the act, there is a section referring to "ceramic production" which specifically mentions "vapour glazing of earthenware or clay with salts". For the craft potter two difficulties arise. The application forms will require detailed figures concerning heat outputs, firing frequency and an analysis of the flue gases emitted from the kiln. This information may have to be collated by an independent professional, which is liable to be a costly exercise and may have to be repeated on an annual basis. Secondly, a fee will be charged on receipt of an application. This fee could be between £800 and £1,800 per kiln. In addition an annual fee will be charged to maintain authorisation. This fee may be between £400 and £800.

The Environmental Protection Agency will have the authority to identify certain emissions of flue gases as "trivial" within the meaning of the act. This is not precisely defined although the phrase " capacity to do harm is insignificant" is also used. The aim of the act is clearly not to out law the activities of small scale craft potters using salt glazing. However the legislation does put in serious doubt the future viability of vapour glazing on a commercial scale.

The pollution hazard caused by the use of sodium chloride as a glazing agent is clear. There are two strategies for avoiding this hazard. Scrubbing the flue gases is one approach. Murray and Myers (1988) describe the use of a wet scrubbing device (figure 1.7). The salt kiln's chimney could be closed by fitting a hinged kiln shelf at the top. This deflected the gases into a stainless steel washing tower which had a swivel jet spray fitted to the top. The diverted gases were sprayed with water. Scrubbing was only carried out during the salting period, the deflector remained open for the rest of the firing. The acidic run-off water was collected in a stainless steel container, the contents of which were neutralised by running over limestone chippings. The other alternative to scrubbing the flue gases was to use the carbonate forms of various alkaline metals, for example, sodium carbonate, sodium bicarbonate, potassium carbonate and lithium carbonate. The resulting emissions from using these materials was carbon dioxide and water. The main difficulty with using these alternative materials was the uneven distribution of vapours through the kiln and the subsequent variable quality in the fired glazes. This was due to

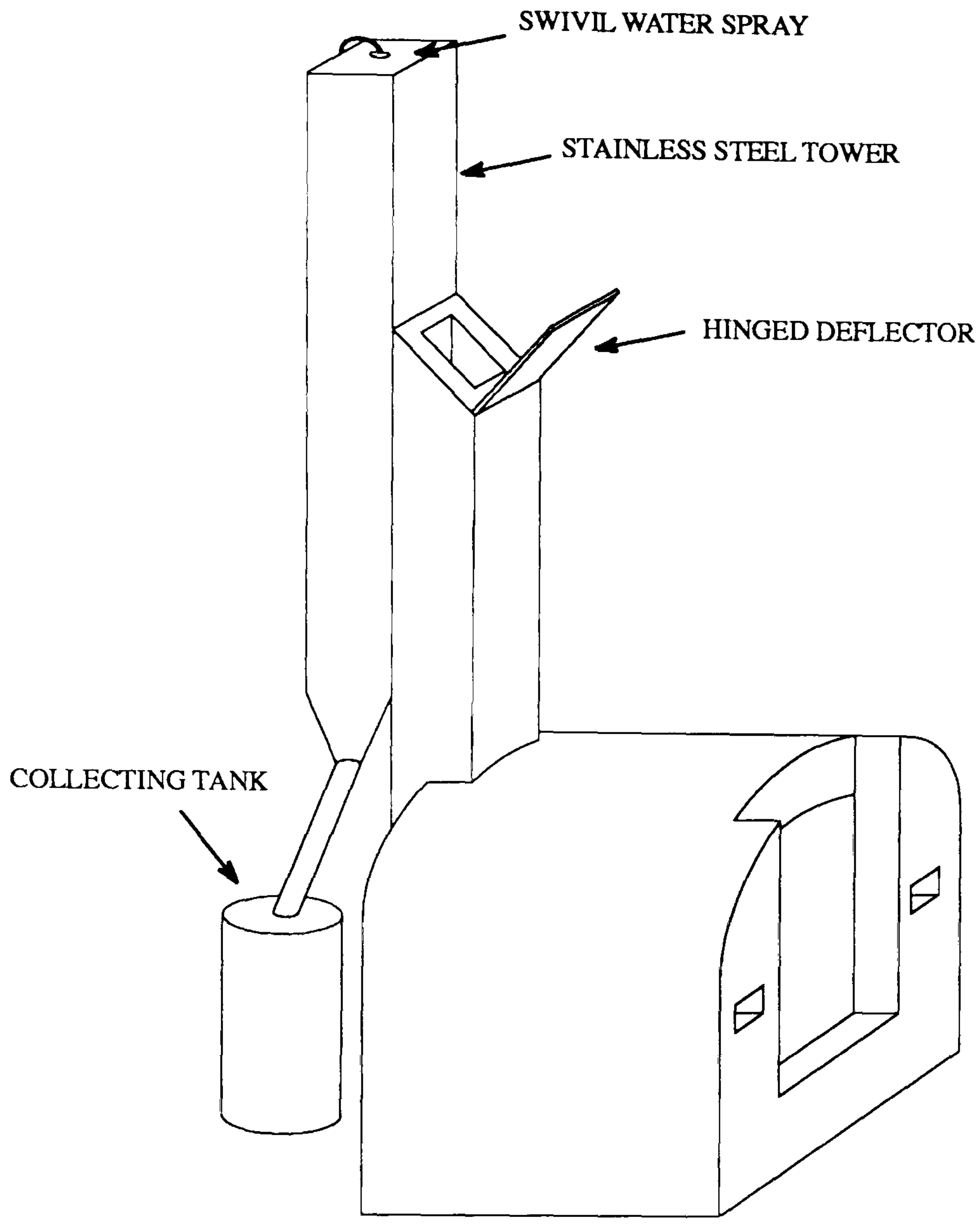


Figure 1.7. Diagram of simple chimney scrubbing device. (adapted from Murray and Myers 1988)

the higher melting point and lower vapour pressure of the carbonate materials. A number of ceramic artists have experimented with alternative salting mixtures.

Whatever salting mixtures are used the effect on the kiln refractories is equally destructive. For this reason the majority of salt kilns are constructed from heavy duty fire bricks. Some kiln designs incorporate a layer of ceramic fibre blanket as secondary insulation (Keeler, Pers. Comm.). The ceramic fibre blanket is laid over the outside of the kiln, well away from direct contact with the kiln atmosphere. Malins (1992) describes the construction of a small soda vapour kiln constructed from low thermal mass fire bricks. The kiln described was thermally more efficient than a conventional heavy duty fire brick kiln. Used as a conventional down draft gas kiln, the kiln described could reach 1280°C in less than three hours if required. However as a salt kiln it was less successful. The bricks used deteriorated rapidly in use and as the pores of the bricks became filled with salt glaze their thermal efficiency was reduced. All the bricks in the vicinity of the salt ports suffered considerable decay (figure 1.5). Brickwork which has been in direct contact with molten salt suffered the greatest damage. Areas of the kiln which have just been exposed to the high alkaline atmosphere suffered less deterioration. The kiln described by Malins was originally to be salted by placing the salt in the kiln, at the commencement of the firing, in small pots. In practice this did not produce satisfactory results because the resulting glaze coating was insufficient. If more than a very light sheen of glaze was desired the packing space needed for pots containing salt would take up most of the available space in the kiln. The kiln was modified so that small packets of salt could be introduced into the fire boxes during the firing through holes in the sides of the kiln.

1.3.4 Special Atmospheres, Safety and Kiln Design

There are many heat treatment processes which require the use of a furnace atmosphere that excludes oxygen. Stratton (1992), describes the potential hazards associated with the use of furnace atmospheres in terms of explosion risk, toxic effects and danger of asphyxiation together with the relevant safety standards.

Shimizu *et al*. (1988) describe the use of an experimental gas kiln designed to evaluate the combustion characteristics of a natural gas pre-mixing burner. The pre-mixing burner produced a more uniform temperature throughout the kiln than low speed diffusion type burners. The average nitrogen dioxide emission from the combustion process was reduced by supplying sub-stoichiometric quantities of primary air to the burner while keeping the total air flow rate constant. The H_2 : CO ratio under reducing conditions was found to depend on temperature as well as the air ratio. The kiln atmosphere was monitored using ceramic samples glazed with a glaze containing copper, colour changes in the glaze indicated whether or not zones within the kiln had been in reduction or oxidation.

Brahmbhatt (1990), describes the principle behind the use of oxygen to enrich combustion gases in a tunnel kiln. Increased oxygen levels were found to lead to greater productivity since the retention time necessary to complete oxidation reactions was reduced and greater fuel efficiency was achieved.

United Kingdom patent G.B. 2 052 030 A, describes the design of a furnace for use with special atmospheres. The walls are constructed from gas permeable refractory and the casing is gas tight. The furnace makes use of a heavy gas to maintain a higher pressure in the insulating cavity thereby retaining the gas in the firing chamber.

1.4 Aims and Research Methodology

The investigations detailed in this thesis encompassed a wide range of analytical techniques. The aim, throughout this research programme, has been to apply the knowledge gained to the design of specialist ceramic kilns. The kiln designs arrived at were intended to be safe to operate, produce a minimum impact on the environment, whilst being capable of producing high quality ceramics. The investigations involved studies of glazes and their raw materials, kiln design and firing atmospheres. The use of perceptual studies designed to assess the aesthetic qualities of the fired results are also described. While the central focus of the research has been intense, the broad range of subject areas covered during the research has meant that some areas could not be investigated in great depth and a number of the firing techniques originally proposed as being worthy of investigation had to be left for future research efforts. The problems which have been identified are mainly of concern to craft potters. This consideration has dictated the scale, complexity and cost of design solutions.

The individual techniques of vapour glazing, Raku, fuming and reduction lustre presented a number of problems worthy of investigation, however time and resources meant it was necessary to concentrate the research effort on one technique only, the results from which would offer the greatest potential for improved practice. A review of the various firing processes was made with the aim of highlighting the research potential of each method. After consideration of the Raku process, it was determined that improvements that could be made to firing procedures and kiln design may conflict with the interactive nature of the technique, for example decision making during the post-firing reduction stage. With this in mind, it was decided that further research into the Raku technique would not be undertaken. The technique of fuming required the design of a specialist kiln dedicated to fuming experiments, however it was likely that the fuming agents would permanently contaminate the kiln used, therefore invalidating other results from other specialist firing techniques attempted such as reduction lustre. Preliminary studies were carried out into the technique of vapour glazing. During the course of the preliminary studies, legislation was introduced to control emissions from salt kilns (Stanbridge, 1991). In the light of this legislation and the need to focus research efforts, vapour glazing was not investigated beyond preliminary studies.

The technique of reduction lustre presents particular difficulties in its execution and can present safety hazards. Through the application of a research programme, these hazards could be overcome. The new methodologies developed during the studies could also have implications for a wide range of ceramic firing techniques, such as the use of reduction atmospheres over a broad range of temperatures. Reduction lustre was therefore the principle focus of the research programme reported in this thesis.

1.4.1 Research Aims

Reduction lustre is recognised as a technique which requires close control of both kiln temperature and atmosphere. Modern technology such as micro-processors and solid state gas probes make it possible to monitor and control complex firing systems at low cost.

There have been many types of kiln used for firing reduction lustre, including wood, coal, gas and electrically fired kilns. (Burton, 1907; de Morgan, 1892; Caiger-Smith, 1985; Taylor, 1983; Peascod, 1981; Clinton, 1991). Both gas fired and electric kilns have been used during this research. Electric kilns lend themselves to computer based control systems. The greater the degree of control the ceramicists has over a firing system, the more versatile the technique becomes. Electric reduction firing has control advantages over other firing systems but as with other reduction kilns, carbon monoxide may be produced and if a hydrocarbon, such as propane, is being used as the reductant there is a possible risk of explosion (Stratton, 1992)

The aims of this project were to investigate the reduction lustre process using chemically, physically and aesthetically evaluated analytical methods, with the aim of designing kilns capable of reproducing reduction lustres in a safe, controllable manner. This involves investigating viable alternative reduction atmospheres, monitoring and controlling the kiln atmosphere and producing lustre effects comparable with existing methods.

1.4.2 Research Methodology

Before research into alternative reduction firing systems could begin, it was necessary to reproduce lustre effects comparable with other contemporary practitioners. Researching acceptable reduction lustre glazes and pigments is an essential prerequisite to improved lustre kiln design. The methodologies adopted can be divided into three areas; glaze research, kiln design research and aesthetic evaluation.

1.4.2.1 Glaze Research Methodology

As a starting point for an investigation into lustre glazes, recipes were obtained from contemporary potters. The glaze recipes could not be used directly however because many of the recipes contained proportions of commercial glazes of unknown formulation. Glazes to some extent are also matched to the clay body being used and the working methods of the potter. For these reasons the glaze recipes obtained were re-formulated so that standard raw materials could be used. A computer glaze calculation programme was used for this purpose (Bryant, 1990). The computer programme allows rapid conversion of recipe to glaze molecular formula and visa versa, making it possible to adjust silica : alumina ratios without altering the range of fluxes present in the glaze. Both successful and unsuccessful glaze results were examined using electron microanalytical techniques. Thermal analysis was used to determine the reduction behaviour of the raw materials used as well as lustre glazes and pigments. Thermogravimetrey was also used to investigate alternative kiln atmospheres. In a further series of experiments using a lustre glaze prepared as a frit a topochemical model of the reduction behaviour of a lustre glaze was explored. Electron microscopy was used to study the glazes in cross-section. Surface concentration of elements were studied by energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS). The results obtained were used to formulate a speculative model of the reduction mechanism occurring within a lustre glaze during its reduction.

In order to carry out specific experiments into the effects of different kiln atmospheres and reduction temperatures, a single in-glaze lustre was chosen as an indicator which displayed a wide range of colour changes under differing reduction conditions.

1.4.2.2 Kiln Research Methodology

Existing lustre kiln designs were examined and contemporary practitioners were visited and interviewed. These included Alan Caiger-Smith of Aldermaston Pottery, Margery Clinton of Haddington Pottery and John Calderwood of Glasgow school of Art, who are recognised practitioners in the field of reduction lustre.

A down draft gas fired test kiln was designed and constructed so that reduction lustre glazes could be fired under a variety of reducing conditions.

For greater control and reproducibility a commercial electric kiln was purchased and extensively modified as a reduction lustre test kiln. Various degrees of manual and automated control were used and instrumentation was calibrated.

New refractory materials were evaluated and methods for investigating design problems were established.

For greater control over kiln atmosphere and temperature, a laboratory muffle kiln was adapted for firing reduction lustres. This kiln allowed the methodical firing of glazed samples under different atmospheric conditions and temperatures.

1.4.2.3 Aesthetic Evaluation Methodology

An important part of this research programme has been the assessment of the aesthetic qualities of the results obtained from the use of new firing systems. A perceptual study was undertaken using a psychological test based on a semantic differential survey (Anastasi, 1988).

The semantic categories were established following a preliminary survey using tiles in a multiple sorting task (Canter *et al.*, 1985). Two surveys were undertaken using the semantic differential test. The first was also a preliminary study using lustred tiles and the second survey made use of lustre glazed vase forms. The results obtained were subjected to statistical analysis to establish whether or not differences recorded were statistically significant.

CHAPTER TWO

2 Lustre Glazes and Clay Paste Pigment Formulation, Test Shape Design and Methods of Application.

2.1 Introduction

The following chapter describes the development of lustre glazes and clay paste lustre pigments, their preparation and the rationale behind the design of suitable substrate test shapes. Methods of application of glazes and pigments onto test samples using screen printing technology and the effect of varying application thickness are described.

2.1.1 Aims of Experiments Described in Chapter Two

The aims of the investigations described in this chapter were therefore:

- To obtain a set of glazes which were compatible with the clay paste recipes and vice versa.

- To obtain a set of in-glaze lustres.

- To design a suitable substrate test shape for evaluating lustre glaze effects.

- To establish suitable methods for the application of lustre glazes and clay paste lustres, and to assess the effects of application thickness on lustre development.

2.1.2 Development of Underglazes

For the development of Clay paste lustres, specific glazes designed to be suitable for use under lustre clay paste pigments must be developed. Although it was stated by both Franchet (1906) and Burton (1907) that any glaze could be used under a clay paste lustre pigment i.e; "it is only necessary to know the softening point of the glaze and then reduce the pigments at that temperature" (Burton, 1907), Caiger-Smith (1985), states that; "this may be correct in theory, but in practice it is hard to put into effect. Even determining the ideal softening point of a glaze may not be straight forward." Certain types of glazes are much more susceptible to forming a lustre than others; for example, under-glazes with a high alkali content (Peascod, 1981). Also important is the matching of the softening point of a glaze to the temperature at which reduction takes place (Burnham and Harder, 1944). This is particularly true for clay paste lustres which have a much narrower temperature range than lustre glazes.

Under-glazes high in alkaline oxides are preferable for use with reduced clay paste lustres. They are generally responsive to lustre metals and unlike high lead glazes, are not susceptible to greying. Alkaline glazes have low softening points, which is a further advantage since the finely divided silver and copper metals are particularly volatile at elevated temperatures. Therefore at lower temperatures less metal is lost. When a lustre is fired too high above its softening point, the metal is said to migrate onto areas adjacent to the applied design. On designs of a more abstract nature this effect may be aesthetically pleasing but if it occurs on more defined patens it can obscure the design. Figure 2.1 shows a series of clay paste lustre tiles which illustrate this point. The tiles have been screen printed with a copper red clay paste pigment and reduction fired over a range of temperatures. The finely divided copper particles have become increasingly mobile as the reducing temperature was increased.

In this study, lustre glazes, under glazes, clay pastes and firing temperatures were tested

Figure 2.1 Screen printed tiles by Margery Clinton. The tiles were fired at differing temperatures. As the temperature increased more of the design is obscured by copper vapour.

in order to arrive at a set of compatible under-glazes and clay pastes and appropriate firing regimes. Once these were established, a standard representative glaze, a clay paste lustre and an in-glaze lustre could be used for carrying out further investigations.

2.1.3 Silk Screen Printing

Screen printing of ceramics involves mixing finely powdered glaze into a medium to form a smooth homogeneous paste which is pressed by a squeegee through the open areas of a fine, stainless steel or polyester mesh stretched on a frame. Designs are formed by selectively blocking the mesh to form a mask. The mask is produced by a photographic process in which the mesh is coated with a photosensitive emulsion and then dried. A transparent positive, which has opaque black areas making up the design, is brought into close contact with the screen prior to exposing the screen to an ultraviolet light source which desolubilises the emulsion. After exposure, the screen is immediately washed in warm water to fix the reaction, allowing the unexposed emulsion to be washed out of the screen, leaving the design in the filaments of the mesh weave.

During printing, the substrate is positioned below the screen and as the screen and substrate come into contact, the paste adheres to the latter in a precise pattern corresponding to the open areas of the design in the screen. The thickness of the coating is dependent on the density of the paste, diameter of the mesh filament, thickness of the emulsion, the distance of the screen from the surface of the substrate, known as the "snap off" distance, and the pressure on the squeegee.

When using screen printing to prepare ceramic transfers, the medium in which the glaze material is dispersed can be either oil, wax or water based. On preparing ceramic transfers, the design is printed onto transfer paper using an oil based medium. After it has dried a water-proof 'cover coat', encapsulating the glaze materials, is printed over the design. When dry, the transfer is floated off the paper backing by immersing it in cold water. The transfer, which consists of the cover coat and the glaze materials is then applied to the ceramic object using a soft, flexible rubber squeegee to flatten it onto the substrate, and to remove air pockets and surplus water. Water based printing mediums are used when prints are made directly onto the substrate. When wax is used as the printing medium, the screen is heated to control the fluidity of the "inks". Industrially, this can be done by passing a small current through the screen itself if a steel mesh is being used, or by infrared radiators positioned above the screen.

The establishment of suitable methods for the application of lustre glazes and clay paste lustres, and the effects of application thickness on lustre development, were carried out using screen printing techniques. Both direct (onto glazed substrate) and indirect (onto transfer paper) screen printing techniques were used for both lustre clay paste pigments and lustre glazes.

The effects of screen mesh size and emulsion thickness were investigated with a view to the possible use of application thickness in the control of the degree of iridescence observed in the fired lustre. In the process of preparing suitable images for printing, computer graphic systems were used.

2.1.3.1 Use of Computers for Graphic Manipulation In the Production of Screen Printed Patterns

In order to evaluate the success of the various lustre glazes and pigments developed during this research project, computer generated graphic designs were used.
The hardware used was an Apple Macintosh IIci computer, Apple digital image scanner and Apple laser printer. The software used included the following Apple Macintosh compatible application programmes: Aldus Free-Hand™, Apple Scan™, Adobi Streamliner™, Adobe Illustrator™.

The starting point for producing a design for use as a screen printed motif can be an original drawing or part of an existing design. The design may be poly-chrome or black and white. If a poly-chrome design is being used as the starting point then the scanner attached to the computer must be capable of scanning colours. The selected image is placed on the scanner window and scanned into the computer. The computer digitises the image and stores it as a 'TIFF' or 'PICT' file (TIFF and PICT are alternative document formats used by a number of graphic and page layout programmes). At this stage parts of the image can be selected out and a limited amount of alteration is possible, however the scale of the image is not altered at this stage. The TIFF or PICT can be electronically traced by the computer using a programme such as Adobe Streamliner™. This procedure is referred to as "anti-aliasing" and eliminates the jagged appearance of curved lines. The file is automatically saved as an Encapsulated Post Script (EPS) file. The EPS file can then be imported into a graphic design application programme such as Aldus Free-Hand™ or Adobe Illustrator™. Once the image has been imported into the graphics programme, it can then be altered in a number of ways. The image can be re-scaled to fit a predetermined shape, for example an oblong design can be re-sized to fit a square shape of precise dimensions. By duplicating the design a repeat pattern can be created. Strips of pattern can be made to follow a "path", such as a circle to form a circular pattern which might become a design for the border of a plate. When the design is complete it is printed out using a laser, or ink-jet printer. If the image is a multi-coloured design, the software can be set to print colour separations. The black and white print-outs are then exposed onto photographic film (Photo Mechanical Transfer, PMT), forming a negative. The PMT is then exposed onto a suitably prepared silk screen which has been coated with a light sensitive photographic emulsion.

2.1.4 Design of Substrate Test Shapes for the Evaluation of Lustre Glazes

The melting behaviour of a glaze is dependent to some extent on the underlying contours of the substrate e.g. convex or concave, vertical or horizontal surfaces. On a horizontal surface, a glaze can flow out to produce a flat layer, on a vertical surface the glaze will tend to flow downwards, producing variations in glaze thickness. The amount of flow which takes place depends on the viscosity of the glaze at its maturing temperature. The unit of viscosity is the 'poise', a 'stiff' glaze with high viscosity may have a rating in the order of 100000 poise, while a 'runny' glaze of low viscosity might have a rating in the order of 1000 poise. The maturing point of a glaze can be defined as the smoothing out of the glaze after the bubblings of the melting reactions (Hamer and Hamer, 1986). Concave and convex surfaces influence the degree of compression or tension at this point.

The shape of the underlying ceramic substrate can have a considerable influence on the optical properties of the fired glaze. It can also affect the way in which heat is dissipated from the substrate surface during firing, which in turn affects the melting behaviour of the glaze and subsequent reduction response. Because reduction effects depend upon the glazes and pigments which come into contact with a reducing gas during firing, the substrate shape has a direct effect on the way the gas impinges on the surface. Two test shapes were designed to take these specific considerations into account. A circular test shape containing a concave, convex, horizontal and vertical surface was produced by slip casting and an extruded sample test shape was also used.

2.2 Materials and Methods

2.2.1 Preparation of Glazes and Pigments.

All the glazes used in the various investigations of this study were prepared in the same manner, the recipes used are listed in tables 2.1, 2.2 and 2.3 (see pp 49-51).

During preparation, glaze constituents were weighed out to amounts specified in individual recipes, water was then added and the glaze mixed. The mixture was then sieved twice through a 100 mesh lawn to achieve a homogeneous state. For the preparation of glazes, mixed, dry glaze constituents were made up to 515 g per litre. For the preparation of clay paste lustre pigments, required ingredients were weighed out, oven dried at 100°C and re-weighed after cooling. The dried mixture was then put into a lidded container and shaken. After shaking, the mixture was transferred to a ceramic crucible and placed in an electric kiln and fired to 700°C with vents open so that the substances were calcined under oxidising conditions. Water was then added (1 litre per 100 g of calcined powder) and the mix ground in a porcelain ball mill for approximately five hours, before being wet sieved through a 100 mesh lawn. If other ingredients, such as dilute (4% v/v) or concentrated acetic acid, or a water-based brush medium were being used, then the material was evaporated to dryness and the resulting dry powder added to the medium to achieve a required consistency for whatever application method (e.g. brush, spray or screen) was being used.

Glazes being prepared for screen printing were dried and calcined to 700°C and then dry sieved through a 100 mesh lawn. The dry glaze powder was then added to the screen printing medium, and mixed to the required working consistency.

2.2.1.1 Ball Milling of Clay Paste Pigments

A one or two litre capacity ball mill (Ratcliffe R.51), with a fixed rotational speed, was used to grind clay paste ingredients. Batches of clay paste lustre pigment were made up to one litre in volume. The mill jar was filled with grinding media to just over half its volume to give the following proportions:

Grinding Media	55 - 60 %
Charge (clay paste material)	20 - 22 %
Water	11 - 18 %

After grinding for at least one hour, the charge was recovered by sieving and washing the grinding media with a fine water spray. The charge could then be dehydrated in an oven to the desired consistency. The procedure followed was based on the recommendations given by Cardew (1975) and Taylor and Bull (1986).

2.2.2 Under-Glazes for Use with Clay Paste Lustres

Under-glazes were tested for their suitability for use under clay paste lustres. The under-glazes tested were designed to mature in the temperature range of 1040 to 1080°C (Orton cone 05 to 03). The softening point of the glaze was more critical since this determined the temperature at which reduction of the clay paste pigments occurred. The softening point of glazes was determined by the use of a gradient kiln.

In order to develop under-glazes for use in investigations, recipes published by established potters working with lustres were tested. These included the following:

Alkaline white tin glaze (1060°C with 1 hour soak) (Fiddis, 1977). This glaze has a poor colour response and crazes badly due to the high alkaline content.

Lead bisilicate tin glaze (Calderwood, 1990). This glaze has a particularly low softening point (<600°C). The high lead content produces a very shiny surface and a good colour response, although the high lead content makes this glaze unsuitable for use on domestic ware. The glaze lustres well but has a tendency to grey under reduction and because of its very low softening point, can easily be over-fired causing the clay paste to adhere to the surface.

Opaque white L16 glaze (1060°C with 1 hour soak) (Clinton, 1991). This glaze is made up from commercial glazes:

Blythe (20306G)	100 parts
Tin Oxide	9 parts
Blythe Alkaline Frit (2012G)	6.5 parts
Blythe (low solubility frit) (21065)	22 parts
Bentonite	2 parts

Clinton's glaze was adapted into a conventional recipe using the molecular formula of the above glaze ingredients (provided by Blythe Colours Limited, Stoke-on-Trent). A glaze recipe was derived which could be made up from standard glaze materials. The resulting glaze was designated as #1, made up from the Seger Molecular formula (SMF) (Table 2.1). This recipe, which had an alumina to silica ratio of 1:8, was modified several times. Initially, bentonite was added to the glaze as a suspension agent. However the high levels of alkaline frit in the glaze meant it had a tendency to flocculate. This tendency was much reduced if bentonite was not used. This recipe was also used as a transparent glaze by simply omitting the tin oxide (#6, table 2.1).

Glazes were applied by dipping. The glazes were fired in a standard earthenware firing to 1060°C and given a one hour soak. Firing the glaze so that it was properly matured was found to be essential if a good lustre was to be obtained. This point is referred to again in chapter four following scanning electron microscopy studies.

Once standard glaze recipes had been established, the glost firing regime was standardised and all the glazes used as part of this research programme were fired in an identical fashion using a computer programmeable kiln.

2.2.2.1 Determination of Glaze Softening-Points Using a Gradient Kiln.

A gradient kiln is constructed such that a temperature gradient is established from the front to the back of the kiln on firing. The temperature of the gradient can range from around 600 °C to 1300°C.

For the determination of glaze softening-points, a test strip made from the substrate was prepared. The strip was glazed and glost fired in a conventional kiln after which, clay paste pigment was applied and the strip fired again in the gradient kiln. After firing, the clay paste was washed off the cooled strip. The softening-point of the glaze was determined from an area of the test strip where the applied clay paste was not washed off and was shown to adhere to the under-glaze. This point of the strip corresponds with a temperature just above that of the softening-point of the glaze.

The upper temperature at which clay paste lustres can be used appears to depend on the volatility of the lustre metals. (Peascod, 1981; Caiger-Smith, 1985)). This upper limit is around 750°C. The lower limit is dependent upon the softening point of the glaze. For glazes based on a soft alkaline frit, this may be as low as 600°C. The optimum softening temperature for a lustre under-glaze is between 660°C and 700°C.

2.2.2.2 Preparation of Silk Screens for Printing Glazes and Clay Paste Pigments

For screens intended for use with glazes, an emulsion called Capillex 80™ (Sericol Limited) was used to apply the design onto the screen. The Capillex emulsion can be obtained over a range of thicknesses. Material of required thickness was cut from an appropriate roll and applied to the down side of a clean, wet, degreased printing screen. On application, the Capillex sticks to the screen and is covered by a protective layer of transparent acetate. The screen was then left for 24 hours to dry before exposure to ultra violet light.

Table 2.1 Underglaze Recipes For Use With Clay Pastes

All the recipes given are fired to 1060°C (Orton Cone 04), requiring a one hour soak period

	ACS *	CF *	JC**	LBW†	#1(L16)	#2(L16-2)	#3(L17)	#4(L18)	#5(L19)	#6(L21-O)	#7(L21-T)
Material				**Percentage of Ingredients**							
Lead Bisilicate	61.00		78.00	27.00	6.33	7.06	8.00	8.00	8.00	7.37	7.37
T Frit					18.80			24.00	22.00		
High Alkaline Frit					19.10	21.97	22.00			23.61	23.61
Cornish Stone	13.00										
Borax Frit	9.00	78.00	11.00	58.00							
Barium Carbonate			10.00								
Calcium Borate Frit						22.30	22.00	24.00	22.00	23.28	23.28
Whiting					3.52	4.12	6.00	4.00	6.00	3.99	3.99
Bentonite					1.40						
China Clay	5.00	10.00	3.00	8.00	21.43	17.44	11.00	18.00	11.00	13.46	13.46
Zinc	2.00										
Flint			7.00		24.64	19.97	31.00	22.00	31.00	23.22	23.22
Tin Oxide	10.00	8.00		7.00	6.44	7.52	5.00	5.00	5.00	5.00	
Zirconium Oxide		4.00									
Alumina : Silica Ratio	0.05	1.70	1:10	1.80	1:10	1:10	1:9	1:10	1:10	1:10	1:10

*Alan Caiger-Smith; Clive Fiddis. Ceramic Review Book of Clay Bodies and Glaze Recipes 1977

** John Calderwood.(Pes. Comm.)

† Clinton (1991)

Table 2.2. Clay Paste Lustre Pigment Recipes

Material	FR1	FR2	HM1	A10	JM1	JM2	JM3	JM4	JM5
Copper Carbonate	30	28	27	12	32	19	22		20
Silver Sulphate		2	7	20	3	2	6	12	
Yellow Ochre				40	30		40	30	50
Red Clay	70	70	66	15					
China Clay					30	63	30	39	
Red Iron Oxide				25	5	16	6	9	6
Tin Oxide				5				10	24

Table Continued:

Material	JM7	JM8	JM9	JM10	JM11	JM12	JM13	JM14
Copper Carbonate	22	20	22	25	25	20	30	20
Silver Sulphate	6		6		1			1
Yellow Ochre				50	50			
Red Clay						56	50	56
China Clay	72	50	72					
Red Iron Oxide		6	6	6	6			
Tin Oxide		24		24	24	24	20	23
Sum	100	100	106	105	106	100	100	100

Table 2.3 Reduction Lustre Glaze Recipes

All the recipes given are fired to 1060°C (Orton Cone 04), requiring a one hour soak period

	#8	#9	#10	#11	#12	#13	#14	#15	#16
	CRL	VCL	MCG	Purple	GS	2BG	Pink	S872	Blue
Glaze Material			**Percentage of Ingredient**						
Lead Bisilicate	23.00			19.00	19.00	9.90	19.00	23.00	19.00
High Alkaline Frit	25.60	21.01	22.89	22.00	22.00	36.50	22.00	25.60	22.00
Calcium Borate Frit	33.10	31 27	32.19	28.00	28.00	40.18	28.00	33.10	28.00
Whiting	1.00	3.23	3.40			0.97		1.00	
Bentonite	1.40	1.00		2.00	2.00	0.97	2.00	1.40	2.00
Ball Clay		2.00							
China Clay	6.14	19.79	20.84	11.00	11.00	2.00	11.00	6.14	11.00
Flint	6.10	19.64	20.68	18.00	18.00	5.93	18.00	6.10	18.00
Copper Carbonate	1.50	1.50	0.33	1.50	1.50	5.89	0.50	0.75	
Cobalt Carbonate	1.00			1.00				0.50	1.00
Manganese Dioxide			0.33						
Iron Oxide			0.33				0.50		
Silver Sulphate			1.5		0.50	2.00		1.00	
Zinc Oxide							1.00		
Tin Oxide							2.00		
Bismuth Oxy-Nitrate	5.00	1.00	1.5	5.00	5.00	2.00			5.00
Alumina : Silica Ratio	1:10	1:07	1:07	1:10	1:10	1:09	1:10	1:10	1:110

Just prior to exposure to ultra violet light, the protective acetate layer was peeled off the screen. The screen was then exposed for 8 minutes to an 800 W ultra-violet light source. The screen was re-exposed for a further 2 minutes in order to harden the emulsion. After exposure, the Cappillex forms a reservoir at the screen surface of approximately 80µm in depth.

Screens prepared using Capillex were used for printing glaze directly onto dipped tiles using a water based screen medium (AJ1144 from CMS Colours Ltd). The medium manufacturers recommend the use of a triple bar mixer and a powder to medium ratio of 1.8 : 1, this mixture being referred to as an ink. However if mixing by hand, the maximum ratio that could be handled was roughly 1:1, this gave satisfactory results. Screen printing onto transfer paper used an oil based medium, the CMS Colours product AA0192 was used. After the design has been printed on to transfer paper, it was allowed to dry before a cover coat was printed over the design. The CMS Colours product CK2636 was found suitable for the cover coat.

An alternative photographic emulsion to Capillex was Dirasol 948. This emulsion was applied to a clean, dry screen as a liquid using an applicator. Layers of emulsion were applied to the screen until the desired thickness was achieved. Dirasol 948 proved to be more versatile and easier to use than the Capillex 80. The exposure times for this product depended on the mesh size being used and on the number of layers applied to the screen.

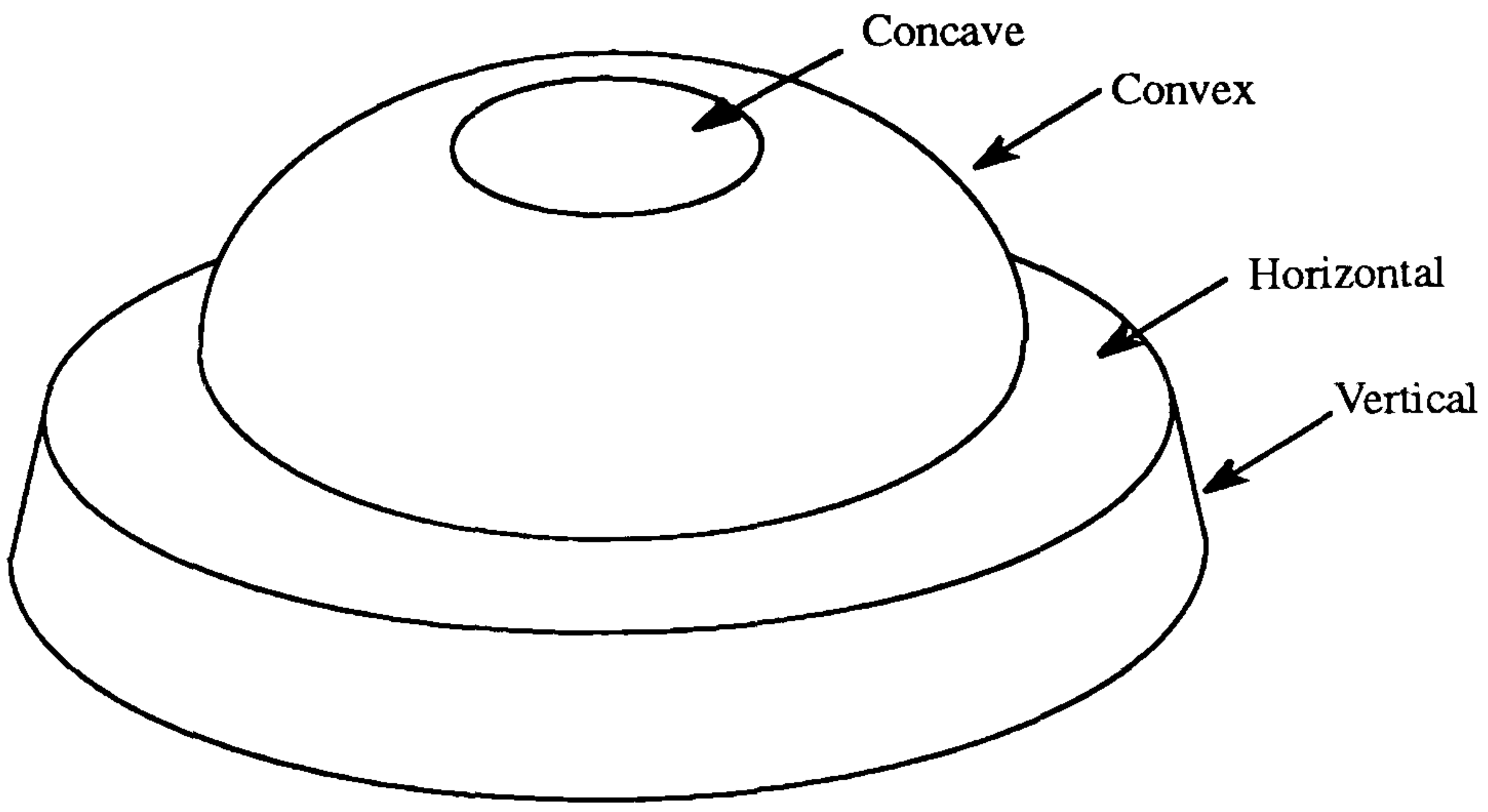
For screen printing onto a substrate, a range of mesh sizes were used, the mesh size being determined by the number of threads per centimetre. The diameter of the threads can also vary with mesh size. The snap-off distance was kept constant once an optimum distance had been established. This was done by using a screen printing table which had an adjustable, hinged frame fitted to it, in which the screen was clamped. The density of the inks was kept constant throughout a particular experiment. The squeegee pressure was not fixed but was kept as constant as possible since all printing was carried out by the same operator. The area covered by the design was also kept to a minimum.

2.2.3 Substrate Shape Design

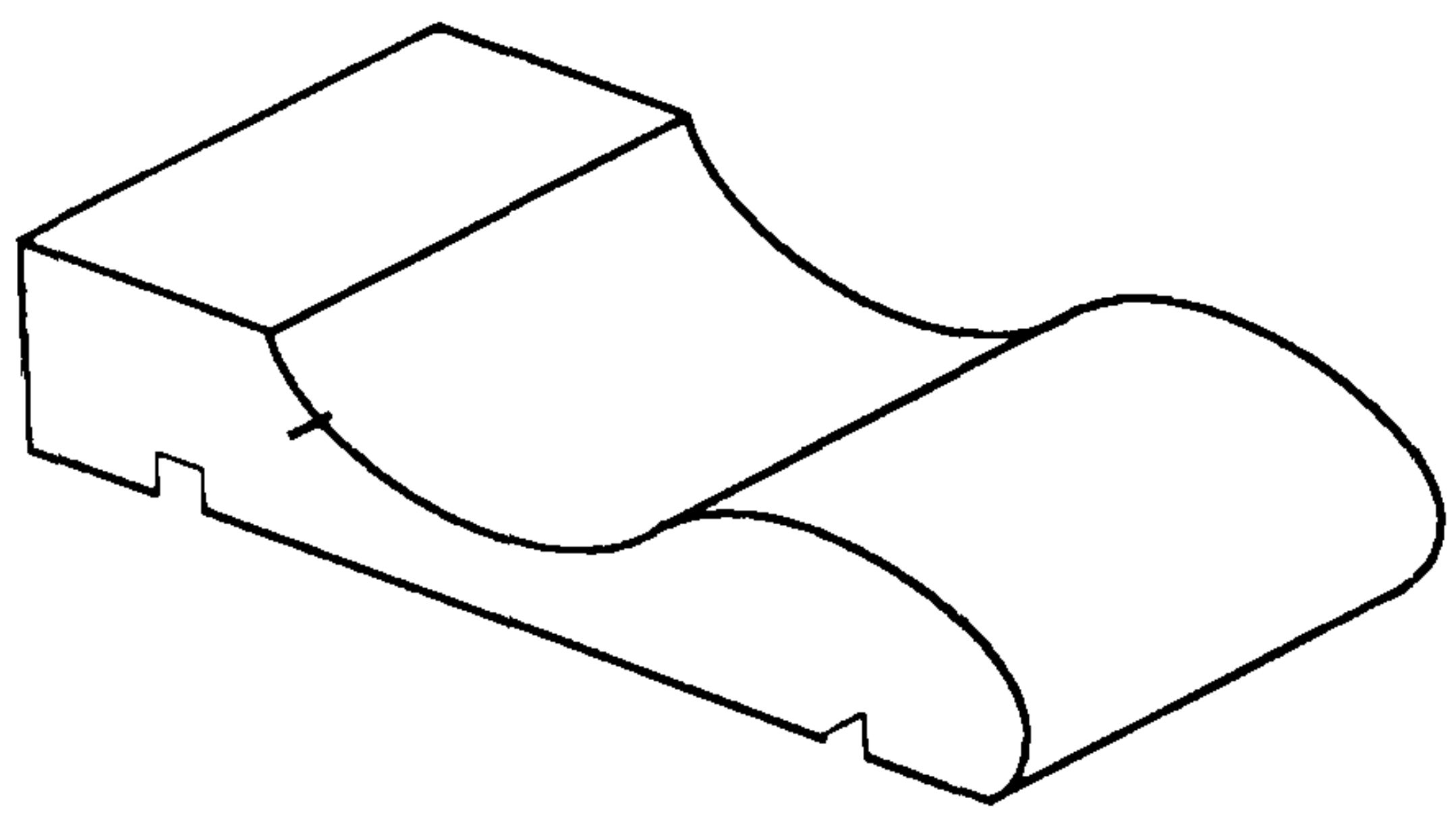
Throughout this investigation, three basic substrate shapes where adopted, these were commercially produced bisque tiles, and two three-dimensional shapes.

Six inch bisque fired commercially produced tiles (H & R Johnsons Tiles Limited; Stoke-on-Trent) were used since these provided a two dimensional surface which was suitable for screen printing directly onto, and a consistent substrate which was easy to cut after firing, enabling samples to be examined in scientific instruments. Glazes fired onto these tiles were all glost fired using tile cranks which held the tiles in a horizontal position during firing. In the reduction firing the tiles were mainly fired in a nearly vertical position.

Two three dimensional shapes where designed. A circular shape made by the slip casting process and an alternative extruded shape. These are illustrated in figure 2.2. Both shapes



Slip cast form



Extruded Form

Figure 2.2. Substrate test shapes used for lustre glaze evaluation.

incorporated a variety of surface contours designed to simulate the surfaces which occur on ceramic objects.

Some later experiments in the electric kiln used actual slip cast pottery. These were used to examine the aesthetic effects of different reduction processes, and to investigate the gas flow patterns occurring within a modified electric kiln.

2.3 Effect of Silk Screen Mesh Size on Application Thickness and Lustre Development.

The application thickness of a clay paste lustre has a marked effect on the final appearance of the lustre. This can be seen clearly when a brush is used to apply the pigments to a glaze, the marks left by the brush stroke show up as variations in the tone of the lustre. Very fine lines or fine deposits produce iridescent effects. This occurs when the thickness of the lustre film is in the region of 300 nm - 400 nm thick, this is due to constructive interference between incident light beams (Caiger-Smith, 1985). Most of the characteristic iridescence observed on a piece of lustre ware is due to the volatile nature of the finely divided metal film which is formed during the reduction.

The thickness of lustre glazes was also observed (section 4.4.4) to have a profound effect on lustre development. It was postulated by this author, that controlling the thickness of the pigment application could allow control over the degree of iridescence formed.

Controlling the thickness of a deposit of glaze or pigment depends on the application method being used. Screen printing was chosen as a possible method of applying a controlled weight of glaze or pigment to a glazed tile. For glazes which generally require a relatively thick deposit of material to form a satisfactory glaze layer, the most effective way to control the application thickness is through varying the thickness of photographic emulsion used to create the stencil on the silk screen. A product such as Capillex or Dirosol 948 can be used for this purpose. For a clay paste pigment, the deposit required to produce a satisfactory lustre can be relatively thin, in the order of 10 - 20 μm. The minimum thickness of screen emulsion would therefore be used. There are a number of ways in which the deposit of pigment can be varied. The density of the material can be altered by increasing the printing medium to powdered pigment ratio. Alternatively the screen mesh can be varied. A series of experiments were undertaken to establish the effect of mesh size on application thickness. Six different mesh sizes were chosen. The range of sizes used were chosen following consideration of particle size analysis data carried out on a typical clay paste pigment. Particle size analysis was carried out using the Malvern Mastersizer, Model E. This is a laser diffraction instrument yielding results in the form of frequency histograms or cumulative frequency curves of volume% vs particle size.. An example is shown as figure 2.3. On the basis of the size distribution results, a series of screen mesh sizes were chosen in the knowledge that these would not exert a seiving action on the glaze. The mesh sizes used ranged from 21 threads per square centimeter to 62 threads per square centimeter.

2.3.1 Experimental Procedure for Screen Application Test

Two pigments, JM 9 and JM 12 (table 2.2), were prepared for screen printing using a water based printing medium (CMS Colours, AJ1144) in accordance with the procedure described in section 2.2.2.2.

The meshes used were as follows:

21 TW, 32.7 SDEUO Orange, 34 TW, 43.8 TW, 55 TW and 62 TW. (Sericol Limited) (numbers refer to threads per centimetre).

Screens used were given a single coat of Dirosol 948 emulsion, applied to the down side of the screen. The image which formed the stencil was prepared using the Aldus Free-Hand programme, running on an Apple Macintosh computer. The image was in the form of precisely measured square shapes (20 x 20 mm), set out as a grid formation with 4 mm

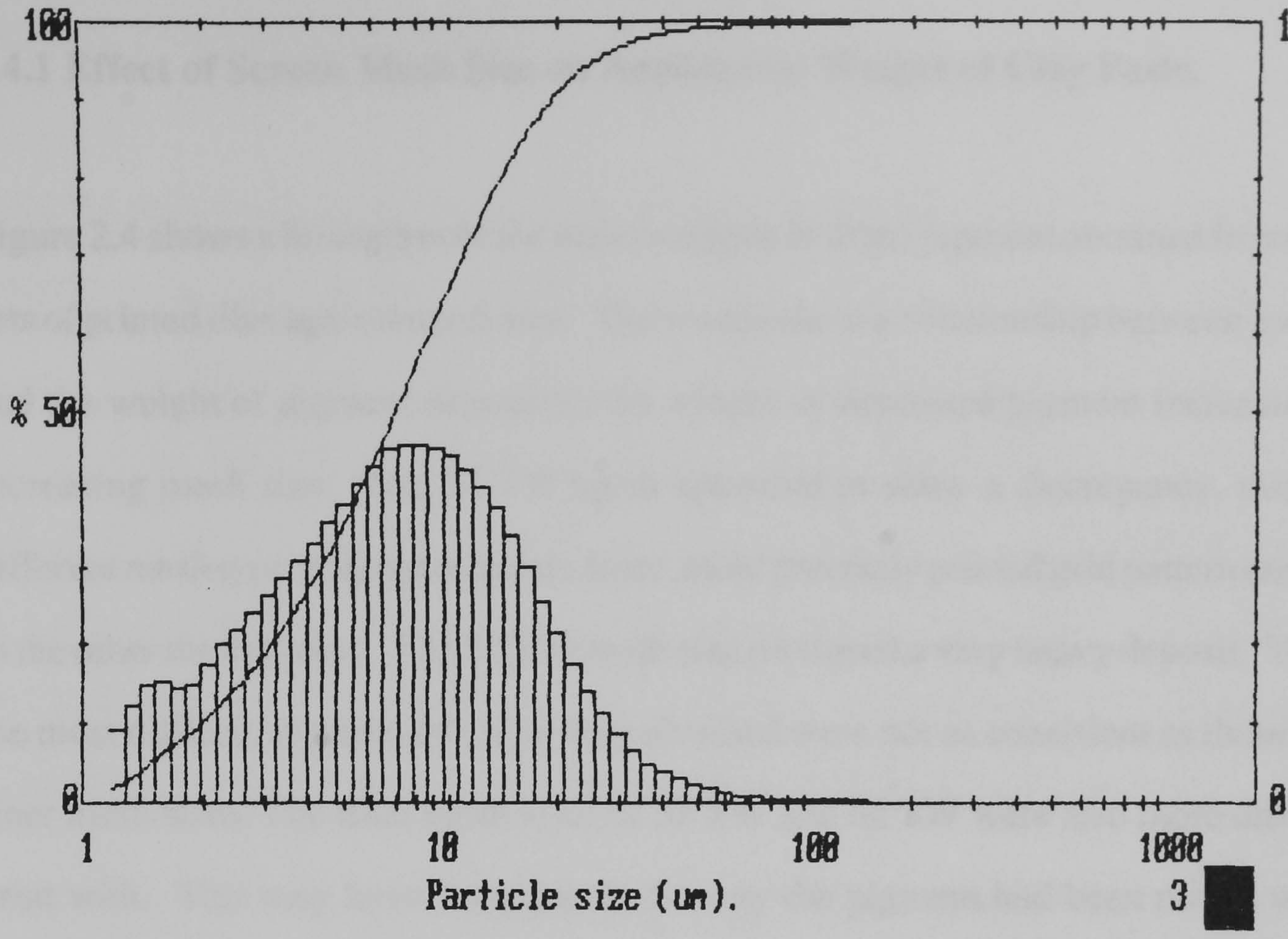


Figure 2.3. Particle size analysis of clay paste pigment JM9 (table 2.2).

gaps between each square on the grid. The grid design provided a convenient sample area over which the pressure of the squeegee would be reasonably even. The grid was produced as a PMT and then exposed onto the screens.

A screen printing bed was used which allowed the screens to be clamped into position and the snap off distance kept constant once an optimum had been established.

Biscuit tiles (150 mm^2) were glazed using under-glaze #7 (table 2.2). Each tile was then printed with the grid pattern before being oven dried at 350°C. Following cooling, the dried pigment of three individual squares of the grid was scraped off the glazed surface of each tile into weighing bottles, and weighed. The three squares were selected from different parts of the surface of each tile.

2.4 Results

2.4.1 Effect of Screen Mesh Size on Application Weight of Clay Paste.

Figure 2.4 shows a histogram of the mean weights of dried pigment obtained from twelve sets of printed tiles against mesh size. The results show a relationship between mesh size and the weight of pigment deposited, the wieght of deposited pigment increasing with increasing mesh size. The 32 TW mesh appeared to show a discrepancy, this was a different mesh type which produced a finer, more precisely printed grid pattern compared to the other meshes used. The 21 TW mesh size produced a very heavy deposit. This was the most difficult to print and the results obtained were not as consistent as those for the finer mesh sizes. The finer mesh sizes of 55 TW and 62 TW were also more difficult to print with. This may have been due to the way the pigment had been mixed with the printing medium.

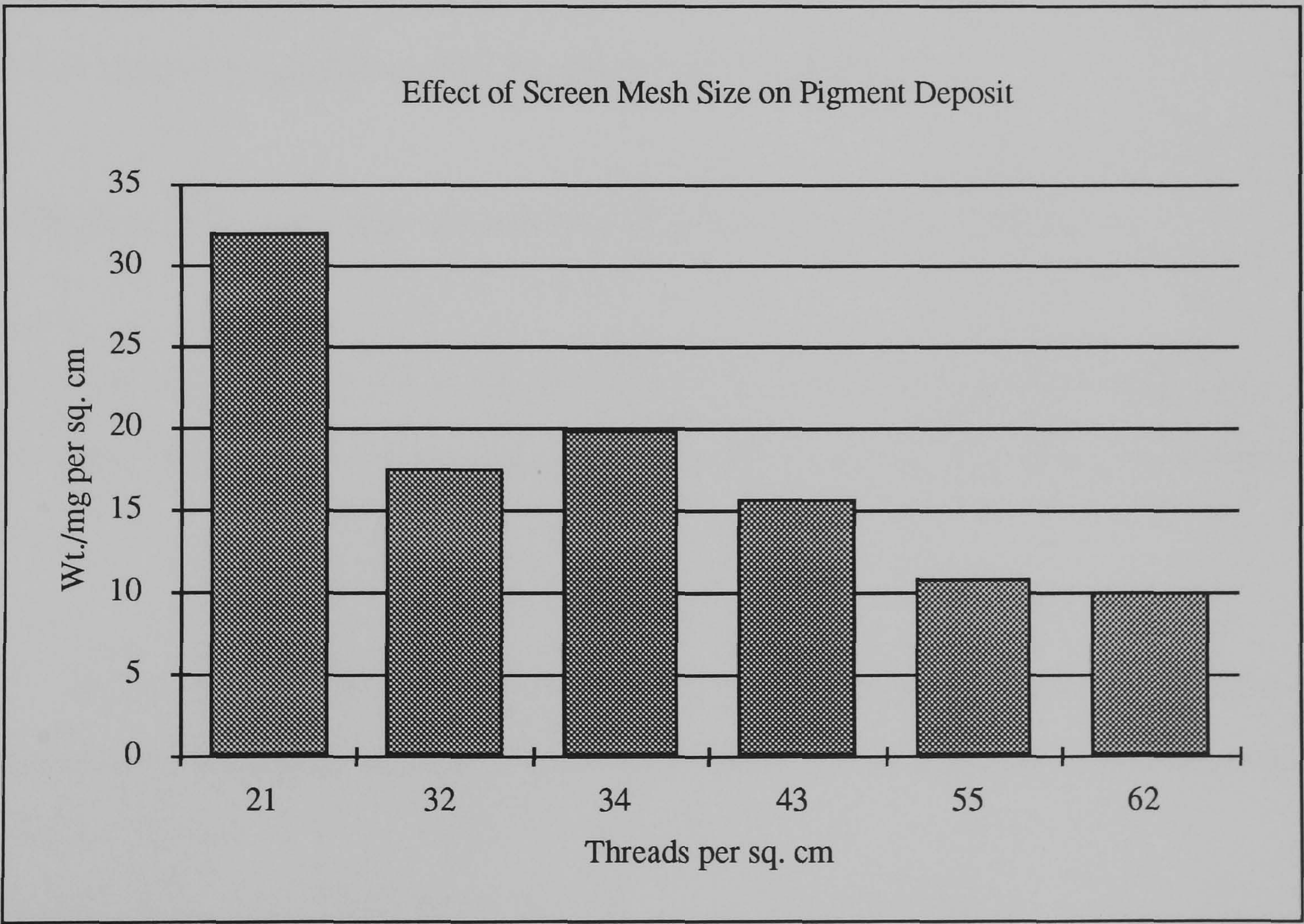


Figure 2.4. Histogram showing the effects of screen mesh size on the weight of pigment deposited on the surface of a glazed tile.

The medium was thixotropic, requiring a mechanical mixer designed for the purpose if it is to be printed without difficulty.

Once the squares of printed pigment had been scraped off the tiles and weighed, the tiles, with the remaining pigment, were reduction fired in the muffle kiln described in section 6.2.1. The reduction temperature was set to 680°C and the reduction time was 40 minutes using 5% hydrogen in nitrogen as the reducing agent. The fired tiles were then cleaned with water to reveal the resulting lustre development. Very little difference was apparent in colour development between the tiles printed with different mesh sizes. From this observation it was concluded that deposits of pigment < 10 mg per cm^2 were sufficient to produce a lustre and deposits greater than this were a waste of material.

CHAPTER THREE

3 Thermal Analysis of Lustre Glaze Materials

3.1 Introduction

The following chapter describes the thermal analytical studies which have been carried out into the raw materials of lustre glazes, the glazes themselves and clay paste lustres. The overall aim of the experiments described in this chapter was to gain an understanding of the processes which take place when lustres are applied to ceramics and fired under reducing conditions. Using lustre glaze #8 prepared as a frit, thermal analytical data was obtained which is explained in terms of the kinetic reduction reactions occurring within the glaze.

3.1.1 Aims of Experiments Described in Chapter Three

The aims of the investigations described in this chapter were as follows:

- To establish the effect of firing individual raw glaze materials under oxidising and reducing atmospheres, and the temperatures at which reduction occurs for those materials.

- To establish the effect of firing mixtures of glaze materials under oxidising and reducing atmospheres, and to establish the temperatures at which reduction occurs for those materials.

- To formulate a topochemical model of the reaction behaviour of a lustre glaze.

3.2 The Use of Thermogravimetry in the Analysis of Lustre Glaze

3.2.1 Thermal Analysis

Thermal analysis (TA) includes a number of techniques which determine temperature dependencies of various physical properties of a material. Table 3.1 gives examples of various thermal analytical techniques together with some of their applications. In many cases, one particular technique can provide all the information required by the investigator. Often techniques are combined, such as thermogravimetry (TG) and differential thermal analysis (DTA), or TG and evolved gas analysis (EGA). A succinct description of these techniques and their applications in the ceramic industry is given by Cooper (1992).

Table 3.1 Thermal Analytical Techniques, Abbreviation and Physical Property Investigated

Technique	Accepted Abbreviation	Physical Property
Thermodilatometry	-	Length
Thermogravimetry	TG	Mass
Derivative Thermogravimetry	DTG	Mass
Differential Thermal Analysis	DTA	Temperature
Differential Scanning Calorimetry	DSC	Enthalpy
Evolved Gas Analysis	EGA	Mass (gas partial pressure)

(Dodd and Tonge, 1987; Cooper, 1992)

Of these techniques, TG and DTG were chosen for use in this investigation because during reduction firing the process results in a measurable weight loss from the glaze. Differential Scanning Calorimetry (DSC) was not used because the instrumentation which was available was limited to a maximum temperature of 600°C and too low for most of the reduction processes being investigated.

For investigations, instrumentation was available which allowed simulation of typical firing schedules. In these schedules glazes, or glaze constituents, could be subjected to controlled pre-programmed temperature rises, soaking periods and controlled cooling and gas change-overs, so that a topochemical model could be developed which was based on a realistic firing system. DTG records differences in temperature between a sample and a reference material, such as alumina, which remains inert over the temperature range of interest. Both sample and alumina are subjected to the same controlled temperature programme. The technique when used in combination with TG produces data as pronounced peaks which show rates of weight changes in the sample during a temperature programme, and make it possible to be more precise as to the temperature at which a reaction is occurring.

A number of experiments were carried out using Programmed Temperature Reduction (TPR), this technique is another thermal analytical method during which the changing H2 concentration of a gas flowing past a sample undergoing a temperature rise is measured. This provides data relating to the reducibility of a solid sample. TPR is a sensitive analytical method which can be used to provide data relating to the starting and finishing temperatures of a reduction process (Jones and McNicol, 1986).

The production of ceramics involves the application of elevated temperatures to materials. Thermal analysis techniques can often provide appropriate methods for the characterisation of ceramics. Cooper (1992) describes the use of DTA for the characterisation of potters plaster and showed that when used in conjunction with TG, the amount of combined water could be accurately determined. The characterisation of bone china with the combined use of DTA and DTG is also described by the same author. A search of the available literature on the subject of thermal analysis as applied to ceramics has revealed a wide range of applications. Kaisersberger *et al.* (1992) describe the application of thermoanalytical techniques including TG and DTG in combination with a variety of supplementary techniques to study the process of identification of sinter-reactive powders and oxygen loss from superconductors during linear heating and isothermal sintering. The results were used to optimise sintering during a firing process and to establish the point at which binders were burned out.

3.2.1.1 Thermogravimetry

Sometimes referred to as thermal gravimetric analysis, TG is defined as a technique in which the mass of a substance is measured, as a function of temperature, whilst being subjected to a controlled temperature programme. From this, a TG curve can be obtained, using a thermal balance, which shows changing weight of sample with time and temperature. The technique enables sample materials to be heated under different atmospheres, for example, the change in mass of a material undergoing a reduction process can be determined by heating the material using a gas containing hydrogen or carbon monoxide. The quantitative nature of TG enables accurate measurements to be made of any reactions during which a change in weight occurs.

Thermogravimetry was used during this research programme to investigate the effect of firing raw glaze materials under oxidising and reducing atmospheres. The technique enabled the temperatures at which reduction occurred for those materials to be determined and the various steps in the reactions to be identified. TG was also used to examine the mixtures of materials as they would appear in a glaze or clay paste lustre. Further experiments using a fritted lustre glaze (#8, table 2.3) were undertaken. A series of isothermal experiments were carried out from which rate constants for reduction processes could be calculated. This allowed the Arrhenius equation to be applied so an activation energy could be estimated. With this information it is possible to formulate a topochemical model for the reduction behaviour of a glaze.

3.3 Materials and Methods

3.3.1. Preparation of Samples for Thermogravimetry

Investigations involving the technique of TG were carried out on raw materials, glazes and clay paste pigments as well as samples of fritted lustre glaze used throughout this study.

Air dried raw material samples of approximately 20 mg were placed into a thermal balance (Metler TA3000, figure 3.1). A TG curve was obtained from which step analysis, using the software of the instrument, was carried out enabling interpretation of the curve. Steps of the curve which represented stages of water loss, decomposition or reduction, indicated by weight losses from samples, were determined.

Analysis was carried out on a number of lustre glazes and clay paste pigments. Sub-samples were taken from glazes after they had been mixed and wet sieved (Section 2.2.1). The sub-samples were oven dried before being placed in a thermal balance. The samples were fired under oxidising conditions in flowing air and under reducing conditions using a mix of 5% hydrogen in nitrogen gas or a hydrocarbon gas mixture. The samples were heated to 900°C, with a temperature rise of 10°C per min.

3.3.2 Preparation Method Used For Fritted Glaze #8

A sample of glaze #8 (table 2.3) was placed into a platinum crucible and fired in a muffle kiln to 1060°C. After rapid cooling the resulting frit was dry ground using a ball mill to form a fine pale blue powder. Sub-samples (40 mg) of the frit were removed and placed in a thermal balance which was programmed so as to simulate a reduction firing similar

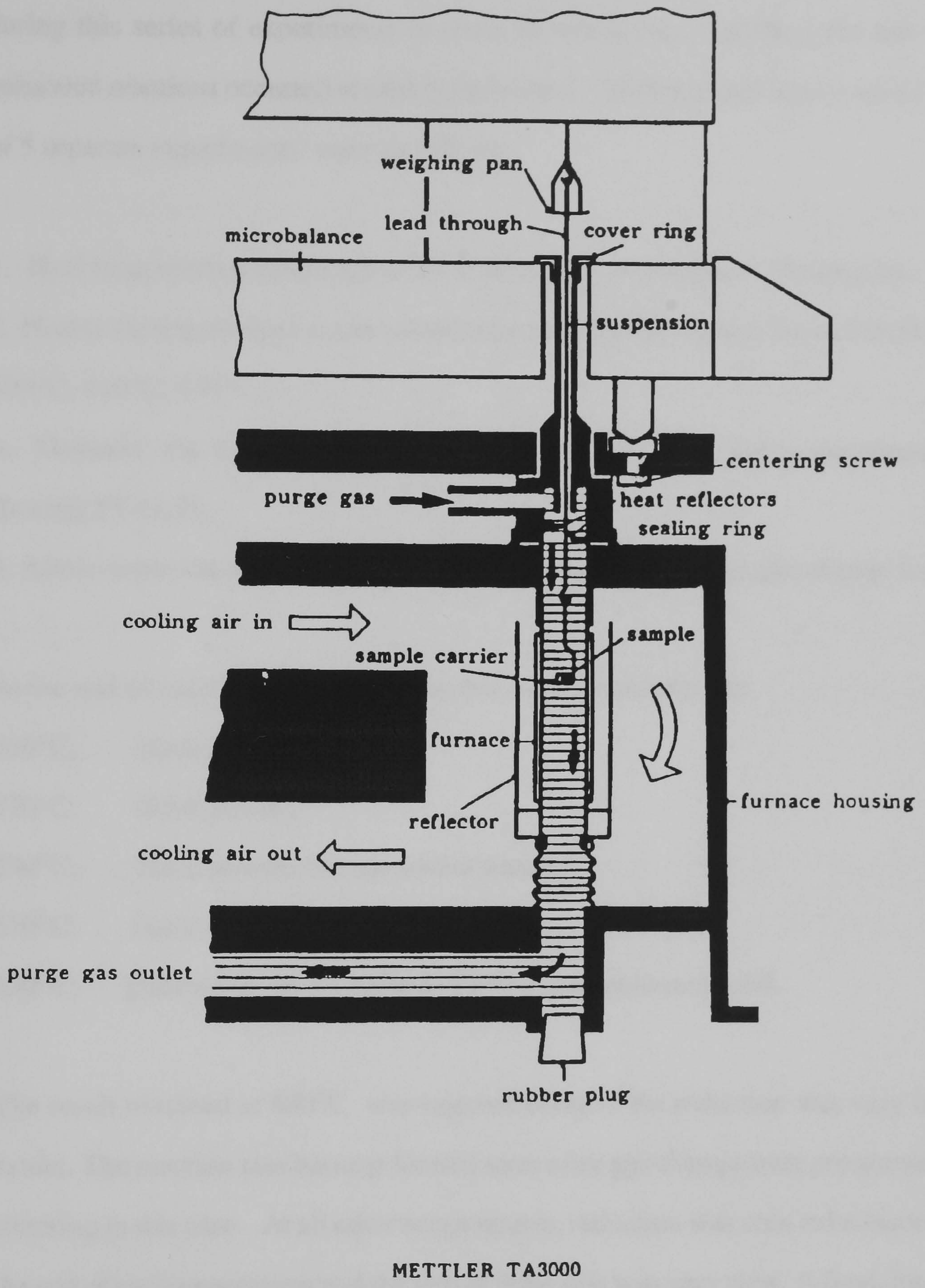


Figure 3.1 Schematic diagram of thermal balance and furnace assembly (adapted from the Mettler TA 3000 Manual).

to that used in a full-scale lustre firing. A range of reduction temperatures were chosen during this series of experiments in order to obtain data regarding the rate at which reduction reactions occurred at each temperature. The firing procedures used in a series of 5 separate experiments were as follows:

1. Heat from room temperature to 35°C and allow to stabilise in flowing air.
2. Heat to the required reduction temperature under oxidising conditions (550°C, 570°C, 590°C, 610°C, 630°C)
3. Maintain the sample at the reduction temperature and change the atmosphere to flowing 5% H_2/N_2
4. Allow reduction to take place and monitor the isothermal weight change for 90 min.

At the end of each experiment, the product was observed to be:

550°C; black powder

570°C; black powder

590°C; black powder but somewhat sintered

610°C; black solid with some gold areas.

630°C; glaze components become a fused gold-coloured solid.

The result obtained at 630°C was rejected because the reduction was very limited in extent. The reaction rate became limited soon after gas change-over presumably due to sintering in this case. At all other temperatures, reduction was seen to be incomplete by the end of each experiment and the rate of reduction was very slow. A final, total weight loss for a complete reduction was not obtained, but could be estimated by visual extrapolation of the weight against time curve. Topochemical and diffusional models of the reduction mechanism were evaluated on the basis of the kinetics of isothermal TG work.

3.4 TG Analysis Results

3.4.1 Results of TG Analysis of Raw Materials

Thermal analysis curves, showing weight change against temperature under different firing regimes, are shown as figures 3.2 - 3.11. The materials tested and the approximate temperature at which reductions occurred are given in table 3.2.

Many of the materials tested were unaffected by the presence of a reducing atmosphere during firing; the curves produced were similar under both oxidising and reducing atmospheres. However some materials, in particular the reducible metal oxides, were affected, demonstrating different weight losses on reduction firing from those observed under oxidising conditions. In the case of copper carbonate, reduction had the effect of lowering the temperature at which weight loss, through decomposition of the carbonate, took place.

Clay minerals such as bentonite and china clay, were unaffected by reduction atmospheres. Weight losses at temperatures of 100°C and 570°C were observed, indicating dehydration of the clay mineral lattice.

Table 3.2 Raw Materials Examined Using Thermogravimetry

Material	Formula	Approximate Reduction Temperature / °C
Whiting	$CaCO_3$	non-reducible
Bentonite	$Al_2O_3.5SiO_2.7H_2O$	non-reducible
Copper carbonate	$CuCO_3$	250
Cobalt carbonate	$CoCO_3$	450
Silver sulphate	Ag_2SO_4	400
Bismuth oxy-nitrate	$BiO(NO_3).H_2O$	550
Manganese dioxide	MnO_2	410
Tin oxide	SnO_2	780
China clay	$Al_2O_3.2SiO_2.2H_2O$	non-reducible
Flint	SiO_2	non-reducible

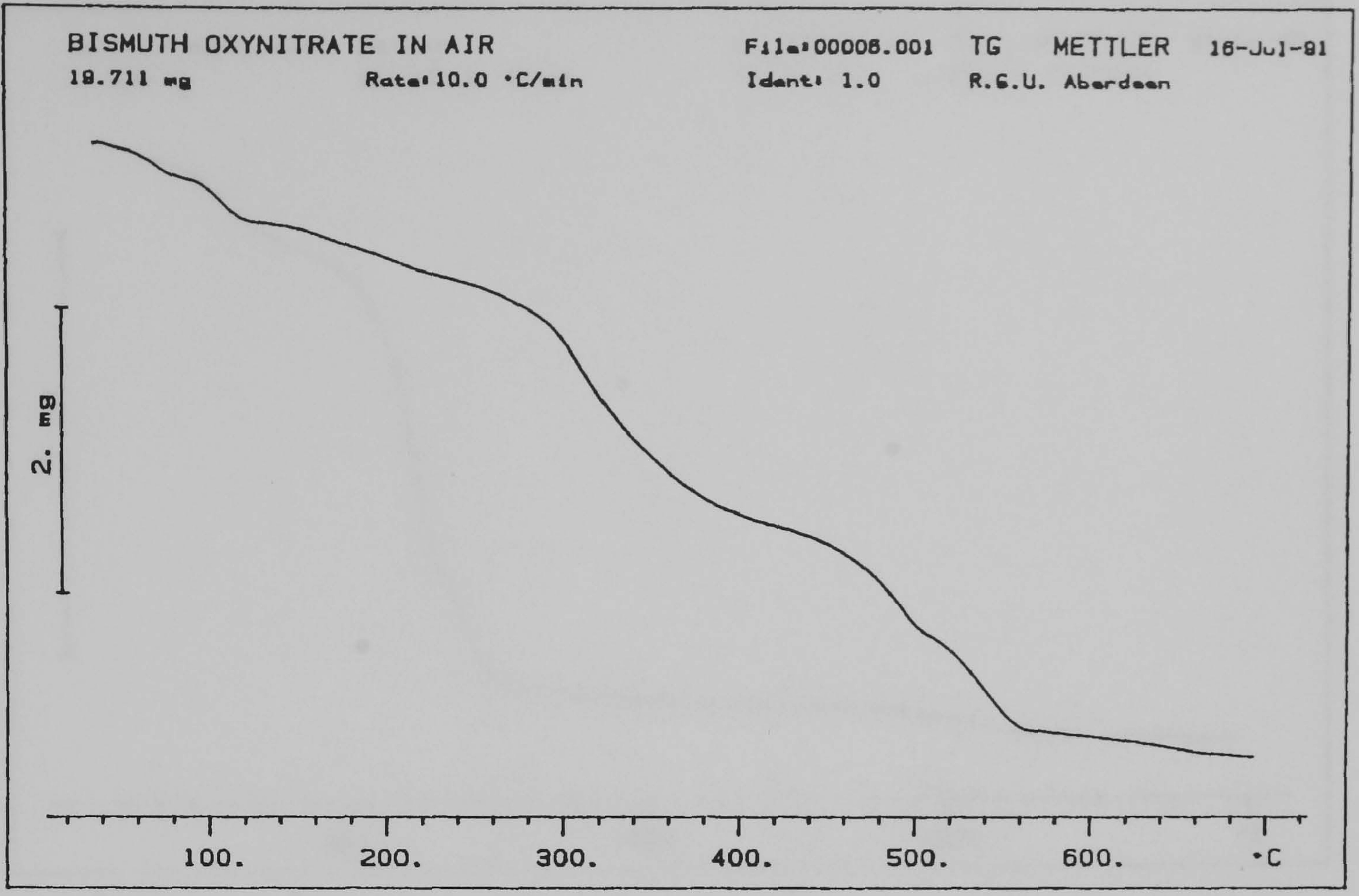


Figure 3.2 TG of bismuth oxy-nitrate heated in flowing air at 10°C per min.

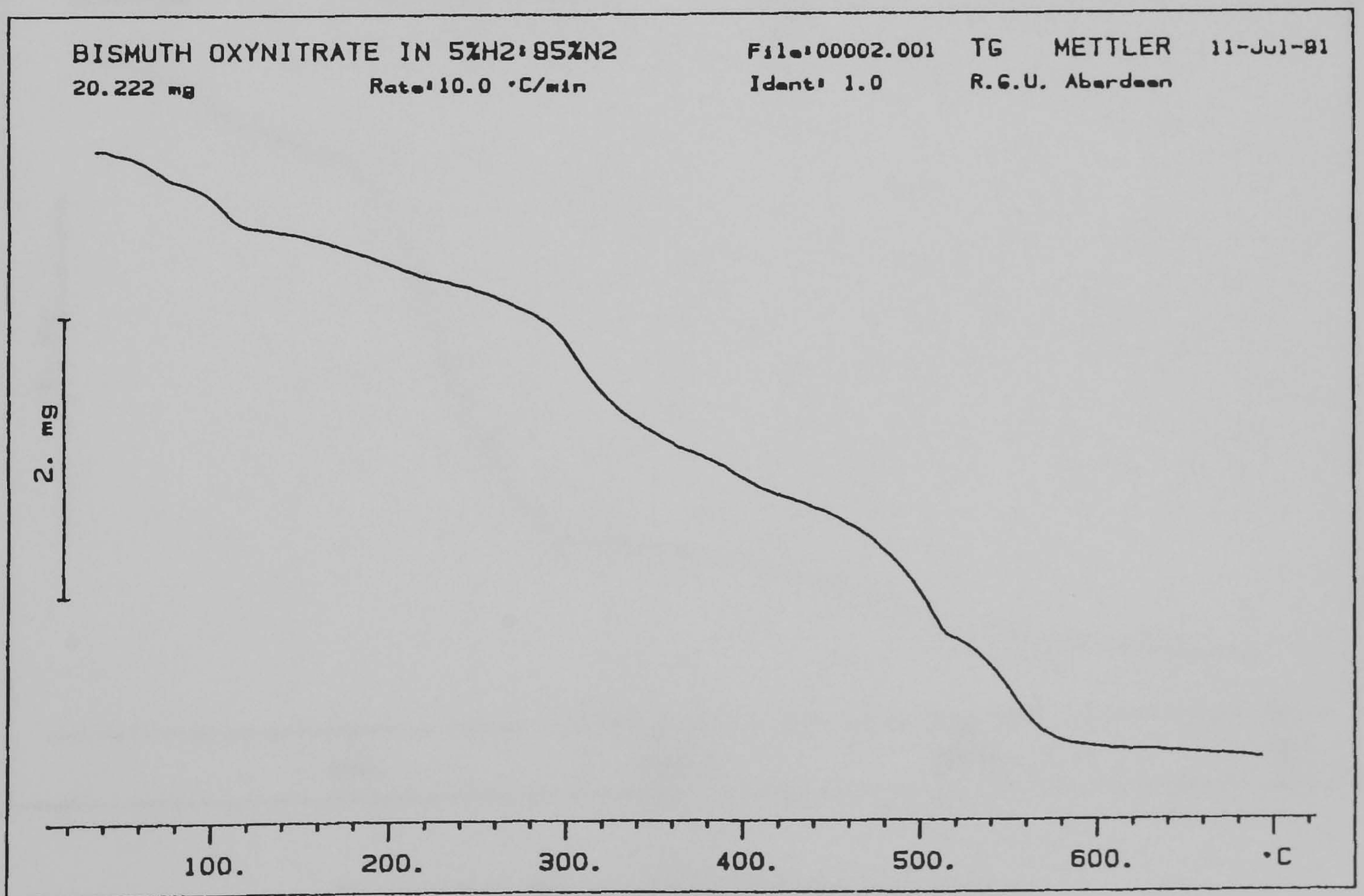


Figure 3.3 TG of bismuth oxy-nitrate heated in 5% hydrogen in nitrogen at 10°C per min.

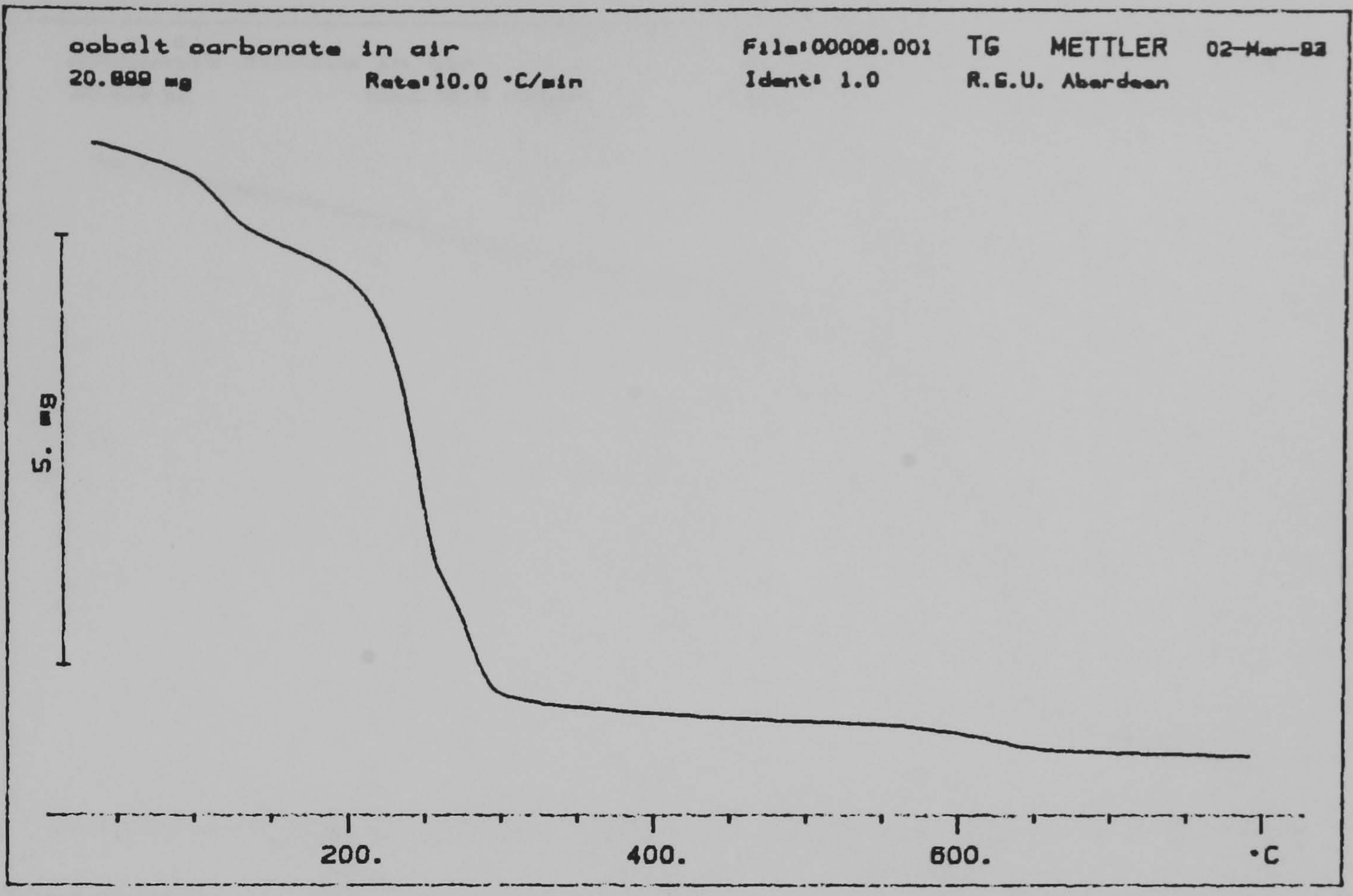


Figure 3.4 TG of cobalt carbonate heated in flowing air at 10°C per min.

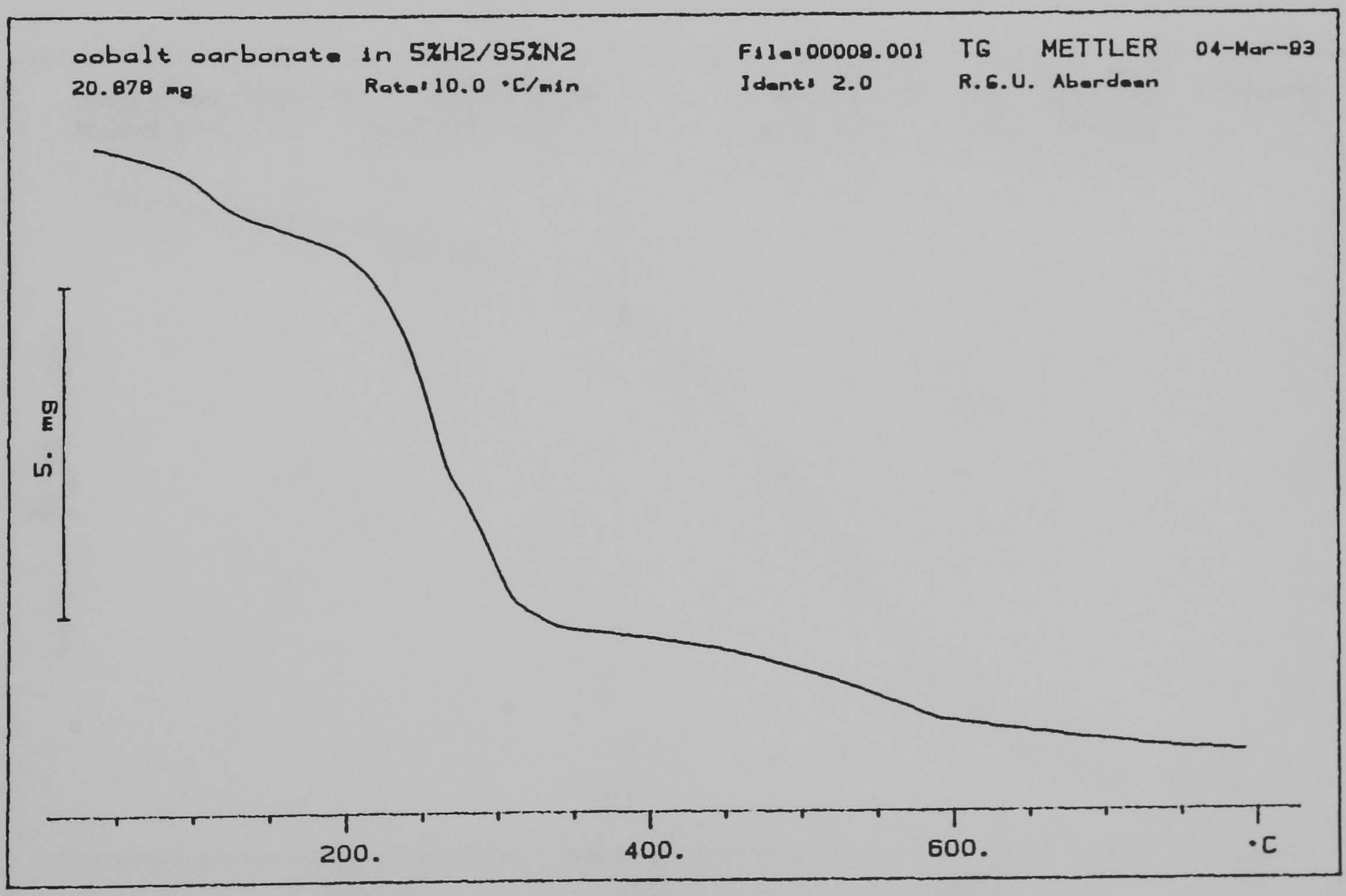


Figure 3.5 TG of cobalt caronate heated in
5% hydrogen in nitrogen at 10°C per min.

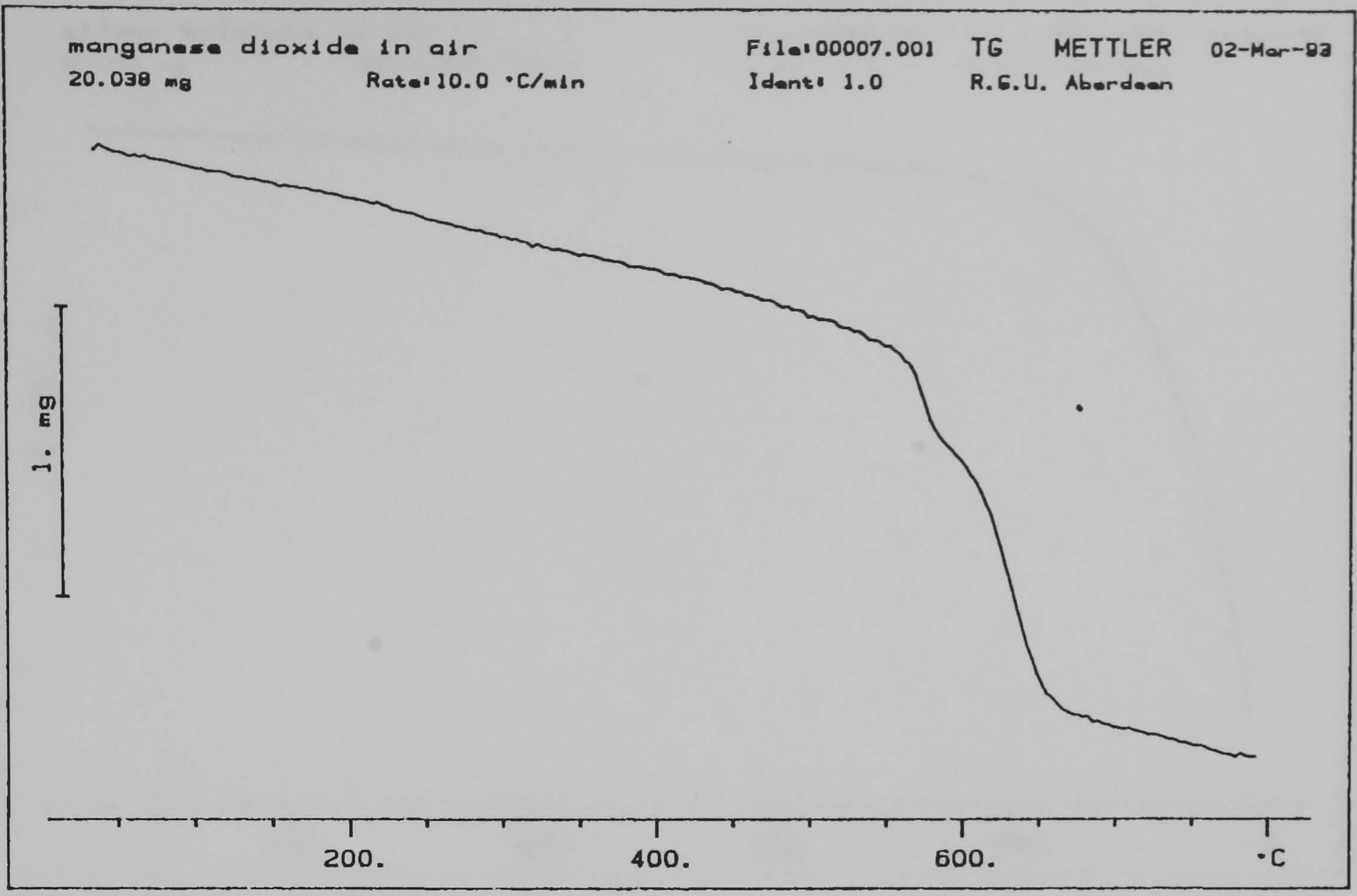


Figure 3.6 TG of manganese dioxide heated in flowing air at 10°C per miN

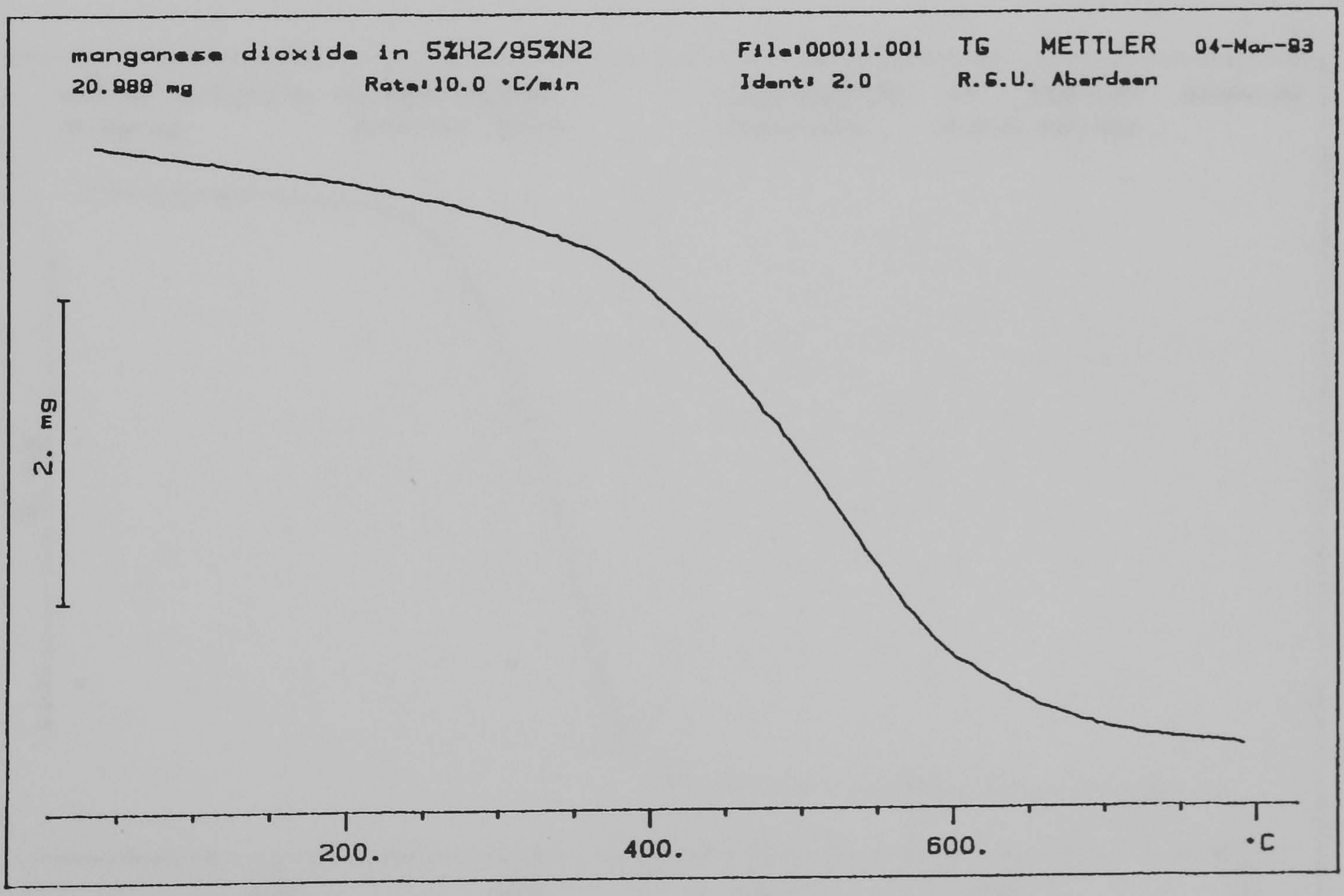


Figure 3.7 TG of manganese dioxide heated in 5% hydrogen in nitrogen at 10°C per min.

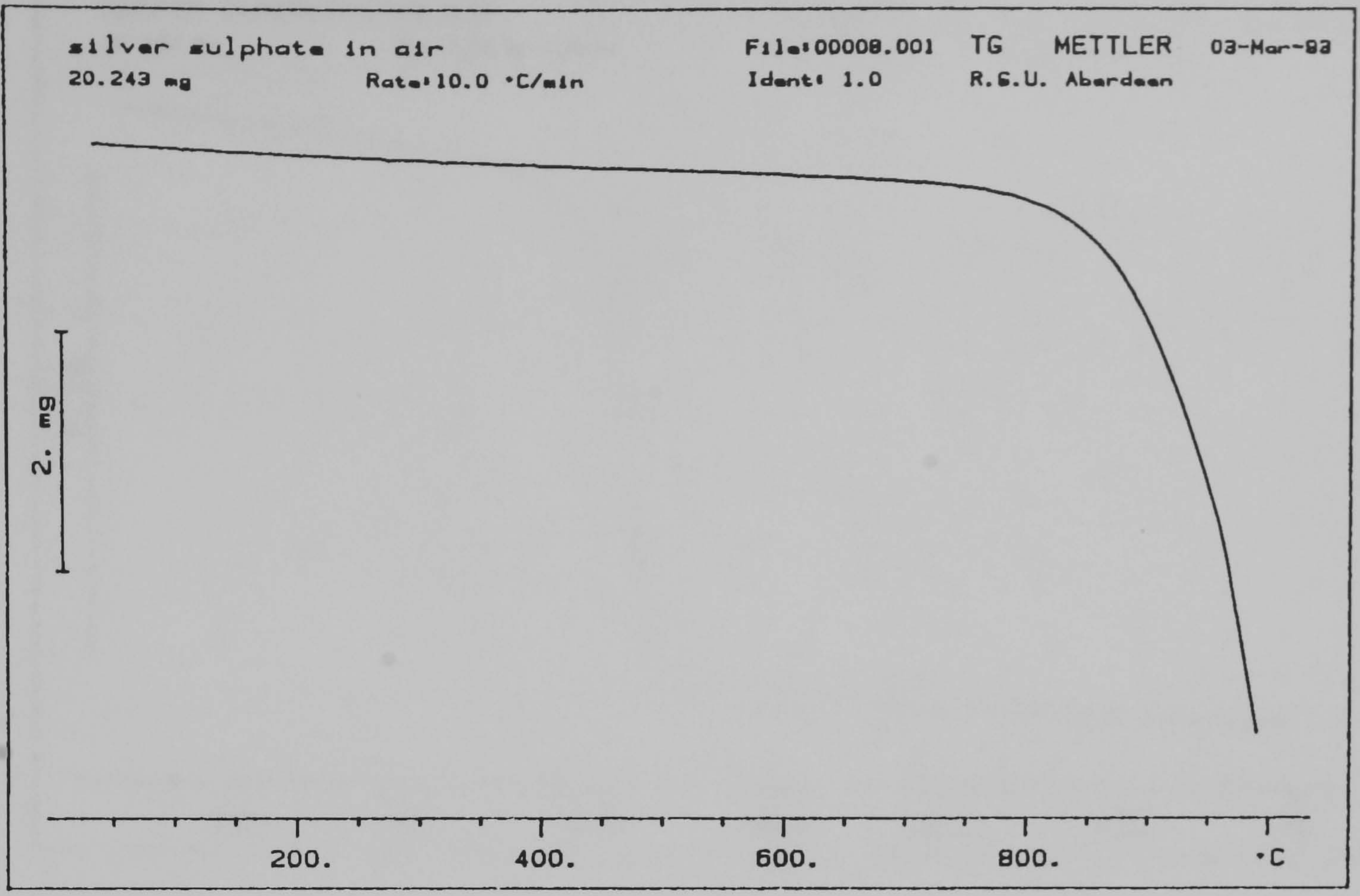


Figure 3.8 TG of silver sulphate heated in flowing air at 10°C per min.

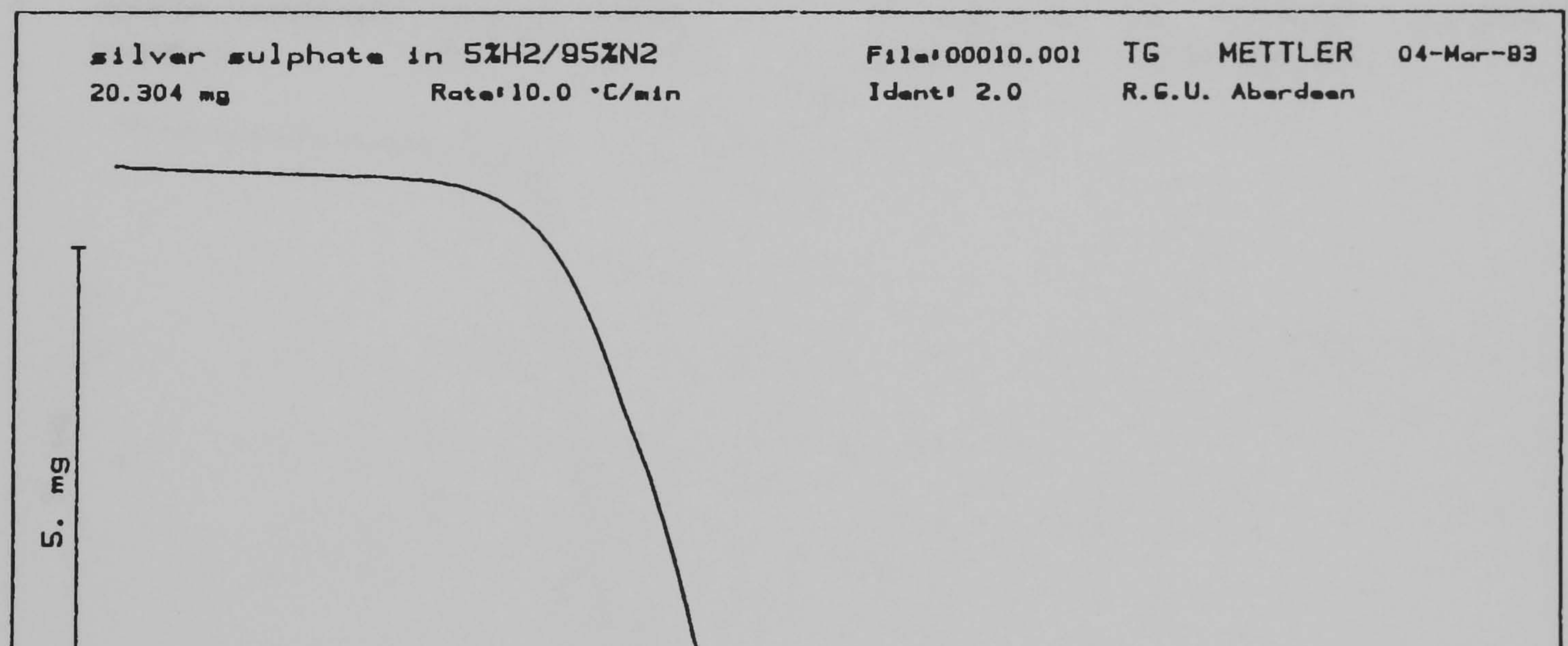


Figure 3.9 TG of silver sulphate heated in
5% hydrogen in nitrogen at 10°C per min. inn2 at 10°C per min.

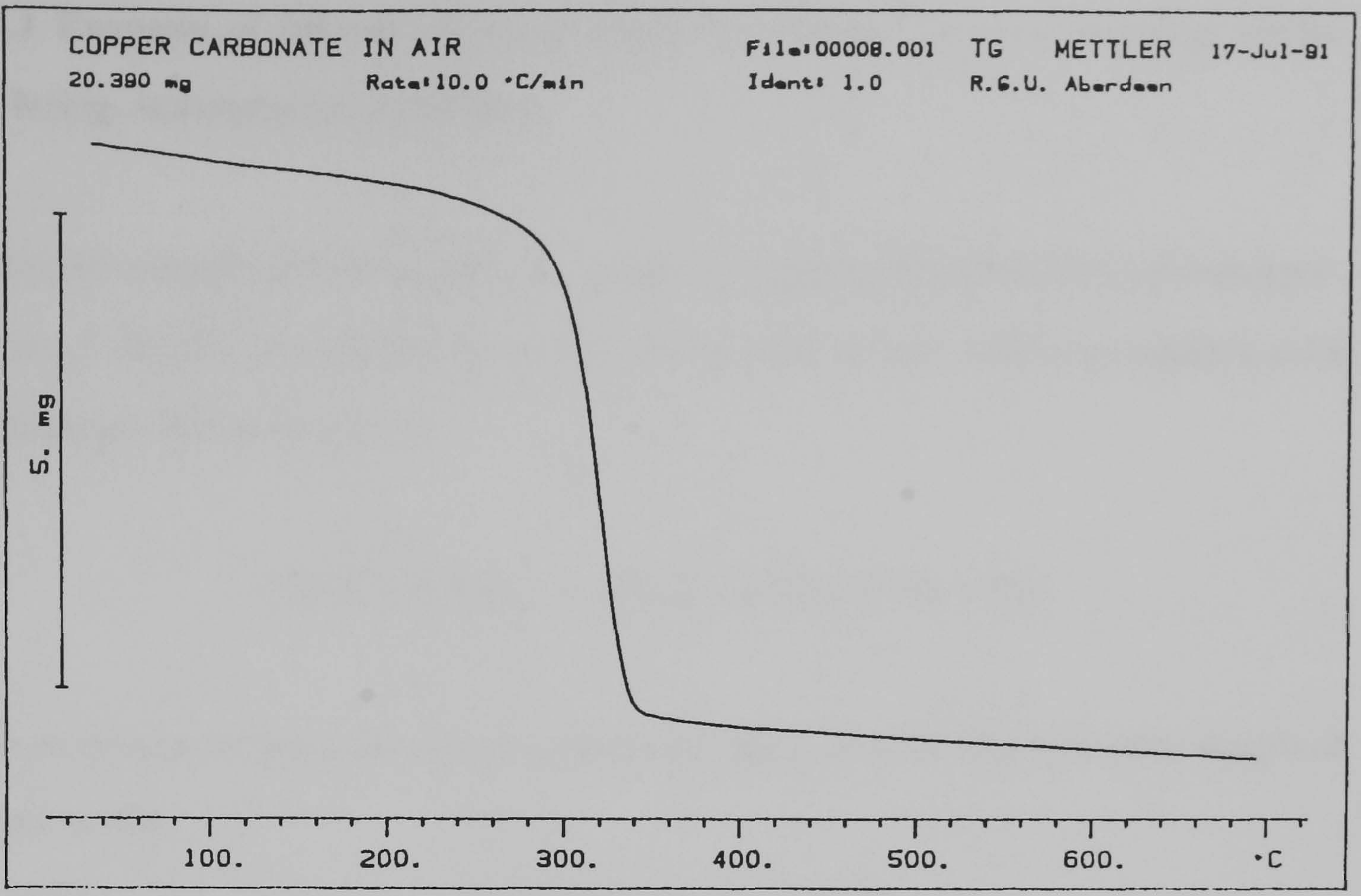


Figure 3.10 TG of copper carbonate heated in flowing air at 10°C per min.

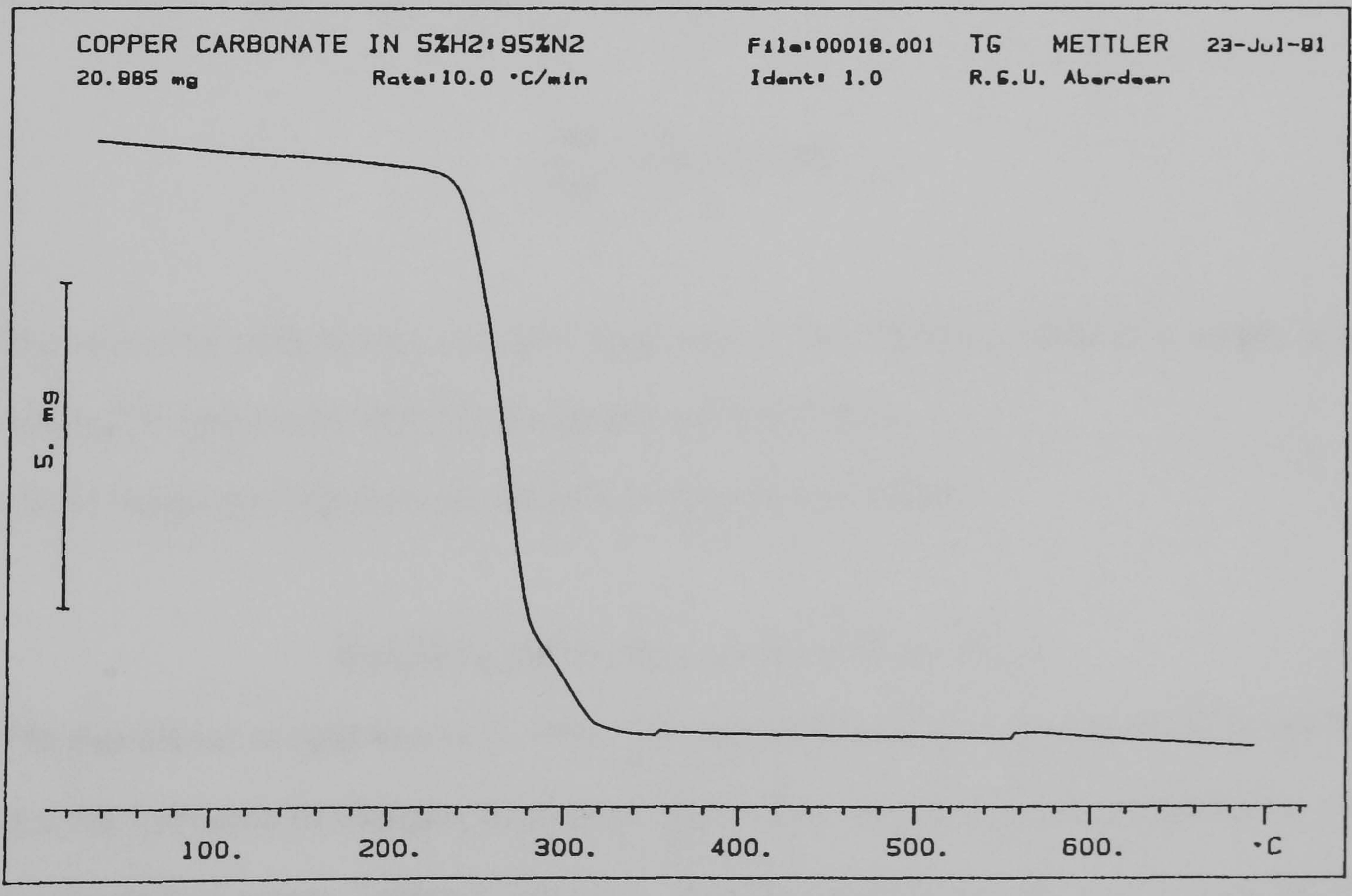


Figure 3.11 TG of copper carbonate heated in
5% hydrogen in nirogen at 10°C per min.

4.1.1 Example of Interpretation of Observed Weight Losses Occurring Under Differing Atmospheric Conditions.

Using the example of bismuth oxynitrate with the formula, $BiO(NO_3).H_2O$, the interpretation of observed weight losses can be demonstrated. Under oxidising conditions the following reaction may occur:

$$2BiO(NO_3).H_2O \rightarrow Bi_2O_3 + 2NO_2 + 0.5O_2 + H_2O$$

The molecular weight of the starting product is 305 x 2 = 610. The molecular weight of Bi_2O_3 = 466.

The percentage weight loss is calculated from the equation:

$$\text{Percentage weight loss} = \frac{\text{weight loss}}{\text{weight of material}} \times 100$$

The theoretical percentage weight loss is therefore:

$$\frac{144}{610} \times 100 = 23.6\%$$

The observed weight loss for this stage was in fact 19.92% (table 3.3) which is in reasonable agreement with the theoretical value (23.6%).

Under reducing conditions the following reaction may occur :

$$BiO(NO_3).H_2O + 2H_2 \rightarrow Bi + NO_2 + 3H_2O$$

The theoretical weight loss is 31.48%. The experimental value was found to be 32.3% in a 5% hydrogen in nitrogen atmosphere (table 3.4), which is in broad agreement with the theoretical value. Tables 3.3 and 3.4 give the results obtained for all the reducible metals tested under oxidising conditions in flowing air and under reducing conditions in a 5% hydrogen in nitrogen atmosphere, respectively.

No weight losses were observed as a result of reduction in the following materials tested:

Bentonite
Calcium borate frit
China clay
Flint
High alkaline frit
Red clay
Whiting (calcium carbonate)

Weight loss on reduction was observed for the following materials when fired in an atmosphere of 5% hydrogen in nitrogen.

Bismuth oxy-nitrate
Cobalt carbonate
Copper carbonate
Lead bisilicate
Manganese dioxide
Silver sulphate
Tin oxide
Yellow ochre

The following materials were found to reduce also in a n-octane nitrogen atmosphere.

Bismuth oxy-nitrate
Cobalt carbonate
Copper carbonate
Manganese dioxide
Silver sulphate

It is likely that the other materials reducible by hydrogen will also reduce in hydrocarbon-nitrogen mixtures, though not all were actually tested.

Table 3.3 Results of Thermal Analysis of Reducible Materials Carried Out in Air

Substance	Approx.Step Temperature / °C	Calculated Percentage Weight Loss	Proposed Product	Observed Percentage Weight Loss
Bismuth Oxy-nitrate				
I$BiO(NO_3).H_2O$	310	18.69	$Bi_2(NO_3)$	19.92
Copper Carbonate				
$CuCO_3$	300	35.77	CuO	29.79
Cobalt Carbonate				
$CoCO_3$	250		CoO	23.14
Manganese Dioxide				
$2MnO_2$	640	9.2	Mn_2O_3	10.29
$3\ Mn_2O_3$	940	3.37	$2Mn_3O_4$	1.98
Silver Sulphate				
$AgSO_4$	905	30.79	Ag	30.59

Table 3.4 Results of Thermal Analysis of Reducible Materials Carried Out in 5% Hydrogen in Nitrogen Atmosphere

Substance	Approx.Step Temperature / °C	Calculated Percentage Weight Loss	Proposed Product	Observed Percentage Weight Loss
Bismuth Oxy-nitrate				
$BiO(NO_3).H_2O$	530	31.48	Bi	32.3
Copper Carbonate				
Cu_2O_3	260	35.62	CuO	32.42
Cu	280	20.11	Cu	10.15
Cobalt Carbonate				
$CoCO_3$	330	37.01	Co	23.14
Co	460	21.35	Co	14.32
Manganese Dioxide				
MnO_2	410	18.4	MnO	20.45
Silver Sulphate				
$AgSO_4$	410	30.79	Ag	31.48
Tin Oxide				
SnO_2	780	21.2	Sn	22.59

3.4.2 Results of TPR analysis of Glazes and Pigment mixtures.

Results from TPR analysis of glazes and clay paste pigment mixtures showed that the average temperature at which reduction occurred was in the region of 350 to 400°C (table 3.5). This is well below the normal temperature at which lustre glazes and clay paste pigments are reduced in a typical lustre firing. This is due in part, to the fact that the powdered unfritted glaze samples do not behave in a way directly comparable with a fired lustre glaze on a piece of ceramic. In the case of lustre firing carried out on fired ceramics, the reduction temperature is typically in the region of 650 to 700°C. The reduction temperature chosen for clay paste lustre is dependent primarily on the softening temperature of the under-glaze.

3.4.3 Results of TG Analysis of Fritted Glaze #8.

The TG's of the friotted glaze #8 under the oxidative ramp heating followed by isothermal reduction are shown in figures 3.12 to 3.15. The interpretation of the isothermal TG data has been in terms of a number of physical models which may have topochemical constraints. Topochemical processes are those in which the rate of reaction is governed not only by the rate of the actual chemical reaction taking place but also by the changing area and geometry of the interface at which the reaction is occurring. Any topochemical model of the reduction process should take into account the sintering process if this is significant. Because of the particulate nature of the fritted solid and the fact that the reduction reaction was taking place at the interface with a gas it was thought that the reduction process might have a topochemical character. A large number of models have been proposed for such reactions (Keattch and Dollimore, 1975). Mathematical analysis of the models has yielded a variety of model equations for the evaluation of experimental data.

Since the reduction process clearly must involve diffusion of gases, and ions or atoms of metallic elements, diffusional models were also considered in the analysis of the TG data.

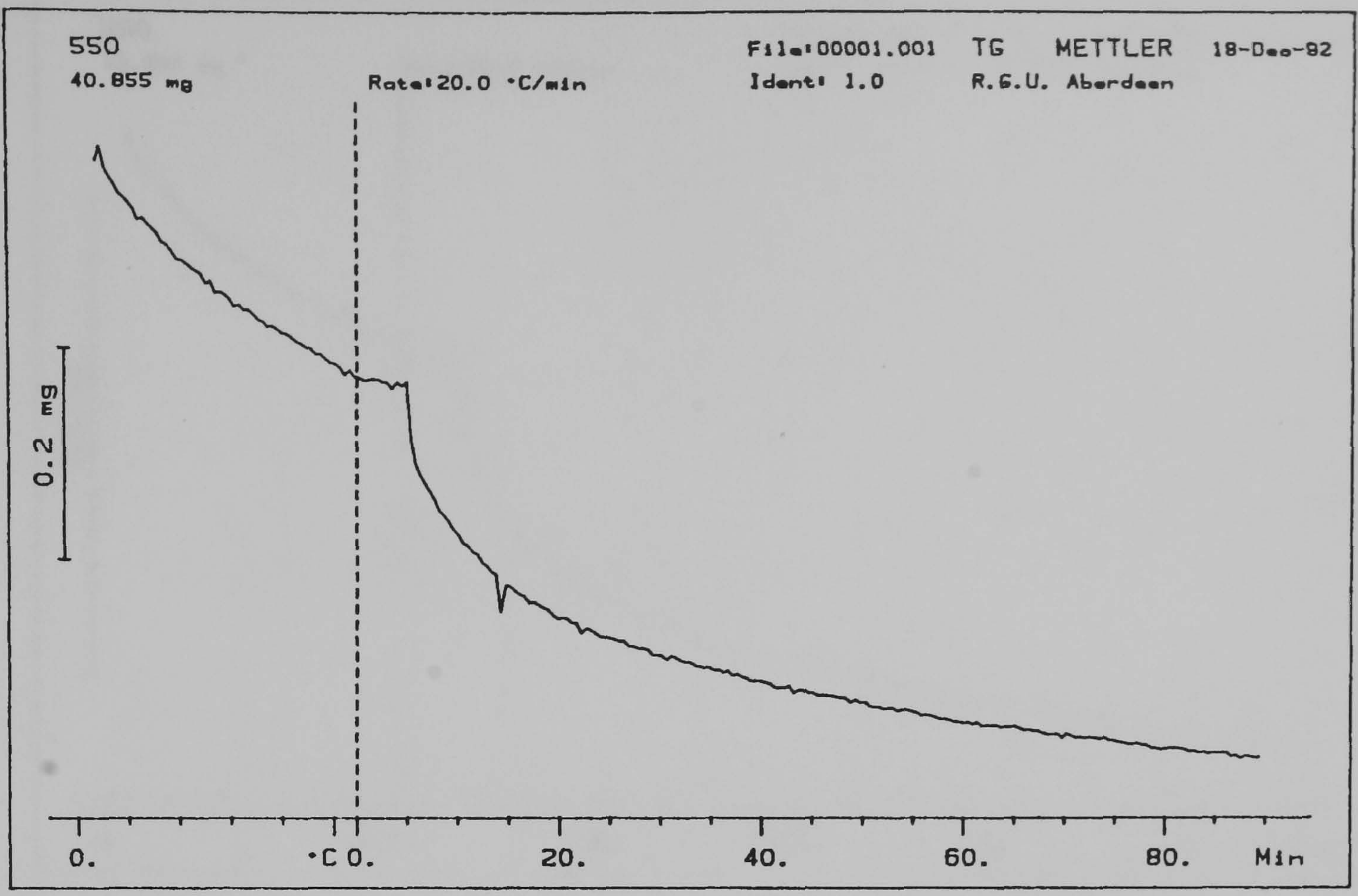


Figure 3.12 TG of Glaze #8 (CRL) frit reduced at 550℃

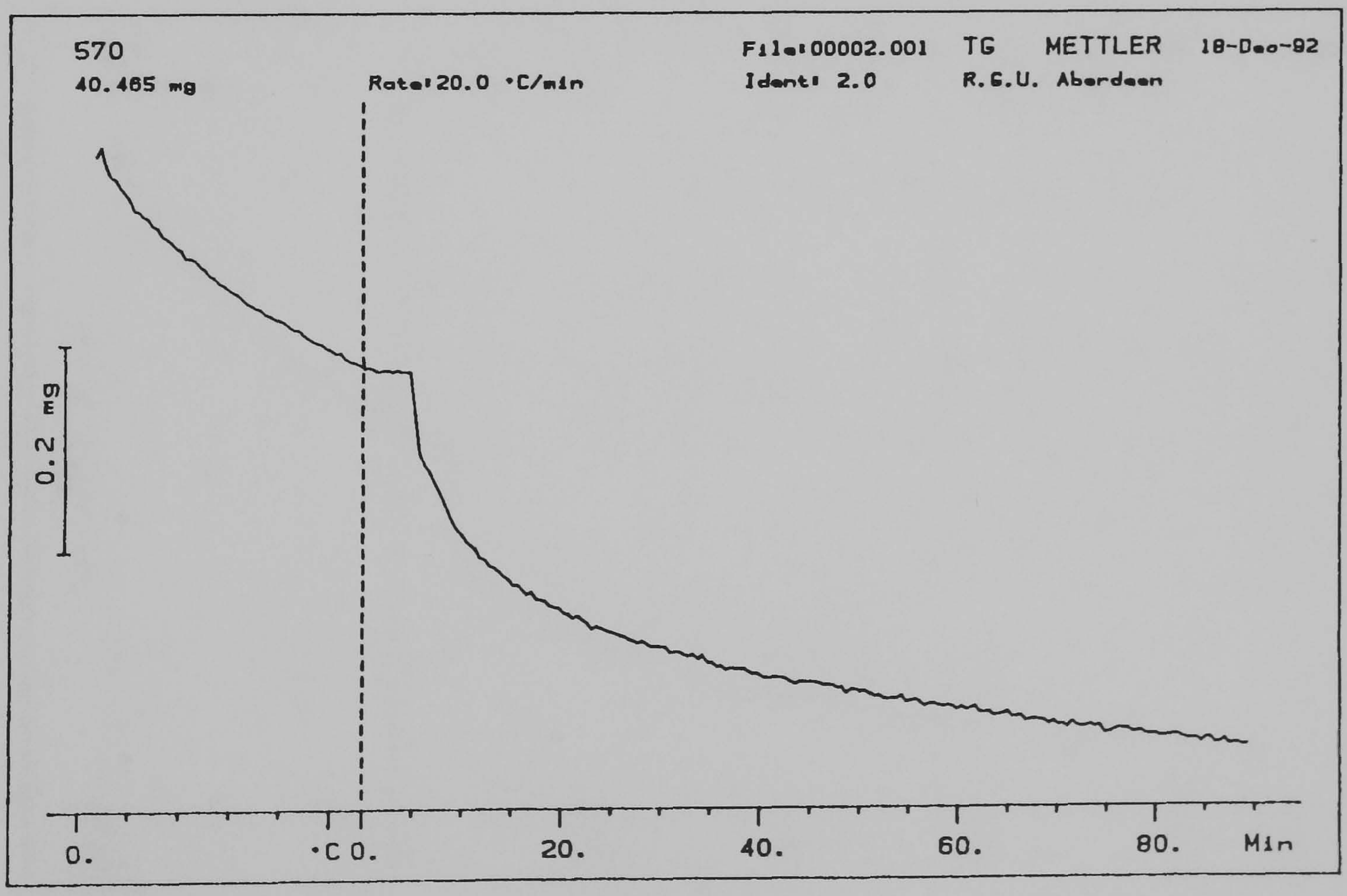


Figure 3.13 TG of Glaze #8 (CRL) frit reduced at 570℃

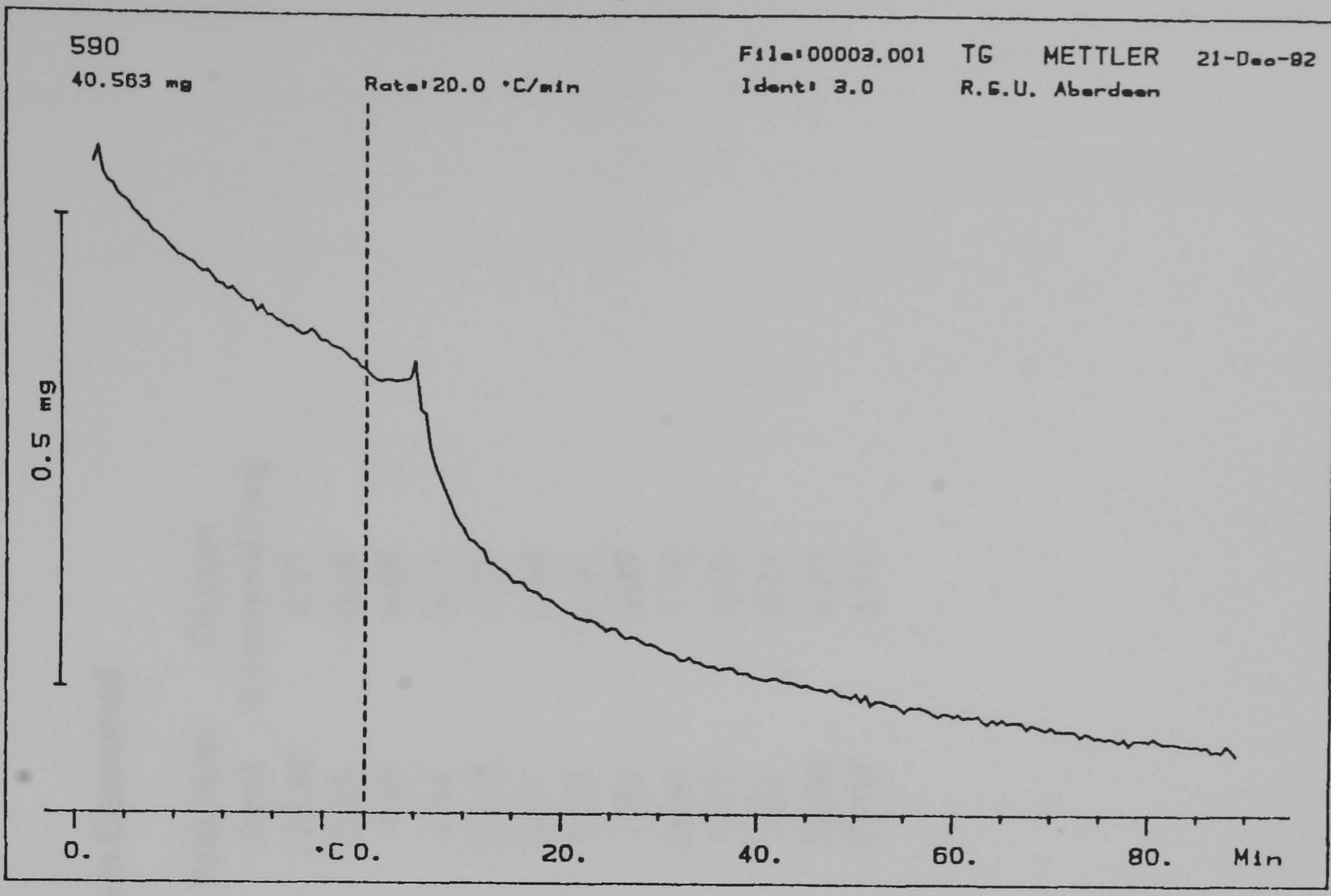


Figure 3.14 TG of Glaze #8 (CRL) frit reduced at 590°C

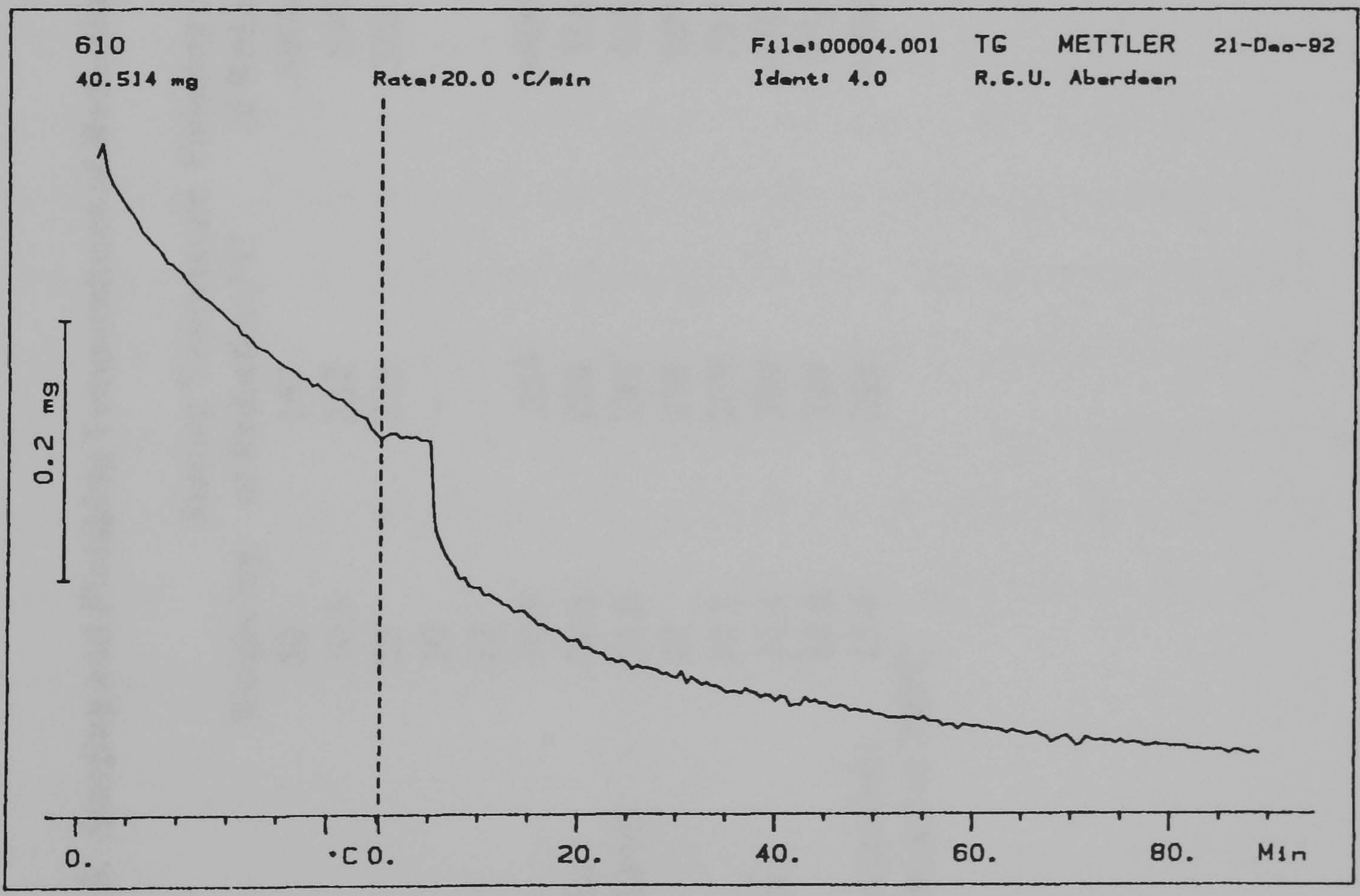


Figure 3.15 TG of Glaze #8 (CRL) frit reduced at 610°C

Table 3.5. Starting and Finishing Temperatures of Reduction and Oxygen Consumed

Sample	Weight/mg	Starting Temperature of Reduction /°C	Finishing Temperature of Reduction / °C	Peak Area /cm2	Oxygen Consumed / mg
A10	50	167	>800	123.45	8.23
FR2	10.5	232	630	2.35	0.16
FRl	25	228	350	9.97	0.66
FRl(c)	10	-	-	4.64	0.31
JM3	12	-	-	26.65	1.78
JM3 (c)	10.6	254	>800	24.5	1.63
#9 (VCL)	10.6	270	326	0.15	0.01
#9 (VCL) (c)	51.6	282	425	1.42	0.09
JMl	42	238	609	26.81	1.78
JMl (c)	12.7	255	554	9.97	0.66
#8 (CR)L	16.4	399	>800	3.81	0.25
JM5	12.8	239	676	35.06	2.34
JM 5 (re-ground)	15.4	234	>790	23.09	1.54

(c) = calcined at 700°C

Having fitted data to a model the analysis often provides information relating to activation energies for the rate controlling processes. (Gentry *et al.* 1979) Under isothermal conditions gas-solid reactions frequently show extent of reaction versus time curves having the characteristic sigmoid shape shown in figure 3.16.

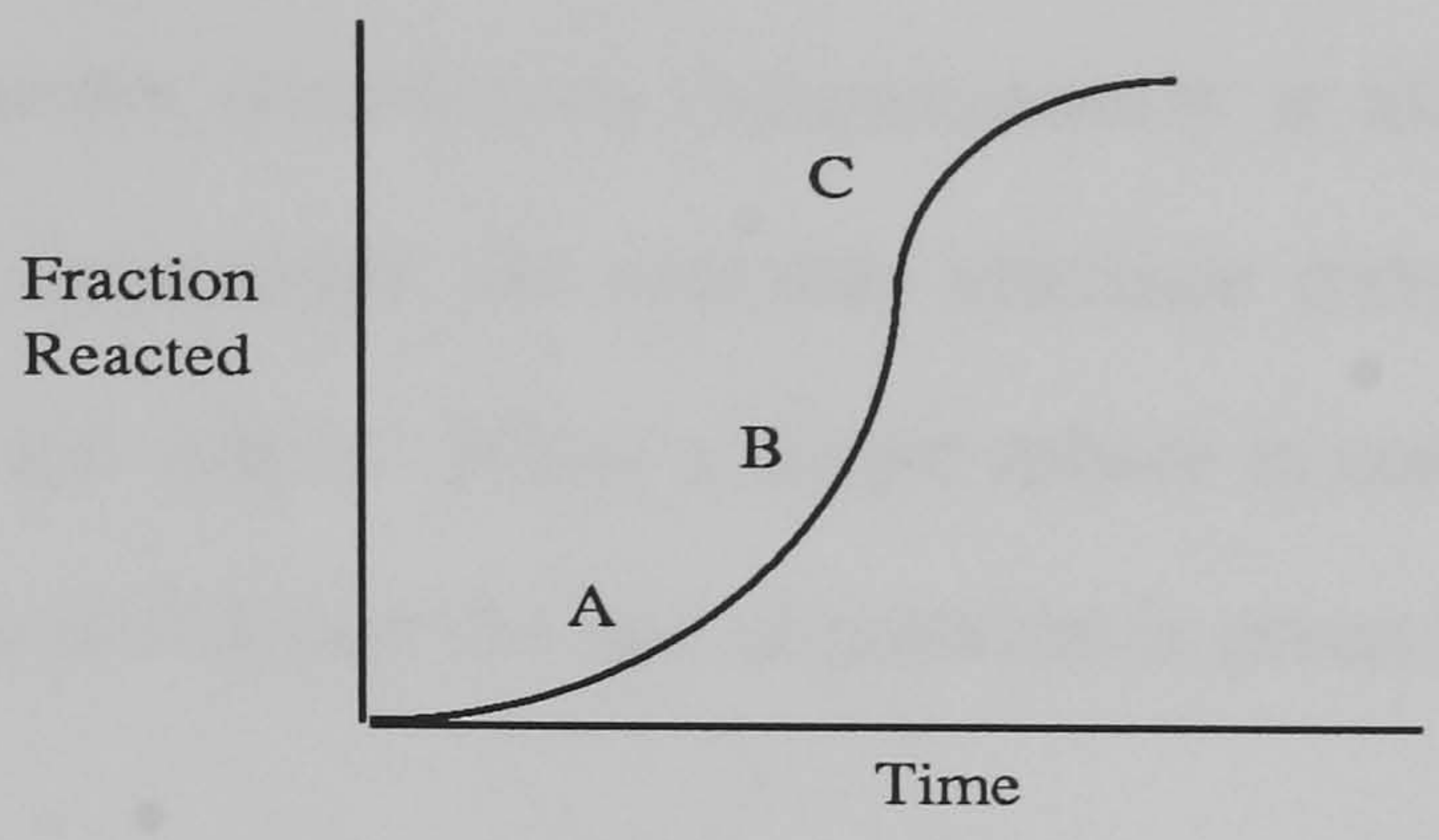


Figure 3.16 Characteristic sigmoid shape curve.

The regions indicated by the letters A, B, C are described as; A 'Nucleation' where the reaction starts at favoured points on the surface of the solid; B 'Growth' where the reaction spreads at constant linear velocity through the solid at an interface which is increasing in area; C 'Decay' where the reaction interface continues to progress at constant speed but now at an interface where interference from the growth regions reduces the overall interfacial reaction area. The relative importance of each region can vary from system to system depending on the detailed mechanism. For example, instantaneous nucleation over the whole surface of a spherical solid particle will result in the interface contracting towards the centre and will give a curve which shows no acceleratory growth phase (usually known as the contracting sphere model). The model and the resulting curve type are shown in figure 3.17.

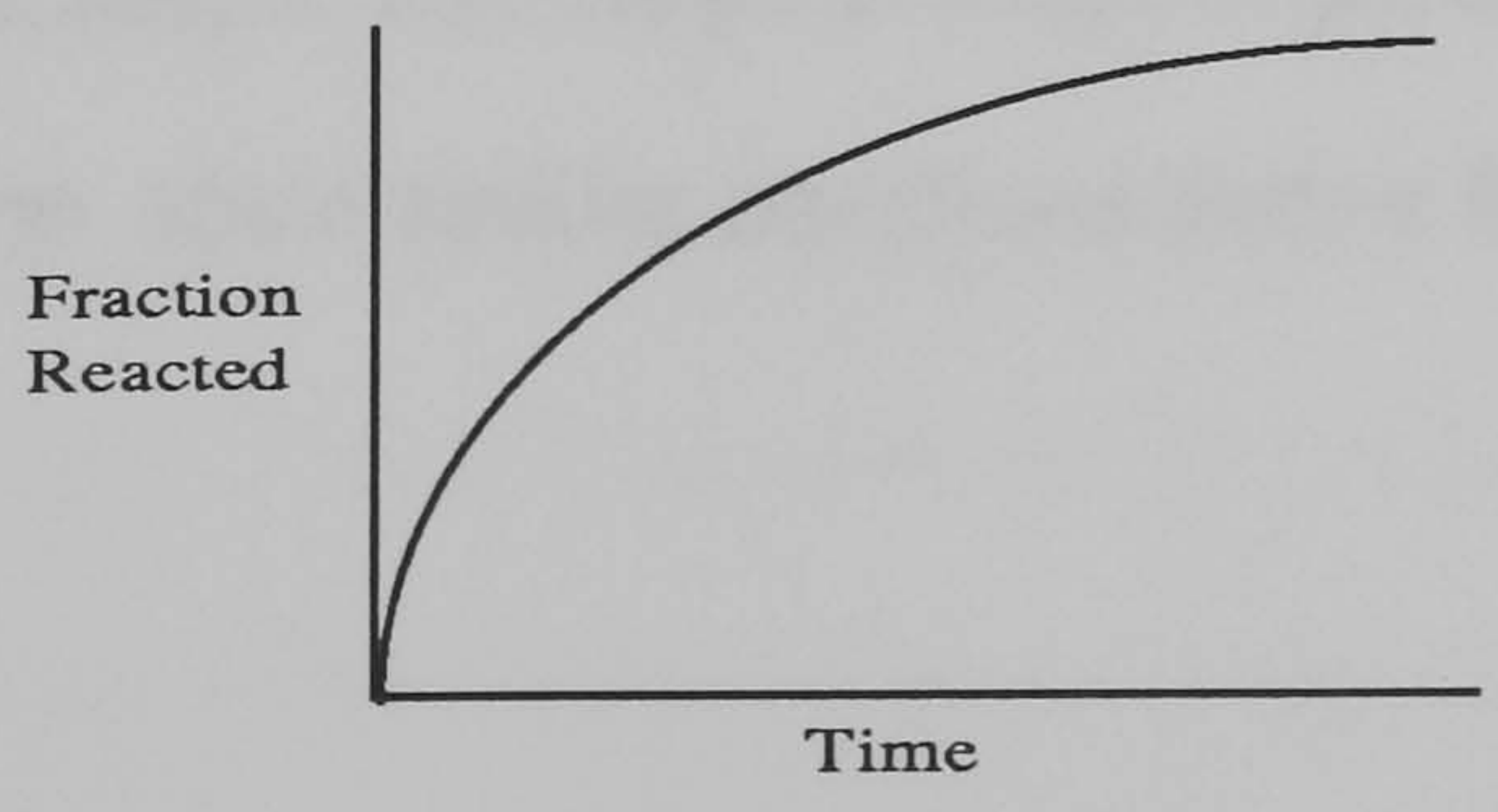


Figure 3.17 Characteristic curve produced when a contracting sphere type reaction is occurring.

3.4.3.1 A topochemical 'Contracting sphere' model with allowance for particle size distribution.

In the contracting sphere model the assumption is made that the particle of solid is spherical and that reaction commences instantaneously at all points on the sphere's surface. At constant temperature the reaction interface travels at constant velocity towards the centre of the sphere. When a single sphere is considered or a number of spheres all of the same initial size the rate of reaction is given by the expression:

$$1-(1-f)^{1/3} = kt$$

where f is the fraction of solid reacted at time t and k is the rate constant at the given temperature. Tonge (1984) has shown that when a particle size distribution is present in the solid the reaction rate decreases more rapidly than predicted by a simple contracting sphere model. This is due to the number of particles decreasing as the reaction in the smaller sized particles become completed whilst the larger sizes continue reacting. The powdered frit was shown (figure 3.18) to possess a wide particle size distribution.

It would be expected that there would be considerable deviation from the simple contracting sphere model in the later stages of reaction when the smaller particles have been consumed.

Apart from the particle size distribution effect it is also expected that the particles would not be perfectly spherical in shape. The irregular shape of particles does not invalidate the use of the $1-(1-f)^{1/3}$ function since similar equations derive for many roughly spherical particulates.

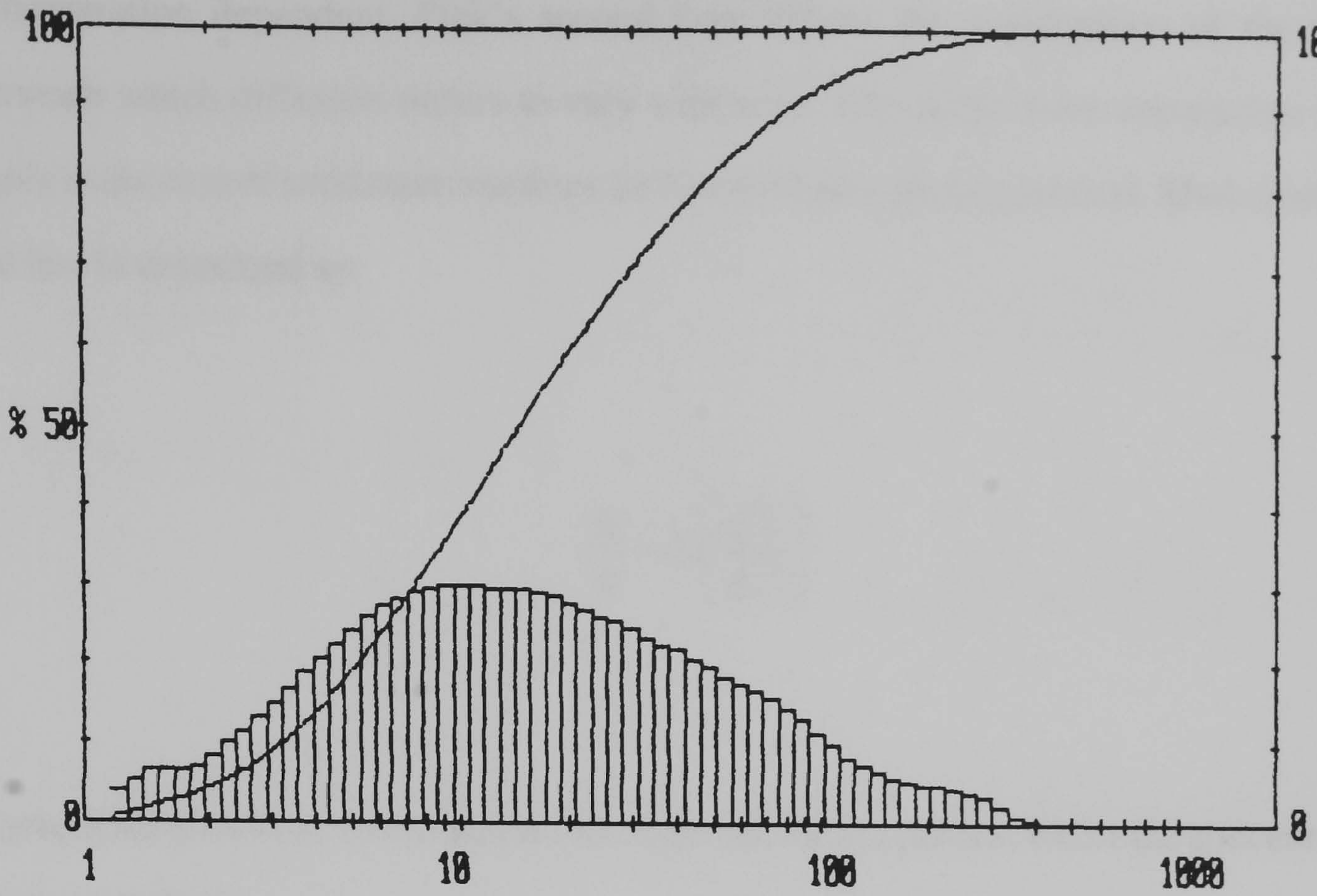


Figure 3.18 Particle size distribution curve for powdered frit #8.

3.4.3.2 Diffusionally controlled reaction models

The kinetics of diffusion phenomena are described by Fick's Laws. The First Law is mathematically expressed as:

$J = -D\left(\frac{dc}{dx}\right)$ where J is the rate of mass transfer

dc/dx is the concentration gradient

and D is a temperature dependent proportionality constant.

Fick's First Law is only applicable to systems in which mass transfer across a boundary is between phases of constant composition. The constant, D, is known as the diffusion coefficient. It varies from system to system and for a given system may also be concentration dependent. Fick's second Law allows the composition of the phases between which diffusion occurs to vary with time. This is the more appropriate law to apply in the case of solid state reactions such as the lustre glazing process. Mathematically the law is expressed as:

$$\frac{dc}{dt} = D\left[\frac{d^2c}{dx^2}\right]$$

where dc/dt shows the time variation of concentration at a point x, where the concentration gradient is dc/dx.

The solutions to Fick's Laws depend upon the boundary conditions, i.e. the limits in the integration of the differential equations shown.

For the lustre glazing process the concentration of hydrogen in the flowing gas can be regarded as constant and reaction takes place in the solid phase by diffusion of hydrogen into the solid, water out of the solid and diffusion of metal atoms and ions within the reaction zone. For the gas/solid diffusion processes such a an experimental set-up (depicted in figure 3.19) is known as a semi-infinite medium.

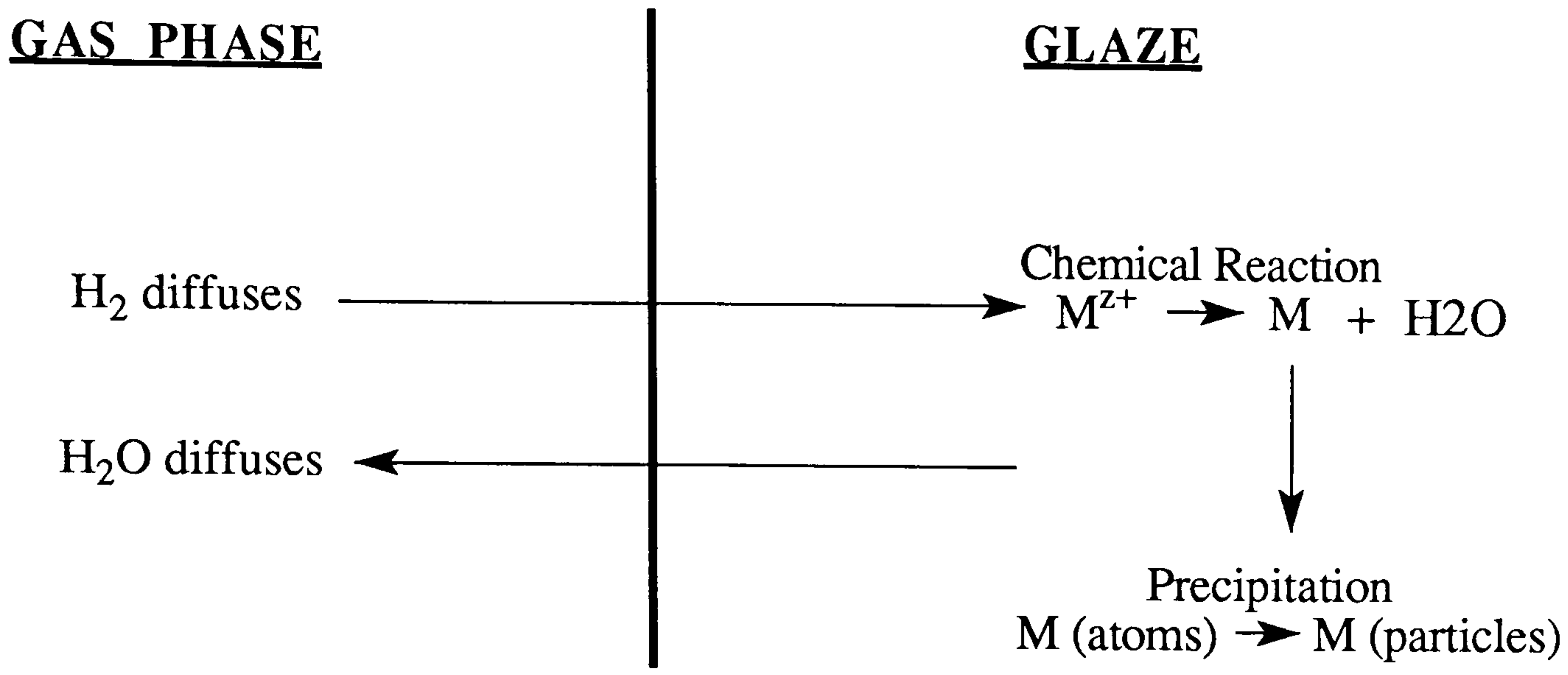


Figure 3.19 Diagram showing diffusion of reactants and products in glaze process

For a semi-infinite medium the solution to Fick's 2nd Law is

$$C = C_o \mathrm{erfc}\left\{\frac{x}{2(Dt)^{1/2}}\right\}$$ (J Crank, 1979)

where Co is the initial, constant concentration of the diffusing species,

and C is the concentration at time t and distance x from the interface across which diffusion is taking place, erfc is the complementary error function which occurs frequently in the solution to diffusion problems and tables of which are readily available. For the TG type of experiment a proportionality wold exist between the square of the extent of reaction and time.

The diffusion of water out of the glaze may be regarded as analogous to a tarnish reaction. In tarnish reactions on metals metal ions diffuse through an increasingly thick oxide layer to the surface where they combine with oxygen to form the tarnish film. As with other diffusion controlled processes the extent of reaction is proportional to the square root of time (or the extent squared is proportional to time). This is the so-called parabolic law.

For the formation of metal clusters a precipitation model may be appropriate. Solution of

Fick's second law for the initial stages of precipitation from a homogeneous solution gives

$$C = C_O \exp(-t/T)^{3/2}$$

where C is the average concentration in the solution at time t

Co is the initial concentration in the solution

T is the relaxation time.

In terms of the TG experiments the rate determining process can be distinguished in that

(a) (weight change)^2 is proportinal to time for gas diffusion

(b) ln(1-f) is proportional to (time)$^{3/2}$ for a precipitation process

3.4.4 Testing the Models Against the Experimental Data

When tested against the experimental data the parabolic law was found to hold over the first 50% of reaction as seen in figures 3.20 to 3.23.

The slopes of the (weight change)^2 versus time curve (i.e. the rate constants) were

62×10^{-6} at 550°C

68.6×10^{-6} at 570°C

68.65×10^{-6} at 590°C

23.7×10^{-6} at 610°C

There is a clear, catastrophic, slowing at the higher temperatures. This is doubtless due to sintering. Indeed at all temperatures there is evidence that as the reaction proceeds the rate becomes less than predicted by extrapolation of the x^2 vs t curve.

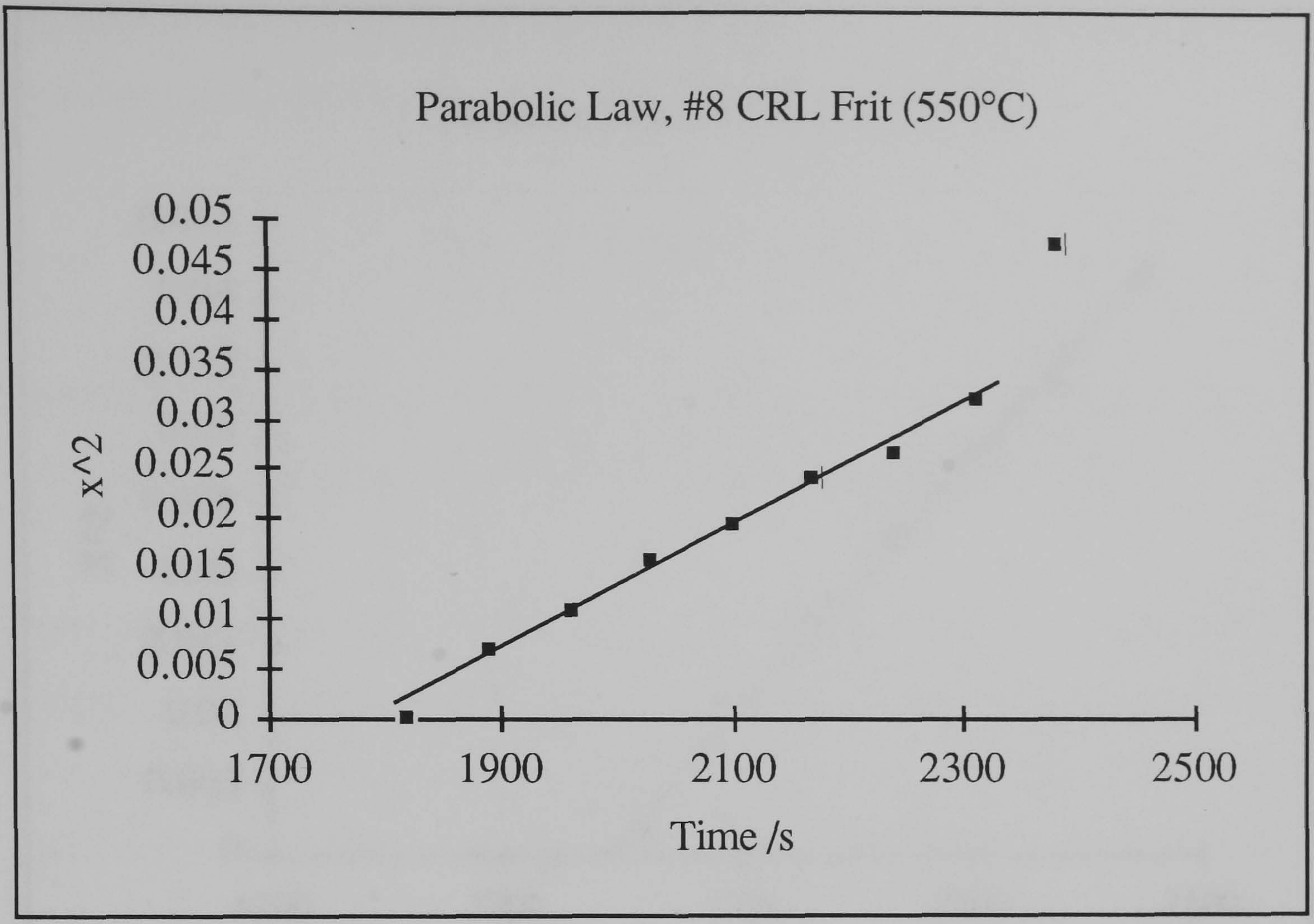


Figure 3.20

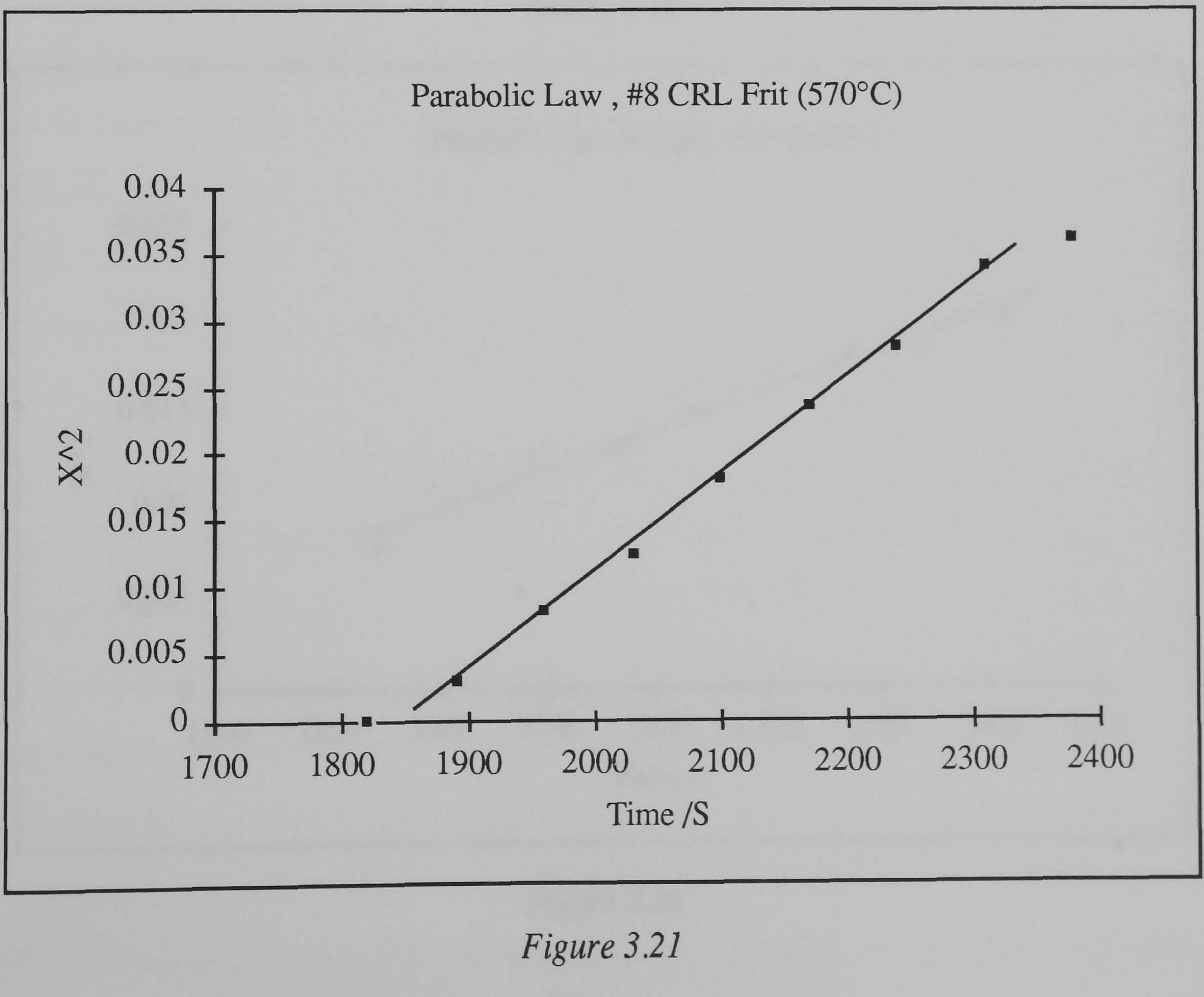


Figure 3.21

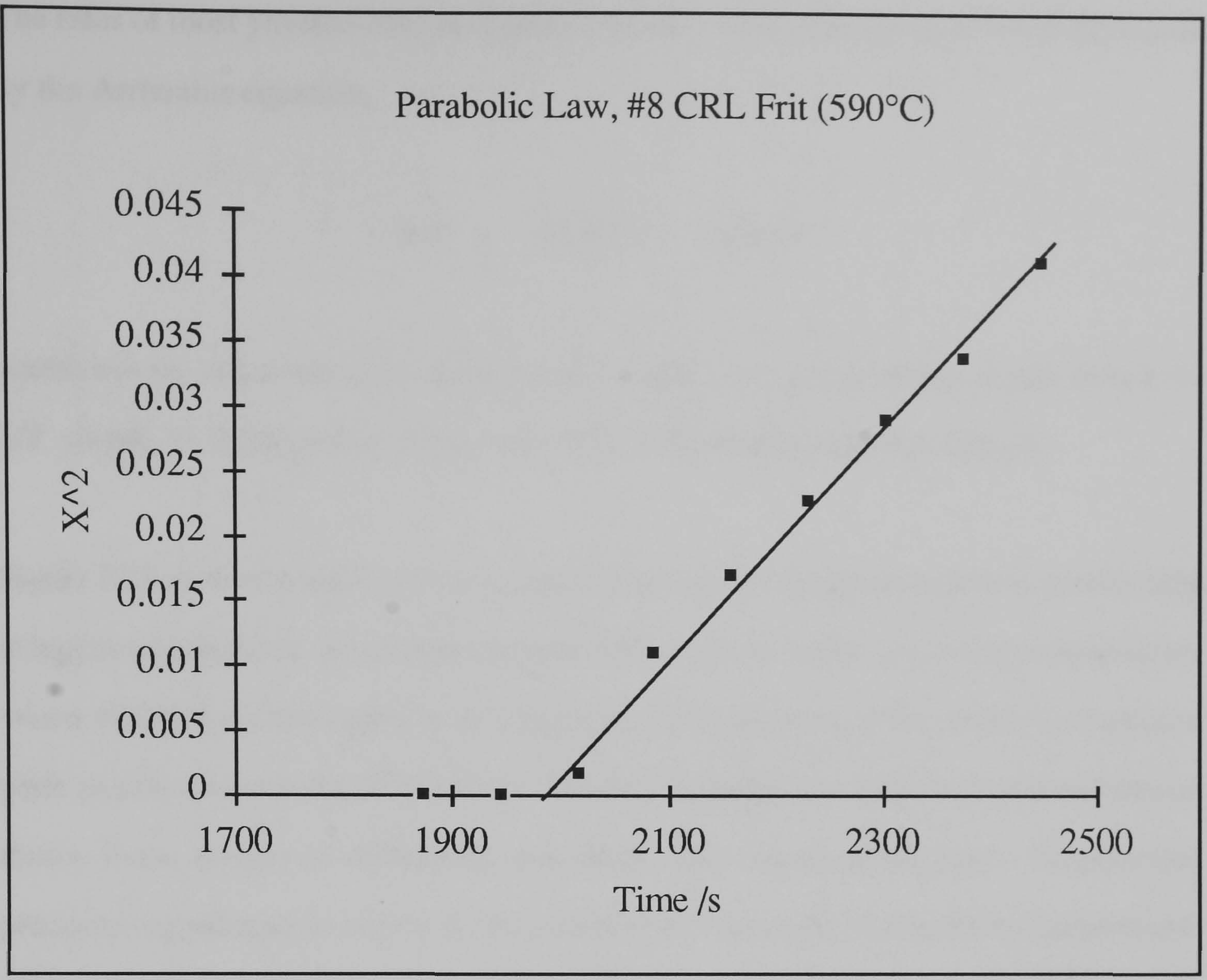


Figure 3.22

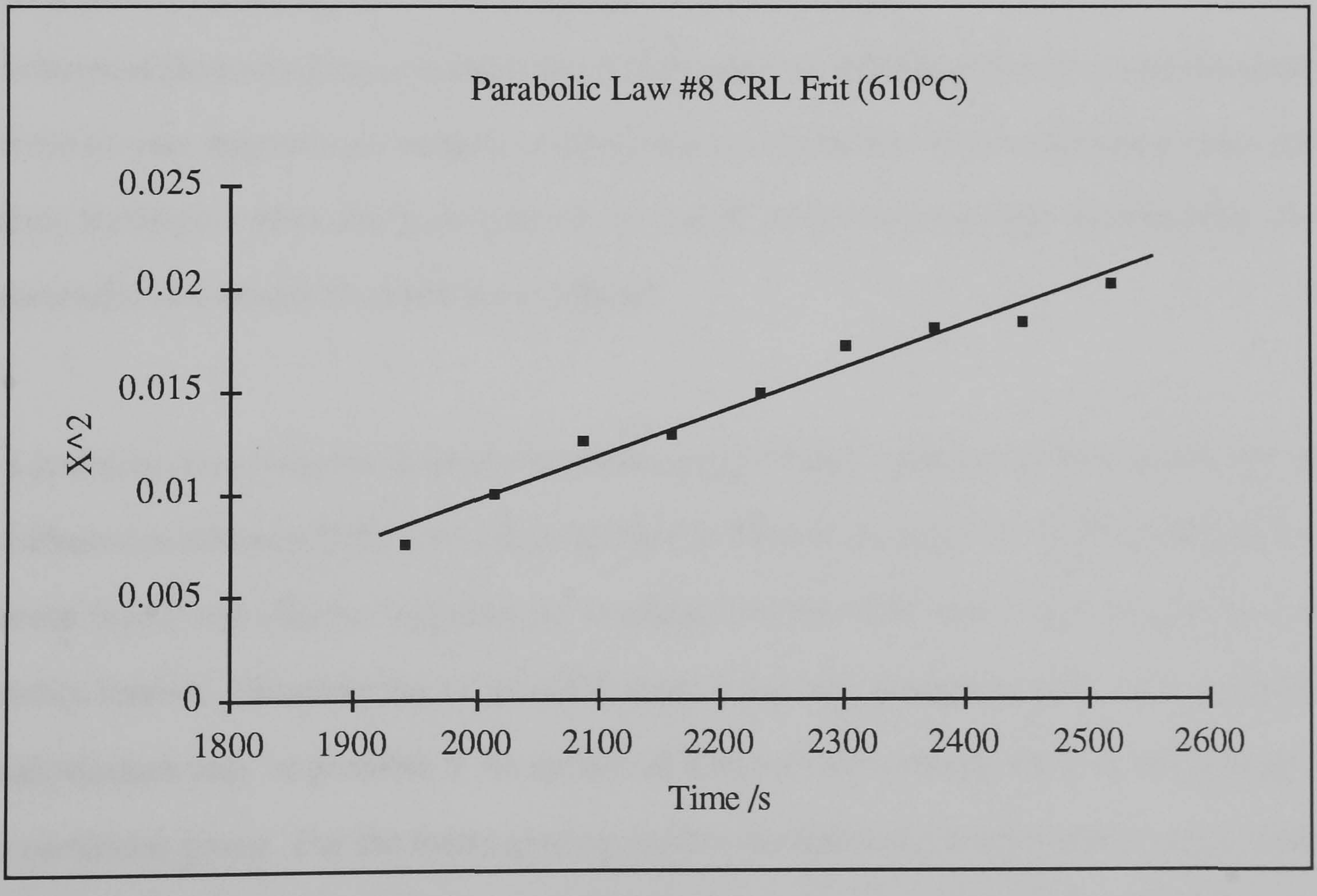


Figure 3.23

The rates of most physico-chemical processes have a temperature depedence expressed by the Arrhenius equation,

$$\ln k = -(E/RT) + \text{constant}$$

where k is the rate constant at temperature T and R is the gas constant. A plot of ln k vs 1/T should be linear and of slope -E/R if the Arrhenius equation is obeyed.

Figure 3.24 shows the failure of the equation in the case of the glaze reduction, particularly at higher temperatures where sintering was most evident. At the two lower temperatures, where sintering did not appear to be significant the application of the Arrhenius equation yilds an activation energy of 30 kJ/mol. This is a relatively low value in physico-chemical terms, more typical of diffusional processes than chemical reactions. Its principal practicall significance however, is that the reduction rate is little affected by temperature. Thus temperature gradients in the reduction kiln can be tolerated. A 40 K difference in temperature results in only a 10 % change in reduction rate.

In terms of the lustre glaze mechanism it is likely that the diffusion of water out of the glaze is the slowest step because water is a rather larger and therefore slower diffusing molecule than hydrogen. Had the precipitation of metal particles been rate determining the parabolic law would not have been obeyed.

A problem often found in dealing with diffusion problems is the lack of availability of the diffusion coefficient D for the system of interest. Empirical methods of calculating D for some liquid and gaseous systems are available but for solid state reactions the data is rarely known. However the values of D tend to fall into groups so order of magnitude calculations may be possible if the system of interest can be categorised as belonging to a particular group. For the lustre glazing system the diffusing species of interest are the hydrogen gas, the reducible ions and the product, water. In oxide systems the diffusion of oxide ions is rarely of importance because of their size in comparison to that of the metal ions.

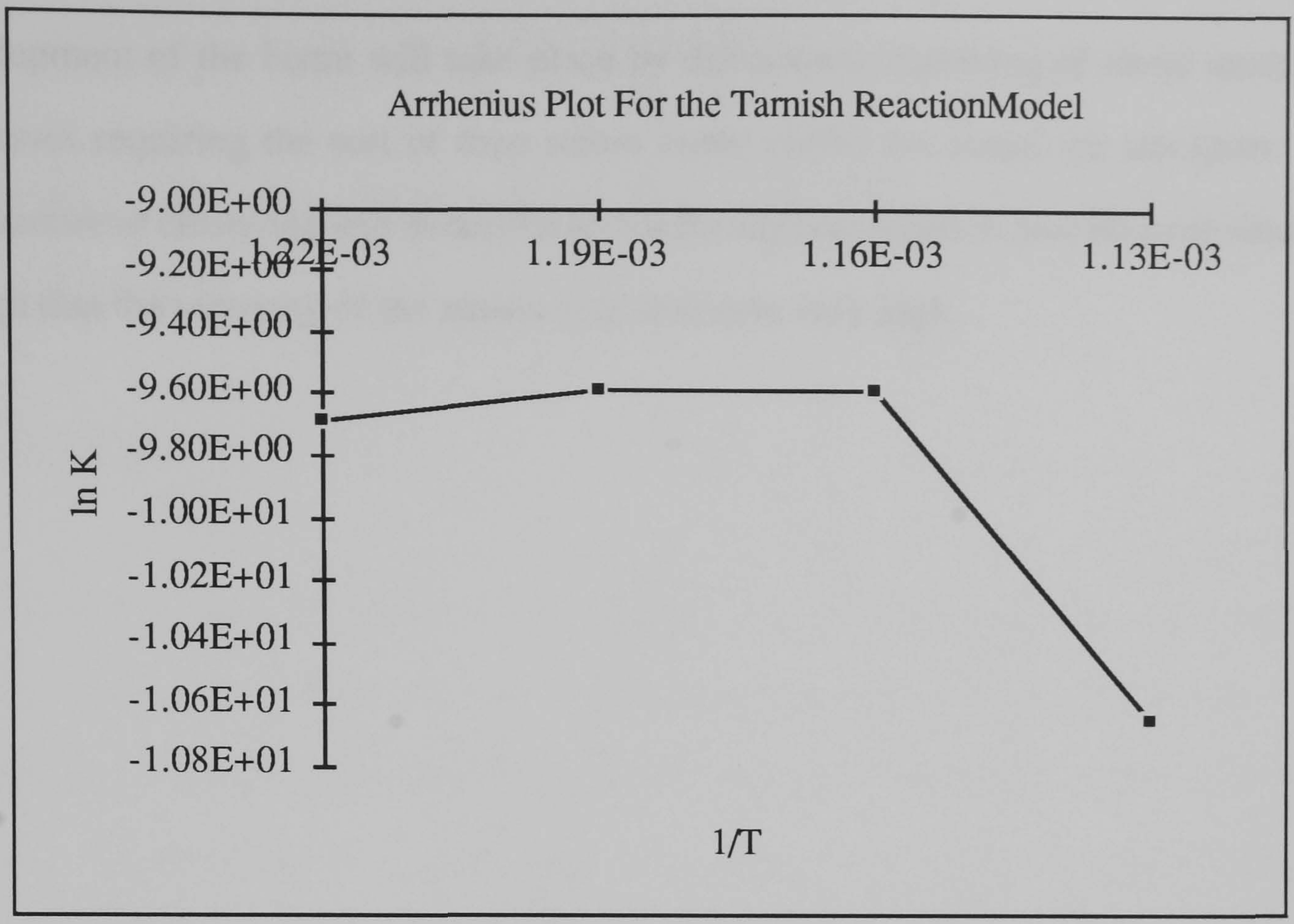


Figure 3.24 Arrhenius plot for diffusion rate data.

Molecular size is an important factor in determining diffusion rates especially where interstitial mechanisms operate. Hydrogen, being of small size has a very high diffusivity. Typically the diffusion coefficient for hydrogen in, for example, metals is of the order of 10^{-8} m^2s^{-1} at the temperatures of interest (Shewmon, 1963). Metal ion diffusion in oxides is generally characterised by much lower diffusion coefficients, about 10^{-13} m^2s^{-1} for vacancy mechanisms (e.g. Ni^{2+} in NiO) and 10^{-20} m^2s^{-1} for interstitial mechanisms (e.g. Fe in Al_2O_3) Askill, 1970).

The hydrogen saturates the top 10 microns in about 1 second. By contrast, the rate at which reduced species in this layer would be replaced by diffusion of ions from the interior of the solid is extremely slow.

The TG studies clearly measure the loss of the product water from the glaze and this is much slower than the rate of reduction of the copper and bismuth ions as would be expected given that the diffusion of a water molecule involves interstitial transport. The development of the lustre will take place by diffusional clustering of metal atoms by processes requiring the sort of time scales noted earlier for metal ion transport. The mechanism of clustering will be similar to that for any precipitation process from solution except that the viscosity of the matrix is in this case very high.

CHAPTER FOUR

4 Scanning Electron Microscopy and X-Ray Microanalysis for the Analysis of Glaze Materials

4.1 Introduction

The following chapter describes studies carried out using the techniques of scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and x-ray photo-electron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA). Scanning electron microscopy was used to examine grain structure of the raw materials used in the lustre glazes and to compare the cross sections of successful and unsuccessful clay paste lustres. EDX was used to determine elemental profiles in fired samples of lustre glazes and a series of samples of glaze #8 reduction fired at different temperatures. Samples of the same glaze were also examined by XPS to determine the valence states of elements within the glaze in order to establish how the observed colour changes relate to changes in the elements present near the surface of the glaze.

4.1.1 Aims of Experiments Described in Chapter Four

The aims of the investigations described in this chapter were as follows:

- To investigate the relationship between the physical structure of the substrate, the glaze or under-glaze and the development of the lustre effect

- To establish the nature of physical and chemical changes occurring in the lustre glaze during the reduction phase of the glaze firing, and to relate these to the visual effects.

- To use the information obtained from the various analytical studies outlined in this chapter, to expand on the topochemical model of the lustre glaze described in the previous chapter.

4.2 Scanning Electron Microscopy

The basic function of a scanning electron microscope (SEM) is to produce a highly magnified image of three dimensional appearance, derived from the action of an electron beam scanning across the surface of a specimen. The size and shape of features on the surface of solid bulk samples can be examined using SEM, as can such surfaces where roughness renders observation very difficult, or impossible by means of light or transmission microscopy (TEM), SEM having a depth of field of at least 300 times greater than that of light microscopy at the limit of resolution. The SEM can have a magnification range of between ten to several hundred thousand, the higher magnification range being limited only by image resolution. For these reasons, the S.E.M. was a suitable instrument to use in order to observe surfaces of various glazes and the changes occurring during different firing regimes.

4.2.1 Energy Dispersive X-Ray Analysis

An additional feature of SEM is the ability to derive chemical information about the samples being investigated through the use of 'energy dispersive X-ray analysis' (EDX). The technique of EDX makes use of the fact that X - Rays are produced whenever an electron beam interacts with matter, as in the SEM, and can be used to provide information about the elemental composition of samples being examined. On bombardment of a sample with an electron beam in vacuo, the amount of energy released by excited electrons in the sample is characteristic of the atomic number of the element exposed to the beam. The method is a non-destructive technique. The equipment available could examine samples up to 100 mm in diameter.

A research study undertaken to find suitable ways of replicating a clay paste lustre finish for conservation purposes, using nacreous or pearlescent pigments, based on an acrylic polymer medium (Tennent, *et al.* in press), six fragments of medieval Spanish lustre ware were examined by SEM, EDX and TEM. The study revealed a uniform distribution of copper crystallites of c 2 - 4 nm in diameter, light scattering from which was thought to be responsible for the lustrous appearance of the shards.

Both SEM and EDX have been used in the qualitative examination of glaze surface flaws. A surface flaw was identified as refractory material which had fallen from the lining of the kiln during the firing (Althof, 1991). The study also revealed contamination of the clay body by silicon carbide, in this case only SEM was used as carbon (atomic number 6) is too low to be detected by EDX. Pinholes at the surface of a glaze were examined by SEM and were revealed to be caused by pyrites leading to iron enrichment in the body, this was detected by EDX. The use of EDX and X-ray microprobes have proved to be valuable techniques in the examination of the chemical structure of ceramic glazes. The elemental composition of inhomogenous glaze layers was determined using EDX by Hammer and Kranz (1986) in the study of origins and ages of East Asian porcelain glazes. Cross sections of Jun (Chun) glazes examined by Kingery and Vandiver (1983) and the elemental composition of crystals formed during cooling of glass-ceramics containing sulphur were examined by Orts *et al.*. (1988). Both employed the technique of EDX.

Gaprindashvili *et al.* (1984), describes a study of the effects of reduction on softened glazes, with the aim of examining the glazes chemical composition, electrical conductivity, and the structure of the glaze layer in which EDX was the investigative technique used. The glaze formula quoted in the paper contained 10% bismuth oxy-nitrate, 1.5% cobalt oxide, the rest of the glaze consisting of a lead-alkaline frit and clay. The glaze described was fired to 950°C and reduced at 660°C. The glaze was a gold-violet colour following reduction. The glaze layer was 120 - 150 μm thick. EDX was used to examine the oxygen distribution across the glaze layer. Attempts at doing this by passing the electron beam across the profile of the glaze were unsuccessful due to the marked heterogeneity of the glaze. An alternative technique was therefore adopted, the surface layers of the glaze were removed 10 μm at a time by polishing. Initial results obtained by the researchers were effected by absorbed moisture from the atmosphere, as a result the oxygen content was above the theoretical value calculated from the glaze components. Samples used in subsequent studies were dried by heating to 350°C prior to examination. The oxygen content of the glaze studied showed a maximum oxygen content at the top surface of the glaze. After removal of 10 μm of glaze the oxygen content was at its minimum. Beyond the 10 μm layer the oxygen content gradually increased with depth. The electrical resistance across the glaze surface was also measured by passing a current between electrodes attached to the glaze with silver paste. The electrical resistance showed a slight increase as the surface layers were removed, these results were also effected by residual moisture. The conclusion reached was that the reduction of bismuth in the glaze was essentially a surface phenomenon, the maximum reduction occurring just below the surface at a depth of 10 μm.

The technique of EDX has been successfully used for the non-destructive chemical analysis of ancient samples of ceramic and glass in an attempt to identify their origin. For example, Rincon and Navarro (1990) analysed samples of ancient glassware found at El Hierro in the Canary Islands. On analysis by EDX, the samples were shown to be too low in manganese oxide and iron oxide to have been manufactured from indigenous materials, which meant the samples had been imported. Ancient samples of ceramic were examined from the same area, using EDX to obtain a chemical analysis in an attempt to identify the origin of the samples (Isidro and Navarro, 1990; Rincon *et al.*, 1990).

The main disadvantages of EDX are that distinctions cannot be made between ionic, non ionic and isotopic species, nor can it detect elements with very low atomic numbers ($Z < 6$). However the technique does provide basic information regarding the relative proportions of the main elements present near the surface of a glaze.

4.2.2 X-ray Photoelectron Spectroscopy

A related analytical technique to EDX is that of X-ray photoelectron spectroscopy (XPS), which employs the use of low energy X-rays rather than high energy electrons. Photoelectron spectroscopy is one of a group of techniques in which photoelectrons are emitted from a sample following excitation by electromagnetic radiation of a suitable wavelength. Photoelectrons excited from the energy levels of atoms within a sample are separated on the basis of their kinetic energies. A photomultiplier and recorder device produces data in the form of electron yield against electron energy. The technique can be used to determine the atomic or ionic state of individual elements present in a sample and provides information on the chemical environment of the constituent atom. The system obeys the Einstein relationship:

$$E_K = hv - E_B$$

Where:

E_K is the kinetic energy of the photoelectron

E_B is the binding energy of the electron

v is the wave number of the incident radiation

h is Planck's constant

hv is the energy of the incident beam.

E_B is equivalent to the binding energy of the electrons in the anode of the instrument.

This is illustrated diagrammatically in figure 4.1, in which the incident beam of x-rays with energy hv excites electrons in a sample. Although the incident x-rays penetrate the sample, collisions between electrons cause the kinetic energy of the electrons to be dissipated in inelastic processes. For this reason only electrons near the surface of the sample (approximately 50Å or 5 nm) have sufficient energy to reach the detector.

The XPS technique can be used to give a qualitative chemical analysis of the surface of

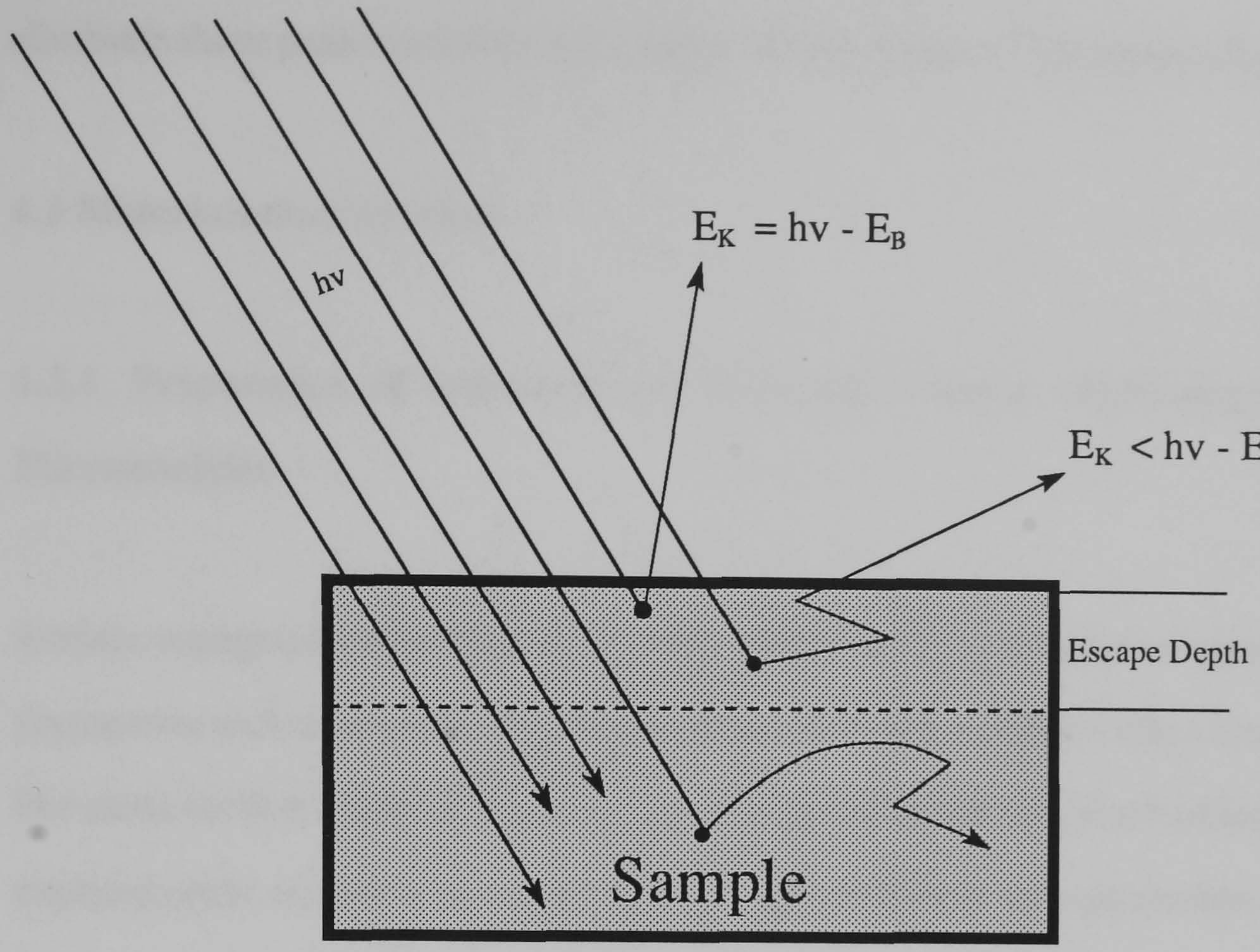


Figure 4.1. Diagram showing the excitation of an electron from near the surface of a sample.

a sample. All elements can be readily identified, with the exception of hydrogen and helium. To acquire data from greater depths the surface of the sample must be removed either by chemical or physical abrasion. Quantitative analysis is also available using XPS since peak areas are directly proportional to atomic concentrations. The area under the peak is calculated by the computer attached to the instrument.

Each element present in a sample can give rise to a number of XPS peaks depending on the energy level from which the electron was excited. In addition to the photo peaks observed from XPS, additional peaks are produced by the Auger process, in this case electrons are emitted as part of a relaxation process following excitation of the iron/atom species. The photoelectrons produced are used as the basis of another related technique, known as Auger Electron Spectroscopy (AES) (Briggs and Seah, 1983). These peaks are distinguishable by their greater line width and the fact that their kinetic energy is independent of the incident radiation. By changing the X-ray source from magnesium to aluminium a shift in the Auger peaks is observed. A computer data base is used to eliminate these peaks and to identify peaks characteristic of particular element species.

4.3 Materials and Methods

4.3.1 Preparation of Specimens for Scanning Electron Microscopy and X-Ray Microanalysis

Surface topography examination of a sample using EDX requires no specialist sample preparative techniques other than ensuring the specimen will fit into the vacuum chamber. For cross section analysis, the sample was first embedded in a block of resin before the exposed cross section area was ground and polished prior to examination.

Specimen preparation for SEM occurred after EDX examination had been carried out, since SEM preparation involved modification of the sample in order to produce an electrically conductive surface. Non conducting specimens become negatively charged during analysis, charge allowed to build up badly affects the quality of the image. Specimens for analysis were coated with a thin layer of gold by sputtering using vacuum evaporation, this provided a low resistance path to earth for the electrons. The thickness of the applied gold layer was below the resolution of the instrument and did not affect the image produced.

On SEM examination of fired samples, images were viewed over a range of magnification between 40 to 300 times. Scanned areas of the samples were re- examined using back-scattered electrons which provided alternative views, demonstrating the presence of discontinuities in the substrate and differences in elements present, for example, differences between elements present in a lustre layer and elements present in the resin in which the samples were embedded. When satisfactory results were achieved, the images were photographed using 35 mm black and white film which was later developed and examined.

Two series of investigations were carried out using EDX. The first was a feasibility study intended to establish whether the EDX technique could be a suitable method for the examination of the chemical composition of lustre glazes. The top surface of a range of samples were examined with the instrument set to a magnification of 30 x and an accelerating voltage of 15 kV. The samples examined, showing reduction times and reducing agents, are listed in table 4.1. The second investigation involved study into the nature of physical changes occurring in the lustre glaze lattice during the reduction phase of the glaze firing.

Table 4.1 Samples Examined By EDX In Preliminary Study

400x Magnification, 15 kV

Sample No.	Pigment / Glaze Used	Reduction time/ min	Reductant
001	JM5 over #3	40	Propane
002	JM 5 over #6	40	Propane
003	JM 12 over #6	40	Propane
004	FR1 over #6	40	Propane
005	#15	none	none
006	#15	20	5% H_2 in N_2
007	JM3 over #6	30	Propane
008	#10	20	Propane
009	#15	20	5% H_2 in N_2
010	JM3 over #6	30	Propane
011	#15	15	Propane

The samples used in the subsequent investigation of lustre glaze development using EDX were prepared in the following manner: Ceramic tiles (150 mm x 150 mm) were glazed using the lustre glaze #8 (table 2.2), chosen as a representative standard lustre glaze and glost fired conventionally to 1060°C with a one hour soak period. The glazed tiles were cut into approximately 75 mm square pieces. The pieces of glazed tile were then fired, under controlled conditions of atmosphere and over a range of temperatures, in a laboratory muffle kiln. During firings at each temperature, the samples of glazed tile were reduced using 5% hydrogen in nitrogen gas for 15 minutes. A temperature range was chosen starting at 580°C and increasing at 50°C intervals to an optimum temperature of 680°C, this being a temperature known from previous studies to produce a good lustre from glaze #8, using 5% hydrogen in nitrogen for 15 minutes reduction time. The temperature was further increased, again at 50°C intervals, until no colour change was observed on the surface of the lustre glaze. Sub-samples were cut from glazed tiles which had undergone reduction firings, these were placed into the SEM vacuum chamber for EDX examination. Data were plotted as temperature against percentage element detected.

Further sub-samples were taken from tiles which had been fired at 580°C, 730°C and 1000°C for cross section analysis. These samples were embedded in resin blocks, ground and polished, so that the cross section of each glaze could be examined by EDX. The resin potted samples were coated in colloidal carbon paste to provide a conducting surface to prevent charge accumulation occurring on the surface of the sample. The sections were examined with the SEM scan coils switched off in order to carry out spot analysis. Readings were taken at 50 μm intervals from the top edge of the glaze.

During the process of EDX analysis, when information on the elemental composition of the surface of a sample was required, a low (30x) magnification was selected. This resulted in a relatively large scan area emitting x-rays. The resulting data produced by the instrument were displayed in the form of peaks, the positions and sizes of which were characteristic of particular elements and their concentrations in the sample. The identification of elements and their relative abundance in the sample were calculated by the instrument. When elements were identified as being present in the specimen, they were selected using a cursor, the instrument calculating their relative percentages. Plots of count rate against energy released were obtained, which were used in the comparison of elements identified from samples which had undergone different reduction regimes. Used in this manner the instrument did not give a complete chemical analysis of the specimen but showed the relative amounts of the selected elements present. The instrument was also used to provide data from a scanned area and also, by switching off the scan coils, provided data from a single spot corresponding to the diameter of the electron beam. Spot analysis was used when the cross section of a material was being examined and an element profile of the cross section was being studied. In this case a series of measurements were made with the beam in a fixed position whilst moving the specimen along one axis at measured intervals.

Only the area being scanned by the SEM will produce x-rays, this area may or may not be representative of the whole sample.

The accelerating voltage being used is another important variable. At high voltages, >10 kV for example, the beam penetrates some way into the specimen. If the material being examined is not homogeneous, varying the accelerating voltage will give differing results. For this reason both the surface and cross-section of specimens were examined.

3.2 Preparation of Specimens for X-ray Photoelectron Spectroscopy

The aim of the investigations using XPS was to try and identify the valency states of the elements present at the surface of the lustre glaze. A sample of glost fired tile glazed with #8 was reduced in an electric kiln using a 5% hydrogen in nitrogen gas mix as the reducing agent. Three distinct zones of colour were evident at the surface of the tile. Tile 2 shown in table 7.2 is similar to the tile used for the XPS investigations. For the purpose of identification the three zones were termed blue, copper and electric blue. The copper and electric blue zones appeared lustrous where as the blue zone did not. Samples (10 mm x 10 mm),were taken from the three zones and given a conducting coating of colloidal carbon and out-gassed for 24 hours prior to being placed in the XPS apparatus. Plots of electron yield versus binding energy were obtained using both Al Kα radiation and Mg

Kα radiation so that Auger peaks could be identified and eliminated from the results.

4.4 Results of Microanalytical Studies

4.4.1 Results of EDX Analysis

When a lustre glaze is fired under particular conditions of temperature and atmosphere, a dramatic colour change at the glaze surface is observed. For example the chosen standard lustre glaze #8 (table 2.2) is dark blue before reduction, after reduction it may become an electric blue colour, a copper metal colour or red or purple red, depending on the firing conditions used. The reduced metal particles are prevented from re-oxidising by a silica-alumina layer at the outer surface of the glaze, which solidifies on cooling. Figure 4.2 shows a typical plot count rate against energy released obtained from EDX examination of samples listed in table 4.2. When samples 005 and 006 (table 4.2) were compared no differences were observed despite a marked difference in their visual appearance. These two samples were the same except 006 had undergone reduction for 20 minutes. This demonstrates the limitations of the technique which was not capable of detecting changes in the valency of the elements in the sample.

Figure 4.3 and 4.4 shows the relative percentages of elements detected in samples of glaze #8 fired at differing temperatures. The results obtained from EDX analysis showed that the proportions of the elements present in lustre glazes vary as reduction temperatures were varied. The glaze sample reduced at 730°C (figure 6.5) showed the strongest copper lustre appearance. At a reduction temperature of 580°C, the lustre glaze was too viscous and no colour change was observed. Alternatively the reaction is occurring too slowly at the lower temperatures. As the temperature at which reduction was carried out increased, lustre appeared to develop more easily. The samples reduced at 830°C and 1000°C appeared cloudy and had lost any lustrous appearance. This may be due to the sintering behaviour of the copper present in the glaze. As the reduction

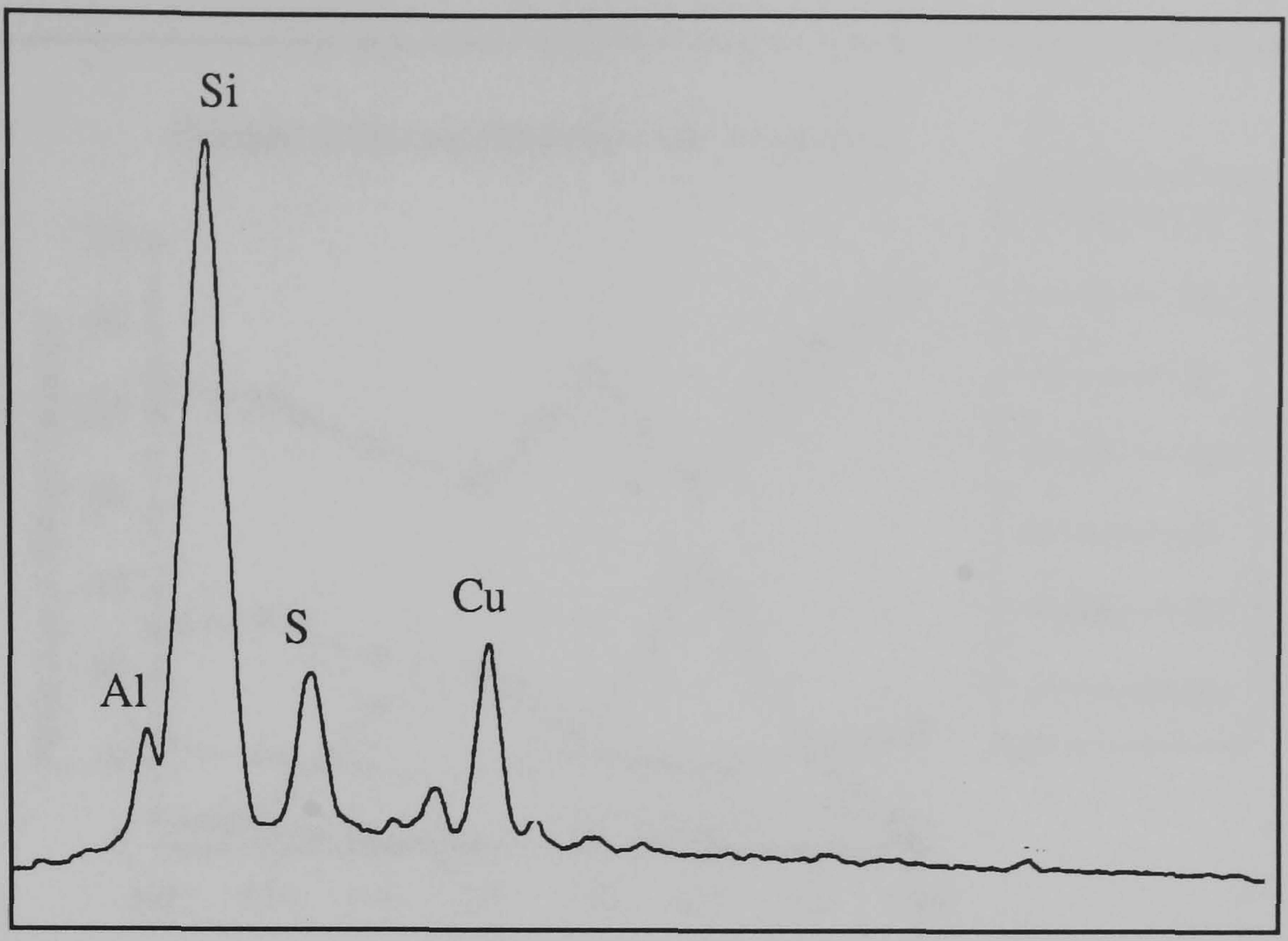


Figure 4.2 EDX plot obtained from the surface examination of lustre glaze #15 following reduction.

temperature increases the reduced copper particles begin to sinter together. As the mass of the sintered copper particles increases the tendency is for the copper to sink into the melt. If lustre glazes are refired to their maturing temperature after undergoing reduction they will revert to the appearance of an unreduced glaze. The lustre can be re-established with a further reduction stage. How many times this procedure can be repeated has not been established. The temperature at which sintering occurs can be estimated from the Tamman temperature (section 3.4.3).

Changes occurring in elements other than copper were less easy to identify. Bismuth for example could not be separated from the EDX peak obtained for lead by the instrument being used, and so changes in the proportions of this metal were not recorded. Examination of samples prepared as cross sections potted in resin were not conclusive. This was thought to be due to the limits of the resolution of the instrument, the lustre layer was localised near the surface of the lustre glaze and was therefore difficult to detect by EDX. A full elemental map of the cross section would need to be performed in order to detect

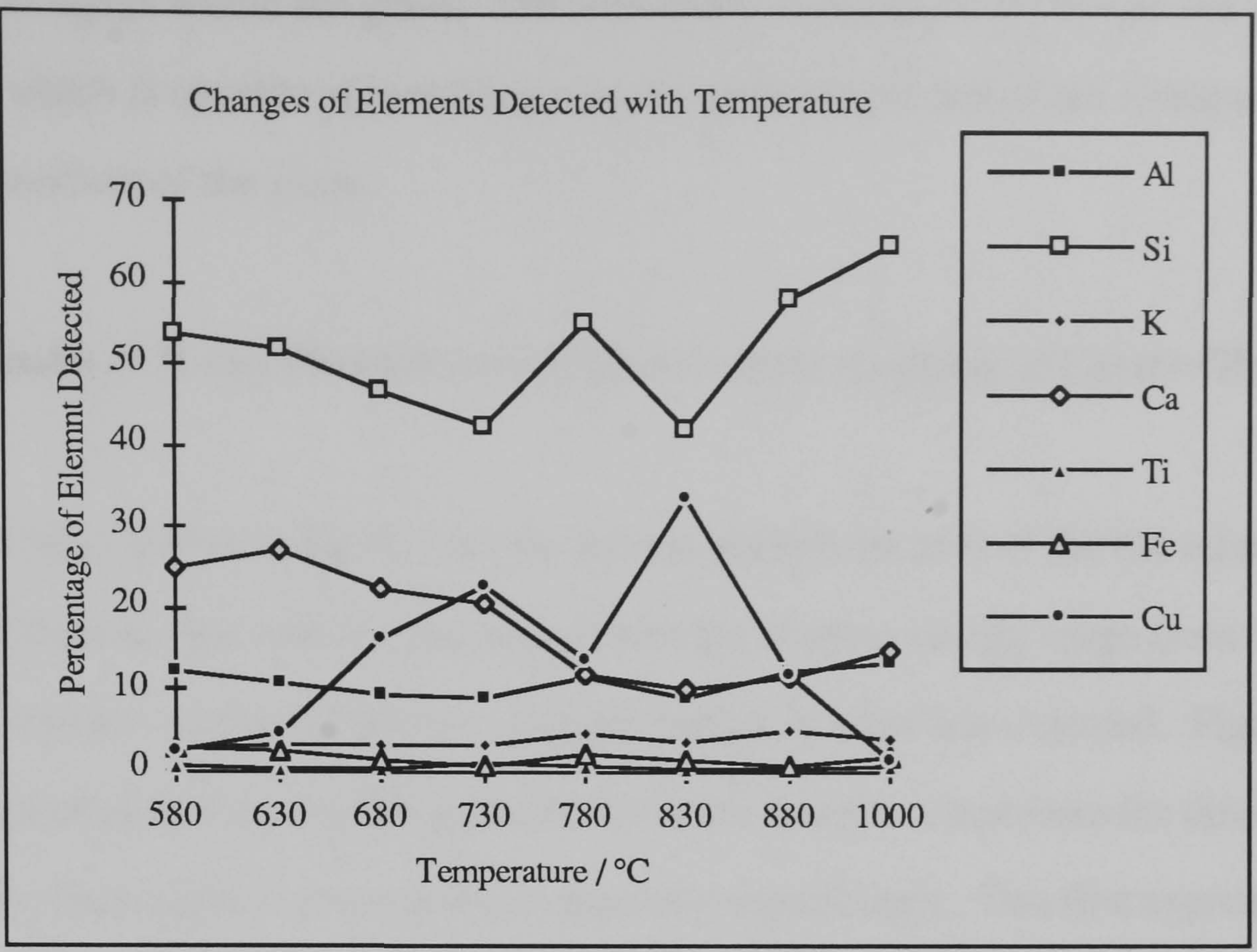


Figure 4.3 Graph shows the relative percentage of elements detected by EDX at different reduction temperatures.

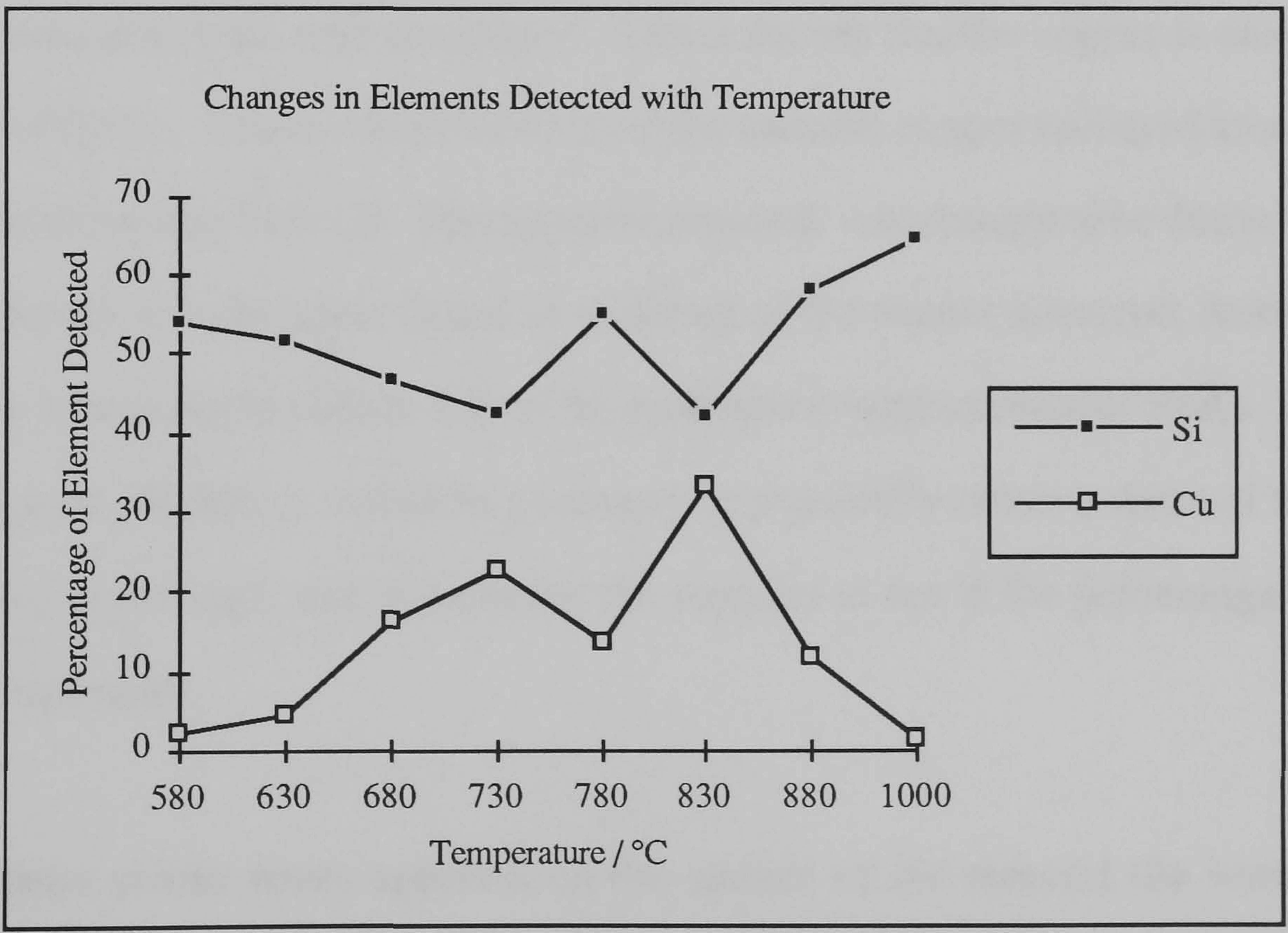


Figure 4.4 Graph generated from the same data as figure 4.3 but only copper and silica has been plotted so as to show the relationship more clearly.

individual layers within the glaze. The limitations of the EDX technique led to the use of XPS, which is capable of providing a more complete picture of the elements present near the surface of the glaze.

4.4.2 Results of X-ray Photoelectron Spectroscopic Analysis of Lustre Glaze #8.

The wide scan shown in figure 4.5, was produced from the area of the tile referred to as being an electric blue colour. The scan covers the binding energy range from 0 to 1000 eV and has been annotated to give a representation of what was detected. Figure 4.6 is a montage of plots showing the peaks for Cu in the samples taken from the three regions of the tile. Each curve is presented at comparable sensitivities . To a first approximation, these plots indicate the relative amounts of Cu present in the three samples. For the top curve, (electric blue in colour) the XPS peak is accompanied by a satellite peak (marked S). The presence of the satellite peaks indicates Cu(II) is present. In the plot produced from the blue glazed area of the tile, there is a lower concentration of copper and the satellite structure is not well developed. This indicates that the copper is most likely in the form of Cu(I). The curve obtained from the metallic copper coloured area of the tile appears to show very little Cu. This apparent anomaly was thought to be due to the copper sinking deeper into the glaze lattice as sintering of the copper occurred, thereby falling below the escape depth (figure 4.1) of the instrument (approximately 50 Å). In order to investigate this further it would be necessary to physically remove some of the sample surface (by polishing), and re-examine the samples to see if the percentage of copper detected increases.

The different colour zones apparent on the surface of the reduced tile were found to correspond to different valency states of the reducible metals present in the glaze. If a tarnish type reaction is operating with atoms of reduced species subsequently clustering to form the increasingly metallic appearance of the surface layer. Metal cluster size changes would be responsible for the changing appearance of the lustre through light

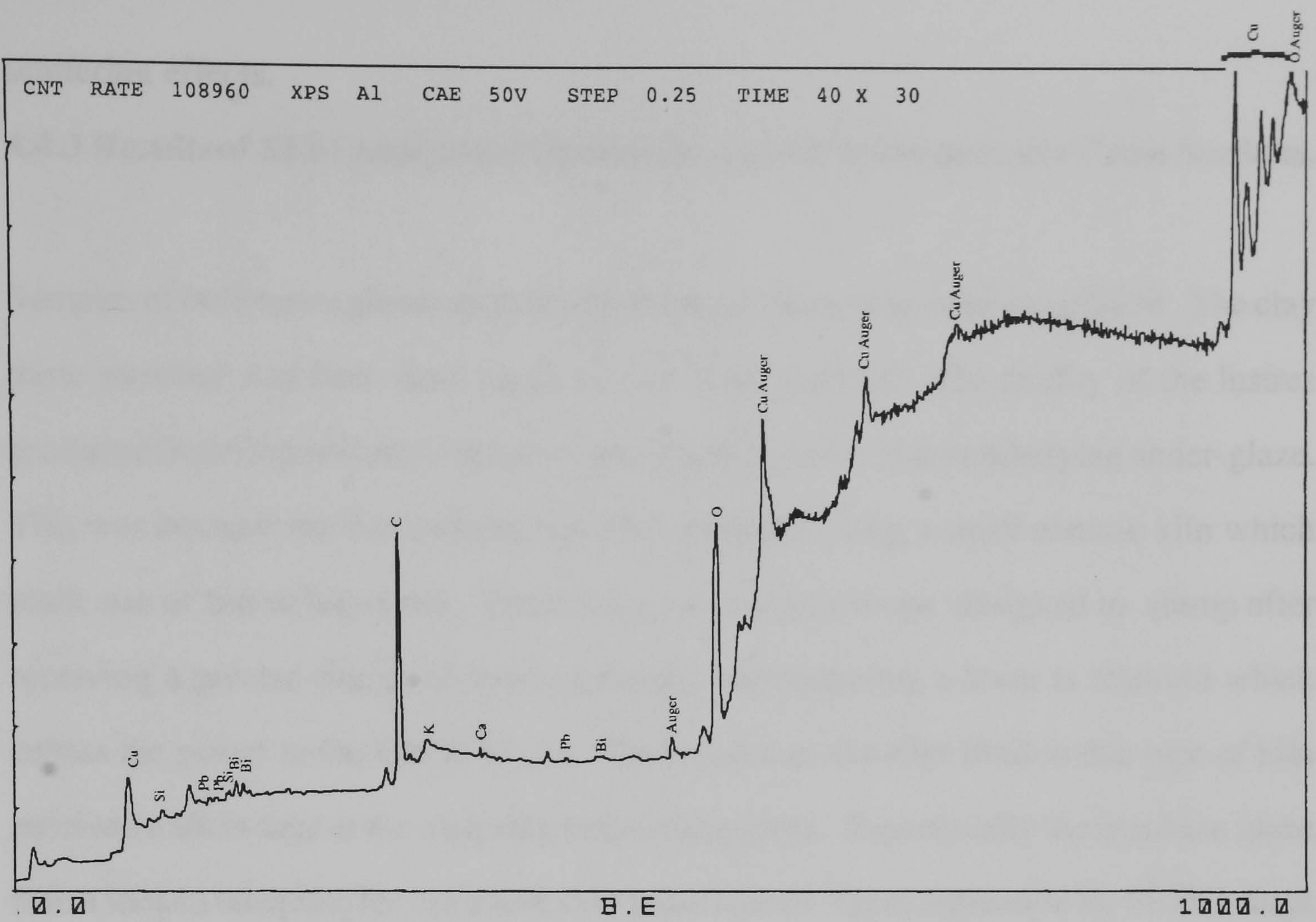


Figure 4. 5 XPS wide scan covering a binding energy range from 0 - 1000 eV illustrating the range of elements detected from the electric blue area of the tile.

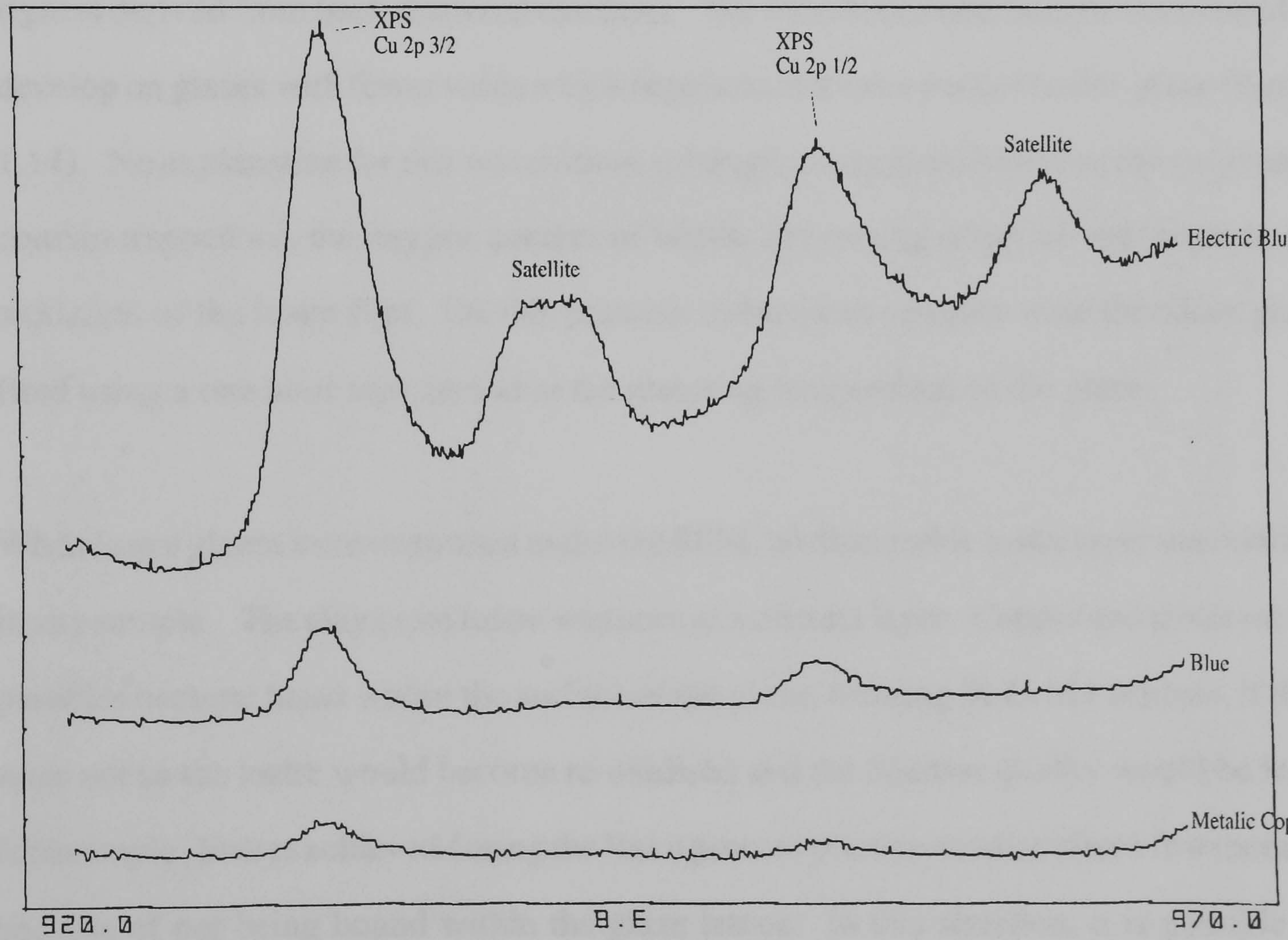


Figure 4. 6 An expanded view of the XPS curves allowing the comparison of the relative amounts of copper detected for each zone of the sample tile.

scattering effects.

4.4.3 Results of SEM Analysis of Under-Glaze and Clay Paste lustre Cross Sections.

Samples of both lustre glazes and clay paste lustres were examined using SEM. The clay paste samples had been fired using a down draft gas kiln. The quality of the lustres produced from this were not consistent, nor was the quality of the underlying under-glaze. This was because the tile samples had been prepared using a small electric kiln which made use of trip or bar cones. These are a form of pyroscope designed to slump after receiving a precise degree of thermal energy. On slumping, a lever is released which causes the power to the kiln to be cut. The result was that tiles fired in this type of kiln received a short time at the maturing point of the glaze. Superficially the resulting glaze finish looked adequate for use under clay paste lustres. On examination by SEM, a large number of voids in the under-glaze were revealed (figure 4.13). Figure 4.13 shows a split screen image. The left side of the image is derived from the secondary electrons and the right is derived from back scattered electrons. The most successful lustres were found to develop on glazes with fewer voids which represented a more mature under-glaze (figure 1.14). No explanation for this was evident although it was speculated that the voids may contain trapped air, the oxygen content of which preventing adequate reduction or re-oxidation of the lustre film. On this premise, subsequent samples were therefore glost fired using a one hour soak period at the maturing temperature of the glaze.

When lustre glazes were examined under the SEM, no discernible lustre layer was visible in any sample. The clay paste lustre was seen as a distinct layer. Copper and silver metal particles become fused within the surface of the glaze, forming Si-O-M+ bridges, if this were not so the lustre would become re-oxidised and the lustrous quality would be lost, for example, lustres achieved during the Raku process often re-oxidise after a few months because of not being bound within the glaze lattice. In this situation, it is possible to overcome this problem by applying a transparent glaze over the top of the glaze containing the reducible metals. This however tends to produce a very glassy appearance which may not be aesthetically sympathetic.

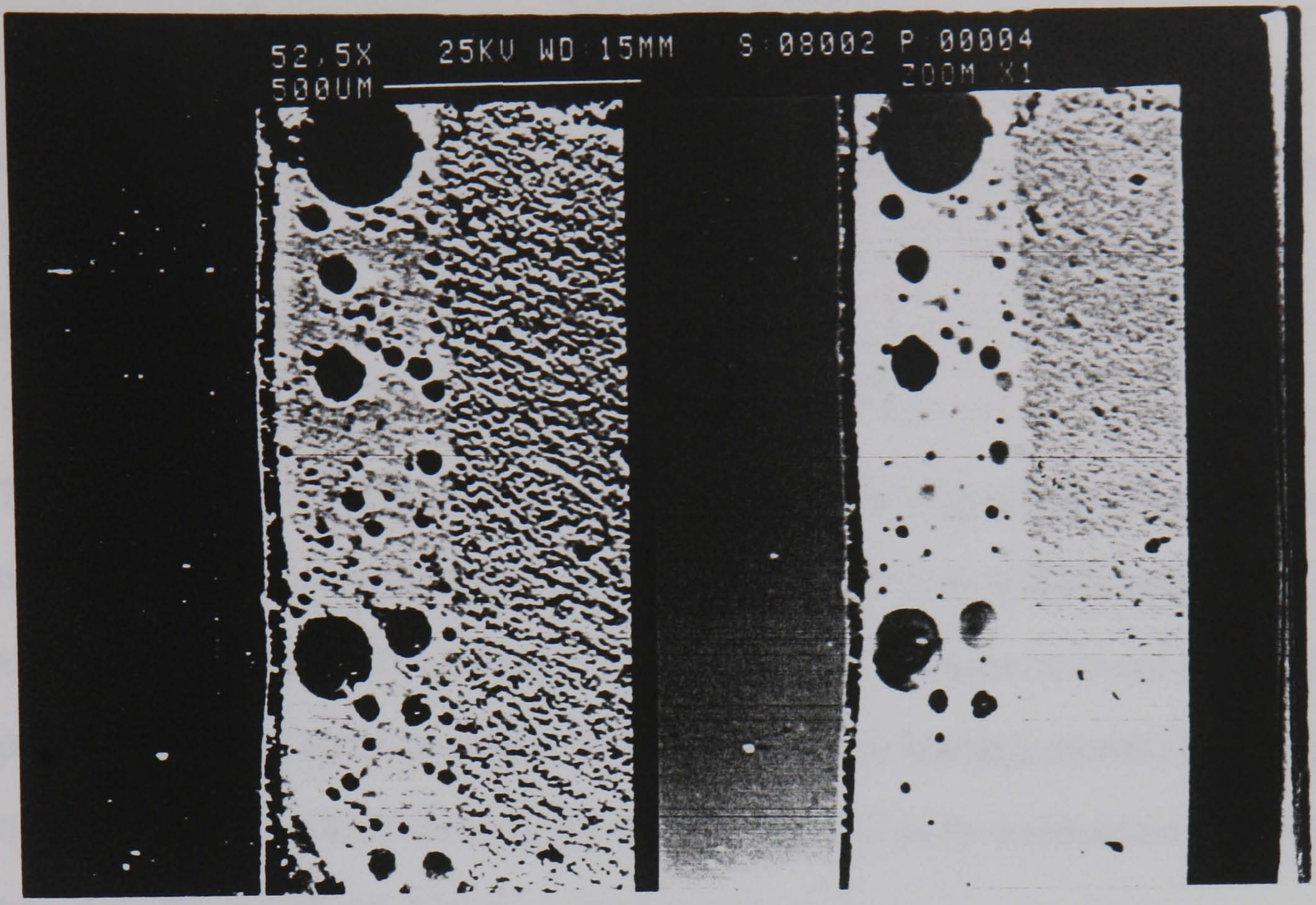


Figure 4.13 SEM photograph of the cross section of a clay paste lustre over an underglaze showing voids due to an insufficient soak period at the maturing point of the glaze.

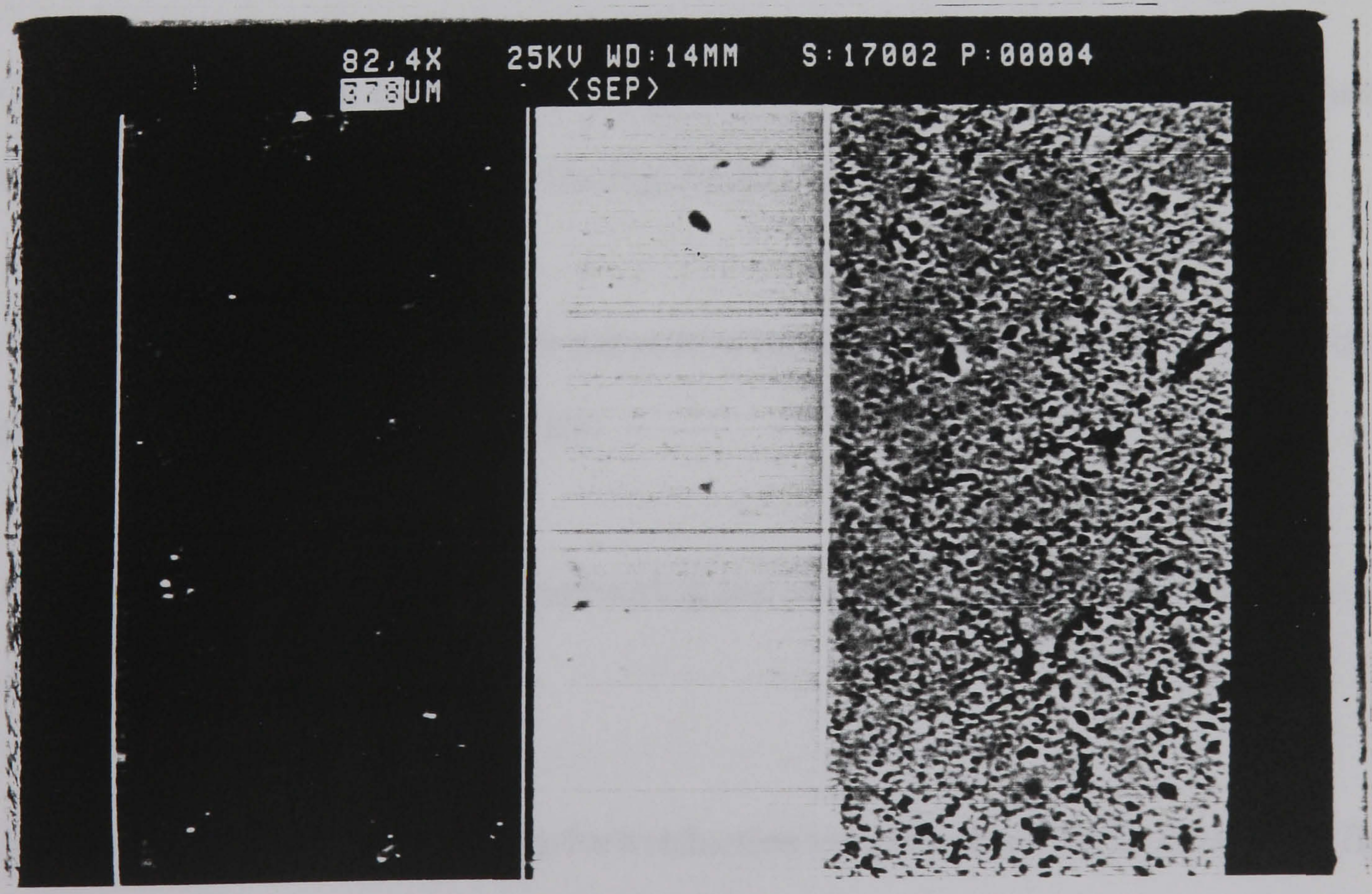


Figure 4.14 SEM photograph showing a more mature underglaze.

CHAPTER FIVE

5 Kiln Design, Construction and Modification for Reduction Lustre Firing

5.1 Introduction

This chapter describes kilns used during this research programme, the rationale behind their design and the modifications which were made. The instrumentation used to monitor and control the kilns during firing is also described. The kilns referred to are a 100 litre propane gas fired down-draft kiln and a 40 litre, front loading, electric kiln. Following observations of the kilns described a hypothetical design for a reduction kiln is outlined, based on the use of a hydrogen - nitrogen gas mixture.

5.1.1 Aims of the Investigations Described in Chapter Five

The aims of the investigations described in this chapter were as follows:

- To design, construct and fire a small gas fired kiln capable of reproducing reduction lustre effects using a variety of reducing agents.

- To modify a small electric kiln for use as a reduction kiln in order to reproduce reduction glaze effects in a controlled manner.

- To design a suitable computer monitoring and control system, compatible for use with an electric reduction kiln.

- To describe a possible new design for a reduction kiln, which would be suitable for firing reduction lustres.

5.1.2 Reduction Lustre Kilns

An examination of historical and contemporary designs of lustre kilns show a wide diversity in design. Successful lustres have been achieved using kilns fired with all types of fuel, for example wood, gas, oil or electricity, and in many configurations, for example up draft or down draft (section 1.2.3). The important factors for reduction firing are that kilns used for lustre can be held at or near the reduction temperature, while the reduction of the lustre is taking place, and that it is possible to produce a strongly reducing atmosphere at the correct temperature, i.e. in the region of 650°C to 750°C.

Kiln temperature control is dependent on the type of fuel being used. Gas kilns rely on convection and conduction to transfer thermal energy from the hot combustion gases to the ware in the kiln. This is normally controlled in craft kilns by altering the gas flow to the burners. The fuel to air ratio directly affects the combustion efficiency. An excess of air or an excess of fuel will result in a decrease in the rate of rise in temperature, or even a temperature drop. Thermal energy transfer is also affected by the way combustion gases flow through the kiln, these are normally controlled through adjustment of the chimney damper which restricts or increases the flow of gases through the kiln. Where atmospheric burners are employed, dampers can be used to restrict the air drawn into the flame path resulting in a reduction atmosphere through incomplete fuel combustion.

Electric kilns rely mainly upon radiation to transfer thermal energy to the ware being fired. Temperature control is achieved either by varying the power to the elements using a rheostat, which varies the current going through the elements, or by switching the elements on and off over predetermined time periods, either is amenable to electronic control. The normal atmosphere within an electric kiln is oxidising. To produce a reduction atmosphere a reducing agent has to be introduced into the kiln, for example a hydrocarbon gas. The introduction of a gas into the kiln causes the temperature to rise, this is partly due to better energy transfer due to convection effects but is mainly due to the greater thermal conductivity of the reducing gases compared to that of air. As well as control of the kiln atmosphere through the introduction of specialised gases into the kiln, the type of fuel being used can also influence the kiln atmosphere. For craft potters, the estimation of the degree of reduction occurring during a firing has largely been a matter of visual observation of for example, the colour of flame emerging from the spy hole, or the amount of smoke emerging from the flue. For lustre firing, the effect of the kiln atmosphere can be monitored using draw trials, small sample pieces of lustred ceramic being taken from the kiln at intervals during the reduction phase of the firing using tongs. A more accurate method of monitoring kiln reduction atmosphere is through the use of oxygen sensors. These instruments can be interfaced with computer control systems. The use of oxygen probes to monitor the kiln atmosphere is not yet common practice among craft potters.

A number of special atmosphere kilns employ a muffle arrangement to prevent direct flame impingement on the ware. This involves an inner refractory chamber which physically separates the ware from the combustion gases. The incorporation of a muffle arrangement in wood-fired lustre kilns is designed to protect the ware from carry-over of ash which may adhere to the soft glaze surface. In the case of coal fired kilns, the muffle protects the ware from the effect of sulphurous gases produced by the burning coal. A muffle may also be used as a way of containing the reducing gases within the ware chamber.

The size of a reduction lustre kiln is dependent on the ware being fired and the requirements of the potter. Davis (1954) suggested an optimum size of "9 cu. ft (0.25 m^3) as it may be difficult to get even circulation of the reducing gases in a larger kiln, although the author goes on to describe the use of a gas fired tunnel kiln," as used in mass production, which was used to produce reduction lustre effects. Distribution of the reducing gases and temperature gradients between different areas within the kiln are important considerations in the design of lustre kilns. The past twenty years has seen many improvements to industrial kiln design. The use of high velocity burners and computer monitoring of pressure differences and natural gas flow patterns through the kiln permits a high degree of control of temperature and kiln atmosphere. Lingl (1985), describes a number of design innovations which are now used in the construction of commercial tunnel kilns. However, much of this new technology is not suitable for small scale craft kilns, either because of the high cost of the equipment or because of physical constraints.

5.1.2 Kiln Atmosphere Sensors

Measurement of the concentration of various gases can be carried out by a variety of solid state sensors or 'probes', for example, methane concentration in endothermic gas generators and furnace atmospheres can be measured through the use of infrared sensors (Poor, 1985), which are also suitable for carbon monoxide, carbon dioxide and methane. Sulphur dioxide gas can also be measured by the use of a similar instrument which uses potassium sulphate as an electrolyte (Anonymous, 1986). An early system based on the 'Orsat' method of volumetric analysis is described by Brodie (1982). This system preceded the solid state probes and whilst slow and requiring a degree of skill to use, had the effect of making craft potters aware of the fuel efficiency that could be achieved through kiln atmosphere monitoring.

Gas monitoring systems based on infrared light have become more advanced over the past two decades. Solid state infrared detectors measure infrared adsorption bands which are then related to the relative concentrations of gases in the reference cell, for example, carbon dioxide. Infrared systems can monitor several different gases simultaneously, the systems being generally more complex and more expensive than other available monitoring systems such as zirconia oxygen probes.

Oxygen measuring systems may consist of one or more, *in-situ* oxygen sensing probe assemblies and an electronic display unit. The oxygen sensing probe assemblies are mounted directly in the kiln in an area that will expose the sensor to rapidly moving flue gases. The oxygen sensor is made of yttria-stabilised zirconia, an electrolyte which has the ability to conduct oxygen ions at temperatures exceeding 600°C. Platinum electrodes on opposite surfaces of the zirconia electrolyte provide catalytic surfaces for the transformation of oxygen molecules to oxygen ions. These ions move through the electrolyte and re-combine on the opposite electrode. The temperature of the sensor is measured using a thermocouple (a porcelain tube protects this assembly). The movement of oxygen ions produces an e.m.f. across the sensor which is a function of three variables:

- The sensor temperature.

- The oxygen partial pressure at the inner surface of the sensor.

- The oxygen partial pressure at the outer surface of the sensor (reference oxygen level).

The furnace atmosphere's oxygen content can be found from the e.m.f. and temperature of the probe.

Oxygen probes first became commercially available approximately twenty years ago. They are now used extensively in a number of heat treatment industries. Poor (1985) describes their use for controlling and monitoring carbon potential in furnace and generator atmospheres . In the ceramics industry, oxygen probes are used to monitor gas kiln atmospheres in order to prevent reduction taking place in white ware production. Atkinson (1985), describes the use of a zirconia oxygen probe to monitor both oxidising and reducing conditions in a wide variety of ceramic manufacturing processes. Campbell (1985) describes how both infrared and zirconia oxygen sensors were used to monitor pollutant gases emitted from a cement plant. Oxygen probes are increasingly being used with gas fired kilns. They indicate the proportion of oxygen, carbon monoxide or carbon dioxide in the chamber or flue. The information obtained can be used to produce the desired kiln atmosphere, i.e. oxidising or reducing or to control the amount of air and gas entering the burners to give the greatest fuel efficiency, that is when a stoichiometric ratio between air and fuel is achieved. For natural gas the stoichiometric ratio is 1:10 (fuel to air) and for propane it is 1:25.

5.1.3 Commercial Electronic Controllers & Programmers

Many different types of kiln controller exist. They can be equipped to operate with various input sensor and output actuator devices. The controllers can accept a wide variety of input sensors, thermocouples of various types, resistance temperature detectors and other transducers. Controllers can be used to drive a variety of output actuators in response to different types of signal. For example, relay output for on/off or time proportioning, to drive contactors, and solenoid valves. Remote outputs may also be provided to indicate an alarm condition, the current set-point, or process variable value.

The controller may be provided with a range of standard and optional extra features depending on the type of process being controlled. The control type may be on/off control, two term control or three term control depending on cost and required accuracy. Communication by serial link, when fitted, enables remote control of the controller and monitoring of the process variables, using a supervisory computer system.

The controller may include a programmer, the purpose of which is to provide a time varying set-point to the controller in response to a user defined sequence. The sequence or programme consists of segments. Typically a ramp segment, where the set-point changes at a linear rate, for example 10°C per hour, up to a target level, a dwell or soak segment, where the set-point remains constant for a specified time interval. In addition there is the step segment where the set-point changes immediately from its current value to a new value. The programmer allows complex firing schedules to be repeated accurately.

5.1.4 Electrically Operated Actuators

An actuator is a device which changes some physical property of the final control element of a process control loop. For example if a valve is used to control gas flow, some mechanism must physically open or close the valve, this is achieved by the use of an actuator. A solenoid and plunger together form an electrical actuator that converts an electrical signal into mechanical motion. The plunger may be spring loaded to return it to its original position once energisation of the coil ceases. Solenoids are used to operate gas or other fuel control valves on a kiln in response to an electrical control signal. Electrically operated actuators can be electromechanical for example, a relay or they can be solid state devices. These devices could also be regarded as signal conditioners, or amplifiers.

In solid state devices, which contain no moving parts, it is possible to have very rapid switching of the device during part of a cycle of the mains supply. By this method it is possible to vary the power the load receives by altering the switching on point of the actuator during each complete mains cycle. This is known as phase control. An alternative method of control is by time proportioning the available power. This is done by varying the On to Off time (t1) of the switching device within a regular total cycle time (t2). The load then has an effective power of: P_{max} t1/t2 where Pmax is the normal power rating of the device. This burst control may use various total cycle times (t2), for slow cycling about 30 - 40 seconds, for fast cycling about 400 milliseconds. By replacing electro-mechanical relays with solid state relays it is possible to adopt burst control which offers a potentially more accurate control system than the normal simmerstat switch.

5.2 Materials and Methods

5.2.1 Gas Fired Lustre Kiln.

A propane gas fired lustre kiln was designed so that the technique of reduction lustre could be successfully reproduced. The plans for this kiln are shown in figure 5.1. The kiln was constructed from low density, MPK LW 130 grade, fire bricks and a 1260 grade, 25 mm ceramic fibre blanket. The kiln shelves used were perforated cordierite. Kiln shelves were used as bag walls and interior brickwork was laid without mortar. The kiln was built in an angle iron frame using 6 mm calcium silicate board as an outer supporting layer. Two atmospheric type burners, manufactured by Aeromatic Barter Limited of London, were used. The burners (No.38 FR1, angle pattern), were fitted with flame failure thermal cut off valves, and manifolded together before being mounted at the rear of the kiln so that they fired horizontally into the fire boxes (as indicated in figure 5.1). Two perforated refractory boxes, constructed from T-material, were placed in the bottom of the fire boxes. These provided zones within each fire box for the combustion of wood, introduced through ports at the front of the kiln as reducing agents and to provide catchment areas for ash, preventing carry-over onto the ware. During introduction of the wood, burners were switched off and the burner ports closed using a sliding shutter arrangement (figure 5.1). The ash boxes were later removed and the wood ports sealed as it was found that reduction could be achieved more easily, and with less temperature fluctuation, by closing the damper and allowing the burners to burn with insufficient air for complete combustion of the fuel. The degree of reduction was achieved by the adjustment of the gas flow valve. During this procedure, any decreases in temperature were rectified by opening the damper slightly, increasing air supply to the burners. Increases in temperature were corrected by switching off the

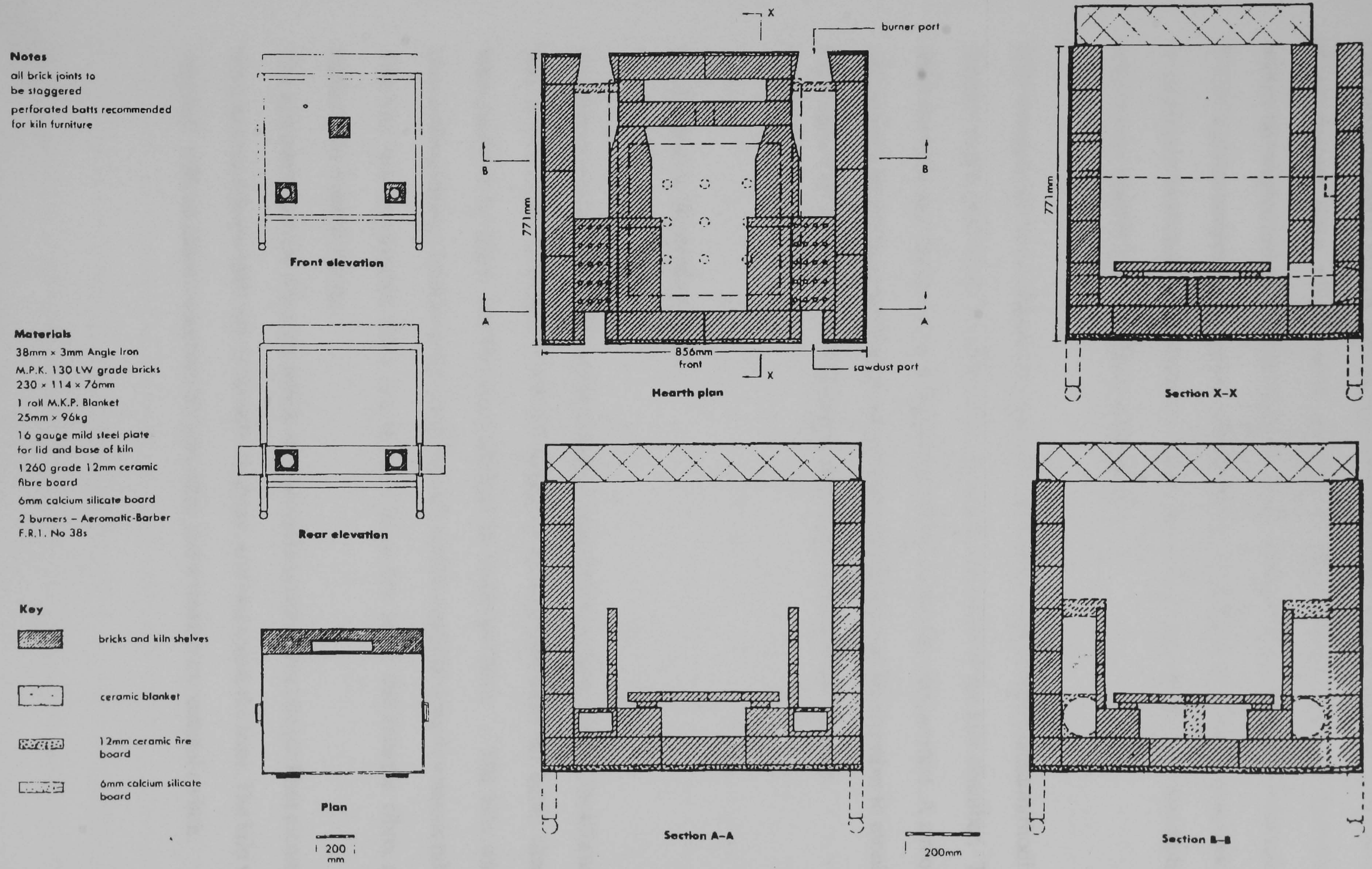


Figure 5.1. Plans of propane fired, down draft gas kiln.

kiln and allowing it to cool. Decreasing fuel to the burners does not prevent an increase in temperature since a higher air to gas ratio is achieved, which increases the thermal energy transferred to the kiln. In practice, the kiln temperature can be maintained to within 5°C of a given temperature for over an hour before temperature begins to rise, making it necessary to switch off the burners. When the burners are off, the kiln atmosphere reverts very quickly to an oxidising atmosphere.

Kiln temperature was measured by use of a 22.5 cm length R type platinum/rhodium thermocouple, positioned roughly half way up the rear wall of the kiln chamber. The thermocouple was connected to a digital pyrometer to monitor temperature. A zirconia cell oxygen probe was also fitted to the kiln near the bottom of the chamber to monitor the progress of the reduction and provide an additional temperature sensor.

5.2.2 Electric Reduction Kiln

A commercial electric kiln was adapted for use as an electric reduction kiln. The kiln used was a 4.76 KW Atmosfire™ KF55T (capacity of approximately 40 cubic litres), manufactured by Kilns and Furnaces Limited of Stoke-on-Trent. The kiln was a conventional design apart from the elements used, which were fitted inside ceramic tubes. The kiln was constructed from low thermal mass fire brick and ceramic fibre, and enclosed in a metal casing.

The kiln contained ten elements which were wired in series as one circuit. Four elements were mounted down each side of the kiln chamber, and two across the base. The kiln was supplied with an electro-mechanical type relay and a simmerstat control switch.

5.3.2 Modifications Made To The Electric Kiln

The kiln purchased was extensively modified in order to produce a controllable electric reduction kiln, a schematic diagram of the kiln is shown as figure 5.2. Three platinum rhodium R-type thermocouples were fitted. These were positioned at the bottom left, centre and top right of the rear wall of the kiln, protruding approximately 30 mm into the chamber. A removable zirconia gas probe was fitted which could be positioned at the bottom centre of the kiln chamber or near the top centre. The vent hole at the top of the kiln was bricked in and a porcelain tube, with an internal diameter of 10 mm, was fitted. The internal surfaces of the chamber were coated with a high alumina coating in order to fill the surface pores of the bricks, reducing surface permeability. The porcelain tubes supporting the element tails were sealed in place using high temperature adhesive cement. The element tails were also sealed in the supporting tubes using a ceramic fibre filler. The wiring of the kiln was altered to include one solid state relay and two electro-mechanical relays, mounted on aluminium heat sinks housed in the wiring cavity beneath the kiln. One of the relays switched the power supply to the elements and was used to control the kiln temperature. The two other relays included were part of a supplementary circuit for remote operation of the solenoid gas valves. A 5V current supplied by a transformer controlled by the monitoring computer opened and closed the relays. The circuit diagrams for the kiln are reproduced as Appendix III.

The kiln was fitted with two gas lines for introducing gases directly into the kiln chamber. Pipe work conveying both purging and reducing gases was made out of stainless steel (6 mm OD) for heat and corrosion resistance. The stainless steel pipes were passed through the casing of the kiln and connected with high temperature cement to porcelain tubes (6 mm ID), inserted into the kiln chamber. To prevent gas leakage, a steel box, held in place with pressure clips, covered the ‘spy hole’ brick in the centre of the kiln door, and a teflon gasket was fitted between the kiln casing and the steel box covering the spy hole. Valves, gauges and flow meters were all mounted on the outside of the kiln outer casing.

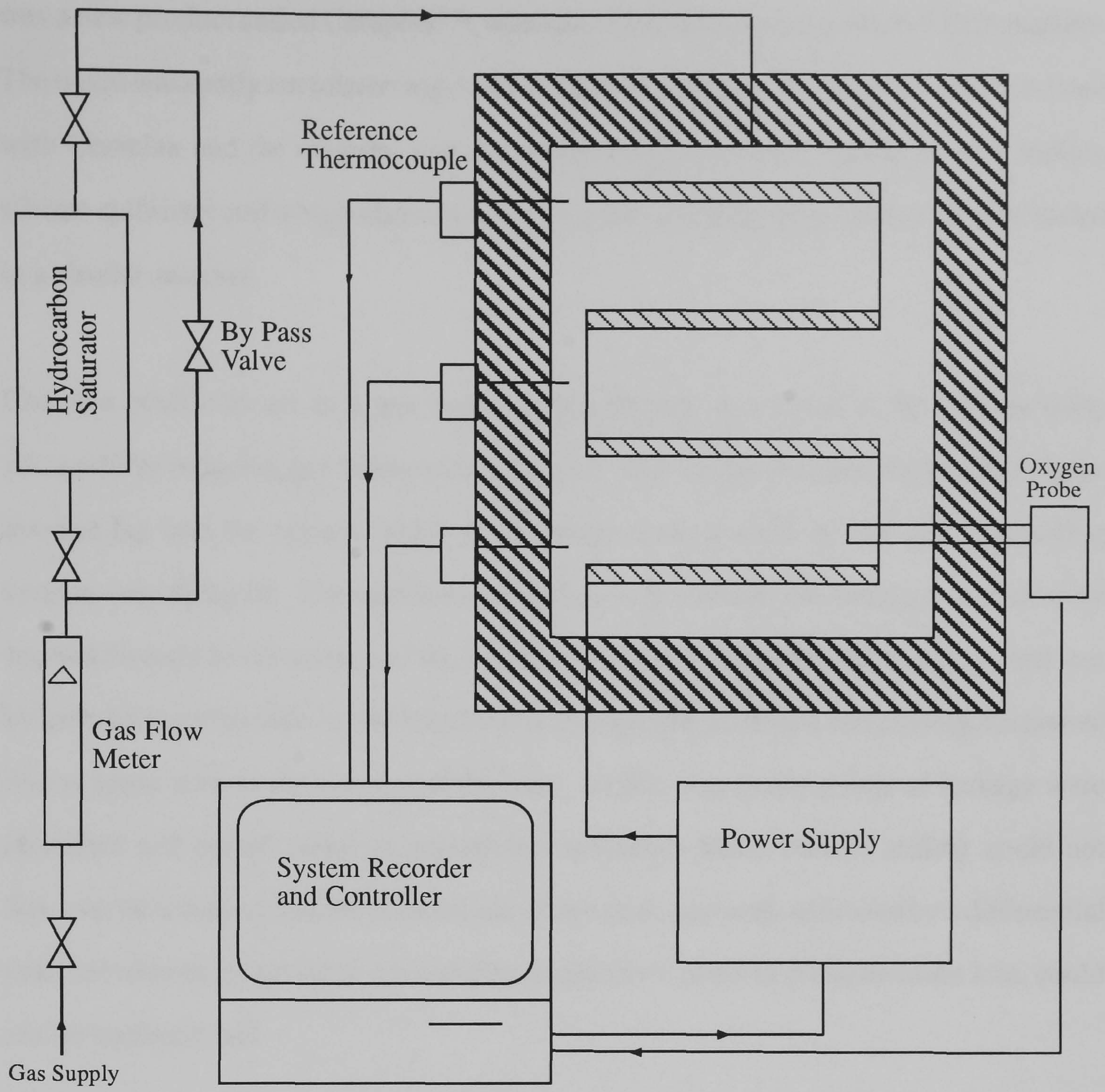


Figure 5.2 Schematic diagram of modified electric kiln with control and monitoring equipment and hydrocarbon saturator.

Flexible pressure hoses were used to connect the valves, gauges and flow meters to gas regulators attached to the top of the gas cylinders.

During modification, one of the main difficulties in adapting the kiln for use with special atmospheres was the prevention of gas leakage from the kiln chamber. The kiln as delivered used ceramic fibre as the door seal and the lining bricks themselves were highly porous so gas leakage was very evident. In an attempt to overcome this problem, a muffle lining was constructed from a light weight alumino-silicate refractory board. The board was a new product called Ceraplax^{TM}, manufactured by Foseco Limited of Birmingham. The board was easily cut (observing dust hazard precautions). The kiln chamber was lined with Ceraplax and the material was then coated with a sealent, consisting of a sodium silicate stabiliser and a high alumina outer coating. The kiln door brickwork was sealed in a similar manner.

Use of a muffle to act as a gas impermeable barrier, was found to be only partially successful in reducing gas leakage from the kiln. The muffle also introduced a very large thermal lag into the system which made temperature control, by the kiln monitoring system, very difficult. The muffle was therefore removed and the sealing materials were applied directly to the surface of the interior brickwork. Leak detection was carried out by introducing ammonia fumes into the kiln through the gas inlets, and placing dampened litmus paper around the exterior of the kiln. In this way major points of leakage were identified and sealed using an appropriate refractory filler. Perfect sealing could not however be achieved and the planned use of an extractor pump, activated by a differential pressure transducer aimed at maintaining a very small positive pressure in the kiln, could not be implemented.

5.2.4 Instrumentation of the Electric Kiln

Instrumentation of the electric kiln described in the previous section was provided by a BBC microcomputer. Platinum rhodium thermocouples and a zirconium oxygen probe, allowed temperature and kiln atmosphere to be monitored. The computer programme listings are reproduced as Appendix IV. The following sections describe the various components of the control and monitoring system in detail.

5.2.4.1 Thermocouples

Several types of thermocouple are available, the different types being designated by their composition. R-type platinum -(13%) rohdium thermocouples (150 mm length) were used, positioned into the bottom left, top right and centre of the rear wall of the kiln chamber, in order to monitor temperature at different areas of the kiln to obtain a more accurate and informative picture of temperature gradients during firing. On insertion, the thermocouples were extended 30 mm into the kiln chamber, protected within a porcelain sheath. Changes in temperature are recorded by thermocouples as a thermoelectric voltage, or 'Seebeck coefficient', approximately linear over small changes in temperature, becoming non linear over larger changes in temperature. This required the use of polynomial equations or 'look up' tables to determine the temperature corresponding to a given voltage.

5.2.4.2 Pyroscopes

Pyroscopes are expendable objects (usually cones) made from carefully proportioned ceramic minerals. They are similar in composition to glazes and thus sinter, fuse and melt at predicted points during a firing at specific temperatures. The temperature / time factor is termed heat-work. Each cone is given a number corresponding to the temperature at which it will collapse through heat-work if that temperature is arrived at through a specified cycle. Cones are normally set at an angle of 82 degrees to the horizontal so that they bend in a predictable, consistent way.

Pyroscopes may be used as a visible check of heat-work during a firing indicating end points in firings which are useful for post-firing diagnosis. On heating at specific temperatures, the cones soften and eventually bend over. The action of bending over, also known as collapsing or squatting, may be observed through the 'spy hole' allowing the kiln operator to see the heat-work taking place within the kiln.

Measurement inaccuracies can occur if cones are fired too rapidly during the early stages of a firing when binders are burning out. In this case, the cone will crust, and collapse will be delayed. However cones containing iron, identified by their brown colour before firing, are affected in the opposite way by reduction and collapse prematurely. Because of the tendency for cones to collapse prematurely under strongly reducing conditions, they were not used extensively in this research programme.

5.2.4.3 The Glen Dale Oxygen Probe

A Glen Dale oxygen probe was the instrument used to monitor changes in oxygen content within the various kilns used throughout this research programme. This probe consists of a zirconia pellet housed in a protective porcelain tube. The electrical terminals, the reference air supply connection point and needle valve assembly are housed in a metal box at the exterior end of the probe. The probe also contains a platinum rhodium thermocouple. During operation, the probe was inserted into the kiln. The probe could be positioned either at the bottom of the chamber or near the top. Where ever the probe is positioned calibration has to be in-*situ* because the probe's output is affected by the way the gases impinge on the sensor. The instrument generates a temperature dependent output which is shown on a voltmeter. The instrument can be calibrated to yield actual oxygen percentages (p), the output voltage (E) conforming to the Nernst equation: $E = E' + S \ln p$ where E' and S are constants at any given temperature. However, in practice the actual output voltage can be used as an indicator of the existence of reducing or oxidising conditions in the kiln. For instance, at 600°C a fully oxidising atmosphere gave an output of about 12 mV and a strongly reducing atmosphere gave about 900 mV.

5.2.4.4 The BBC 'Model B' Microcomputer

The BBC Microcomputer has a variety of High level programming languages available in Read Only Memory (ROM) form. The High level language BASIC, is supplied as standard. The model 'B' is fitted with a Disc Drive interface to communicate with various types of Disc Drive units for programme and data storage/retrieval. The computer is provided with a Centronics parallel printer port and an eight bit bidirectional "User Port".

It also has an RS423 serial port, "1MHz Bus" for peripheral expansion, "Tube" port for second processor operation, a four channel 12 bit Analogue to Digital (A to D) converter, Audio Cassette, RGB and Video Monitor ports (Coll). The machine was considered suitable for use as a kiln controller as it was already equipped with an A to D converter, which was used to convert the analogue signal from the thermocouples and oxygen sensor into a digital signal for use by the computer.

The output from the thermocouples during use was small, in the order of millivolts, and was subject to noise interference from the electrical equipment in the vicinity of the kiln. For this reason signal amplifiers where built and fitted to the rear of the thermocouples, screened wire was used to carry the signal between the amplifiers and the computer. The gain of the amplifiers was between 100 and 150 times, thereby giving a signal output in the order of several millivolts. Firing tests were monitored using the centrally placed thermocouple wired directly to a portable pyrometer and twin pen chart recorder, the other amplified thermocouples were connected to the A to D port of the computer.

5.3 Discussion of Lustre Kilns Described in Chapter Five

5.3.1 Down Draft Gas Kiln

The down draft gas kiln was a practical design for the reproduction of reduction lustre effects. The design of this kiln was such that burner ports (figure 5.1) were kept as small as possible so as to facilitate the achievement of a strongly reducing atmosphere and the maintenance of a reduction temperature once reached, however this prevented the kiln from firing efficiently to temperatures above 800°C. If enlargement of the burner ports were later found to be necessary, it would have been easy to make adjustments, since the bricks were removable and could be cut without difficulty. The kiln was not suitable as an indoor kiln because of the high levels of carbon monoxide given off during reduction.

A log of the firings undertaken in the gas kiln was kept. A typical firing record is shown in table 5.1, showing temperature verses time. The log recorded the type of samples being fired, the reduction temperature and duration and the e.m.f. generated by the oxygen probe. In this particular example, the lustre firing was not successful in terms of it producing a copper red lustre. It was subsequently found that a higher reduction temperature of 700°C was necessary for this particular combination of under glaze and clay paste pigment. For general purpose use this kiln would normally be satisfactory, however due to the fact that this kiln was situated outdoors and was therefore exposed to changing weather conditions, changes in air pressure and humidity were found to alter the performance of the kiln in an unpredictable manner. For this reason, it was not possible to gain sufficient control over firing cycles. Identical firing conditions for each experiment, where precise reproduction of a particular result was required, could not be achieved.

Table 5.1: Firing Schedule for Gas Fired Lustre Kiln

Date: 6,8,91
Samples: FR1 Clay Paste Lustre over L21/o

Time	Temperature /°C	Gas Setting *	O2 Probe output /mV	Comments
11:00	18	5	-	Damper fully open
12:00	400	10	-	
12:30	500	10	-	
1:15	620	20	13	
1:24	660	20	15	Close damper
1:50	665	15	800	1st draw trial, Pink stain
2:05	667	15	860	2nd draw trial, dark pink
2:20	667	15	850	3rd draw trial, no change
2:30	668	15	900	4th draw trial, blotchy pink
2:40	670	15	870	5th draw trial, no change

Firing discontinued. Results disappointing. No lustre achieved./
* Maximum gas setting was 30

5.3.2 Modified Electric Kiln

The electric kiln described in this chapter was a commercial product not specifically designed as a reduction kiln and even after extensive modification was not ideal. The kiln could not be sealed adequately and the ceramic tubes used to house the elements did not give protection from the reducing atmosphere since they were not sealed at the ends. The tubes did however, increase the thermal lag in the system and make accurate temperature control more difficult.

A series of test reduction firings were carried out in the kiln using 25 mm x 50 mm test tiles glazed with #8 (CRL). These were placed throughout the kiln chamber at varying heights. The results obtained gave an indication of the pattern of the gas flow within the kiln. The original gas inlet for the reducing gas was placed near the bottom of the chamber, entering from the middle of the side wall. When a kiln shelf was used in the kiln, half way up the chamber, gases were restricted to the bottom of the kiln, despite the use of perforated kiln batts. As a result of this observation a second inlet at the top of the kiln was made.

In order to investigate the flow of gases through the kiln chamber a series of firings was undertaken in which samples of tile glazed with #8 (25 mm x 75 mm), were placed in the chamber supported on kiln props at differing heights. Colour changes in the samples indicated where the reducing gases had flowed. Figure 5.3 shows a colour diagram of one of these test firings. In this particular experiment the reducing atmosphere was generated with the use of 5% hydrogen in nitrogen. The gas was introduced at the top of the chamber and at the side (see figure 5.3). The colour changes indicate that samples placed near the centre in the lower half of the chamber had been reduced but samples near the top rear of the chamber had not undergone reduction. On samples which had been partly reduced the gas flow patterns are clearly

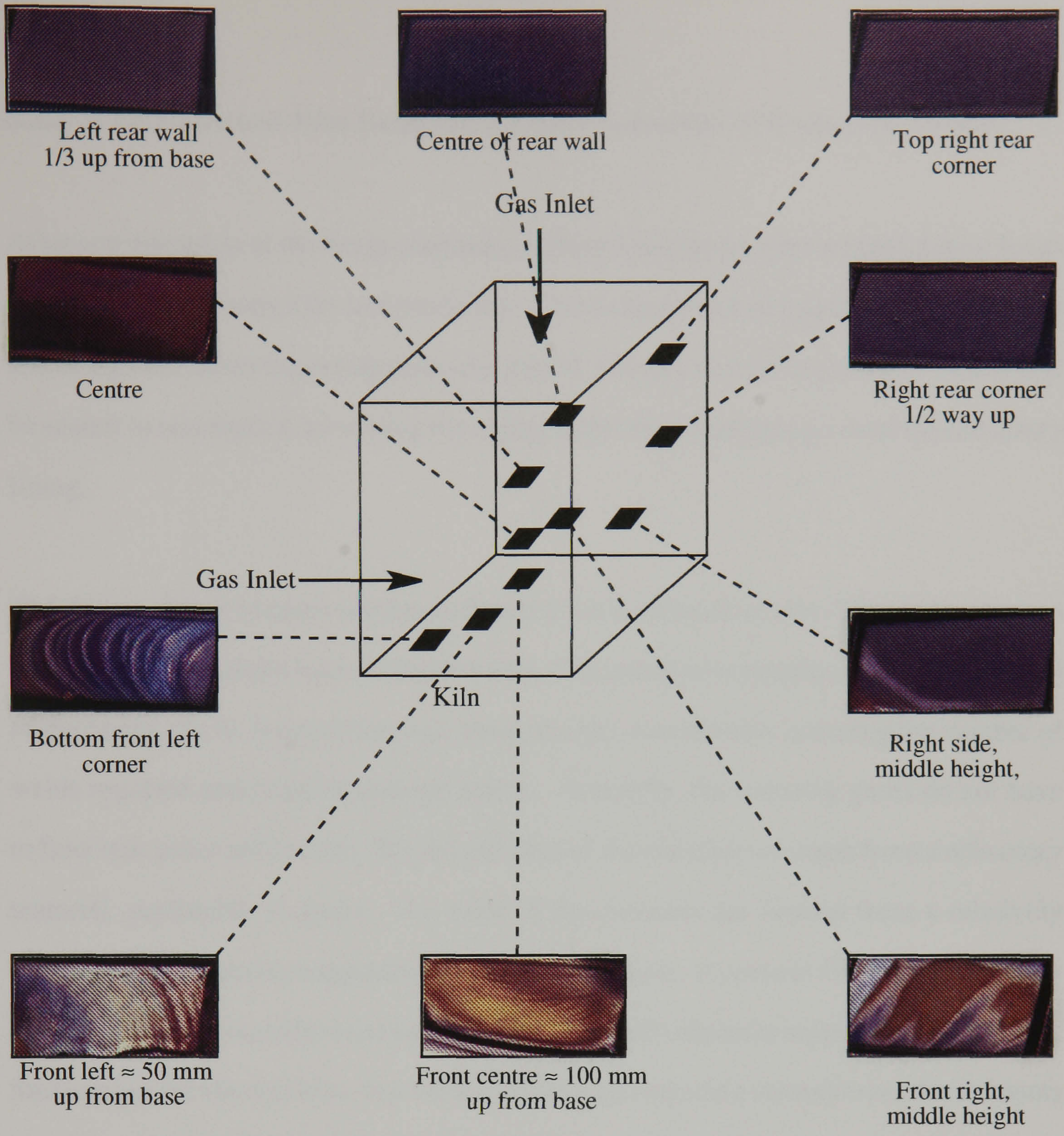


Figure 5.3 Diagram showing the effect on samples of tile glazed with #8 lustre glaze placed at differing points throughout the modified electric kiln.

visible. Because of the permeable nature of the refractories lining the chamber and the difficulty in making the kiln gas tight, the gas pressure within the chamber was barely measurable.

5.3.3 A Hypothetical Kiln Designed for the Production of Reduction Lustres.

After consideration of the design limitations described above , a theoretical design for an electrically fired lustre kiln was produced. This is illustrated as figure 5.4. In arriving at this design the following points were considered. The kiln should be gas tight. This would be easiest to accomplish by sealing the casing rather than attempting to seal the refractory lining.

The design shown in cross section in figure 5.4 is a cylindrical kiln. This shape has two main advantages over a square chamber kiln. Construction is simpler, since the main part of the casing can be formed from one sheet of steel, considerably reducing the number of welds required and possible leakage points. Secondly, the reducing gases do not have to flow into awkward corners. The lid and base of the chamber are made from a refractory material, permeable to gases. The sides of the chamber are formed from a relatively impermeable refractory supporting the electric elements. A ceramic fibre material or low density fire brick could be used as insulation behind the element supporting refractories. Since using the electric kiln in a variety of strongly reducing atmospheres the elements have not suffered unduly. When initially fired the elements were heated in an oxidising atmosphere, to a temperature in excess of 1054°C, this allowed a protective aluminium oxide layer to form on the surface of the elements. This layer did not appear to suffer any deterioration under the various reducing conditions established in the kiln, although the oxidising layer will reform even if reduction of the aluminium oxide occurs. It is therefore not considered necessary to use embedded elements. As an alternative silicon carbide elements could be used.

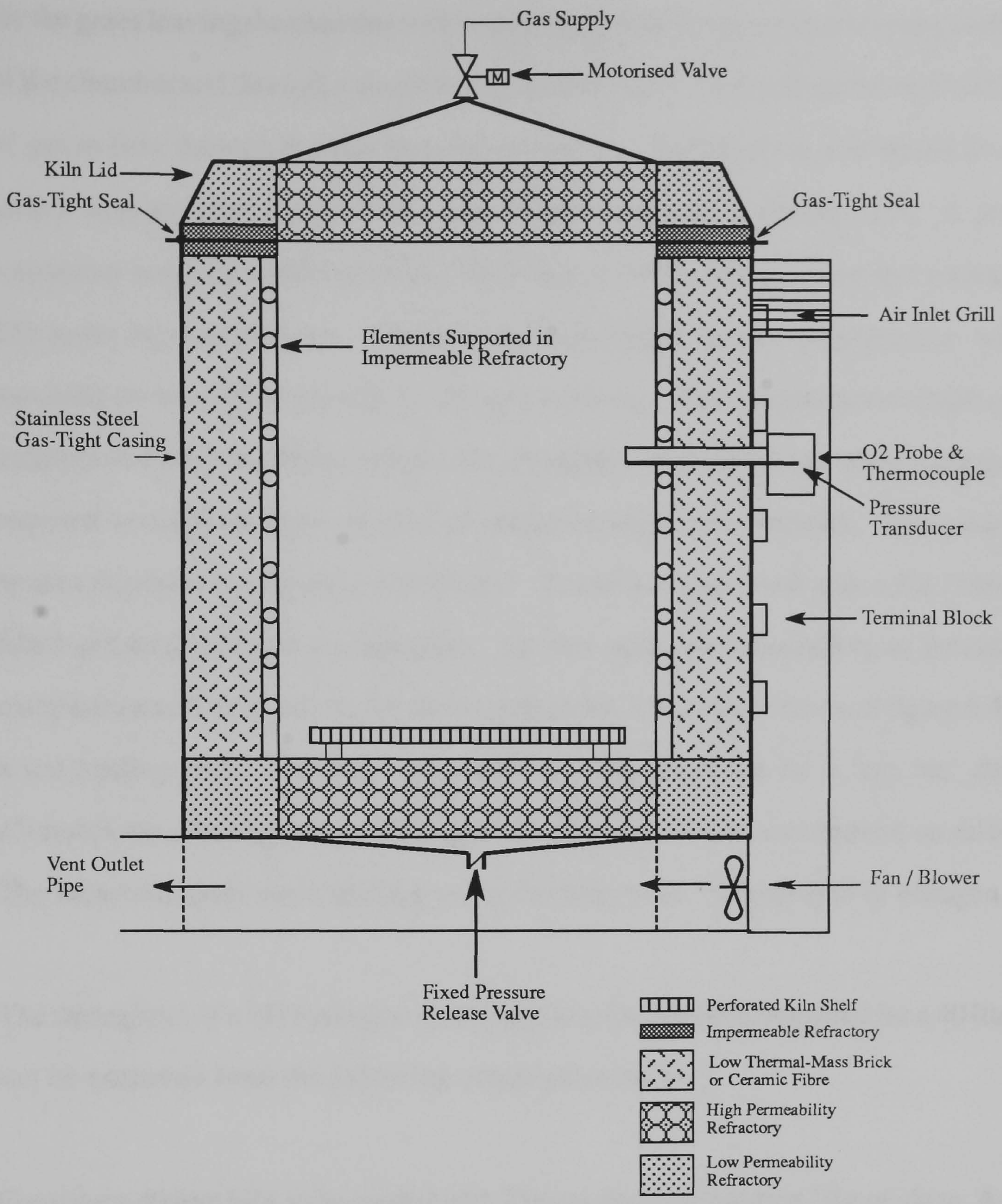


Figure 5.4 Hypothetical design (shown in cross section) for a reduction kiln based on the use of a hydrogen in nitrogen gas mixture.

Silicon carbide elements however are brittle and very much more expensive in comparison with conventional iron-chromium-aluminium wire elements. The design shown in figure 5.4 is essentially a down draft configuration. This is not essential, there is no reason why the configuration could not be reversed. The reducing gases enter at the top of the kiln illustrated in figure 5.4. The inlet valve is motorised so that gas flow can be moderated by the controlling computer, to maintain a specified flow rate. The only outlet for the gases leaving the chamber is through a layer of gas permeable refractory at the base of the chamber and through a single fixed pressure valve. This arrangement allows a plug of gas to flow through the kiln from top to bottom. The lid of the kiln would be sealed with a heat resistant plastic o-ring and pressure resistant fastening clips. A pressure transducer could be used to provide closed loop control of the gas flow and maintain the kiln at the required pressure. The kiln is pictured fitted with an oxygen probe, which is mounted on the side of the kiln in a boxed-in cavity. The oxygen probe could also be incorporated into the control system, the instrument would indicate when more gas was required to maintain a pre-set level of reduction within the chamber. This cavity also houses the element terminals and relays. The kiln is also fitted with a fan / blower to dilute and safely exhaust the kiln gases. Air inlet vents provide cooling air for electrical components and reference air for the oxygen probe. The design shown in figure 5.4 is for a top loading kiln. There is no reason why this could not be a 'top hat' design . Alternatively a lozenge shape for larger capacity kilns would also present no difficulty. The reduction gases envisaged for use in this kiln were 5% hydrogen in nitrogen.

The throughput of a 5% hydrogen in nitrogen gas that would be required for a 40 litre kiln can be estimated from the following rough calculation:-

Consider a 40 litre kiln to be loaded with 25 tiles, each tile holding 10 g of glaze. Assume the glaze contains 2.5% copper as Cu^{2+} and that all of this will be reduced to copper metal. The total quantity of hydrogen gas required is :-

Total moles of Cu = $(10 \times 2.5 \div 100$ g Cu per tile$) \times (25$ tiles$) \div (63.5)$

≈ 0.1 moles (approx.)

Total moles of H_2 required = moles of Cu = 0.1 moles [because reduction is $Cu^{2+} + H_2 = Cu + 2H^+$] Since the kiln holds 40 litres of gas which, at STP, is approximately 2 moles at 1000 K the kiln holds $(273 \div 1000) \times 2 = 0.5$ moles approximately. The reduction atmosphere is actually only 5% hydrogen so the kiln at 1000 K contains 0.5 x (5/100) moles = 0.025 moles of hydrogen in a static atmosphere.

The kiln atmosphere, if not replenished from a continuous supply would only be capable of reducing one quarter of the total copper.(i.e. 0.025 ÷ 0.1) If the lustre effect is only produced in the outer skin of the glaze then this may be sufficient. However an advantage of using a flowing gas stream is that the reduction will not be inhibited by an accumulation of gaseous reaction products (namely, water vapour). The effect of gas pressure on the rate of reduction has not been investigated during this research programme. Operating the kiln at two atmospheres pressure would double the collision frequency of the hydrogen atoms, while maintaining a safe gas mixture. Temperature control will always present some difficulties. Hydrogen has seven times the thermal conductivity of air. This phenomenon is exploited by the katharometer in a gas chromatograph, where small changes in the hydrogen to nitrogen ratio composition are exploited to give large changes in thermal conductivity, thus making the katharometer a more sensitive instrument. A kiln designed specifically for reducing lustres which was not capable of higher temperature firings would be of limited use and only marginally cheaper to build. At a reduction temperature of 700°C the heat loss from a kiln insulated for potential operating temperatures of 1300°C will be insufficient to avoid a rise in temperature. This could be countered by increasing the flow of cold gas through the chamber. The key to the hypothetical design being described, is the permeability of the different refractories used in its construction and the use of a gas-tight casing.

CHAPTER SIX

6 Kiln Atmospheres For Reduction Lustres

6. 1 Introduction

This chapter describes experiments carried out using 5% hydrogen in nitrogen and various paraffinic hydrocarbons in nitrogen gas mixtures as possible sources of reductants, for use in an electric kiln, for the reduction of lustre glazes.

The experiments were carried out using two kilns. The larger kiln was the modified electric kiln described in the previous chapter (section 5.2.2), which reproduced conditions close to those that would pertain to craft practice and could be used to produce objects for aesthetic evaluation. A smaller kiln, described here was capable of close control and was used to produce glaze specimens for scientific evaluation.

6.1.1 Aims of Experiments Described in Chapter Six

- To evaluate the use of 5% hydrogen in nitrogen as a safe, viable alternative reducing agent to the use of flammable undiluted hydrocarbon gases such as butane, propane or natural gas (methane).

- To evaluate the possible use of hydrocarbon saturated nitrogen gas mixtures for use as sources of reductants in a reduction lustre kiln.

- To establish the effect of using alternative sources of reductant on the colour development of lustre glazes.

- To evaluate the effects of temperature and reduction duration on the development of reduction lustre glazes.

6.1.2 Special Kiln Atmospheres

Special atmospheres are routinely used in industry for the heat treatment of metals (Stratton, 1992). These atmospheres may consist of nitrogen, to produce an inert atmosphere, or hydrogen, carbon monoxide, carbon dioxide, natural gas, methanol and ammonia, which generate reducing, carburising or nitriding atmospheres. When such gases are used to create special atmospheres, strict safety precautions are required to prevent oxygen from entering the kiln or furnace. The presence of oxygen may lead to a potentially explosive situation. Normally an inert gas, such as nitrogen is used as a purge prior to the introduction of a flammable gas (Clinton, 1991; Stratton, 1992). The nitrogen physically displaces the atmosphere within the chamber.

Producing a reducing atmosphere within a kiln is normally achieved by reacting a hydrocarbon fuel gas with insufficient air for complete combustion. The reaction can occur within the kiln or externally in a gas generator (Stratton, 1991). The external exothermic generator allows for a greater degree of control, the products of combustion (water and carbon dioxide), can be removed before the remaining gases (nitrogen, carbon monoxide and hydrogen) enter the kiln. Stratton (1991), describes the use of an alternative to the use of hydrocarbon generated atmospheres in the form of premixed high purity nitrogen and low percentage hydrogen gases. The hydrogen combines with the oxygen to form water, maintaining a neutral atmosphere and preventing reoxidation.

6.2 Materials and Methods

6.2.1 Electric Muffle Kiln

The electric kiln which had been adapted as a reduction kiln (section 5.2.2) was found not to be suitable for use where a closely controlled firing environment was required. For example, the size of the chamber and the distribution of the elements within the chamber, resulted in the presence of temperature gradients during firing. There were also large variations in the composition of gases making up the kiln atmosphere. These limitations, together with the need for a more controlled experimental firing environment, led to the adaptation of a small (5 litre) laboratory muffle kiln for reduction firing. The muffle kiln was small enough to be housed in a fume cupboard, which meant that any fumes escaping from the kiln could be safely vented. The kiln was placed adjacent to a tube furnace which was adapted for use as a gas pre-heating system. This was achieved by winding stainless steel tubing (6 mm) around a mandrill to form a coil and thus extend gas residence time within the furnace long enough to pre-heat the gases flowing through the tubing to a similar temperature of that pertaining in the muffle kiln. The end of the tube was branched forming two inlets into the front of the muffle kiln, one allowing gas into the front area of the muffle chamber and the other delivering gas to the rear of the chamber. Figure 6.1 is a schematic diagram of the muffle kiln and monitoring apparatus. The front of the kiln was fitted with a gas impermeable heavy duty fire brick. Holes drilled through the brick allowed for the two gas inlets and the insertion of a zirconia oxygen probe. The brick was sealed in place each time the kiln was fired, using china clay mixed with water to a paste consistency.

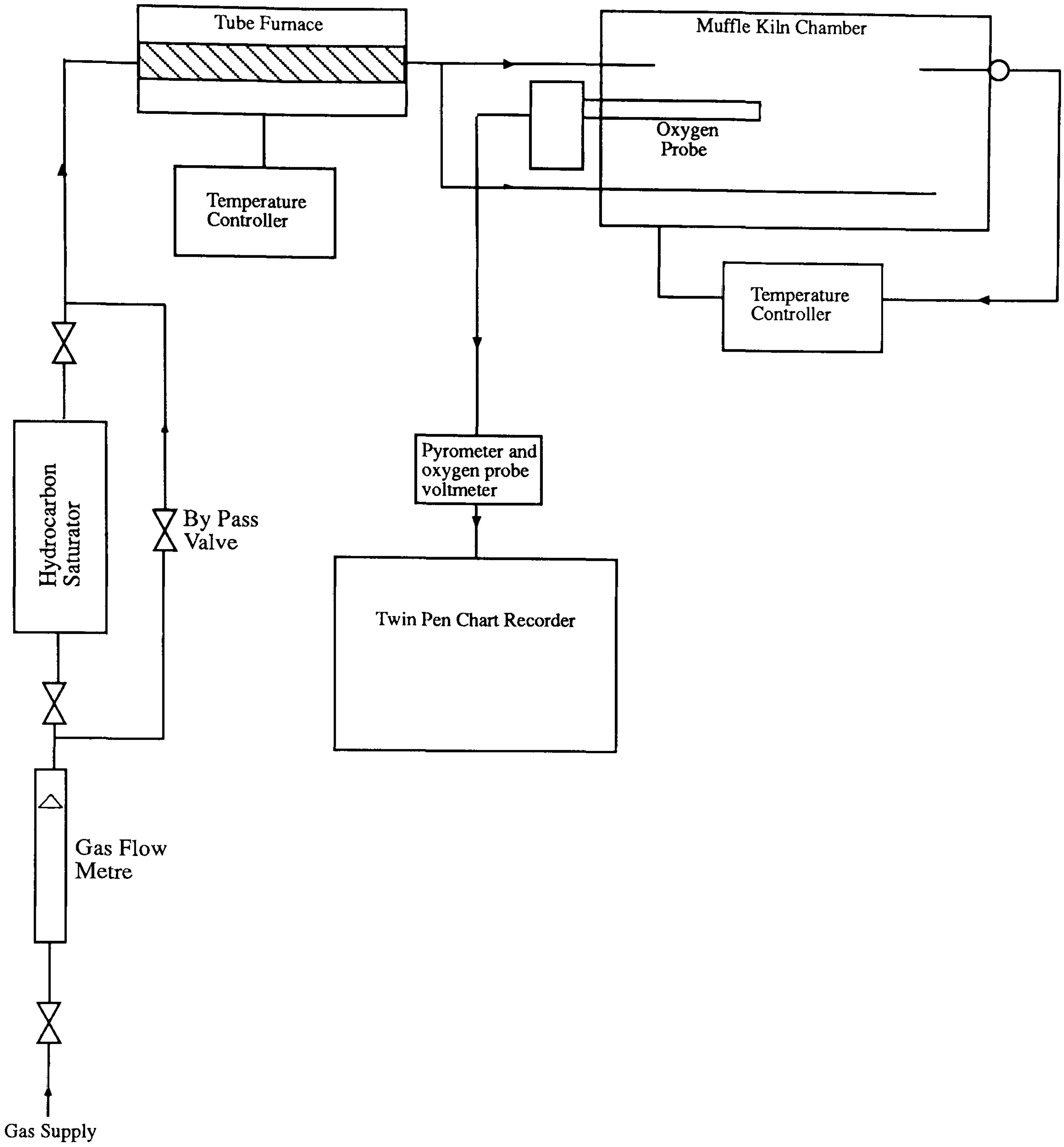


Figure 6.1 Muffle kiln, gas pre-heating system, hydrocarbon saturator, temperature controller and monitoring apparatus.

6.2.2 Hydrocarbon Gas Saturating Apparatus

Hydrocarbon saturated gas was generated by bubbling oxygen-free nitrogen gas through bottles containing liquid hydrocarbon. This apparatus is shown schematically as figure 6.2. The saturator consisted of two 500 ml Dreschel bottles containing approximately 300 ml of *n*-alkane liquid. A Buchner flask was included to prevent droplets of alkane liquid from entering the gas pipeline. The liquid was maintained at an ambient temperature (25°C) by immersion in a thermostatically controlled water bath. In passing through the liquid the nitrogen gas becomes saturated with hydrocarbons which are then carried forward into the kiln. During a reduction firing using hydrocarbon saturated gas, the kiln was heated to its set point temperature and allowed to equilibriate for approximately 20 minutes. The kiln was then purged with nitrogen for five minutes before the gas was diverted through the saturator by opening valves 1 and 2 and closing valve 3 (figure 6.2). After a chosen reduction time, both gas flow and kiln were switched off. Investigations were carried out using a variety of hydrocarbon sources as reducing agents, ranging from unleaded petrol to refined, normal alkanes. These included *n*-pentane (C_5H_{12}), *n*-hexane (C_6H_{14}), *n*-heptane (C_7H_{16}), *n*-octane (C_8H_{18}) and *n*-decane ($C_{10}H_{22}$).

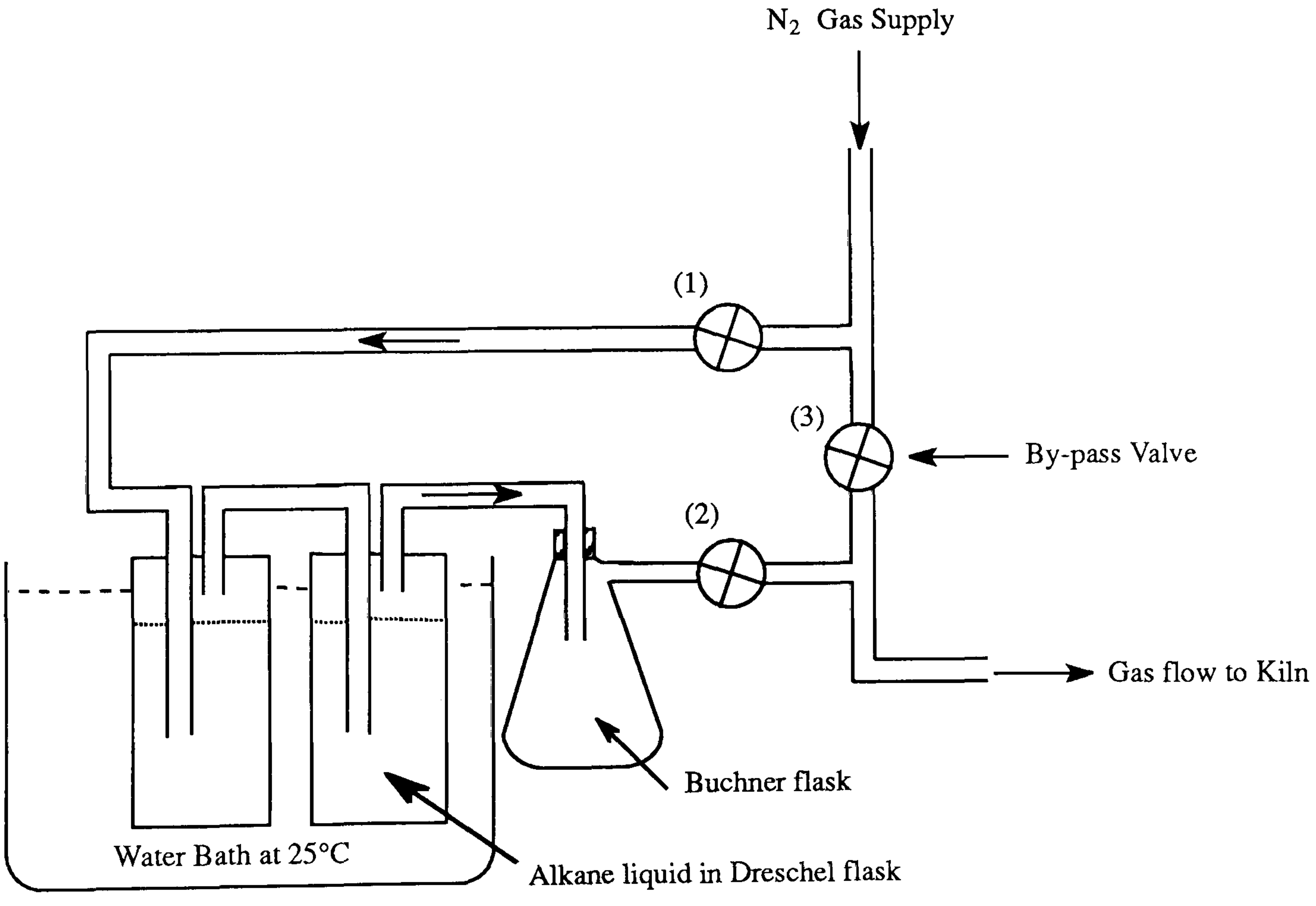


Figure 6.2 Diagram of gas saturator apparatus.

6.2.3 Temperature and Atmosphere Monitoring and Control of Muffle Kiln

Temperature control of both the muffle kiln and the tube furnace was achieved through the use of separate proportional temperature controllers. The output from the oxygen probe was logged using a twin-pen chart recorder. One channel of which recorded the output from the zirconia cell and the other channel recording the output from the sensor's thermocouple, providing a simultaneous record of both kiln temperature and atmosphere within the chamber. The samples used in experiments in the muffle kiln consisted of glazed tiles (76 mm x 76 mm) which were supported vertically in tile cranks at an angle of approximately 80° to the horizontal .

Figure 6.3 shows a typical example of a firing record obtained during a reduction test firing in the muffle kiln. The temperature is shown ramping up to a plateau. After approximately twenty minutes at the pre-set temperature, nitrogen was introduced into the chamber and the output from the oxygen probe is seen to rise to approximately 50 mV. After five minutes the 5% hydrogen in nitrogen gas mixture was introduced into the chamber and a slight temperature rise was recorded as the output from the oxygen probe increases rapidly, to a maximum of approximately 900 mV. The slight temperature rise at this stage was due to the increase in the thermoconductivity of the kiln atmosphere which consisted of 5% hydrogen at this point. After 15 minutes both the gas and the power to the kiln were switched off. The output from the oxygen probe falls rapidly as air leaks into the firing chamber.

The modified laboratory muffle kiln enabled repeated firings to be carried out under reproducible conditions of atmosphere and temperature. A series of firings were carried out in the muffle kiln, using oxygen free nitrogen gas saturated with different *n*-alkanes as the source of hydrocarbon as well as the 5% hydrogen in nitrogen mixture. In the first series of experiments the reduction time was varied at constant temperature. Then a set of experiments were carried out in which the temperature was varied with a fixed time of reduction.

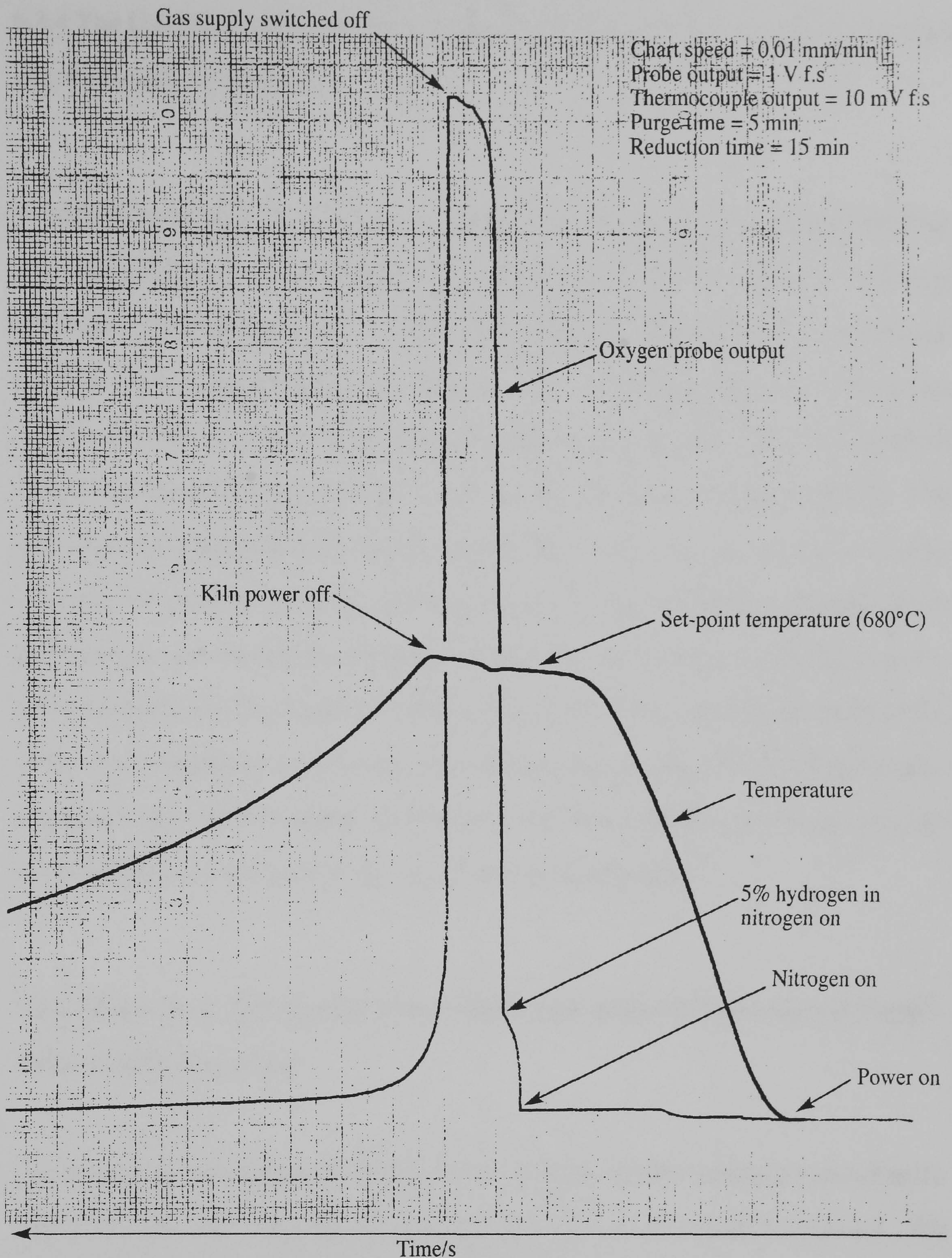


Figure 6.3 Typical chart recording of a reduction lustre test firing carried out in the laboratory muffle kiln.

6.2.4 The Use of Unleaded Petrol as a Source of Hydrocarbons for the Production of a Reducing Atmosphere.

In order to produce a cheap, readily available source of hydrocarbon saturated reducing gas, unleaded petrol was considered as a possible agent for use in the gas saturating apparatus. An investigation was carried out to assess the suitability of unleaded petrol to create the required reducing atmosphere within a modified electric kiln. Four tiles glazed with #8 were placed vertically, supported in tile cranks, within the kiln chamber. The same reduction firing procedure was followed as that used in the muffle kiln. The procedure was repeated for several firings using the original sample of petrol. In order to assess the consistency of the reducing atmosphere by this method, samples of the saturated gas were obtained using a 5 ml syringe from the gas line leaving the saturator. This was repeated a second time 15 minutes later prior to the end of the reduction. This meant that samples of gas were obtained at the start and end of a period of gas saturation. Changes in the relative quantities of different petrol-derived hydrocarbons present in the reducing gas were assessed by the use of gas chromatography.

6.2.4.1 Gas Liquid Chromatography in the Identification of Hydrocarbon Components of Reducing Gases

Gas liquid chromatography (GC) is a technique which enables separation and identification of individual components of a complex mixture of volatile substances. The apparatus consists of a long narrow column packed with an inert support material of uniform particle size, for example silica gel that has been coated with a non volatile liquid 'stationary phase'. The column is housed in a thermostatically controlled oven. The sample to be analysed is carried through the column by an inert gas 'mobile phase'. As the sample passes through the column, individual components become separated by the stationary phase. The retention time of each component in the column depends upon its chemical properties and type of column used. On elution, separated components are detected by electrical or thermal conductivity, and recorded as peaks. Additional software can display and identify the data by reference to a stored data base.

The second method of using the instrument was intended to analyse the gases leaving the kiln during the reduction phase of the lustre firing. In this case a stainless steel capillary tube was inserted into the kiln chamber and a sample of the gases in the kiln was withdrawn using a syringe.
The instrument used in this project was a Hewlett Packard GC 5890 series II using a 25 m silicon gum capillary column using helium as the carrier gas, with a HP 5971A mass selective detector.

6.2.5 Quantitative Reducing Power of *n*-Alkanes

The degree of reduction, or reducing power, achieved by a particular hydrocarbon saturated gas is related to the number of hydrogen and carbon atoms present in the molecule. The reducing power is also dependent on the vapour pressure (P) of the substance because this determines its concentration in the gas. The pressure of vaporisation of a liquid can be calculated using the Clausius-Clapeyron equation:

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where:

P_1 is the vapour pressure at temperature T_1

P_2 is the vapour pressure at T_2

T_1 is the normal boiling point of the liquid (in Kelvin)

$T_2 = 298K$ (ambient temperature)

R is the gas constant, 8.31 J $K^{-1}mol^{-1}$

ΔH is the latent heat of vaporisation

Since each carbon atom reduces 2 oxygen atoms (C → CO_2), during combustion and each hydrogen ion reduces half an oxygen molecule (H → ½ H_2O), thus *n*-pentane (C_5H_{12}) has an intrinsic reducing power (IRP) of 16 (oxygen atoms). A nett reducing power (NRP) can be defined as follows:

Nett Reducing Power (NRP) = Intrinsic Reducing Power (IRP) x Vapour Pressure (P_2) which takes into account the variable concentrations of hydrocarbons in the nitrogen gas stream from the saturator. Thus for *n*-pentane which has a normal boiling point of 309.1 K, the vapour pressure (P_2 atmospheres) at 298 K is obtained from:

$$\ln\frac{P_2}{1} = \frac{-23.8\times10^3}{8.314}\times\left(\frac{1}{298}-\frac{1}{309.1}\right)$$

giving $P_2 =$ 0.67 atm.

Nett Reducing power of pentane = 16 x 0.67 = 10.72

Table 6.1 was compiled from similar calculations for all the alkanes used as reducing agents in the saturating vessel illustrated in figure 6.2.

Table 6.1 Reducing Power of Various *n*-Alkanes in Nitrogen Saturated at 298 K and 5% Hydrogen in Nitrogen

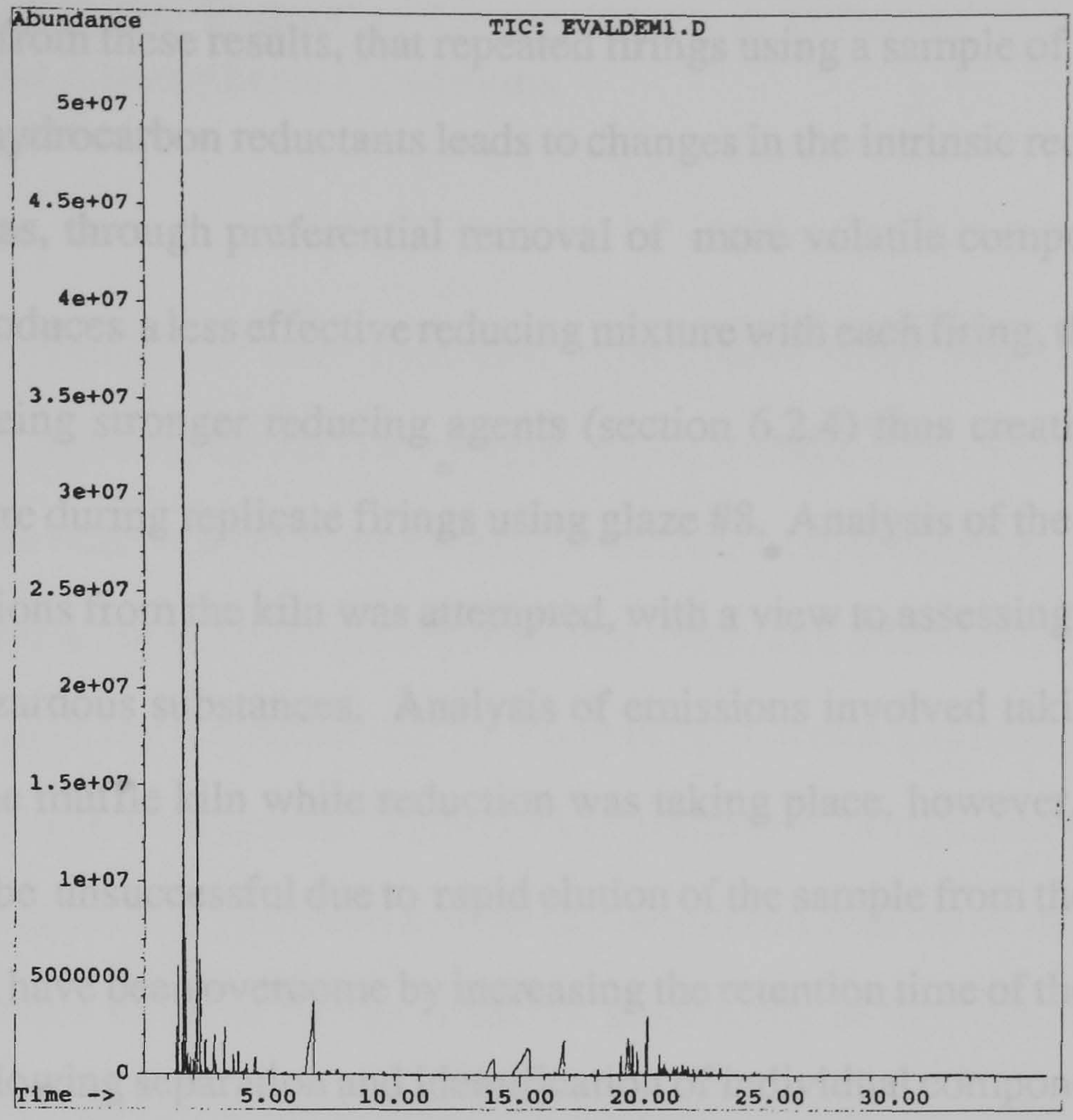
System	Number of carbon atoms per molecule	Number of hydrogen atoms per molecule	IRP	Vapour pressure	NRP
n-pentane	5	12	16	0.67	10.72
n-hexane	6	14	19	0.3	5.77
n-heptane	7	16	22	0.05	1.11
n-octane	8	18	25	0.02	0.49
n-decane	10	22	31	0.002	0.06
5% H_2	–	2	1	0.05	0.05

6.3 Results of Experiments Investigating Kiln Atmospheres

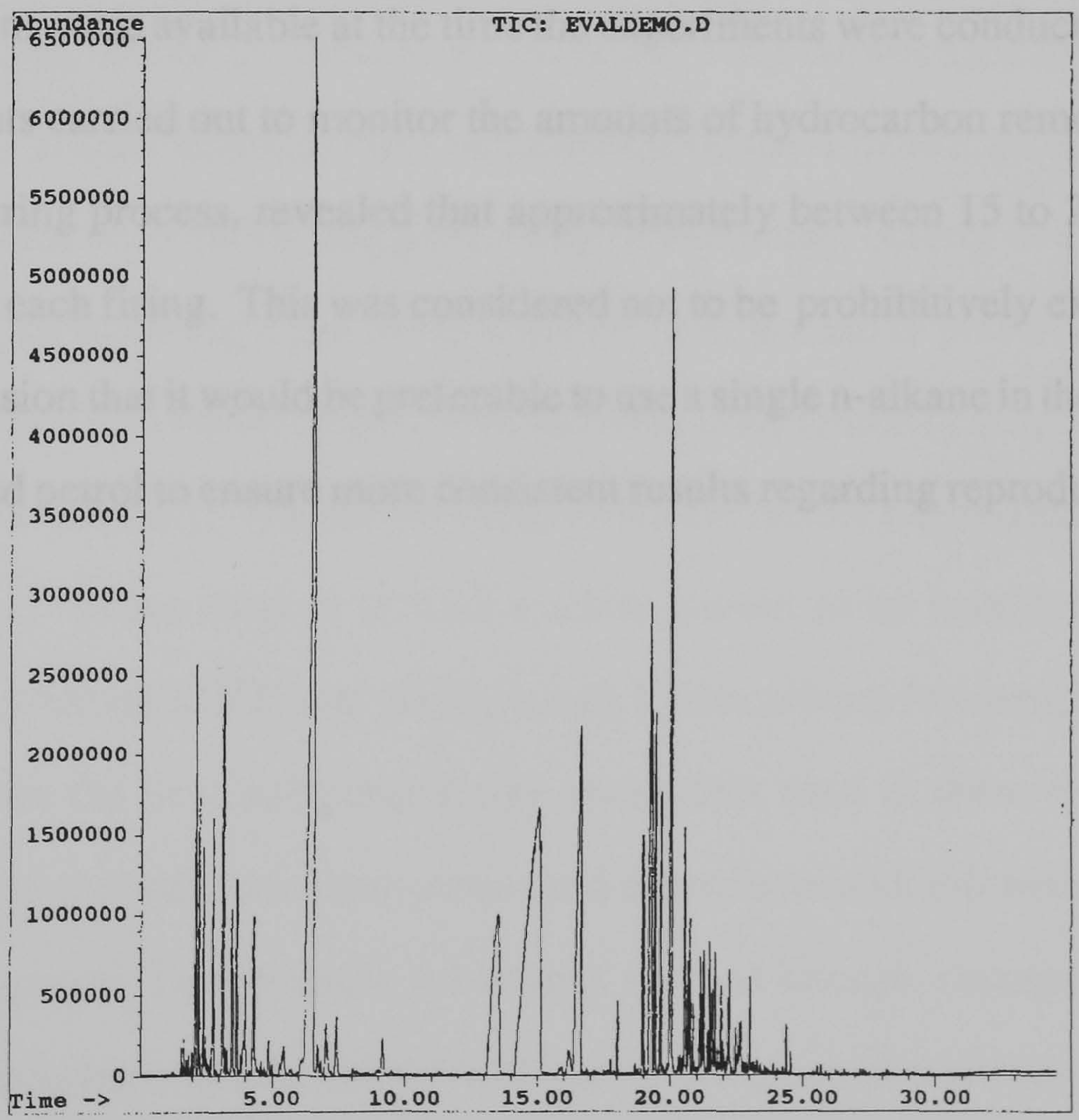
6.3.1 Changes Occurring to Hydrocarbon Components of Reducing Gases During Reduction

Unleaded petrol provided a cheap source of potential reducing agents in the form of various hydrocarbons. With repeated reduction firings it was found that the volume of petrol used from the saturator was not constant, with replicate firings appearing to use different amounts of reductant. The degree of reduction, as observed by colour changes in the standard lustre glaze, #8, also varied with replicate firings, the reducing power of the petrol appearing to be less effective with time.

Chromatographic analysis of samples taken from the gas line prior to saturated gas entering the kiln chamber, showed changes in the proportions of volatile hydrocarbons present before and after a reduction firing. The results showed that the mixture of hydrocarbons in the gas changed as the more volatile, lighter components were taken up by the nitrogen carrier gas in preference to the heavier components. The amount of alkane used up during a reduction firing was found to be dependent on the volatility of the alkane and the gas flow being used. Figure 6.4 shows data obtained from the GC. from two samples of hydrocarbon saturated gas. The data obtained is shown as peaks which represent individual hydrocarbon components of the gas sample identified by the instruments computer data base. The elution time of each component from the column (shown along the y axis) is indicative of its molecular weight and volatility, the area of the peak representing relative concentration. Graph 1 shows the data obtained from a sample taken at the beginning of a firing cycle. The data shows a large proportion of highly volatile hydrocarbons being eluted from the column, less volatile hydrocarbons being eluted at a slower rate, and present at much lower concentrations. Graph 2 shows the data obtained from a sample taken after 15 minutes into the reduction cycle. On comparison with graph 1, the proportion of less volatile hydrocarbons in the sample appeared to increase, with a decrease in the relative amounts of more volatile compounds.



Graph 1



Graph 2

Figure 6.4. Gas chromatographs of unleaded petrol before (graph 1) and after

It can be seen, from these results, that repeated firings using a sample of unleaded petrol as a source of hydrocarbon reductants leads to changes in the intrinsic reducing power of the reducing gas, through preferential removal of more volatile components from the liquid. This produces a less effective reducing mixture with each firing, the more volatile components being stronger reducing agents (section 6.2.4) thus creating inconsistent degrees of lustre during replicate firings using glaze #8. Analysis of the composition of gaseous emissions from the kiln was attempted, with a view to assessing the presence of potentially hazardous substances. Analysis of emissions involved taking gas samples from within the muffle kiln while reduction was taking place, however, these attempts were found to be unsuccessful due to rapid elution of the sample from the column. This problem could have been overcome by increasing the retention time of the sample within the column, allowing separation and identification of individual components. Retention time in such a system can be increased by either taking a larger sample volume or by cooling the collumn in a cryogenic system, thus making the sample more viscous. Neither of thee options were available at the time the experiments were conducted. Gravimetric measurements carried out to monitor the amounts of hydrocarbon removed from petrol during the firing process, revealed that approximately between 15 to 20 g of reductant were used at each firing. This was considered not to be prohibitively expensive and led to the conclusion that it would be preferable to use a single n-alkane in the saturator rather than unleaded petrol to ensure more consistent results regarding reproducibility of lustre effects.

6.3.2 Results of Firing Reduction Lustre Glazes at Different Temperatures and Under Different Atmospheric Conditions

A number of ceramicists have described experiments using alternative sources of hydrocarbon as reducing agents (De Morgan, 1892; Burton, 1907; Peascod, 1981). No differences were observed between alternative sources of hydrocarbon. However it was not clear how much control over the experimental conditions was exercised and no record was documented of any researcher using a 5% hydrogen in nitrogen mixture as a reducing agent for firing reduction lustres. The series of controlled firings undertaken using the lustre glaze #8 (table 2.3) produced a range of colours and degrees of lustre. The results achieved from this series of firings is shown graphically in figure 6.5. The coloured squares shown in the figure were taken from the fired samples. A computer was used to 'frame grab' a video image of the sample. The framed grabbed image was scaled to fit into the diagram. The resulting colours are not accurate due to the limitations of the printing process, but it is possible to see the relationship between the treatments given to the samples. Similar colours could be produced by the different alkanes but not at the same rate. This observation suggests a way of extending control over the lustre firing for example, by selecting a less volatile alkane (e.g. hexane in preference to pentane) a slower reduction rate would be achieved, allowing interruption of the process at a desired point more successfully. Not shown in figure 6.5 are further experiments using *n*-octane and *n*-decane. These sources of hydrocarbon proved to be insufficiently volatile at ambient temperature (25°C), to yield enough hydrocarbons for reduction of the lustre glaze #8 under the time and temperature constraints used in these experiments. The reduction time, the reduction temperature and the reductant all influence the final colour of the lustre glaze. Less volatile substances such as hexane, successfully produced a reducing atmosphere which reacted with the lustre glaze at a slower rate than that of heptane for example.

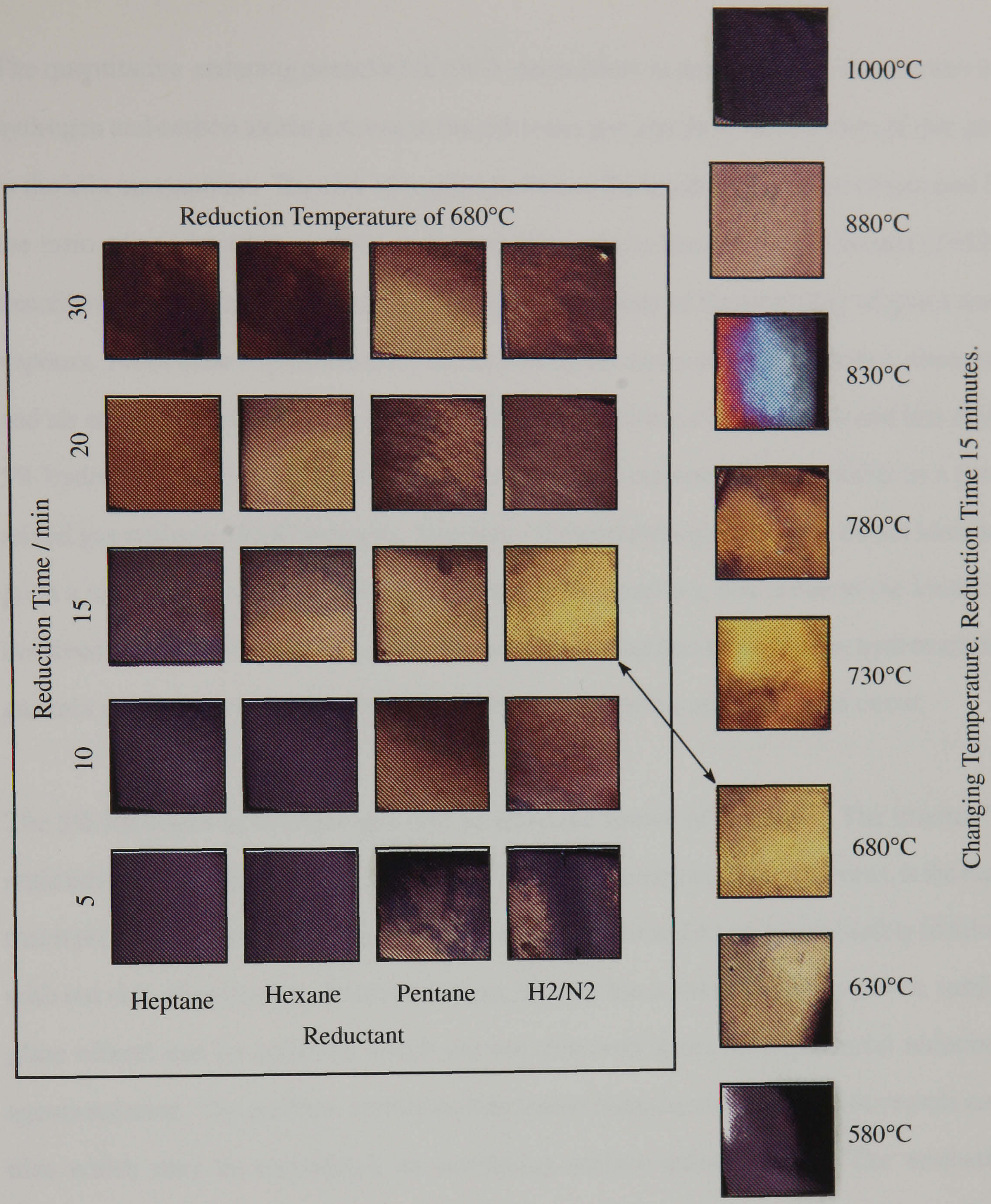


Figure 6.5 Diagram showing the effect on samples of glazed tile (#8 table 2.3) reduced for differing periods of time using differing reductants (left) and the effects on similar samples using a fixed reduction time of 15 min whilst varying the reduction temperatures using 5% hydrogen as the reductant.

The quantitative reducing potential of a kiln atmosphere is dependent on the number of hydrogen and carbon atoms present in the reductant gas and the concentration of that gas in the kiln atmosphere. The risk of explosion from a flammable gas can be eliminated if the ratio of combustible material to inert carrier gas is low enough. Coward (1952) describes experiments carried out to determine the limits of flammability of gases and vapours. From these experiments it was calculated that no mixture of hydrogen, nitrogen and air at atmospheric pressure would ignite if the resulting mixture contained less than 5% hydrogen. A 5% hydrogen in nitrogen mixture is commercially available as a pre-mixed gas mixture (BOC limited). Nitrogen - hydrocarbon gas mixtures do not have as great a reducing potential as nitrogen/hydrogen gas mixtures, this is due to the kinetics involved in the reactions taking place. In the case of reduction by a nitrogen hydrocarbon gas mix a larger number of bonds have to be broken before reduction can occur.

The 5% hydrogen in nitrogen gas was an effective source of reductant. The mixture's main advantages over the use of alternative hydrocarbon saturated gas mixtures, is the fact that it produces no harmful emissions to the environment and it can be used safely in kilns with out risk of explosion. Because the gas mixture has a lower reducing power, subtle glaze effects can be achieved which are not observed when more powerful reducing agents are used. The gas flow within the kiln leaves patterns on the surface of vessels and tiles which may be considered an interesting surface enhancement. The aesthetic potential of this effect could be exploited if it was considered worthwhile to do so. The following chapter describes the use of samples prepared using both hydrocarbons and hydrogen in an aesthetic evaluation survey.

CHAPTER SEVEN

7 The Aesthetic Evaluation of Ceramics

7.1 Introduction

The following chapter describes the development of a methodology for the statistical assessment of the aesthetic qualities achieved by some of the different firing regimes described in this thesis. A multiple sorting task was carried out so that meaningful criteria could be established for use in a perceptual survey. The technique adopted for the survey was based on a semantic differential method.

A feasibility study was carried out using lustre glazed ceramic tiles and a further study was undertaken using two groups of lustre glazed ceramic vases which had been fired under different reducing conditions. The resulting data was analysed to establish whether significant differences were perceived between the two groups of vases by the respondents.

7.1.1 Aims of Experiments Described in Chapter Seven.

- To establish a method of assessing the aesthetic qualities of ceramic glazes in an objective manner.

- To use the method to make statistically significant comparisons between alternative firing systems.

- To investigate the possibility of relating specific aesthetic responses to characteristics of the glaze or firing process.

7.1.2 Aesthetic Evaluation Techniques

One of the central aims of this research programme has been to improve an existing method of producing a decorative glaze effect. The improvements sought were concerned with the control and safety of the firing system and the elimination of harmful emissions from the kilns used to produce the glaze effect. This was to be achieved without deterioration in the aesthetic quality of the fired results. It can be relatively straight forward to determine whether or not a piece of equipment or process is less hazardous than an existing system. For example a kiln which produces no toxic emissions may be considered to be an improvement on a kiln designed for the same purpose that produces large quantities of carbon monoxide. It is a much more complex task to determine the aesthetic qualities of the finished results in an objective manner if the two systems are designed to produce a similar effect. Aesthetic decisions are by nature highly subjective. A method is therefore required which can assess the aesthetic qualities of a finished product objectively and in such a way that the responses obtained can be correlated with particular aspects of the technique being used. In this way, aspects of the new system can perhaps be altered so as to gain a more favourable response. For example, if a characteristic of the new system, which could be controlled, were the degree of variance in the colour of the fired lustre, this characteristic could be enhanced or suppressed to bring about a more favourable response from the majority of observers or to select minorities who preferred that characteristic..

Testing psychological responses to external stimuli is known to be notoriously complex. One way of attempting to simplify the problems of interpreting human responses to aesthetic stimuli is to attempt to reduce the stimulating object to its basic components. For example separating out shape or form from colour by using coloured rectangles or using black shapes on a white background (Berlyn, 1971). Unfortunately even this approach has its inherent difficulties. Even under precisely controlled experimental conditions any results obtained tend to be of limited value since isolated coloured rectangles bear little relationship to a real stimulus such as an actual painting or piece of ceramic. One of the first experiments carried out in this field in 1865 recorded preferences among rectangles (Berlyn, 1971). The first example of an empirical investigation of reactions to works of art took place in 1871 when two versions of Holbein's *Madonna with Burgomaster Meyer* were displayed next to each other in a Dresden museum. There was some doubt as to the authenticity of one of the versions on display. Visitors to the exhibition were asked to write down their judgements. The experiment did not fulfil its primary objective. However it did form the basis of an important methodology. It introduced the practice of answering psychological questions pertaining to aesthetics by obtaining and recording the reactions of a sample of subjects representing a particular population. This experiment was recorded by the German physicist, philosopher and psychologist, G. T. Fechner, who is credited as being the founder of experimental aesthetics. He published his theories in a volume entitled *Elemente der Psychophysik* (Elements of Psycophysics, 1860).

The procedures for obtaining and recording judgements have increased in sophistication since Fechner's pioneering work was undertaken. Subjects might, for example be asked to rank-order a collection of objects from the most to the least preferred. One common method used for doing this is paired comparison, in which objects are presented for judgement two at a time, so that the preferred number of each pair can be indicated. This is equivalent to rank-ordering two objects at once. Similarly, rank-ordering by threes involves the presentation of three objects at a time, in this case the most and the least preferred is indicated on every trial. Another technique requires respondents to select a number representing degree of preference or liking for each object in the collection in turn. The aim of experiments of this nature is to relate preferences to particular properties apparent in the object or work of art, which was Fechner's objective.

A contemporary technique which has been found useful as a method of obtaining objective judgements on matters of taste is the semantic differential test. Anastasi (1988) reports that the technique was first developed by Osgood and his associates (Osgood *et al.* 1957) as a tool for research on the psychology of meaning, although its potential for personality assessment was also recognised. The Semantic Differential is designed as a standardised and quantified procedure for measuring the perceptual responses of any given concept for the individual. The test consists of a series of bipolar adjectives placed at opposite ends of a 7-point scale, for example 'bright' and 'dull'. Approximately 15 scales are used to test any particular concept. The test developed by Osgood consisted of 50 scales and subsequent analysis revealed three major categories of concept; *evaluative*, with high loadings in such scales as good-bad, valuable-worthless, and clean-dirty; *potency*, found in such scales as strong-weak, and heavy-light; and *activity*, described in such scales as active-passive, fast-slow, and sharp-dull. The concepts rated by a single individual can be analysed quantitatively by computing the "score" of each concept in the three principal factors described above. For this research programme the test was used to evaluate groups of individuals' aesthetic responses to pairs of ceramic tiles or related groups of ceramic vessels which differed in one aspect, that is the manner in which they had been reduction fired. The scales used in the survey were *evaluative* in nature.

The semantic differential technique has been used to study a wide variety of aesthetic and perceptual topics. A recent research study into the chemical cleaning of historic buildings applied this technique to gain an understanding of the way different groups of people perceived the appearance of buildings before and after cleaning. (Webster, 1992). The technique can be applied to subjects that are of a somewhat abstract nature such as the aesthetics of works of art, or in this case ceramic glazes. Although the procedure has been used in many different situations it has not been applied to the assessment of the aesthetic qualities of ceramic glazes and the objective assessment of a new firing procedure. The combining of the scientific study with the aesthetic survey is an original approach in this area of study.

7.2 Experimental Procedure

7.2.1 Multiple Sort Task

The bipolar adjectives, which make up the categories used in the semantic differential survey, were arrived at following a preliminary survey based on the application of a multiple sorting task. Sorting items into categories is a common activity. In some cases this is done on the basis of a personal categorisation scheme and even when selection is not overtly involved, judgements are based on an implicit categorisation scheme. The aim of the multiple sorting task was to reveal these personal schemes. The general procedure followed for a multiple sorting survey is detailed by Canter *et al.* (1985). The instructions to participants, derived from the method described by Canter, are reproduced in Appendix II together with the proforma form used to record responses. The form was designed to record the number of sorts and the categories chosen. No limitations were placed on how the sorting of the tiles was to be done. If particular comments where made about individual tiles, these where recorded on the last page of the form.

Participants carrying out the multiple sort task were asked to look at a number of ceramic tiles, the purpose of the survey was briefly explained and it was emphasised to each participant that their own categories chosen to describe the tiles presented were of particular interest. Each individual was then asked to sort the tiles into groups so that all the tiles in any given group had something important in common which distinguished them from the tiles in other groups. After the initial sort, individuals were then asked to sort the tiles again using new criteria. If odd tiles did not fit conveniently into the chosen categories they were placed in a separate group referred to as 'other'. This did not influence the outcome of the survey. Participants were asked to continue to sort on the basis of new categories as many times as they felt able to do so. The number of tiles used in the survey was twenty, this proved to be rather too many to handle easily, making the test time consuming. In addition to sorting tiles according to their own categories, individuals were asked to sort the tiles into sets that matched possible settings of their choice, relating to the possible environment that might be chosen by the participant for the tiles. Examples might be bathroom or kitchen.

The tiles used in the sorting task had been produced during the development of lustre glazes and related experiments. The tiles were glazed mainly with different lustre effects. Roughly half the tiles had been reduction fired using the down draft gas kiln described in section 5.2.1. The other half had been fired using the electric kiln described in section 5.2.2, using a variety of reducing agents. Two of the tiles had been glost fired but had not yet received a reduction firing, these were included to establish whether or not 'lustre' would be perceived as a specific quality by an average individual with no specialist knowledge of ceramics. The two unreduced tiles were both undecorated, one being dark blue and the other pale green. Table 7.1 lists the tiles used for the multiple sorting task together with details of their preparation.

Participants taking part in the multiple sorting task where chosen at random and did not have specialist knowledge of ceramics. Approximately fifty percent of the participants chosen were staff or students working at Gray's School of Art. The other participants were drawn from the staff and students working in the science faculty of the university. Approximately equal numbers of males and females were asked to participate and ages ranged from early twenties to late fifties.

Each tile used in the study was identified by a number placed on the back of the tile. After each sort, tiles were turned over and their numbers recorded along with the corresponding categories chosen by each participant. As soon as this was done, the tiles were rearranged and re-sorted according to a new set of criteria chosen by the respondent.

This procedure was repeated until participants could no longer suggest new criteria.

Table 7.1. Description Of Tiles Used For Multiple Sorting Task

Tile Number	Glaze	Decoration	Kiln Used*	Reduction Time/ mins	Reductant	Reduction Temp/ °C
1	Matt Black	#10 Art nuvo print	LK1	15	Propane	665
2	Matt Black	#8 Lustre glaze print	LK1	10	Propane	665
3	L21/T	#8 Brushed diagonal lines	LK1	15	Propane	665
4	#8 (CRL)	None	No reduction	-	-	-
5	#10 (MCG)	Sun Flower print	LK1	20	Propane	665
6	#6 (L21/o)	JM3 Clay Paste Transfer	LK1	20	Propane	665
7	#13 (2BG)	None	LK2	15	N2/H2	680
8	#11 (Purple)	None	LK2	20	N2/h2	700
9	#13 (2BG)	None	LK1	10	Propane	665
10	#9 (VCL)	None	No reduction	-	-	-
11	#12 (GS)	#12 Lustre glaze print	LK1	10	Propane	665
12	Johnsons White	#8 Islamic pattern	LK2	20	Petrol	700
13	#10 (MCG)	None	LK1	15	Propane	665
14	L21/T	JM3 Art nuvo print	LK1	20	Propane	665
15	#10 (MCG)	None	LK2	15	Petrol	700
16	#16 (Blue)	Sun Flower print	LK1	20	Propane	665
17	#15 (S872)	None	LK1	15	Propane	665
18	#9 (VCL)	None	LK2	20	Petrol	700
19	#8 (CRL)	None	LK2	20	Petrol	700
20	#6 + JM 9	None	LK2	30	H2/N2	700

*LK1 = Gas Kiln and LK2 = Electric kiln

Participants were not prompted in any way and were not shown previous individuals' responses. Although numerical data was recorded from this initial survey, it was not analysed since the survey's purpose was to establish a list of categories upon which a semantic differential survey could be based. In theory it would be possible to enter the responses into a spreadsheet/data base, after which it would be possible, for example, to obtain a description of each tile based on the views of all the respondents.

7.2.2 Results of Multiple Sort Task

Listed below are the categories and subdivisions identified by respondents taking part in the multiple sort task.

- Warm or Cold
    - (a) Warm
    - (b) Intermediate
    - (c) Cold
- Degree of Reflectiveness
    - (a) None
    - (b) Muted
    - (c) Medium
    - (d) Reflective
    - (e) Very reflective
    - (f) Highly reflective
- Degree of Iridescence
    - (a) No interference pattern
    - (b) With interference pattern
- Surface Texture
    - (a) Some
    - (b) None
- Degree of Pattern
    - (a) Patterned
    - (b) Dotted

    - (C) Plain
- Shiny or dull
    - (a) Dull
    - (b) Not so dull
    - (c) Shiny
    - (d) Very Shiny
- Predominant Colour
    - (a) Blue
    - (b) Green
    - (c) Red
    - (d) Yellow
- Surface Pattern
    - (a) Plain colour, dotted surface, metallic
    - (b) Plain colour, smooth, non metallic
    - (c) Dark patterned
    - (d) Bright patterned
    - (e) Plain, smooth, metallic
- Aesthetically Pleasing
    - (a) Personally pleasing
    - (b) Generally pleasing
    - (c) Neutral
    - (d) Displeasing
- Expected Monetary Value
    - (a) Expensive
    - (b) Less expensive
    - (c) Average
    - (d) Low budget
    - (e) Cheap and nasty
- Patterned or None Patterned
- Metallic or Non Metallic
- Type of Surface Pattern

The most common categories were related to colour, metallic or non metallic, and surface pattern. A minority of participants made a distinction between iridescence and reflectiveness. The total number of interviewees was less than thirty, this was considered sufficient in order to establish categories and to meet the aims of the survey. The environment in which the tiles were viewed would be expected to have a strong influence on the perceptions of individuals participating in the survey, for example the presence of artificial lighting compared to natural light. This also relates to the number of replicate sample tiles exhibiting similar surface effects. For example, some individuals regarded random patterns formed by an uneven reduction as a possible flaw in the glazing process. If this had been a feature common to a number of replicate tiles, it may have been perceived as intentional.

7.3 Semantic Differential Survey

Following analysis of the multiple sorting task, the following bipolar adjectives were derived and included in a semantic differential survey proforma. The proforma and instructions are included in Appendix III. The categories are set out below:

Semantic Differential Categories
1 Bright..Dull
2 Metallic .... Non metallic
3 Reflective ....Non reflective
4 Iridescent ....Non iridescent
5 Expensive................................Cheap
6 Pleasing...................................Displeasing
7 Smooth ....Rough
8 Hand made ....Industrial
9 Domestic Setting................. ...Non domestic
10 Warm.......................................Cold
11 Shallow...................................Deep
12 Abstract ....Non abstract
13 Transparent.............................Opaque
14 Modern ....Old fashioned
15 Attractive ....Unattractive

It may be noted that the more negative terms of each adjective pair are predominantly listed on the right hand side of the proforma. This was designed to make completion of the proforma easier for the participant, and to simplify the interpretation of the results.

Two semantic differential surveys were undertaken to validate a method of aesthetic assessment. The first study was used as a feasibility study only, using tiles (150 mm x 150 mm) to represent regular 2-dimensional surfaces, allowing comparisons to be made between glazed finishes, avoiding distractions related to substrate shape. The second survey consisted of two separate groups of vase forms which were representative of typical 3-dimensional lustre glazed surfaces. This added complexity to the appearance of the glaze due to the influence of the underlying form. The properties of observed differences having a statistical significance could be tested using the Willcoxon matched-pairs signed ranks test or Mann-Whitney U tests (Bartz, 1988), these two tests have been shown to be mathematically equivalent. These tests are similar to the Student t-test in that they are designed to establish whether or not paired groups of data are significantly different or whether the difference can be attributed to sampling error. The tests generate a p value or probability factor. If p is < 0.05 then the 'null hypotheses' is rejected and the difference is regarded as significant at the 0.05 level. At $p < 0.01$ the difference is regarded as highly significant. If on the other hand the value of p is > 0.05 the differences may not be of real significance but could be due to sampling error. P values can be directly compared between sample populations and shows the relative degree of significant difference.

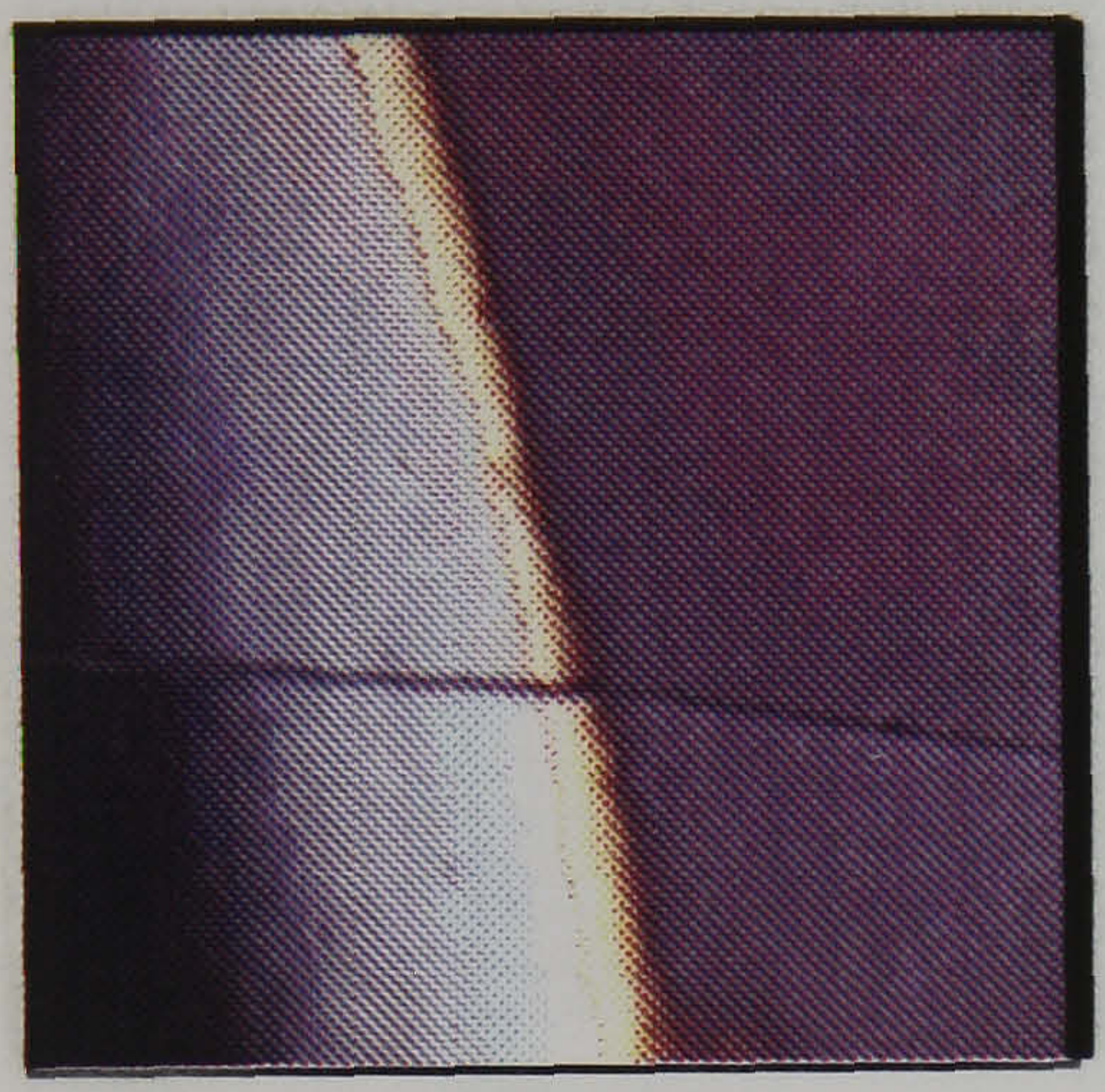
7.3.1 Semantic Differential Survey Using Tiles

The preliminary semantic differential test using tiles, was carried out among ceramic artists attending an international ceramics workshop. Eight tiles were used, selected from a wide range of reduction glazed tiles produced during the course of this research program. The group of tiles were chosen such that comparisons could be made between pairs of tiles which differed in one respect only. For example tiles 1 and 2 described in table 7.2, differ only in the reductant used (note, the crack shown in tile 2 occurred after the survey had been completed).

Table 7.2. Description of Tiles Used in Preliminary Semantic Differential Study.

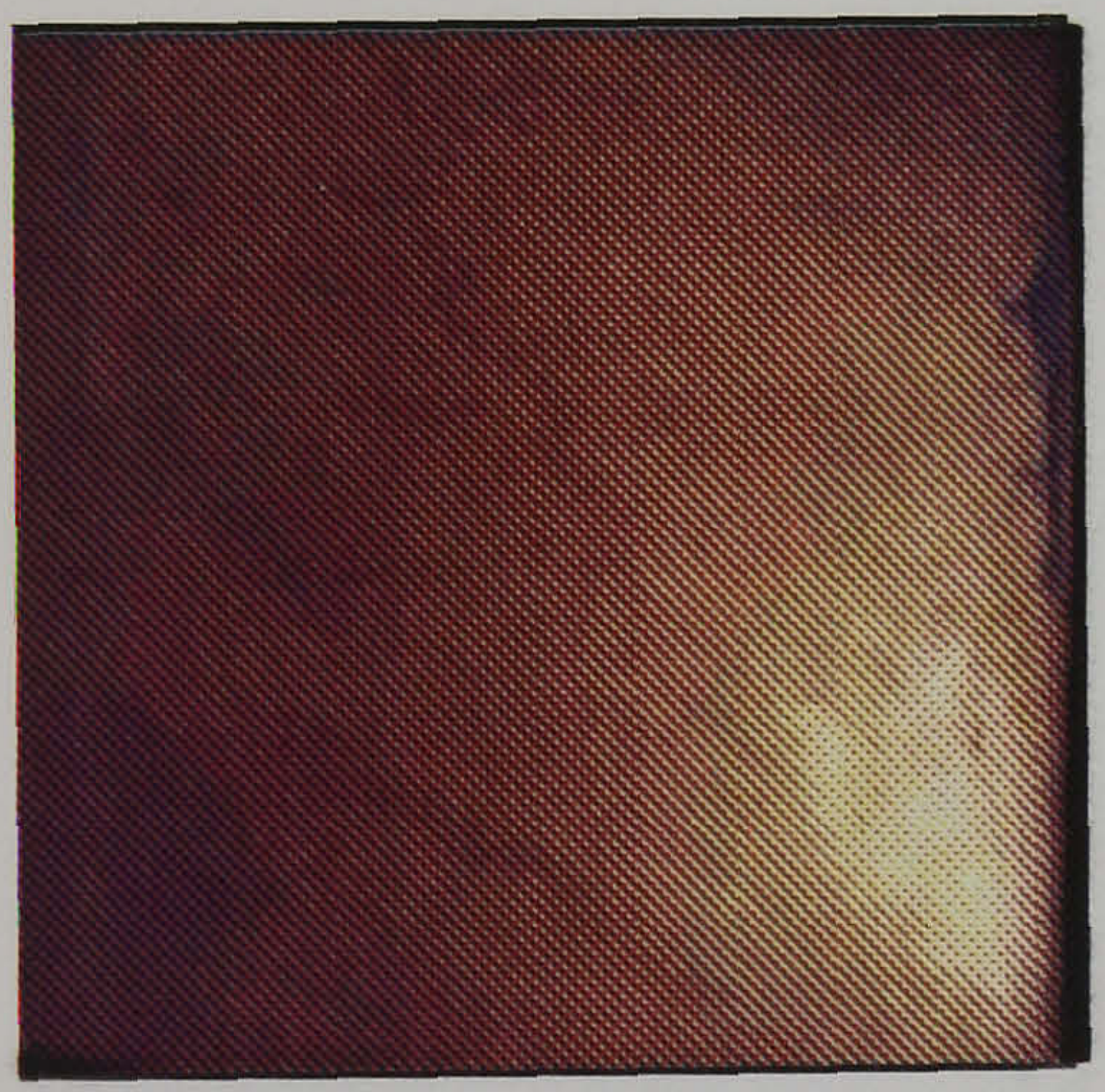
Tile 1

Glaze(s) Used	#8 (CRL)
Kiln Used	Electric kiln
Reductant Used	hexane in nitrogen
Reduction Time	15 minutes
Reduction Temperature	680°C



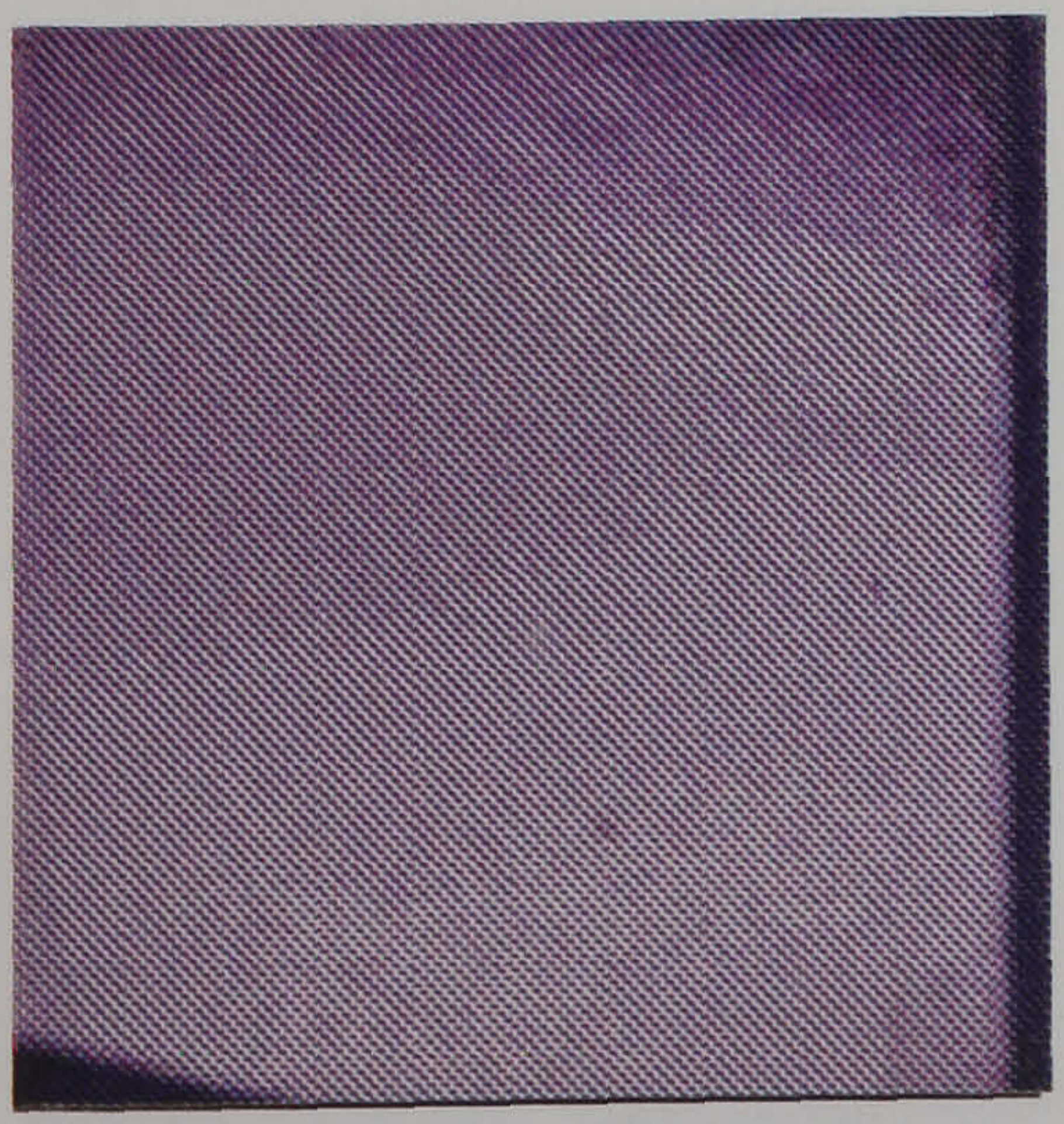
Tile 2

Glaze(s) Used	#8 (CRL)
Kiln Used	Electric kiln
Reductant Used	5% hydrogen in nitrogen
Reduction Time	15 minutes
Reduction Temperature	680°C



Tile 3

Glaze(s) Used	#8 (CRL)
Kiln Used	Electric kiln
Reductant Used	pentane in nitrogen
Reduction Time	15 minutes
Reduction Temperature	680°C



Tile 4

Glaze(s) Used	#8 (CRL)
Kiln Used	Electric kiln
Reductant Used	None
Reduction Time	None
Reduction Temperature	None

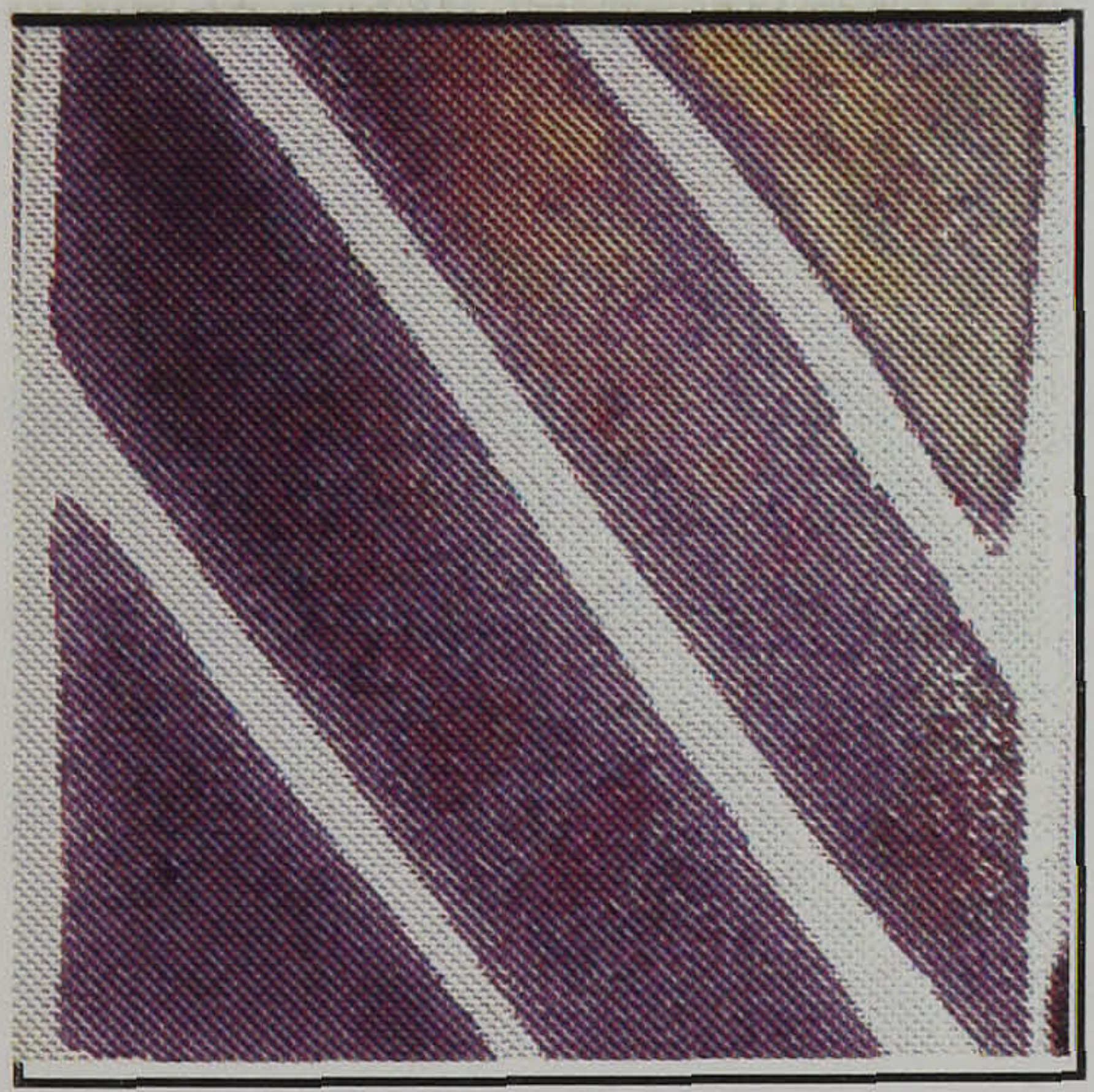
Table 7.2 Continued :-

Tile 5

Glaze(s) Used	#8 (CRL)
Kiln Used	Electric kiln
Reductant Used	Unleaded petrol
Reduction Time	15 minutes
Reduction Temperature	680°C

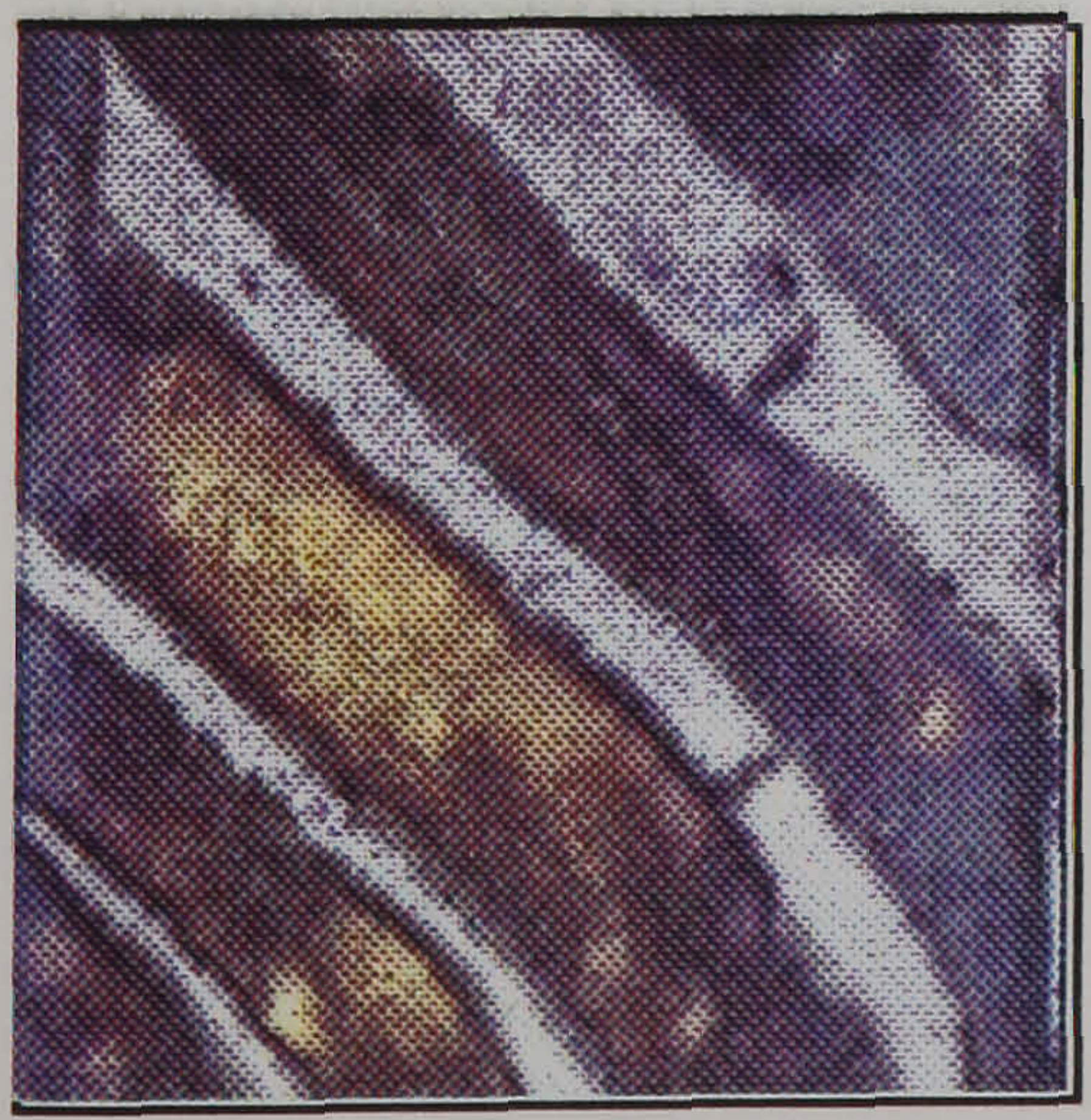
Tile 6

Glaze(s) Used	#8 (CRL)
Kiln Used	Electric kiln
Reductant Used	5% hydrogen in nitrogen
Reduction Time	20 minutes
Reduction Temperature	700°C



Tile 7

Glaze(s) Used	#7 over dark blue engobe
Decoration	# 13 brushed over
Kiln Used	Electric kiln
Reductant Used	5% hydrogen in nitrogen
Reduction Time	15 minutes
Reduction Temperature	680°C



Tile 8

Glaze(s) Used	Matt white
Decoration	# 13 transfers
Kiln Used	Electric kiln
Reductant Used	5% hydrogen in nitrogen
Reduction Time	15 minutes
Reduction Temperature	680°C

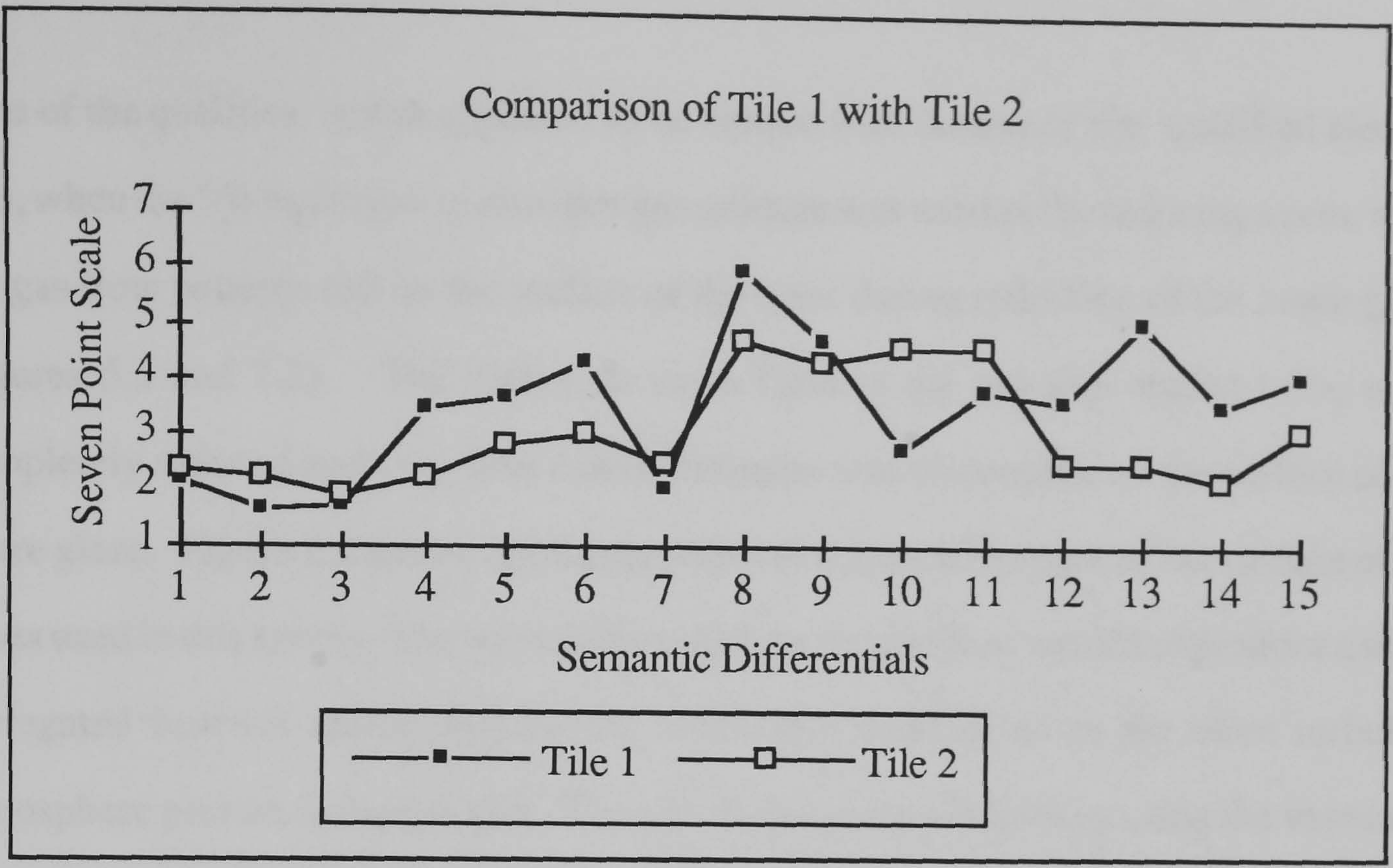
7.3.2 Results of Semantic Differential Survey Using Tiles

Using the eight tiles from the semantic differential survey, various comparisons could be made between tiles which had undergone different firing procedures. In this example the t-test was used to assess the statistical significance between the responses to the different tiles. Tiles 1, 3, 5 and 6, described in table 7.2, had all been glazed using #8 but had undergone reduction firings using different reductants. Table 7.2 shows colour representations of the tiles used in the survey, together with the glaze and firing details. Any tile can be compared with any other tile in the table provided they only differ in one respect. When comparing tiles 1 and 2, which only differ in the reductant used, it would be possible to investigate whether or not a variegated, predominantly blue, lustre is preferred to a more even, (more reduced) red colour. Comparison between tile 3 and 4 allows comparison between a tile with a lustre and one without any lustre. Tile 5 and 6 are very similar in colour but tile 6 has a more mottled surface quality. Tiles 7 and 8 are perhaps too different for a comparison by this survey technique. However tile 8 was given a coating of dark blue engobe under a transparent glaze before a lustre glaze was applied in broad stripes over. The effect produced a lot of iridescent colours and a quality of depth. Tile 7 had a similar pattern but had a more ridgid design quality owing to the use of glaze transfers rather than brush to apply the lustre glaze pattern and much flatter appearance due to the use of an opaque white background glaze. Tiles 7 and 8 were included in the survey to investigate the aesthetic qualities represented by the semantic differential terms 'hand made - industrial' and 'deep - shallow' and to judge the reaction to the category referring to degree of iridescence. Respondents were asked to complete a separate response form for all eight tiles.

Where the glaze appearance was markedly different due to the different kiln atmospheres used, for example between tile 1 and tile 2 (table 7.2), statistical analysis showed a number of significant differences occurring between the semantic differential categories (figure 7.1). The glaze used for each tile was the same (#8 (CRL)). The difference in the tiles' appearance was solely due to the different reducing agents which had been used, hexane in nitrogen for tile 1 and 5% hydrogen in nitrogen for tile 2.

From figure 7.1 it can be seen that significant differences were recorded between tiles 1 and 2 for categories 4, 6, 8, 10, 13, 14 and 15. Tile 1 was therefore considered less iridescent, less pleasing, more industrial, warmer in colour, more opaque, less modern and less attractive than tile 2.

From this initial survey using lustre glaze tiles, two problems were identified. Firstly, using eight tiles simultaneously in one survey proved to be impractical since the test became too time consuming for the respondents to complete. As a result the number of respondents who completed all the response forms was low, less than 30 which is below the minimum recommended sample size for this type of survey. Secondly, the choice of tiles used in the survey was found to be unsatisfactory, being either visually too similar or by differing too much in the glazing methods used in their production. For example, a comparison between tile 1 and tile 8 was not valid since the treatments used varied in more than one respect, making it impossible to attribute the differences identified by the survey to a specific aspect of the tiles' firing treatment. The large number of tiles also meant respondents were liable to become bored by repetition and were therefore less likely to give considered responses when completing the questionnaire. For these reasons only one set of comparisons is presented here as figure 7.1, which is only included as an example of how the semantic differential survey data can be interpreted.



	Semantic Differential Categories	**P Values**
1	Bright.........................Dull	0.556
2	Metallic.......................Non-Metallic	0.126
3	Reflective....................Non-Reflective	0.549
4	Iridescent.................... Non-Iridescent	0.003 *
5	Expensive.................. Cheap	0.074
6	Pleasing...................... Displeasing	0.004 *
7	Smooth....................... Rough	0.150
8	Hand Made................ Industrial	0.013 *
9	Domestic Stetting....... Non-Domestic	0.347
10	Warm.........................Cool	0.005*
11	Shallow......................Deep	0.125
12	Abstract...................... Non-Abstract	0.067
13	Transparent................ Opaque	0.000 *
14	Modern....................... Old Fashioned	0.000 *
15	Attractive.................... Unattractive	0.000 *

* Significant at $P < 0.05$

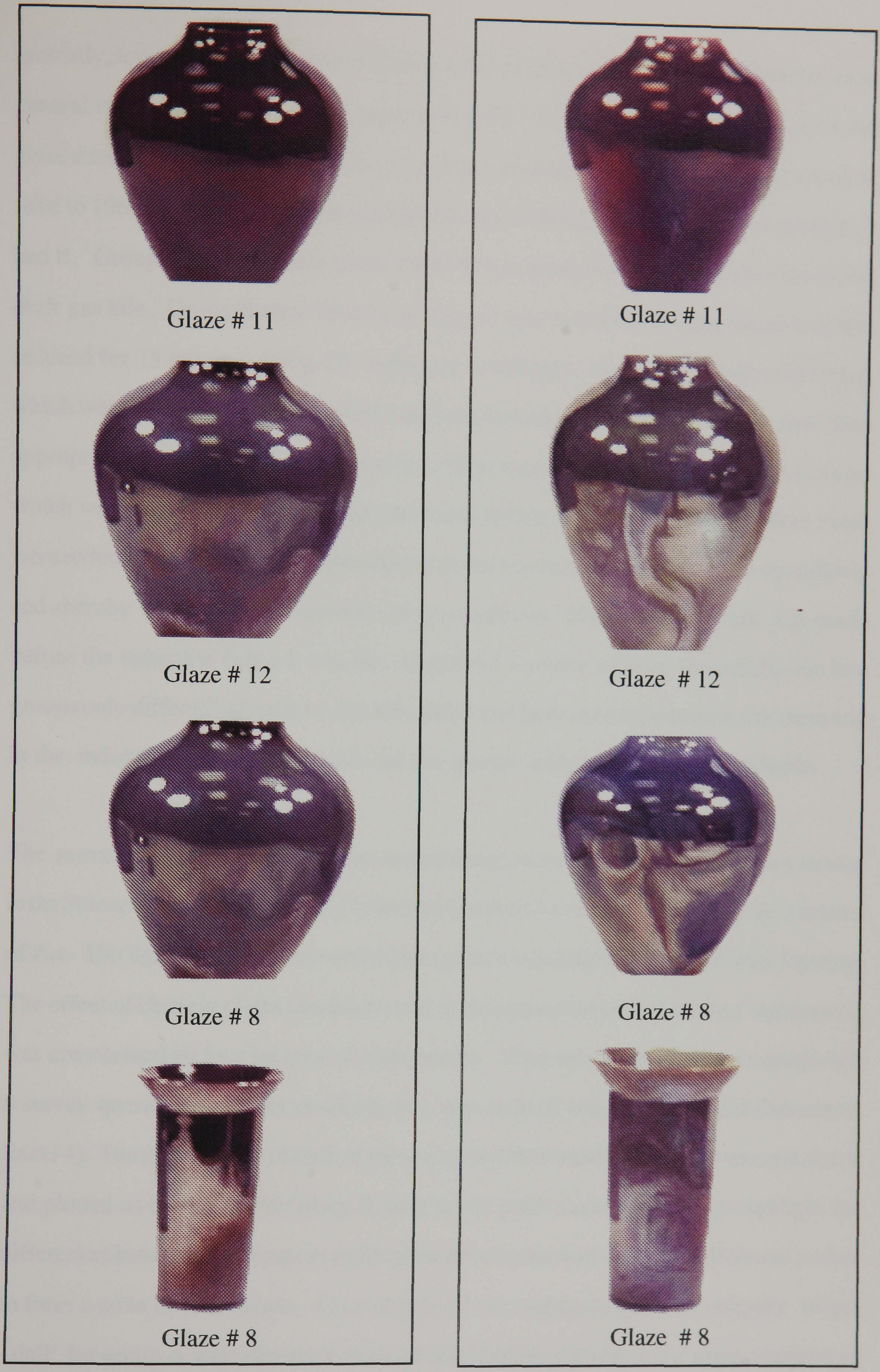
Figure 7.1 Results of semantic differential survey using tiles 1 and 2 (table 7.2).

7.3.3 Semantic Differential Survey Using Lustre Glazed Vases.

One of the qualities, which appeared to be unique with the use of the modified electric kiln, when the 5% hydrogen in nitrogen gas mixture was used as the reducing agent, were the gas flow patterns left on the surface of the ware during reduction of the lustre glaze (figures 5.5 and 7.2). The glazes on vases fired in the gas kiln tended to be more completely reduced and very little colour variation was discernible on the surface of the lustre glaze. Figure 7.2 shows digitised computer enhanced images of the surface of the vases used in this survey. The wave patterns left by the gas flow tended to produce a more variegated lustrous appearance on the vases than those fired in the more turbulent atmosphere present in the gas kiln. The aim of this particular survey using the vases was to determine whether the semantic differential technique could be used to

make comparisons between the different qualities achieved by the two firing systems. The down draft gas kiln was representative of a traditional method of firing lustres and the modified electric kiln, using 5% hydrogen in nitrogen, was representative of a new reduction system. The survey described in this section was designed to test the hypothesis that the new firing system was capable of producing reduction lustre effects of comparable quality to those produced by the more traditional method. The electric kiln was capable of being programmed to repeat a specific firing cycles which could either emphasise the wave patterns left by the reducing gases, or the reduction time could be extended so that the final result would be closer to the quality of lustre achieved in the down draft gas kiln.

Groups of vases which had undergone reduction in each kiln were used in the survey as opposed to selected individual pieces from each firing. This was intended to prevent a potential source of bias occurring through personal preference of the researcher setting up the survey. The vases used in the aesthetic evaluation survey were slip-cast in a white bone china body, high bisque and glazed in a variety of lustre glazes. The forms were not



Group A **Group B**

Figure 7.2 Digitised video images of the two groups of vase forms used in the semantic differential survey.

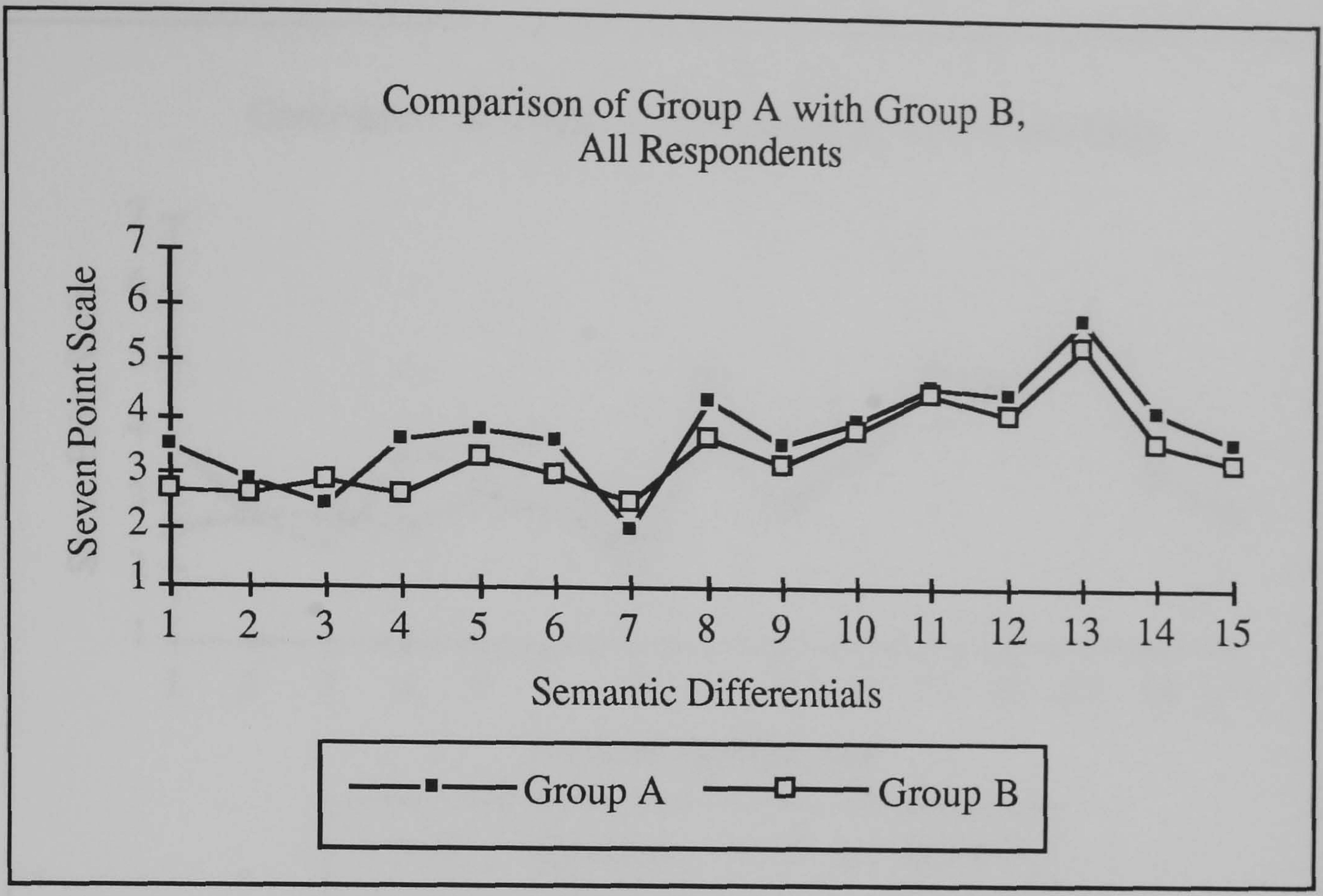
specially designed but were chosen from a range of shapes which were representative of general vase forms. Glazes were applied by spray. This led to some unevenness in the glaze thickness which also contributed to colour variations on firing. The vases were glost fired to 1060°C in a conventional electric kiln before being separated into two groups; A and B. Group A were reduction fired at 860°C using propane, for 15 minutes in a down draft gas kiln. Group B were fired in an electric kiln to a similar temperature and also reduced for 15 minutes, using 5% hydrogen in nitrogen. Four vases from each firing, which were the same shape and which had been identically glazed (figure 7.2), were then appropriately labelled on their bases as belonging to group A or B. The selection of vases which were to be used in the survey was made before the reduction firing. More vases were reduction fired than were to be used in the survey in order to fill the kilns completely and thereby simulate more realistic firing conditions. Since this selection was made before the reduction firing it was not considered a source of bias. Essentially the two groups only differed in respect to the kiln which had been used to reduction fire them and in the reductant used. Despite this the two groups were visually distinguishable.

The semantic differential survey was carried out at two sites over a period of two weeks, in the Science Faculty building of The Robert Gordon University and at the Gray's School of Art. The lighting conditions varied from good natural light to total artificial lighting. The effect of changing light conditions and subsequent change in the vases' appearance was commented on by a number of respondents. Over seventy respondents completed a survey questionnaire. The resulting data was entered into a spreadsheet (Microsoft Excel 4). The mean values of each of the semantic differential categories were calculated and plotted as Group A and Group B, on a seven point scale In order to highlight the differences between the groups A and B, pairs of columns were subtracted from each other to form a table of 15 columns. For example all the responses given to category 'bright - dull' for group A were deducted from all the responses given in the same category to group B. The Wilcoxon matched-pairs signed-ranks test (Bartz, 1981)was then applied to the 15 column table comparing the difference in scores with zero to establish whether or not differences which were visually discernible were significant at $P < 0.05$. The data was entered into the spreadsheet so that respondents' scores for group A and group B were on the same row of the work sheet, together with details of age, gender and whether they were from the Art School or the Science department belonging to the University. Entered in this way the data could be sorted by the computer, according to origin, sex or age group. This allowed for a more detailed analysis of the data. For example the question of whether respondents from the Art School would give different responses when presented with the two groups of vases, than those given by the members of the science faculty, could be investigated. This was in fact done and the results are given in section 7.4.1. Similarly it would also be possible to compare responses between male and female respondents or between younger and older respondents.

7.3.4 Results of Semantic Differential Survey Using Two Groups of Lustre Glazed Vases.

Figure 7.3 shows the results obtained from the respondents to the aesthetic evaluation survey taken as a whole. The two sets of responses are generally similar. This was expected since both sets of vases were basically the same, except group A had been fired using propane as the reducing agent in the down draft gas kiln and group B had been fired using a hydrogen in nitrogen gas mixture in the modified electric kiln. Further analysis of the results obtained was then carried out. Splitting the responses into those given by members of the Science Faculty and those given by the Art School, figures 7.4 and 7.5, show the Art School respondents making greater distinctions between the two groups, than those made by the Science Faculty respondents. The differences in the responses given by the members of the Art School compared with the Science Faculty can be assessed by comparing the p values shown in figures 7.4 and 7.5.

Although the differences between group A and B as perceived by all respondents, were not large, ten out of the fifteen categories showed significant differences were perceived

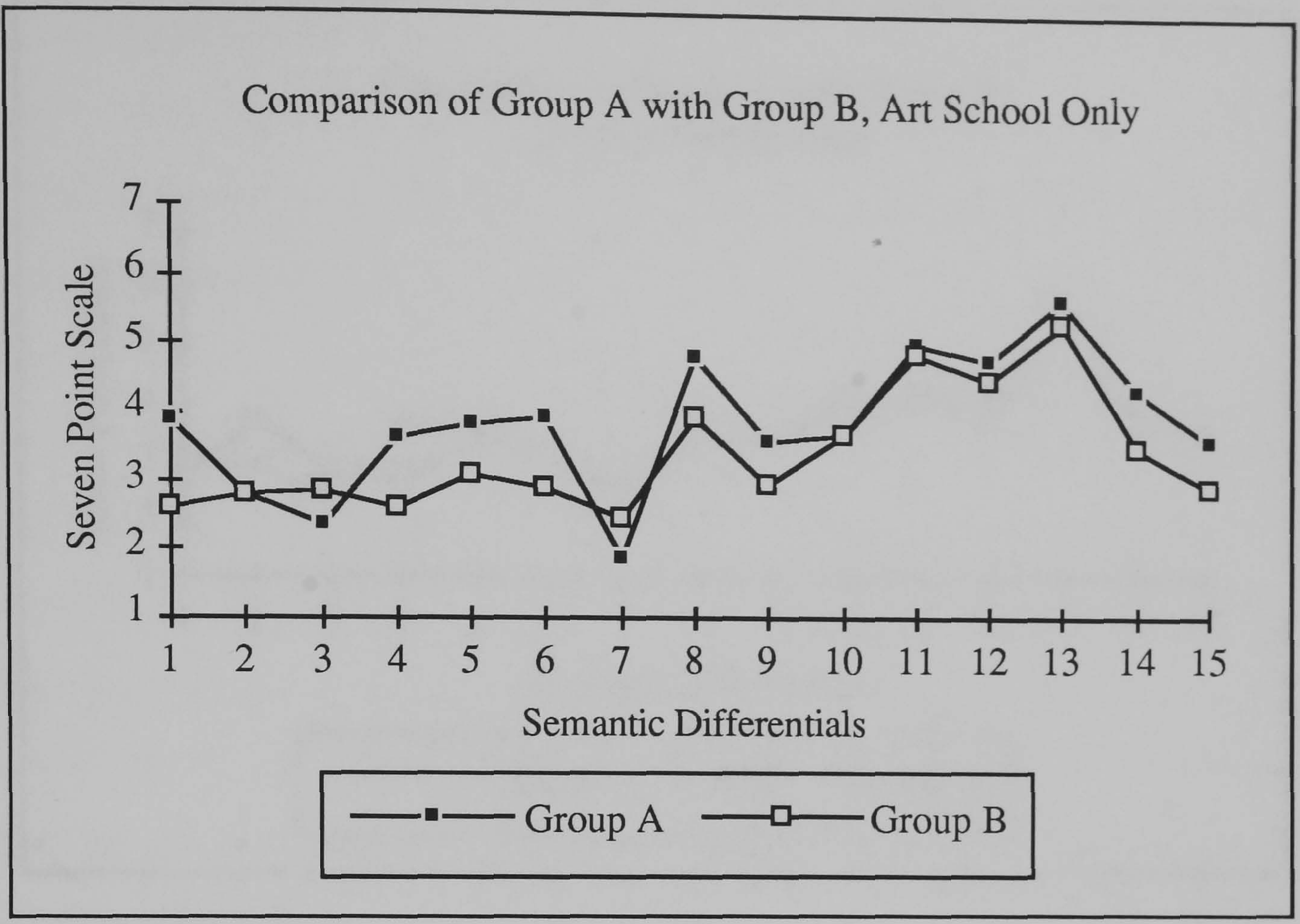


Comparison of Group A with Group B, All Respondents

	Semantic Differential Categories	**P Values**
1	Bright.........................Dull	0.001 *
2	Metallic...................... Non-Metallic	0.064
3	Reflective....................Non-Reflective	0.01 0 *
4	Iridescent.................... Non-Iridescent	0.000 *
5	Expensive................... Cheap	0.024 *
6	Pleasing...................... Displeasing	0.006 *
7	Smooth........................Rough	0.006 *
8	Hand Made................. Industrial	0.000 *
9	Domestic Stetting....... Non-Domestic	0.147
10	Warm..........................Cool	0.739
11	Shallow.......................Deep	0.273
12	Abstract.......................None Abstract	0.043 *
13	Transparent................. Opaque	0.014 *
14	Modern....................... Old Fashioned	0.005 *
15	Attractive.................... Unattractive	0.087

* Significant at $P < 0.05$

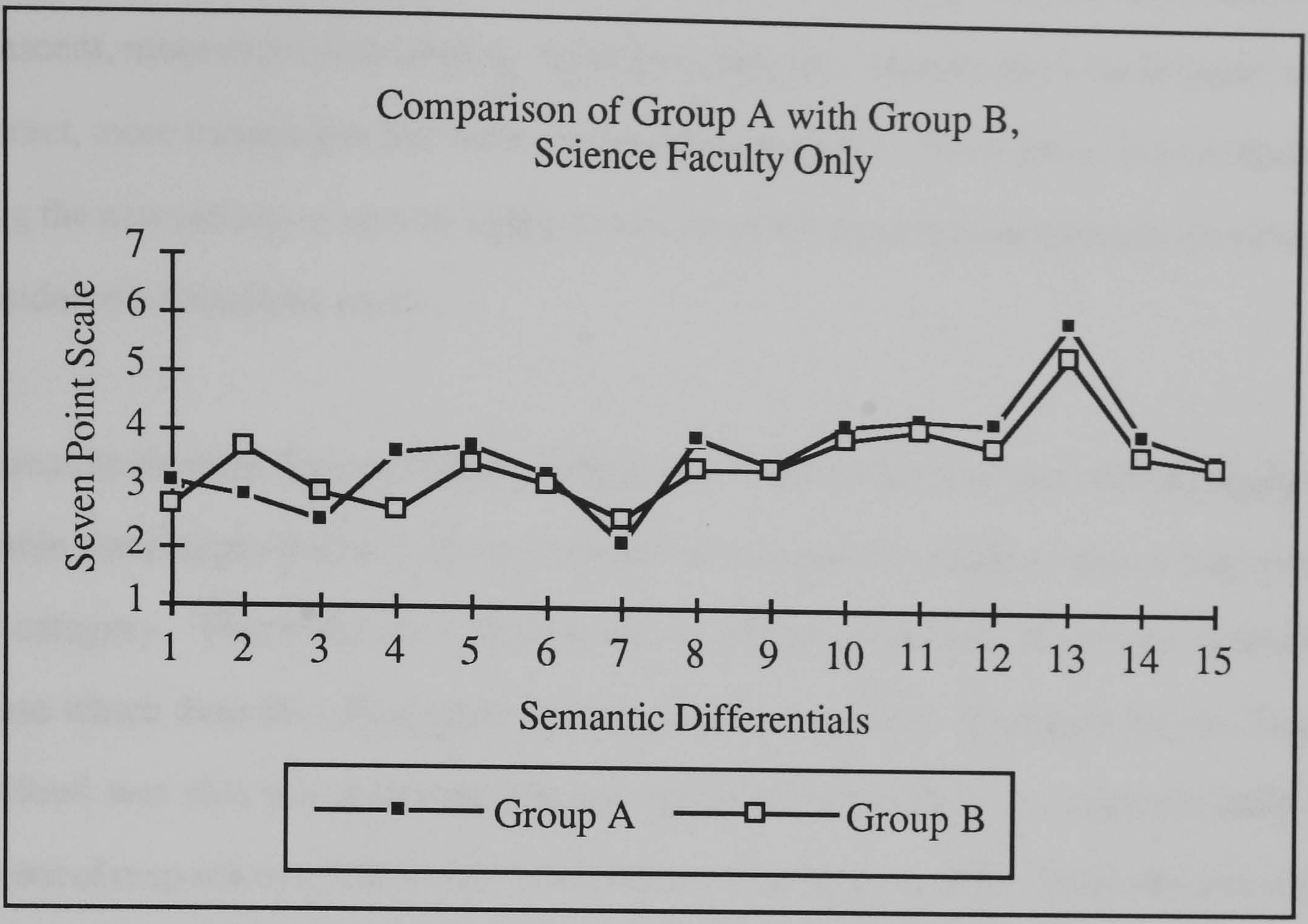
Figure 7.3 Semantic differential survey results taken from all participants.



	Semantic Differential Categories	**P Values**
1	Bright.........................Dull	0.001 *
2	Metallic......................Non-Metallic	0.855
3	Reflective...................Non-Reflective	0.068
4	Iridescent................... Non-Iridescent	0.001 *
5	Expensive.................. Cheap	0.025 *
6	Pleasing...................... Displeasing	0.002 *
7	Smooth.......................Rough	0.029 *
8	Hand Made................. Industrial	0.002 *
9	Domestic Stetting....... None Domestic	0.067
10	Warm.........................Cool	0.853
11	Shallow......................Deep	0.433
12	Abstract......................Non-Abstract	0.360
13	Transparent................ Opaque	0.414
14	Modern...................... Old Fashioned	0.016 *
15	Attractive................... Unattractive	0.055

*Significant at $P < 0.05$

Figure 7.4 Semantic differential survey results taken from respondents based at Gray's School of Art



	Semantic Differential Categories	P Values
1	Bright.........................Dull	0.203
2	Metallic..................... Non-Metallic	0.021 *
3	Reflective....................Non-Reflective	0.086
4	Iridescent.................... Non-Iridescent	0.000 *
5	Expensive.................. Cheap	0.354
6	Pleasing.......................Displeasing	0.589
7	Smooth........................Rough	0.097
8	Hand Made................ Industrial	0.034 *
9	Domestic Stetting....... Non-Domestic	0.810
10	Warm.......................... Cool	0.439
11	Shallow...................... Deep	0.432
12	Abstract......................Non-Abstract	0.031 *
13	Transparent................ Opaque	0.005 *
14	Modern...................... Old Fashioned	0.126
15	Attractive.................. Unattractive	0.648

*Significant at $P < 0.05$

Figure 7.5 Semantic differential survey results taken from respondents based at the Science Faculty .

between the two groups of vases. Group B was considered brighter, less reflective, more iridescent, more expensive looking, more pleasing, less smooth, more hand made, more abstract, more transparent and more modern than group A. Since group B were reduced using the new reduction system based on the use of 5% hydrogen in nitrogen, this may be considered a fortuitous result.

The results obtained for the category 'Iridescent - None iridescent' may not be considered reliable since approximately twenty percent of respondents failed to give a response to this category. This indicates a fault in the experimental design, clearly an alternative phrase which describes the degree of iridescence is required. Category eleven 'Deep - Shallow' was also not understood in the context of this survey by approximately ten percent of respondents. These adjectives were included to describe the differences which exist in the depth of a glaze, referring to the three dimensional quality possessed by certain types of glaze surface.

A number of respondents commented on the way the appearance of the lustre glazes changed as the lighting conditions in the room where they had been placed changed. Since many of the iridescent qualities in particular depend on the quality of light available, this is a particular problem with a survey of this nature. A further consideration is that of the effect of the surrounding physical environment. Lustre glazes are highly reflective and therefore take on the colour of the materials in the immediate vicinity. It was also noted that the distance between the two groups of vases was also of importance for similar reasons. Positioning the groups adjacent to each other allowed direct comparison between the groups. An alternative strategy would be to display the two groups in separate rooms. This would also allow the use of a control group. The control group would consist of two identical groups of vases placed in separate rooms, the subsequent survey should produce no significant differences between the groups.

The use of groups of vases rather than individual vases for the aesthetic evaluation survey was a source of confusion. Groups were use so that the sample of ware from the two kilns could be considered as representative, however in retrospect this presented difficulties due to variations in the firing atmospheres within the kilns used.

The correlation of results obtained from the semantic differential survey with glaze recipes or firing schedules is possible in theory, since all the information is contained within compatible data base systems. However many more surveys would need to be carried out to build up a more accurate picture of the way particular aspects of glaze and firing effect the finished result.

The semantic differential survey technique has been shown to be a sensitive method of assessing aesthetic qualities. Further refinement of the survey technique would be required before the results obtained could be used for more than just broad comparisons between two objects that differ in a specific manner. The number of bipolar adjectives could be increased with out the survey proforma becoming over long. Where a concept presents some difficulties in being expressed by one pair of adjectives such as the degree to which a design is abstracted, several pairs of adjectives could be included in the proforma to increase the sensitivity of the test to this concept.

CHAPTER EIGHT

8 General Discussion and Recommendations for Future Research

8.1 General Discussion

The overall aim of the research programme described in this thesis has been to examine specialist firing techniques used by craft potters with the aim of designing kilns and firing procedures which are safe, environmentally innocuous, economic to use and capable of producing aesthetic results comparable with existing systems.

Following initial studies of the techniques of vapour glazing, Raku, fuming and reduction lustre, the focus of the research has centred on the technique of reduction lustre. During the research a range of lustres were developed and tested using kilns constructed for the purpose. After reproducible lustres were achieved, a lustre glaze, underglaze and clay paste lustre pigment were chosen as representative recipes. Controlled laboratory studies were then undertaken using the selected recipes. The glazes and pigments chosen were also used in the evaluation of kilns, reducing atmospheres and in the aesthetic evaluation studies. The implications of the conclusions of the research as they apply to craft potters and industrial manufactures are considered separately under different headings.

8.1.1 Reduction Lustre Glazes

Initial experiments carried out using TPR (table 3.5) showed that both clay paste pigments and lustre glazes would begin to reduce at temperatures well below the temperatures normally used for reduction firing. The reducible ingredients used in lustre glazes, when fired in a 5% hydrogen in nitrogen atmosphere, also reduced at temperatures below that normally used to fire lustres (tables 3.2 and 3.4). The reduction temperature chosen for a clay paste lustre firing was, as expected, dependent on the softening temperature of the underglaze rather than the reducing temperature of the clay paste ingredients.

The softening points of the glazes used in this study were estimated from experiments carried out using a gradient kiln. Adjustment of the softening point was made by altering the alumina to silica ratio of the glaze. A ratio of 1:10 was found to be satisfactory and this is in agreement with that found by Caiger-Smith (1985). A more precise method for determining the softening point of a glaze would be to prepare the glaze as a frit and use a technique, such as DTA or DSC, to record changes in enthalpy as would occur during phase transitions of a glaze, for example softening or melting.

Following examination of cross sections of successful and unsuccessful clay paste lustres by SEM disclosed the presence of a large number of gas bubbles left in the underglaze of less successful lustres (figure 4.13). No direct cause was determined for this observation, however it was clear that best results were obtained after the underglaze had received at least a one hour soak period at the maturing point of the glost firing. The air trapped within the glaze may be sufficient to cause reoxidation of the lustre at the surface of the glaze.

The iridescent colours, which are a feature of clay paste lustres, are caused by constructive interference of light waves. Colour effects are evident when a microfine layer of reducible metals is formed at the surface of the glaze during firing. Experiments designed to produce fine layers of clay paste lustres at the surface of the glaze, by means of screen printing techniques, revealed that the degree of iridescence was not controllable through varying the application thickness of the pastes. The microfine layers formed during firing could not be simulated by the techniques described in chapter two. The degree of iridescence was however found to be affected by temperature (figure 2.1). At more elevated temperatures reducible metals become more volatile, causing, for example blurring of a design or contamination of adjacent ware.

The data obtained from TG studies following isothermal experiments, using a fritted lustre undergoing reduction by hydrogen, were best interpreted in terms of a diffusional model. At the temperature at which reduction of the lustre glaze occurs, hydrogen diffuses rapidly through the glaze, reacting to form metal atoms and water. Weight loss, as recorded by TG, indicated the rate of water loss from the sample. Precipitation of metals eventually leads via lustrous phases to the formation of metallic particles. In the specific example of inglaze lustre #8 using hydrogen as a reductant an intermediate electric blue colour was observed as a lustrous phase during the firing process. When reduction was continued the blue colour changed to a fully metallic copper lustre. Precipitation of metal particles appears to deplete the surface layer of metal putting it out of range of surface analysis methods such as XPS. The XPS study described in section 4.4.2 detected the highest levels of copper when the electric blue area of tile was examined and a minimum when the copper coloured area was examined. The existence of the lustre particles in a sub-surface layer explains their stability towards re-oxidation in the long term in normal conditions. When reduced lustre glazes are refired to their softening temperature, the lustre appearance is lost as the glaze becomes reoxidised. Subsequent reduction firings were found to reinstate a lustre layer. In order to verify the hypothesis, that the copper particles are sub-surface, the samples would have to be systematically polished to reveal by say XPS examination deeper layers within the glaze.

The low activation energy for the reaction, estimated from the Arrhenius plot, suggests the reaction is being controlled by transport phenomena. There may be a number of rate limiting steps in the reactions taking place, diffusion of metal cations through the lattice, diffusion of hydrogen or diffusion of water from the solid. On the basis that molecular size is likely to be an important factor in determining diffusion rates it is suggested that water diffusion out of the solid, or highly viscous glaze is rate determining. The practical significance of the low activation energy is that temperature variations of 5 or 10 degrees through a kiln may be tolerated during the reduction process.

The much shorter reduction time required for in-glaze lustres as opposed to the clay paste type is explained by the proximity of the reducible metals within the glaze and by the eutectic effect of the bismuth. Both clay paste and in-glaze type lustres can be used in combination with each other on the same piece of ceramic although the in-glaze lustre tends to be over reduced compared to a somewhat under reduced clay paste lustre. The consequence of over reduction is a tendency towards darker, increasingly brown coloured glazes.

1.2 Lustre Kilns

Both gas fired and electric kilns were used during this research for firing reduction lustre. It was found that a controllable lustre kiln could be developed from a conventional electric craft kiln. The kiln was successfully interfaced with a micro computer which was capable of controlling temperature, monitoring oxygen levels and recording the various outputs. Appendix VIII shows both the down draft gas kiln and the modified electric kiln being fired together with some examples of fired reduction lustres. Satisfactory lustres were obtained when a reducing gas consisting of 5% hydrogen in nitrogen was used. The product of the reduction reaction when using this gas is water vapour, so no special extraction facilities are required. The 40 litre electric kiln described in chapter five used approximately 10p of gas per minute of reduction time. This could be considerably reduced if a more gas tight system were being used. Cheaper sources of reductant were assessed in the form of a hydrocarbon saturated nitrogen gas. A nett reducing power for the hydrocarbon saturated gases was derived (table 6.1) which indicated that the lighter more volatile hydrocarbons had the greatest reducing potential. The 5% hydrogen in nitrogen gas has a nett reducing power similar to that of n-decane, however it actually performed as a reducing agent more like n-pentane. This is due to the kinetics of the reactions taking place. When hydrocarbons are used cracking of the substance must occur before reduction takes place, this is in contrast to the hydrogen nitrogen gas mixture which is free to diffuse rapidly through the glaze (section 3.4.4). The relationship between the hydrocarbon and hydrogen in nitrogen reductants tested was illustrated in figure 6.5. Earlier researchers using various sources of hydrocarbon stated that the final result was unaffected by the reductant used (Burton, 1907; De Morgan, 1892). However the rate at which reduction occurs was found to depend on the reductant, as well as temperature. This can be exploited to gain additional control over the reduction firing. By using a refined liquid hydrocarbon of known formula in the saturating vessel reproducible results can be obtained. Using lustre glazed samples placed at strategic points in the firing chamber was found to be an effective method of monitoring a reduction procedure. The hypothetical kiln design described at the end of chapter five incorporates the main features required for a kiln designed specifically for reduction lustre. Many of the ideas contained in this design would equally be applicable to larger scale firing systems. The kiln design is based on the use of a gas mixture such as 5% hydrogen in nitrogen and a gas tight outer casing. Feedback from the pressure transducer, zirconia oxygen probe and thermocouple to a kiln controller/programmer could be set to allow only sufficient gas into the chamber to reduce the ware. To be economic a design such as that described in section 5.3.3 would also have to be capable of firing to stoneware temperatures. Stoneware reduction may also be possible using the same low percentage hydrogen in nitrogen gas, however further research would be needed to investigate this.

The research programme reported in this thesis has encompassed several disciplines, as a result some of the areas investigated lack the depth which would be expected from a study dedicated to a single aspect of this research topic. However, the bringing together of a scientific investigation of materials and firing systems as well as carrying out an assessment of the aesthetics of the fired results has allowed new knowledge to be established. A similar approach could be adopted for the investigation of other processes which have an end product aesthetically determined. For example a research programme setting out to find an environmentally friendly, economic and safe alternative to salt as a vapour glazing agent could benefit from adopting a similar approach to that reported in this thesis. Thermal analytical techniques such as TG and EGA could be used to evaluate alternative salting mixtures. The vapour pressure and critical temperatures of the mixtures as well as the gases given off during volatilisation could be obtained using these techniques. SEM and EDX could be used to observe the surface topography, measure the glaze thickness and obtain a chemical analysis of the glaze coating. A muffle kiln with a gas preheating system similar to that described in chapter six could be used to evaluate vapour glazing mixtures and concentrations together with the assessment of alternative refractory kiln linings. Larger scale experiments would also be needed to assess the effectiveness of alternative vapour delivery systems. Finally the aesthetic qualities of the fired results could be objectively compared with traditional salt glazes using a method based on a semantic differential survey.

8.1.3 Implications For Craft Practice

The underglazes listed in table 2.1 with an Al:Si ratio of 1:10 were found to be successful underglazes when used in conjunction with the clay paste recipes listed in table 2.2.

The down draft gas kiln (figure 5.1) was a successful design for use as an out door lustre kiln, however it does require a degree of skill to obtain reproducible results, and does not represent any innovation in the design of reduction lustre kilns. The principles explored in the design of an electric kiln which exploits a non toxic, non flammable gas may offer greater potential. The lustre effects achieved in the modified electric kiln when using 5% hydrogen in nitrogen gas as the reductant gave a more positive response when assessed by the semantic differential technique described in chapter seven. A survey of this nature is unlikely to be used by a craft potter to evaluate his or her output. However the multiple sorting task did produce a considerable amount of feedback on the various glaze effects produced during this research.

The solid state zirconia oxygen probe described in section 5.2.4.3 allowed monitoring of oxygen levels within the kiln. If a conventional hydrocarbon gas such as propane or natural gas were being used in an electric kiln in conjunction with a nitrogen purge, an oxygen probe would indicate when the kiln had been adequately purged.

It is recommended that on both safety and environmental grounds a 5% hydrogen in nitrogen gas mixture is used as the reducing agent when firing reduction lustres in an electric kiln.

8.1.4 Implications For Industrial Applications

Clay paste reduction lustres are not suitable for industrial applications owing to their lack of resistance to acid attack. In-glaze reduction lustres have been used industrially in the past and still have potential as a contemporary industrial product given technical advances in kiln control and monitoring systems. The glazes used during this study were not formulated to be lead free or especially abrasion resistant. However it would be a relatively simple matter to adapt a lead free glaze for reduction lustre. The bismuth in reduction glazes has very similar fluxing characteristics to those of lead and has no known toxic effects. A very wide range of lustrous colours can be obtained with the use of zirconia stabilised glaze stains.

The use of reduction glazes in combination with other glazes presents some difficulties. When used over white earthenware glazes the volatile metals tended to stain adjacent areas and produced yellowing effects and a blurring of the pattern. When reduction lustres were applied to matt earthenware, or felspathic stoneware glazes, a good colour contrast could be achieved. The use of reduction lustre glazes over stoneware glazes presents other difficulties in terms of glaze fit and the need for additional glost firings.

Firing reduction lustre glazes can be carried out in conventional intermittent gas kilns adapted for the purpose, however the large volumes of carbon monoxide which would be produced would require that the kiln be fitted with an after burner system and air monitoring in the vicinity of the kiln. These special precautions could be avoided with the use of a low percentage hydrogen in nitrogen gas mixture. If reduction lustre glazes are being used on their own, or in combination with other earthenware glazes, a once-fire manufacturing process could be adopted by introducing the reduction phase of the firing on the cooling cycle after the glost stage has been completed.

The use of a non flammable reduction gas would allow the adaptation of continuous kiln designs such as tunnel or carousel type kilns. A reduction zone would be established within the chamber. Figure 8.1 shows a possible method for maintaining a reduction zone by the use of a fitted refractory tray containing the ware which travels through the kiln in a similar manner to a kiln car in a tunnel kiln. The gas could be recycled through the chamber provided a suitable gas sensor was being used to maintain the correct level of hydrogen within the reduction zone. This is not intended to be a complete design, there are obvious problems with the gas sealing arrangements but these are not insuperable.

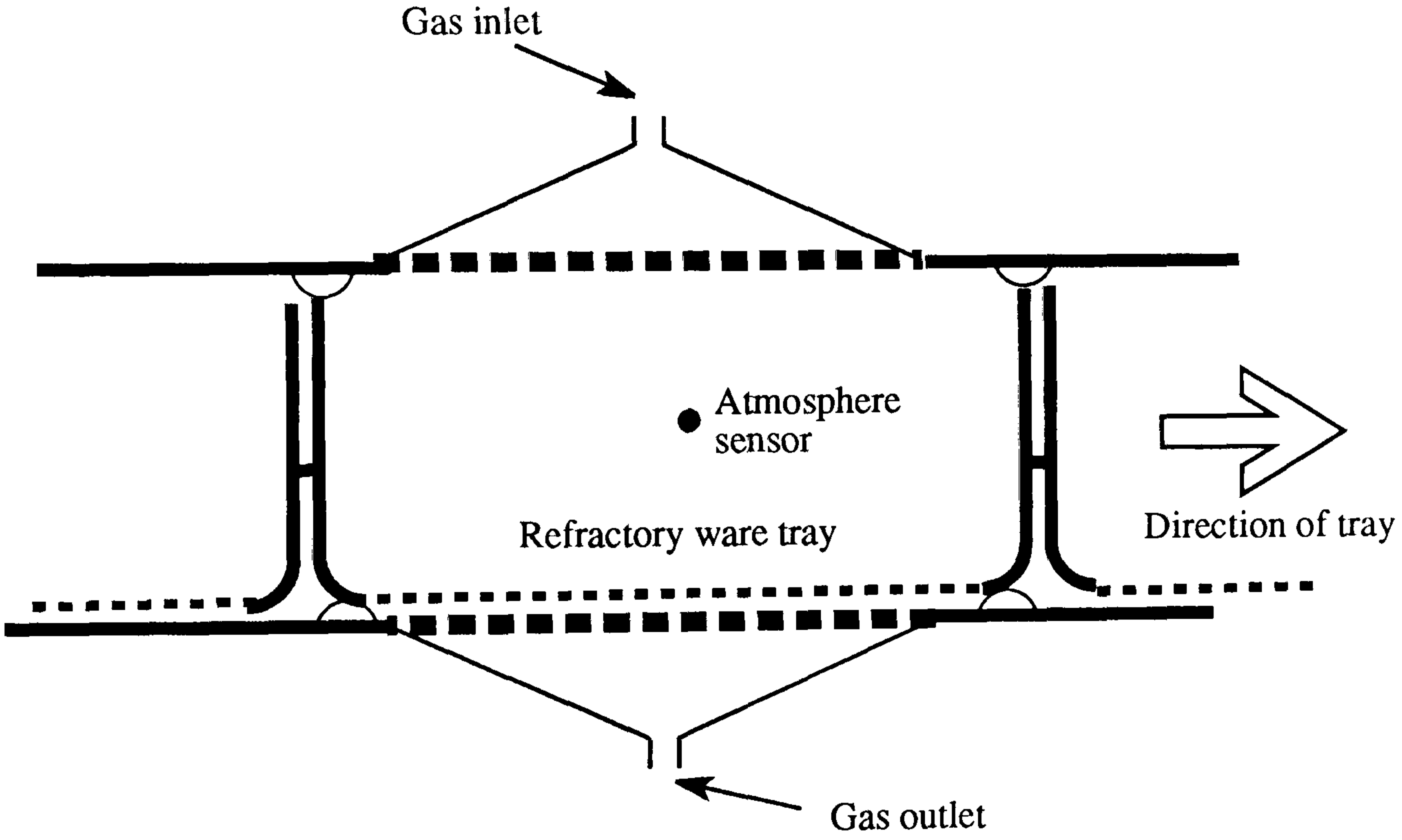


Figure 8.1 Diagram of reduction zone in a continuous firing system created by moving refractory trays.

The firing systems developed in this thesis are appropriate for use by craft potters, schools and colleges and could be used safely and economically to produce lustre effects comparable with more traditional firing systems. The methodologies adopted during this research programme could equally well be applied to other processes which present environmental problems and which require an objective method of assessing the quality of the product.

8.2 Recommendations For Future Research

8.2.1 Laboratory Studies

Because of the broad range of investigative techniques covered in this research project there are a considerable number of topics which warrant further study. There has not been sufficient time to explore the many ways in which lustre glazes can be applied to ceramics. The combination of clay paste lustres and in-glaze lustres used over high fired glazes offers a virtually infinite number of possibilities for new glaze effects. Likewise, using commercial glaze stains in combination with lustre glazes, means the colour range can be extended to encompass almost any colour.

Following experiments carried out to establish the acid resistance of the lustre glazes it was found that colour changes were observed on the surface of tiles glazed with reduced #8 after being exposed for 1 week to a 5% aqueous solution of conc. sodium sulphide. The copper coloured lustre had become an electric blue coloured lustre. Whether this is due to chemical abrasion of the surface or partial denucleation of the metal ions within the glaze was not established. However the post reduction firing alteration of lustre glazes by chemicals may present a possible patterning process.

Thermogravimetry has been shown to be a useful technique for the investigation of reduction mechanisms in glazes. By preparing a glaze in the form of a ground frit and using simulated firing conditions it is possible to investigate the optimum firing conditions and the effect of alternative kiln atmospheres for any reduction glaze.

The use of a gas tight outer casing for a reduction kiln would allow the use of a gas recycling system to minimise the use of reducing gases and for controlling temperature gradients within the kiln chamber. The use of a sealed kiln with a pre-heated gas inlet system and filtered outlet would allow the injection of metal salts into the kiln atmosphere. Using this arrangement fuming agents could be tested without danger to the operator or detriment to the environment. A similar system could be used to investigate the use of alternative sources of alkali for vapour glazing by injecting a solution at various concentrations of salts into the gas inlet stream just prior to pre-heating. The carrier gas would distribute the vapour throughout the kiln chamber and allow the use of a muffle type electric kiln and thus greater temperature control. Such a muffle kiln arrangement would allow the testing of alternative refractory lining materials. The most promising materials for this purpose are those based on zirconia.

8.2.2 Perceptual Studies

The methodology for the aesthetic evaluation of fired ceramics using a perceptual study based on a semantic differential test requires further study. The effect of more complex ceramic forms and differing environmental conditions need to be assessed. When used in combination with suitable data bases the technique could be used for quality assessment and control. The design of the test requires further refinement in the number and type of bipolar adjectives chosen to make up the semantic categories. The design of suitable controls also need further investigation. The effect of environmental conditions on peoples' perceptions also requires further study.

Various methods of cataloguing the fired results were attempted including the use of reflectance spectroscopy and a chromometer. Both of these methods were unsuccessful due to the highly reflective nature of the glaze surface. For similar reasons standard colour photography was also unsatisfactory as a method of cataloguing fired results. In an attempt to circumvent this problem a video camera connected to a computer capable of digitising the video signal was used. This is potentially a very good way of cataloguing fired ceramics. The video image grabbing card used was not of sufficient quality to allow accurate colour representation but the technology is available and could be used in future research programmes.

REFERENCES

Acero, R. E. (1975) A Fuming Technique. *Ceramics Monthly,* **23**, 48 - 50.

Allan, J.W. (1973) Abu'l-Qasim's Treatise on Ceramics, Ashmolean Museum, Oxford.

Althof, J. (1991) Possibilities of Failure Analysis for Glazes and Bodies by Means of Electron Microscopy. *Keramische Zeitschrift.,* **43** (6), 387-388.

Anastasi (1988) Psychological Testing. 6th ed. Collier Macmillan, London.

Anonymous (1986). Newly Designed Cables Signals Flue Gas Analyzer For Increased Combustion Efficiency. *Industrial Heating,* June, 40-41.

Askill, J. (1970) Tracer Diffusion Data for Metals, Alloys, and Simple Oxides. Plenum, New York.

Atkinson, M. P. (1985) Oxygen Analysis of Kiln Flue Gases. *Ceramic Industries Journal* , **94**, 38 - 39.

Bartz, A. E. (1981). Basic Statistical Concepts. 3rd ed. Macmillan Publishing, New York.

Behrens, R. (1976) Ceramic Glaze Making: Experimental Formulation and Glaze Recipes. Professional Publications Inc., Columbus, Ohio pp57-59.

Berlyn, D. F. (1971) Aesthetics and Psychobiology. Merdith Corporation, New York.

Berlyne, D.E. (1974) Studies in the New Experimental Aesthetics. John Wiley & Sons, Chichester.

Brahmbhatt, S. R. (1990) Oxygen: An Important Chemical for the Clay Industry. *Ceramic Bulletin* , **69** (2), 243 - 246.

Bransburg, F.S. and Karacharov, T. S. (1946) Gigina i Sanit, Moscow. 7.8.28 [Cited by Fairhall, L. T. (1957).] *In*:: Industrial Toxicology. Williams and Willkins, Baltimore, MD.56.

Briggs, D. and Seah, M. P. (1983) Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy. John Wiley & Sons, Chichester.

Brodie, R. C. (1982) The Energy Efficient Potter. Watson Guptill, New York.

Bryant, V. (1990) CERAM-Info-Calc. Terracotta Software, Kingston Upon Themes.

Budworth, D.W. (1970) An Introduction to Ceramic Science. Pergamon, Oxford.

Burnham, F. and Harder, C. (1944) Practical Production of Once-Fire lustre Glazed Pottery. *Journal of American Ceramics Society,* **27** (2), 62 - 64.

Burton, D. L. (1992). William Burton and Pilkingtons Tiles Limited. *Journal of the Tile and Architechtural Society,* **4**, 29-35.

Burton, W. (1907) Lustre Pottery. *Journal of the Society of Arts,*. **IV**.

Byers, I. (1990) Raku. B. T. Batsford, London.

Caiger-Smith, A. (1984) Lustre and Light - The Decorated Forms of Alan Caiger-Smith. *Ceramic Review,* No. 90, 6-8.

Caiger-Smith, A. (1985) Lustre Pottery. Faber and Faber, London.

Campbell, M. (1985) Effective Kiln Waste Gas Analysis Combats Environmental Pollution. *World Cement,* April, 90 - 92.

Canter, D., Branner, M., Brown, J. (1985) The Research Interview, Use and Approaches. Academic Press, London.

Cardew,M. (1975) Pioneer Pottery. Longman, London. p278.

Casson, M. (Personal Communication).

Chornewy, A. (1986) Contemporary Decorative Effects and Application Techniques. *Ceramic Engineering Society Proceedings,* **7** (11- 12), 1362 - 1363.

Clark, P.W., Cannon, J.H., White, J. (1953) Further Investigations on the Sintering of Oxides. Transactions of the British Ceramics Society, **52**, 1 - 49.

Clark, T.J. and Pellerin, R.J. (1988) Microcomputer Control of Multiple Electric Curing Ovens at Norton Plant. *Industrial Heating,* April, 36-39.

Clinton, M. (1991) Lustres. Batsford Limited, London.

Clinton, M.(1987) Elusive Lustres. *Ceramic Review,* No. 103, 6 - 8.

Coombs, C. H.(1964) A Theory of Data. John Wiley and Sons, New York.

Cooper, E. (1981) A History of World Pottery. 2nd Ed. B. T. Batsford Limited, London.

Cooper, J. (1992) The Role of Thermal Analysis in the Ceramic Industry. *Global Ceramic Review,* **1**, 22 -25.

Coward, H. E. *et al.* (1952) Limits of Flammability of Gases and Vapours. Bureau of Mines, Washington DC. pp20 - 21.

Crank, J. (1979) The Mathematics of Diffusion. Clarendon, Oxford

Davis, V. C. (1954) Reduced Lustres. *Ceramic Age*, **64**, 44 - 47.

De Morgan., W. (1892) Lustre Ware. *Journal of the Society of Arts*, June 24, 756-767.

Elkins, H.B. (1959) The Chemistry of Industrial Toxicology. Wiley Interscience, New York, p74.

Fiddis, C. (1977) *In* : The Ceramic Review Book of Clay Bodies and Glaze Recipes. (Cooper, E. and Lewenstein, E. Ed.) Craftsmen Potters Association, London. p25.

Franchet, M. L. (1906) Etude sur les Dépots Métalliques Obtemus sur les Emaux et sur les Verres. *Annales de Chimie et de Physique*, 8e série, **IX**, Paris. Translation by Clinton, M. and Home, O. (Pers. Comm.).

Frank, S. (1984) Gold, Ruby, Glass. *Technology,* **25** (17), 47 - 50.

Gaprindashvili,G.G., Odzelashvili, D.G., Kutateladze, D. S., Zhgenti, É. P. (1983) Properties of the Internal Layers of Reduced Glazes. *Steklo i Keramika* , **8**, 26 - 27., Georgian Polytechnic Institute.

Gempper, C. Parks, R. Gillier, D. (1989) Gold and Lustre Decoration in the Tile Industry. *'Improved Ceramic Materials':South African Ceramics Society Symposium Proceedings., June. 29 - 31.*

Guller, D. (1987) Gold and Lustres for the Ceramics Industry. *Ceramic Engineering Society Proceedings.*, **8** (11 - 12), 1184 - 1187.

Hamer, F. and Hamer J. (1986) The Potters Dictionary of Materials and Techniques. A & C Black, London.

Hammer, H. and Kranz, J. (1986) Investigating Porcelain Glazes with the Aid of Scanning Electron Microscopy and an Electron Microprobe. *Berichte der Deutzche Keramishe Gesellscheft,* 4/5, 204 - 211,

Henderson,Y. and Haggard,H.W. (1943) Noxious Gases. Reinhold, New York, p126.

Hendricks, C. and Piltcher, D. (1972) Salt Glazing: The Pollution Aspects of Salt Glaze Firing, *Ceramic Review,* 7-9.

Hornewy, A. (1986) Contemporary Decorative Effects and Application Techniques. *Ceramic Engineering Society Proceedings,* **7** (11 - 12), 1362 - 1363.

Hunt, I. R. (1979) Gold In The Pottery Industry. *Gold Bulletin* ,**12.**

Isidro, A. and Navarro, F. (1989) XRD Analysis of Ancient Ceramics from the El Hierro (Canary Islands). *In:* Y Technologica de los Materiales Ceramicos Y Vitreos (Rincon.

J.M. Ciencia, ed.) Espana Faenza Editrice Liberica SL., pp271 - 276.

John, W. D. and Baker, W. (1951) Old English Lustre Pottery. Newport, Monmouth.

Kaisersbertger, K., Janoschek, J., Davis, P. (1992) Application of Thermal Analysis in Modern Ceramic Technology. Special Ceramics 9. *British Ceramic Proceedings* , No. 49, (April). Institute of Ceramics.

Keattch, C. J. and Dollimore, D. (1975) An Introduction to Thermogravimetry, Heyden, London.

Keeler, W. (Personal Communication).

Kingery , W. D. and Vandiner, P. B.(1983) Song Dynasty Jun (Chun) Ware Glazes. *American Ceramic Society Bulletin,* **62**, 1269 - 1274.

Lane, A. (1946) Early Hisparno-Moresque Pottery: A reconsideration. *Burlington Magazine* , **88.**

Lingl, H. (1985) The Latest Developments in Tunnel Kiln Construction and Kiln Control. *Ziegelindustrie International,* **38** (6), 336 - 342.

Malins, J. P. (1992) A Soda Vapour Kiln. *Ceramic Review,* **135**, 9 - 12.

Mallet, J. V. G. (1979) Francesco Urbini in Gubio and Deruta. *Faenza/*, **65**, 279 - 285.

Mansfield, J. (1991) Salt-Glaze Ceramics: An International Perspective. A&C Black, London.

Mellor, J. W. (1922) A comprehensive Treatise on Inorganic and Theoretical Chemistry. Langman Green & Co., London. 99 - 100.

Moles A. (1966) Information theory and esthetic perception. University of Illinois Press, London.

Murray, M. J. and Myers, C. (1988) Salt Glazing at Frankston. *Pottery In Australia,* 27. No. 1.

Orts, M. J., Rincon, J. M., Rivera, E., Celaya, L. E.(1988) SEM/EDX Microanalysis of a Na_2O-CdO-SiO_2 Glass-Ceramic Containing Sulphur. *Materials Letters* , 7 (3), 106 - 109.

Osgood, C. E., Suci, G. J., Tannenbaum, P. H. (1957) The Measurement of Meaning. Urbana, University of Illinois Press, London.

Paterson, E. Swaffield, R. (1993) X-Ray Photoelectron Spectroscopy. Macaulay Land Use Research Institute, Aberdeen (in press).

Patty, F.A. (1963) Industrial Hygeine and Toxicology., volume 2. Wiley Interscience, New York. p851.

Peascod, A. (1981) High Temperature Lustre Firing. *Pottery in Australia,* **20**, 27-29.

Poor, R. P. (1985) Furnace Atmosphere Control Using Modern Technology, Part 1. *Industrial Heating* , **52**, 16 - 17.

Poor, R. P. (1985) Furnace Atmosphere Control Using Modern Technology, Part 2. *Industrial Heating* , **52**, 26-27.

Rackham, B and Van De Put, A. (1934) Li Tre Libri dell' Arte del Vasio (The Three Books of the Potters Art) by C. C. Piccolpasso, 1558, Victoria and Albert Musium, London.

Randall, R. H. Jr.(1956-57) Lusterware of Spain. *Metropolitan Museum of Art Bulletin,* **15**, 213 - 221.

Rincon, J. M. and Navarro, F. (1990) Microstructural and Microanalytical Characterisation by SEM/EDX of Ancient Glasses from El Hierro (Canary Islands). *In:* Ciencia Y Technologica de los Materiales Ceramicos Y Vitreos. (Rincon, J.M. & Ciencia, Eds.) Espana '89 Faenza Editrice Liberica SL., pp277 -283.

Rincon, J. M., Barba, M. F., Navarro, F (1990) Macro and Micro Analytical Study of Ancient Ceramics from El Hierro (Canary Islands) *In:* Ciencia Y Technologica de los Materiales Ceramicos Y Vitreos (Rincon, J.M. & Ciencia, Eds.) Espana Faenza Editrice Liberica SL., pp265 - 270.

Schlandt, W. (1986) Reducing Fluorine Emissions and Recovering Flue-Gas Energy. *Ber. Dt. Keram. G es.* 9/10-85, 459 - 464.

Shewmon, P. G. (1963) Diffusion in Solids. McGraw-Hill, New York.

Shimizu, S., Wakamatsu, M., Takeuch, N., Kurihara, G., Shimuzu, S. (1988) The Oxidizing and Reducing Characteristics of Flame Produced by a Premixing Ceramic Kiln Burner. *Nippon Seramikkusu Kyokai Bakujutsu Ronbunshi,* **96**, 225 - 230.

Soames, M.R. (1986) Automatic Kiln Controllers in the Pottery Industry. *Ceramic Industries Journal,* August, 19-20.

Stanbridge, P. (1991) A Wound in the Salt. *British Ceramic Review,* No. 85, 52.

Starkey, P. (1978) Salt Glaze. Pitman, London.

Stratton, P. (1991) Nitrogen - Based Protective Atmospheres For Ferrous Treatments. *Metals and Materials,* **7**, 671 - 674.

Stratton, P. (1992) An Introduction to Furnace Atmosphere Safety: Heat Treatment of Metals. *Journal of the Wolfson Heat Treatment Centre*, **1**, 10 -13.

Taylor, J. R. and Bull, A. C. (1986) Ceramic Glaze Technology. Pergamon Press, Oxford

Taylor, S. (1983) Lustred Earthenware. *Ceramic Review*, **82**, 6 - 9.

Tennent, N. H., Baird, T., Kerr, J., Slager, M. (in press) The Conservation and Technical Examination of Some Spanish Lustre Ceramics, Glasgow University, Department of Chemistry.

Tichane, R. (1985) Reds Reds Copper Reds. The New York State Institute for Glaze Research, New York.

Tonge, K. H (1984) Particle Size Effects in Temperature Programmed Topochemical Reactions. *Thermochimica Acta*, **74**, 151 - 166.

Tromans, S. The Environmental Protection Act 1990, Text and Commentary. Sweet and Maxwell 1991.

Troy, J. (1977) Salt Glaze Ceramics. Watson Guptill, New York; Pitman, London

Van De Put, A. (1909) Hisparno Moresque Ware of the Fifteenth Century. The British Museum.

Wakamasu, M., Takeuchi, N., Nagai, H. (1989) Chemical States of Copper and Tin in Copper Glazes Fired under Various Atmospheres. *Journal of the American Ceramics Society,* 72, 16-19

Wakamasu, M., Takeuchi, N., Nagai, H., Ono, Y., Ishida, S. (1985) Effects of Furnace Atmosphere on Colour of Copper Glaze. *Yogyo-Kyokai-Shi,* April, 10-16.

Wakamasu, M., Takeuchi, N., Shimizu, S. Ishida, S. Yu, K. (1986) Colour of Iron Oxide Containing Glaze Fired in Various Atmospheres. *YogyoKyokai-Shi,* April, 677-679.

Warterberg, E.W. (1984) The Refinement of Glazed Ceramic Surface: A Process for Depositing a Metalloid Coating in the Gas Phase. *DKG* **61** (2), 75 - 85.

Warterberg, E.W. (1984) The Refinement of Glazed Ceramic Surface: A Process for Depositing a Metalloid Coating in the Gas Phase. *DKG* 61(2), 75 - 85.

Watkin, R. (1922) Degree to which Different Glaze Compositions Take Vapour Lustres. *Journal of the American Ceramics Society,* **5**, 28 - 36.

Webster, R. G. M. (Ed.) (1992) Stone Cleaning and the Nature, Soiling and Decay Mechanisums of Stone. Donhead, London.

The subject matter and range of techniques used in the execution of this project have been very extensive. Methodologies have been drawn from the disciplines of chemistry, physics, ceramics and social psychology. This short glossary is intended to make the contents more accessible to those whose specialities do not include all of the above fields.

Calcine. To heat to red heat or beyond. Calcining may cause chemical decomposition, burning off of carbonaceous substances, and sometimes melting.

Chun (Jun). A pale blue opalescent stoneware glaze fired in a reducing atmosphere.

Clay Body. Clay minerals combined according to a recipe to achieve specific handling and firing properties.

Cone. Elongated triangular pyramids of ceramic materials having precise softening and melting characteristics. When placed in a kiln cones can be used to monitor the heat work input through complex firing schedules.

Cordierite.A mixture of clay minerals having refractory properties and used for the manufacture of kiln furniture.

Damper. A device for constricting the flue in order to control the air flow and hence degree of reduction within a kiln.

Energy Dispersive X-ray analysis (EDX). A laboratory technique for determining the surface elemental composition of a material. Restricted to higher mass atoms and gives no information on the chemical state of these. Generally carried out as a supplementary technique in scanning electron microscopy. (q.v.)

Engobe. A coloured clay suspension (slip) applied to bisquit fired ware.

Flux. (see also unity formula) Fluxes lower the melting point of a glaze. They are represented as oxides with the general formula R_2O or RO. Also includes some accepted exceptions in the sesquioxides, e.g. boric oxide and bismuth oxide. Fluxes may be introduced into a glaze in a variety of chemical forms.

Frit. A combination of ceramic materials that has been fired to form a glass, which is then ground to powder. Materials are fritted in order to render soluble materials insoluble, reduce hazards from materials such as lead and free silica, reduce the volatility of some components and remove the water and carbon constituents. Frits may be used to improve control over glaze melting behaviour, and prepare stains and colours.

Glost. The process of firing a glaze to maturity.

In-vacuo. A procedure carried out in a vacuum.

Lustre. A surface decorative effect on ceramic glazes, consisting of an iridescent or metallic sheen

Multiple sorting. A method of categorising the descriptions used when choosing objects. Used to collect bipolar descriptions of objects for use in a semantic differential survey, e.g. good - bad, bright - dull, expensive - cheap.

Parameter In mathematics a parameter is a variable quantity, which under set conditions has a fixed value.

Raku. A traditional Japanese firing technique which uses rapid firing course bodied clays and low temperature glazes. Cooling in a combustible material such as saw dust results in reduction of the glaze and clay body and the characteristic crazing of the glaze.

Ramp. A segment of a firing cycle in which the kiln temperature is changing at a constant rate with time.

Reduction. A chemical process in which metal oxides are converted to metals by the removal of oxygen . Chemicals which are capable of extracting oxygen are known as reducing agents or reductants.

Resinate Lustre Sometimes referred to as liquid lustre. The resinate material is a natural resin such as balsam used to suspend finely divided precious metal. Resinate lustres are fired under oxidising conditions (c.f. reduction lustres q.v.).

Scanning Electron Microscopy (SEM). A laboratory technique for viewing the surfaces of objects under high magnification.

Semantic Differential. A scale on which a personal opinion may be expressed between two extremes, for example good / fair / poor / bad.

Shard. A broken piece of ceramic.

Soak. A period of time over which the temperature in a kiln is kept constant.

Spalling. The loss of surface layers from a ceramic, particularly kiln brickwork, due cracking under thermal stress.

Specifically 273.15 K and 101325 Pascals. In conventional units this is 25oC and 1 atmosphere pressure.

Stoichiometric. Combined in simple proportions in accordance with the chemical requirements for compound formation.

STP (Standard Temperature and Pressure).

Thermal analysis. Laboratory techniques for studying the effects of heat on the chemical and physical behaviour of materials. Examples are thermogravimetry (TG or thermogravimetric analysis) in which materials are weighed as they are heated and temperature programmed reduction (TPR) in which changes in the reducibility of a material are observed as it is heated.

Thixotropy A reduction in viscosity which occurs sometimes when suspensions are stirred. Thixotropes revert to their less fluid form on standing.

Unity formula or Seger Molecular Formula (SMF). Refers to a way of tabulating the chemical formulae of the glaze constituent oxides. The alkaline, amphoteric and acidic oxides are set out in three columns such that the oxides with formulae R_2O or RO are in the first column and add up to one. The rest of the oxides are expressed as a ratio to this column. Laid out in this manner glaze compositions can be compared so the effect of making adjustments can be predicted.

Wadding. A highly refractory clay mixture used to prevent salt glazed ware from sticking to kiln furniture.

X-ray Photoelectron Spectroscopy (XPS) A laboratory technique for determining the surface elemental composition of a material. Also known as electron microscopy for chemical analysis (ESCA). Can give information on the chemical species present as well as surface composition.

Appendix I

Burnham and Harder (1944)
Once Fire Lustre Glaze Molecular Formulas

			Glaze No.		
	1	2	3	4	5
PbO	0.87	0.54		0.20	
CaO		0.35	0.18	0.51	0.69
K_2O		0.10	0.08		
Na_2O	0.13		0.59	0.23	0.30
ZnO			0.15		
Al_2O_3	0.18	0.18	0.36	0.38	0.43
B_2O_3			0.28	0.81	1.10
SiO_2	2.50	1.53	2.34	2.19	2.80
Range (Cones)	010 - 08	06 - 04	02 - 04	02 - 04	02 - 1

Appendix II

This appendix contains the proforma forms and instructions to participants taking part in the various aesthetic evaluation surveys described in Chapter Seven.

Tile Sorting

I am carrying out a study into what people think about tiles. I would like you to help me by looking at a number of tiles and then to sort them into groups in such a way that all the tiles in a group of tiles are similar to each other in some important way and different from those in other groups. You can put the tiles into as many groups as you like and put as many tiles into each group as you like. It is up to you to decide what characteristics you use to group the tiles.

When you have sorted the tiles into groups, I would like you to tell me the reasons for your sorting and what the tiles in each group have in common.

When you have sorted the tiles once I will ask you to do so again using any different principles you can think of and we will carry on as many times as you feel able to produce

MULTIPLE SORTING TASK RECORDING SHEET

Number [ ]

Subject Name:________________________________

Male/ Female Age:_____

Occupation: ________________________________

==

SORT NUMBER [ ] CRITERIA:-

____

SORT NUMBER [ ] CRITERIA:-

Instructions for semantic differential survey:-

- We are trying to compare the aesthetic appeal of different tiles.
- Please tick the appropriate box to indicate how you rate the various qualities of each tile.
- For example if you think the tile is bright, rather than dull, put your tick to the left of the row labelled BRIGHT — DULL.
- You can rate each quality on a scale from 1 — 7.
- If you don't understand the meaning of a phrase just skip that row.

THANK YOU FOR ASSISTING US.

Name: ______________________________

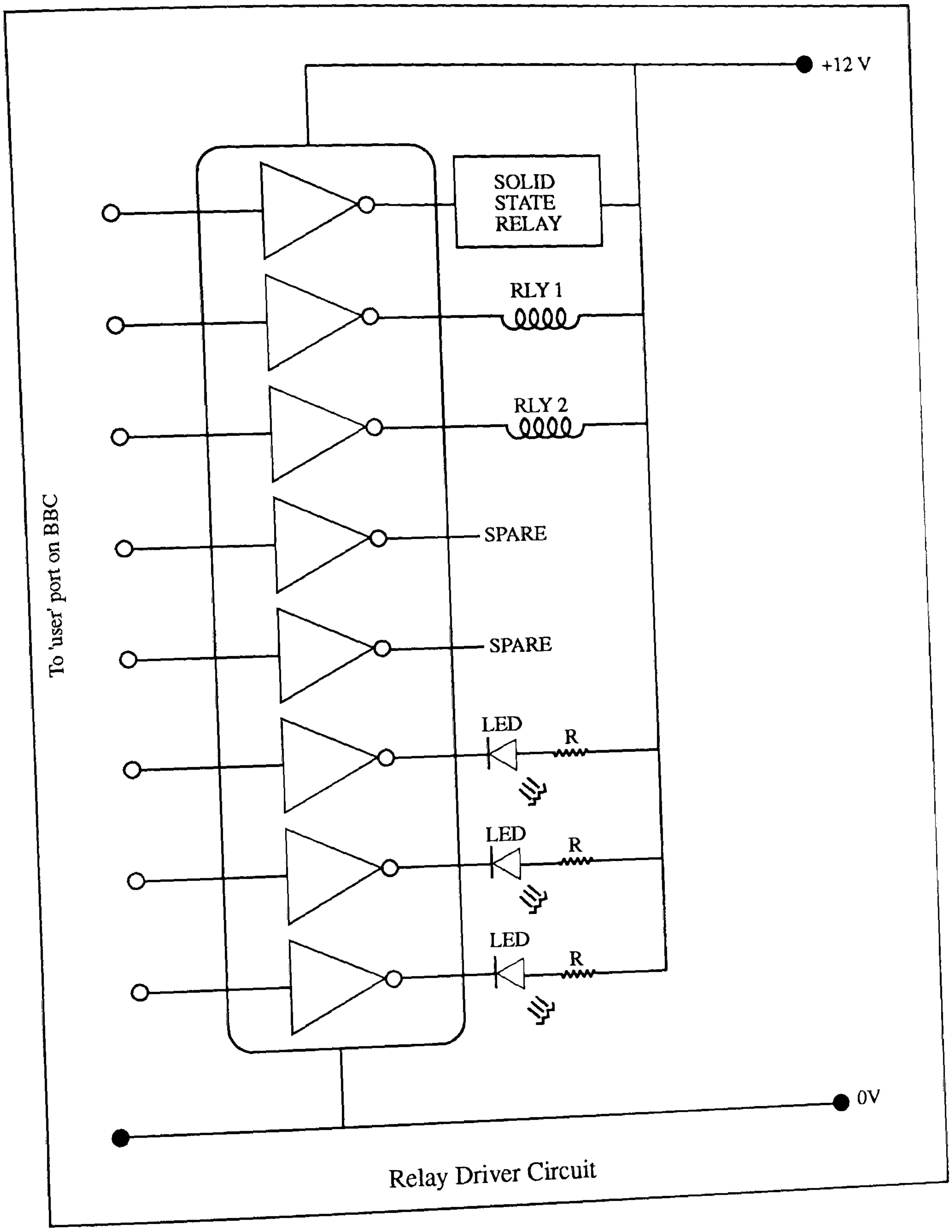
Occupation ______________________________

Male/Female Age ______________

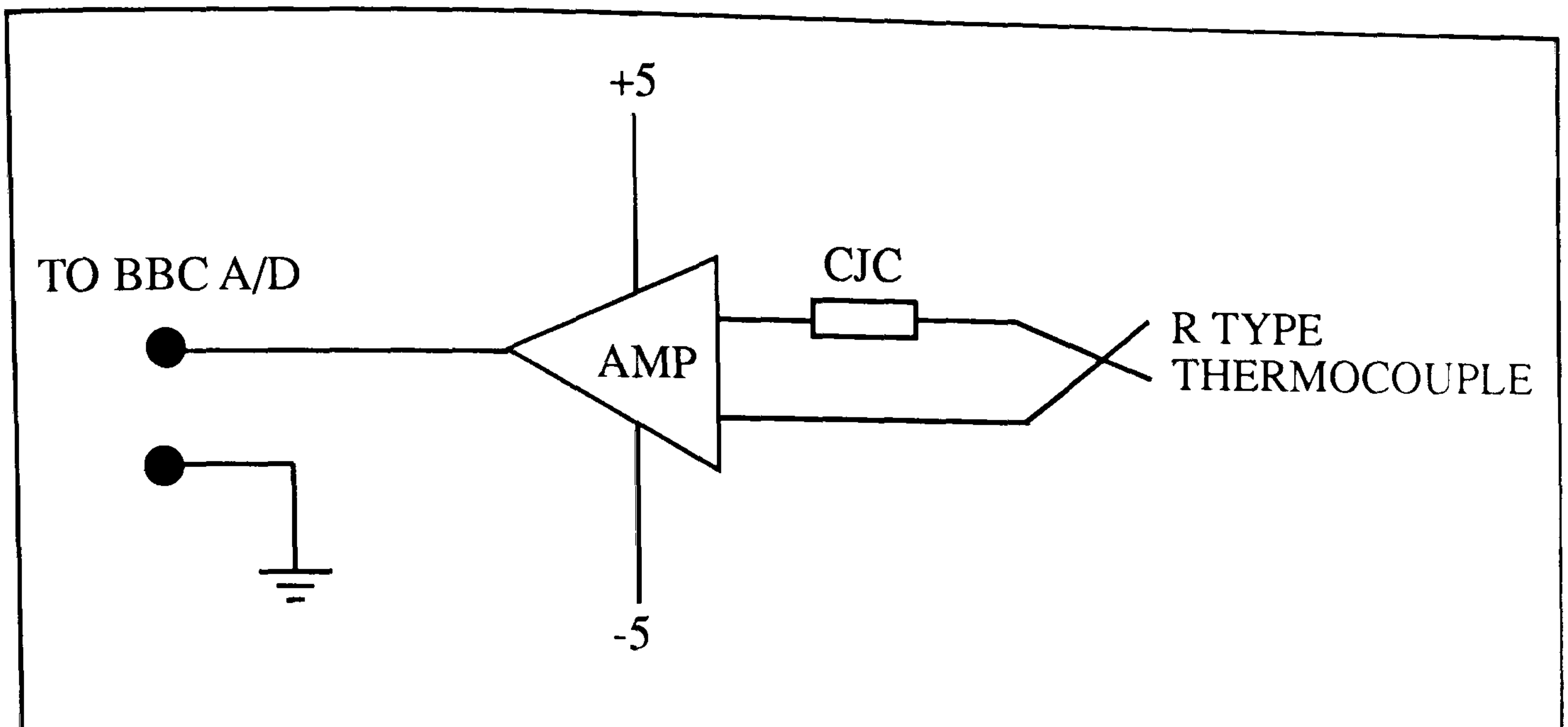
Semantic differential proforma.

	1	2	3	4	5	6	7	
BRIGHT	☐	☐	☐	☐	☐	☐	☐	DULL
METALLIC	☐	☐	☐	☐	☐	☐	☐	NON METALLIC
REFLECTIVE	☐	☐	☐	☐	☐	☐	☐	NON REFLECTIVE
IRIDESCENT	☐	☐	☐	☐	☐	☐	☐	NON IRIDESCENT
EXPENSIVE	☐	☐	☐	☐	☐	☐	☐	CHEAP
PLEASING	☐	☐	☐	☐	☐	☐	☐	DISPLEASING
SMOOTH	☐	☐	☐	☐	☐	☐	☐	ROUGH
HAND MADE	☐	☐	☐	☐	☐	☐	☐	INDUSTRIAL
DOMESTIC SETTING	☐	☐	☐	☐	☐	☐	☐	NON DOMESTIC
WARM	☐	☐	☐	☐	☐	☐	☐	COOL
SHALLOW	☐	☐	☐	☐	☐	☐	☐	DEEP
ABSTRACT	☐	☐	☐	☐	☐	☐	☐	NON ABSTRACT
TRANSPARENT	☐	☐	☐	☐	☐	☐	☐	OPAQUE
MODERN	☐	☐	☐	☐	☐	☐	☐	OLD FASHIONED
ATTRACTIVE	☐	☐	☐	☐	☐	☐	☐	UNATTRACTIVE

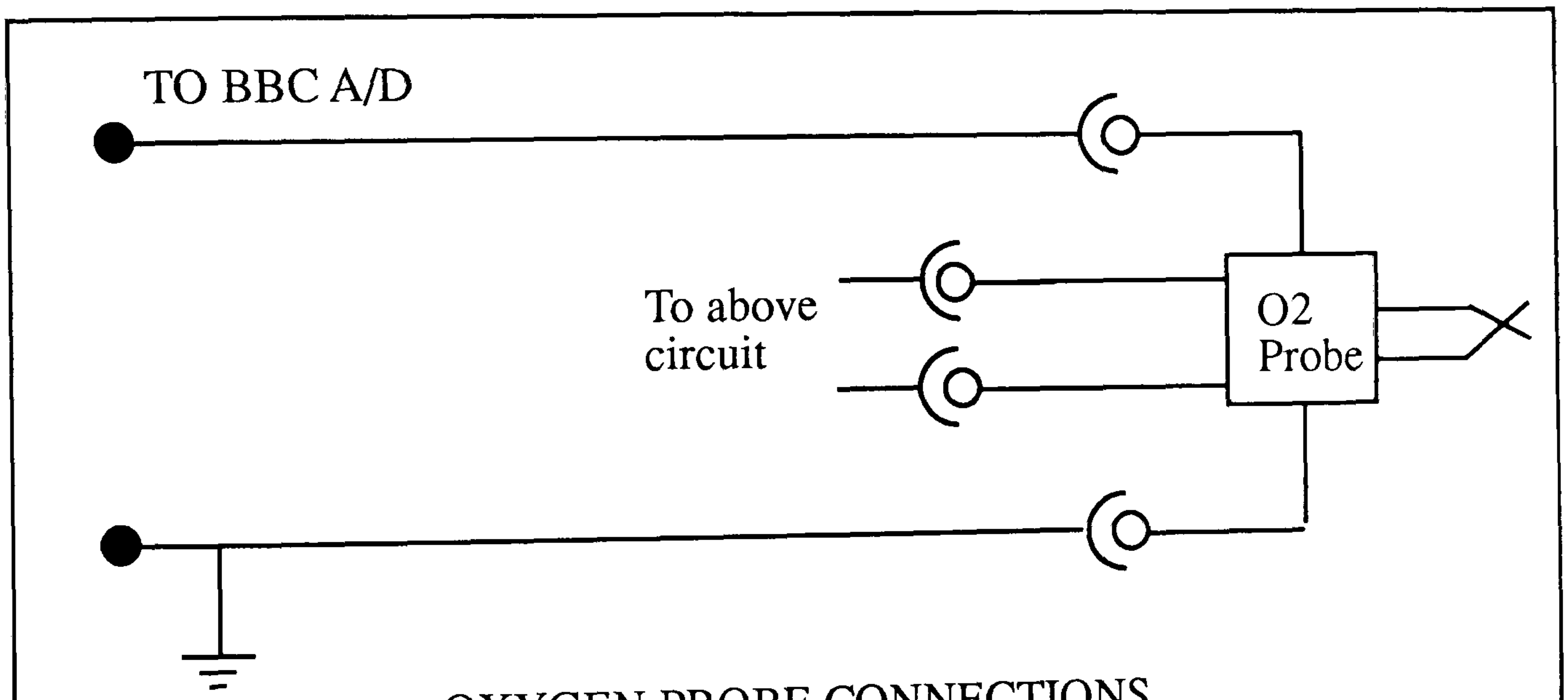
Appendix III



Relay Driver Circuit



THERMOCOUPLE CONETIONS



OXYGEN PROBE CONNECTIONS

Appendix IV

Kiln control programme listings used in conjunction with the BBC micro computer.

Firing Cycle Programme:

```
 10 MODE 7
 20 VDU14
 30 ON ERROR REPORT:CLOSE#0:END

 35 REM main programme now calls these procedures.
 40 PROCINIT
 50 PROCTITLE
 60 REPEAT
 70 PROCQTN1
 80 PROCQTN2
 90 PROCQTN3
100 PROCQTN4
110 PROCQTN5
120 PROCQTN6
130 PROCQTN7
140 PROCQTN8
150 PROCQTN9
160 PROCCHK
170 CLS
180 UNTIL EXIT$=”T”
185 CHAIN “KILN_1”
190 END

195 REM initialise variables.
200 DEFPROCINIT
210 CLS
220 X1=0:X2=0:X3=0:X4=0:X5=0:X6=0
230 X7=0:X8=0:X9=0:X10=0:X11=0
240 Y1=0:Y2=2:Y3=5:Y4=7:Y5=10:Y6=12
250 Y7=15:Y8=17:Y9=20:Y10=22:Y11=25
260 ENDPROC

265 REM display programme title and copyright notice.
270 DEFPROCTITLE
280 VDU23;8202;0;0;0;
290 PRINT:PRINT
300 PRINT CHR$(141);”   KILN FIRING CYCLE PROGRAMMER “
310 PRINT CHR$(141);”   KILN FIRING CYCLE PROGRAMMER “
320 PRINT:PRINT
330 PRINT CHR$(141);”         BY SIMON HAWLEY”
340 PRINT CHR$(141);”         BY SIMON HAWLEY”
350 PRINT:PRINT:PRINT
360 PRINT CHR$(141);”       (C) R.G.I.T. 1992  “
370 PRINT CHR$(141);”       (C) R.G.I.T. 1992  “
380 FOR I=1 TO 6000:NEXT I
390 CLS
400 ENDPROC


405 REM obtains from user the first setpoint.
410 DEFPROCQTN1
420 PRINT TAB(X1,Y1);CHR$(141);”SET POINT ONE :?”
430 PRINT TAB(X1,Y1+1);CHR$(141);”SET POINT ONE :?”
```

```
440 INPUT A1
450 Y=VPOS
460 PROCCLR(Y)
470 PRINT TAB(X1+16,Y1);A1;CHR$(151);CHR$(33)”C”
480 PRINT TAB(X1+16,Y1+1);A1;CHR$(151);CHR$(33)”C”
490 ENDPROC
500 DEFPROCCLR(Y)
510 PRINT TAB(0,Y-1)”    “
520 ENDPROC

525 REM obtains from user the time to first setpoint.
530 DEFPROCQTN2
540 PRINT TAB(X2,Y2);CHR$(141);”TIME TO SET-POINT ONE :?”
550 PRINT TAB(X2,Y2+1);CHR$(141);”TIME TO SET-POINT ONE :?”
560 INPUT,A2
570 Y=VPOS
580 PROCCLR(Y)
590 PRINT TAB(X2+24,Y2);A2;” MINS.”;
600 PRINT TAB(X2+24,Y2+1);A2;” MINS.”;
610 ENDPROC

615 REM obtains from user the second setpoint.
620 DEFPROCQTN3
630 PRINT TAB(X3,Y3);CHR$(141);”SET POINT TWO :?”
640 PRINT TAB(X3,Y3+1);CHR$(141);”SET POINT TWO :?”
650 INPUT A3
660 Y=VPOS
670 PROCCLR(Y)
680 PRINT TAB(X3+16,Y3);A3;CHR$(151);CHR$(33)”C”
690 PRINT TAB(X3+16,Y3+1);A3;CHR$(151);CHR$(33)”C”
700 ENDPROC

705 REM obtains from user the time at second setpoint.
710 DEFPROCQTN4
720 PRINT TAB(X4,Y4);CHR$(141);”TIME AT SET-POINT TWO :?”
730 PRINT TAB(X4,Y4+1);CHR$(141);”TIME AT SET-POINT TWO :?”
740 INPUT,A4
750 Y=VPOS
760 PROCCLR(Y)
770 PRINT TAB(X4+24,Y4);A4;” MINS.”;
780 PRINT TAB(X4+24,Y4+1);A4;” MINS.”;
790 ENDPROC

795 REM obtains from user the third setpoint.
800 DEFPROCQTN5
810 PRINT TAB(X5,Y5);CHR$(141);”SET POINT THREE :?”
820 PRINT TAB(X5,Y5+1);CHR$(141);”SET POINT THREE :?”
830 INPUT A5
840 Y=VPOS
850 PROCCLR(Y)
860 PRINT TAB(X5+18,Y5);A5;CHR$(151);CHR$(33)”C”
870 PRINT TAB(X5+18,Y5+1);A5;CHR$(151);CHR$(33)”C”
880 ENDPROC

885 REM obtains from user pre-reduction delay time.
890 DEFPROCQTN6
900 PRINT TAB(X6,Y6);CHR$(141);”PRE-REDUCTN DELAY AT S.P. :?”
910 PRINT TAB(X6,Y6+1);CHR$(141);”PRE-REDUCTN DELAY AT S.P. :?”
920 INPUT,A6
930 Y=VPOS
```

```
940 PROCCLR(Y)
950 PRINT TAB(X6+28,Y6);A6;” MINS.”;
960 PRINT TAB(X6+28,Y6+1);A6;” MINS.”;
970 ENDPROC

975 REM obtains from user valve one opening time.
980 DEFPROCQTN7
990 PRINT TAB(X7,Y7);CHR$(141);”GAS ONE ON TIME :?”
1000 PRINT TAB(X7,Y7+1);CHR$(141);”GAS ONE ON TIME :?”
1010 INPUT A7
1020 Y=VPOS
1030 PROCCLR(Y)
1040 PRINT TAB(X7+18,Y7);A7;” MINS.”;
1050 PRINT TAB(X7+18,Y7+1);A7;” MINS.”;
1060 ENDPROC

1065 REM obtains from user valve two opening time.
1070 DEFPROCQTN8
1080 PRINT TAB(X8,Y8);CHR$(141);”GAS TWO ON TIME :?”
1090 PRINT TAB(X8,Y8+1);CHR$(141);”GAS TWO ON TIME :?”
1100 INPUT,A8
1110 Y=VPOS
1120 PROCCLR(Y)
1130 PRINT TAB(X8+18,Y8);A8;” MINS.”
1140 PRINT TAB(X8+18,Y8+1);A8;” MINS.”
1150 ENDPROC

1155 REM obtains from user a valid response to save settings prompt.
1160 DEFPROCQTN9
1170 REPEAT
1180 PRINT TAB(X9,Y9);CHR$(141);”SAVE SETTINGS (Y/N) :?”
1190 PRINT TAB(X9,Y9+1);CHR$(141);”SAVE SETTINGS (Y/N) :?”
1200 INPUT,A9$
1210 Y=VPOS
1220 PROCCLR(Y)
1230 PRINT TAB(X9+22,Y9);A9$”   “
1240 PRINT TAB(X9+22,Y9+1);A9$”   “
1250 UNTIL A9$=”Y” OR A9$=”N”
1260 ENDPROC

1265 REM action user response to save settings prompt.
1270 DEFPROCCHK
1280 IF A9$=”N” THEN PROCFINISH ELSE PROCQTN10: PROCFLWR:
PROCFINISH
1290 ENDPROC

1295 REM obtains from user the name for settings file, creates named file and
writes variables to file.
1300 DEFPROCQTN10
1310 REPEAT
1320 PRINT TAB(X10,Y10);CHR$(141);”SETTINGS DATA FILE NAME :?”
1330 PRINT TAB(X10,Y10+1);CHR$(141);”SETTINGS DATA FILE NAME :?”
1340 INPUT,A10$
1350 Y=VPOS
1360 PROCCLR(Y)
1370 PRINT TAB(X10+26,Y10-1);A10$
1380 PRINT TAB(X10+26,Y10);A10$
1390 UNTIL A10$<>””
1400 ENDPROC
1410 DEFPROCFLWR
```

```
1420 *DISC
1430 *DR.2
1440 Z=OPENOUT(A10$)
1450 PRINT#Z,A1,A2,A3,A4,A5,A6,A7,A8
1460 CLOSE #0
1470 *DR.0
1480 ENDPROC

 1485 REM obtains user response to enter new settings prompt, and processes re-
sponse      obtained.
 1490 DEFPROCFINISH
 1500 REPEAT
 1510 PRINT TAB(X11,Y11);CHR$(141);”ENTER NEW SETTINGS (Y/N) :?”
 1520 PRINT TAB(X11,Y11+1);CHR$(141);”ENTER NEW SETTINGS (Y/N) :?”
 1530 INPUT A11$
 1540 Y=VPOS
 1550 PROCCLR(Y)
 1560 PRINT TAB(X11+27,Y11-4);A11$”   “
 1570 PRINT TAB(X11+27,Y11-3);A11$”   “
 1580 UNTIL A11$=”Y” OR A11$=”N”
 1590 IF A11$=”N” THEN EXIT$=”T” ELSE EXIT$=”F”
 1600 ENDPROC
```

Kiln 1

```
   5 REM this programme fires the kiln using predefined settings.
  10 MODE 7
  20 VDU14
  30 ON ERROR GOTO 2260

  40 REM main programme now calls these procedures.
  50 PROCINIT
  60 PROCTITLE
  70 PROCQTNFCP
  80 PROCFLRD
  90 PROCQTNDFN
 100 PROCFLOPEN
 110 PROCKEY
 120 PROCCLR
 130 PROCDSLY
 140 PROCPOWER
 150 PROCRDCTN
 160 END

 170 REM initialise data direction register, close contact, initialise variables.
 180 DEFPROCINIT
 190 ?&FE62=&FF
 200 *MOTOR 1
 210 HR=360000:MIN=6000:SEC=100
 220 TA=0:W=0
 230 CL1=1.0:CL2=1.0:CL3=1.0:CL4=1
 240 X1=7:Y1=23
 250 X2=14:Y2=11
 260 X3=1:Y3=2
 270 X4=27:Y4=2
 280 ENDPROC
```

```
290 REM display programme title and copyright notice.
300 DEFPROCTITLE
310 VDU23;8202;0;0;0;
320 PRINT:PRINT
330 PRINT CHR$(141);”  KILN CONTROL AND MONITORING “
340 PRINT CHR$(141);”  KILN CONTROL AND MONITORING “
350 PRINT:PRINT
360 PRINT CHR$(141);”      BY SIMON HAWLEY”
370 PRINT CHR$(141);”      BY SIMON HAWLEY”
380 PRINT:PRINT:PRINT
390 PRINT CHR$(141);”     (C) R.G.I.T. 1992  “
400 PRINT CHR$(141);”     (C) R.G.I.T. 1992  “
410 FOR I=1 TO 3000:NEXT I
420 CLS
430 ENDPROC


440 REM obtains from user the name of settings data file
450 DEFPROCQTNFCP
460 REPEAT
470 INPUT”FIRING CYCLE PROGRAMME”,FCP$
480 UNTIL FCP$<>””
490 ENDPROC

500 REM opens named settings data file, reads firing variables from file.
510 DEFPROCFLRD
520 *DISC
530 *DR.2
540 Z=OPENUP(FCP$)
550 INPUT#Z,SP1,TSP1,SP2,TSP2,SP3,RDLY,G1T,G2T
560 CLOSE #0
570 ENDPROC

580 REM obtains from user the name for log file.
590 DEFPROCQTNDFN
600 REPEAT
610 PRINT
620 INPUT”DATA FILE NAME”,DFN$
630 UNTIL DFN$<>”” AND DFN$<>FCP$
640 ENDPROC

650 REM creates named log file, writes firing variables to start of file.
660 DEFPROCFLOPEN
670 *DISC
680 *DR.2
690 Z=OPENOUT(DFN$)
700 PRINT#Z,SP1,TSP1,SP2,TSP2,SP3,RDLY,G1T,G2T
710 ENDPROC

720 REM prompts user to press a key to continue, loops until keypress detected.
730 DEFPROCKEY
740 PRINT:PRINT
750 PRINT”PRESS ANY KEY WHEN READY”
760 *FX15,1
770 REPEAT
780 A=INKEY(25)
790 UNTIL A<>-1
800 ENDPROC

810 REM clears user display screen to black.
```

```
820 DEFPROCCLR
830 CLS
840 ENDPROC

850 REM displays outlines and titles for each virtual instrument.
860 DEFPROCDSLY
870 PRINT TAB(X2-1,Y2);CHR$(255)
880 PRINT TAB(X2,Y2)”————————”
890 PRINT TAB(X2,Y2-1)” PERCENTAGE”
900 PRINT TAB(X2,Y2+4)”  OXYGEN “
910 PRINT TAB(X2-1,Y2+3);CHR$(255)
920 PRINT TAB(X2,Y2+3)”————————”
930 PRINT TAB(X2+12,Y2);CHR$(255)
940 PRINT TAB(X2+12,Y2+3);CHR$(255)
950 PRINT TAB(X3-1,Y3);CHR$(255)
960 PRINT TAB(X3,Y3)”————————”
970 PRINT TAB(X3,Y3-1)”THERMOCOUPLE”
980 PRINT TAB(X3,Y3+4)” NUMBER ONE “
990 PRINT TAB(X3-1,Y3+3);CHR$(255)
1000 PRINT TAB(X3,Y3+3)”————————”
1010 PRINT TAB(X3+12,Y3);CHR$(255)
1020 PRINT TAB(X3+12,Y3+3);CHR$(255)
1030 PRINT TAB(X4-1,Y4);CHR$(255)
1040 PRINT TAB(X4,Y4)”————————”
1050 PRINT TAB(X4,Y4-1)”THERMOCOUPLE”
1060 PRINT TAB(X4,Y4+4)” NUMBER TWO “
1070 PRINT TAB(X4-1,Y4+3);CHR$(255)
1080 PRINT TAB(X4,Y4+3)”————————”
1090 PRINT TAB(X4+12,Y4);CHR$(255)
1100 PRINT TAB(X4+12,Y4+3);CHR$(255)
1110 ENDPROC

1120 REM heats kiln up to reduction temperature.
1130 DEFPROCPOWER
1140 PROCon
1150 REPEAT
1160 PROCCALC
1170 PROCRECORD
1180 PROCUPDT
1190 PROCtime
1200 UNTIL TAVE>=SP2
1210 ENDPROC

1220 REM heating elements de-energise and extinguish led indicator.
1230 DEFPROCoff
1240 ?&FE60=?&FE60 AND &ED:REM CLR 16&2
1250 ENDPROC

1260 REM heating elements energise and light led indicator.
1270 DEFPROCon
1280 ?&FE60=?&FE60 OR &12:REM SET 16&2
1290 ENDPROC

1300 REM obtain sample, convert to engineering units, set variables
1310 DEFPROCCALC
1320 TH1=((ADVAL(1)/65536)*1.8)*CL1
1330 TH2=((ADVAL(2)/65536)*1.8)*CL2
1340 TH3=((ADVAL(3)/65536)*1.8)*CL3
1350 EMF=((ADVAL(4)/65536)*1800)*CL4
1360 T1=FNTEMP(TH1)
```

```
1370 T2=FNTEMP(TH2)
1380 T3=FNTEMP(TH3)
1390 IF T3<600 THEN POXY=20.9 ELSE POXY=FNNERNST(EMF,T3)
1400 TAVE=(T1+T2)/2
1410 ENDPROC

1420 REM convert sampled voltage to temperature in Celsius.
1430 DEFFNTEMP(TH)
1440 X=(TH/150)
1450 A0=0.263632917:A1=179075.491:A2=-48840341.37:A3=1.90002E10
1460 A4=-4.82704E12
1470 A5=7.62091E14:A6=-7.20026E16:A7=3.71496E18:A8=-8.03104E19
1480 =A0+X*(A1+X*(A2+X*(A3+X*(A4+X*(A5+X*(A6+X*(A7+X*A8)))))))

1490 REM convert sampled voltage to percentage oxygen, given the probe tempera-
ture.
1500 DEFFNNERNST(EMF,T3)
1510 =(1/(EXP(EMF/((T3+273)*0.0215))))*20.9

1520 REM produce audible indication, write sample counter and data to log file.
1530 DEFPROCRECORD
1540 VDU7
1550 PRINT#Z,W,T1,T2,T3,POXY
1560 ENDPROC

1570 REM display data in engineering units on virtual instruments.
1580 DEFPROCUPDT
1590 @%=&20209
1600 PRINT TAB(X2+3,Y2+1);CHR$(141);POXY;”    “
1610 PRINT TAB(X2+3,Y2+2);CHR$(141);POXY;”    “
1620 @%=&10
1630 PRINT TAB(X3+2,Y3+1);CHR$(141);INT(T1);CHR$(151);CHR$(33)”C”
1640 PRINT TAB(X3+2,Y3+2);CHR$(141);INT(T1);CHR$(151);CHR$(33)”C”
1650 REM @%=&20209
1660 PRINT TAB(X4+2,Y4+1);CHR$(135);INT(T2);CHR$(151);CHR$(33)”C”
1670 PRINT TAB(X4+2,Y4+2);CHR$(135);INT(T2);CHR$(151);CHR$(33)”C”
1680 @%=&10
1690 ENDPROC

1700 REM wait for three seconds, increment sample counter.
1710 DEFPROCtime
1720 TIME=0
1730 REPEAT UNTIL TIME=300
1740 W=W+0.05
1750 ENDPROC
1760 REM purge and reduce kiln, whilst maintaining reduction temperature.
1770 DEFPROCRDCTN
1780 PROCV1on
1790 FOR C=1 TO G1T*20
1800 PROCCALC
1810 IF TAVE>=SP3 THEN PROCoff
1820 IF TAVE<SP3-1 THEN PROCon
1830 PROCRECORD
1840 PROCUPDT
1850 PROCtime
1860 NEXT
1870 PROCV1off
1880 IF POXY>=5 THEN GOTO 2260
1890 PROCV2on
1900 FOR D=1 TO G2T*20
```

```
1910 PROCCALC
1920 IF TAVE>=SP3 THEN PROCoff
1930 IF TAVE<SP3-1 THEN PROCon
1940 PROCRECORD
1950 PROCUPDT
1960 PROCtime
1980 NEXT
1990 PROCV2off
2000 PROCoff
2010 PROCCLR
2020 PRINT
2030 PRINT CHR$(141);” FIRING COMPLETED “
2040 PRINT CHR$(141);” FIRING COMPLETED “
2050 *MOTOR 0
2060 ?&FE60=0
2070 CLOSE #0
2080 ENDPROC

2090 REM turn on valve one.
2100 DEFPROCV1on
2110 ?&FE60=?&FE60 OR &01:REM SET 1
2120 ENDPROC

2130 REM turn off valve one.
2140 DEFPROCV1off
2150 ?&FE60=?&FE60 AND &FE:REM CLR 1
2160 ENDPROC

2170 REM turn on valve two.
2180 DEFPROCV2on
2190 ?&FE60=?&FE60 OR &F7:REM SET 8
2200 ENDPROC

2210 REM turn off valve two.
2220 DEFPROCV2off
2230 ?&FE60=?&FE60 AND &F7:REM CLR 8
2240 ENDPROC

2250 REM Exception handling routine follows.
2260 *MOTOR 0
2270 ?&FE60=0:CLOSE#0:PRINT”ERROR”:END
```