A STUDY OF THE CHEMICAL DETERIORATION OF PAPER USING FOURIER-TRANSFORM INFRARED SPECTROSCOPY, AND THE ~~STABILIZATION AND~~ STRENGTHENING OF MECHANICAL WOOD PAPERS

AND STABILIZATION

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To my parents and to the memory of my brother.

ABSTRACT

The composition and mode of deterioration of a number of old and modern papers of different types were investigated using a variety of techniques including Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Special emphasis was placed on papers based in whole or in part on mechanical wood pulps, as these are particularly noted for their poor preservation, and have not been so widely studied as the lignin-free papers. FTIR was used to investigate chemical changes occuring in papers as a result of ageing, and to identify paper types and additives on a chemical basis by comparison with standards of known composition treated in different ways. DSC was used to look for changes in stability of papers as a result of ageing and following chemical modification.

The causes of paper deterioration have been reviewed and discussed, and the role of acidity and pollutants in paper deterioration further investigated and assessed. Alternative methods of deacidification have been tried, particularly those based on vapour-phase reagents, in an attempt to overcome some of the disadvantages of existing techniques.

Two particular aspects of the conservation of wood-pulp based papers have been investigated. The strengthening of new and already partially deteriorated papers by chemical means has been tried, as has the use of reagents to stabilize the lignin and to limit future deterioration of such papers.

Prospects for the preservation of modern papers of low permanence have been discussed in the light of the work described above.

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ABBREVIATIONS

Text

FTIR	Fourier transform infrared spectroscopy
TMP	Thermo mechanical pulp
DSC	Differential scanning calorimetry
DETA	Dielectric thermal analysis

Spectroscopy data

b	broad
D	doublet
k	kink
m	medium
s	small
st	strong
sh	shoulder
T	triplet
v	very
w	weak

Ac	Acetylated
ac	acid
alco.	alcohol
ald.	aldehyde
ali.	aliphatic
aro.	aromatic
bond.	bonding
C	cellulose
conj.	conjugated
def.	deformation
equit.	equatorial
G	glucose
gL	guaiacyl lignin
grp.	group
HC	hemicellulose
H.W.	hard wood
int.	internal
keto.	ketone
L	lignin
4-MGX	4-O-Methyl-D-Glucuronoxylan
P	polysaccharide
pri.	primary
PU	Polyurethane sizing
rock.	rocking
S	sucrose
sat.	saturated
sec.	secondary
skelet.	skeletal
sL	syringyl lignin
str.	stretching
subst.	substituted
S.W	soft wood
s.w.L	soft wood lignin
sym.	symmetric
V	vanillin
van.	vanallyl
vib.	vibration
W	wood
X	xylan

Sample list

Arc.	Archaeological
Mis.	Miscellaneous
bri.	British

atm.	atmosphere
B	book
bl.	blue
br.	brown
cal.	calandered
co.	coated
com.	computer
e	early
E	Europian
exp.	exposed
fib.	fibre
ge	gelatin
g.w.	ground wood
h.m.	hand made
J	journal
l	light
m	manufacturer
ma. fo.	manifold
mat.	material
m.m.	machine made
N	Newspaper
New Z.	New Zealand
no.	number
o.w.	off white
pre.	present
pri.	printed
p.w.	pure white
qua.	quality
sh.	sheet
S.L.	Sri Lankan
S.W.	soft wood
U.K.	United Kingdom
w	white
y	yellow

PREFACE

This project was initiated with the hope of developing a technique for the conservation of paper. It was realised that in developing a reasonably good practical method of conservation, the reasons for the condition of the paper and the processes of deterioration should be identified. Hence, this project was planned to investigate the deterioration of paper in more detail, evaluate some of the existing techniques for the conservation of paper, and if possible, to establish new or modified processes which can be used even in developing countries.

In the evaluation of previous work regarding deterioration, factors affecting the process such as raw materials, storage conditions, acidity, and the types of deterioration have been discussed. The analytical techniques used, i.e. differential scanning calorimetry and particularly Fourier transform infrared spectroscopy (FTIR), were examined along with the published literature. In respect of conservation, the literature about deacidification processes, and consolidation methods such as lamination and graft copolymerization, were investigated in particular.

In this project, a range of analytical techniques which had previously been used for paper analysis was employed, along with FTIR spectroscopy which had not been widely used in analysing paper. The author used this technique as it is essentially non destructive, and also as it could be helpful in determining the composition of the main components of paper, together with its additives and changes caused by deterioration. Also, in addition to being a versatile technique, FTIR was used in the hope of establishing it as a routine analytical technique in the analysis of books and archival materials, being non destructive and very rapid. The author managed to run over one thousand FTIR spectra of different paper samples while investigating the deterioration, stabilization and strengthening of paper.

One hundred and eight different samples of paper both old and modern were collected from books, periodicals and newspapers of known date. These represented a wide range of types of paper in different stages of deterioration. Whatman No.1 filter paper was used as the standard pure cellulosic paper, and fresh newsprint as a reference source of lignin-containing paper. In addition, paper pulp samples of known origin were also used. FTIR spectroscopy was used to monitor the changes occuring on deterioration, and for this purpose many of the samples were also artificially aged.

In this study mechanical wood and rag papers were examined to evaluate their deterioration. Since the deterioration of rag papers had been thoroughly investigated previously, major attention was given to mechanical wood papers which had not been studied extensively.

With regard to the conservation of paper from books, periodicals, newspapers and documents, the author tried out various methods for stabilization and strengthening paper. For the stabilization of paper, deacidification processes have been known and established for a long time. Strengthening of paper was also widely used, although it has not yet been developed as a large-scale process.

In the case of rag papers, stabilization has been limited to the process of deacidification, which is sufficient to stabilize these, as their main degradation process is acid hydrolysis. In the case of lignin-containing papers, i.e. mechanical wood papers, neutralization is not sufficient, as oxidation takes place readily, while in rag papers, it is very limited. If rag papers are kept in a good environment in the absence of light, they oxidise only very slowly.

The deacidification processes which already exist are also applicable to mechanical wood papers. Many of the deacidification processes used at present are complicated and involve toxic material. Hence, the author investigated a modified technique using entirely non-toxic material, which can be used in developing countries. A number of existing processes which can be used in developing countries have been assessed as well.

The use of other stabilization techniques for mechanical wood papers has hitherto been extremely limited. This limitation is due to the large quantity of the material which has to be treated, and the difficulty in finding a successful technique which is capable of being used as a bulk treatment without disbinding bound volumes. For this reason only vapour phase processes were considered, and several different reagents which were expected to react with the functional groups in lignin were investigated.

The same criteria must apply to strengthening. It has already been shown that the C-ray induced polymerization of vinyl monomers can be used successfully to strengthen paper. This, however, requires irradiation facilities which are not widely available or affordable in developing countries. Therefore, it was decided to investigate the use of monomers which would autopolymerize in contact with paper, in order to achieve an adequate degree of strengthening without blocking the adjacent sheets.

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Chapter 1

INTRODUCTION

1. Paper

Paper is a felted sheet formed by the interlocking of cellulose fibres derived from a variety of sources such as cotton, linen (flax), hemp, jute, ramie, manila, esparto, mulberry, straw, bamboo, or wood. An aqueous suspension of the chosen fibres is drained on a grid to give a suitable thickness of mat which is dried, subjected to appropriate finishing processes (for example sizing) and is then ready for use as newsprint, writing paper, art paper, packaging, or other purpose.

1.1 Raw materials

Paper is made out of fibrous raw materials which contain cellulose, hemicellulose and lignin, with the addition of sizes, fillers and coatings. Since the major ingredient, cellulose, is introduced through plant fibres, and the quality of paper depends on the nature of the fibres, it is necessary to consider the composition of the plant fibres used for paper-making. The three main components, cellulose, hemicellulose, and lignin, each make its own special contribution to the development of paper strength. Cellulose is the main structural element forming the fibrous structure of paper, reinforced by lignin in differing amounts, while hemicellulose and low molecular weight fractions of cellulose contribute to the formation of fibre-to-fibre bonds within the sheet (Akim, 1977).

1.1.1 Plant fibres

Until the middle of the 19th century, the most commonly used fibres were rag, i.e.cotton (*Gossypium* sp.) and flax (*Linum usitatissimum* L.), which contain about 98% cellulose and 80% cellulose (Higham,1963) respectively. Hemp (*Cannabis sativa*) and jute (*Corchorus* spp.) yielding 77% and 60% cellulose respectively and esparto (*Stipa tenacissima*) which yields 46-58% cellulose, 26-32% hemicellulose and16-19% lignin (Emerton, 1980) were used as substitutes in addition to straw (*Triticum* spp)which contains 31-40% cellulose, 35-50% hemicellulose, 15-25% lignin and 4-8% mineral matter (Emerton,1980), and bamboo (*Cephalostachyum pergracile* Munso) which consists of 56-66% cellulose (Higham, 1963).

Wood fibres are obtained from hardwood (deciduous) and softwood (coniferous) (Emerton, 1980). Hardwoods contain larger amounts of hemicelluloses, but are lower in their lignin content (Kiran, 1986). According to Fan, Gharpuray and Lee (1987), the hemicellulose content is similar in hardwoods and softwoods, and the cellulose content is generally higher and the lignin content is lower in hardwoods than in softwoods.

It is necessary to state that in addition to the fibre pulped directly from vegetable sources, secondary fibre obtained by re-pulping paper, board, rope, and textile (i.e. used rags) is also used for the manufacture of paper.

A general comparison of wood compositions is given in Table 1.1 (Emerton, 1980).

	% cellulose	hemicellulose	lignin
Conifer - normal wood	44	27	29
(range)	(41-47)	(22-32)	(26-32)
Conifer - compression wood$_a$	30	31	39
Deciduous - normal wood	44	35	21
Deciduous - tension wood$_a$	57	30	13

a - values found by Meier (1964) for a single species in each case

TABLE 1.1: General composition of wood

1.1.1.1 Cellulose

Cellulose is a high molecular weight, stereoregular, linear polymer of ß -D-glucopyranose (anhydrous glucose) units linked by 1,4,-glycosidic bonds (Figure 1.1) (Emerton, 1980). In native cellulose up to 10,000 ß -anhydroglucose residues are linked, while cellulose contained in pulp and filter paper usually has a degree of polymerisation ranging from 500 to 2,100 (Fan, Gharpuray and Lee, 1987). ß -1,4-links in cellulose are nominally straight as a result of intra-chain hydrogen bonding along its length (Figure 1.2) (Emerton, 1980; Hermans, 1949). In addition to ß -1-4-links and the intra-chain hydrogen bonding, hydrogen bonds form between the free hydroxyl groups of neighbouring cellulose molecules and bind them together (Emerton, 1980). These hydrogen bonds strongly influence the chemical reactivity and solubility of cellulose (Ekman et al., 1986). The glucosidic linkage acts as a functional group, and this along with the hydroxyl groups mainly determines the chemical properties of cellulose. All significant chemical reactions occur at these locations (Fan, Gharpuray and Lee,1987).

The free hydroxyl groups in cellulose react as in alcohols, and it forms complex compounds with alkalis, and gives esters and ethers on oxidation which can be converted into aldehydic and carboxylic groups. Hence cellulose behaves as an aliphatic compounds with alkalis, and gives esters and ethers on oxidation which can be converted into aldehydic and carboxylic groups. Hence cellulose behaves as an aliphatic poly-alcohol (Heuser,1944). The hydroxyl groups in positions 2 and 3 are secondary hydroxyl groups, whereas the one in position 6 is a primary hydroxyl group. The acidity of these hydroxyl groups increases in the order OH-6 < OH-3 < OH-2 . However when OH-2 is ionized or substituted, the acidity in position 3 is lowered and the hydroxyl group in position 6 may then be the more acidic one (Ekman et al., 1986). It has been reported recently that the hydroxyl group in the 3-position is bound by an intramolecular hydrogen bond to the ring oxygen atom of the next chain unit (Sihtola and Neimo, 1975; Fan, Gharpuray and Lee, 1987).

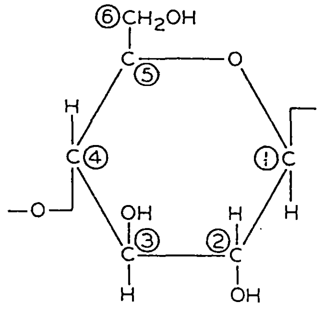


Figure 1.1 (a)

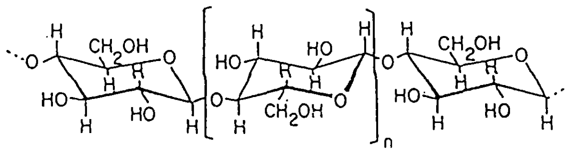


Figure 1.1 (b)

Figure 1.1: (a) Anhydroglucose unit and (b) schematic molecular structure of cellulose

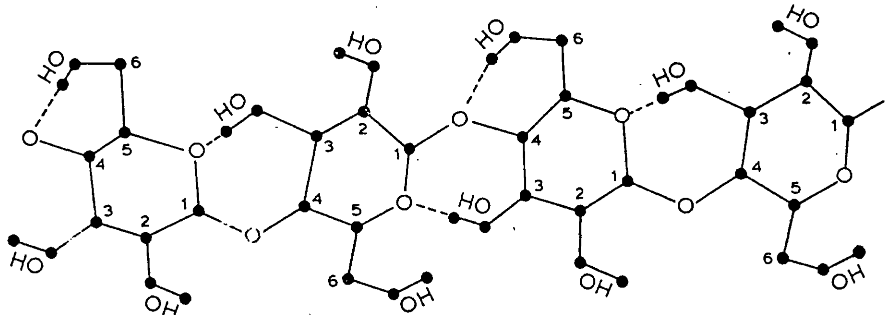


Figure 1.2: Intra-chain hydrogen bonding of cellulose

Cellulose is crystalline in nature, although it is not uniform (Emerton, 1980), and it is insoluble in water. However, strong acids and strong alkalis have the capacity to swell or

1987). Native cellulose consists mainly of α-cellulose which may degrade to β-cellulose through oxidation or hydrolysis during cooking and bleaching in the process of making pulps, and also to water soluble γ-cellulose with the further increase in de-polymerisation (Browning, 1977). Hydrolysis, oxidation, photochemical degradation or even mechanical action can cause the scission of the chain thus lowering the molecular weight.

1.1.1.2 Hemicellulose

Hemicellulose, which exists in an amorphous form in its natural state (Fan, Gharpuray and Lee, 1987), can be termed a non-cellulosic carbohydrate, which yields pentosans and hexosans together with some uronic acids on hydrolysis (Haun, 1970; Emerton, 1980; Heuser, 1944). Hemicelluloses are soluble in water or in aqueous alkali, and the degree of polymerisation is very much lower than that of cellulose (Emerton, 1980). According to Browning (1967), hemicelluloses are for the greater part soluble in alkaline solutions, both because of their relatively low degree of polymerisation and the presence of carboxyl groups. As in cellulose, hydrogen bonding between the functional groups of hemicellulose which are polar in nature, binds hemicellulose and cellulose together (Emerton, 1980).

The content of hemicellulose varies according to the different origins of the fibres. Most of the hemicelluloses which go into paper manufacture are from wood fibres. Hemicelluloses assist in internal fibrillation of the fibres in paper-making although they easily break down during digestion and are lost in the form of by-products, due to their short-chain structure (Higham, 1963).

Hardwood hemicelluloses are rich in xylan polymers with a small amount of mannan, whereas softwood hemicelluloses are rich in mannan polymer and contain significant quantities of xylans (Browning, 1967; Haun, 1970). Xylan is a polymer of 4-O-methylglucuronoxylan and 4-O-methylglucuronoarabinoxylan linked by a β-D-(1→4)-bond, similar to the linkages of the glucose units in cellulose (Marchessault, 1964; Fan, Gharpuray and Lee, 1987). The structures of 4-O-methyl-D-glucuronoxylan and 4-O-methyl-D-glucuronoarabinoxylan are given in Figure 1.3.

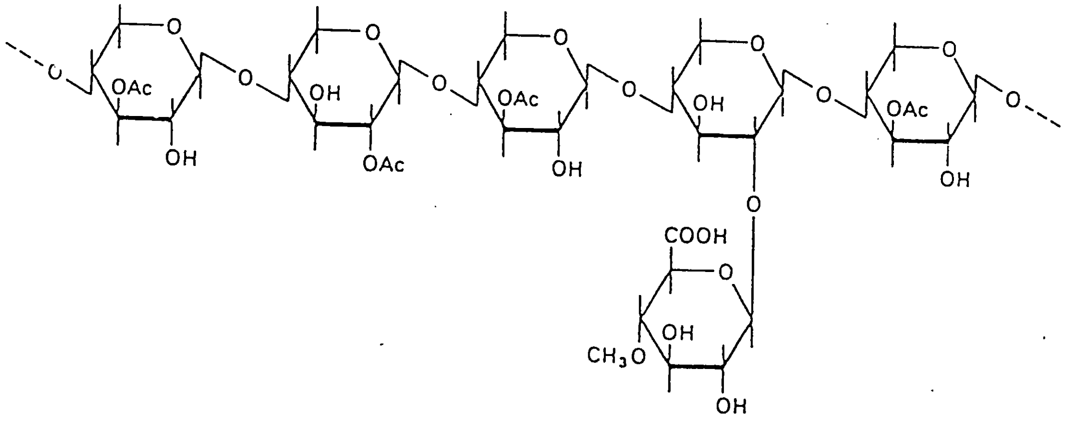


Figure 1.3 (a)

(softwood) are different; the former is characterized by the absence of galactose units. Thus, it is assumed that the glucomannans have a linear structure so that there is no branching at either of two carbon positions, namely (C-2) or (C-3). The presence of short side-chains of galactose units in the glucomannans from coniferous woods may be considered to be certain (Fan, Gharpuray and Lee; 1987). The structure of glucomannan is given in Figure 1.4.

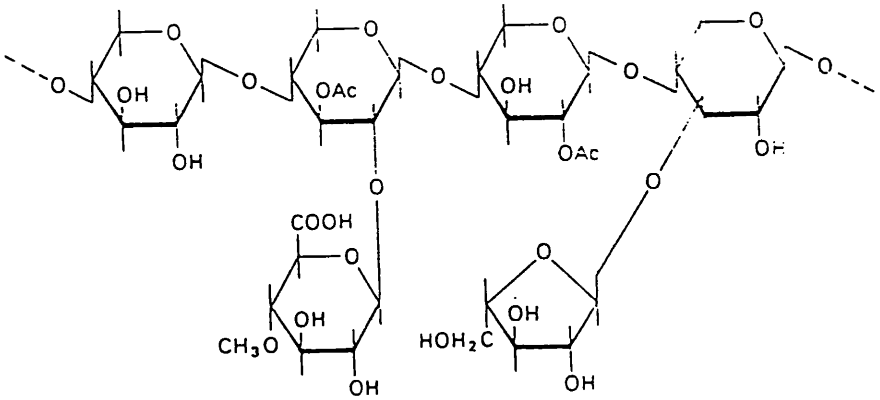


Figure 1.3 (b)

Figure 1.3: Molecular structures of (a) 4-O-methyl-D-glucuronoxylan and (b) 4-O-methyl-D-glucuronoarabinoxylan

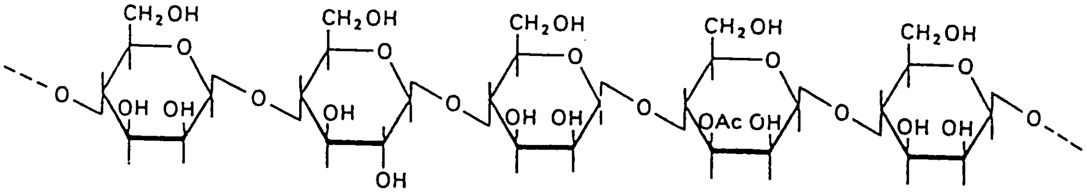


Figure 1.4: Molecular structure of glucomannan

The principal sugar residues of wood hemicelluloses are given in Figure 1.5.

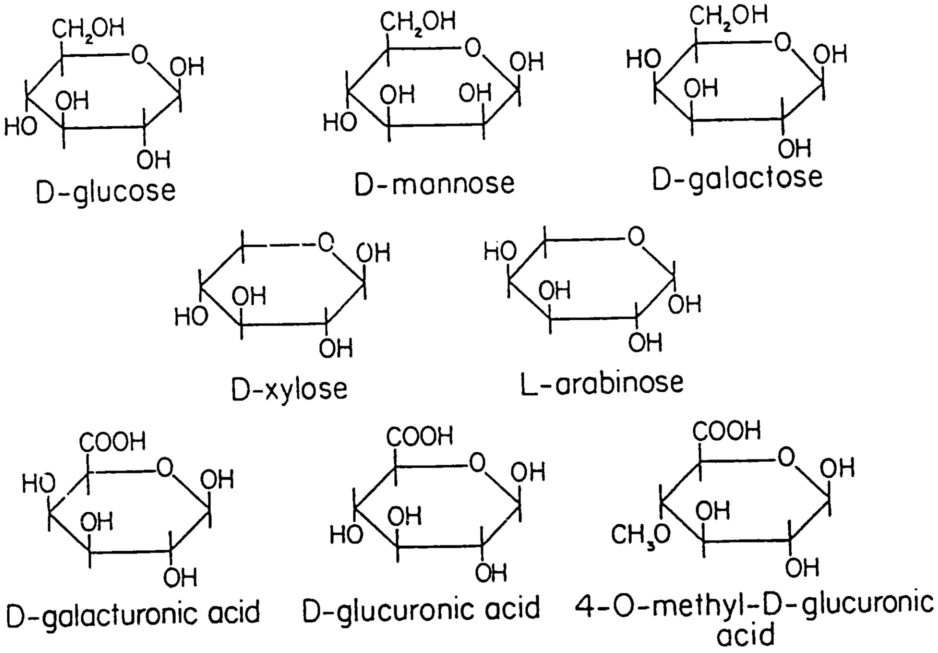


Figure. 1.5: Principal sugar residues of wood hemicellulose

1.1.1.3 Lignin

Lignin is an amorphous material which is partly aromatic in nature and contains methoxyl groups and aliphatic and aromatic hydroxyl groups as its characteristic functional groups (Browning,1967), but according to Emerton (1980) it remains ill-defined and in fact its constitution may not be precisely definable. Lignin is essentially a three-dimensional phenylpropane polymer with phenylpropane units held together by ether linkages and carbon-carbon bonds (Forss and Fermer, 1975; Fan, Gharpuray and Lee, 1987). The schematic molecular structures of spruce lignin (Adler et.al., 1969; Fan, Gharpuray and Lee, 1987) and beech lignin (Leisola and Fiechter, 1985) are given in Figures 1.6 and 1.7 respectively.

Iskikawa and Takaichi (1956) concluded that lignin contains both conjugated and non-conjugated phenolic hydroxyl groups (Brauns and Brauns, 1960). According to these workers, lignin contains phenolic and aliphatic hydroxyl groups, and the number of phenolic hydroxyl groups varies with the type of lignin, both due to variations inherent in different wood species, and also the conditions under which it was isolated.

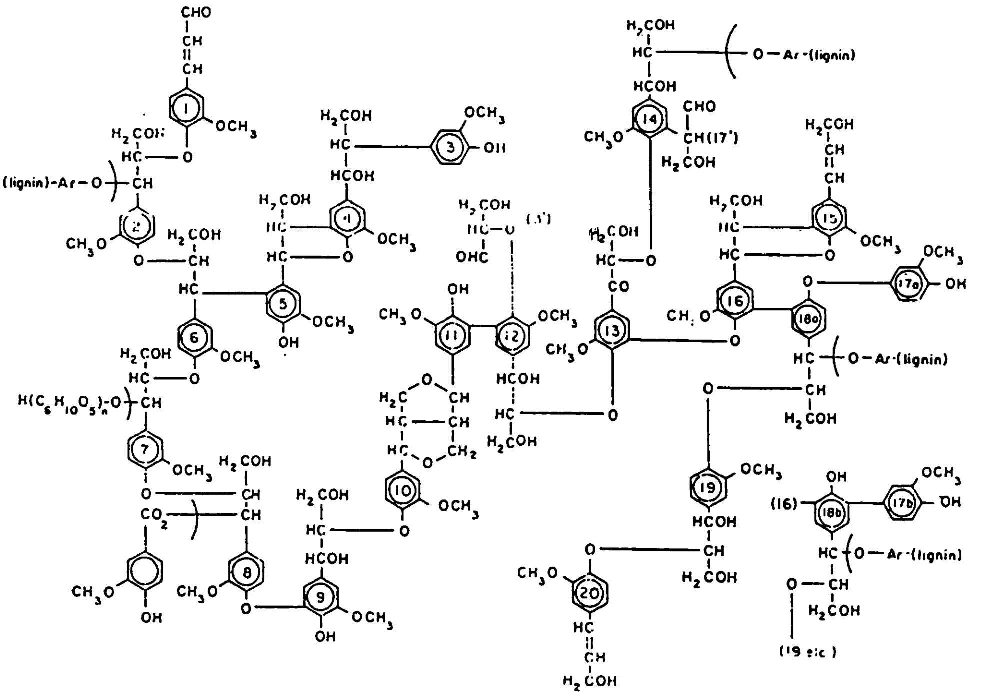


Figure 1.6: Schematic molecular structure of spruce lignin; represents soft wood lignin

The lignin from grasses, soft woods and hard woods differ somewhat in composition, mainly in methoxyl substitution and the degree of linkage between phenyl groups (Fan, Gharpuray and Lee, 1987). Gymnosperm lignin which is in softwoods is a dehydrogenation polymer of coniferyl alcohol; and angiosperm lignin, which is in hardwood, is a mixed dehydrogenation polymer of coniferyl and sinapyl alcohols; and grass lignin is composed of a mixed dehydrogenation polymer of coniferyl, sinapyl and p-coumaryl alcohols (Higuchi, 1981). Schobinger (1956) concluded from infrared (IR) absorption studies that milled wheat-straw lignin contains the β-keto acid ester grouping (Brauns and Brauns, 1960). The molecular structures of coniferyl, sinapyl and p-coumaryl alcohols are given in Figure 1.8. The lignin in conifers is more condensed and less susceptable to chemical attack than the lignin in hardwoods.

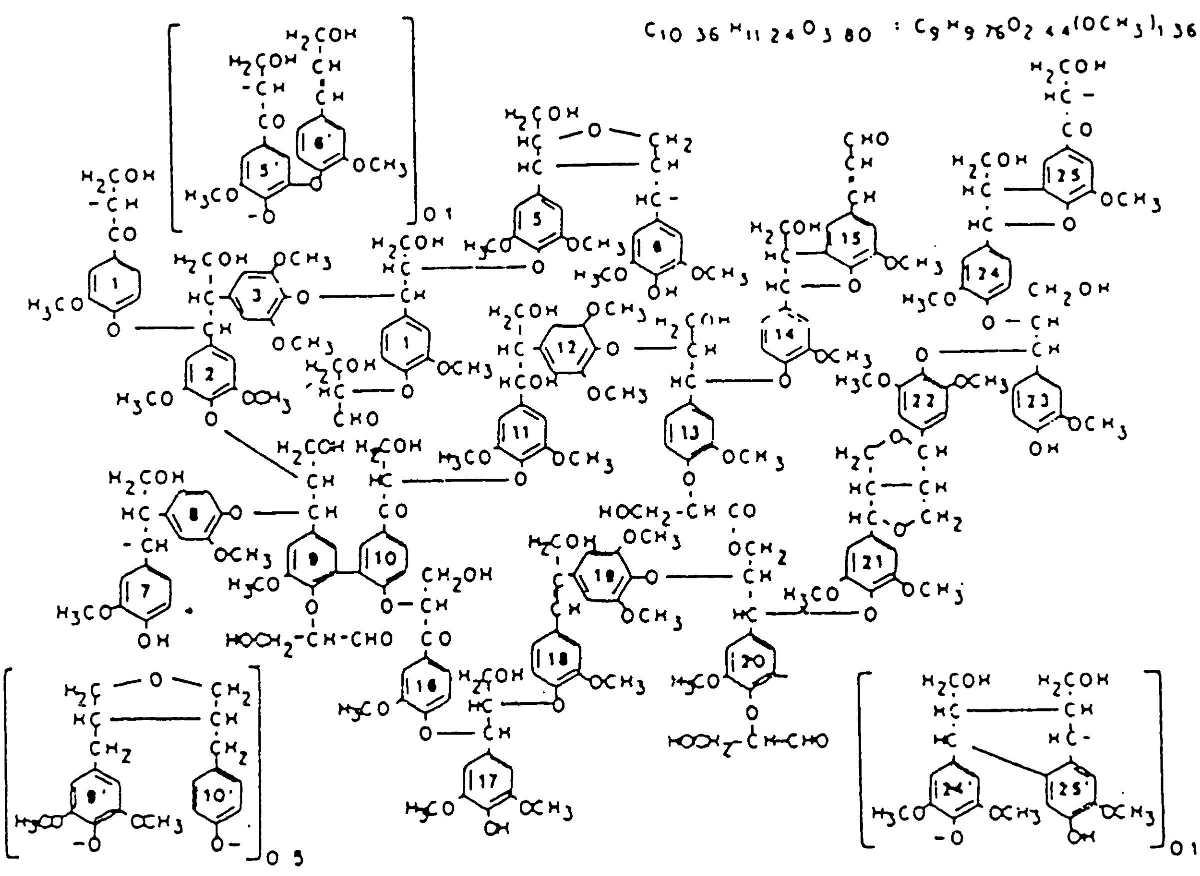
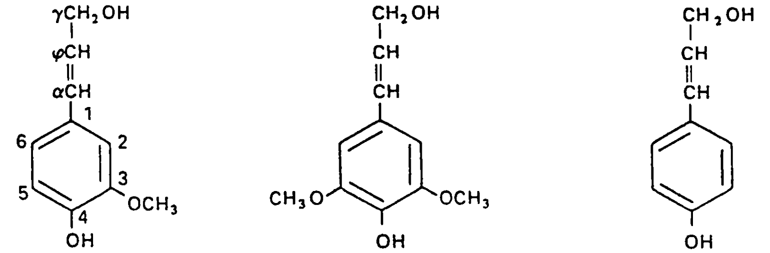


Figure 1.7: Schematic molecular structure of beech lignin; represents hard wood lignin



(1) Coniferyl alcohol
(2) Sinapyl alcohol
(3) *p*-Coumaryl alcohol

Figure 1.8: Molecular structures of coniferyl, sinapyl and p-coumaryl alcohols

Lignin is insoluble in water, common organic solvents and acids, although it is partly soluble in alkaline solutions. Lignin, in the presence of strong mineral acids, is subject to condensation reactions and is readily attacked and solubilized by oxidising agents (Browning, 1970). Lignin is present in groundwood and unbleached pulps used in paper manufacture, to a considerably greater extent in the former than the latter. The bleaching process essentially removes all the lignin present in unbleached pulps. However, small quantities of residues derived from lignin may remain (Browning, 1967).

1.1.2 Non-fibrous materials

1.1.2.1 Water

The most important non-fibrous material in paper is water. The uptake of water allows the crystallites to open up to release some internal hydroxyl groups of cellulose, which leads to the development of adhesion forces, mainly hydrogen bonds, between the cellulose chains of adjacent fibriles and microfibriles (Higham, 1963). Paper contains typically 6% water, depending on ambient relative humidity.

1.1.2.2 Sizes

In order to introduce an amount of hydrophobic characteristic into paper, sizes are added. Animal glue, gelatin, starch and rosin were the most commonly used sizing materials in paper manufacture before the introduction of synthetic sizes.

Introducing sizes can be done in three ways; as an internal size, as an external size, and as the adhesive in a pigment coating (Browning, 1977). Sizing can vary in different papers according to the material and quantity used. Internal sizing is a factor inducing resistance of the paper to the penetration of water. Surface sizing contributes to the increase of properties such as water and abrasion resistance, abrasiveness, creasibility, finish, printability, smoothness and surface bond strength, as well as a decrease in porosity and surface fluff (Roberts and Etherington, 1982).

1.1.2.2.1 Starch

Starch is probably the oldest of sizing agents, and was re-introduced in European paper-making from around 1800 (Norris, 1952; Browning, 1977).

Starch assists water retention, and has a certain amount of binding effect on the sheet (Norris, 1952). For use in paper-making, starch can be obtained from corn, potato, sorghum and tapioca (Browning, 1977).

Starch is made up of a long chain of glucopyranose units joined together through oxygen by $\alpha(1\rightarrow4)$ glucosidic bonds, to produce a branched polymer, amylopectin, and a linear polymer, amylose, and yields glucose alone on complete hydrolysis. Although the ratio of the two polymers varies according to the source of the starch, its major component is always amylopectin (Prosser, 1989).

Starch, when used as a paper size, can be employed in all three of the ways mentioned in 1.1.2.2. It increases the strength and smoothness when used as an internal size, and gives water resistance when applied as an external size. (Browning, 1977).

1.1.2.2.2 Gelatin

Gelatin is a complex protein of the scleroprotein class, derived from animal glue, having a molecular weight varying from about 40;000 to 100,000 and it is obtained from hydrolysed collagen (Roberts and Etherington, 1982). Gelatin is a purified form of animal glue and was used for sizing almost all European hand-made papers, and good quality machine-made papers. The fibres of gelatin-sized papers are partially protected from oxidising agents in the atmosphere, and hence they are more durable (Clapperton and Henderson, 1952; Browning, 1977).

1.1.2.2.3 Animal glue

Animal glue, which is a related but less pure protein than gelatin, was used as a tub-sizing agent, i.e. it was applied after the sheet was made. It is derived from the simple hydrolysis of collagen, and is essentially composed of polyamides of certain α-amino acids and consists largely of gelatin, but also contains impurities such as keratin, elastin, mucin, and chondrin (Prosser,1989).

1.1.2.2.4. Rosin

Rosin is a resinous material obtained from pine trees. It was introduced for sizing in 1807 (Browning, 1977), and paper-makers have found rosin more effective and less expensive than starch (Norris, 1952). Rosin consists mainly of resin acids with a small amount of neutral material. Rosin is insoluble in water, and when exposed to light and air it changes into a crystalline substance losing its amorphous quality and becoming friable (Higham, 1963).

Alum had long being used as a hardener for gelatin sizes, and it was employed for similar purposes with rosin sizes, the alum acting as a mordant by attaching the polar ends of the size molecule to the hydroxyl groups of the cellulose (Higham, 1963). Its effect is to decompose the sizing agents (an emulsion of free rosin in aqueous sodium resinate), and to deposit the resin on the fiber (Heuser, 1944)

1.1.2.2.5 Feculose

Feculose, which is an acetate derivative of starch, is sometimes used for tub-sizing of writing papers, but not on its own. It was used always with either gelatin or rosin size (Clapperton and Henderson, 1952).

1.1.2.3 Adhesives

Adhesives are added to pulp stocks to enhance the strength, to reduce the air permeability, to decrease the tendency for the surface to fluff and to increase the ink retention of the paper, and they are also used as coatings (Emerton, 1980).

1.1.2.4 Coatings

The coating of papers improves the smoothness and printing quality of the surface, and also increases the opacity of the sheet (Browning, 1977).

The chief components of the coating are the pigment and a coating adhesive. The largest proportion is pigment, and its properties will affect the characteristics of the coated surface. Some of the properties which characterise the coating are particle size and shape, and range of particle size, which affect the finish of the coating, and the refractive index which affects the opacity and the brightness of the pigments (Prosser, 1989)

Clay (kaolin) is the pigment component most frequently and widely used. Calcium carbonate is also used to some extent, and the other pigments used include talc, titanium dioxide, satin white, barium sulphate and calcium sulphate. Two or more pigments may be used in the same formulation. (Browning, 1977; Higham, 1963).

Coating adhesives bind the pigment particles to each other and to the paper surface. Casein, gelatin and starch were used as adhesives (Higham, 1963), and animal glue was an important coating adhesive in England during the 1920's (Prosser, 1989). Synthetic adhesives such as styrene-butadiene latex, polyvinyl alcohol, polyvinyl-acetate latex and acrylic dispersions are some of the coating compounds widely used (Browning, 1977). The properties affected by the use of synthetic lattices include gloss (due to easier calendering), smoothness, higher flexibility, increased ink and varnish hold out, reduced tendency to curl, higher pick strength and higher wet-rub resistance (Prosser, 1989).

1.1.2.5 Fillers and loadings

Fillers are introduced mainly to create a smooth surface, to improve opacity and to increase dimensional stability. Kaolin and calcium carbonate are of great importance. Calcium sulphate, calcium sulphite, calcium silicate, magnesium silicate and kieselguhr are also employed as fillers (Browning, 1977; Emerton, 1980; Higham, 1963).

The word loading is reserved for those heavy minerals that are embodied in a sheet chiefly to increase its opacity. Titanium dioxide is pre-eminent among these (Emerton, 1980).

1.2 Chemical deterioration of paper

The degradation or breakdown of paper, which results both from the materials used during the manufacturing process and from natural aging due to the substances in paper and the effect of the environment comprises chemical deterioration, and is the factor controlling the permanence of the paper material.

1.2.1 History

In the thirteenth century the Holy Roman Emperor Frederick I expressed doubts about the useful life of paper which was then being introduced into Europe (Walton, 1929; Williams, 1970), and the Benedictine abbot Johann Tritheim also recorded similar reservations about paper in the fifteenth century (Grove, 1966; Williams, 1970). In July 1823 the journal *Annals of Philosophy* published an article about frauds and imperfections of paper making, and in the same month John Murray wrote an article in the *Gentleman's Magazine* calling attention to the state of the "wretched compound called paper" (Grove, 1966; Williams, 1970).

Murray had recognised that the employment of sulphate of lime and other compounds in the pulp, and that bleaching the rags previously, or the paper subsequently, with oxymuratic acid gas (chlorine) are the chief causes of self-destruction of paper (Grove, 1966; Williams, 1970). In 1825 Thomas Hansard talked about unbound books crumbling to dust (Hansard, 1825). In 1856, Herring found that paper perished as a result of not being thoroughly washed after bleaching (Herring, 1856).

The poor quality of newsprint was a matter of great concern during the late nineteenth century. Justin Winsor tried to persuade Boston Newspapers to use more durable paper; it was feared that the "permanency of literature" was threatened by inferior paper (Johnson, 1891; McAllister, 1898; Williams, 1970). The durability of paper-making materials has been discussed by Cross (1897). A report of a conference held by Italian libraries on paper deterioration appeared in the New York Library Journal of 1897. Paper deterioration was also the subject of reports by Evans (1898) and by the Librarian of Congress in 1898 (Williams, 1970).

In 1902 Paul Klemm wrote in *Papier-Zeitung* that the intensity of discolouration is generally proportional to the iron content in the paper (Klemm, 1902). In 1903 Little emphasized the distinction between groundwood papers and wood fibre papers (chemically treated papers) (Little, 1903) and in 1907 Davenport wrote about the unreadable condition in the future of modern books (Williams, 1970). In 1908 Veitch had pointed out the effects of insufficient cooking or over-cooking and using oxidising agents as bleaches in paper-making operations, in an article written on "suitable paper for permanent records".

It is recorded that the American Library Association (ALA) had a committee on the deterioration of newspapers from 1910 to 1913 and again from 1918 to 1920 (Williams, 1970). In 1912 Schoeller had stated in *Wochenblatt für Papierfabrikation*, that the most important cause of the discolouration of paper was the rosin size, which had as a result the development of a darker colour on standing due to the polymerisation or auto-oxidation of rosin (Schoeller, 1912). In the same year Hjelmsatter concluded as a result of scientific

(Herzberg, 1914; Williams et al., 1977). In 1913 Briggs and Zschokke respectively had identified mechanical wood and rosin as factors in paper discolouration. Hitchins (1918) wrote that the amounts of size and iron present are important factors, and are more or less proportional to the degree of yellowing of paper. In 1920, Sindall concluded that rosin size and impurities due to careless manufacture were frequent sources of trouble.

Kohler and Hall concluded in 1925 that the root of the degradation was the acidity produced by the use of aluminium sulphate (Kohler and Hall, 1925; Williams et al., 1977), and in 1928 Hoffman had written about the effect of residual acid on the rate of deterioration of paper. In 1957 W. J. Barrow conducted a substantial and important study of the deterioration of modern book papers and in 1960 the Barrow Laboratory and the Association of Research Libraries (ARL) committee discussed paper deterioration as a result of a report written on a study of the deterioration of modern book papers in 1959 . In the same year Robert Kingerly presented a paper on the extent of the problem of paper in research collections and comparative costs of available solutions (Kingerly, 1960; Williams, 1970).

The effect of acidity in accelerating the deterioration of paper and its various aspects have been studied in detail by Smith (1970 a). Koura and Krause (1978) have carried out experimental studies on a series of papers and revealed that factors such as acidity and the organic substances present are of importance for the decay of paper. In 1980, Krause pointed out that paper-making techniques and acidity of the suspended fibres and pulp additives are the factors causing paper decay (Krause, 1980). Suryawanshi has described the results of a survey of raw materials in old papers and their role in deterioration (Suryawanshi, 1983). The causes of acidity in paper were discussed briefly by Cali (1985). Inaba and Sugishita (1986) have studied the effect of dossa, which consists of animal glue and alum, i.e. glue size, on the deterioration of Japanese papers.

1.2.2 Types of chemical deterioration

Chemical deterioration is the end result of chemical action taking place in paper mainly due to hydrolytic degradation, oxidative degradation and photochemical degradation.

1.2.2.1 Hydrolytic degradation

The hydrolysis of cellulose always results in enhanced reducing properties owing to the increased number of end groups (Browning, 1967), and as a result of that, paper which is subjected to hydrolysis is liable to undergo a number of other chemical changes.

The main reactions of lignin with water are the solvolitic splitting of α and β -linkages (Wallis, 1971). Sakakibara and Nakayama (1962) have reported that on hydrolysis, gymnosperms yield coniferyl alcohol, p-coumaryl alcohol, coniferyl aldehyde and vanillic acid, and angiosperms yield sinapyl alcohol, coniferyl alcohol, coniferyl aldehyde, syringic acid and vanillic acid (Pearl, 1967).

acid, and angiosperms yield sinapyl alcohol, coniferyl alcohol, coniferyl aldehyde, syringic acid and vanillic acid (Pearl, 1967).

Hydrolytic degradation can occur in the presence of hydrogen ions or in the presence of hydroxyl ions, and these processes are known as acid hydrolysis and alkaline hydrolysis respectively.

1.2.2.1.1 Acid hydrolysis

Hydrolysis is most often brought about by hydrogen ions linked with the presence of acidic materials in the paper. The most significant factor is usually considered to be the widespread use of aluminium sulphate (commonly known as alum) with rosin in sizing (Priest, 1987). The rate of hydrolytic degradation is determined by the total concentration of protons which catalyse the reaction, and the temperature (Smith, 1968). Acid hydrolysis of the cellulose molecule proceeds as a heterogeneous process with weaker acids and as a homogeneous process with strong acids (McGinnis and Shafizadeh, 1980), and rapidly at a pH of less than 5.6, until the chain length is reduced from about 5000 glucose units to about 500, at which point the paper becomes weak and brittle.

In the process of acid hydrolysis the initial attack is confined to the amorphous regions in cellulose (Browning, 1967), and the crystalinity index increases as hydrolysis proceeds (Fan, Gharpuray and Lee, 1987) owing to the removal of the amorphous portion (Davidson, 1943; Browning, 1967).

Cellulose, which is the major component of paper, forms oligosaccharides and ultimately forms D-glucose in the presence of acid during the process of hydrolysis (Browning, 1967). The β-1, 4-glucosidic bonds of a cellulose molecule are split by the addition of water molecules in an acid medium, and yield fragments of shorter chain lengths while preserving the basic structure (Wenzl, 1970; Fan, Gharpuray and Lee, 1987).

The mechanism of acid hydrolysis of cellulose involving protonation of glucosidic oxygen is widely accepted (Barker and Vail, 1967; Nevell and Upton, 1976; Sharples, 1971 and Szejtli, 1975) although there are different ideas about the involvement of the primary site in protonating either the cyclic oxygen (Bunton et al., 1955; Fan, Gharpuray and Lee, 1987) or the glucosidic oxygen (Bunton et al., 1955; Fan, Gharpuray and Lee, 1987; Nevell and Upton, 1976) or both types of oxygen (Bunton et al., 1955; Szejtli, 1975). A model of the mechanism of acid hydrolysis is given in Bunton et al. as in Figure 1.9. Paths A-1 and A-2 are unimolecular, and path B is bimolecular. The path A mechanism, i. e. protonating both oxygen atoms, according to Szejtli, and the path B mechanism, according to Nevell and Upton, for the acid hydrolysis of cellulose are given in Figures 1.10 and 1.11 respectively. This protonation is followed by the slow rate-determining scission of the glucosidic bond adjacent to C_1 (Bunton et al., 1955; Sharples, 1971). In the presence of excess water the reaction is first order, although in many cases the reaction was not studied in detail with the result that data can be fitted equally well to a zero-order plot (Sharples, 1971).

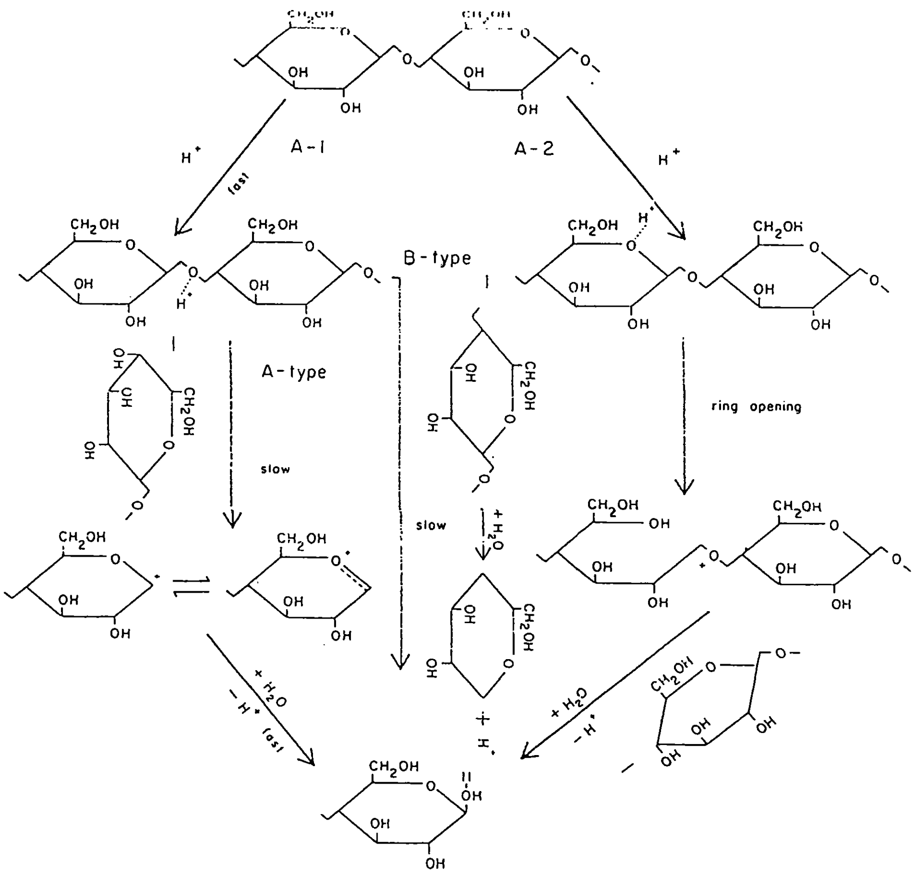


Figure 1.9: Mechanism of acid hydrolysis of cellulose; given by Bunton et al.

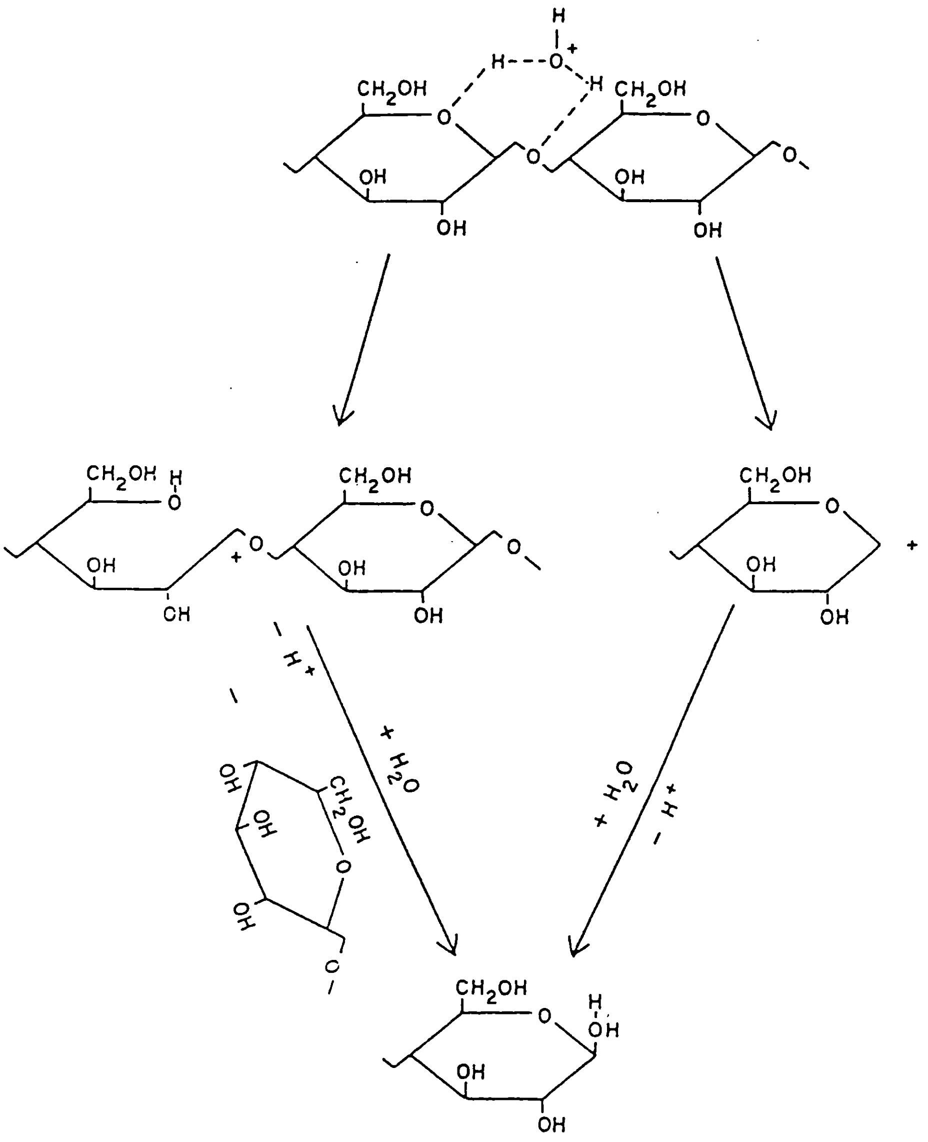


Figure 1.10: Mechanism of acid hydrolysis of cellulose; path A, according to Szejtli

In the initial stages of hydrolysis cellulose maintains its original fibrous form, and on its continuation, it decreases in physical strength until finally the fibre becomes brittle and is ultimately reduced to a powder (Browning, 1967).

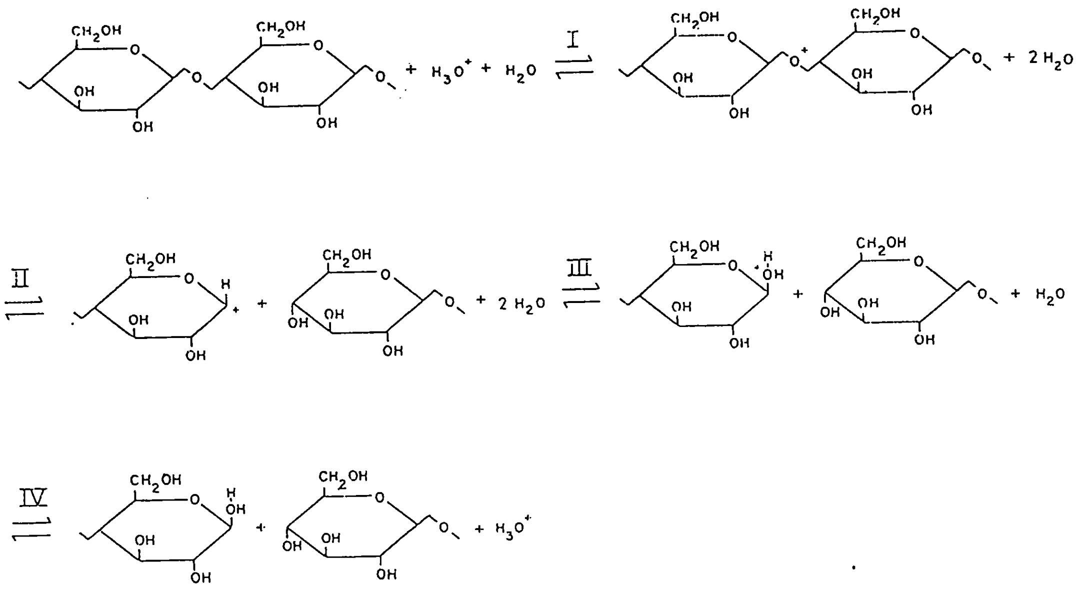


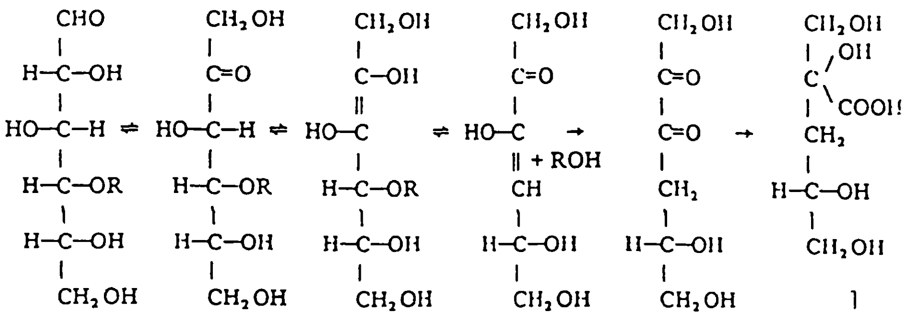
Figure 1.11: Mechanism of acid hydrolysis of cellulose; path B, according to Nevell and Upton

Wood cellulose is less resistant to continued hydrolysis than cotton cellulose (Immergut and Ranby, 1956). The discoloration of paper may also be influenced by the role of internally generated acids, i.e. carboxylic acids, in the process of acid hydrolysis (Butler et al., 1986).

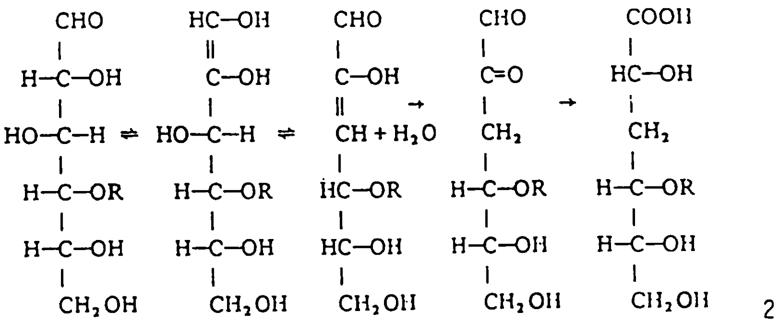
Due to atmospheric pollution, sulphur dioxide may become absorbed into paper and react with the free water in cellulose. The resulting sulphurous acid is oxidised by air under the catalytic influence of traces of iron and other impurities in the paper to form sulphuric acid which, being involatile, accumulates almost without limit (Seeley and Barker, 1979).

1.2.2.1.2 Alkaline hydrolysis

In the presence of a significant concentration of hydroxyl ions, i.e. in highly alkaline papers, degradation of cellulose occurs by random cleavage of glucosidic linkages and by stepwise elimination of monomer units from the reducing end (Gentile, Schroeder and Atalla, 1987; Meller, 1960 a ; Richards, 1971), in competition with another reaction which stabilizes cellulose against alkaline degradation by converting the reducing end group to an alkali-stable carboxylic acid group. The former is known as the peeling reaction, and the latter as the stopping reaction (Gentile, Schroeder and Atalla, 1987), which is denoted in Figure 1.12 according to McGinnis and Shafizadeh (1980).



Peeling reaction



Stopping reaction

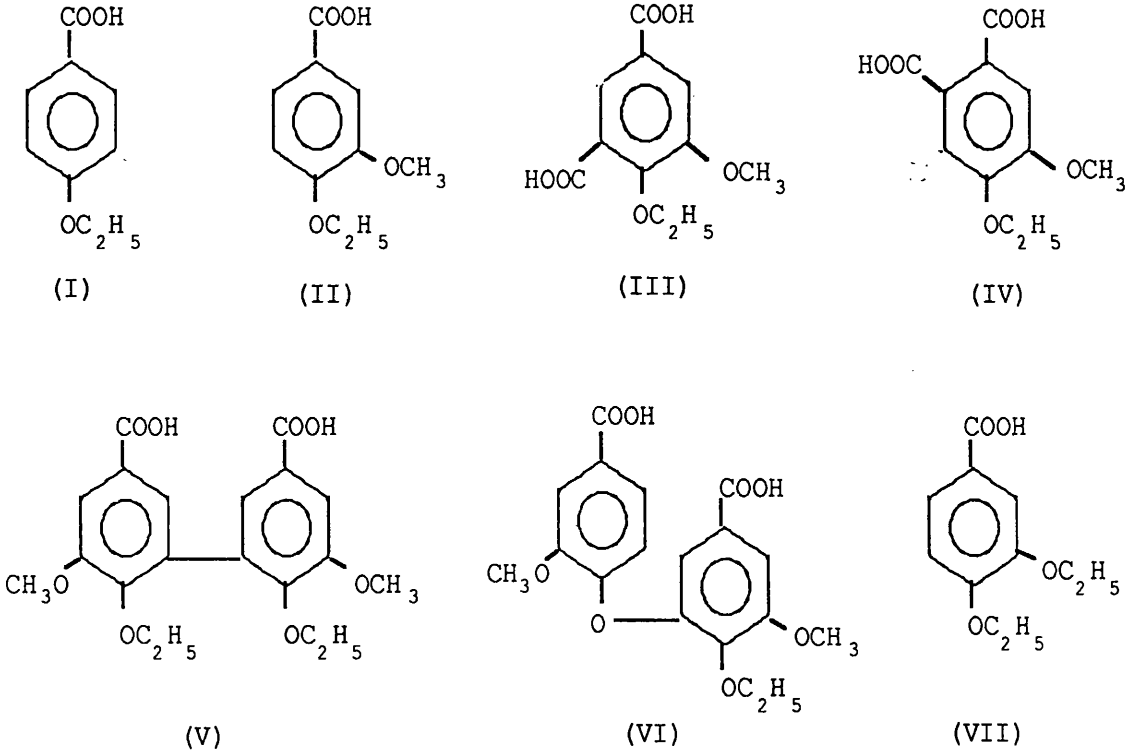
1 = isosaccharinic acid 2 = metasaccharinic acid end group R = cellulose

Figure 1.12: Non-destructive alkaline degradation reactions of cellulose

occurs, depending on the nature and location of the substituents on the phenyl ring (Wacek and Kesselring, 1962; Browning, 1967).

1.2.2.2 Oxidative degradation

Oxidative degradation takes place as a result of oxidation, and its effect is to decrease the content of aldehyde groups in the molecular chains of hydrocellulose, and increase the content of carboxyl groups (Achwal et al., 1959; Davidson and Nevell, 1957 and 1959; Meller, 1955; Fan, Gharpuray and Lee, 1987). Limited oxidation of cellulose occurs by the conversion of the alcoholic hydroxyl groups at the 2-, 3- and 6-positions of the anhydroglucose unit to carbonyl groups. A ketonic carbonyl groups can be formed at C_2, C_3 or both. The aldehyde (hemiacetal) group at C_1 of the terminal reducing group of the chain can be oxidized to a carboxylic acid group (Browning, 1967) as the hydroxyl groups and the terminal reducing ends are the most susceptible to attack in the process of oxidation (McGinnis and Shafizadeh, 1980).



I 4-ethoxy benzoic acid
II 3-methoxy 4-ethoxy benzoic acid
III 5-methoxy 6-ethoxy iso-phthalic acid
IV 4-methoxy 5 ethoxy phthalic acid
V 2, 2'-diethoxy 3, 3'-dimethoxy-biphenyl 5, 5'-dicarboxylic acid
VI 2, 3'-dimethoxy 2'-ethoxy-diphenyl-ether-4, 5'-dicarboxylic acid
VII 3, 4-diethoxy benzoic acid

Figure 1.13: Degradation products of lignin due to oxidation

Although oxidation is not such an acute problem as acid hydrolysis due to alum, it can be accelerated by the presence of minute quantities of certain metallic salts such as copper and iron which can be picked up by the paper from processing equipment (Priest, 1987). The significance of oxidation grows as the amount of non-cellulosic material present in the paper fiber increases (Smith, 1968). It is been observed that oxidation induces some changes in the structure of cellulose and these changes may influence its properties (Meller, 1953 and 1961; Fan, Gharpuray and Lee, 1987).

Certain paper fibre components such as lignin are particularly liable to oxidation and decompose, causing the paper to discolour. Tatsumi and Terashima (1985) suggested that the lignin macromolecule can be degraded to low molecular weight substances via the cleavage of the biphenyl linkage and the rupture of the aromatic ring by oxidation, and also oxidative deterioration of phenolic hydroxyl groups tends to increase the number of quinone carbonyl groups (Allan, 1971), which is suspected as the reason for colour change. According to Gellerstedt et al. (1986) the degradation products of lignin due to oxidation are given in Figure 1.13. Besides the discoloration of paper, loss of strength and embrittlement also takes place due to oxidation (Smith, 1968).

Zavyalov et.al. (1968) concluded that oxidative degradation of lignin is an auto-catalytic process. It is a type of chain reaction which involves free radicals, and at the initial stage the formation of peroxide groups occurrs. Structures of the β-diketone type form as a result of the decomposition of peroxide groups, and have a strong tendency to enolization. The enols are easily auto-oxidised to give cyclic peroxides, which in turn are decomposed with the rupture of the side chains.

1.2.2.3 Photochemical degradation

Photochemical degradation is not a serious cause of paper deterioration, but it does not take place in isolation, and the presence of oxygen and water vapour profoundly influence many photochemical reactions (Feller, 1964).

The exact mechanism of the photo-degradation of cellulose is difficult to ascertain, and most investigators have drawn some analogy with acid hydrolysis to assume a cleavage of the glucosidic bond (Baugh and Phillips, 1971). It was proposed that the major possibility of rupturing the glucose residues is in the vicinity of C_1, C_2, or C_3, rather than at the glucosidic linkage (Launer and Wilson, 1943 and 1949; Baugh and Phillips, 1971).

Light can affect components of paper such as glue, starch and casein (Feller, 1964 ; Hon, 1981). Whelan and Peat (1949) have discussed the degradation of starch. A few pigments, especially certain forms of titanium dioxide and zinc oxide, can hasten the photo-deterioration of paper (Feller, 1964). At low intensities, the process of photochemical degradation will be retarded, but will not be completely arrested. The short wavelengths of visible and ultraviolet (UV) radiation are the most energetic, and hence represent a greater photochemical hazard (Feller, 1964). When paper is exposed to UV radiation, ozone is formed in air and oxidizes the paper, increasing the oxidation state of the surface, and damaging the fibre wall seriously, while the damage is rather less when exposed to ordinary sunlight (Li, 1987).

The papers containing lignin rapidly discolour on exposure to light, and the discolouration is usually accompanied by embrittlement. Lin and Kringstad (1970 a) stated that photochemical reactions of lignin which produces chromophores consist of several steps, i.e. the primary process, absorption of light, and the secondary photochemical process which may include photochemical elimination, decomposition, polymerisation, substitution, molecular rearrangement, and chain reactions. Most of these involve free radical intermediates. They also suggested that α-carbonyl groups and conjugated carbon-carbon double bonds may play a major part in the photochemical yellowing of the lignin (Lin and Kingstad, 1970 a). According to Tschirner and Dence (1988) light induced formation of chromophores, i.e. quinonone moieties, are responsible for the discolouration of groundwood papers, and these are shown in Figure 1.14.

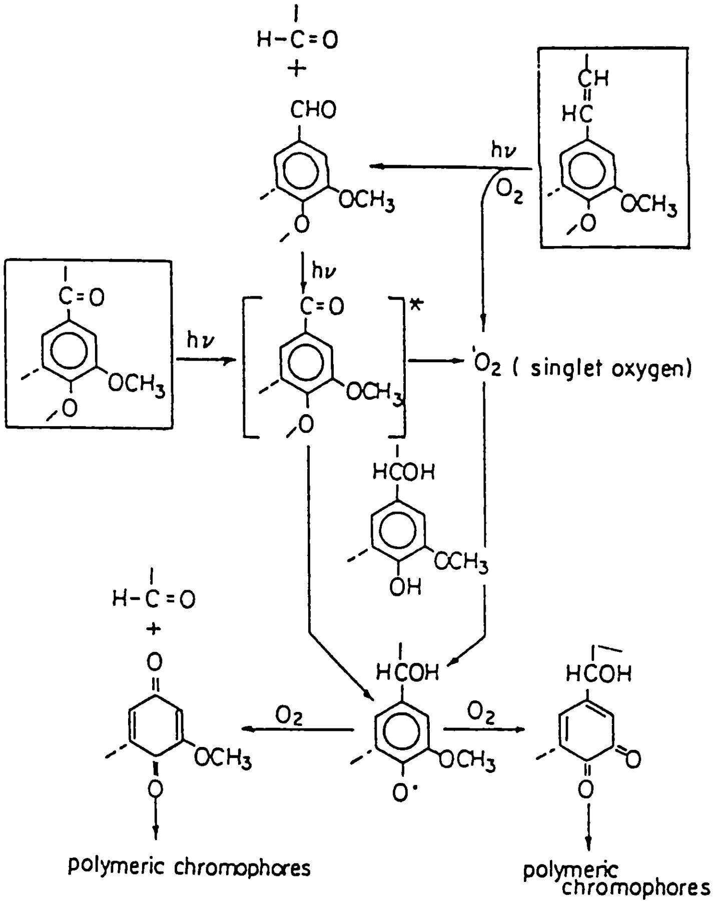


Figure 1.14: Light-induced formation of chromophores in lignin

With the ozonation of lignin, complete degradation of an aromatic nucleus occurs forming an aliphatic acid, which carries the original side-chain attached to the carboxylic group originating from the C_1 of the aromatic nucleus. The oxidative degradation of aromatic nuclei by ozone is shown in Figure 1.15

Since the newer high-yield hybrid pulping processes (e.g. the chemithermomechanical process) still retain substantial proportions of lignin which will rapidly discolour, they are likely to give continuing problems with colour change, although they may appear initially well bleached, white and bright (Priest, 1987).

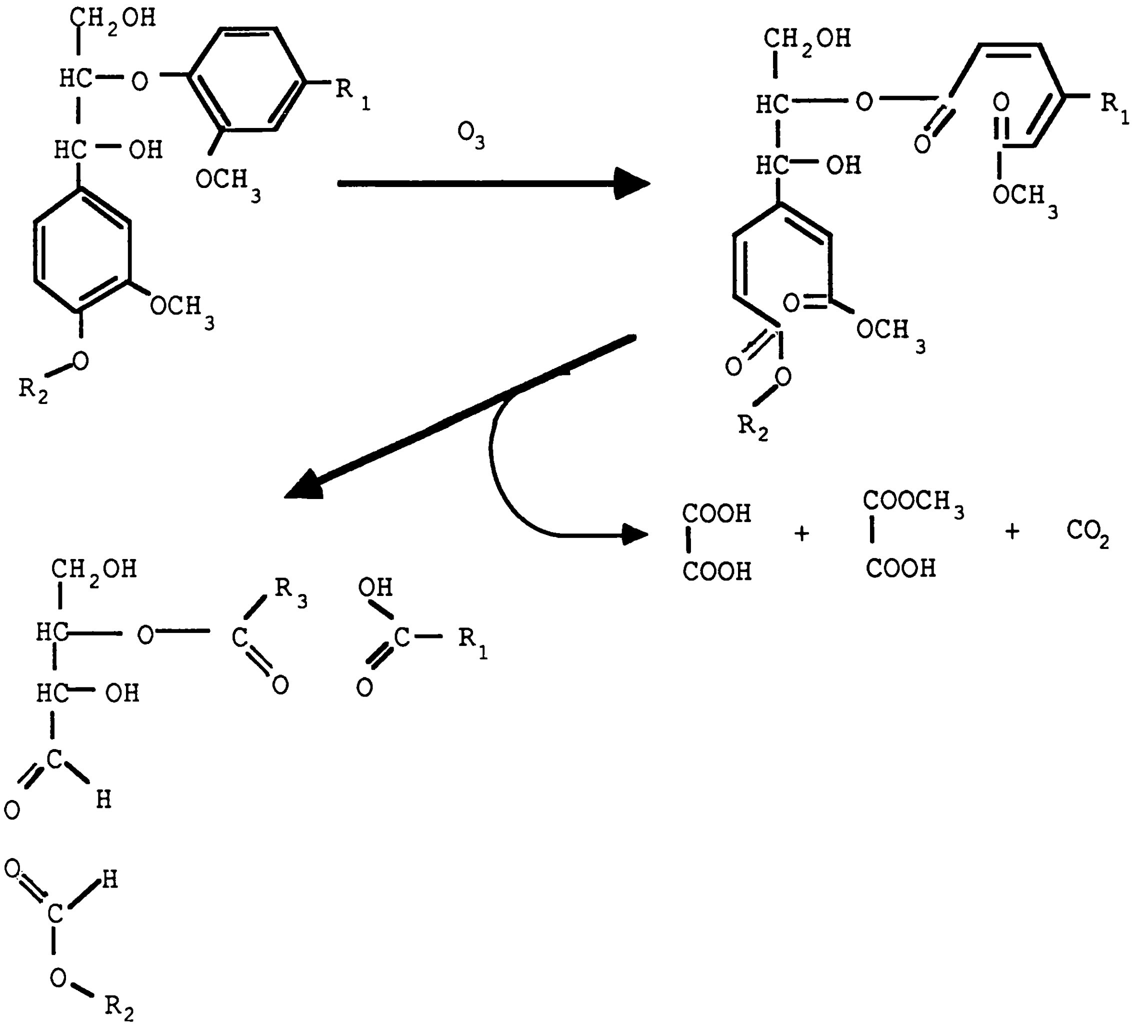


Figure 1.15: Oxidative degradation of lignin by ozone

1.2.3 Factors affecting chemical deterioration

Chemical deterioration occurs mainly due to raw materials, manufacturing processes and storage conditions which lead to the acidity, humidity, temperature and light.

1.2.3.1 Acidity

Acidity may be determined as the amount of water-soluble acid (or alkali) or as the hydrogen ion concentration (pH) of the paper extract (Brandon, 1981). Acidity results primarily from methods of manufacture of the paper, which introduce alum as a mordant in rosin sizing, from bleaching, and from acidic components in the atmosphere such as sulphur dioxide and nitrogen dioxide. Although alum itself does not contain hydrogen ions, when it is dissolved in water it releases hydrogen ions from the water as a result of hydrolysis and forms a series of basic aluminium sulphates; the free sulphuric acid formed as a result, makes the solution acidic (Browning, 1977, Priest 1987). If nitrogen dioxide is present it gives rise to some nitric acid, and it too adds to the hydrolytic degradation of paper. The role of nitrogen dioxide in the deterioration of paper has not been investigated as extensively as that of sulphur dioxide (Wessel, 1970).

1.2.3.2 Moisture

Moisture in paper is present in two states, absorbed and bound moisture, of which only the former component varies with atmospheric relative humidity. It is stated that in general the moisture content increases with the lignin content or as the paper quality falls, and extra lignin moisture is present in a relatively strongly-bound condition (Anderson, 1976).

The moisture content of paper and the RH of the air are not linearly related because of bound moisture (Anderson, 1976). Moisture affects the rigidity, the flexibility and the elasticity of paper (Brandon, 1981). The presence of excessive water content, i. e. high RH, can cause damage to paper materials due to hydrolysis. Fluctuations in water content can cause mechanical damage, while the mere presence of water can accelerate certain chemical changes.

1.2.3.3 Temperature

The effect of heat on paper varies greatly, depending upon the quality of the paper and the nature of the various constituents used as fillers. The influence of temperature on paper is of such importance that heating of paper is used as an accelerated aging test to predict its long term durability (Feller, 1964). Most chemical reactions increase in rate with an increase in temperature. However, the sensitivity of reaction-rates to temperature is not linear or the same for all reactions, but is an exponential function of both the temperature and the activation energy of the reaction (Erhardt, 1989). The reactions of cellulose tend to have high activation energies in the range of 25-30 kilo calories per mole, and such reactions increase in rate about four to five times for every 10°C rise in temperature (Erhardt, 1989).

Average annual storage temperature		Average annual storage relative humidity							
Fahrenheit	Centigrade	70%	60%	50%	40%	30%	20%	10%	0%
95°	35°	0.14	0.16	0.19	0.23	0.30	0.41	0.68	1.90
86°	30°	0.32	0.37	0.43	0.52	0.67	0.93	1.53	4.30
77°	25°	0.74	0.85	1.00	1.22	1.56	2.17	3.57	10.00
72.5°	22.5°	1.14	1.31	1.54	1.88	2.40	3.34	5.50	15.40
68°	20°	1.76	2.02	2.38	2.90	3.71	5.16	8.49	23.80
63.5°	17.5°	2.74	3.14	3.70	4.52	5.77	8.02	13.20	37.00
59°	15°	4.30	4.94	5.81	7.08	9.05	12.60	20.70	58.10
50°	10°	11.10	12.70	15.00	18.30	23.40	32.60	53.50	150.00

Table 1.2: Effect of storage temperature and relative humidity on paper permanence

The variation of paper permanence with the temperature is given in Table 1.2. This is a computer-based estimate of the probable life of book papers stored at different temperatures and relative humidities with respect to material stored at 25°C and 50% RH which is defined as having a life expectation of unity (Smith, 1970b).

1.2.3.4 Light

Light causes photochemical degradation, as the sunlight which contains UV rays can act as an initiator in chemical reactions, especially in the presence of oxygen (Feller 1964), and can induce effects on paper such as a bleaching action which causes some whitening of paper, and discolouration of lignin-containing papers.

Lignin-containing high yield pulps turn yellow when exposed to light. Lignin absorbs UV light strongly, and results in a radical reaction as described in section 1.2.2.3. According to Feller, light can also cause deterioration of size. Upon exposure to sunlight, rosin and starch sized papers have been found to be less sensitive to change in writing qualities than glue-sized papers (Feller, 1964) . It is reported that once exposed to light, paper may deteriorate at an accelerated rate when it is removed from the light and stored (Feller, 1964).

1.3 Stabilization of paper

In order to preserve paper from chemical degradation, stabilization may be carried out in two ways, by deacidification, and stabilization of lignin which had hardly been carried out previously.

1.3.1 Deacidification

Deacidification is a method of preserving paper, and more particularly a method of neutralizing the acidity of paper and buffering it to the alkaline side to improve its permanence. Deacidification cannot strengthen weak or embrittled paper, although an alkaline condition does restrict the activity of trace metals like copper and iron, and also it does not decrease the probability of biological attack. Deacidification does not prevent oxidative or photochemical attack, although the alkaline buffer neutralizes the acidic byproducts of these reactions. The application of a deacidification agent to the paper inhibits the chain breaking process causing deterioration, although it cannot rejoin the broken chain back together again (Sparks, 1982).

1.3.1.1 History

The first attempt at a deacidification treatment was undertaken by Sir Arthur Church in 1891, to stabilize early paper which had become acid. He used a solution of barium hydroxide in methanol to deacidify the backings of Raphael cartoons (Banik, 1988). In 1936 Schierholtz immersed paper in, or sprayed paper with, aqueous solutions of barium, calcium or strontium bicarbonates or hydroxides, and he recommended a carbon dioxide gas treatment to convert hydroxides to carbonates (Smith, 1970 a) and obtained a patent. Barrow (1942) originally used the calcium bicarbonate immersion method and during 1940's he developed his two stage process using calcium hydroxide and calcium bicarbonate. In 1957 Gear modified the single stage process using magnesium bicarbonate (Gear, 1965). In 1959 a saturated solution of calcium and magnesium bicarbonates was recommended for spray deacidification (Church, 1959).

The possibility of using deacidification agents other than calcium and magnesium salts were considered in the 1960s (Barrow, 1964). Russian workers expanded the list of choices to include pH-buffered solutions of borates and phosphates (Pravilova and Istrubsina, 1965, Smith, 1970 a). Baynes Cope, no doubt influenced by Church, proposed the use of about 1% solution of barium hydroxide in methanol for the non-aqueous deacidification of paper (Baynes Cope, 1969-70). The Regnal process for non-aqueous deacidification which was introduced before 1976 uses magnesium acetate dissolved or suspended in polyvinyl acetal in organic solvents (Kelly, 1976). Various attempts have been made to deacidify paper with ammonia or other volatile amines and have been proved unsuccessful for various reasons (Kathpalia, 1962, Langwell, 1969).

In 1966 Langwell introduced vapour phase deacidification using a volatile base salt, cyclohexylamine carbonate (CHC) (Langwell, 1966). Smith introduced magnesium methoxide in methanol or a low-boiling halogenated hydrocarbon solvent for non-aqueous deacidification of books (Smith, 1970 b) followed by ethylene oxide exposure in 1972 (Smith, 1972). In 1971 Kusterer and Hind described the impregnation of paper with hexamethylenetetramine, produced as a result of the reaction of ammonia and formaldehyde and formaldehyde in gaseous form (Kusterer and Hind, 1971). In 1973, Kusterer et al. disclosed a method of impregnating and neutralizing paper by exposing it to gaseous morpholine and in 1975 Williams et al. introduced a process using calcium chloride and ammonium carbonate. In 1976 Walker developed a process based on impregnation with a mixture of morpholine vapour and water vapour (Walker, 1977) and Kelly introduced methyl magnesium carbonate (magnesium methoxy carbonate) (Kelly, 1976). A diethyl zinc process was introduced in the same year by Williams and Kelly and developed by them through the early 1980s.

In Germany, a technique was developed using calcium bicarbonate, manufactured under pressure, in 1980 (Udowski, 1980). Rao and Kumar (1986) carried out aqueous deacidification using 1% sodium dehydroacetate (SDHA) and observed the improvement of strength of deacidified papers. Koppers deacidification process, which dispersed the alkaline particles of basic metal oxides, hydroxides or salt of the size 0.01 to 0.9 μ in a gas or liquid (hydrocarbons or freons) was tried out and then dropped. A U.S. patent was granted in 1985 and the U.K. patent application was published in 1986 (Kundrot, 1986). The Lithium Corporation of America developed the Lithco process which is effective in both deacidification and strengthening paper in bound books using long chain polyfunctional magnesium alkoxides in hydrocarbons and freons.

1.3.1.2 Deacidification processes

In a good deacidification process, the deacidification agent must be uniformly distributed throughout the entire sheet of paper, the pH of the paper must be raised to a level of between 7 and 8, the alkaline reserve in the paper should be 2-3% to neutralize any future acidic component acquired. The process must be time efficient and the treatment must be permanent and should neither impart odour nor have any toxic risk to people. It should have minimum side effects and be carried out at a reasonable cost (Sparks, 1982)

The three classes of technique used for deacidification and buffering paper are :

a immersion in one or more solutions of a suitable base or bases ;

b spraying with an aqueous or non-aqueous solution;

c vapour phase deacidification (Seeley, 1985).

1.3.1.2.1 Immersion methods

The immersion technique neutralizes the acid and, the neutralized product can be removed by washing. Aqueous or non-aqueous solutions can be used, provided that the inks are non labile. This method is only suitable for single-sheet treatments, and hence can be used for unbound or disbound material, and also, the process is expensive as the rate of treatment is slow and requires extensive drying facilities. Both of Barrow's processes, Williams' buffering and washing process, Kopper's process and the Lithco process belong to this group.

1.3.1.2.2 Spraying method

The spraying method can be used on bound material although it does not always completely deacidify the spine. It carries very little risk to labile inks and also has the advantage of the possibility of treating only a selected area if necessary.

Baynes Cope's barium hydroxide, magnesium methoxide and methoxy magnesium carbonate processes belong to this method as the chemical treatments are generally done by spraying the chemical to the paper though it also can be done by immersion. The spraying technique can be applied in Kopper's process and the Lithco process as well. At present magnesium methoxide treatment is widely used although the magnesium methoxide leads to gelling, clogging of spray jets and the deposition of a white film of magnesium hydroxide on the surface of the paper due to extreme sensitivity towards water. It could also impart adverse effects on certain inks and dye stuffs (Kelly, 1976). In this process magnesium methoxide is converted into magnesium hydroxide and methyl alcohol by moisture in the paper and atmosphere. With atmospheric carbon dioxide, magnesium hydroxide becomes magnesium carbonate (Kelly, 1976). Methoxy magnesium carbonate is also a non-aqueous process which appears excellent as it neutralizes the paper and buffers it with magnesium carbonate while also being non-sensitive towards moisture.

1.3.1.2.3 Vapour phase method

In general, bound materials can be safely treated provided no part is adversely affected by vapour phase deacidification.

Langwell's vapour phase process, morpholine process, Information Conservation, Inc. process, Kathpalia's ammonia process and diethyl zinc process belong to vapour phase deacidification. Out of these, Langwell's vapour-phase and Kathpalia's ammonia processes are unable to provide successful buffering action due to escape of the volatile base, and they also have side effects such as producing unpleasant or toxic volatiles into the atmosphere and causing stains due to the oxidation of amines (Williams and Kelly, 1976). These processes might lead to give high pH which might harm certain alkali matters and cellulose (Smith, 1970 a).

Langwell's treatment appeared to destroy the effect of rosin sizing and decrease the brightness of papers treated (Dupuis, Kusterer and Sproull, 1969-70). The morpholine process, which belongs to this category is a mass process, which shows an indication of fumigation (Walker, 1977) in addition to deacidification. Morpholine is toxic and it was found to be unsatisfactory, as it makes newsprint yellow and gives weak pH and negligible alkaline reserve (Klinger, 1983).

Although the diethyl zinc process also belongs to vapour phase, it does not possess the above drawbacks. The mechanism of the diethyl zinc process is not very well known, as at the begining it was stated that when a paper was treated with diethyl zinc, it reacts with residual moisture in the paper and hydroxyl groups on cellulose, and deposits zinc hydroxide, and reacts with aldehydes and forms stable alcohols (Williams and Kelly, 1976). At present it is being illustrated as follows. When diethyl zinc reacts with hydroxyl groups such as those in cellulose, it forms an ethylene-oxycellulose group, C_2H_5ZnO-R which hydrolyses to form ethane, zinc oxide and cellulose hydroxy group when exposed to air. It was hoped that hydrolysis in the presence of carbon dioxide would cause the zinc to form carbonate directly rather than oxide (Kelly and Williams, 1981). On the other hand it is stated that when a material is treated with diethyl zinc, it neutralizes free acid and slowly reacts with the hydroxyl groups of cellulose and hydrolysis the ethyl zinc substituent of the cellulose to give zinc hydroxide, ethyl alcohol and unsubstituted cellulose. Thus ultimately the zinc hydroxide will probably be converted into basic zinc carbonate which acts as a buffer. Papers and books treated with diethyl zinc show a promising aspect (Cunha, 1986). The disadvantages of this method are that, the solution must be handled carefully, and personnel have to use protective clothing and equipment as diethyl zinc is extremely flammable and might cause very serious skin burns and specially irritate the lungs and eyes by vapours and smoke (Williams and Kelly, 1976). Whitmore and Bogaard (1989) stated that high-quality cellulose papers containing (non-alkaline) zinc salts degraded more rapidly than an untreated, high quality control sheet, in accelerated oven aging.

Kathpalia's ammonia process has been discontinued as ammonia being volatile, loses the alkalinity obtained due to the treatment, with time and because of the absence of alkaline reserve on treated paper.

1.3.2 Stabilization of lignin

Launer and Wilson (1943) observed an increase in the light stability of lignin, when newsprint was treated with sodium bicarbonate solution. The phenolic groups in lignin molecules are associated closely with its oxidation to coloured quinonoid products (Luner, 1960; Hon, 1981). Hence, the possibility of blocking the phenolic hydroxyl groups of lignin by etherification or esterification, which might lead to protection against photochemical discoloration, was suggested by Andrews and Des Rosiers (1966), and Leary (1968).

Lyall has tried out some chemical methods for stabilizing lignin in groundwood papers, and pointed out that although potassium borohydride reduced the colour in aged papers it was not permanent, and the stability of colour was greatly improved on acetylation using acetic anhydride after bleaching the paper with hydrogen peroxide (Lyall, 1982).

Tschirner and Dence (1988) attempted to photostabilize lignin in thermomechanical pulp (TMP) by chemical modifications such as the removal of carbonyl groups with reducing agents, ie. sodium borohydride, sodium dithionite, thiourea dioxide and diborane, separately and in combination, and alkylation of pre-reduced TMP with diazomethane or propylene oxide. The latter was able to block the phenolic groups and had a very favourable impact on photostability (Tschirner and Dence, 1988). Manchester et al. found out that methylation using diazomethane did not photostabilize groundwood (Manchester et al., 1960), but according to Gierer and Lin (1972) it could partially photostabilize lignin.

Singh (1970) used alkylating agents with a view to blocking phenolic hydroxylgroups in groundwood and found out that propylene oxide, butylene oxide, dimethyl sulphate, benzoyl chloride, and methyl chlorocarbonate were partially or totally effective in photostabilizing pulp (Tschirner and Dence, 1988). Tschirner and Dence (1988) stated that their observed trends suggest that the removal of carboxyl groups varied in number and type with different reducing agents.

It should be pointed out that the work reported above relate to pulps, and that the majority of these reactions require conditions which could not be applied to paper in its final form.

1.3.3 Other

Stabilizing effects of chelates, such as oxyethylenediphosphonic (OEDP) and diethylenetriamine pentaacetic acid (DTPA) and calcium chealate compounds on paper was evaluated (Blank and Dobrusina, 1984).

A reduction treatment using sodium borohydride solution was further investigated and a patent was awarded for the stabilization of paper. Although this treatment is most effective in retarding the aging of paper, it cannot yet be applied as a conservation treatment (Tang and Kelly, 1983).

It was found out that polyethylene glycols having a molecular weight higher than 1000 in the amount of 20 gm^{-2} of paper, prevent discolouration to some extent (Minemura and Umehara, 1986) and newspapers coated with an ultraviolet curable resin and dried for 15 minutes at 60°C are resistant to yellowing (Sato and Sato, 1984).

1.4 Consolidation of paper

To strengthen paper, consolidation by means of lamination, impregnation, rapid cure radiation and graft copolymerisation can be applied (Burstall et al; 1984 and 1986; Davis et al., 1981) and further research is being carried out at present, mainly on graft copolymerisation, in Britain.

1.4.1 Lamination

Lamination which was considered as the state of the art process in the conservation field from the 1940s through the 1960s (Roger, 1987), is a technique in which a sheet of treatment material is applied to each side of a sheet of paper by means of heat and pressure or an adhesive, which enables the handling of fragile documents freely without any accidental damage.

1.4.1.1 History

The earliest examples of lamination are the ones of very fine silk attached to either side of a sheet of paper using an adhesive such as animal glue. All later lamination techniques work on a similar principle, by which a sheet of material is attached to one or both surfaces of deteriorated paper in order to strengthen it.

Lamination in the modern sense was first started in the mid 1930s in the U.S.A, using only cellulose acetate film (Hummel and Barrow, 1955-56), and in the late 1930s cellulose acetate film containing thermoplastic and pressure sensitive adhesives was developed (Hummel and Barrow, 1955-56). Later, following deacidification, lamination with cellulose acetate film and tissue giving a five-layer sandwich was introduced and it is known as the Barrow method of lamination (Hummel and Barrow, 1955-56). Kathpalia in India introduced solvent lamination with cellulose acetate film and acetone (Kathpalia, 1958).

A dry-mounting process which uses a plastic film or sheet of thin tissue paper coated with a pressure-sensitive adhesive (PVC), in addition to Lamatec, Crompton tissue and Postlip Duplex tissue, developed by W.H. Langwell, were introduced for the lamination

(Langwell, 1964). After the World War II, cellulose acetate, polyester and polyacrylate foils were used for lamination in the Federal Republic of Germany . Polythene was used for lamination in Hungary from 1958 and in Germany since 1968 (Feindt, 1982-83).

From the late 1960s, foils without adhesives, especially polyethylene and polyethylene coated, were used in Germany (Feindt, 1982-83). In 1973 Regnal patented the lamination method using polyvinyl acetal (Hanzlova, 1988). Lal (1975) initiated a process of lamination using polythene with a rotating drum type lamination machine in India. In Germany, polyester sieve, Japanese tissue and polyethylene foil were used for lamination from 1976 (Feindt, 1982-83). In Prague, a new and efficacious mixture based on acrylic water disperson of methyl hydroethyl cellulose with an admixture of sodium hydroxide as buffer, was introduced as a cold lamination process (Hanzlova, 1988).

1.4.1.2 Lamination processes

As a measure of stabilizing paper, i.e. to protect the document, to add strength as well as to provide resistance to tears, creases, folds, soil and liquids (Rieke, 1985), lamination is being carried out in different ways and mainly these processes can be categorized into heat lamination and cold lamination. There are two methods of heat lamination, heat-sealing and dry mounting, the first of which uses a high temperature.

Lamination has several disadvantages besides being practically irreversible. In the case of heat lamination, the exposure to high temperature facilitates deterioration of the material and may even cause distortion. Laminating materials deteriorate, and become brittle. In some cases the machinery is very expensive. The paper and the tissue used for lamination can expand and contract in different degrees with climatic changes, and this could lead to cockling of the document (Wettasinghe, 1989).

1.4.1.2.1 Heat lamination

1.4.1.2.1.1 Heat sealing method

Lamination with cellulose acetate film and tissue both, can be categorized into this group. The application of cellulose acetate film, to a sheet of paper did not increase its resistance to tearing. Hence a high quality tissue was chosen as a material with good tear resistance which could be incorporated in the laminate to give it added strength (Hummel and Barrow, 1955-56). A five layer sandwich was made by placing the sheets paper between two sheets of cellulose acetate, and then placing the three layer sandwich so formed, between the two sheets of alpha-cellulose tissue. This was then passed through a special heated press. Unless the document has been deacidified and buffered, the high temperature to which it is subjected enhances deterioration. After the treatment a thicker sheet is produced, which no longer resembles the original material. Delamination, without damage of the treated paper is possible, but it leaves behind traces of adhesive, and for this reason the process has been criticised (M. Woods, pers. comm.).

The use of other kinds of laminating film, such as polyvinyl chloride (PVC) and polyethylene have not been very successful as PVC seems to be unstable and could form hydrochloric acid in paper, while polyethylene laminates are not easily reversible (Turner, 1980). Although the polyethylene laminates are softer and more elastic than those laminated with cellulose acetate, polyethylene being a polyolefin, is liable to oxidative degradation, due to elevated temperature or UV light (Dadic and Ribkin, 1969-70). According to Lal (1975) lamination with polythene has the added advantage of being lower in density, non-combustible and economical when compared with cellulose acetate.

1.4.1.2.1.2 Dry mounting

Dry mounting is a process by which a plastic film or sheet of thin tissue paper coated with a pressure sensitive adhesive is attached to the sheet of paper using moderate pressure at a relatively low temperature (Turner, 1980). Three most widely available commercial films are Lamatec, Crompton tissue and Postlip Duplex tissue and out of these Crompton tissue appears to be the most satisfactory as it can be easily applied and is readily reversible in methanol (Turner, 1980). Lamatec strengthens books printed on mechanical paper (Turner, 1980) and it appears to be suitable for routine archival material (Shaw, 1982). Although it was claimed originally that the paper so treated could be delaminated by steeping in cold water for 5 minutes, experience has shown that it is very hard to reverse fully, especially from soft paper (the tissue is removed, but not the PVA adhesive) (Turner, 1980). The Postlip Duplex Lamination Process is similar to Lamatec, except that the PVA adhesive is impregnated with an acid neutralising salt, such as magnesium acetate (Turner, 1980). Although this process claims to strengthen and deacidify the paper, it has been shown that magnesium acetate is harmful to paper (Turner, 1980).

1.4.1.2.2 Cold lamination

The modification of the heat sealing process which includes impregnating a mixture based on acrylic water disperson of methyl hydroyethyl cellulose with an admixture of sodium hydroxide buffer (Hanzlova, 1988) and preparation of a five layer sandwich, by dissolving cellulose acetate using acetone (Turner, 1980) are known as solvent lamination and belong to this category.

In the impregnating process, the mixture makes it possible for the damaged leaf to be reinforced with strong, thin, and translucent paper (preferably Japanese) and the laminated leaf exhibits elasticity and does not manifest any undesired gloss or yellow tint (Hanzlova, 1988). The missing parts of a damaged leaf can be replaced at the same time and the method is relatively simple, and less time consuming (Hanzlova, 1988). This method does not use any toxic solvents (Hanzlova, 1988).

Solvent lamination, dispenses with both the elaborate equipment and the high temperatures of the heat sealing method, although great skill is needed to ensure a perfect bond. There are disadvantages as the acetone must be handled with great care as its fumes are harmful and also some inks are soluble in acetone and the process is very slow (Turner, 1980).

1.4.2 Monomer treatments

Porous materials other than paper are commonly consolidated by impregnating with a solution of an appropriate polymer in an organic solvent. On evaporation of the solvent, the polymer remains in the material and consolidates it by means of adhesive action. Such a method cannot be used for paper, because adjacent sheets would self adhere, leading to blocking, and the inability to open a volume so treated. The alternative approach is through the use of monomers, which may be absorbed into the paper fibres and polymerized in situ by chemical or physical curing methods. If in the process the polymer becomes chemically bonded to the paper substrate, the process is known as graft copolymerisation.

1.4.2.1 History

In 1978, Garnett and Major commmenced a project on the application of radiation polymerisation techniques to the restoration of library materials (Garnett, 1981) using rapid curing and grafting techniques, but no serious follow up of the approach appears to have been made (Burstall, Mollett and Butler, 1984).

The Parylene process, a pre-existing method licensed by Union Carbide, is being developed by Nova Tran, Inc. in Wisconsin and is under investigation, for the strengthening of brittle books. This process enables 4-6% deposition of the polymer (Bruce, 1986).

During the past 36 years, modification of cellulosic substrates by graft copolymerisation has been studied extensively (Arthur, 1970; Burstall et al., 1984). In the aspect of preservation purpose, graft copolymerisation experiment has been carried out (Davis et al , 1981) by the begining of 1981 (Davis et al). The work along graft copolymerisation began in 1981 and by 1984, the British Library carried out graft copolymerisation experiments with new and aged papers on a laboratory scale with encouraging results (Burstall et al., 1986). Hon (1982) carried out some experiments and reported that graft copolymerisation of methyl methacrylate onto papers seemed to be able to maintain their strength, even after 16 months of natural ageing.

1.4.2.2 Situ formation

An insitu can be formed as a result of the exposure of the material to oligomer or monomer with a sentisizer alone,as well as with the use of rapid cure technique, in addition to solution. Situ formation due to homopolymerisation of a monomer, resulting in a film possesing flexibility, water permeability and acid and alkaline resistance (Garnett and Major, 1982) could be used for restoration purposes, although Garnett and Major make no specific mention of strengthening properties. Archival materials which are cellulosic in nature are amenable to treatment by rapid cure technique, which needs very short time (Garnett and Major, nd)

1.4.2.3 Graft copolymerisation

Graft polymerisation is a method of bonding supple new plastic-like molecules to the brittle cellulose fibres that make up a sheet of paper (Strange, 1988). Copolymerisation of monomers is a convenient and useful one step method for modifying the properties of polymers such as cellulose. It is particularly attractive for improving the properties of wet and dry strength and brittleness (Davis et al., 1981).

The grafting process can be initiated by chemical means or by radiation but the latter is more convenient. According to the degree of penetration, of the mode of initiation should be selected (Burstall et al., 1984 and 1986) and it is stated that UV light is adequate for grafting to the surface of cellulose, while gamma rays are needed for internal grafting (Burstall et al., 1984). The mechanism of graft copolymerisation is a free radical mechanism (Garnett, 1986).

Graft copolymerisation offers a way by which old and new material, may be deacidified, strengthened and made proof-resistant to further attack in a single treatment (Burstall et al, 1986).

1.4.2.3.1 Process

In the graft copolymerisation process, developed for the British Library by the University of Surrey, paper can be treated as received, apart from the removal of oxygen by flushing nitrogen (Burstall et al., 1984). Promising results were obtained by the use of a mixture of ethyl acrylate (EA) and methyl methacrylate (MMA) in the ratio of 5:1. as a pure liquid or as a vapour, using 0.4 M rad (Burstall et.al., 1984 and1986). It is stated that an amine substituted alkyl methacrylate such as dimethylaminoethyl methacrylate can be added into the mixture for neutralizing acids and preventing future acid attacks in the paper. It could be readily grafted to both chemical and mechanical papers under usual conditions and treated sheets have maintained their fold endurance (Burstall et al., 1986).

The presence of basic residue in the polymer had no adverse effect (Burstall et al., 1986). At the dose level used, radiation damage to the cellulose was negligible (Burstall et al., 1984 and 1986). At the dose of 8 kGy, although the decrease in folding endurance was insignificant, it was very rapid after accelerated ageing (Hanus, 1985).

The strength gain obtained, generally rose with the amount of polymers incorporated and 15 to 20% polymer level is accepted as a reasonable value (Burstall et al., 1986).

The tensile strength, fold endurance and acid resistance of chemical paper may be considerably enhanced by reaction with acrylic monomers (Schwab et al., 1962). However lignin containing papers react much less readily (Kobayashi et al., 1971) while oxygen has a strongly retarding effect (Burstall et al., 1984).

The thickness of paper is not affected and the appearance of the paper is not altered appreciably although a slight discolouration was observed (Burstall et al., 1984 and 1986). Plastic covers are occasionally softened. The ink migration was negligible (Burstall et al, 1984 and 1986).

1.4.3 Impregnation technique

The Vienna process which belongs to the impregnation technique category was developed specially for newspapers. In this process, the newspaper blocks were kept in a vacuum machine to create a vacuum, so that the air was substantially withdrawn from the fibre intersites and then the text blocks were flooded with the strengthening solution, an aqueous mixture of celluloses and polyvinyl acetate and magnesium carbonate (as a neutralising agent), for about two hours. After pressing out the solution, the blocks were subjected to freeze drying for a month (Wachter, 1987).

Although this process strengthens, neutralises and buffers the paper at the same time and is economical (Wachter, 1987), the swelling of the material during the process might cause harm in the long run and might not be easy to reverse, after some time.

1.5. Analytical techniques

Number of physical tests such as tensile strength, bursting strength and folding endurance and chemical tests such as pH, copper number, viscosity are commonly used for evaluating the paper and the deterioration of paper. The above mentioned physical testing needs quite a big sample which gets spoiled, while the testing proceedure takes place. pH can vary according to the testing method and can be destructive except in surface measurement. To get the copper number one has to disintegrate the paper in a grinder and this method, in evaluation, cannot apply meaningfully, to papers containing unbleached pulps and groundwood (Browning, 1977). Although the viscosity method is useful, the application of it, for papers containing groundwood is inadvisable and difficulties may be experienced in dissolving unbleached pulps (Browning, 1977). It can also produce erratic and sometimes contradictory results when applied to book papers (Seeley and Wettasinghe, 1988).

Infrared spectroscopy is very commonly used for the chemical identification of solids

(Sharp, 1983). The infrared (IR) spectrum of paper, provides a distinctive and permanent record which constitutes a "finger print" based on the components present (Wise and Smith, 1967). Although IR spectra are often difficult to interpret owing to the complex composition of paper, they may aid in establishing the identity of two specimens and tracing the source of a single specimen (Wise and Smith, 1967).

Most of the existing test methods are destructive as mentioned above. Even to obtain diffuse reflectance IR, except FTIR, one has to grind the sample in most of the cases, which prevents determining the moisture content and crystalinity of the cellulose. FTIR technique has proved to be a useful, non-destructive method (Wise and Smith, 1967; Hon, 1986), for the identification of acidic impurities (Hon, 1986), crystallinity, moisture content and chemical characteristics of cellulose, using a very small sample of paper. Hon (1986) mentioned that FTIR technique proved to be satisfactory in analysing paper and it is a promising field of research in paper studies.

Methods such as Differential thermal analysis (DTA), proved to be useful for the evaluation of historical paper. Differences found in the thermal behaviour, e.g., shape and position of the DTA peaks in function of temperature could be assigned to changes in the composition of paper (Wiedemann, 1985). Although DTA does provide information regarding energy transformation or enthalpy of a reaction, Differential scanning calorimetry (DSC) provides the same information more directly (Chatterjee and Schwenker, 1972). DSC could be valuable, particularly for lignin analysis and its suitability for wood analysis, especially for the determination of lignin modification and degradation has been investigated (Reh, Kraepelin and Lamprecht, 1987).

In the assesment of the state of deterioration of book papers, several alternative methods were explored, and Fourier transform infrared (FTIR) and differential thermal analysis were selected as being most promising (Seeley and Wettasinghe, 1988).

1.5.1 Fourier transform infrared spectrometry

FTIR is the technique, obtained as a result of minimizing energy limitations by using interferometers of the Michelson type rather than the conventional prism and grating instruments (Hon, 1986). FTIR spectrometers combine an interferometer with a sensitive detector and a digital processer. By passing light from an infrared source first through the interferometer and then through the sample a characteristic interferogram is obtained which can be stored in digital form. The desired infrared spectrum is obtained by Fourier transformation of the digital data in the on-line computer (Bruker, nd).

The interferometer has two plane mirrors placed perpendicular to each other. One is fixed (F) and the other one (M) moves in the direction which is perpendicular to its plane (Figure 1.16). A beamspitter (B) which is semi-transparent, is located between the mirrors and this reflects a portion of light to the moveable mirror. The moving mirror causes varying path differences which introduce an interference between the beams when they are combined. The beams return to the beam splitter where they recombine and again are partly transmitted to the detector (D) and partly reflected to the source (S). For a single frequency and constant mirror velocity, the signal is a sine wave with the maxima occuring when the beams are in phase and the minima when they are at 180° out of phase. The beam directed to the detector is passed through the sample where portions of the radiation are absorbed, hence the intensities are changed. The spectral information obtained from FTIR spectrometry is measured from the change in intensity of the beam directed to the detector. This variation is measured as a function of the path difference (Griffiths and de Haseth, 1986; Shearer, 1990).

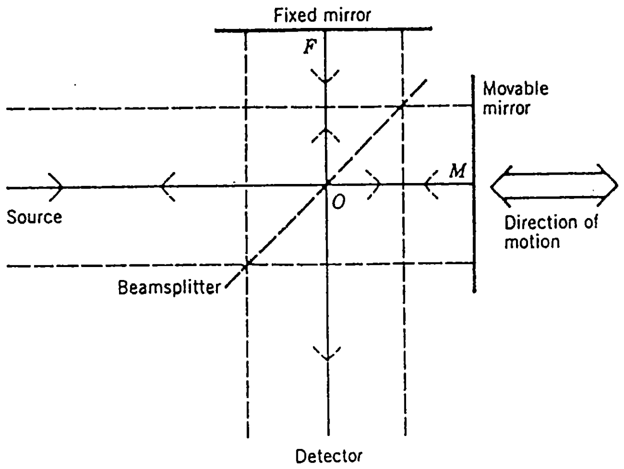


Figure 1.16: Schematic representation of a Michelson interferometer

By 1975, FTIR spectrometry had become the accepted technique for measuring high quality spectra (Griffiths and de Haseth, 1986). It is both efficient and rapid in collecting the data (Banwell, 1983; Hon, 1986) and also less susceptible to stray radiation (Hon, 1986). Fourier transform spectroscopy, provides simultaneous and almost instantaneous recording of the whole spectrum in the infrared regions (Banwell, 1983). FTIR can improve signal-to-noise ratio by performing many scans easily and can obtain good difference spectra, by digital substraction, as a computer is necessary (Hon, 1986) for the measurements.

To obtain a FTIR spectra, the sample can be used as it is and only a small amount of it is needed, while many other IR techniques need sample preparation, in obtaining spectra.

In contrast to dispersive instruments, the scanning interferometer effectively modulates each infrared wavelength to reach the detector during the entire measurement period. The spectra are obtained via a frequency analysis (Fourier transform) of the recorded signal. This multiplexing of the infrared signals results in a significant signal-to-noise enhancement. The electronics detect and amplify the signal, digitally encode it, and transmit it to the dedicated mini-computer. There the interferogram is Fourier analyzed into a recognizable infrared spectrum (Painter, Coleman and Koenig, 1982).

1.5.1.1 Diffuse reflectance

Diffuse reflectance is an easy way to measure infrared spectra of solids and obtain high quality results (Shearer, 1990). Diffuse reflectance can be described as light reflected from a matt surface. In this case, the radiation passes into the bulk of the material, undergoes reflection, refraction, scattering and absorption in varying degrees before re-emerging at the sample surface. The light reflected in this manner is distributed in all directions of the surrounding hemisphere (Griffiths and Fuller, 1982).

Griffiths and Fuller (1982) showed that diffuse reflectance spectrometry should be superior for microsampling than conventional transmission techniques.

Diffuse reflectance measurements in the infrared were possible only after the development of FT-IR spectrometers commercially in 1979 (Griffiths and Fuller, 1982).

5.1.1.2 Theory

Frie and MacNeil have described in detail the parallel relationship to Beer's law for transmission and the Kubelka-Munk theory for reflectance from solids and showed reasonable relationships for the concentration of various components in a mixture whereby one can determine quantitative information from diffuse reflectance of materials (Willey, 1976).

In practice, Kubelka and Munk theory may be written in the form,

$$f(R) = \frac{(1-R)^2}{2R} = \frac{k}{S} \qquad \text{———————} \quad 1.2$$

where R is the ratio of the diffuse reflectance of the sample at infinite depth (i.e. at a depth beyond which the signal does not change) to that of a selected standard, k is an absorption constant, and S a scattering constant (Chalmers and Mackenzie, 1985).

1.5.1.3 History of FTIR in paper analysis

Although IR spectroscopy has been used in the analysis of paper from 1967 (Wise and Smith, 1967), the use of FTIR spectroscopy for paper analysis was started only in 1986 (Hon, 1986). The experimental work carried out in the study of paper documents using FTIR has been described by Hon (1986).

1.5.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) which was developed by Clarebrough et al. (1952), is a technique whereby the energy transformation during a reaction can be directly determined from the recorded measurements. The temperature differences between the sample and reference are measured as functions of time and/or temperature in DTA, whereas in DSC, the differences in energy required to maintain the same temperature in both the sample and the reference are measured in millicalories per second. The recorded tracing of DSC has the same appearence as that of the DTA, except the ordinate, which reads the heat flow in millicalories or calories per second instead of δT. Thus the area of peak represents the enthalpy of transformation (Chatterjee and Schwenker, 1972).

The DSC method has several advantages such as the possibility of obtaining reproducible thermograms without any pretreatment of the sample except mechanical disintegration, and the use of a small quantity of the sample (Reh, Kraepelin and Lamprecht, 1987). It also has been recognised that by using the technique, it is possible to obtain accurate thermodynamic data for both chemical reactions and physical processes such as transitions undergone in solid state, with an understanding of the possible sources of errors (McNaughton and Mortimer, 1975).

1.5.2.1 Theory

In DSC, the sample and the reference are each provided with individual heaters and this enables to use the null-balance principle (McNaughton and Mortimer, 1975).

The slope of the leading edge of a melting endotherm of a pure sample is given by $(1/R_0)(dTp/dt)$, where (dTp/dt) is the programmed scanning rate and Ro is the resistance between pan and holder.

Although the peak shape can be affected by the change in R_0 the peak area does not get affected by it (McNaughton and Mortimer, 1975).

Chapter 2

EXPERIMENTAL TECHNIQUES

2.1 Introduction

Paper samples from the 18th century to date both chemically treated and untreated were analysed, mainly using Fourier transform infrared (FTIR) spectroscopy, and occasionally differential scanning calorimetry (DSC), as a means of understanding the composition, changes on ageing, and changes occurring due to chemical treatment.

DSC was used to investigate the chemical changes which occurred, if any, due to the treatments undertaken with a view to the stabilization of groundwood papers, as this can alter the positions, shapes and areas of exotherms and endotherms.

Mechanical testing was carried out to assess the mechanical strength of the samples for the purpose of evaluating the treatments in strengthening paper.

2.2 Sample preparation

Samples of size 10x10 cm were taken from books and newspapers (List of samples in Appendix 1) and kept in a desiccator conditioned to 40-45% RH at room temperature, i.e. 18-22°C. Depending on the treatment, smaller samples of varying size were taken from the conditioned sample. Whatman No.1 filter paper was always taken as the standard reference sample, as it consisted of high α-cotton cellulose and only about 0.25% lignin.

2.3 Artificial ageing

Paper was artificially aged to simulate its condition after many years under ambient conditions, as it would take many years to check the outcome of a treatment and the condition of the treated material in a real situation.

Artificial ageing was carried out by exposing paper samples in the fadeometer, to daylight, to ozone and to oven ageing. To check the effect on ageing with time, samples were artificially aged for different time periods varying from two days to three months.

2.3.1 Exposure in fadeometer

Equipment used Fadeometer fitted with medium pressure mercury discharge lamp.

Procedure

Paper samples (7.5 x 2.5 cm) were attached to glass slides with paper-clips, placed in the fadeometer and exposed for 96 hours. This normally showed a reasonable change when analysed with FTIR, especially in the case of groundwood papers. For the purpose of comparison only, the period of exposure was occasionally varied.

2.3.2 Exposure to daylight

Procedure

Samples of Whatman No.1, different types of modern newsprint and old newsprint, each of 10 x 4 cm, were fixed onto the inside of a window in the laboratory, by placing their edges in mounts made out of Whatman No.1, which were then attached to the window with Sellotape for three months.

2.3.3 Oven ageing

Procedure

Paper samples of 6 x 6 cm and 10 x 6 cm were suspended in an airtight bottle containing a saturated potassium iodide solution to maintain a RH of 50%, and placed in an oven set to 70°C. Since all the samples became yellowish, which could have been the result of the liberation of iodine, the potassium iodide solution was replaced by a sodium nitrite solution and maintained at 60% RH and temperature of 60°C for the remaining batches of samples. For normal ageing, samples were kept in the oven for 7 days.

2.3.4 Ozone treatment

Procedure

Paper samples were suspended from a glass rod and placed in a perspex chamber containing an ozonizer for 9 weeks. To test for the presence of ozone, a strip of Whatman No.1 dipped in a starch solution followed by adding two drops of potassium iodide solution was placed in the chamber.

2.4 Chemical treatments

Paper samples, especially Whatman No. 1, were subjected to a number of chemical treatments in order to investigate the resulting changes in the FTIR spectra, and thus to interpret the spectra of paper and assign the individual absorbtion peaks to functional groups.

Some of the samples were treated with acid, and some of these were artificially aged after the acid treatment to monitor their deterioration. Alkaline treatments were carried out on some samples to investigate the effects of deacidification on papers.

Several chemical treatments were carried out on different types of paper with the aim of chemically stabilizing and strengthening them.

2.4.1 Acid treatments

Whatman No.1 paper samples (6 x 6 cm) were dipped in 0.001N sulphuric acid and one of them was washed with water. Other batch of Whatman No.1 paper samples (6 x 6 cm) was dipped in 2N sulphuric acid solution for 5 minutes, and one of these was washed with water. Other treated samples and an untreated one were placed in the oven at 60°C for different time periods ranging from 1 to 7 days, then washed with water and some of them were deacidified using calcium hydroxide and calcium bicarbonate solution. All the samples were analysed by FTIR.

2.4.2 Alkali treatments

Whatman No.1 and other paper samples were treated with a number of alkalis used for deacidification. The processes are described below.

2.4.2.1 Barrow's single stage process, using calcium hydroxide solution

Preparation of calcium hydroxide solution

One gram of calcium hydroxide was dissolved in 500 ml of distilled water and kept overnight in a closed glass bottle in order to allow the excess calcium hydroxide to settle. The calcium hydroxide solution was then decanted off and diluted with water in the ratio of 1:1.

Calcium hydroxide treatment

The samples were placed in a beaker containing 250 ml of the dilute calcium hydroxide solution and kept for 10 minutes. These were then transferred to another beaker containing fresh dilute calcium hydroxide solution for a further 10 minutes and removed. They were left on a clean glass plate to dry. The weights were recorded before and after the treatment under controlled RH conditions.

2.4.2.2 Barrow's two stage process

Preparation of calcium bicarbonate solution

3 grams of calcium carbonate were placed in a 1 litre syphon which was filled with distilled water up to the mark and closed. One bulb of carbon dioxide was injected, and the syphon was well shaken at intervals over about 30 minutes.

Calcium hydroxide solution

As above (see 2.4.2.1, Barrow's single stage process).

Treatment

The paper samples were placed in a beaker containing 250 ml of 1:1 saturated calcium hydroxide solution and water for 10 minutes and then transferred to a beaker containing freshly prepared calcium bicarbonate solution for a further 10 minutes. The samples were left to dry on a clean glass plate. Weights were recorded before and after the treatment, under controlled RH conditions.

2.4.2.3 Barium hydroxide treatment

Procedure

The paper samples were placed in a beaker containing 2% barium hydroxide solution which was then covered with aluminium foil. The samples were kept for an hour in the solution and allowed to dry on a clean glass plate.

2.4.2.4 Magnesium hydroxide colloidal suspension treatment

Details are given in chapter 4.

2.4.3 Formaldehyde treatment

Details are given in chapter 4.

2.4.4 Ethylene oxide treatment

Details are given in chapter 4.

2.4.5 Diazomethane treatment

Details are given in chapter 4.

2.4.6 Trimethoxymethyl silane treatment

Details are given in chapter 5.

2.4.7 Cyanoacrylate monomer treatment

Details are given in chapter 5.

2.4.8 Other treatments

To fully interpret the FTIR spectra of different types of paper, various treatments were carried out in order to relate peak positions and changes to chemical composition.

2.4.8.1 Sodium borohydride treatment

Two grams of sodium borohydride were dissolved in 100 ml of distilled water. Two samples from each paper type were immersed in this for 5 minutes, and then one sample of each was washed in distilled water. All samples were dried on a glass plate and analysed using FTIR.

2.3.8.2 Sodium hydroxide treatment

A 2% sodium hydroxide solution was prepared, and the procedure used for the sodium borohydride treatment was repeated with the sodium hydroxide solution. All samples were dried on a glass plate and analysed using FTIR.

2.4.8.3 Bleaching

To check the effect of bleaching on paper, bleaching was carried out with hydrogen peroxide and sodium hypochlorite, which are common bleaching agents used in paper conservation.

2.4.8.3.1 Hydrogen peroxide treatment

Two samples from each paper type were treated with 100 volumes hydrogen peroxide for 2 minutes, and of these one sample of each was washed in distilled water. All samples were analysed using FTIR.

2.4.8.3.2 Sodium hypochlorite treatment

Sodium hypochlorite solution was prepared by dissolving 2 grams of sodium hypochlorite in 100 ml of de-ionized water. Two samples from each paper type were treated with sodium hypochlorite solution, and one sample from each was rinsed with water, and all were dried on a glass plate. The samples were analysed using FTIR.

2.4.8.4 Sizing

To identify the presence of sizing agents an attempt was made by treating Whatman No.1 samples with different sizing agents.

2.4.8.4.1 Gelatin treatment

A 2% gelatin solution was prepared, and a sample of Whatman No.1 was immersed in it and dried on a glass plate. The sample was analysed using FTIR.

2.4.8.4.2 Rosin sizing

Preparation of rosin solution

0.2631 grams of rosin was dissolved in 2 ml of a 2% sodium hydroxide solution and boiled for 6 hours, while boiling water was added to keep the volume constant at about 2ml, i.e. to maintain the ratio of resin and sodium hydroxide to 7:1 (Clapperton, 1952).

4% alum solution was also prepared.

Treatment

One sample of Whatman No.1 was immersed in the cooled rosin solution until the sample was saturated with the solution. The sample was then placed in the 4% alum solution for 5 minutes, until a white precipitate was deposited on the paper. The sample was washed twice using distilled water and allowed to dry on a glass plate and was then analysed using FTIR.

Control treatments omitting rosin

One sample of each paper type was dipped in 2% sodium hydroxide solution for 5 minutes and one Whatman No.1 sample was dipped in 4% alum solution for the same time period. Another Whatman No.1 sample was treated with 2% sodium hydroxide for 2 minutes and

4% alum solution for another 2 minutes respectively and then washed in distilled water. These samples were dried on a glass plate and analysed using FTIR.

2.4.8.5 Deuterium oxide treatment

Treatment	Sample No.			
	9	3	4	56
Drying in the oven at 60°C for 2 hrs	9AV$_5$	3AV$_5$	4AV$_5$	56AV$_5$
Drying in the oven at 60°C for 2 hrs and treating with D_2O	9AV5m	3AV5m	4AV5m	56AV5m
Drying in the oven at 60°C for 2 hrs, treating with D_2O and in the desiccator for a day	9AV$_5$md	3AV$_5$md	4AV$_5$md	56AV$_5$m.d

Samples: 9 (Whatman No.1), 3 (buffered good quality paper), 4 (old newsprint) and 56 (modern newsprint) were placed in open sample tubes in an oven at 60°C for 2 hours to dry them. The lids were closed in the oven itself. Four drops of deuterium oxide were added to two tubes containing the same sample and the same was done for each type of paper and all sample tubes were kept at room temperature for 2 days. One out of each pair was kept in the desiccator for a day.

The samples were analysed using FTIR without allowing them to absorb water.

2.5 Mechanical testing

Folding endurance and tensile strength were measured in the samples treated with strengthening agents, and also the untreated control samples.

2.5.1 Tensile strength measurement

Apparatus used Hounsfield Tensometer; model W 6935 (Plate 2.1).

Procedure

Paper samples were cut into 10 x 1 cm strips in the machine direction (MD) and cross direction (CD) using an aluminium template and scalpel. By recording the length of the mercury column of the tensometer at the breaking point of the sample, the tensile strength was measured. Six strips were measured from the same sample and the average was taken.

2.5.2 Folding endurance measurement

Apparatus MIT fold endurance tester (Plate 2.2).

Procedure

Samples were prepared and taken in the same procedure as in 2.5.1. The number of folds the paper sample could undergo before breaking was measured under 1 kg of tension. Results were averaged as in 2.5.1.

2.6 Analytical methods

A number of analytical tools were used to assist in the interpretation of the composition of the paper samples, and the changes resulting from the treatments.

2.6.1 Measurement of acidity

Acidity was measured in two ways, i.e. by measuring the pH of the paper surface and by analysing the water extract of the paper. Since the surface measurement cannot give very accurate results, although it is the only feasible method to use in archive conservation, the water extraction method was also used to check for the presence of soluble and insoluble acids.

2.6.1.1 Surface pH

Apparatus used pH meter; model EIL 7055 (Corning), flat surface combination electrode containing Ag/AgCl reference electrode (Corning).

Procedure

After calibrating the pH meter with buffer solutions, the flat surface electrode was washed and dipped in de-ionized water which had a pH of about 7. Paper samples were placed on a Mylar sheet supported by a glass plate on the bench. The electrode which was in the beaker containing de-ionized water was taken out and placed on the paper sample, carrying a drop of water to the surface. The reading was taken after 20 seconds.

2.6.1.2 pH of water extraction

Apparatus used pH meter model EIL 7055, combination electrode with Ag/AgCl reference electrode (Corning), MSE homogeniser.

Procedure

One batch of samples from each book was cut into small pieces and placed separately in 500 ml beakers. 60 ml of boiling de-ionized water was added to each beaker, and the paper samples were stirred to make sure that each piece was covered with water. Every beaker was covered and kept for one hour at room temperature. Titrations were carried out with 0.01 N sodium hydroxide solution.

The other batch of samples from each book was also cut into small pieces and placed separately in 500 ml beakers. 60 ml of boiling de-ionized water was added to each beaker, and the paper samples were stirred to make sure that each piece was covered with water. The beakers were covered and kept for 5 minutes. Then the contents of each beaker was poured into the homogeniser and milled. The milled contents were filtered separately using sintered glass funnels. The residue in each case was washed with another 15 ml of boiled de-ionized water and allowed to filter. The extracts were titrated with 0.01 N sodium hydroxide solution.

In all cases, the volume of sodium hydroxide solution needed for neutralising the extract (i.e. the volume needed for the pH value to become 7) was measured.

2.6.2 Spot tests

To identify the constituents of the paper, spot tests were carried out. The Raspail test for rosin (TAPPI T 408), the iodine test for starch (TAPPI T 419), the hydroxyproline test for glue (TAPPI std. T 504), the Biuret test for protein (Browning, 1977), the Millon test for casein (TAPPI std. T 415) and the phloroglucinol test for groundwood (Browning, 1977) were used for a selection of the paper samples.

2.6.3 Fourier transform infrared spectroscopy

2.6.3.1 Choice of diffuse reflectance

FTIR spectroscopy can be done in the transmittance or reflectance mode. In the transmittance mode, sample preparation is usually necessary. In preparing the samples, attention should be given to obtaining the right thickness of the sample and in making the discs. Preparation of samples could change the actual composition of the paper, such as the water content and crystallinity. Hence, to avoid sample preparation, the diffuse reflectance mode was used. In addition to eliminating all these disadvantages of the transmittance mode, it was found that the reflectance mode also gave sharper spectra.

2.6.3.2 Experimental work

Apparatus used Bruker IFS 45 FTIR spectrometer (Plate 2.3).

Procedure

A 5mm square paper sample was placed in an aluminium sample holder and examined by diffuse reflectance, using the Bruker IFS 45 FTIR spectrometer. The instrument was purged with nitrogen and the reference spectrum was taken using a mirror, prior to the analysis of the samples. Although different numbers of scans (400, 600, 800) were tried, in most instances spectra were accumulated for 200 scans, under 4 cm^{-1} resolution, and plotted out.

Peak intensities in FTIR spectra of some samples were recorded using the "Calcpeak" programme. The "Calcpeak" programme has been designed to calculate the intensity and/or area of peak(s) within a known region of wave length.

2.6.3.3 Peak assignments

Peak assignments were mainly based on the published literature. The author has surveyed a number of publications about FTIR and IR, with relevance not only to paper, but to related substances such as wood, lignin, cellulose and hemicellulose. The assignments collected are given in Appendix 4. These published peak assignments were collected and rationalised on the basis of experimental work carried out by the author.

2.6.3.4 Experimental results used to establish the FTIR peak assignments

Sodium borohydride treatment

The spectra of Whatman samples treated with sodium borohydride showed the appearance of a new strong broad peak at 2260 cm^{-1}, an intensity increase in the peaks at 1639 cm^{-1}, an intensity decrease at 1205 cm^{-1} and 897 cm^{-1} and a change in shape, of the very small peak at 897 cm^{-1}. Also, a shape difference was observed of the region 1500-1000 cm^{-1}. With washing all the changes disappeared and it showed a similar spectrum to the untreated sample (Figure 2.1)

The disappearance of the peaks at 1733 cm^{-1} and 1510 cm^{-1}, the appearance of a broad peak at 2260 cm^{-1}, the shape difference in the peak at 1280 cm^{-1} and in the region of 1020-800 cm^{-1} were observed as the two peaks at 1003 and 897 cm^{-1} merged to become a broad single peak, with a very small peak at 1003 cm^{-1}, in the spectrum of old newsprint treated with sodium borohydride. After washing, the change that had occurred in the peak at 1733 cm^{-1} remained while other changes due to the treatment disappeared and showed similar features as in the spectrum of the untreated sample, although there was a slight change in the shape of the region 1050-750 cm^{-1} (Figure 2.2)

The spectrum of modern newsprint treated with sodium borohydride showed an intensity decrease in the peak at 1733 cm^{-1} which virtually became a shoulder and an increase in the intensity of the peaks at 1600 cm^{-1} and 1173 cm^{-1}. A decrease in the intensity of the peaks at 1510 cm^{-1}, 1269 cm^{-1} and 897 cm^{-1} were observed. The small peaks at 1205 and 1235 cm^{-1} had become bends, the shape of the region 1500-800 cm^{-1} was changed and a new broad peak at 2260 cm^{-1} was observed. With washing, all the changes observed due to the sodium borohydride treatment disappeared, except for the change in the peak at 1733 cm^{-1}, and also an overall intensity increase of the peaks at 1173, 1128 and 1086 cm^{-1} was observed. (Figure 2.3)

Sodium hydroxide treatment

The spectrum of the Whatman No.1 sample treated with sodium hydroxide showed an intensity increase in the peak at 1649 cm^{-1}, shape differences in the peaks at 1280 and 1245 cm^{-1}, an intensity decrease in the peaks at 1325 and 1205 cm^{-1}, an appearance of a shoulder at 880 cm^{-1} in the peak at 897 cm^{-1}, and a shoulder between 840-800 cm^{-1}. With washing, all the changes observed due to the treatment disappeared. (Figure 2.4)

Spectra of modern newsprints treated with sodium hydroxide showed the appearance of two peaks at 810 and 830 cm^{-1}, disappearance of the peak at 1733 cm^{-1}, a very considerable decrease in the peak at 1510 cm^{-1}, an intensity decrease in the peak at 1168 cm^{-1} and an intensity increase in the peaks at 820 and 875 cm^{-1}, while the peak at 897 cm^{-1}

became a shoulder. Overall shape difference in the peaks in the region 1500- 1000 cm^{-1} was also observed. With washing, the peak at 1510 cm^{-1} reappeared to the same extent as in the untreated sample. All other changes observed due to the sodium hydroxide treatment disappeared, except the intensity decrease of the peak at 1168 cm^{-1} and the disappearance of the peak at 1733 cm^{-1} (Figure 2.5).

Sodium sulphate treatment

There was no change in the spectrum of the Whatman No.1 treated with sodium sulphate except a slight increase in intensity of the peaks at 636 and 680 cm^{-1}. With washing the intensity of both the peaks decreased to almost the similar level of the untreated sample, and the peak at 680 cm^{-1} became a doublet (Figure 2.6)

Alum treatment

Only the shape difference of the peak at 1235 cm^{-1} was observed in the spectra of the alum-treated Whatman No.1 sample. (Figure 2.7)

Sodium hydroxide and alum treatment

In the spectra of the Whatman No.1 samples subjected to sodium hydroxide and alum treatment, an intensity decrease in the peak at 1092 cm^{-1}, an increase in the peak at 636 cm^{-1} and a shape difference in the peak at 1235 cm^{-1} were observed (Figure 2.8).

Sodium hydroxide, alum and washing

There was no difference in the spectrum of Whatman treated with sodium hydroxide and alum followed by washing, compared with the untreated sample, except for the appearance of very small peaks in the region 2000-1500 cm^{-1} and an intensity increase of the peak at 636 cm^{-1}. These small peaks may be due to the moisture (Figure 2.9)

Gelatin treatment

The spectrum of the Whatman No. 1 sample treated with gelatin showed weak peaks at 1541 and 1552 cm^{-1} and an increase in intensity of the existing peak at 1639, which shifted to 1650 cm^{-1} (Figure 2.10)

Barium hydroxide treatment

In the spectrum of the Whatman No.1 sample treated with methanolic barium hydroxide, a shape difference in the peaks in the region 1650-1500 cm^{-1}, the appearance of the peaks at 1650 and 1580 cm^{-1}, a small kink at 860 cm^{-1} and an intensity increase in the peaks at 636, 575 and 520 cm^{-1} were observed (Figure 2.11).

Calcium hydroxide treatment

The appearance of a small peak or a shoulder at 875 cm^{-1}, an intensity increase in the peak at 636, 1320 cm^{-1} and an intensity decrease in the peaks at 1380, 1092, 570, 520 and 440 cm^{-1} and an intensity decrease in the peaks at 1380, 1092, 570, 520 and 440 cm^{-1} were observed in the spectra of the Whatman No.1 samples treated with calcium hydroxide (Figure 2.12)

Sodium hypochlorite treatment

The spectrum of the Whatman No.1 sample treated with sodium hypochlorite showed a shape difference, an intensity decrease in the region of 1500-1000 cm^{-1}, an intensity increase of the peaks at 1639 cm^{-1} and 636 cm^{-1}, an appearance of a shoulder at 1724 cm^{-1} and a peak at 854 cm^{-1} and the loss of the peak at 897 cm^{-1}. (Figure 2.13)

Deuterium oxide treatment

The spectra of modern newsprints immediately after the treatment with deuterium oxide showed new peaks at 3845 cm^{-1} and at 2692 cm^{-1} and a decrease in intensity of the broad band in the region of 3725-3700 cm^{-1}. All peaks in the region of 1750 to 400 cm^{-1} became less resolved (Figure 2.14,). Spectra of samples dried after the treatment showed a better resolution in the region of 1750 to 400 cm^{-1} (Figure 2.14)

The spectra of Whatman No.1 samples also showed similar changes to modern newsprint in the region of 4000-2000 cm^{-1} with deuterium oxide treatment, even after drying. In the region of 2000-400 cm^{-1}, not all the peaks were properly resolved due to the treatment. When the samples were dried after the deuterium oxide treatment, the peaks in the region of 2000-400 cm^{-1} were resolved to a small extent, a new peak appeared at 880 cm^{-1} and the peak at 1639 cm^{-1} disappeared. (Figure.2.15)

It was found that the old newsprint behaved in the same manner as the modern newsprint.

Magnesium hydroxide and aluminium hydroxide

The FTIR spectrum of magnesium hydroxide showed a very sharp peak at 3700 cm^{-1}, while other metal oxides such as aluminium hydroxide did not show this peak in the FTIR spectrum (Figure 2.16).

Milled wood lignin

In the spectrum of milled wood lignin it was clear that the strong peak at 1510 cm^{-1} is the same as the characteristic peak for mechanical wood papers (Figure 2.17).

Unbleached and bleached pulps

The major difference observed in the FTIR spectra of unbleached and bleached softwood sulphite pulp was in the region 1733-1500 cm^{-1}. The peaks at 1510 cm^{-1} and 1733 cm^{-1} had become shoulders in the FTIR spectrum of bleached sulphite pulp (Figure 2.18).

It was obvious that one could identify the bleached from unbleached paper using FTIR. In addition it was apparent that, in the process of bleaching, all the lignin products were not removed, as the spectrum showed shoulders at 1510 cm^{-1} and 1733 cm^{-1} (Figure 2.18).

Bleached sulphate and sulphite pulps

In the case of softwood, the appearance of a shoulder at 1724 cm^{-1} was observed in the FTIR spectrum of bleached sulphite pulp. There was no other difference except in overall intensity changes. In the case of hardwood, the appearance of a very small shoulder was observed in both cases, i.e. in bleached sulphate and sulphite pulp (Figure 2.19).

Hence, the author concludes that FTIR cannot distinguish the process so as to identify whether paper has been made by the sulphate or sulphite process.

Thermomechanical pulp and groundwood pulp

In FTIR spectrum of groundwood pulps, the peaks at 1733, 1160, 1606 cm^{-1} and 1510 cm^{-1} were apparent. Thermomechanical pulp also showed a similar spectrum except for a shoulder at 1733 cm^{-1} instead of the peak, an intensity decrease of the peaks at 1510, 1280 cm^{-1} and 820 cm^{-1}, an increase in the intensity of the peak at 1178 cm^{-1} and the appearance of a shoulder at 2940 cm^{-1} (Figure 2.20).

Softwood and hardwood pulp

The FTIR spectra of softwood and hardwood pulp showed the similar spectrum except that the appearance of a peak at 820 cm^{-1} only in softwood (Figure 2.21) .

Hence one could identify the softwood from hardwood using FTIR.

2.6.4 Scanning Electron Microscope

Apparatus used Scanning electron microscope, Hitachi model S-570; Edwards cool sputter coater, model S150 B; Edwards coating unit, model 12E 6/1136.

Procedure

Some of the samples treated with magnesium hydroxide colloidal suspension were coated with carbon using the coating unit, and examined in the SEM, and the elements present were analysed on both surfaces of the sample, using the X-ray fluorescent analyser, and the results plotted out.

Some of the samples treated with magnesium hydroxide and cyanoacrylate monomer were coated with gold using the cool sputter coater, and observed under the SEM and photographed at 15kV and 300x magnification .

2.6.5 Differential Scanning Calorimetry

Apparatus used Perkin Elmer DSC 7 with the TADS 7 data station (Plate 2.4); Mettler FP-82 stage heater.

Procedure

Samples of 6mm diameter were selected from an area without any printing, and placed in aluminium crucibles. Heating was carried out in oxygen, maintaining a flow rate of 60 cm^3/min., and heating rates of 10°C/min. and 40°C/min.

Samples were also heated on the Mettler FP-82 stage heater at from 5°C/min to 300°C. The temperature of onset of discolouration and subsequent charring observed was recorded using the microscope.

2.6.6 Dielectric Thermal Analysis

Apparatus used PL- dielectric thermal analyser.

Procedure

Small rectangular samples (7.5mm wide) from an area without printing, were examined at frequencies of 0.1 kHz, 1Hz and 10 Hz. Tan-δ was recorded on a plot over the temperature range 0°C to 200°C.

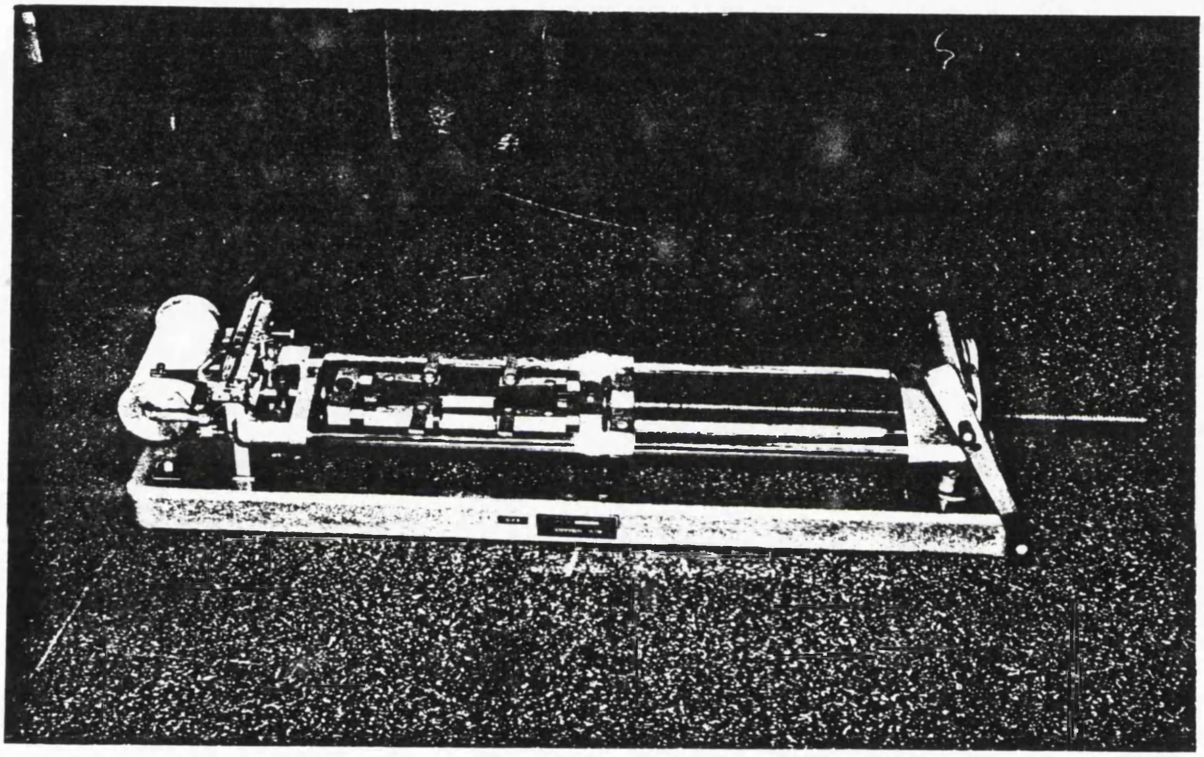


PLATE 2.1: Hounsfield Tensometer

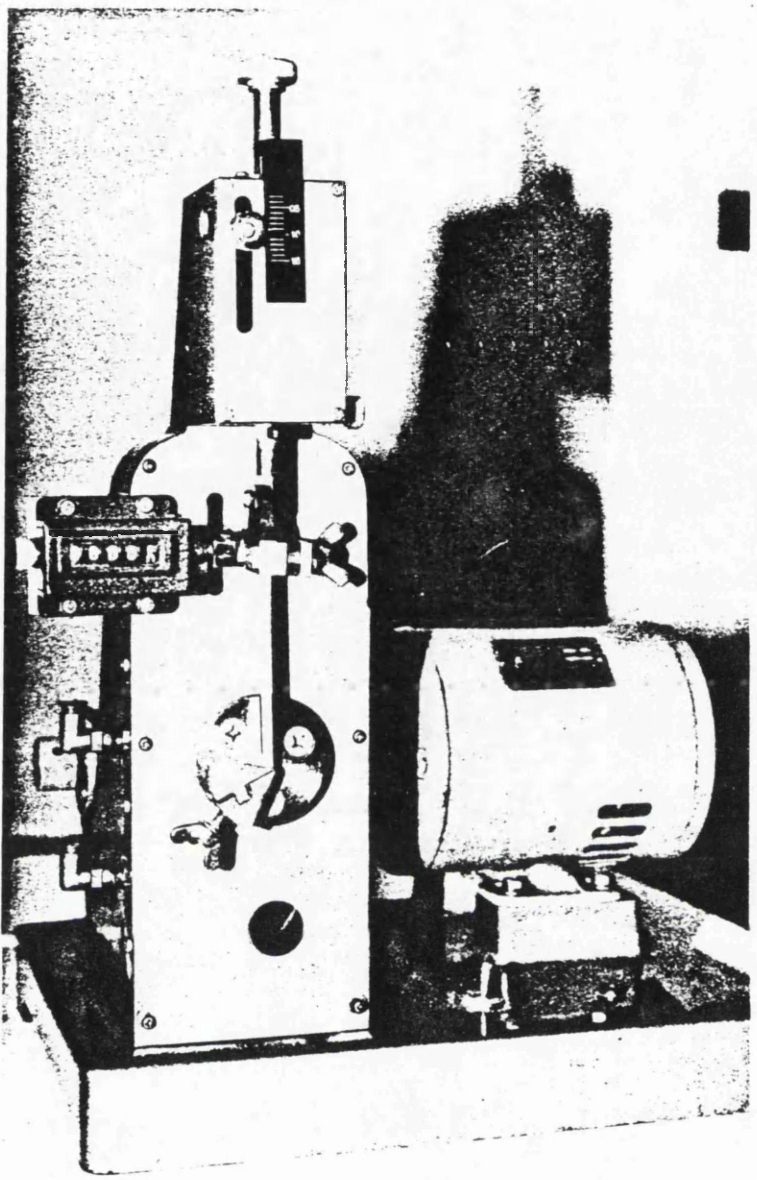


PLATE 2.2: MIT fold endurance tester

PLATE 2.3: Bruker IFS 45 FTIR spectrometer

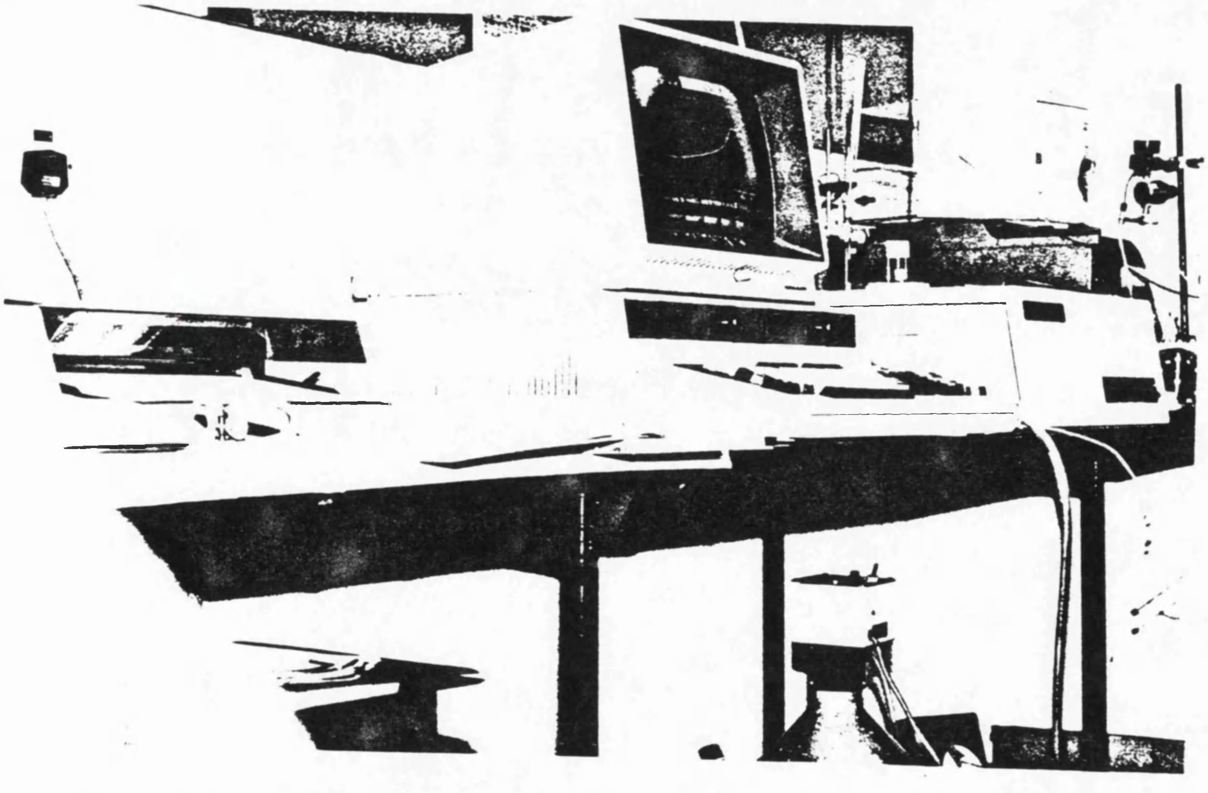


PLATE 2.4: Perkin Elmer DSC 7 with the TADS 7 data station

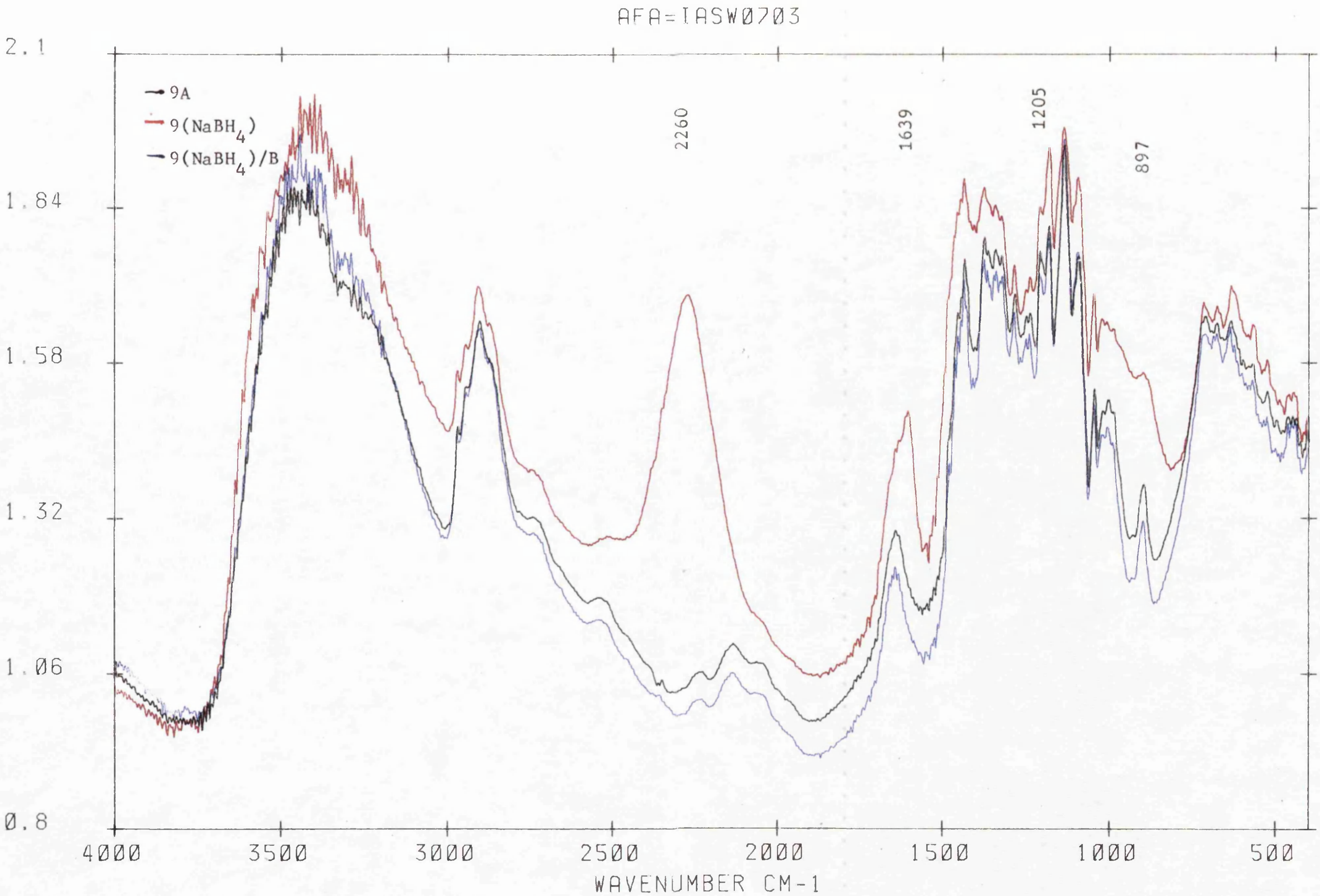

AFA=IASW0703
9A
9(NaBH$_4$)
9(NaBH$_4$)/B
2260
1639
1205
897
2.1
1.84
1.58
1.32
1.06
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.1

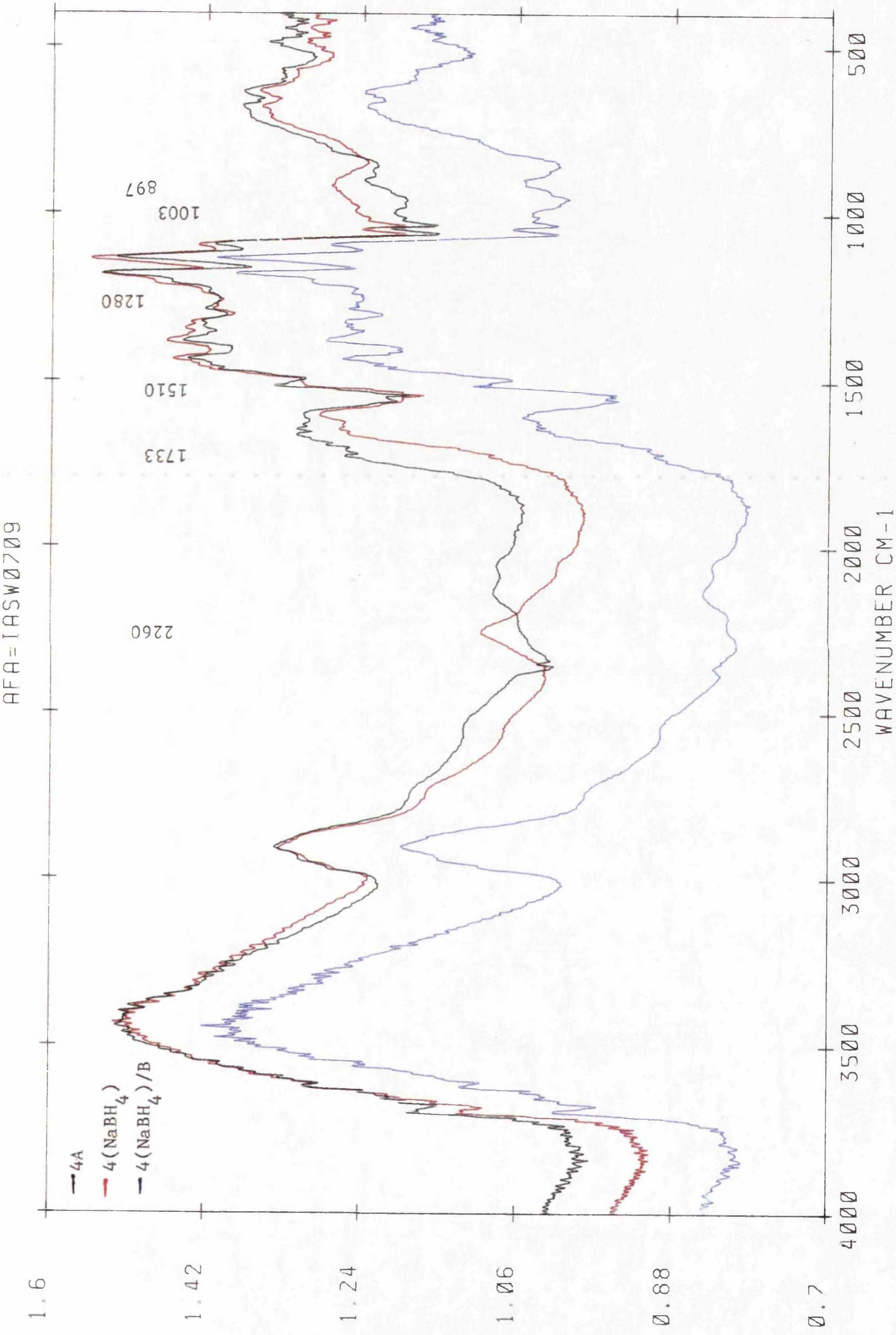

AFA=IASW0709
4A
4(NaBH$_4$)
4(NaBH$_4$)/B
2260
1733
1510
1280
1003
897
1.6
1.42
1.24
1.06
0.88
0.7
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.2

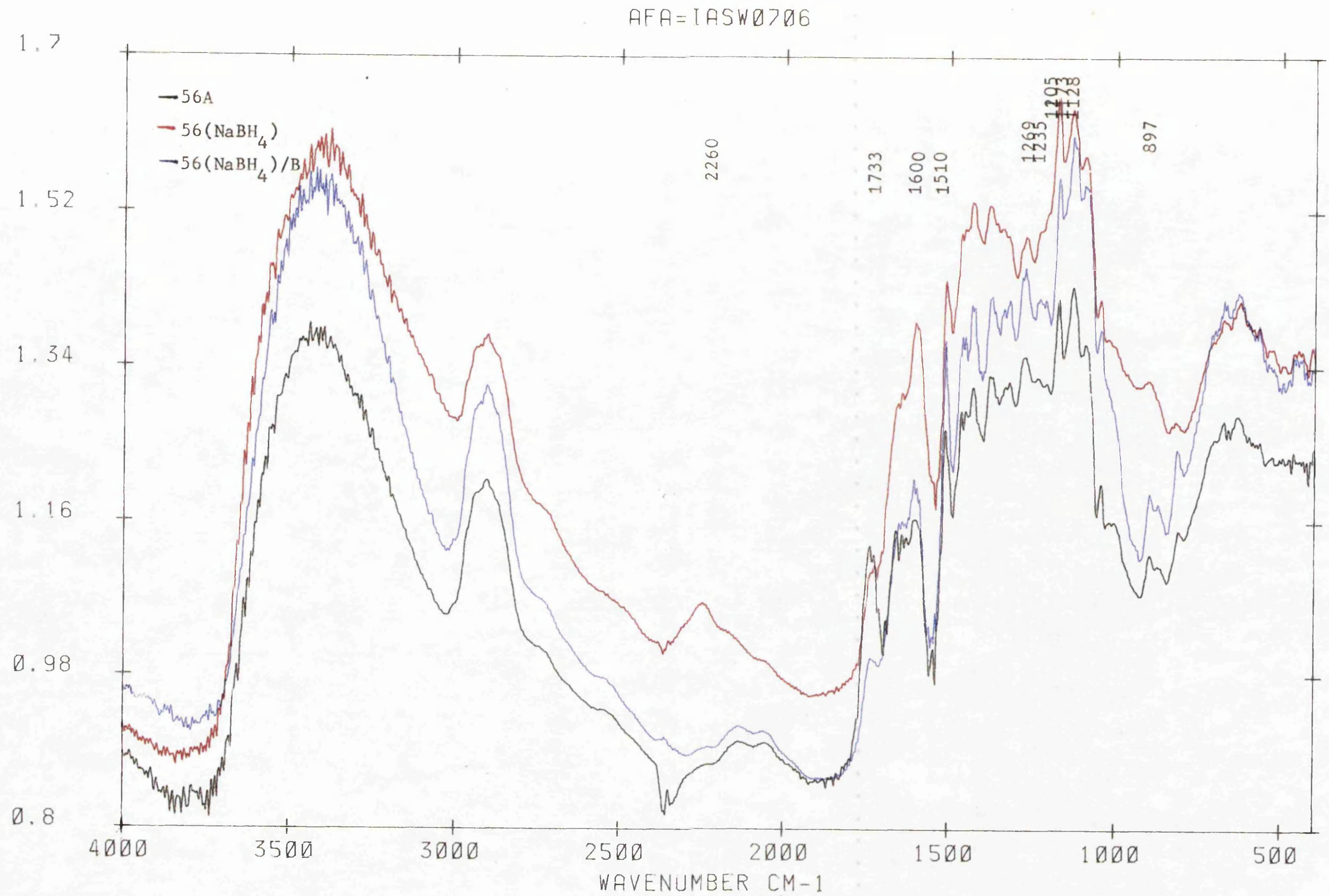

AFA=IASW0706
1.7
1.52
1.34
1.16
0.98
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1
56A
56(NaBH4)
56(NaBH4)/B
2260
1733
1600
1510
1269
1235
1205
1173
1128
897

Figure 2.3

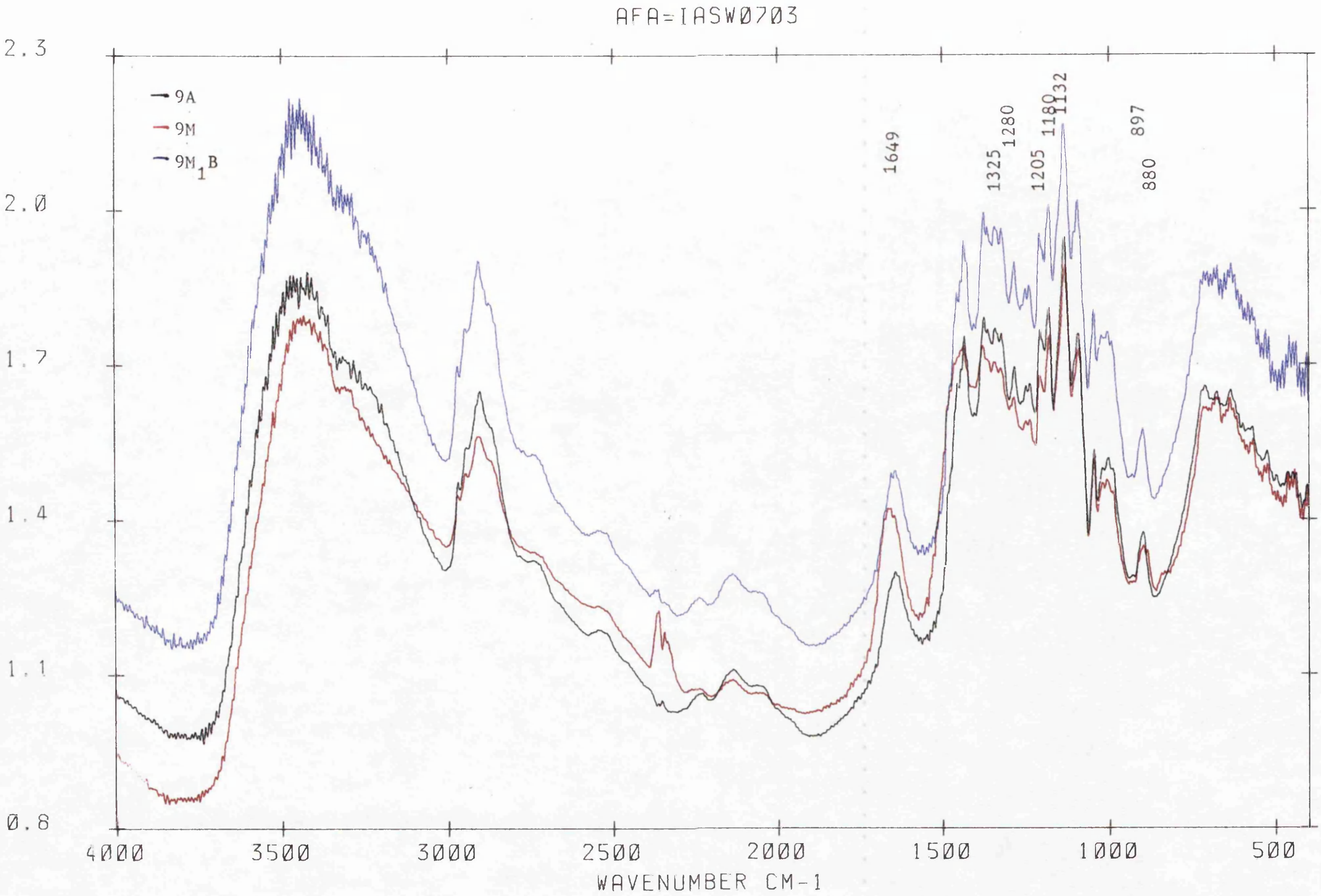

AFA=IASW0703
9A
9M
$9M_1B$
1649
1325
1280
1205
1180
1132
897
880
2.3
2.0
1.7
1.4
1.1
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.4

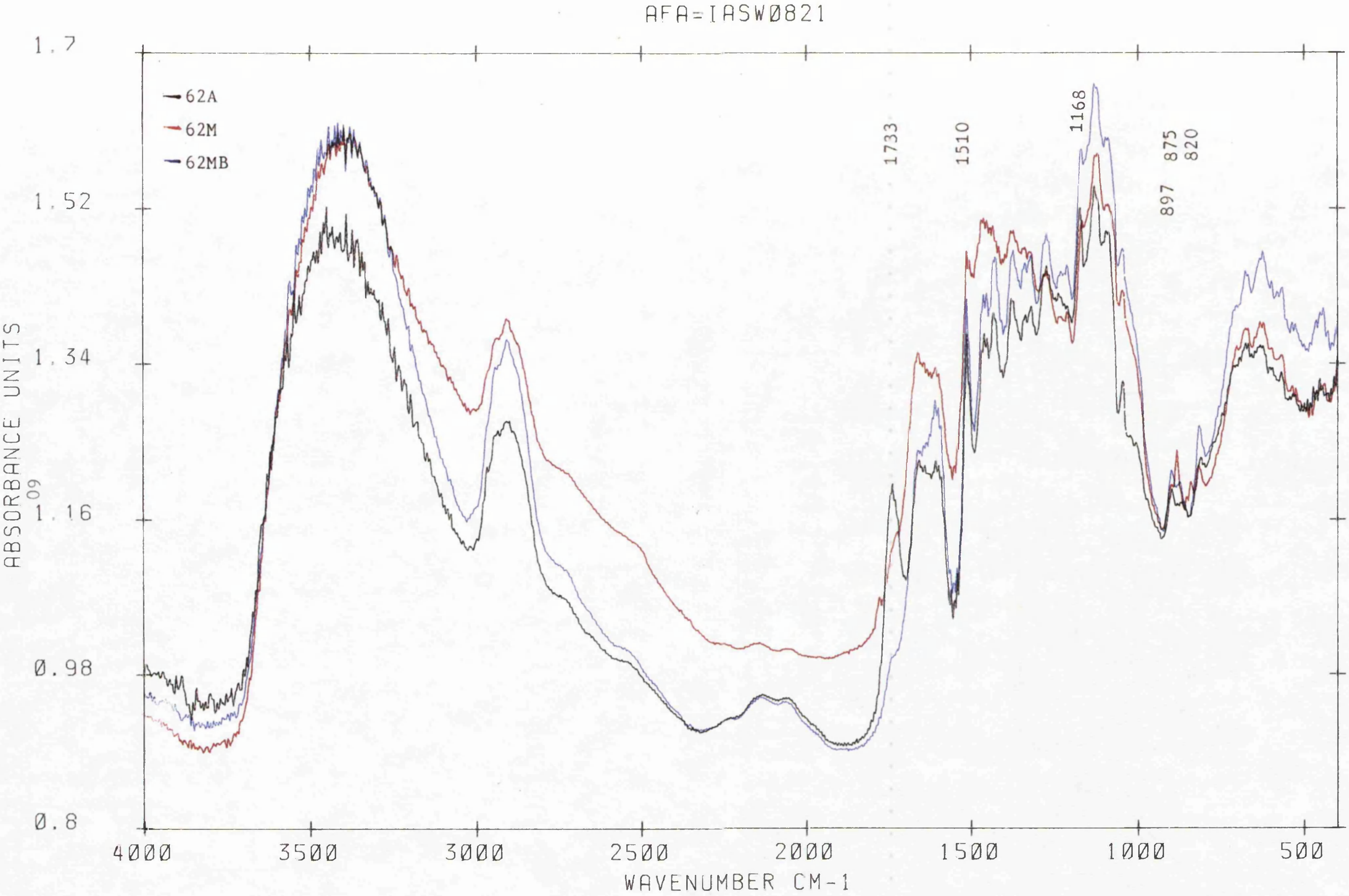

AFA=IASW0821
1.7
1.52
1.34
1.16
0.98
0.8
ABSORBANCE UNITS
62A
62M
62MB
1733
1510
1168
897
875
820
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.5

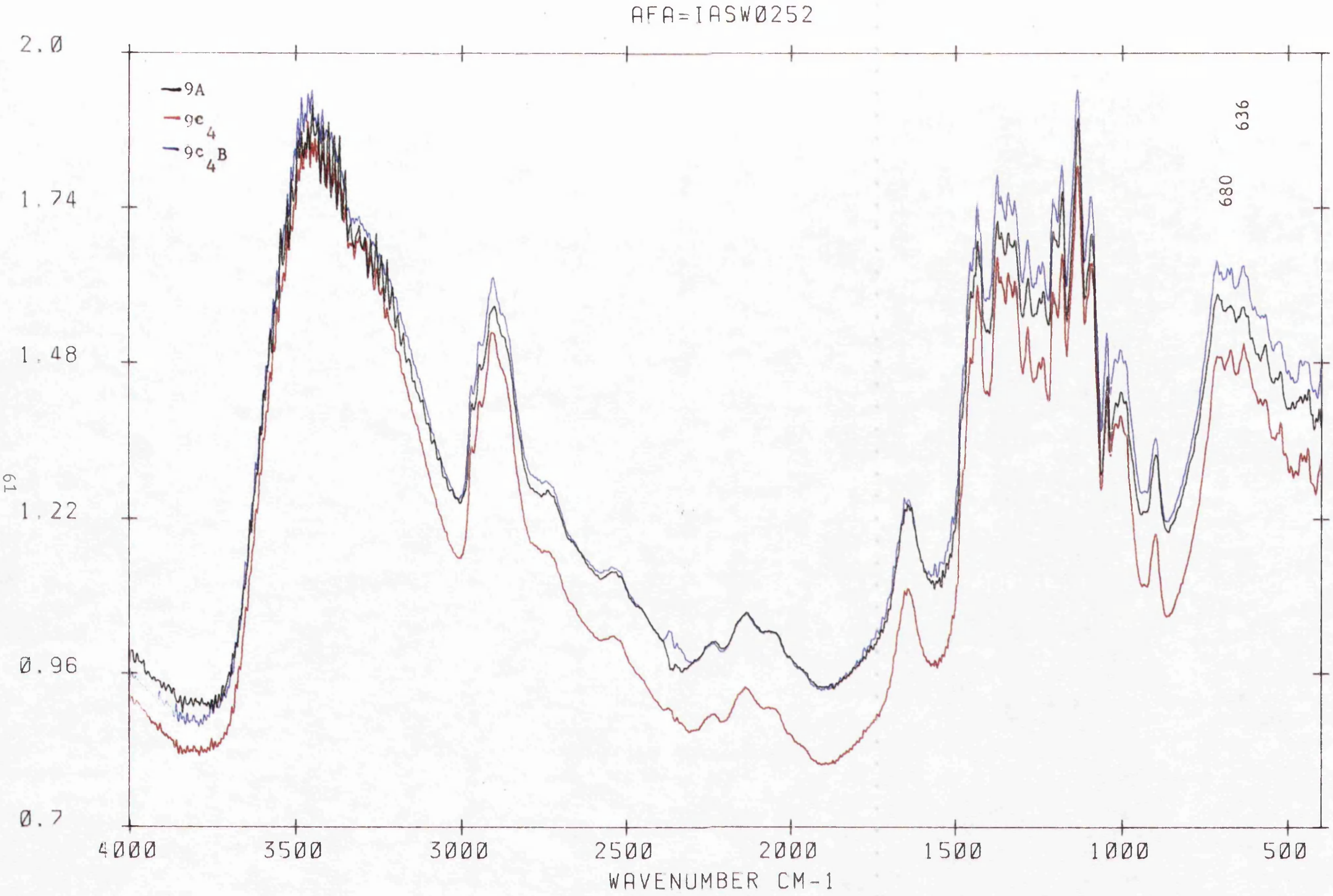

AFA=IASW0252
—9A
—9c4
—9c4B
636
680
2.0
1.74
1.48
1.22
0.96
0.7
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.6

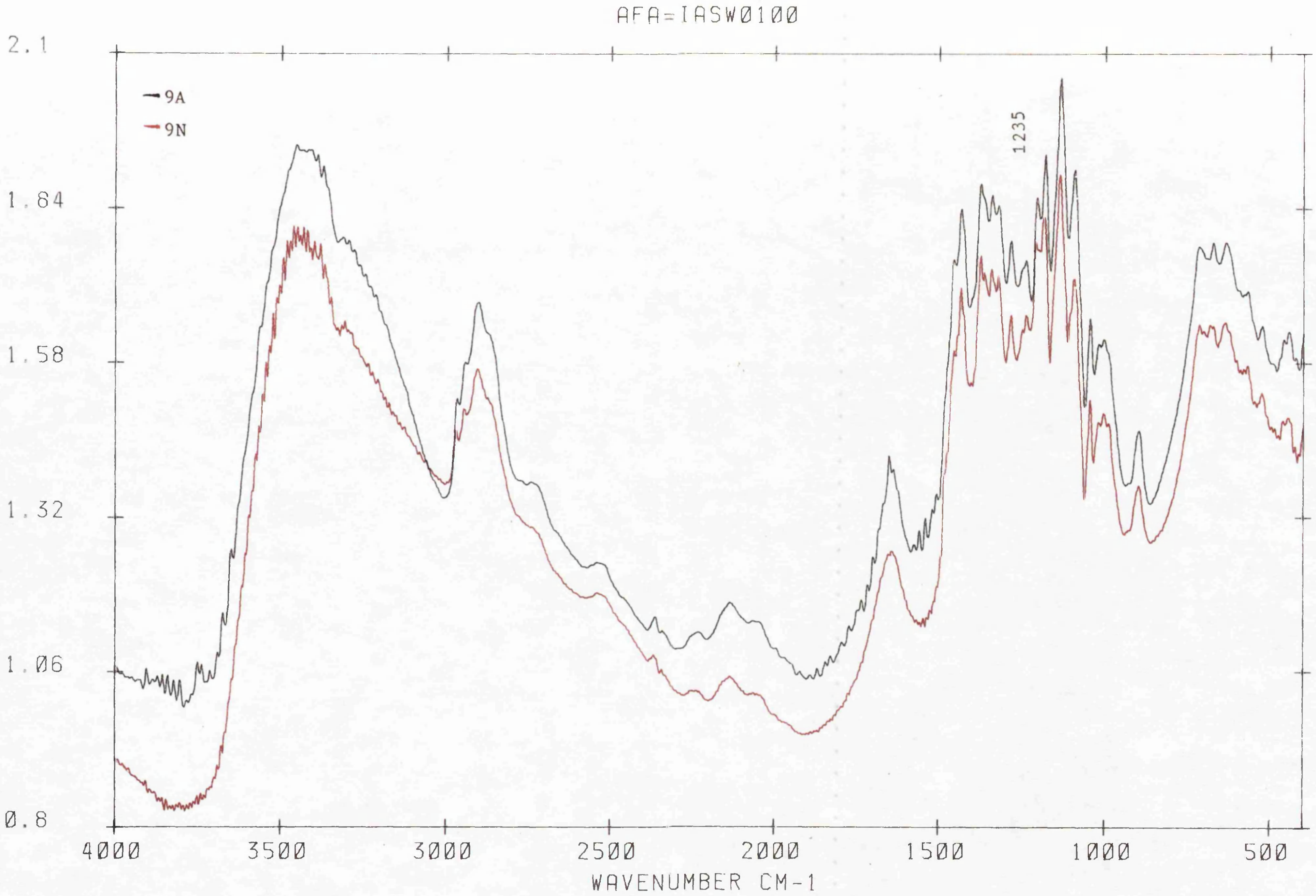

AFA=IASW0100
2.1
1.84
1.58
1.32
1.06
0.8
9A
9N
1235
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.7

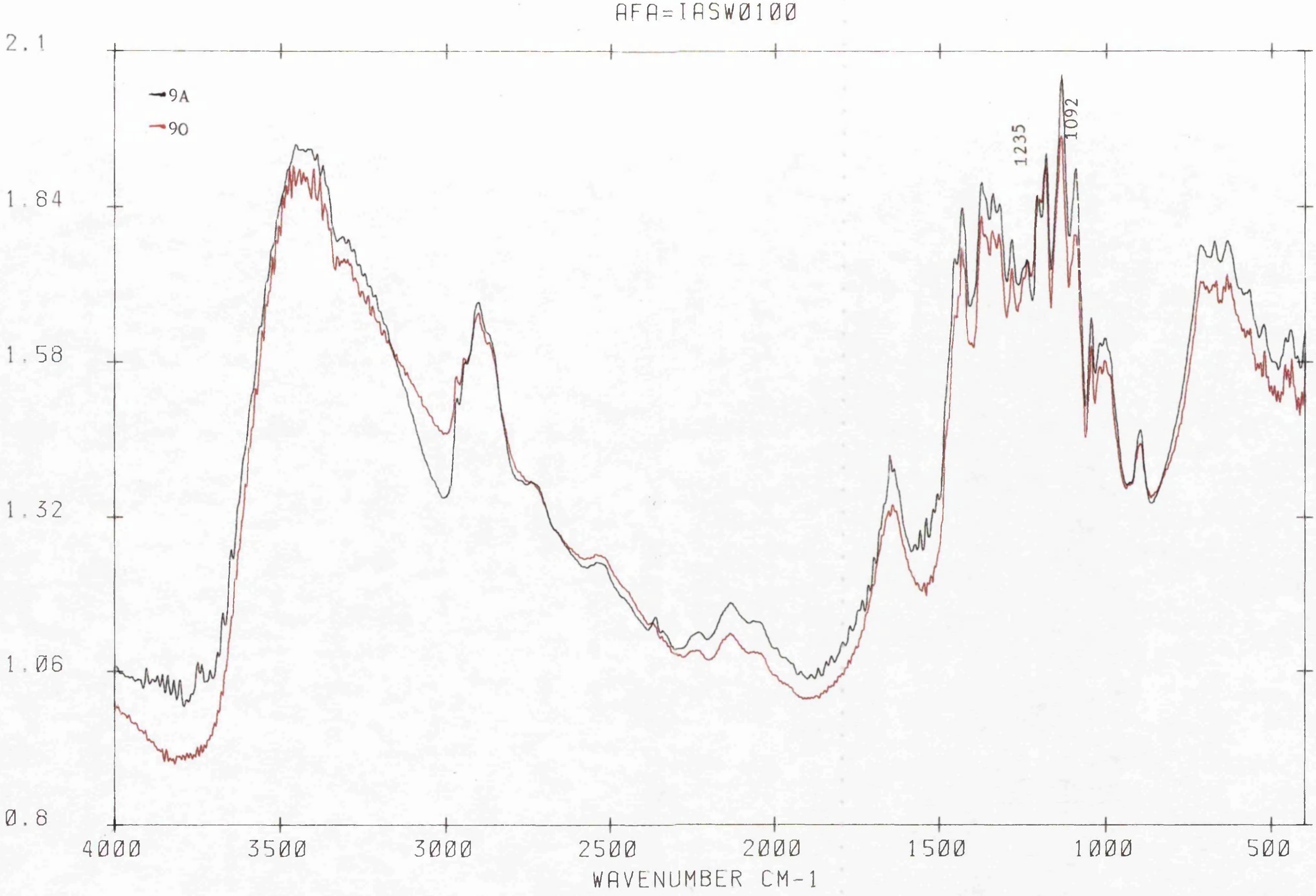

AFA=IASW0100
9A
90
1235
1092
2.1
1.84
1.58
1.32
1.06
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.8

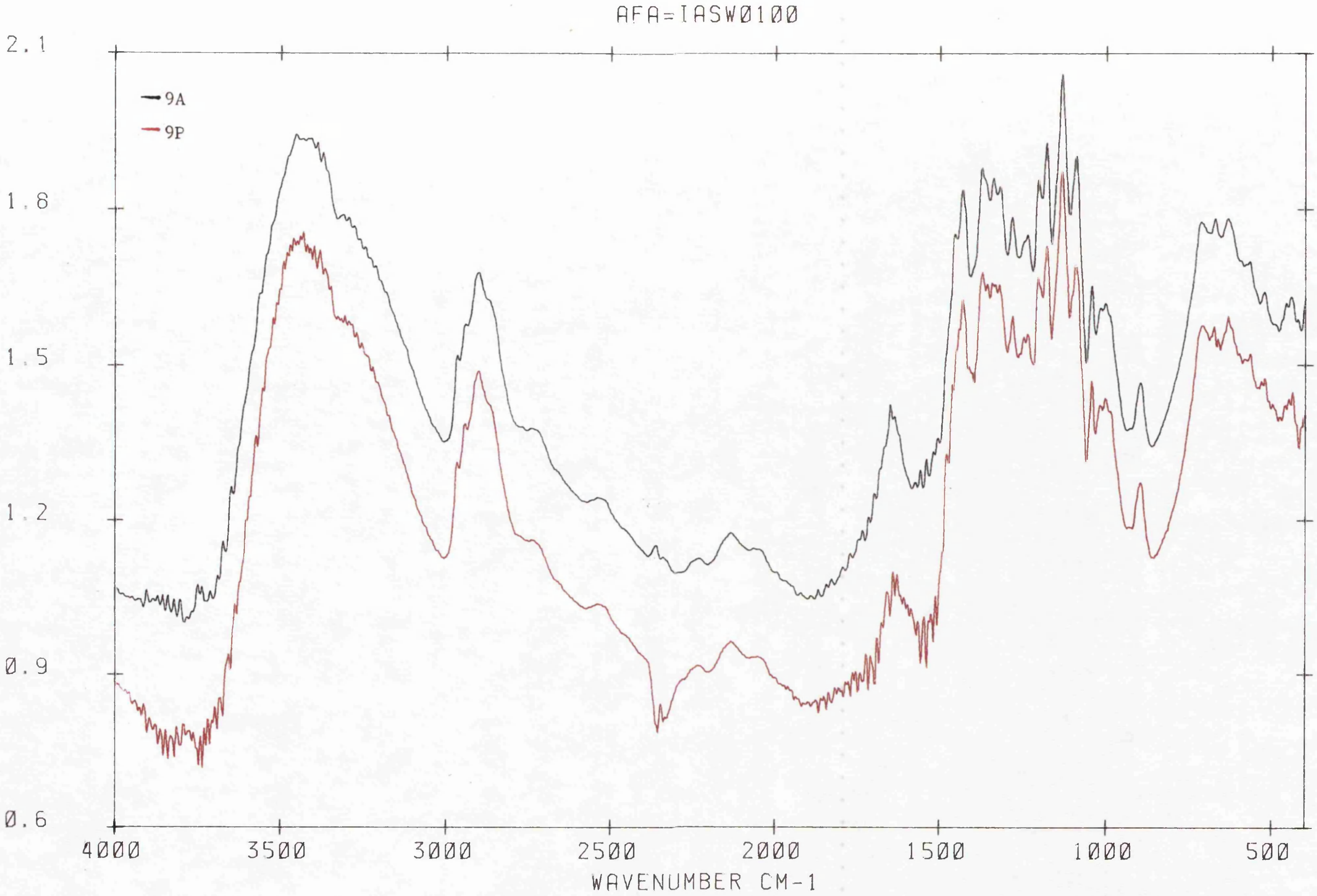

AFA=IASW0100
9A
9P
2.1
1.8
1.5
1.2
0.9
0.6
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.9

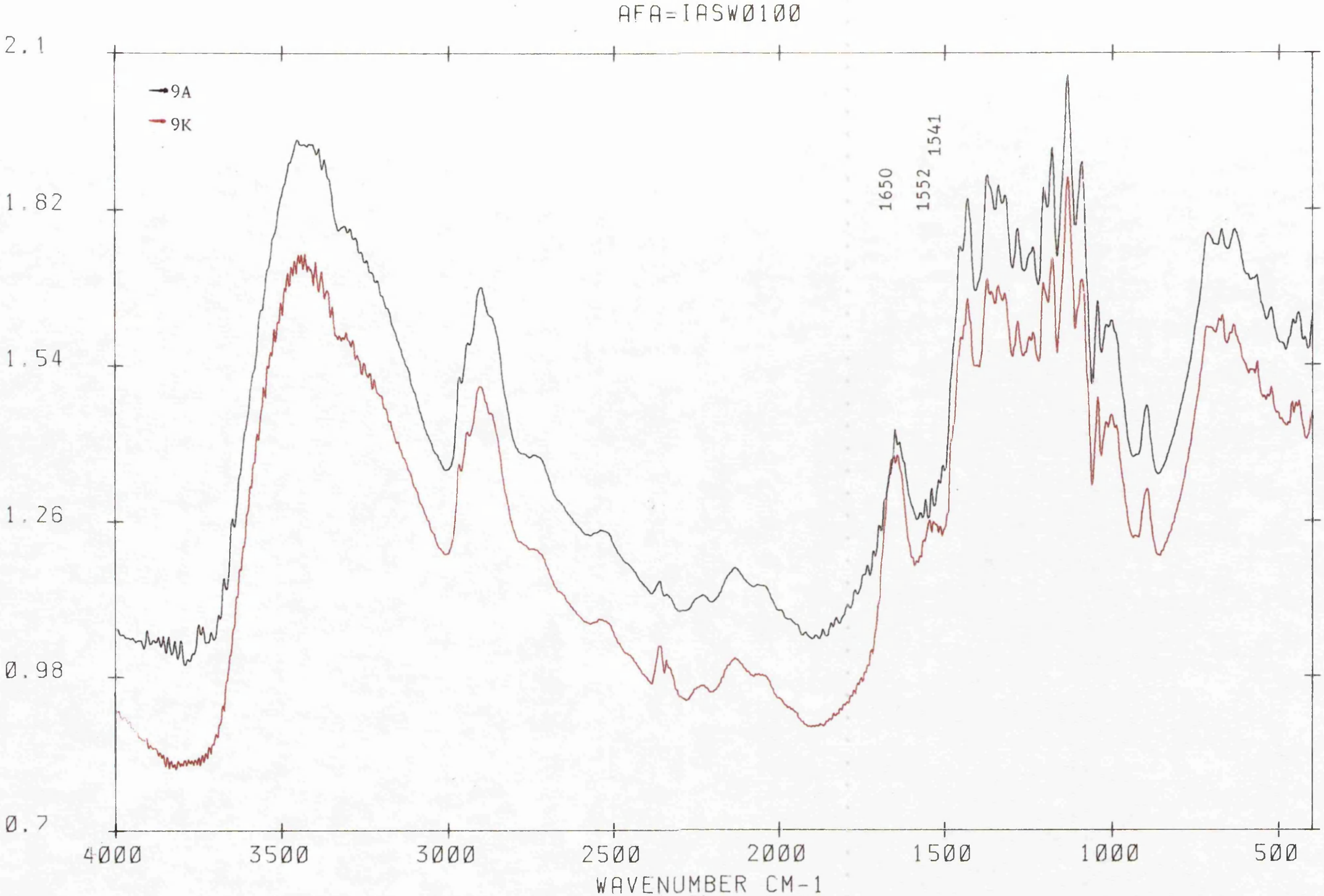

AFA=IASW0100
2.1
1.82
1.54
1.26
0.98
0.7
9A
9K
1650
1552
1541
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.10

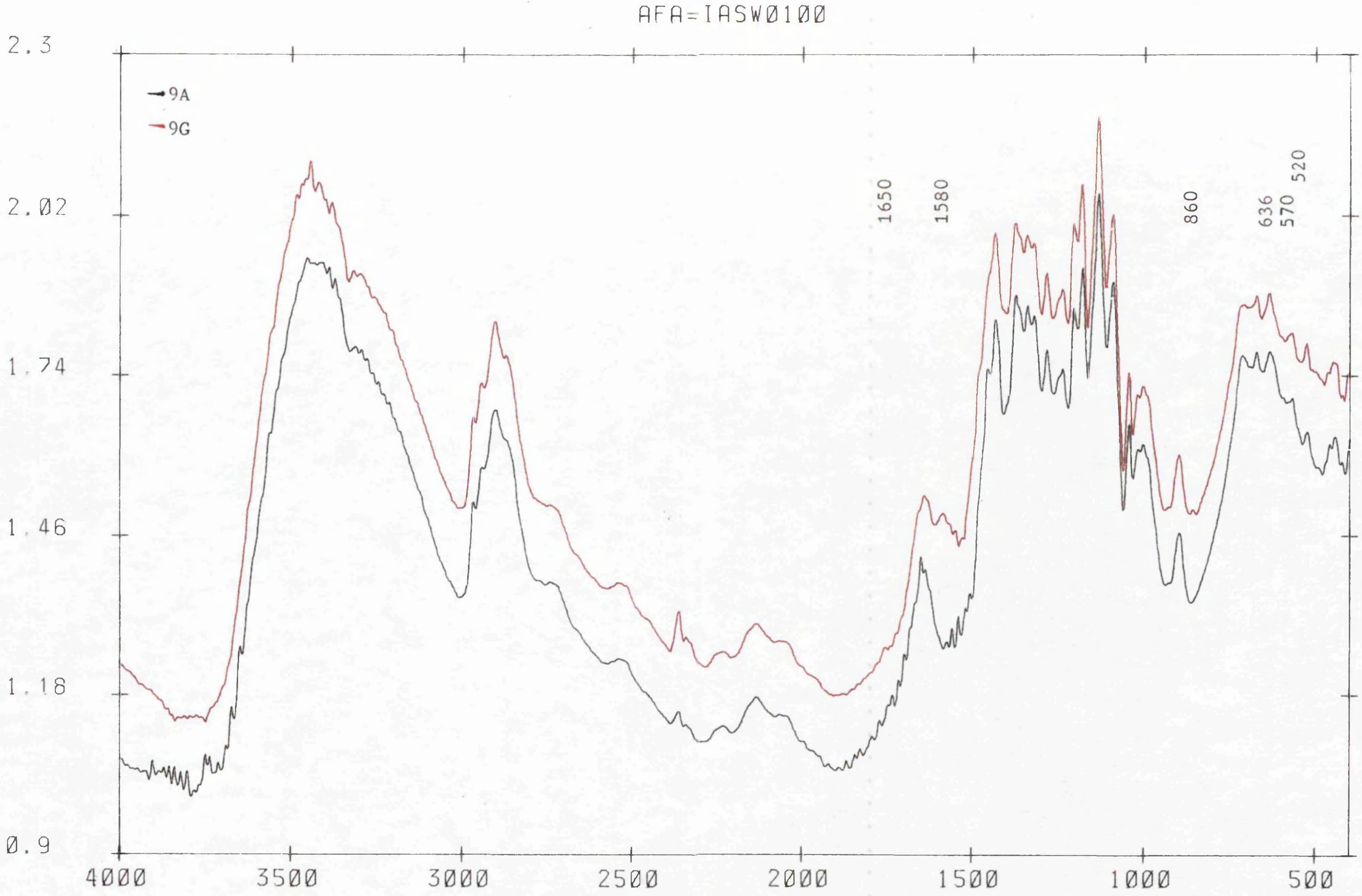

AFA=IASW0100
9A
9G
2.3
2.02
1.74
1.46
1.18
0.9
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1
1650
1580
860
636
570
520

Figure 2.11

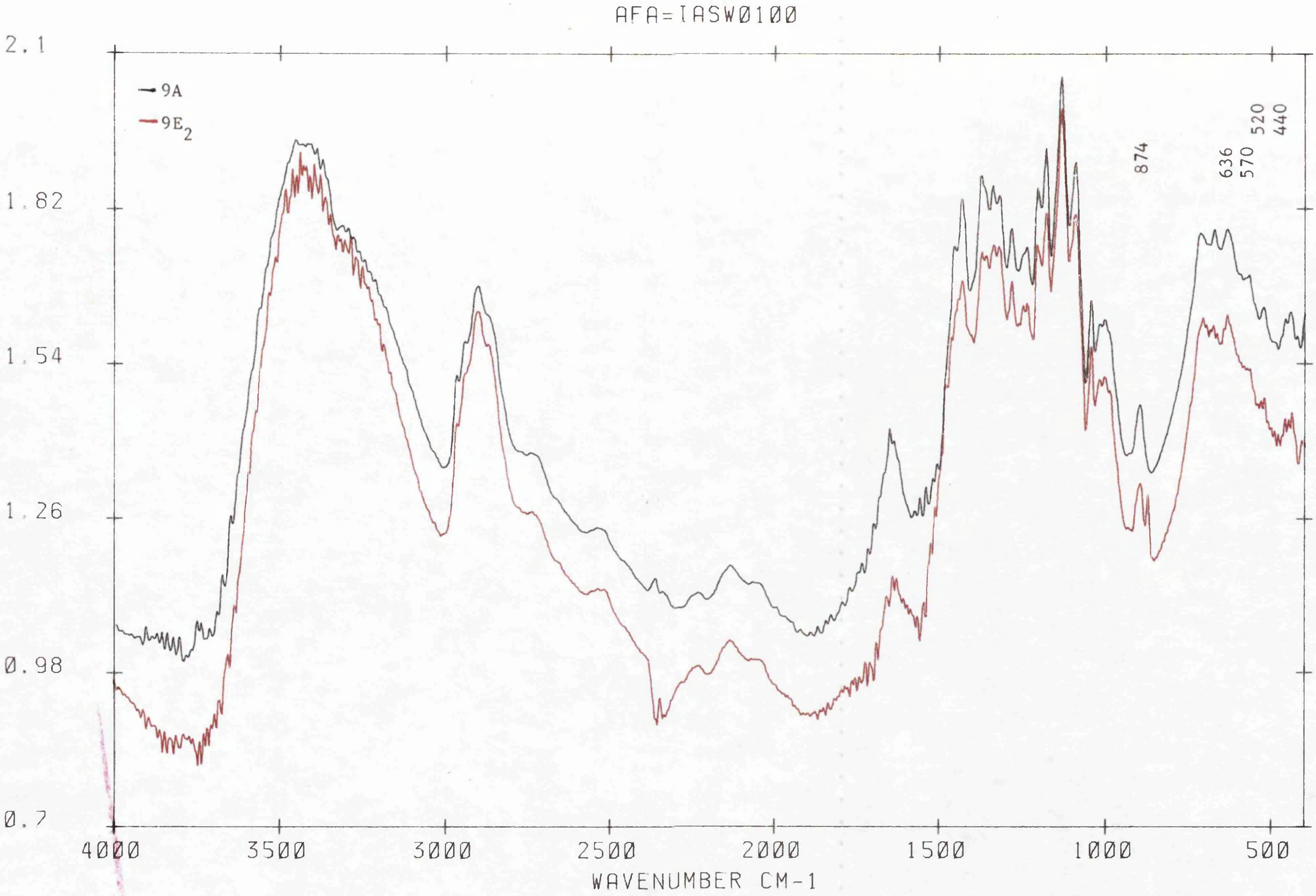

AFA=IASW0100
9A
9E$_2$
2.1
1.82
1.54
1.26
0.98
0.7
874
636
570
520
440
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.12

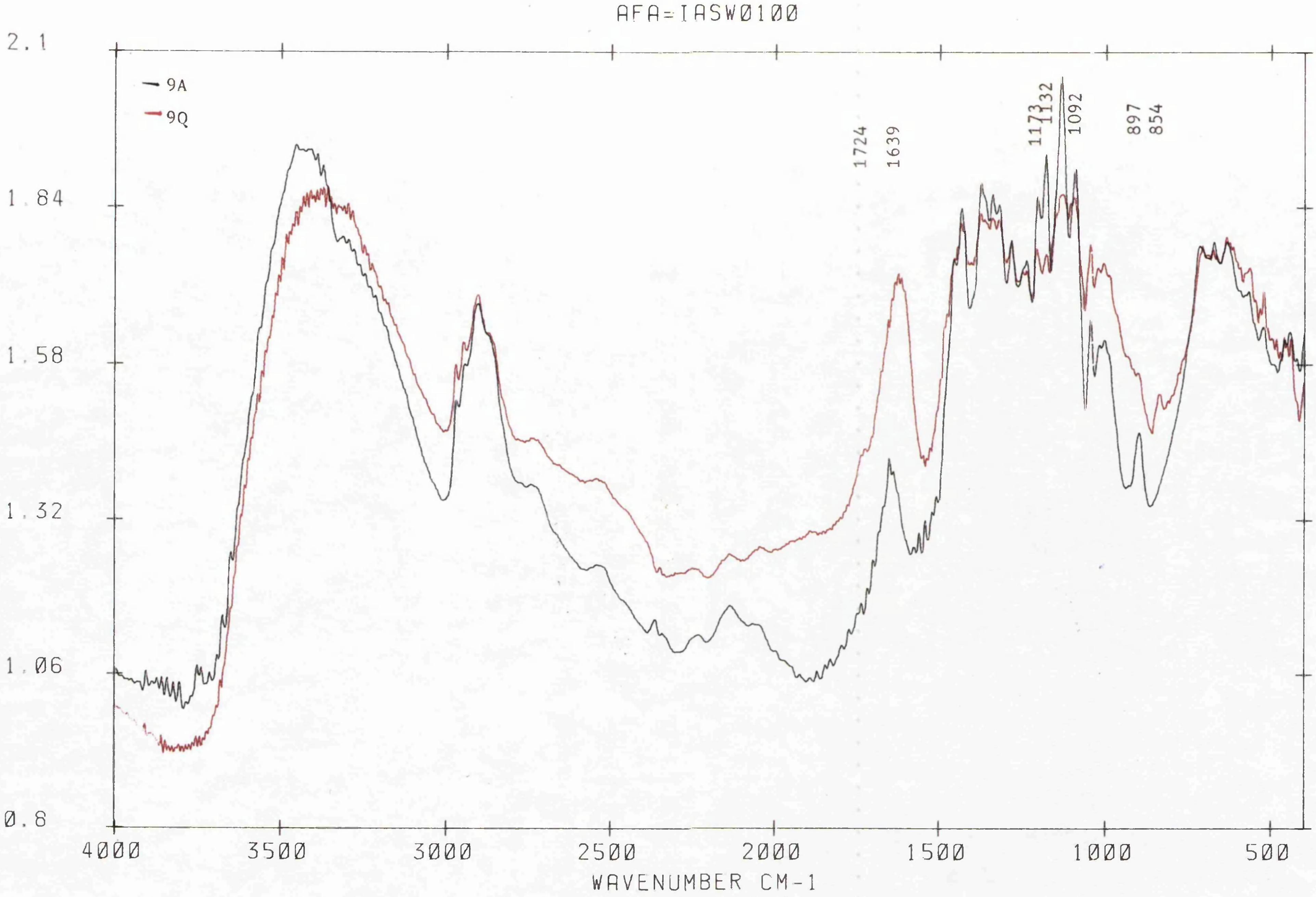
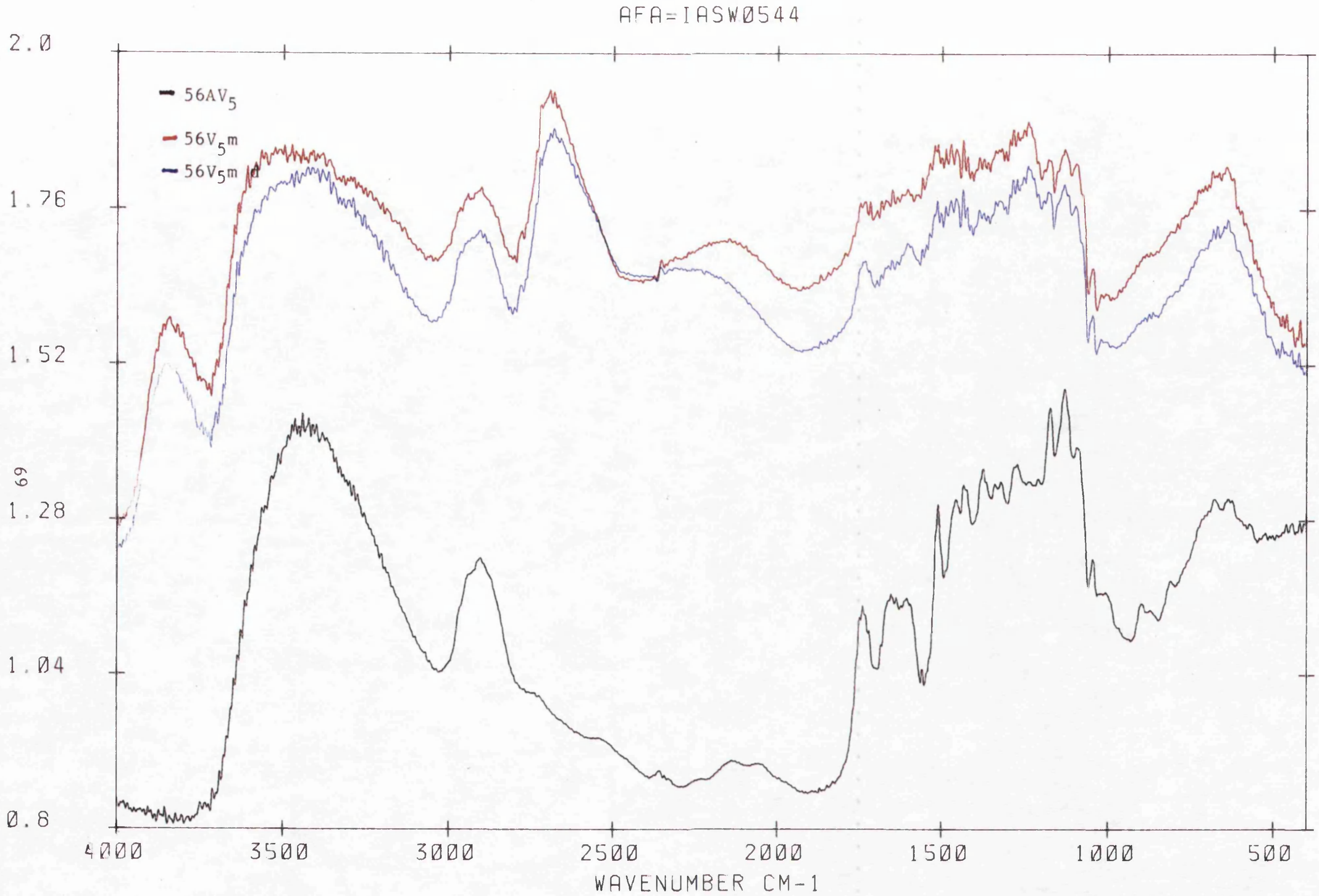

AFA=IASW0100
9A
9Q
2.1
1.84
1.58
1.32
1.06
0.8
1724
1639
1173
1132
1092
897
854
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.13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56AV5
56V5m
56V5m d
2.0
1.76
1.52
1.28
1.04
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.14

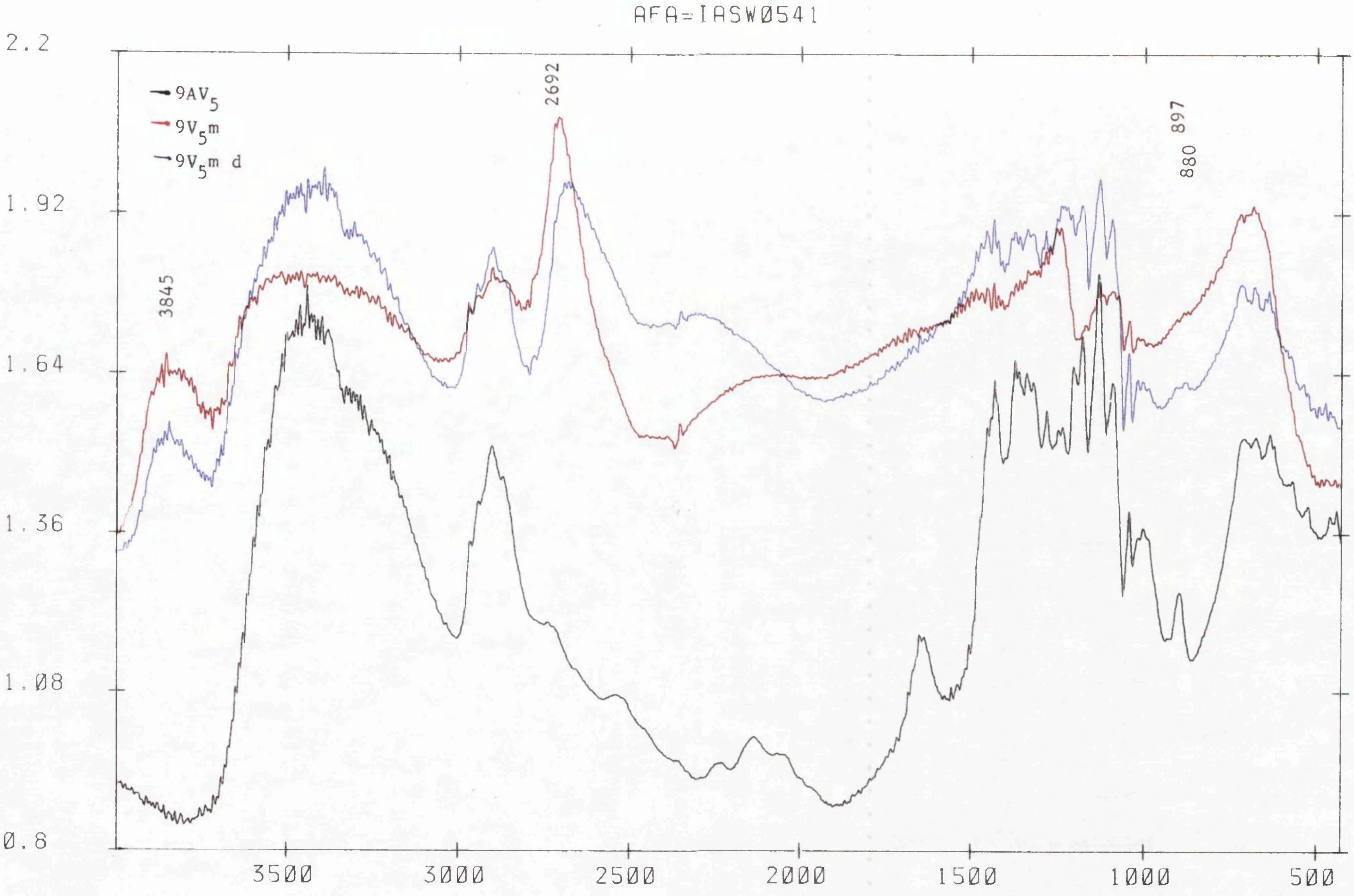

AFA=IASW0541
2.2
1.92
1.64
1.36
1.08
0.8
$9AV_5$
$9V_5m$
$9V_5m$ d
3845
2692
880
897
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.15

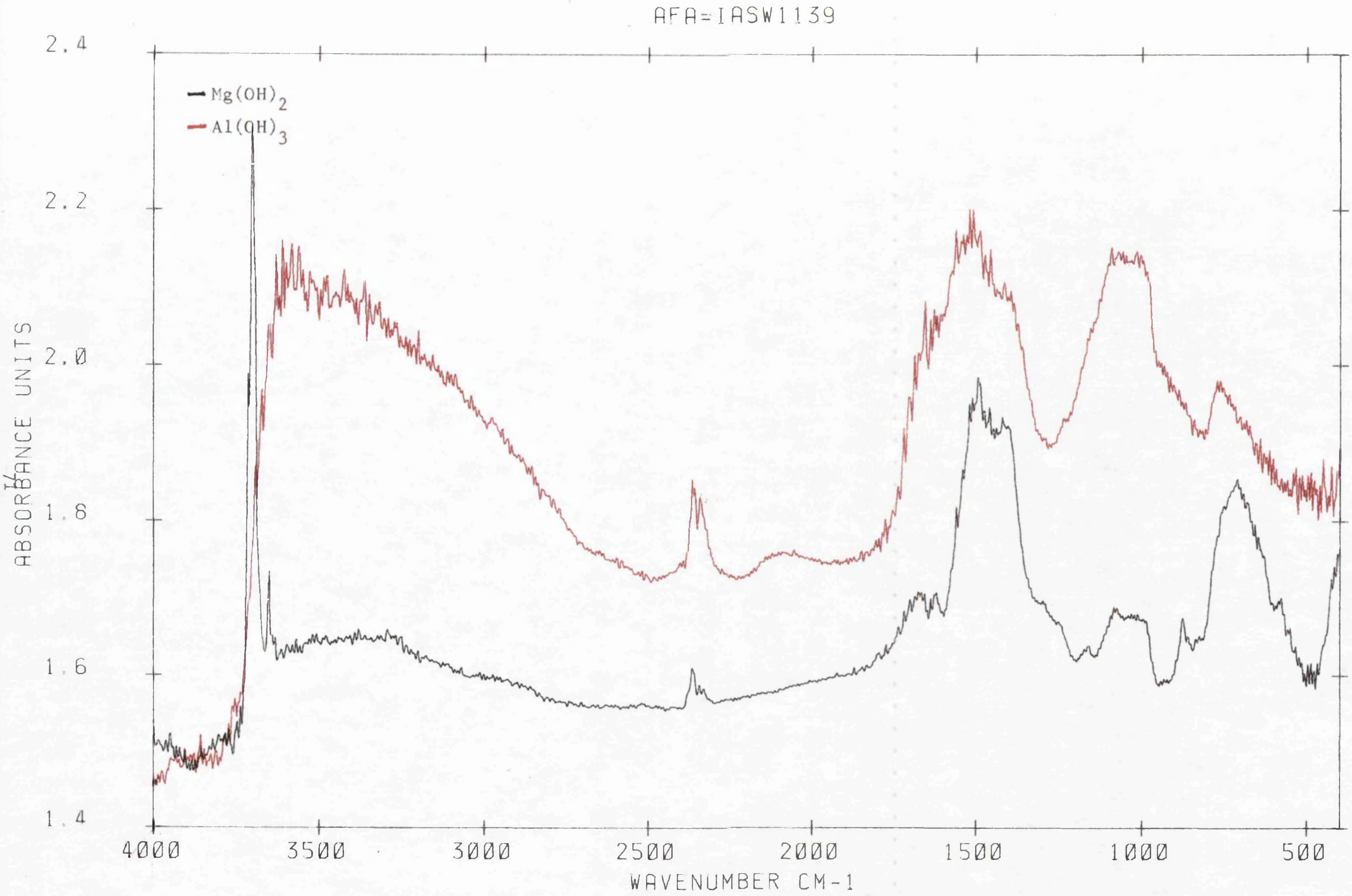

AFA=IASW1139
Mg(OH)2
Al(OH)3
ABSORBANCE UNITS
2.4
2.2
2.0
1.8
1.6
1.4
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.16

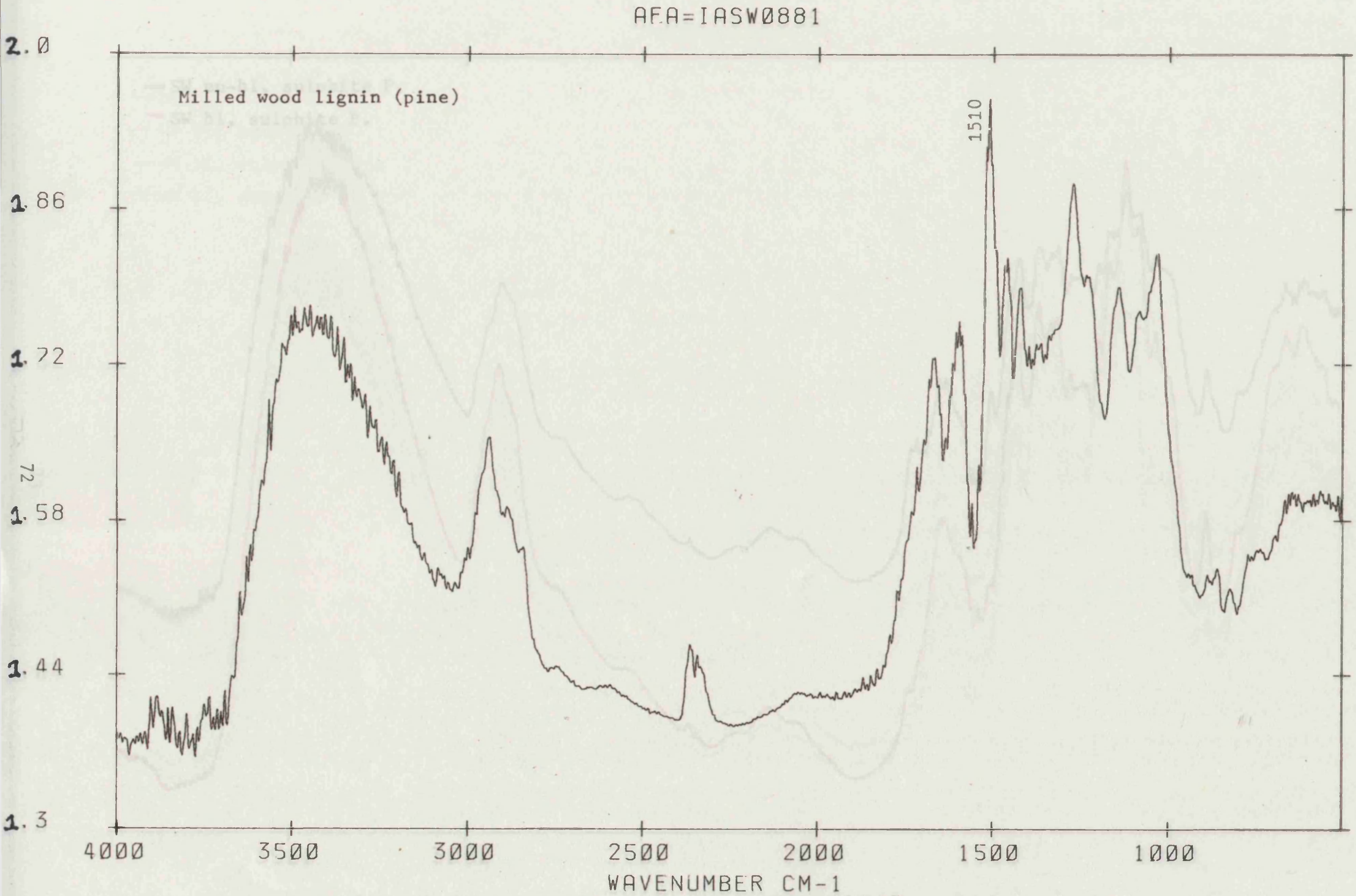

AFA=IASW0881
Milled wood lignin (pine)
1510
2.0
1.86
1.72
1.58
1.44
1.3
4000
3500
3000
2500
2000
1500
1000
WAVENUMBER CM-1

Figure 2.17

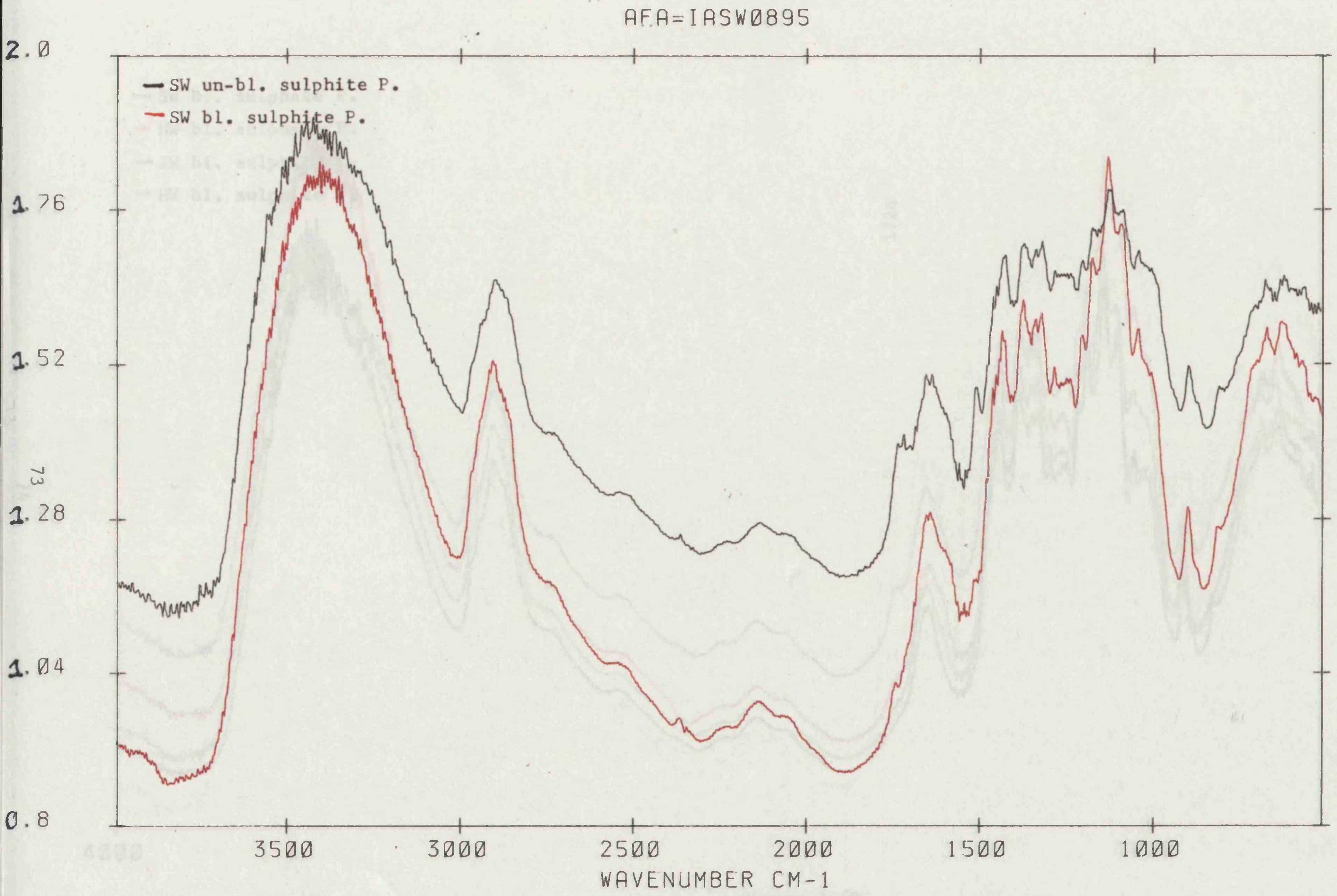

AFA=IASW0895
SW un-bl. sulphite P.
SW bl. sulphite P.
2.0
1.76
1.52
1.28
1.04
0.8
3500
3000
2500
2000
1500
1000
WAVENUMBER CM-1

Figure 2.18

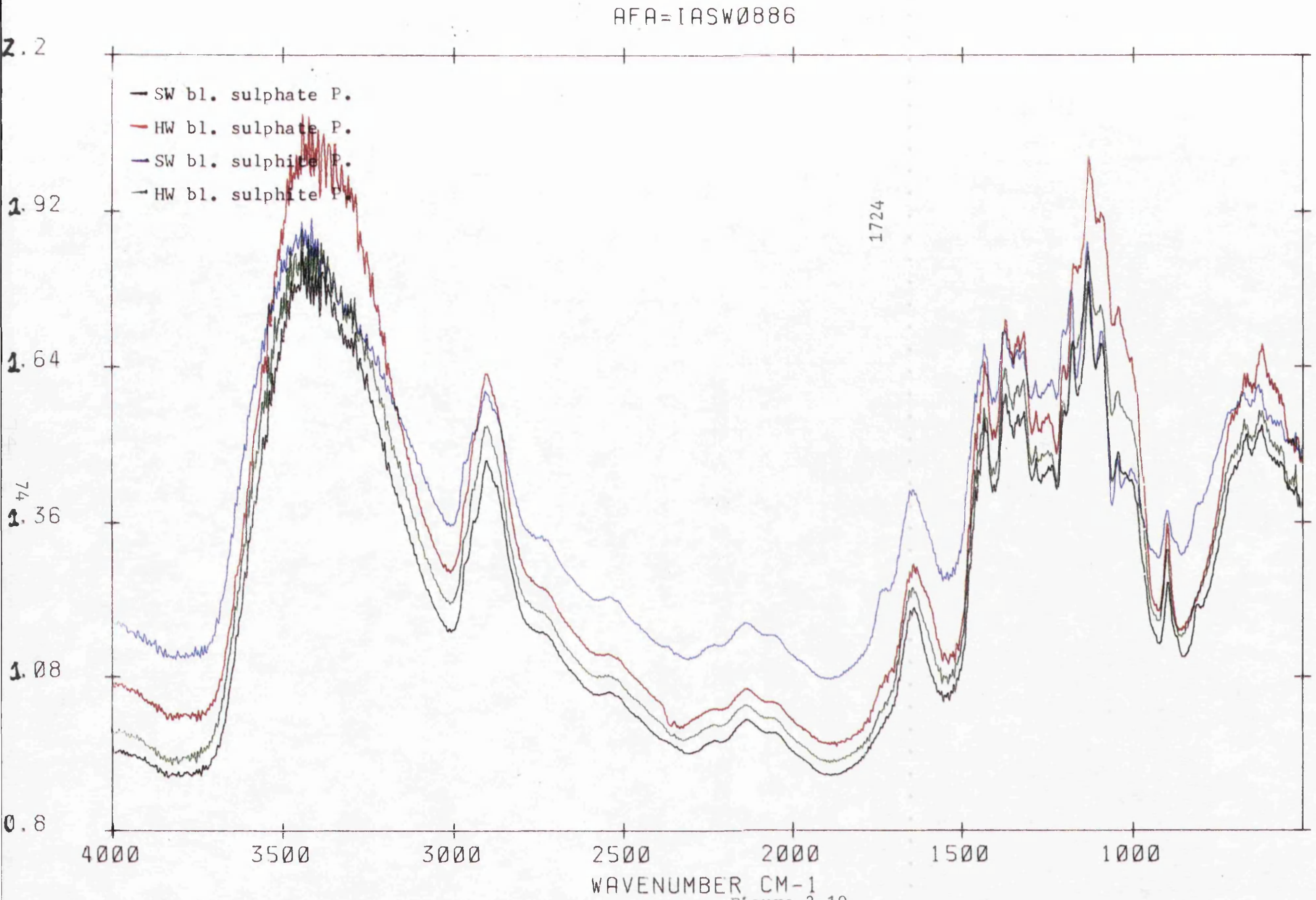

AFA=IASW0886
SW bl. sulphate P.
HW bl. sulphate P.
SW bl. sulphite P.
HW bl. sulphite P.
1724
2.2
1.92
1.64
1.36
1.08
0.8
4000
3500
3000
2500
2000
1500
1000
WAVENUMBER CM-1

Figure 2.19

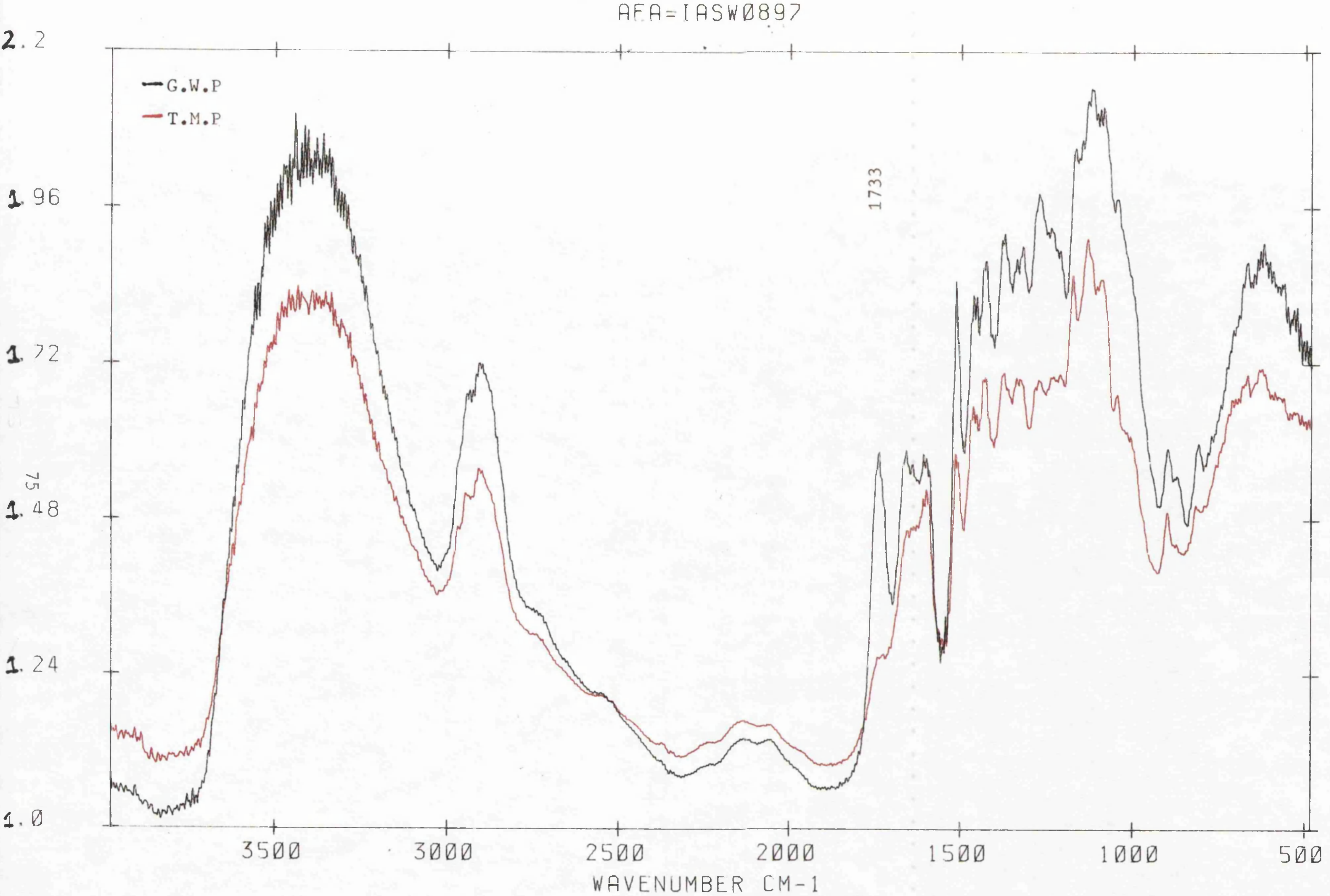

AFA=IASW0897
G.W.P
T.M.P
1733
2.2
1.96
1.72
1.48
1.24
1.0
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 2.20

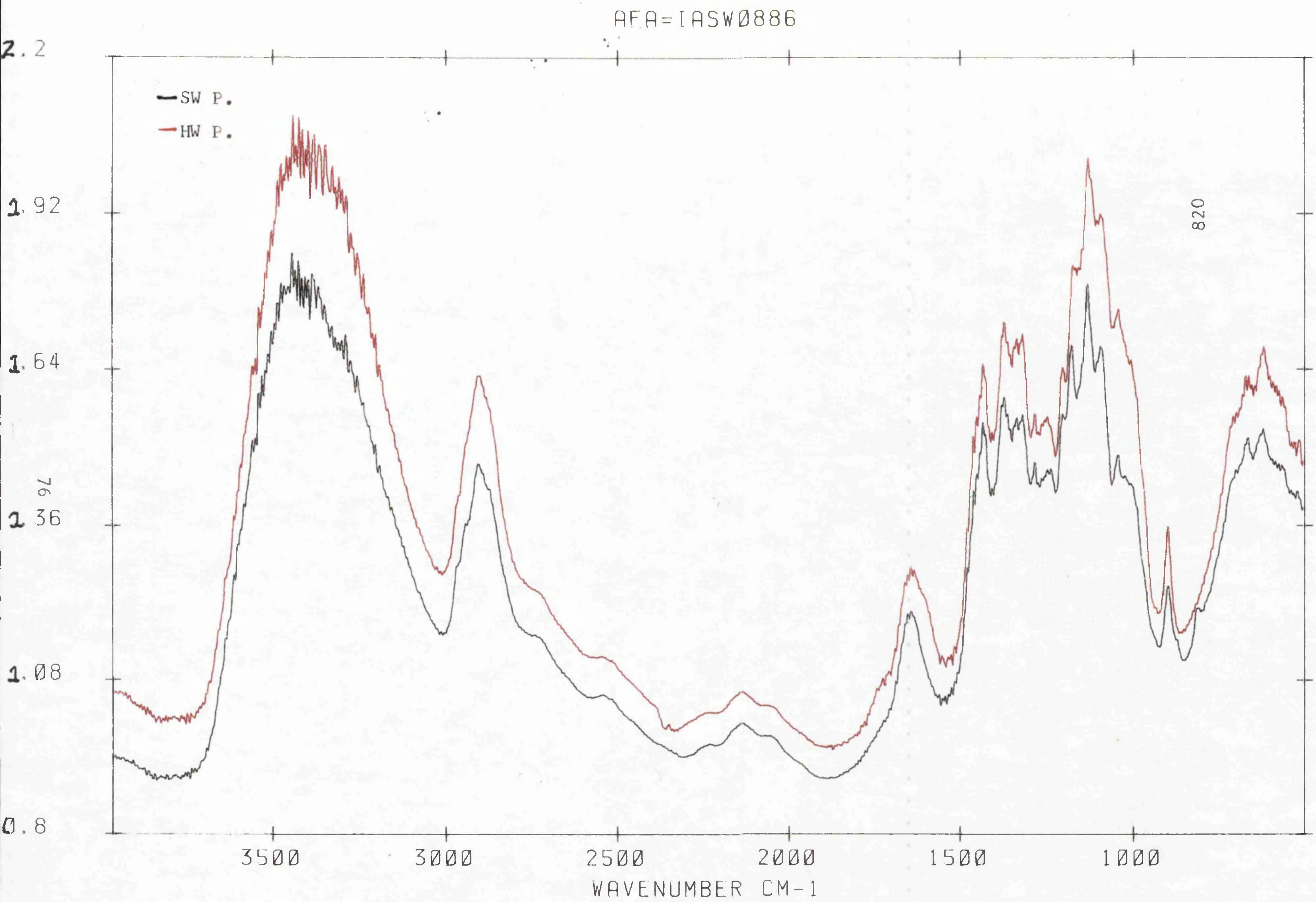

AFA=IASW0886
SW P.
HW P.
2.2
1.92
1.64
1.36
1.08
0.8
3500
3000
2500
2000
1500
1000
WAVENUMBER CM-1
820

Figure 2.21

Chapter 3

DETERIORATION

3.1 INTRODUCTION

This chapter will discuss the deterioration of paper, which was investigated using Fourier transform infrared spectroscopy, measurement of pH and tensile strength. Acidity, one of the major causes of chemical deterioration, was measured and studied in detail. The interpretation of FTIR spectra was based on the information already existing in the published literature.

3.2 RESULTS AND OBSERVATIONS

3.2.1 Light ageing

Light ageing, which was carried out in two different ways (details are given in the second chapter) is reported under their respective sub-headings.

3.2.1.1 Exposure to daylight

Sample No.	No. of days of treatment	Wt. gain/loss %	Surface pH	Tensile strength (kg)
4A 50	0	0.45	5.2	0.4
4 h 50	2	0.17	5.2	0.3
4 h 51	7	0.15	5.1	0.3
4 h 52	14	0.10	5.0	0.3
4 h 53	30	-0.32	5.0	0.2
4 h 54	90	-0.64	4.4	0.2
62 A 50	0	0.63	6.0	2.8
62 h 50	2	0.84	6.0	2.6
62 h 51	7	0.88	6.0	2.4
62 h 52	14	0.08	5.9	2.4
62 h 53	30	0.08	5.9	2.4
62 h 54	90	-0.82	4.3	1.9
63 A 50	0	0.74	6.5	3.0
63 h 50	2	0.74	6.5	2.4
63 h 51	7	0.56	6.5	2.2
63 h 52	14	0.56	6.5	2.1
63 h 53	30	0.51	6.2	2.0
63 h 54	90	1.12	5.2	1.9

TABLE 3.1: Changes in weight, surface pH and tensile strength of old and modern newsprint and Whatman No.1 on daylight ageing

Modern newspaper samples exposed to daylight for three months became yellowish and showed an obvious decrease in intensity of the peak at 1510 cm^{-1} (Figure 3.1), although old newsprint which was partly deteriorated did not show much change in colour or intensity of the 1510 cm^{-1} peak (Figure 3.2). The peak at 1456 cm^{-1} in groundwood papers decreased or disappeared on exposure to dayight. Whatman No. 1 did not show any noticeable change in physical appearance or in FTIR spectra except for the sample exposed to daylight for three months, which showed the disappearance of the peaks at 897 cm^{-1}, 1020 cm^{-1}, an overall decrease in intensities of the peaks mainly in the region of 1000 - 1500 cm^{-1}, and the appearance of a peak at 1724 cm^{-1} (Figure 3.3).

When samples were exposed to daylight for various periods up to three months, weight change, surface pH, tensile strength (Table 3.1) and peak intensities of the peaks at 1510 cm^{-1} and 1724/1747 cm^{-1} were recorded with reference to the peak intensity at 1433 cm^{-1} (Table 3.2).

Sample No.	No.of days of the treatment	Rel. pk intensities w.r.t. the peak at 1433 cm^{-1}	
		1724/1747	1510
4A 50	0	0.2043	0.3414
4h 50	2	0.2064	0.3281
4h 51	7	0.2222	0.2997
4h 52	14	0.2051	0.2928
4h 53	30	0.2616	0.2771
4h 54	90	0.2708	0.2656
62 A 50	0	0.2667	0.4268
62 h 50	2	0.2792	0.4009
62 h 51	7	0.2957	0.3683
62 h 52	14	0.3246	0.3370
62 h 53	30	0.3696	0.2929
62 h 54	90	0.3955	0.2458
63 A 50	0	0.0983	
63 h 50	2	0.0923	
63 h 51	7	0.0909	
63 h 52	14	0.0901	
63 h 53	30	0.0976	
63 h 54	90	0.2705	

TABLE 3.2: Variation of FTIR peak intensities with time on daylight ageing of old and modern newsprint and Whatman No.1.

3.2.1.2 Exposure in Fadeometer

Fadeometer ageing for 96 hours, which is equivalent to direct sunlight exposure for 960 hours, caused a remarkable change in colour and also in the FTIR spectra of modern groundwood papers (Figure 3.4). The FTIR spectra of old newsprint exposed for 96 hours, also showed a change, although not as prominent as in modern newsprint (Figure 3.5). The obvious changes noted are the decrease of the peaks at 1510 cm^{-1} and 1456 cm^{-1} , and an increase of the peak at 1724 /1747 cm^{-1} in the FTIR spectra of both old and modern newsprint aged for 96 hours. In addition, the specta of modern newsprint showed a decrease in intensity of the peak at 1280 cm^{-1}. The FTIR spectra of Whatman paper did not show any change on 96 hours exposure in the fadeometer.

Among the Whatman samples exposed in the fadeometer for significantly longer periods, the sample exposed for three months showed a change, in the form of the appearance of a new peak in the FTIR spectra at 1724 cm^{-1} (Figure 3.6).

Sample No.	No. of days of treatment	Wt. gain/loss %	Surface pH	Tensile strength (kg)
4A 50	0	0.45	5.2	0.4
4 U 50	2	-0.33	3.9	0.3
4 U 51	7	-1.35	3.5	0.2
4 U 52	14	-2.94	3.5	0.1
4 U 53	30	-6.53	3.5	0.0
4 U 54	90	-10.43	3.2	0.0
62 A 50	0	0.63	6.0	2.8
62 U 50	2	-0.04	4.1	2.6
62 U 51	7	-1.95	3.5	2.0
62 U 52	14	-4.22	3.1	1.0
62 U 53	30	-8.81	2.9	0.8
62 U 54	90	-12.36	2.8	0.8
63 A 50	0	0.74	6.5	3.0
63 U 50	2	0.49	5.5	2.6
63 U 51	7	0.34	5.0	2.4
63 U 52	14	-0.13	4.8	2.3
63 U 53	30	-0.59	4.6	1.7
63 U 54	90	-1.32	3.9	1.4

TABLE 3.3: Changes in weight, surface pH and tensile strength of old and modern newsprint and Whatman No. 1 on fadeometer ageing

Modern and old newsprint showed a considerable increase in the intensity of the peak at 1724/1747 cm^{-1}, and a considerable decrease in the intensity of the peak at 1510 cm^{-1}, which varied with increased time of ageing. The intensity increase of the peak at 1680 cm^{-1}, compared with that of 1724/1747 cm^{-1}, is negligible in newsprint exposed in the fadeometer for different periods of time varying from 96 hours up to three months.

The weight loss, surface pH, tensile strength (Table 3.3) and intensities of the 1510 cm^{-1} and 1724/1747 cm^{-1} peaks with respect to that at 1433 cm^{-1} (Table 3.4), were recorded.

3.2.2 Heat ageing

Samples (Whatman no.1, modern and old newsprint) were aged in an oven at 60°C and 60% RH for different time periods up to three months. FTIR spectra of these samples did not show any obvious differences except for the decrease or disappearance of the peak at 1456 cm^{-1}. The relative intensities were recorded as in 3.2.1.1, but did not show any effects similar to light ageing in any of the samples. The weight loss, surface pH, tensile strength and relative intensities recorded are given in Tables 3.5 and 3.6.

Sample No.	**No. of days of treatment**	**Rel. pk. intensities w.r.t the peak at 1433cm^{-1}**	
		1747/1724	**1510**
4A 50	0	0.2043	0.3414
4U 50	2	0.2395	0.2649
4U 51	7	0.2678	0.2063
4U 52	14	0.2873	0.1306
4U 53	30	0.2759	0.1049
4U 54	90	0.3078	0.0163
62 A 50	0	0.2667	0.4268
62 U 50	2	0.3478	0.3445
62 U 51	7	0.4002	0.2005
62 U 52	14	0.4193	0.0448
62 U 53	30	0.4515	0.0149
62 U 54	90	0.4525	0.0026
63 A 50	0	0.0983	
63 U 50	2	0.0942	
63 U 51	7	0.0943	
63 U 52	14	0.0943	
63 U 53	30	0.0942	
63 U 54	90	0.1628	

TABLE 3.4: Variation of FTIR peak intensities with time on fadeometer ageing of old and modern newsprint and Whatman No.1.

3.2.3 Chemical ageing

Paper samples were chemically aged as described in chapter 2.

3.2.3.1 Acid treatments

A Whatman No.1 sample was treated with 0.001N sulphuric acid, and another sample was treated with the same acid, followed by rinsing with water. The latter did not show any changes, but the spectrum of the sample treated with acid showed a change in the shape of the peak at 3330-3550 cm^{-1}, and the intensity of the peak at 3325 cm^{-1} increased (Figure 3.7). Other samples of Whatman No.1 were treated with 2N sulphuric acid followed by oven ageing at 60°C for periods of 1 day, 7 days and 10 days, and rinsed with water; and samples were also treated under the same conditions, except for subsequent deacidification with calcium hydroxide and calcium bicarbonate. The FTIR spectra of samples treated with sulphuric acid and oven aged for 7 days ($9X_2B$) and 10 days ($9X_4B$) showed a change in the shape of the peak at 1235 cm^{-1} and the appearance of a peak at 1724 cm^{-1} as a branch of 1639 cm^{-1} peak. Samples treated with calcium hydroxide and calcium bicarbonate after the acid treatment and ageing ($9X_5BF$), showed the disappearance of 1724 cm^{-1} peak, and the peak at 1235 cm^{-1} changed back to its normal shape in the FTIR spectrum (Figure 3.8).

Sample No.	No. of days of treatment	Wt. gain/loss %	Surface pH	Tensile strength (kg)
4A 50	0	0.45	5.2	0.4
4 V 50	2	0.35	5.0	0.3
4 V 51	7	0.87	4.9	0.3
4 V 52	14	1.59	4.8	0.2
4 V 53	30	0.86	4.6	0.1
4 V 54	90	0.92	4.0	0.1
62 A 50	0	0.63	6.0	2.8
62 V 50	2	0.83	5.8	2.6
62 V 51	7	1.77	5.8	2.5
62 V 52	14	2.87	5.3	2.2
62 V 53	30	1.60	5.3	2.0
62 V 54	90	1.42	5.0	2.0
63 A 50	0	0.74	6.5	3.0
63 V 50	2	0.84	5.9	2.6
63 V 51	7	1.60	5.9	2.6
63 V 52	14	2.65	5.9	2.6
63 V 53	30	0.37	5.8	2.6
63 V 54	90	1.64	5.4	2.6

TABLE 3.5: Changes in weight, surface pH and tensile strength of old and modern newsprint and Whatman No.1 on heat ageing

Sample No.	No.of days of the treatment	Rel. pk. intensities w.r.t the peak at 1433 cm^{-1}		Peak Area 3700-3000 (OH region)
		1724/1747	1510	
4A 50	0	0.2043	0.3414	91.60
4V 50	2	0.1924	0.3368	118.30
4V 51	7	0.2056	0.3100	91.19
4V 52	14	0.2032	0.3048	89.04
4V 53	30	0.1758	0.2735	119.72
4V 54	90	0.2203	0.3106	86.19
62 A 50	0	0.2667	0.4268	174.29
62 V 50	2	0.2435	0.4117	214.40
62 V 51	7	0.2384	0.4072	193.40
62 V 52	14	0.2450	0.4163	183.08
62 V 53	30	0.2462	0.4231	212.11
62 V 54	90	0.2547	0.4183	195.95
63 A 50	0	0.0983		262.05
63 V 50	2	0.1026		291.00
63 V 51	7	0.0815		290.43
63 V 52	14	0.0844		282.91
63 V 53	30	0.0913		286.93
63 V 54	90	0.1093		269.52

TABLE 3.6: Variation of FTIR peak intensities and peak area of the hydroxyl region with time on oven ageing of old and modern newsprint and Whatman No.1

3.2.3.2 *Ozone treatment*

After exposing paper samples (Whatman, old and modern newsprint) to ozone for two months, no changes were observed in the paper itself or in the FTIR spectra, except in the case of modern newsprint which showed a decrease in the intensities of the peaks at 1456 and 1510 cm^{-1} (Figure 3.9).

3.2.4 Acidity

In order to investigate the nature and quality of the acidity in papers, the various paper samples were examined. The recorded peak areas in the range 3700-3000 cm^{-1} in the FTIR spectra, the surface pH of the paper samples, and the acid content present in filtered and unfiltered extracts of paper samples, are given in Table 3.7.

Sample No.	Surface pH	Extract pH	Acidity (µm/g)	Ratio of the acid content	Buffering action	Peak area 3700-3000 cm^{-1}
1a	6.0	6.0	7.2	2.9: 1	pH 7	-
1b	6.0	6.6	2.5			-
2a	4.7	4.6	31.9	1.8: 1	pH 7	178
2b	4.9	5.2	18.2			221
3a	6.5	7.2	0.0			186
3b	7.0	7.2	0.0			146
4a	4.0	3.7	143.6	1.9: 1	pH 7	94
4b	4.0	4.0	75.2			118
5a	4.6	5.3	12.5	1.2: 1		158
5b	4.6	5.3	10.1			146
6a	4.7	4.7	15.1	2.8: 1	pH 4.7	109
6b	4.7	5.5	5.4		pH 4.7	141
7a	4.0	4.3	60.7	1.8: 1	pH 7.0	77
7b	4.0	4.9	33.3		pH 7.0	60
8a	4.3	4.4	42.8	1.6: 1		301
8b	4.3	4.6	26.9			316
17a	4.4	4.2	88.4	2.6: 1	pH 7.0	187
17b	4.3	4.5	33.5			172
54a	4.8	5.2	18.2	2.5: 1		210
54b	4.7	6.0	7.4			199
55a	4.2	4.2	73.0	1.9:1	pH 4.2	81
55b	4.2	4.5	39.2		pH 4.2	86

a - extracted and unfiltered   b - extracted and filtered

TABLE 3.7: Acidity and peak area of the hydroxyl region in FTIR spectra of different paper samples

3.3 DISCUSSION AND CONCLUSIONS

3.3.1 Deterioration

Deterioration has been discussed in two sections under ageing and acidity, on which the author has carried out experiments under this investigation.

3.3.1.1 Ageing

As described previously the ageing has been carried out in different ways in order to evaluate the deterioration.

3.3.1.1.1 *Heat ageing*

Heat ageing did not show any changes in the spectra of Whatman samples. The FTIR spectra of old and modern newsprint only showed an increase in the intensity of the peak at 1456 cm^{-1} in the early stages (i.e. five days) of ageing, and was then followed by a decrease in the intensity of that peak, which finally disappeared on prolonged ageing. It may be that the other functional groups which are affected by heat ageing, except for the group represented by the peak at 1456 cm^{-1}, do not clearly show up in the spectra, due to masking of that particular group (s) by another group (s). At the beginning of the treatment the intensity of the peak at 1456 cm^{-1} increased, perhaps due to a change in crystallinity, as the oven ageing was carried out at 60% RH. The decrease in intensity and final disappearance of the peak at 1456 cm^{-1}, which has been assigned to C-H stretching in OCH_3 (Appendix 4), may be interpreted as a result of decomposing the methoxy group. The other changes which occurred may also have been very small and unable to be detected by FTIR . Cellulose is remarkably stable towards thermal degradation (Kilzer, 1971). Back et al. (1963) suggested that cross-linking occurs during thermal treatment of ligno-cellulosic and cellulose papers, and discussed the effect of auto-cross-linking (Back et al., 1967) on the thermal softening of cellulose, which has been defined as the melting transformation of cellulose crystallities (Goring, 1963 and 1966; Gupta, 1962; Chaterjee and Schwenker, 1972). If there was auto-cross-linking to a significant extent, the FTIR spectra of heat-aged samples should show a decrease in the peak area of the hydroxyl region as a result of the formation of additional hydrogen bonding. The data in Table 3.6 indicates that there was no consequential decrease in peak areas with the increase in the duration of ageing.

It is believed that moisture and oxygen play important roles in the thermal degradation at or below 100°C (Wiegerink, 1940; Heuser, 1944; Chatterjee and Schwenker, 1972). Since heat ageing was carried out at 60% RH, there was every possibility of initiating degradation, although no changes except for the intensity change in the peak at 1456 cm^{-1} in groundwood papers were visible. The initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration and decarboxylation (Chatterjee and Schwenker, 1972). Rogers and Ohlemiller (1980) proposed a depolymerization mechanism, assisted by oxidation, for cellulosic materials. They proposed that a hydroxyl radical was first produced from a C_1 radical of the glycoside linkage and then cyclization by oxygen achieved leading to carbonyl segments, as a result of the cleaving of molecular chains and the hydroxyl radical being driven off. This radical reaction leads to the formation of aldehyde and carboxyl groups in the initial stage of cellulose oxidation (Rogers and Ohlemiller, 1980). If there was any such change to a significant extent, the FTIR spectra should indicate them, unless the relevant peaks were masked by others. Although the FTIR spectra did not show much change, this does not mean that there was no heat ageing in the samples under the conditions of treatment, but it appears that heat ageing, i.e. mainly hydrolysis, of Whatman and old and modern newsprint cannot be readily detected using FTIR.

3.3.1.1.2 *Light ageing*

When the samples are exposed to visible light or ultraviolet (UV) light, photochemical reactions take place. Since paper mainly consists of cellulose, it is advisable to consider the behaviour of cellulose towards light ageing. The degradation of cellulose by light leads to the formation of oxidized cellulose (oxycellulose) (Harrison, 1914, Baugh and Phillips, 1971). The degradation results in the production of carboxyl and carbonyl groups in the cellulose (Turner, 1920; Barr and Hadfield, 1927; Scharwin and Pakschwer, 1927; Haller and Wyszewianskii, 1936; Baugh and Phillips, 1971) and a decrease in the tensile strength of the material (Herman and Sommer, 1925; Baugh and Phillips, 1971). Whatman paper, which is almost pure cellulose, does not show any changes in the FTIR spectra of samples aged in the presence of daylight and in the fadeometer for up to 30 days. A Whatman sample aged for three months in the same manner, showed a change in the FTIR spectrum, by the appearance of a new peak at 1724 cm^{-1} (Figures 3.3 and 3.6) which has been assigned to free carboxylic acid groups (Appendix 4). Hence, it supports the evidence for the production of carboxylic acid groups in the process of light degradation, although the degradation starts at a later stage than in other papers, proving that pure cellulose papers are generally very stable. When the samples were exposed to light, thermal degradation could also have occurred, as the light source provided some heat. The peak at 897 cm^{-1}, which can be assigned for the C_1 group frequency and/or the C-OH stretching frequency (Appendix 4), disappeared in the spectra of Whatman samples exposed to daylight for 3 months. Hence, this may be evidence in support of Rogers and Ohlemillers proposition of oxidatively assisted depolymerization in light ageing, which induces thermal degradation and/or the production of carboxyl and carbonyl groups (Barr and Hadfield, 1927; Baugh and Phillips, 1971), as a result of the oxidation of the C-OH group. It was also observed that the tensile strength decreased with the increase of time of ageing (Tables 3.1 and 3.3) and hence the author agrees with Herman and Sommer .

3.3.1.1.2.1 Cellulose

The exact mechanism of the photochemical degradation of cellulose is difficult to ascertain, and some analogy may be drawn with acid hydrolysis, i.e. cleavage of the glucosidic bond, which has been assumed by most investigators (Baugh and Phillips, 1971). The mechanism of acid hydrolysis of cellulose is also interpreted in different ways (Section 1. 2.2.1.1). From the name of the process itself, it is understood that acid hydrolysis takes place as a result of protonation of oxygen in cellulose, although it is not yet certain whether the protonation occurs at a ring oxygen or a glucosidic oxygen or both. The mechanism and the reaction products may vary according to the location of the protonation. In acid hydrolysis, the possibility of rupturing in the vicinity of C_1, C_2, or C_3 of the glucose residues, rather than at the glycosidic linkage, was suggested by Launer and Wilson (1943, 1949, Baugh and Phillips, 1971). The disruption of the bond between C_1 and C_2 would not necessarily cause an immediate rupture of the cellulose chain. It is also stated that the photochemical reaction occurs at the lactol carbon atom, which is consistent with the view that this is the primary absorbing site, as the initial product of photodegradation is D-gluconic acid, and is followed by the production of D-arabinose (Baugh and Phillips, 1971). FTIR spectroscopic analysis only shows the appearance of new carboxylic acid groups in the context of the pure cellulose paper (Whatman) in the process of deterioration . Hence, it is difficult to identify the mechanism of acid hydrolysis, i.e. the location of the oxygen atom(s) subject to protonation in cellulose, using FTIR studies alone.

Modern and old newsprints contain a reasonable amount of lignin and hemicellulose in addition to the main component which is the cellulose. Both lignin and hemicellulose are less stable than cellulose. Lignin can be oxidized very easily in the presence of oxygen and light.

3.3.1.1.2.2 Lignin

With exposure to daylight and in the fadeometer, the FTIR spectra of the newsprints showed a decrease in the peak intensities at 1510 cm^{-1} and 1456 cm^{-1} (Figures 3.1, 3.2, 3.4 and 3.5) which have been assigned as the lignin peaks (Hergert, 1971) and the C-H stretching in OCH_3 (Appendix 4) respectively, and an increase in the intensity of the peak at 1724/1747 cm^{-1} which has been assigned for free carboxylic acid groups and carbonyl groups in esters (Appendix 4). The decrease in the peak intensities at 1510 cm^{-1} (Table 3.2 and 3.4) and at 1456 cm^{-1} even after exposure to light for only 2 days shows the instability of lignin. It is stated that on irradiation by daylight the methoxyl content of lignin decreases (Forman, 1940; Leary, 1968; Sinclair and Vincent, 1964; Lin and Kringstad, 1970 b). It was observed that especially when modern newsprints were exposed to daylight or in the fadeometer, the peaks at 1510 cm^{-1} and 1456 cm^{-1}

disappeared first. Thus, if one accepts Forman's idea, the methoxy (OCH_3) group in lignin can be assigned to the peak at either 1510 cm^{-1} or 1456 cm^{-1} or both . When a modern newsprint was treated with sodium hydroxide solution, the peak at 1510 cm^{-1} disappeared, and it reappeared when the sample was subsequently washed with water. It seemed, therefore that sodium hydroxide could replace the functional group(s) which represent the peak at 1510 cm^{-1}. In general, OCH_3 groups are stable. The observations suggest that, since the peak at 1510 cm^{-1} disappears in the presence of light, the functional group which represents the peak cannot be assigned to the methoxyl group, as the group involved reacted with sodium hydroxide and was regenerated in washing, which is not a characteristic of a methoxy group. Thus this group is not a methoxy group. The peak at 1510 cm^{-1} might be due to phenolic OH, as it might have formed a sodium salt with the sodium hydroxide treatment, which could hydrolyse on washing. Nevertheless there is a possibility that phenolic OH can undergo free radical reactions easily when exposed to light. Photochemical reactions of lignin involve free radical intermediates (Lin and Kingstad, 1970 a). According to the literature, the peak at 1510 cm^{-1} is due to aromatic skeletal vibrations (Appendix 4). Hence the 1510 cm^{-1} peak can be assigned as the aromatic skeletal vibrations in phenolic compounds and phenolic hydroxyl groups in lignin. Thus the disappearance of the peak at 1510 cm^{-1} apparently results from a loss in phenolic and aromatic character. The peak at 1456 cm^{-1} can be assigned for C-H stretching in OCH_3 groups in lignin as is suggested in the literature (Appendix 4), and is also consistent with the observations described here, in considering the fact that on irradiation the methoxyl content decreases in lignin (Forman, 1940). Although the author agrees with Forman, the possible mechanism involved in losing the methoxy group is far from clear. In the process of photochemical reactions of lignin, the oxidation of phenolic compounds to quinonoid structures occurs, and hence results in the yellow colouration in newsprints (Hon, 1981; Lyall, 1982) , and also, the degradation of lignin by light can form vanillin and some organic acids (Figure 3.10).

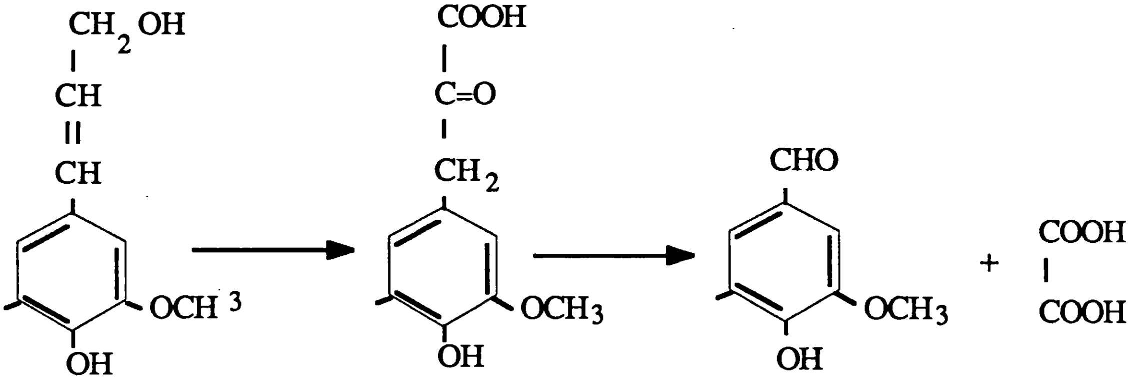


FIGURE 3.10: Formation of organic acids in lignin degradation

The results observed show an intensity decrease or disappearance of the peaks at 1510 cm^{-1} and 1456 cm^{-1}, and an intensity increase of the peak at 1724/1747 cm^{-1} (Figures 3.1, 3.2, 3.4, 3.5 and Tables 3.2, 3.4) , in FTIR spectra of old and modern newsprints exposed to light. They confirm that the photochemical reactions involve free radical intermediates, and form organic acids in the process of light ageing of lignin. Thus lignin is subject to oxidation in the presence of UV light. It was observed that the fadeometer exposure showed remarkable changes and slight changes in modern newsprints and old newsprint respectively, even on exposure for only two days . When the paper is exposed to UV radiation, ozone can be formed in air and it can oxidize paper and increases the oxidation state of the surface. It can seriously damage the fibre wall in paper, while the damage to the same is slight on exposure to sunlight (Li, 1987). Although the old newsprints showed changes in FTIR spectra, they were not as intense as in the modern newsprints, and this may be due to the fact that the existing lignin in old newsprints was already partially degraded, as lignin is highly unstable. Browning (1967) has stated that the intensity of the band at 1500 cm^{-1} is affected only a little by many of the chemical reactions of the lignin, and it can be used to determine lignin content. With the FTIR spectroscopic studies undertaken in this project, the author has already showed the changes which occur in the peak at 1500 cm^{-1} (1512 cm^{-1}) with various chemical reactions, and hence disagrees with Browning in this respect.

3.3.1.1.3 *Chemical ageing*

The experiments were carried out as discussed in the chapter 2 and results have been reported under the following headings as acid and ozone play a predominant role in the deterioration of paper.

3.3.1.1.3.1 Acid treatment

FTIR spectra of the samples of acid-treated Whatman paper which was then oven aged, indicated the presence of carboxylic acid groups (the appearance of a peak at 1724 cm^{-1}), which were formed due to the acid hydrolysis and oxidation of cellulose. They also showed a change in the shape of the peak at 1235 cm^{-1}, which has been assigned to C-O stretching (Appendix 4) , and which may be due to the protonation of the oxygen atom in the glucose ring resulting in a change in C-O stretching.

3.3.1.1.3.2 Ozone treatment

It is concluded that the fact that there are no changes in the FTIR spectra of the Whatman samples treated with ozone may be because of the difficulty in observing the degradation of pure cellulose, as cellulose is highly stable towards oxidation . In the case of lignin, complete degradation of an aromatic nucleus occurs because of the ozonation, forming mainly an aliphatic acid, which causes the original side chain attached to the carboxylic group, originating from the C_1 of an aromatic nucleus (Matsumoto, Ishizu and Nakano, 1986). Hence, FTIR spectra should show the appearance of, or an increase in, a peak at 1724 cm^{-1} which has been assigned for free aliphatic carboxylic acid groups (Appendix 4), and a decrease in the intensity of the peak at 1510 cm^{-1} which is assigned for aromatic skeletal vibrations and phenolic hydroxyl groups (Appendix 4) in groundwood paper samples. Although there was no change in the FTIR spectra of old newsprints treated with ozone, it was observed that there was the disappearance of the peak at 1456 cm^{-1} and a decrease in intensity of the peak at 1510 cm^{-1} in FTIR spectra of modern newsprint treated with ozone (Figure 3.9). Although there was no indication of a peak appearing at 1724 cm^{-1}, the observations support the mechanism of losing aromatic character and phenolic hydroxyl groups in the process of ozonation as the result of oxidation. Also, it showed a loss of methoxyl groups in the process of ozonation. As the old newsprints have already been subjected to the process of degradation, there was no possibility in observing the changes described above.

3.3.1.2 Raw materials

The degradation of paper depends on a number of factors, one of them being the raw materials used in its manufacture. The identification of the raw materials and additives in paper was attempted using FTIR spectroscopy. The papers containing groundwood could easily be distinguished by the additional peaks in the region 1500-1700 cm^{-1}, which are not to be seen in chemically treated wood papers and rag papers (Figure 3.11). The thermomechanical wood papers can be distinguished from groundwood papers, as the peak at 1733 cm^{-1} in FTIR spectra of groundwood pulp is not visible in FTIR spectra of thermomechanical pulp (Figure 2.20). An attempt was made to distinguish softwood from hardwood fibres. It is stated that the IR spectra of softwood and hardwood lignins show essentially the same absorption bands, differences being observed in their intensity. In some cases, weak bands which do not exist in the spectra of softwood lignins, are observed in those of hardwood lignins (Philipchuk et al., 1968). Balhar and Miklosova (1970) concluded that in the identification of softwood and hardwood the respective bands at 822-825 cm^{-1} and 835-842 cm^{-1} due to CH vibrations can be used. The author observed that the spectra of paper pulps prepared from softwood and hardwood are essentially the same, except that the peak at 820 cm^{-1} is visible only in softwood pulps (Figure 2.21). The asymmetrically tri-substituted compounds of the guaiacyl type with different substituents in position one, all showed a band at 822-825 cm^{-1} (Balhar and Miklosova, 1970). Although both types of lignin contain a guaiacyl nucleus, in hardwood it is a mixture of guaiacyl and sinapyl together, while softwood only contains a guaiacyl nucleus. The latter may give rise to a bend at 820 cm^{-1}, which is too weak to see in the case of hardwoods.

3.3.1.3 pH

In all the cases of degradation, the surface pH decreases with the increase of the duration of ageing (Tables 3.1, 3.3 and 3.5). The decrease in pH is due to the production of acids in the process of ageing, and details of their formation have already been discussed.

3.3.1.4 Tensile strength

As in the case of surface pH, tensile strength also decreases with the increase in the duration of the ageing process.

Tensile strength is the maximum tensile stress developed in a tension test carried out to rupture the paper under prescribed conditions (Britt, 1970), which is generally expressed as the breaking load or force applied per unit width of the test sample. The decrease in tensile strength on ageing results largely from the weakening of fibres following a reduction in the mean length of the cellulose chains. As expected, it was observed that the tensile strength decreased with the increase of time of ageing (Table 3.1, 3.3 and 3.5).

3.3.1.5 Conclusions

This study enabled the author to come to certain conclusions not only about the deterioration process, but also about the peak allocations for lignin in FTIR. It is concluded that the peak at 1510 cm^{-1}, which is the predominant peak in lignin, is due to aromatic skeletal vibrations and the phenolic hydroxyl group in lignin. The peak at 1456 cm^{-1} must be due to methoxyl groups in lignin. The author concludes that FTIR spectroscopy is a very convenient way to identify lignin-containing papers in a very short time, in addition to differentiating between softwood and hardwood in paper and detecting the presence of other additives.

It seems certain that on irradiation by light the methoxyl groups, aromatic character and phenolic character in lignin decrease and, in addition, on heat ageing methoxyl groups decrease. These conclusions contribute to an understanding of the reasons for the rapid deterioration of groundwood papers. In the process of lignin deterioration, mainly by oxidation, free radical phenomena occur and phenolic hydroxyl groups play a major role in the deterioration of mechanical wood papers. Although cellulose is highly stable it tends to deteriorate with time, and hence even pure cellulose papers are not indefinetely permanent. However, if the paper is alkaline, deterioration is limited to photo-oxidation.

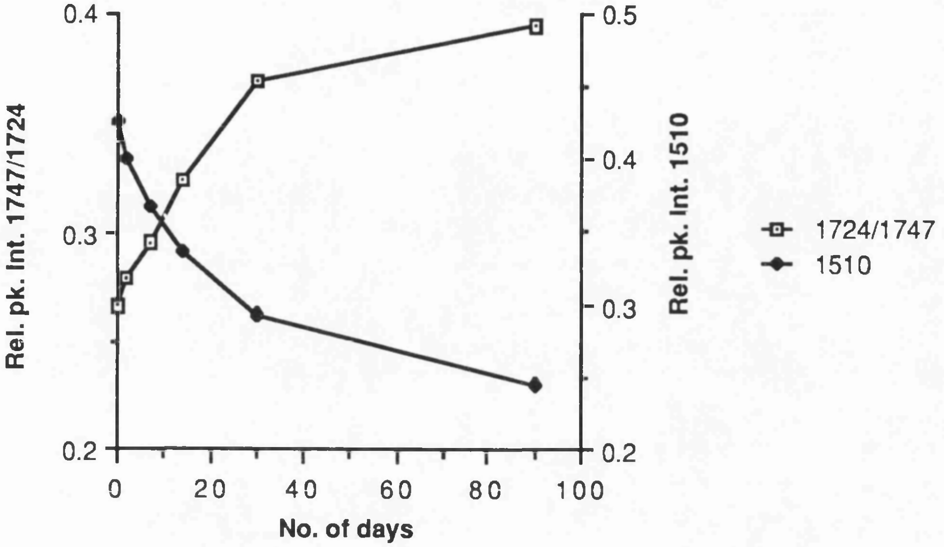
FTIR did not show significant changes in paper on heat ageing, although it showed very encouraging results in detecting light ageing in lignin-free papers as well as lignin-containing papers, and the changes observed in the latter were spectacular. The author concludes that although FTIR is an analytical technique with limitations in paper analysis, and it can be recommended for studies in ageing of mechanical wood papers.

3.3.2: Quantitative peak intensity measurements

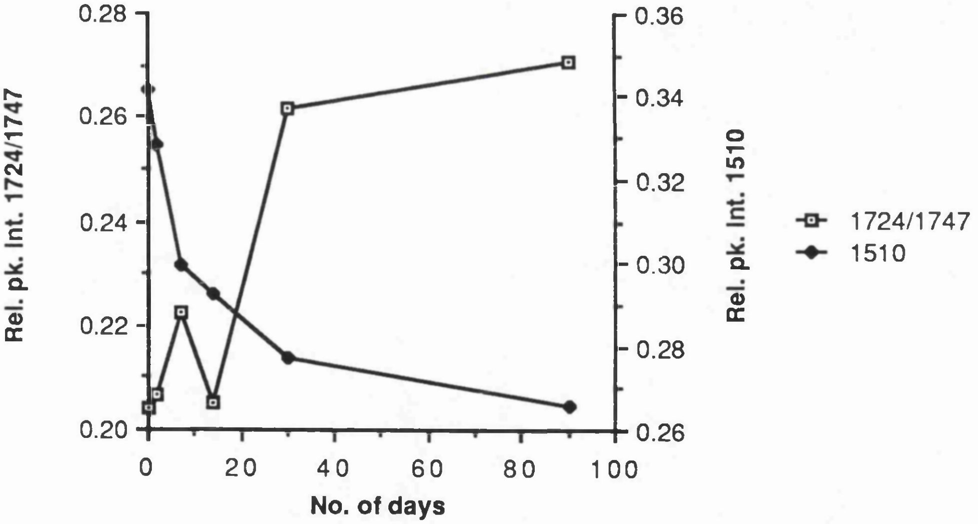
In order to detect small changes in peak intensity resulting from ageing and chemical reactions in the laboratory, it was necessary to normalize spectra with respect to a peak which could be considered to be non-variable.

The CH_2 vibration mode at 1433 cm^{-1} is reported to be one of the few almost pure group frequencies in this region; most of the other predicted modes are more complex, consisting of motions of numerous atoms (Blackwell, 1977). In their work, Yang et al. (1987) normalised the carbonyl peak intensity against the peak intensity at 1430 cm^{-1}, which represented the CH_2 bending in cellulose molecules. In addition to the published information, the author has studied a number of spectra of different paper samples, and of the samples subjected to different chemical treatments. This work identified the peak at 1433 cm^{-1} which has been assigned for C-H stretching in CH_2 groups in cellulose, as the peak which remains without a change or with a very slight change which may be ignored. Hence, the intensities of the peaks at 1510 cm^{-1} and 1724/1747 cm^{-1} were calculated with respect to the peak at 1433 cm^{-1}, and were recorded as relative intensities. The quantified observations (Tables 3.2, 3.4, 3.6) clearly showed that the intensity of the peaks at 1724 / 1747 cm^{-1} was inversely related to the intensity of the peak at 1510 cm^{-1} (Graphs 3.1, 3.2) mainly on light ageing.

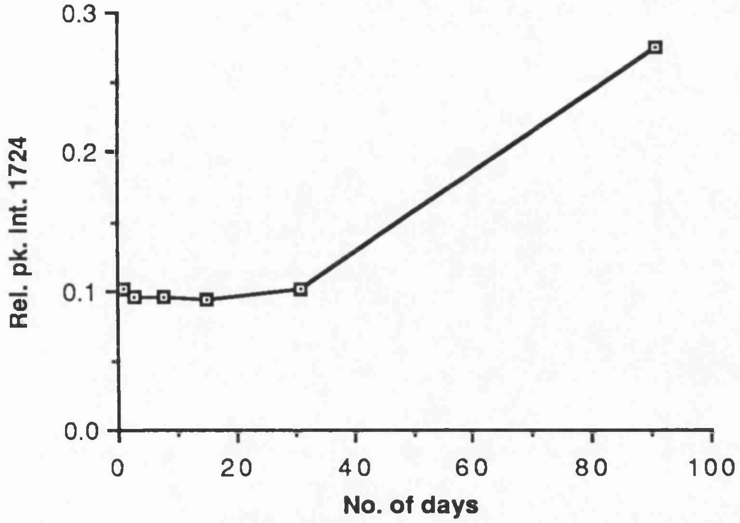
These graphs clearly indicate that the production of acid on ageing was mainly related to the decrease in lignin, in other words the degradation of lignin. Hence, the acidity seems mainly to be due to lignin breakdown products rather than to the alum used in sizing or to atmospheric pollution, in case of mechanical wood papers.



Graph 3.1 (a)

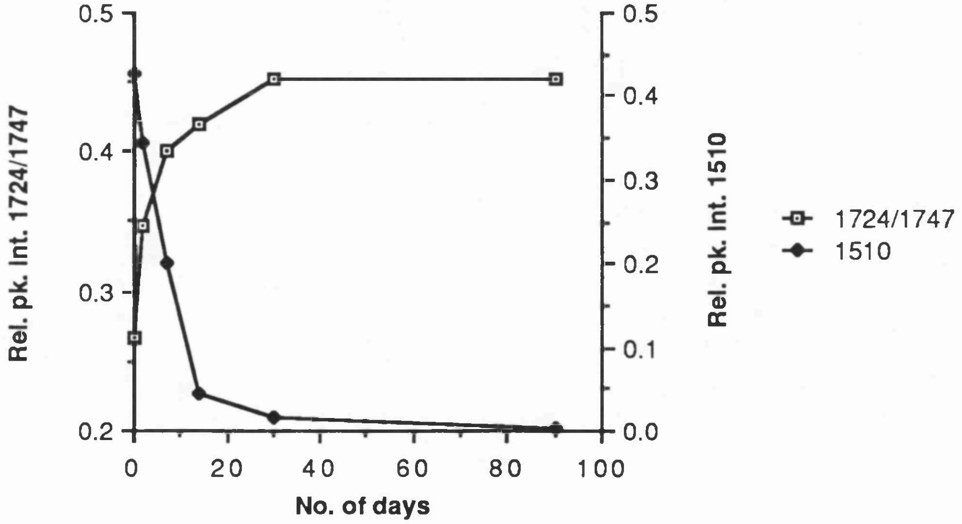


Graph 3.1 (b)

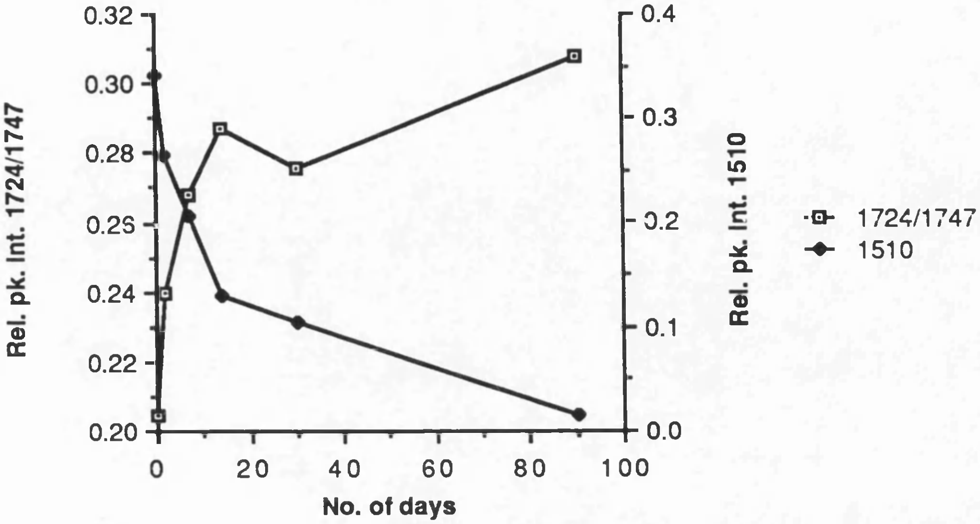


Graph 3.1(c)

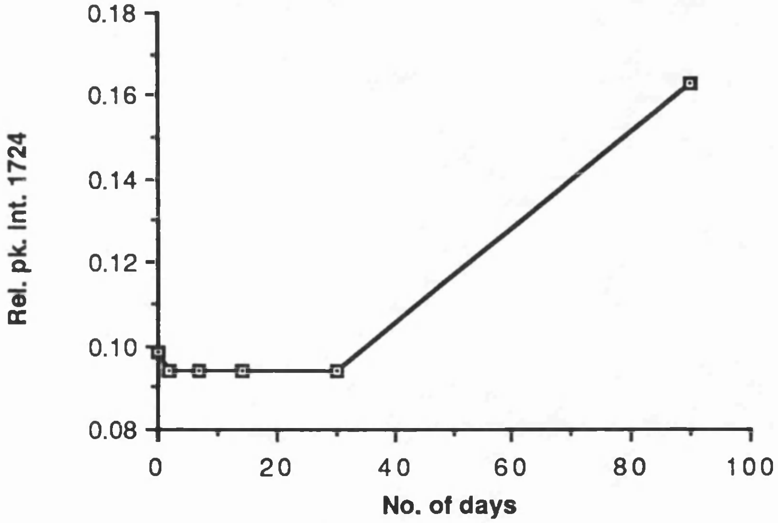
GRAPH 3.1: Variation in relative intensities of the peaks at 1510 cm^{-1} , and at 1724/1747 cm^{-1}, in FTIR spectra of (a)modern newsprints, (b) old newsprints, (c) Whatman no.1, samples on daylight ageing



Graph 3.2 (a)



Graph 3.2 (b)



Graph 3.2 (c)

GRAPH 3.2: Variation in relative intensities of the peaks at 1510 cm^{-1}, and at 1724/1747 cm^{-1} in FTIR spectra of (a) modern newsprint, (b) old newsprint, (c) Whatman no.1, samples on ageing in fadeometer

3.3.3 Acidity

Acidity is one of the major causes of paper deterioration. In conserving archival materials, knowledge of the acid content is very important. Hence, the author investigated the methods of evaluating acidity in paper.

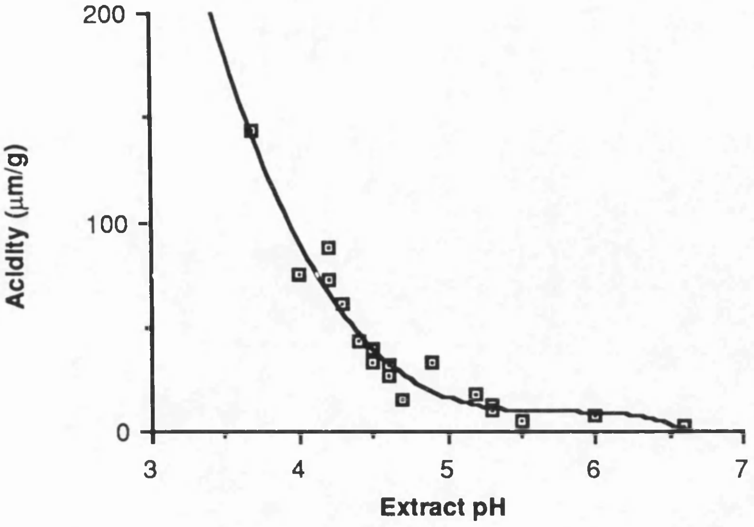
3.3.3.1 Measurement of acidity

According to Browning (1977), the pH found by aqueous extraction is in approximate agreement with the spot test results, while the surface pH can be compared to the extraction values only for a homogeneous paper. Although Hudson and Milner (1959) found a close correlation between the surface measurement method and the conventional extraction method, for some samples this did not hold (Flynn and Smith, 1961).

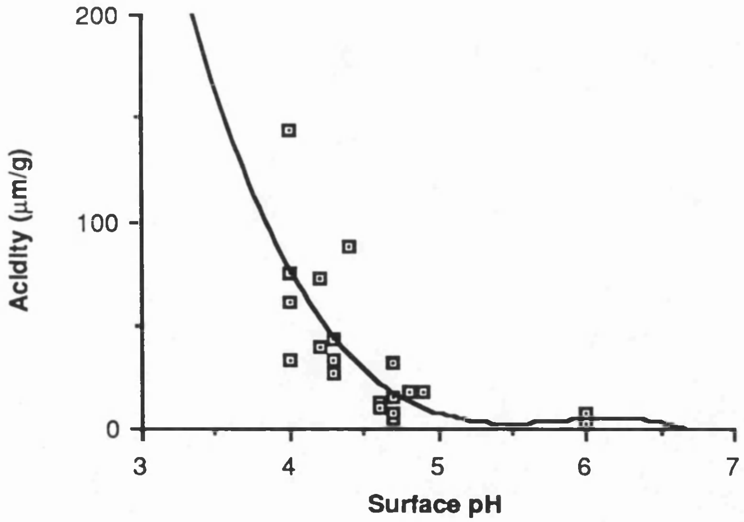
From the present work (Table 3.7), it is seen that the results support the views of Flynn and Smith, as the surface and extraction pH values are in approximate agreement in some of the samples only .

It is obvious that the acid content of paper can be more accurately estimated by the extraction method as compared to surface measurement, as the acid content and extracted pH gives a better fit (Graph 3.3) than the acid content and surface pH (Graph 3.4). It is also seen that there is a correlation between surface pH and extracted pH, although this is not very significant (Graph 3.5).

The total amount of acid in paper can be determined by titration of the water extract to neutrality (Browning, 1977). It was observed that the graphs did not show normal acid-base titration curves (Graph 3.6), mainly due to the buffering action of paper discussed below. Hence, the titration method cannot be used for accurate measurement of the total acidity of paper.



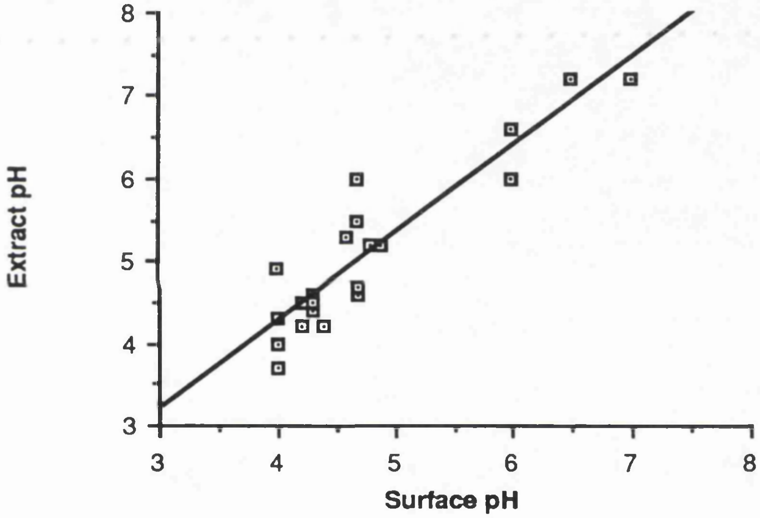
GRAPH 3.3: Correlation of the acid content and extract pH of different paper samples



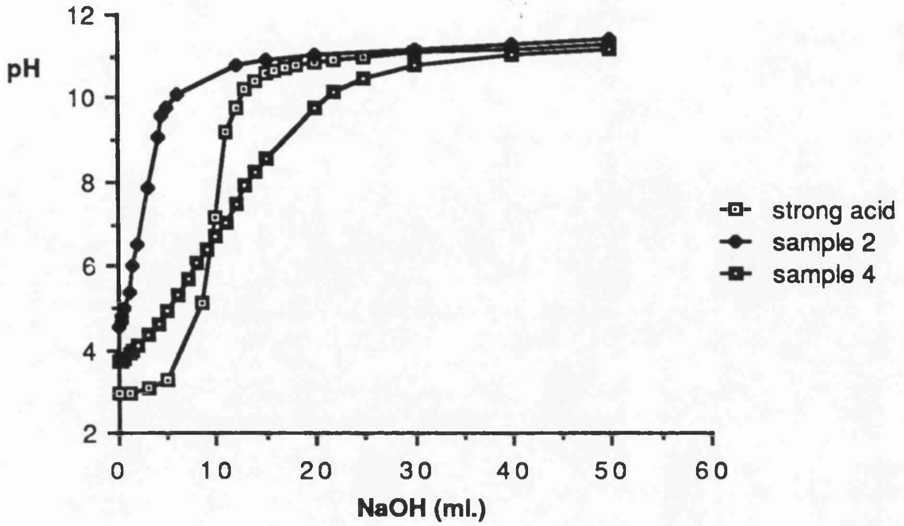
GRAPH 3.4: Correlation of the acid content and surface pH of different paper samples

3.3.2.2 Soluble and insoluble acid

It was also observed that the milled and filtered extracts gave a higher pH than that of the unfiltered extracts, except in the case of samples 3 and 5. This may occur as a result of one or more factors such as the presence of water-insoluble acids in the paper, or not all of the acid content coming out in the extract although additional washing was carried out. The measurements of samples 3 and 5 gave essentially the same pH values. From the observed results, the most probable conclusion is that there are insoluble acidic components in most degraded papers in addition to the soluble acidic components present in the paper, and hence the compounds contributing to acidity are a combination of both.



GRAPH 3.5: Correlation of surface pH and extract pH of different paper samples



GRAPH 3.6: Titration curves of paper samples and strong acid, each against strong base (NaOH)

3.3.2.3 Causes of acidity

According to the available literature, the presence of sulphur dioxide and/or sulphur trioxide leads to the formation of sulphuric acid, and its formation has been proposed as the main cause of acidity in paper. It was observed (Table 3.7) that the lowest pH value was given by sample 4, which contained groundwood. Sample numbers 1, 2 and 3 are pure rag papers, and sample 1 contains a very small amount of acid and sample 2 contains a small amount of acid, which may be due to the absorption of acidic gases from the atmosphere. Sample 3 is alkaline, which is due to the buffering effect given by the calcium carbonate present in it. All other samples except sample 17 contain mixed fibres including chemically treated wood, and they also give high values of acidity. Sample 17, which contains groundwood, has a high level of acidity although it is only 26 years old, mainly due to the lignin decomposition products. The highest values of acidity are observed in samples 4 and 17, which consist of groundwood. Hence it is clear that lignin and lignin decomposition products play a major role in paper acidity in groundwood papers, rather than the sulphuric acid which has traditionally been credited with this effect, which is supported by FTIR results in this study.

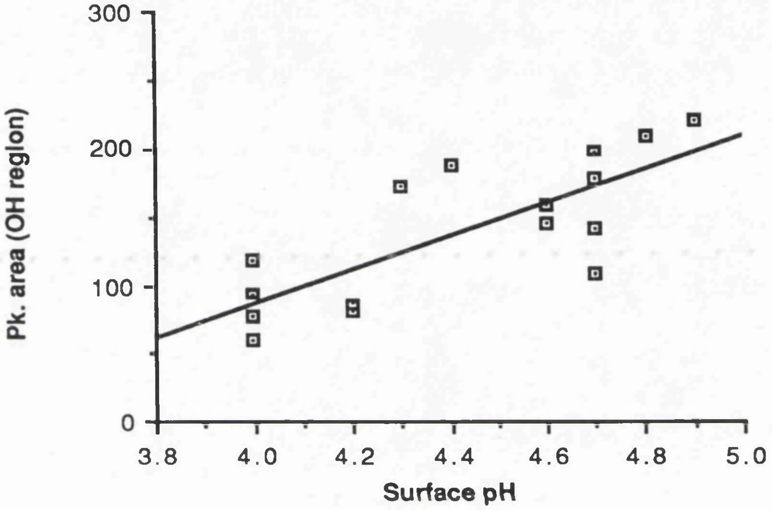
3.3.2.4 Buffering action

During the pH titrations, a buffering action at pH 7 was observed in some of the water extracts, both with and without paper being present. This may be due to the polyhydroxylic character of cellulose, hemicellulose, their decomposition products, or some substance added in the process of paper manufacture. Some of the extracts exhibited buffering action at the initial pH, which may be due in part to the high acid concentration of the solution. In some of the extracts buffering action was not observed, even though they contained pieces of paper, and it cannot therefore be the case that the buffering action is due to either cellulose or lignin alone.

3.3.2.5 Role of FTIR in detecting/measuring acidity

Acidity in a paper sample can also be identified by observing the FTIR spectrum of the sample, as the peaks related to acidity will appear or disappear and/or change in shape according to the acidity or alkalinity of the paper. The peaks at 1724 cm^{-1}, due to the aliphatic carboxylic acid groups, 1680 cm^{-1} due to the aromatic carboxylic acids such as vanillic acid, and the broad peak from 3700-3000 cm^{-1} due to the hydroxyl groups, are the three characteristic peaks which help in evaluating the acidity in paper. At 1724 cm^{-1} a small peak can be seen in the spectra of chemically treated wood pulp papers, and a small peak can be observed at 1680 cm^{-1} in the spectra of mechanical wood papers which have low pH values (Figure 3.12). The FTIR spectrum of a Whatman sample exposed in the fadeometer for 96 hours indicated a very small peak at 1724 cm^{-1}, while groundwood paper subjected to the same exposure, indicated a medium doublet at 1724 / 1747 cm^{-1} in addition to the peak at 1680 cm^{-1} (Figure 3. 13) according to the amount of acid and other degradation products such as esters present. Untreated Whatman samples sometimes also showed a very small peak at 1724 cm^{-1}, which can be accounted for by the presence of free carboxylic acid groups as a result of the oxidation of cellulose due to the bleaching in the process of manufacture. The appearance of a peak due to the free carboxylic acid groups, which lies at 1724 cm^{-1} in lignin free papers, helps in determining the acidity qualitatively. It cannot however be taken into account in quantitative analysis, as it is a very small peak except in the sample aged for 3 months in the fadeometer or in the presence of daylight, and this peak will not contribute much in quantitative analysis where a minute amount of acid is present. In the process of de-acidification, this particular peak should disappear or decrease in intensity, but it is hard to identify that feature in the treated samples (Figure 3.14) as that specific region 2000-1500 cm^{-1} is quite susceptible to noise and the interference of moisture.

The broad peak which lies in the region of 3700-3000 cm^{-1}, changed its shape in the presence of acid and alkali (Figure 3.14). Even when the acid itself did not show up in the spectrum, the change in the shape of the OH region was remarkable, and hence this is a quite sensitive feature to observe in determining acidity using FTIR spectra. With the expectation in getting some information quantitatively using FTIR spectroscopy, measurements were made of the area of the broad peak lying at 3700-3000 cm^{-1} (Table 3.7) . A general correlation was in fact found, and there was a trend in increasing peak area of that range with the increase in surface pH for many samples (Graph 3.7). Sample no. 3, which is a buffered paper, and sample no 8, which is a highly coated paper, did not show the trend. It may be that the buffering agents and coating agents affect the peak area, and hence it does not comply with the normal trend. Hence the author suggests that the peak area of the region 3700-3000cm^{-1}, i.e. the hydroxyl region in FTIR, can be useful in determining the acidity in paper samples within certain limits .



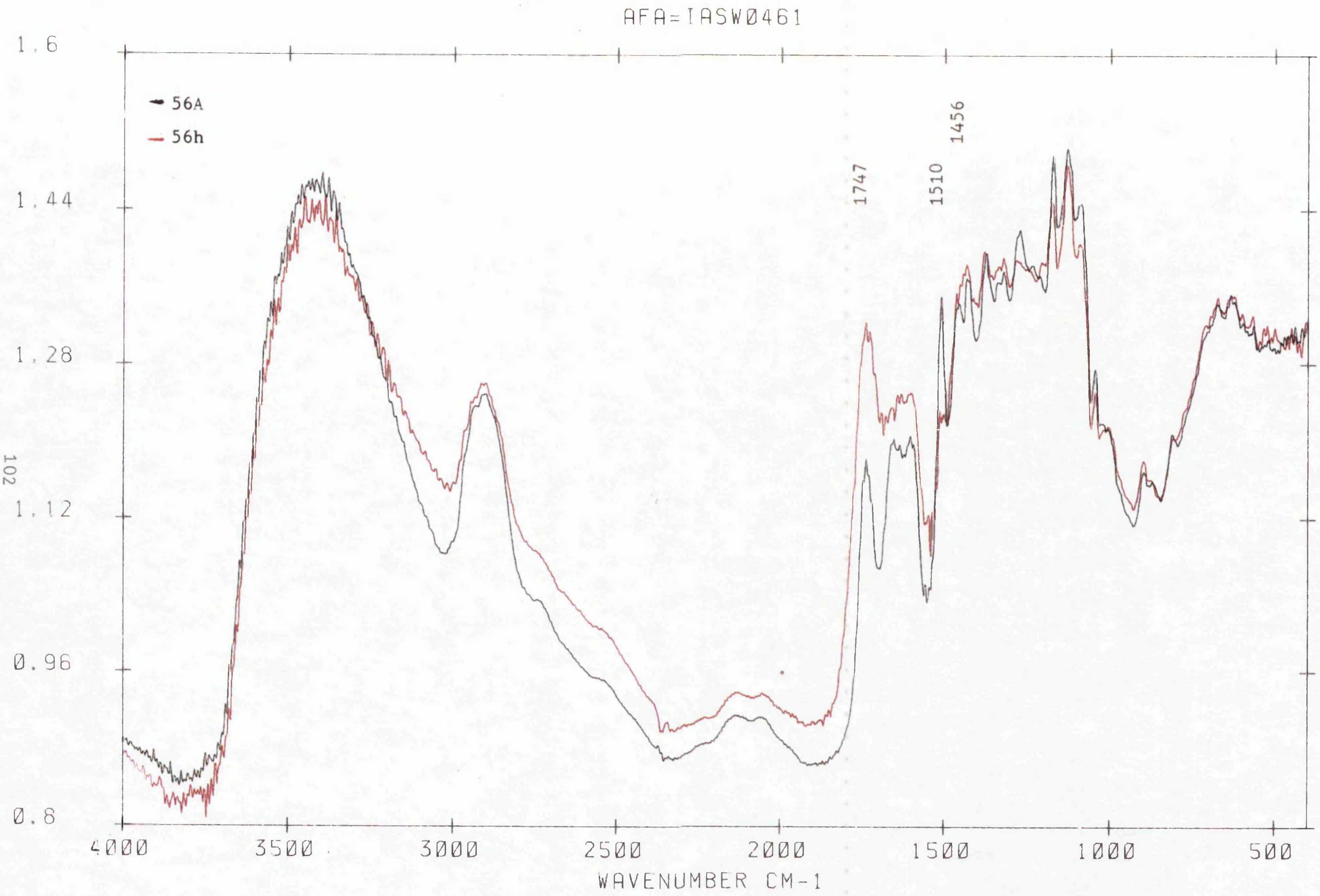
GRAPH 3.7: Correlation of the surface pH and the peak area of the hydroxyl region in FTIR spectra of different paper samples

3.3.2.6 Conclusion

The author concludes that there are usually both soluble and insoluble acids present in paper. Insoluble acids are all organic, and must be weak. Soluble acids can be either or both. Also, it is concluded that the acidity of paper arises mainly due to the lignin and lignin degradation products in lignin containing papers, although there is a contribution from sulphuric acid present as a result of the processes due to sizing and atmospheric pollution.

In case of the measurement of acidity, measuring the pH of an extract containing paper samples can be recommended, and to get an approximate value, especially in dealing with archival materials which cannot be sampled, surface pH measurements can be used. The author warns of possible errors in the method of determining acidity using normal acid base titration methods, as the titrations of paper do not always comply with the normal titration patterns, largely due to the buffering action of the paper.

The FTIR spectra can also be useful in measuring acidity by identifying the presence of the peak at 1724 cm^{-1} and the intensity increase of the peak at 1680 cm^{-1} in groundwood papers, and the shape difference of the region 3700-3000 cm^{-1}, although there are limitations in the latter two as these need experience in recognising the changes. The author would also like to state that the quantitative measurement of the region at 3700- 3000 cm^{-1} in the FTIR spectra of paper might also be useful in measuring the pH of paper within certain limits.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1747
1510
1456
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2500
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1500
1000
500
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Figure 3.1

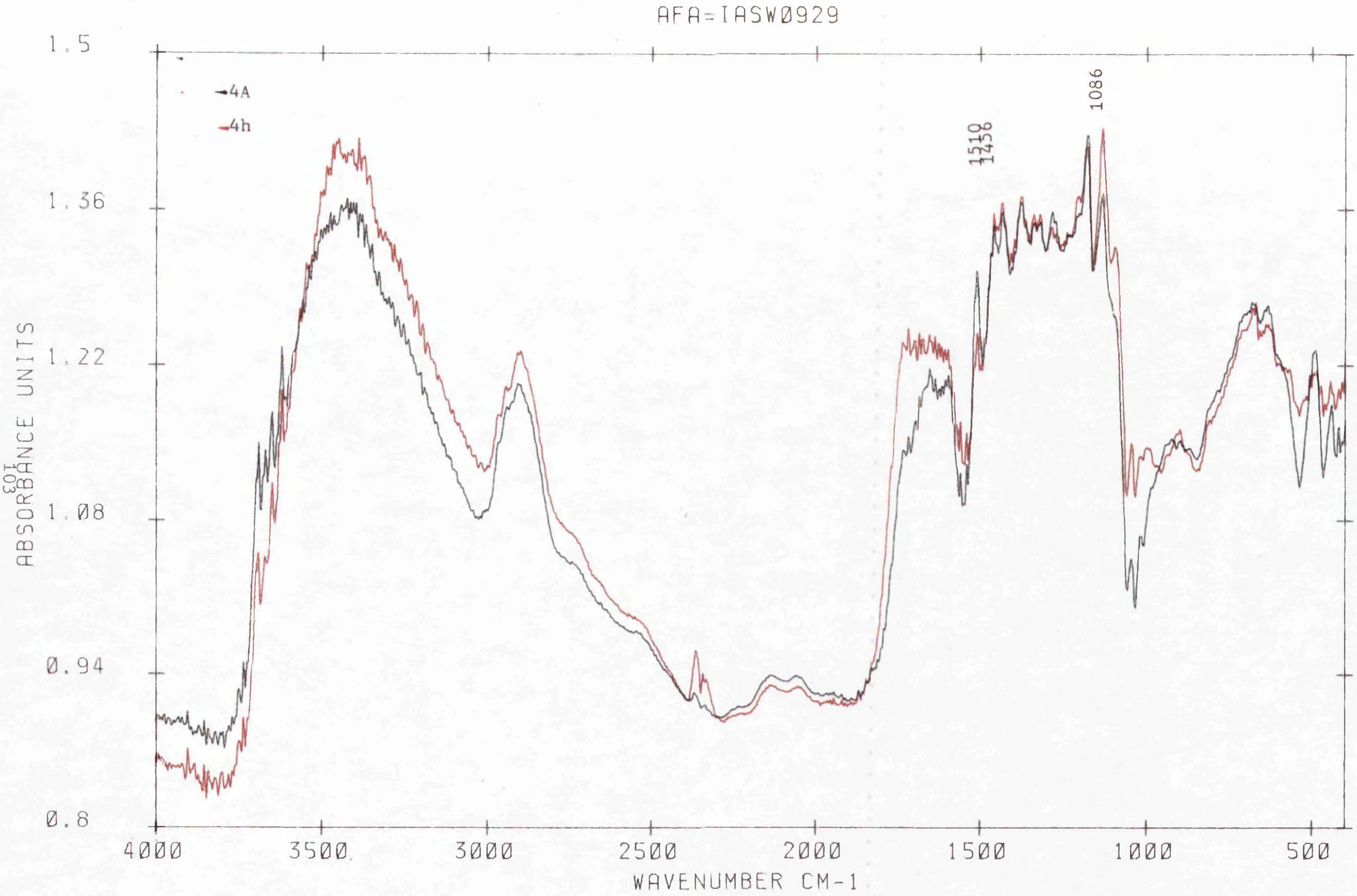
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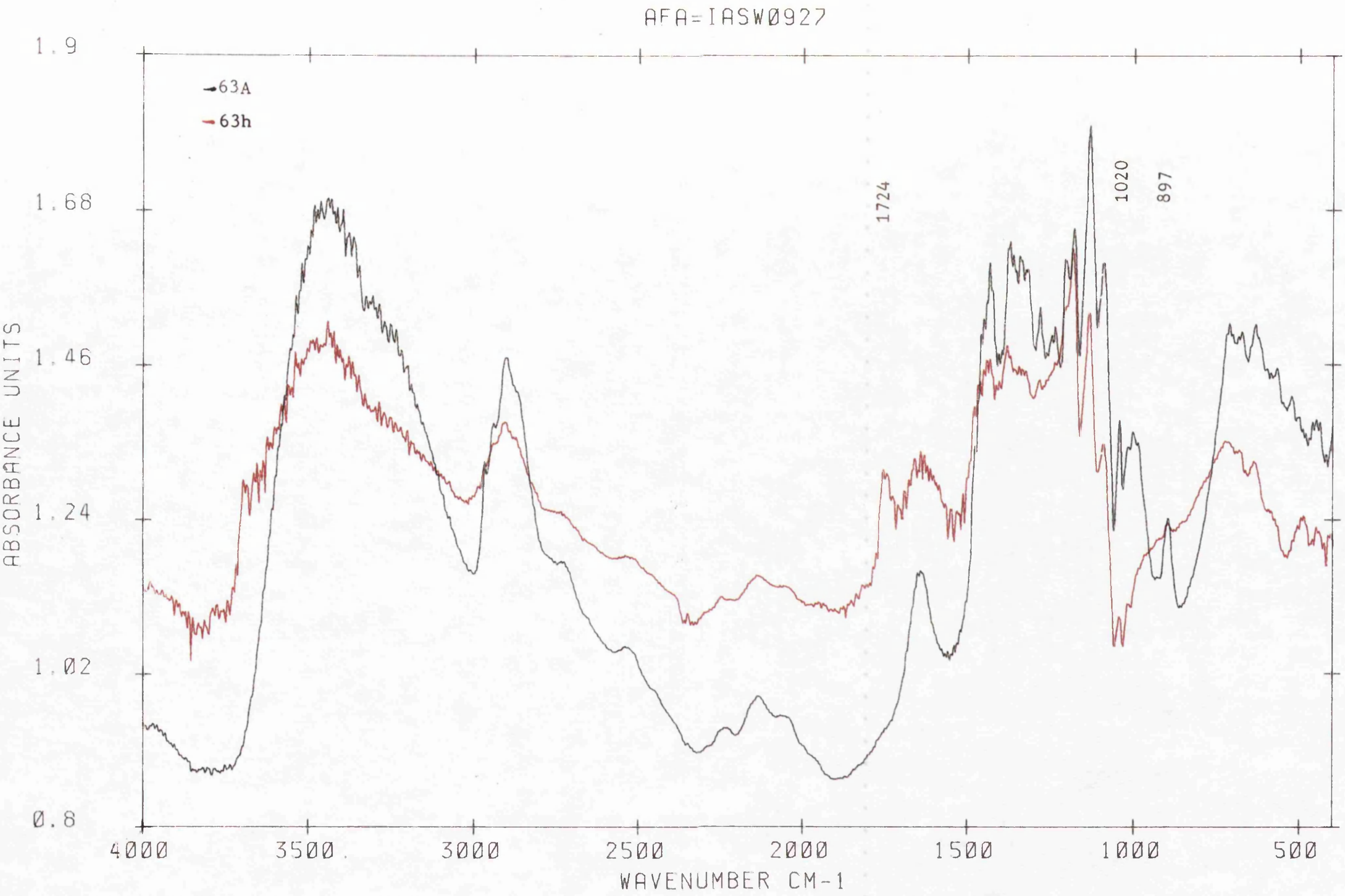
Figure 3.2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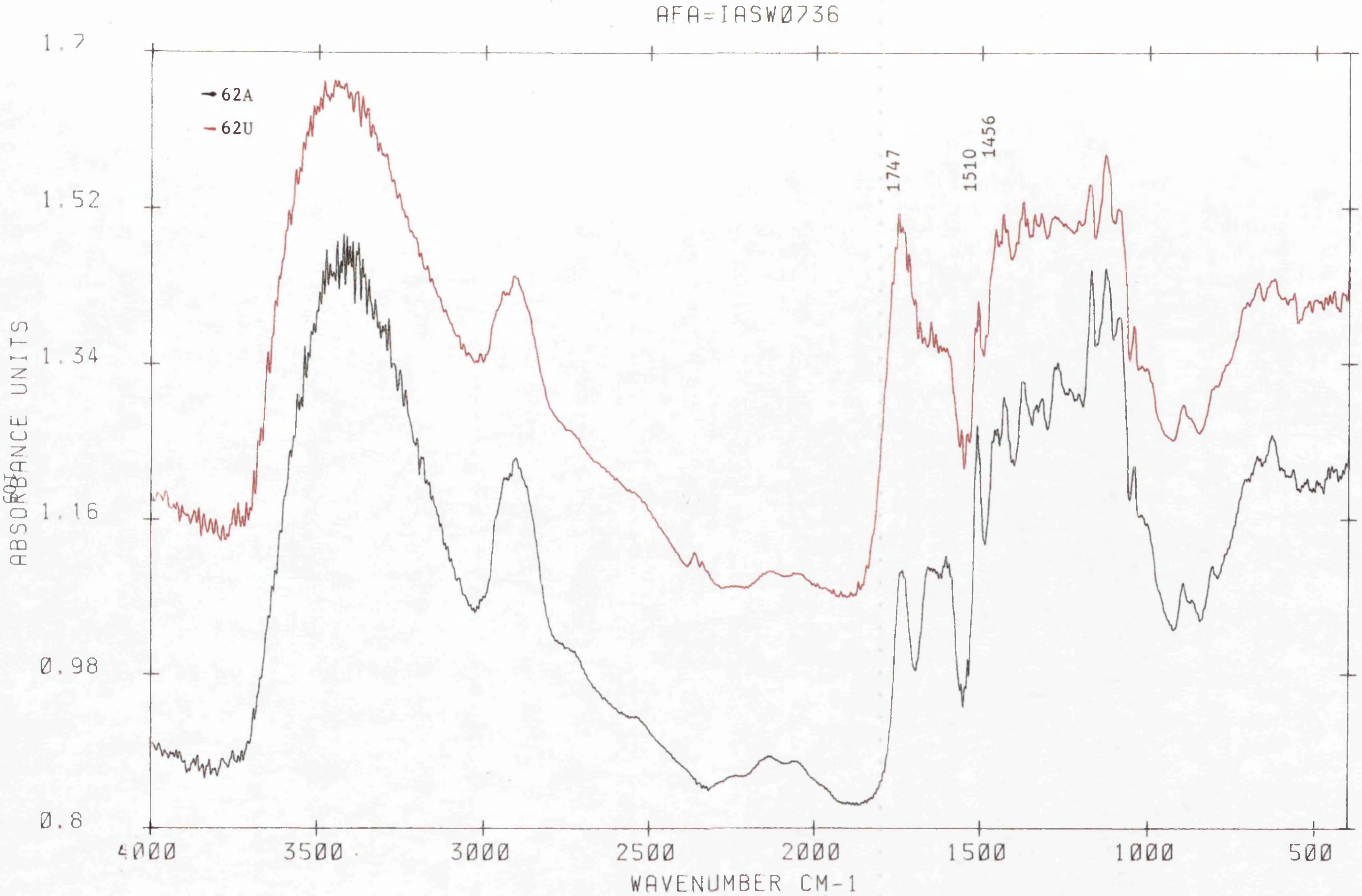
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 3.3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1510
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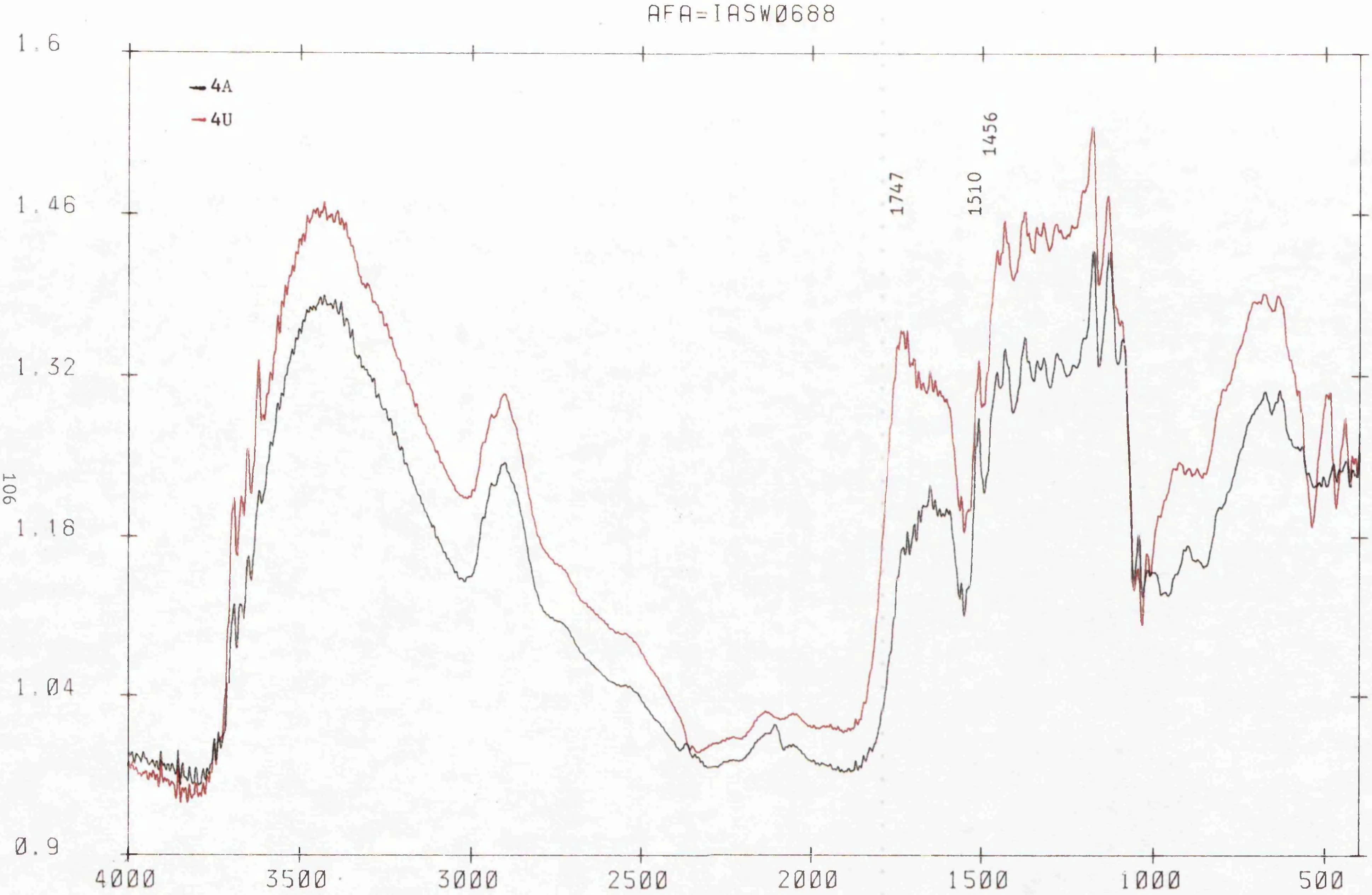
1500
1000
500
WAVENUMBER CM-1

Figure 3.4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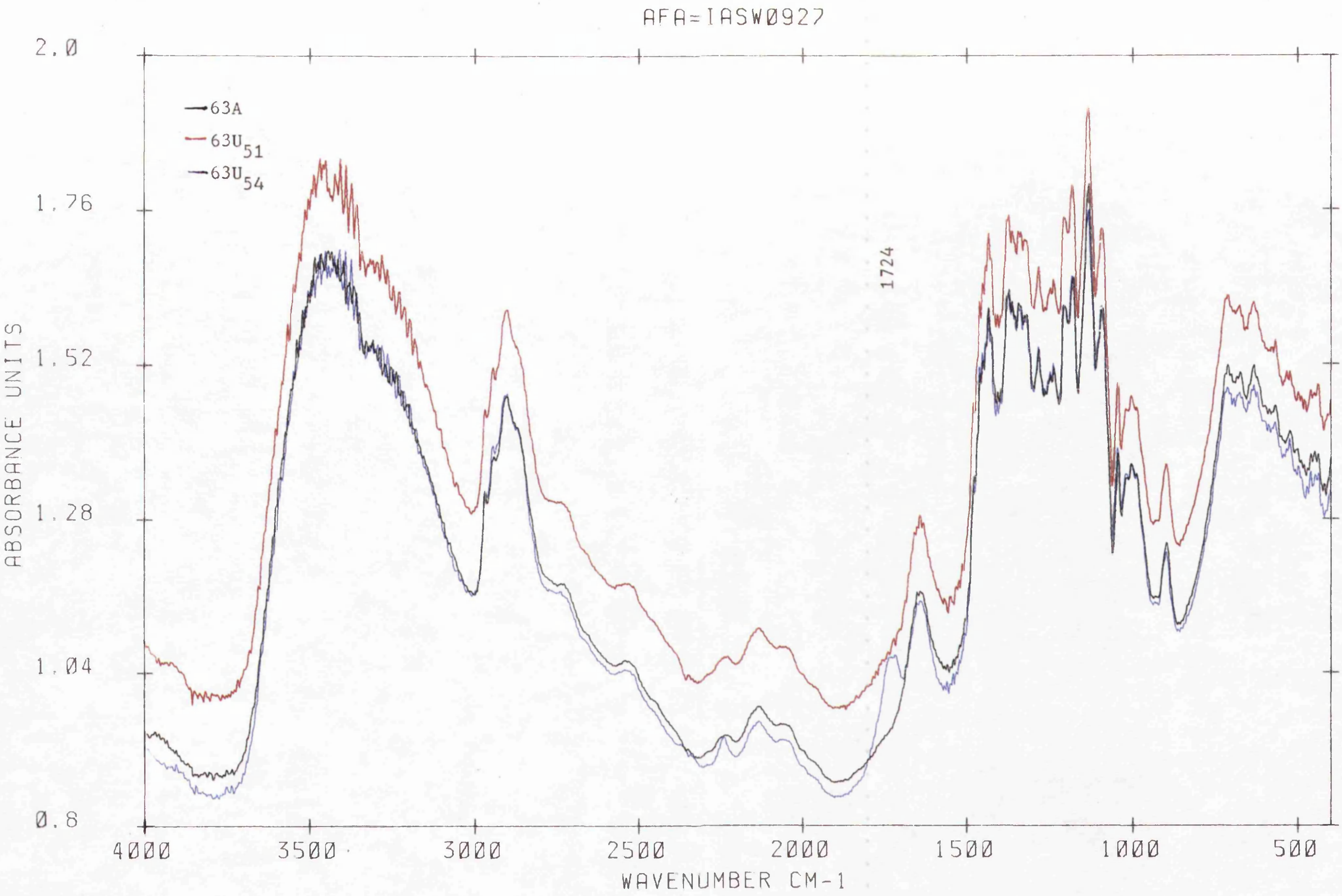
WAVENUMBER CM-1

Figure 3.5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WAVENUMBER CM-1

Figure 3.6

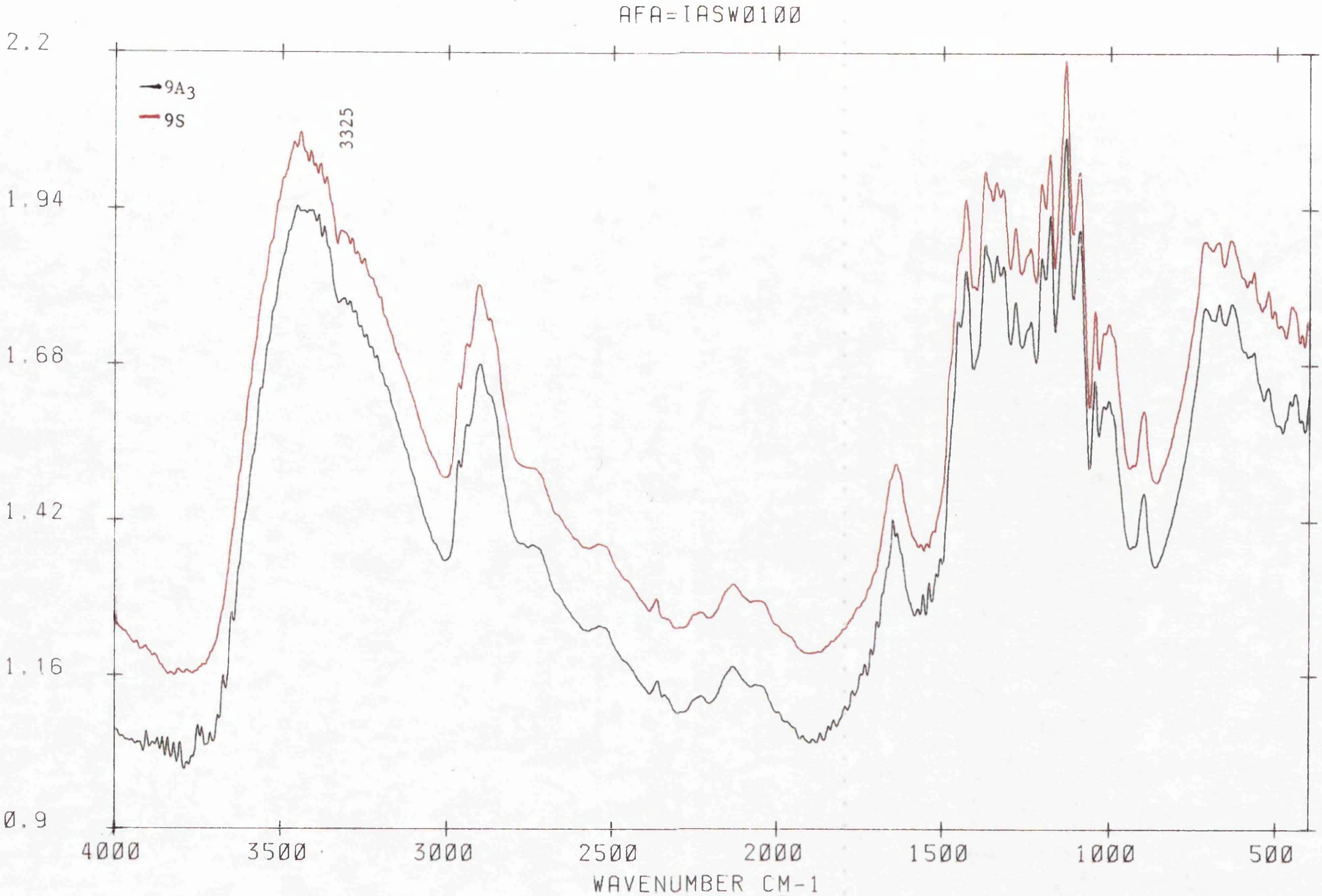
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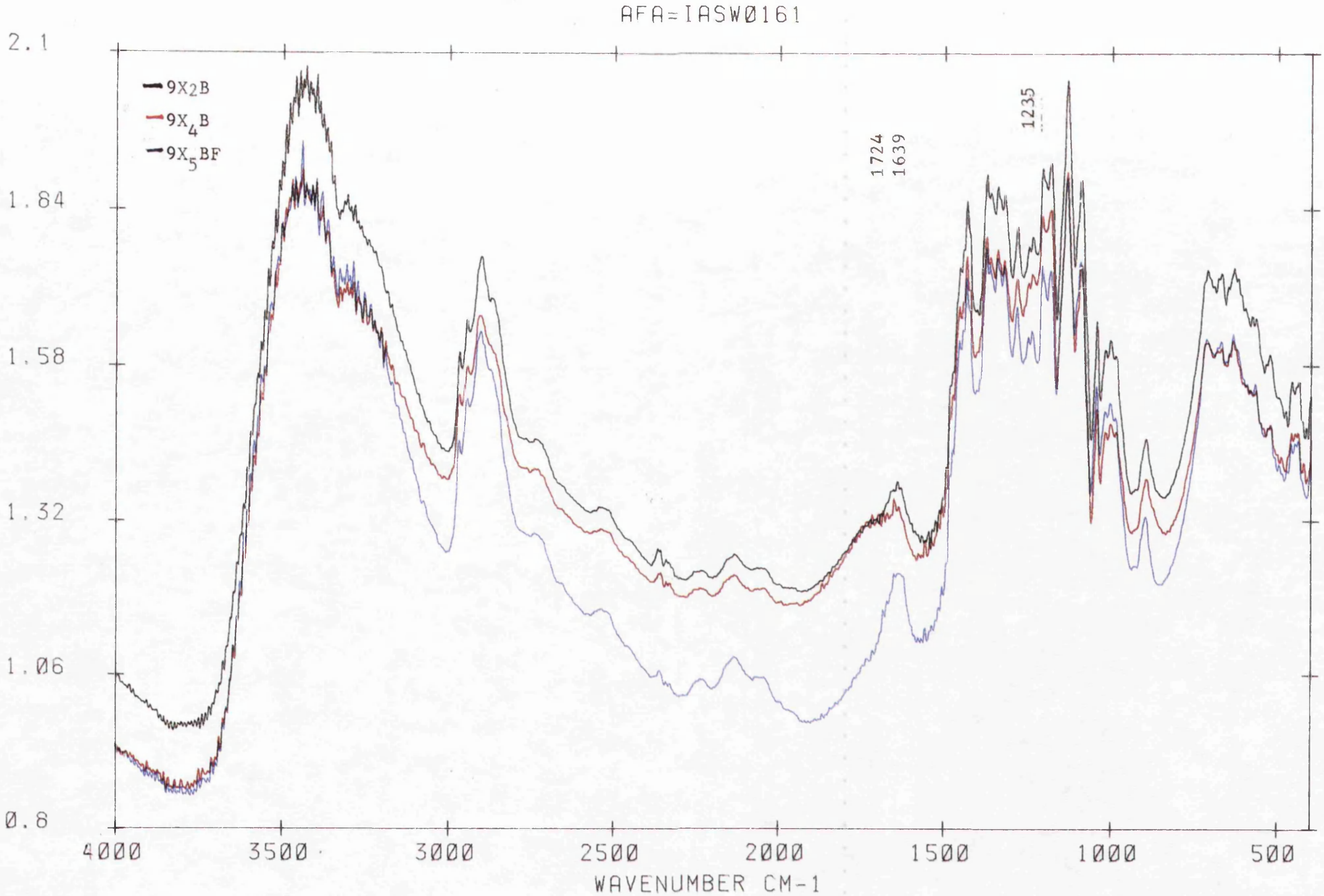
Figure 3.7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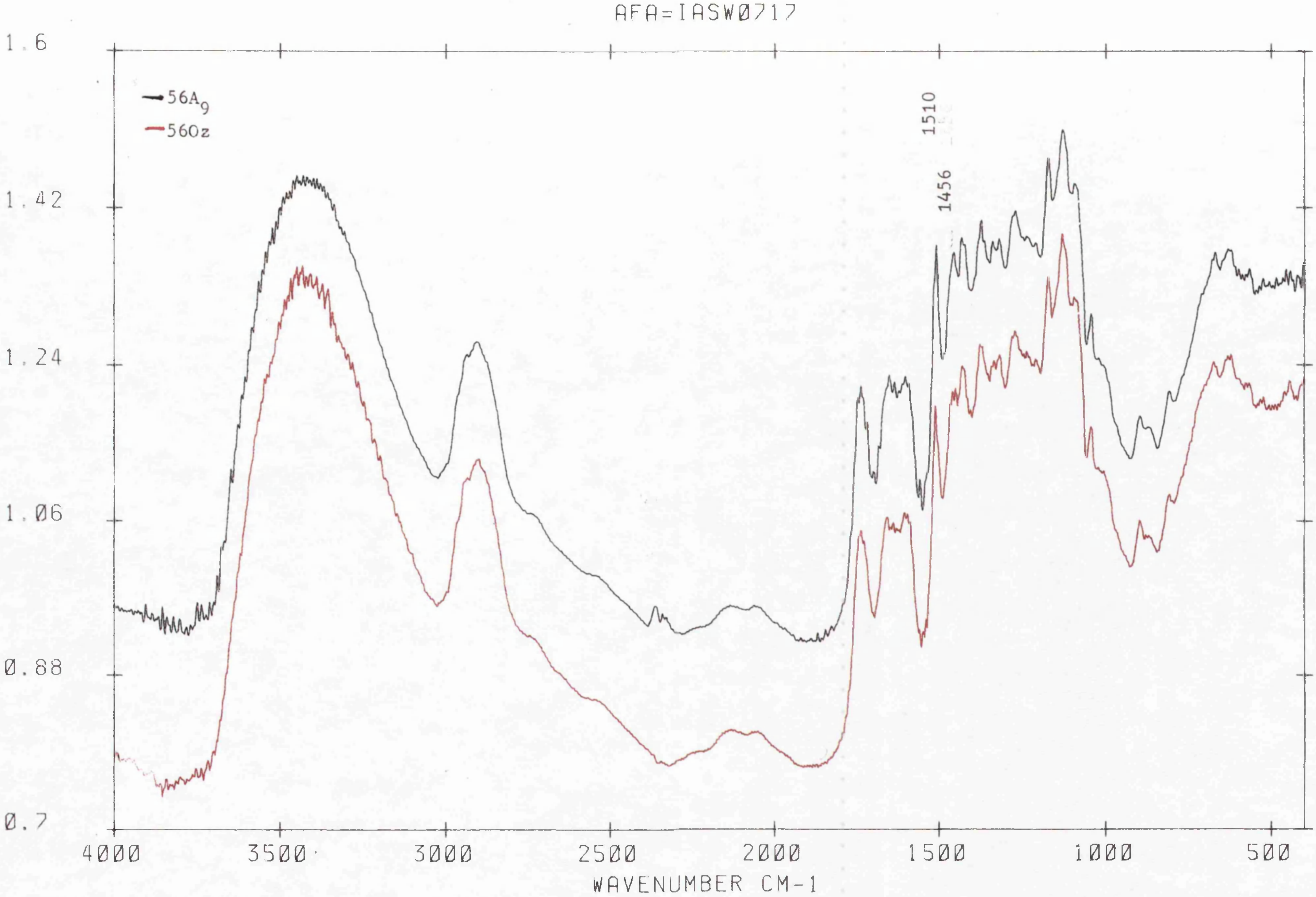
WAVENUMBER CM-1

Figure 3.8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1.6
1.42
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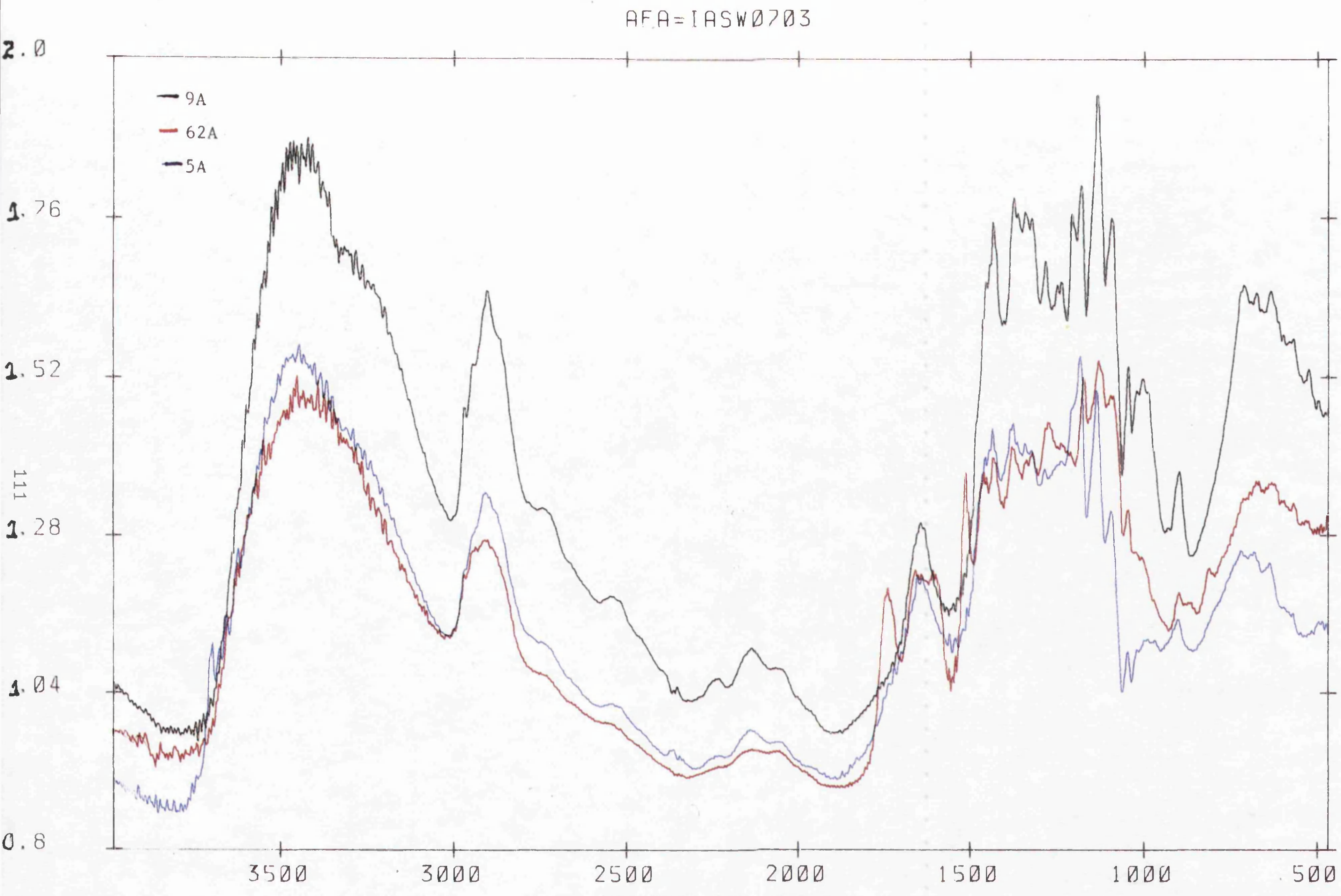
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 3.9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5A
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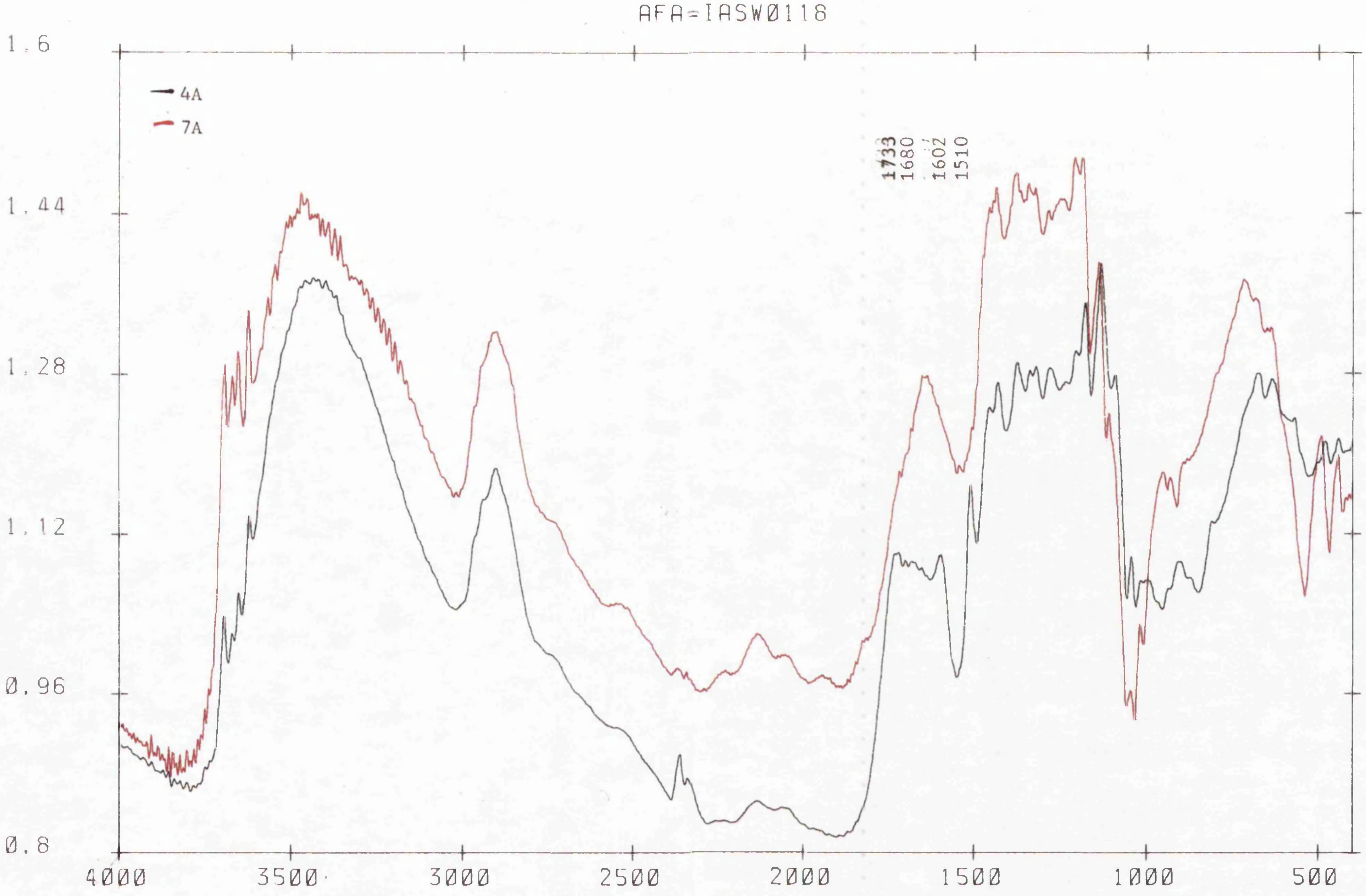
WAVENUMBER CM-1

Figure 3.11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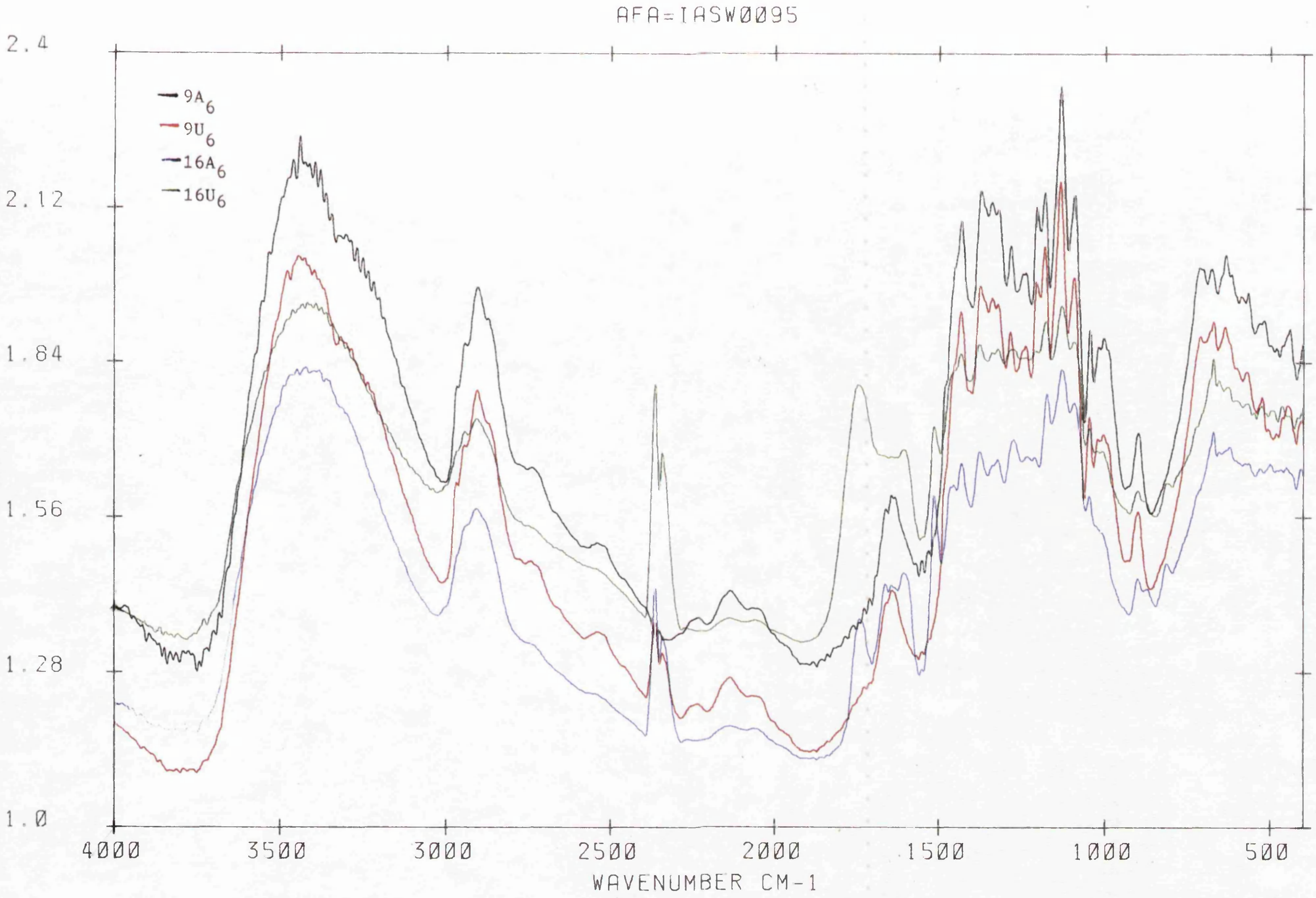
7A
1733
1680
1602
1510
1.6
1.44
1.28
1.12
0.96
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 3.12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16A6
16U6
2.4
2.12
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1.56
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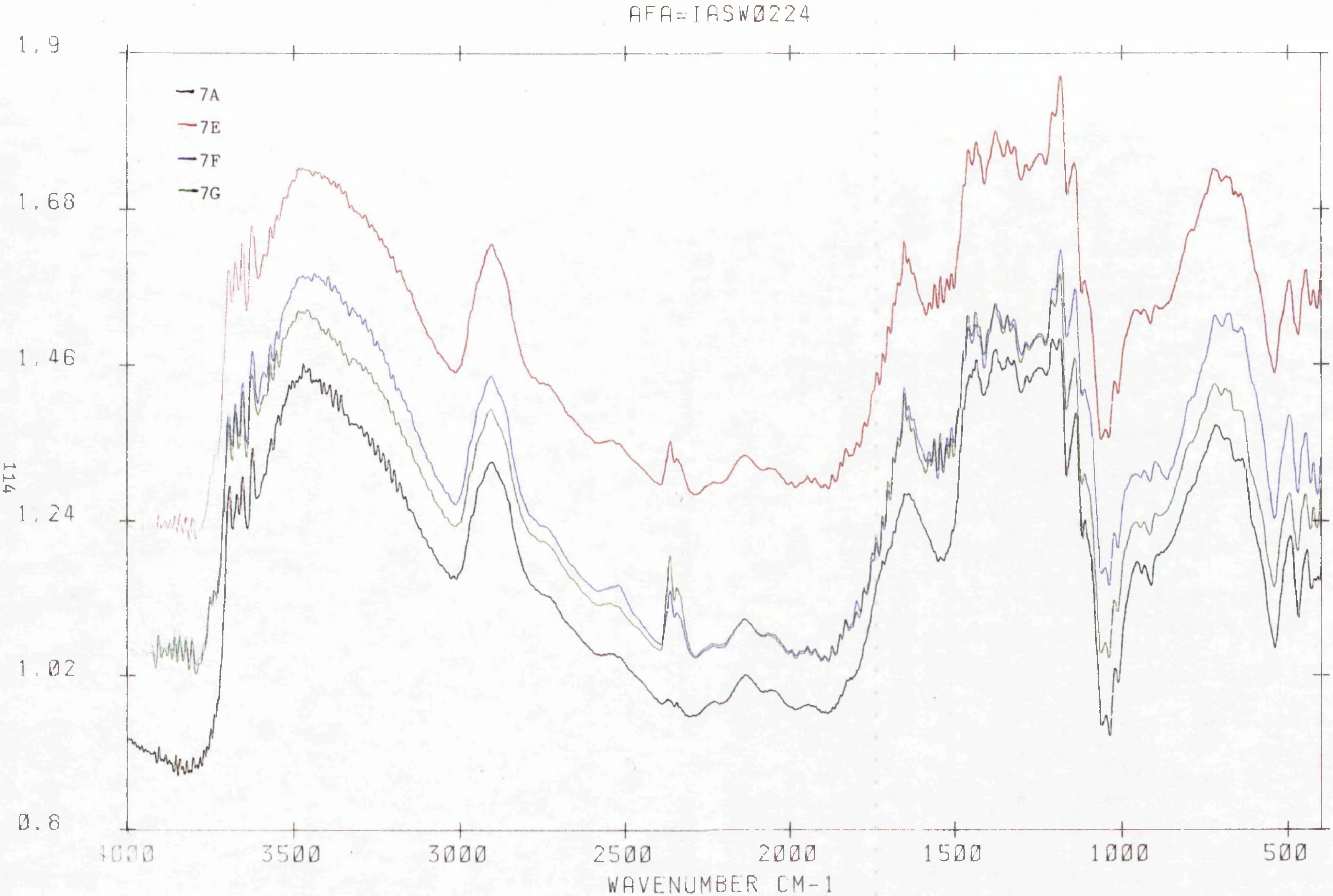
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 3.13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0.8
7A
7E
7F
7G
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 3.14

Chapter 4

STABILIZATION

4.1 INTRODUCTION

In the process of paper conservation, stabilization is one of the main options available at present to retard or to prevent deterioration, and this has been discussed in the first and third chapters.

Since the introduction of rosin/alum sizing in 1807, the majority paper manufactured has been of an acidic nature and even today the major proportion of paper produced is sized with these reagents and also manufactured with groundwood pulp containing lignin, hence much archival and library material is readily subject to degradation resulting in the characteristic yellowing and embrittlement of the paper. Hitherto one of the principal solutions to this problem has been neutralisation of the acid present and buffering to prevent further acid accumulation.

Since the existing deacidification processes have certain limitations (section 1.3.1.2), the author tried out another method using a mixture of colloidal magnesium hydroxide (milk of magnesia) in IMS, which was chosen as being safe since magnesium hydroxide is non toxic and IMS of low toxicity and both are easily available and low in price.

Mechanical wood papers in particular become yellowish upon exposure to daylight at a much higher rate than fully bleached chemical pulp papers and rag papers, and produce acidic components on ageing, owing to the fact that they also contain lignin which has functional groups such as phenolic hydroxyl, conjugated double bonds, and at some stages α-carbonyl groups, which may be subject to oxidation and hydrolysis. The blocking of these functional groups using specific reagents was considered as it might lead to the stabilization of these unstable compounds and might retard or arrest the yellowing of paper and the production of acid. Formaldehyde reacts with phenol to give a resin (Finar, 1964) and Nikitin and Rudneva (1935) studied the reaction of ethylene oxides with lignin at 70°C (Mallinovskii, 1965) and diazomethane can methylate phenolic hydroxyl groups and carboxylic groups. Thus in terms of stabilization of paper, the possibilities of capping lignin using formaldehyde, ethylene oxide and diazomethane were investigated using FTIR and at some stages DSC to follow the reactions.

4.2 DEACIDIFICATION USING MAGNESIUM HYDROXIDE COLLOIDAL SUSPENSION

4.2.1 Reasons for the the choice

Magnesium compounds satisfy the criteria for effective deacidifying agents. Being a non aqueous method, which can be applied by spraying, this process does not require disbinding and can be used on many sensitive and fragile materials.

4.2.2 Experimental method

12 ml of "Milk of Magnesia" mixture was placed in a centrifuge tube and the water was separated using a centrifuge. After removing the water, IMS was added and centrifuging continued. This process was carried out until pure magnesium hydroxide was separated. The amount of magnesium hydroxide separated was calculated and a 2% suspension was prepared by adding to IMS and shaking well.

Treatment

Paper samples including Whatman No.1 were weighed and sprayed with magnesium hydroxide suspension and left to dry. They were then reweighed. Over the period of a week the weight was recorded, and the surface pH on each surface was also measured. One batch of samples was sprayed twice, and in another batch both the surfaces were sprayed and the results were compared. Some of the treated samples were examined by scanning electron microscopy in addition to FTIR.

Selected samples treated on both surfaces with the magnesium hydroxide suspension were artificially aged using the oven and the fadeometer. Oven ageing was done at 80°C at 75% RH, using sodium chloride solution, for 7 days. Fadeometer ageing was carried out by exposing the samples for 96 hours.

4.2.3 Results and observations

4.2.3.1 Surface pH

The samples which were treated with magnesium hydroxide/IMS in colloidal suspension by spraying onto one surface of each sample then drying and repeating these stages once more, showed a weight gain and an increase in the surface pH. When the samples were subjected to measurement of both the surfaces, after certain time intervals, the reverse surface of the sample showed an increase in pH, while the top surface showed a reduced pH value as compared to that immediately after treatment (Table 4.1).

It was observed that the decrease in surface pH in ageing was less following the treatment, compared to the surface pH of untreated aged samples (Table 4.2).

4.2.3.2 FTIR

Spectra of the Whatman samples treated with magnesium hydroxide/IMS once and twice showed the same changes, which could be identified as the appearance of a new peak at 3700 cm^{-1} and an intensity decrease in the peak at 636 cm^{-1} (Figure 4.1).

Sample No.	Surface pH													
	1day		2 days		3 days		7 days		15 days		30 days		5 months	
	T	R	T	R	T	R	T	R	T	R	T	R	T	R
$1A_4$	6.0	6.2	5.9	6.2	6.0	6.2	6.2	6.1	5.9	6.2	6.2	6.3	6.2	6.2
1f,s,1sp	8.2	6.2	7.9	6.8	7.2	6.7	7.3	6.7	7.4	6.6	7.3	7.1	7.4	7.1
1f,s,2sp	8.9	6.8	8.8	7.2	8.8	7.2	8.7	7.2	8.5	7.5	8.4	7.5	8.1	7.9
1f,b,1sp	8.8	8.5	8.8	7.8	8.3	7.2	8.0	8.5	7.8	8.2	8.1	8.3	8.1	8.0
2A4	4.7	4.9	4.7	4.8	4.9	4.8	4.9	4.9	4.8	4.7	4.7	4.8	4.9	5.0
2f,s,1sp	7.7	5.3	7.3	5.8	7.4	5.8	7.1	6.1	7.1	6.0	7.1	6.4	7.1	6.4
2f,s,2sp	8.0	5.9	7.8	6.2	7.5	7.1	7.6	7.1	7.8	7.2	7.6	7.3	7.8	6.5
2f,b,1sp	7.8	7.6	7.4	7.4	8.1	7.6	7.3	7.7	7.8	7.8	7.5	7.1	7.7	7.6
$4A_4$	3.8	3.6	3.7	3.9	3.8	3.9	3.9	4.0	3.8	3.9	4.2	4.0	3.9	4.0
4f,s,1sp	6.1	3.9	6.0	4.2	6.9	4.2	6.7	4.6	6.5	4.6	5.9	4.8	5.8	5.4
4f,s,2sp	7.0	4.9	7.3	4.6	7.8	7.0	7.6	6.5	7.7	5.3	7.3	5.2	7.5	5.4
4f,b,1sp	7.0	7.2	7.6	7.4	7.2	7.0	7.4	7.0	7.6	6.2	7.4	7.0	7.3	7.2
$6A_4$	4.7	4.8	4.7	4.7	4.9	4.8	5.0	5.2	4.9	5.1	4.9	5.0	5.2	5.2
6f,s,1sp	7.7	5.1	7.4	5.8	7.2	5.8	7.1	5.7	7.4	6.3	7.3	6.8	7.2	6.9
6f,s,2sp	8.0	5.4	7.8	5.6	7.5	5.5	7.6	5.8	7.8	5.7	7.4	6.1	7.5	6.4
6f,b,1sp	7.8	7.5	7.5	7.4	7.4	7.5	7.2	7.2	7.7	7.5	7.4	7.3	7.5	7.4
$9A_{14}$	5.8	5.8	5.6	5.5	5.5	5.4	5.8	5.9	5.5	5.5	6.6	6.5	6.2	6.2
9f,s,1sp	8.5	7.1	8.0	7.6	8.9	8.1	8.5	7.6	8.7	8.6	8.8	7.9	8.7	8.8
9f,s,2sp	8.2	8.1	9.0	8.7	9.2	7.7	8.9	7.7	9.0	8.0	8.8	9.1	8.6	9.2
9f,b,1sp	8.4	9.0	9.0	9.6	9.0	9.0	8.0	8.7	9.1	9.4	9.3	8.5	9.6	9.4

b - both surfaces   f - $Mg(OH)_2$/IMS treatement   R-reverse surface   s-single surface
T- top surface   1sp- single spary   2sp-double spray

TABLE 4.1: Change in pH on natural ageing after the magnesium hydroxide/IMS treatment

Sample No.	Initial pH	pH just after the treatment	pH oven aged, foll. treatment	pH oven aged	pH fadeom aged, foll. treatment	pH fadeom aged
9	5.3	8.0	7.5	5.0	6.5	4.5
4	3.9	6.6	5.5	3.6	4.3	3.5
50	5.8	9.6	7.1	5.0	5.3	3.0

foll. - following   fadeom - fadeometer

TABLE 4.2: Change in pH on artificial ageing due to the $Mg(OH)_2$/IMS treatment

The spectra of the old newsprint resulting from the magnesium hydroxide treatment indicated an increase in the intensity of the existing peaks at 3700, 3680, 3660 and 3620 cm^{-1}, and changes in the strong peak at 1130 cm^{-1} to a shoulder, and a shoulder at 1205 cm^{-1} to a weak peak, and an intensity increase in the peak at 1086 cm^{-1}, and a change in shape between 1100-800 cm^{-1}. (Figure 4.2)

Modern newsprints showed the appearance of a new peak at 3700 cm^{-1}. Other changes which were observed in Whatman and old newsprint were not observed in this case (Figure 4.3).

With the spectroscopic results, it was observed that the newsprints treated and then oven aged showed a decrease in intensity of the peak at 1747 cm^{-1}, while untreated and then oven aged samples did not show that particular change (Figure 4.4).

Spectra of the samples exposed in the fadeometer normally showed an increase in intensity of the peak at 1747 cm^{-1}, while magnesium hydroxide/IMS treated samples followed by fadeometer exposure showed a decrease in intensity (Figure 4.5).

4.2.3.3 Scanning electron microscopic analysis

The SEM photographs taken from the samples treated with magnesium hydroxide/IMS, showed small bright particles, which were absent in photographs of untreated samples (Plate 4.1).

X-ray fluorescent analysis of the samples indicated that all the surfaces sprayed with magnesium hydroxide contain magnesium . Although there was no indication of the presence of magnesium immediately after the treatment on the reverse surface of Whatman and old newsprint samples, the presence of magnesium on the reverse surface which was not treated was detected when analysed six months after the treatment (Appendix 5).

4.2.4 **Discussion and Conclusions**

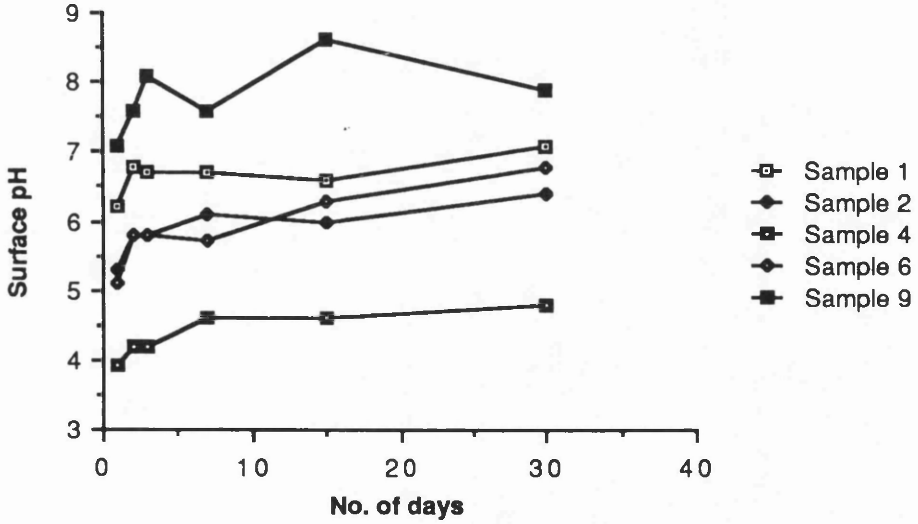
The difficulties and defects of aqueous deacidification processes have lead to the development of non-aqueous solvent-based techniques. A number of magnesium compounds have been used in solvent deacidification and found to be active, even though certain limitations such as the solutions being poisonous and having the ability to attack inks and colours and spread them through the book do exist and are well known. Magnesium compounds are particularly attractive as deacidification agents, as they tend to be more soluble compared to calcium or other alkaline earths, which makes their use more convenient and makes the attainment of an adequate alkaline reserve somewhat easier. It was also reported that magnesium compounds may stabilize some wood pulps (Robert et al., 1965).

4.2.4.1 Surface pH

Samples obtained as a result of spraying twice on each surface showed a small increase in pH over that of samples treated once with the suspension on each surface (Table 4.1). The increase in pH of the reverse surface of the single surface treated samples is given in Graph 4.1. This clearly shows diffusion of either the acid in the paper or of the magnesium compound. The results and observations indicated that the treatment was neutralising the acid, fully or partially. It is a known fact that, if the paper becomes too alkaline, it can undergo alkaline hydrolysis (Section 1.2.2.1.2). High pH values may also cause tinting or colour changes in inks, and yellowing of paper made from ground wood (Williams et al., 1977). In this process, the pH of paper never exceeds ten, therefore no risk of alkaline hydrolysis and colour changes mentioned above exists.

The pH of the fresh suspension was found to be 10.1 initially, falling to 9.7 on standing for three weeks, possibly as a result of carbonation.

Artificial ageing of treated samples resulted in a decrease in pH, but this was less in treated samples compared to the untreated samples (Table 4.2). The decrease in pH of treated samples was probably due to neutralisation of acidic groups of the cellulose and lignin. From the above results and observations it is certain that this treatment could be used to deacidify all types of paper completely, although as a spraying technique it is applied only to the surface.



GRAPH 4.1: Correlation of surface pH and time elapsed after $Mg(OH)_2$/IMS treatment

4.2.4.2 FTIR

The FTIR results were not particularly informative. No reduction in the intensity of the peak at 1724 cm^{-1} due to the COOH group or an increase in the peaks at 1560 cm^{-1} or 1402 cm^{-1} due to COO^- were observed. This may be a result of the very low concentrations or the fact that simple salts were not formed.

The peak at 3700 cm^{-1} was not seen in Whatman papers and modern newsprints, but was present in all samples treated with magnesium hydroxide. The intensity of the peak increased in papers which already showed the peak. The peak at 3700 cm^{-1} is difficult to explain, but it may be due to the association of certain metal ions with cellulose. It is stated that the spectra of the hydrated magnesium carbonate minerals is unique, and in addition to the usual broad peak in the hydroxyl region, one or more very sharp peaks occur (White, 1974). The author observed the presence of the peak at 3700 cm^{-1} only in the spectrum of magnesium hydroxide, out of the spectra of several hydroxides taken, in order to determine the group represented by this particular peak. Hence the peak at 3700 cm^{-1} is due to magnesium hydroxide and it leads to an assumption that the papers which exhibit this peak may contain some inorganic compound consisting of another magnesium compound such as talc.

Exposure to air should convert any excess of magnesium hydroxide to the carbonate. This might be expected to give peaks at 747, 887 and 1485 cm^{-1} (White, 1974). These peaks were not observed, possibly due to the slowness of the reaction, or because the concentrations were too low. Similarly, the peaks corresponding to $MgCO_3.3H_2O$ neither appeared nor was there an intensity increase in existing peaks where expected at 852, 1097, 1415, 1469 and 1518 cm^{-1}. Data for $MgCO_3.5H_2O$ has not been reported.

In old newsprints, an increase in intensity of the peak at 1086 cm^{-1} was observed. The peak at 1086 cm^{-1} can be assigned to a C-O-H vibration in cellulose, and a hydroxyl vibration in lignin (Appendix 4). Since there was no change in the spectra of Whatman samples, it must be due to a change in the hydroxyl group in lignin. Since the change was observed only in old newsprints, it implies that magnesium hydroxide has reacted with a group in lignin resulting from deterioration, which might be a phenate ion. Hence the intensity increase in the peak at 1092 cm^{-1} may be due to the formation of a compound containing hydroxyl groups. Thus, this treatment could prevent further deterioration which occurs due to a phenolic free radical mechanism in mechanical wood papers.

4.2.4.3 Scanning electron microscopic analysis

Since the X-ray fluorescent analysis indicated the presence of magnesium on the reverse untreated surface, it is clear that in a period of less than six months after the treatment the magnesium buffer diffuses throughout the paper, possibly as magnesium bicarbonate.

The SEM has found wide-ranging applications in pulp and paper technology as the surface of a specimen can be brought into focus over an area of several square millimetres, in addition to obtaining a remarkable depth of the field in scanning electron microscopy (Browning, 1977). The SEM photographs indicated minute particles of magnesium hydroxide on the treated surface. Therefore it confirmed that the particles introduced are minute and are evenly spread on the paper in this treatment.

4.2.5. Conclusions

The magnesium hydroxide /IMS treatment increases the pH of the sample, and also the buffer which was formed diffuses through the paper, enabling the process of neutralisation to occur although this is a surface treatment.

Being a non aqueous and spraying method, this process facilitates deacidification of bound as well as unbound documents in addition to fragile documents.

FTIR analysis clearly showed that this treatment could stabilize mechanical wood papers.

Hence this process can be recommended for deacidifying a variety of materials, without the necessity for elaborate safety precautions.

4.3 CAPPING LIGNIN

As a proposed measure for stabilizing paper, the capping of lignin was attempted in order to block the functional groups in lignin which undergo chemical reactions governing the deterioration of mechanical wood paper. The choice of reagents was determined by the requirement to block the phenolic OH of lignin as the phenate ion is mainly responsible for yellowing paper and undergoing photochemical reactions. The other requirement was that the reagent should be volatile, so that vapour phase treatments could be used. Treatments with the following reagents were carried out for modern newsprints mainly as they contain all possible functional groups responsible for yellowing which could be subjected to blocking, and old newsprints were made use of on some occasions, and when clarification was needed Whatman samples were treated with the reagents. Sample identifications are given in tables 4.3 , 4.4 and 4.13.

4.3.1 Formaldehyde treatment

4.3.1.1 Reasons for the choice

Formaldehyde reacts with phenols. Since lignin contains phenolic groups, it is very likely that formaldehyde will react with lignin and also furthermore formaldehyde being volatile renders it suitable for vapour phase treatment.

4.3.1.2 Experimental method

Newspaper samples were suspended in a fumigation tank containing concentrated formaldehyde solution in an evaporating dish at room temperature (20°C) for 5 days. Similar experiments were carried out at 45°C and 55°C for different periods of up to 7 days. The samples exposed to formaldehyde vapour were subjected to fadeometer aging with an untreated control to assess the effect of treatment.

Temperature °C	Length of the treatment (days)	
	5	7
	Batch No.	
20	i1, i4	
45		i2
55		13

4.3.1.3 Results and Observations

4.3.1.3.1 FTIR

Spectra of the formaldehyde treated samples showed no difference, except that in those samples treated at 20°C for 5 days the peak at 897 cm^{-1} and the shoulder at 874 cm^{-1} decreased greatly, and in others the decrease was a slight. It was observed that the peak which decreased, subsequently increased as in untreated paper when the sample was subjected to fadeometer ageing (Figure 4.6).

The spectra of Whatman samples treated with formaldehyde at 20°C for 5 days ($9i_4$) showed an intensity decrease of the peak at 897 cm^{-1} (Figure 4.7).

4.3.1.3.2 Weight

Weight changes recorded are given in Table 4.3

Sample No.	Wt. gain (%)	Surface pH	Colour
4A	-		brown
$4i_4$	7.4		brown
$4i_4U$			brown
56A	-	5.9	off white
56AU			dark yellow
$56i_1$		4.3	off white
$56i_1U$			dark yellow
$56i_2$		6.0	off white
$56i_2U$			dark yellow
$56i_3$		6.4	off white
$56i_3U$			dark yellow
$56i_4$	15		off white
$56i_4U$			dark yellow
9A	-		white
$9i_4$	7.6		white
$9i_4U$			white

i - formaldehyde treatment

TABLE 4.3: Changes in weight, surface pH and colour on formaldehyde treatment

4.3.1.3.3 Surface pH

Recorded surface pH are given in Table 4.3

4.3.1.3.4 Physical appearance

Recorded physical appearance is given in Table 4.3

4. 3. 1.4 Discussion and Conclusions

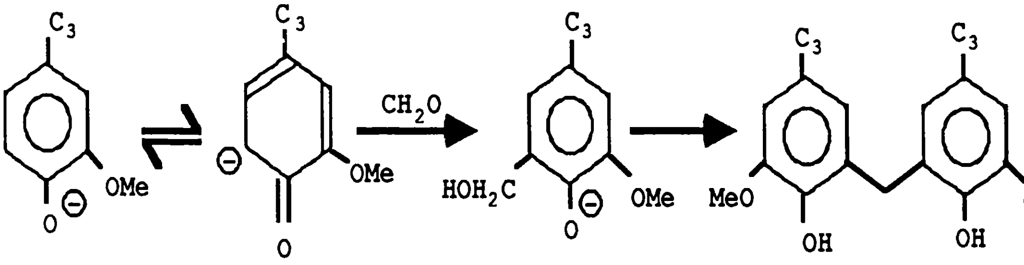
When paper samples are treated with formaldehyde, a number of possible reactions can occur, including a) reaction of formaldehyde with cellulose

b) reaction of formaldehyde with lignin

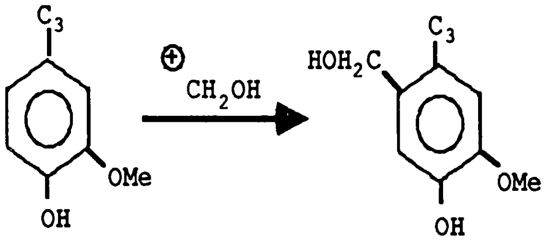
c) reaction of formaldehyde with both cellulose and lignin

d) formation of condensation products of formaldehyde, and their reaction with cellulose or lignin or with both.

The reaction of formaldehyde with lignin can result in a condensation reaction (Billington, Simmonds and Baird, 1933), which would develop methylated lignins similar to the widely used phenol formaldehyde adhesive resins (Carroll and Wallin, 1965; Allan,1971). In alkaline media only those lignin units having a free phenolic hydroxyl group are capable of nuclear reaction (Allan, 1971). In acid solution the protonated formaldehyde can react with the aromatic groups in the lignin units, whether or not they contain a free phenolic hydroxyl group, to afford a methylated lignin (Allan, 1971). The reactions of formaldehyde with lignin can be denoted as in equations 4.1 and 4.2, illustrating the mechanism in alkaline media and in acid media respectively. (Allan, 1971).



—— 4.1



—— 4.2

4.3.1.4.1 <u>FTIR</u>

Since paper contains free water, formaldehyde may form methylene glycol as a result of hydration, when absorbed into paper. In dilute aqueous solutions, formaldehyde is almost 100% hydrated to form methylene glycol (Bieber et al., 1947; Finar, 1964) as in equation 4.3.

$$CH_2O \; + \; H_2O \quad \rightarrow \quad CH_2(OH)_2 \qquad \text{----------} \; 4.3$$

IR spectroscopic details of $CH_2(OH)_2$ have not been reported, and time did not permit the author to investigate it further. However, if methylene glycol was formed, the peaks related would have been obscured by the cellulose peaks in the FTIR spectrum.

When a formaldehyde solution is evaporated to dryness, paraformaldehyde $[(CH_2O)n.H_2O]$ polymer is formed which evolves formaldehyde on heating (Finar, 1964). When the samples were treated at 45°C and 55°C, this possibility could have occurred as paper would have been in a dry state. IR spectroscopic details of paraformaldehyde are not reported in the literature, and hence the author is unable to comment on the formation of paraformaldehyde.

There is also a possibility of forming a trimer, trioxymethylene, when paper is treated with formaldehyde at room temperature. Formaldehyde slowly polymerises to form trioxymethylene (metaformaldehyde, trioxan) $[CH_2O]_3$ when allowed to stand at room temperature (Finar, 1964). If it was formed, there would not have been a reaction, as it neither shows any reducing properties nor does it contains any reactive functional groups. Since it is a polymer, it could polymerise onto paper without taking part in a reaction, and hence the author would have observed changes in the FTIR spectra, with appearance of peaks at 2857, 1408, 1163, 1064, 962 and 930 cm^{-1} due to trioxymethylene (Pouchert, 1970). The FTIR spectra of the samples treated with formaldehyde did not show any of these peaks.

The greater intensity decrease of the peak at 897 cm^{-1}, in modern newsprint and Whatman paper on treatment at room temperature for 5 days, and a small decrease in the intensity of that peak under the other conditions, means that a compound has formed which could modify the group CH_2-OH (Appendix 4) which absorbs at that frequency. And also it was observed that on exposure to the fadeometer the change disappeared, hence the compound formed decomposes on exposure to light and/or heat. The compound formed can only be a weak addition compound, which decomposes readily. Hence this reaction is reversible.

4.3.1.4.2 Weight

With the indication of weight gain (Table 4.3), it was obvious that some reaction had taken place and/or a polymer had been deposited. The extent of the reaction was greater in modern mechanical wood papers, and it may be that the reaction had taken place or polymerisation occurred mainly due to fresh (unbroken) lignin.

4.3.1.4.3 Surface pH

With the pH measurements, it was observed that pH decreased in the samples treated at 20°C for 5 days which may be due to the formation of formic acid. In other conditions, the pH increased with the treatment, and if formic acid was formed it must have been vaporised at higher temperatures. If formic acid was produced and retained in paper, it could harm the paper. Hence this treatment is not suitable in that respect.

4.3.1.3.4 Physical appearance

On fadeometer exposure, all treated papers also became yellowish as did the untreated samples. The formaldehyde treatment did not stop the process of yellowing lignin-containing papers, although there is a possibility that partial stabilization occurs with the treatment at 45°C and 55°C, as the yellowing was slightly less intense.

4.3.1.4 Conclusion

This reaction is not peculiar to lignin and does not lead to stabilization. So it was not investigated further.

4.3.2 Formaldehyde and ammonia treatment

4.3.2.1 Reasons for the choice

As mentioned in section 4.3.1.1 formaldehyde can react with lignin. Ammonia which is an alkali might increase the rate of the reaction in addition to the effect of deacidification. And also being volatile, can be used even for fragile documents.

4.3.2.2 Experimental method

Whatman No.1 and a modern newsprint were exposed to ammonia vapour and formaldehyde vapour simultaneously, by suspending the samples in the same way in the tank containing evaporating dishes with formaldehyde solution and 0.880 ammonia solution respectively for different periods at different temperatures. One batch was treated in the same way for 7 days in the presence of water. Some samples were treated for 3 days at room temperature (20°C), in daylight and in the dark for comparison.

Temperature	Length of treatment (days)			
°C	1	3	6	7
	Batch No.			
20	n_5	n_4	n_1	n_8
20		*n_6		°n_7
35		n_3		n_2

* in the dark

o in presence of water

4.3.2.3 Results and observations

4.3.2.3.1 FTIR

Spectra of the samples of newsprint treated with formaldehyde and ammonia under all conditions except at 20°C for 3 days (n_4) and at 35°C for 7 days (n_2) showed a decrease in intensity or disappearance of the peak at 1733 cm^{-1}. An increase in the intensity of the peak at 820 cm^{-1}, a shape difference and a shift to 2906 cm^{-1} in the peak at 2902 cm^{-1}, was observed in spectra of the samples treated under almost all conditions, except at 20°C for 6 days. The newsprints treated at 20°C for 3 days showed some differences in the spectra compared with the spectra of other treated samples, and showed an intensity increase in the peaks at 1456, 1380, 1235 cm^{-1} and 712 cm^{-1}, the appearance of a weak peak at 780 cm^{-1} and very weak peaks at 1830 cm^{-1}, 1950 cm^{-1} and 2010 cm^{-1} and no identifiable change in intensity of the peak at 1733 cm^{-1} (Figure 4.8). Even when the samples were treated in the dark, there was no difference in the spectra compared to the other treated samples except in those treated at 20°C for 3 days under normal conditions. A slight decrease in intensity of the peak at 1510 cm^{-1} was observed in spectra of the sample treated for 3 days at 35°C

The spectra of Whatman samples did not show any changes resulting from the treatment.

Sample No.	Wt. gain (%)	Surface pH	Colour
4A	-	4.3	brownish
$4n_{7-1}$	8.5	8.0	brownish > 4A
$4n_8$	6.0	8.3	brownish > 4A
56A	-	6.5	off white
$56n_1$		6.2	brownish
$56n_2$		7.0	off white
$56n_3$	7.0	7.7	brownish
$56n_4$	16.0	6.9	yellowish white
$56n_5$	12.0	7.8	yellowish
$56n_6$	6.0	7.3	yellowish < 56n5
$56n_{7-1}$	10.0	7.2	yellowish
$56n_8$	6.0	8.3	brownish
9A	-	5.5	white
$9n_2$		6.3	white
$9n_3$	6.0	6.6	white
$9n_4$	4.0	6.0	white
$9n_5$	8.0	6.5	white
$9n_6$	5.5	6.3	white

TABLE 4.4: Changes in weight, surface pH and colour on formaldehyde and ammonia treatment

With the ageing treatments, it was observed that although the intensity of the peak at 1733 cm^{-1} increased and became 1747 cm^{-1}, the change was less in the treated samples (3 days at

20°C and 35°C) compared with the untreated ones. Even the samples which showed differences in the spectra due to the treatment, showed no difference to other treated and aged samples with ageing (Figure 4.9) .

4.3.2.3.2 Weight

Weight changes recorded are given in Table 4.4

4.3.2.3.3 Surface pH

Surface pH recorded is given in Table 4.4

4.3.2.3.4 Physical appearance

All the samples treated became yellowish.

4.3.2.4 **Discussion and Conclusion**

The reactions with formaldehyde have been discussed in 4.3.1.4. When ammonia reacted with mechanical wood papers the latter became yellowish, which was not observed in Whatman samples. Hence definitely, ammonia reacts with lignin and results in a yellowish paper.

In the presence of weak alkalies, formaldehyde can polymerise to a mixture of sugars known as farmose or α-acrose (Finar, 1964). If these polymers have been deposited on paper, the spectra of treated samples should indicate peaks due to farmose and α-acrose which should be similar to cellulose peaks.

When treated with ammonia, formaldehyde gives hexamethylenetetramine (Finar, 1964) which can be denoted as in equation 4.4.

$$6HCHO \ + \ 4NH_3 \ \text{----->} \ (CH_2)_6N_4 \ + \ 6H_2O \quad \text{----------} \quad 4.4$$

4.3.2.4.1 FTIR

If hexamethylenetetramine was deposited on the paper, there should have been peaks at 2941, 1449, 1370, 1235, 1053, 1010, 813 and 671 cm^{-1} (Pouchert, 1970) in the spectra of treated samples. From the observations it was recognised that there was no formation of hexamethylenetetramine as could be identified using FTIR.

Whatman samples did not show any changes in FTIR spectra, colour or transparency except for the weight gain. Hence whatever the change which occurred in cellulose, it was not detected by FTIR. Either the changes are on a minute scale or they were not involving the functional groups detected by FTIR.

The disappearance or decrease in the intensity of the peak at 1733 cm^{-1} which has been allocated to C=O in unconjugated ketone and/or acetyl and uronic ester (Appendix 4) in FTIR spectra of newsprints, due to the treatment under certain conditions (6 days, 1day and 3 days in the dark at 20°C, and 3 days at 35°C) indicated that reduction had occurred and formed an aldehyde or alcohol. This feature was observed in thermomechanical wood pulp, which is supposed to be somewhat stable compared to mechanical wood. Hence it is a possibility that formaldehyde and ammonia treatment can stabilize mechanical wood in certain respects. If a reaction had taken place with a phenolic group of lignin, the peak at 1510 cm^{-1} which has been assigned for aromatic stretching and skeletal vibrations and phenolic groups in lignin (Chapter 3 and Appendix 4), should change in intensity or in frequency. These changes were not observed, except in the spectra of the sample treated for 3 days at 35°C. Possibly the change was not observed as there was no reaction as such or the reaction occurred on a small scale and FTIR could not detect it. Since the sample treated for 3 days at 35°C did not show a great increase in intensity of the peak at 1724/1747 cm^{-1} with ageing compared to untreated and other treated samples, not much free acid and/or ester which is a lignin degradation product had been formed, and it indicated that at least partial stabilization had occurred. The sample treated for 3 days at 35°C may have undergone partial stabilization of phenolic groups too.

Since the spectra of the same sample at different locations showed slight changes on many occasions, it is certain that the treatment is not uniform or the paper itself is not homogeneous.

4.3.2.4.2 Weight

Since there was a weight increase in every sample (Table 4.4), it is obvious that some sort of resin or polymer had been deposited.

4.3.2.4.3 Surface pH

The pH of the treated samples of Whatman was moreover the same or slightly increased, this may be due to ammonia adsorption.

The surface pH measurement of mechanical wood papers showed an increase with the treatment. This may be due to the product formed as a result of the reaction or due to ammonia. Since it increases the pH, the treatment can stabilize paper in respect of removing acid and becoming alkaline. If this increase of pH was due to ammonia, it is not a significant factor to be considered as ammonia is volatile, hence the pH will be decreased within a very limited time period.

4.3.2.4. 4 Physical appearance

Since all the treated samples became yellow or brownish, this treatment is not very suitable in that respect either.

With ageing, the samples became brownish making the treatment even less attractive.

4.3.2.5 **Conclusion**

Although this treatment may result in small amount of stabilization, the colour change makes it unacceptable for development as a practicable treatment.

4.3.3 **Ethylene oxide treatment**

4.3.3.1 **Reason for the choice**

A reaction of ethylene oxide with lignin had been reported by Nikitin and Rudneva (1935). Ethylene oxide is a gas and hence it can be used for any type of document, i.e. for bound as well as disbound and fragile items.

4.3.3.2 **Experimental method**

Paper samples were exposed to ethylene oxide gas in an airtight fumigation chamber (Honeywell Pern) at different temperatures (20°C, 70°C) and for different time intervals (3, 5, 7, 9, 20, 30 and 94 hours). One batch of samples was exposed to the vapour from 5% ammonia solution for 30 minutes before the treatment. Weight gain or loss and surface pH were recorded.

Temperature	Length of treatment (hours)						
	3	5	7	9	20	30	94
		Batch No.					
20°C	g_{13}	g_{11}	g_{12}		g_4	g_{10}	g_9
70°C	g_8	g_5	g_7	g_{14}			
		*g_6					

* pre-exposure to ammonia

4.3.3.3 **Results and observations**

4.3.3.3.1 Weight

Recorded weight gains are given in table 4.5

Sample No.	Temp.	Wt. gain or loss(%)						
	°C	[3]	[5]	[7]	[9]	[20]	[30]	[94]
4	20	0.1	0	0.6		-0.4	1.2	1.2
	70	1.3	1.5 *1.6	2.6	4.9			
62	20	0.1	-0.3	0.8		-1.4	1.0	0.7
	70	1.2	1.9 *2.5	2.7	4.7			
63	20	0	-0.3	0.8		-0.9	0.6	0.6
	70	0.9	0.9 *1.6	2.3	4.0			

- wt. loss

* NH_3 pre-exposure

TABLE 4.5: Change in weight on ethylene oxide treatment

Sample No.	Temp °C	Surface pH							
		[0]	[3]	[5]	[7]	[9]	[20]	[30]	[94]
4	20	4.3	4.8	4.3	5.5		4.8	4.6	4.8
	70		4.9	5.2 *6.0	5.6	5.7			
62	20	5.8	5.9	6.0	6.2		6.0	6.2	6.2
	70		6.1	6.3 *6.3	6.4	6.6			
63	20	6.7	6.6	6.5	6.4		6.5	6.1	6.1
	70		6.7	6.6 *6.6	6.5	6.6			

[...] hours

* NH_3 pre-exposure

TABLE 4.6: Change in surface pH on ethylene oxide treatment.

4.3.3.3.2 Surface pH
Recorded surface pH is given in Table 4.6

4.3.3.3.3 Physical appearance

The samples treated with ethylene oxide did not show any colour change, except in the case of ammonia pre-exposed modern newsprints. It was observed that when the modern newsprint sample was exposed to ammonia for 30 minutes, it became yellowish.

In the process of artificial ageing, the samples became yellowish, irrespective of the treatment.

4.3.3.3.4 FTIR

Spectra of Whatman samples did not show any change except for an intensity increase in the peaks at 1092, 1043 and 1003 cm^{-1} in samples treated at 70°C (Figure 4.10), while modern newsprint samples showed a decrease in intensity of the peaks at 1456, 1086/1092 and 1178 cm^{-1} at 70°C (Figure 4.11). Old newsprint treated with ethylene oxide did not show characteristic differances, except the intensity decrease of the peak at 1086 cm^{-1} and in the case of the ammonia pre-treated sample, in which the peak at 1205 cm^{-1} altered to a shoulder.

The subtraction of spectra of untreated from those of ethylene oxide treated samples did not reveal any other noticeable feature.

4.3.3.3.5 DSC

The DSC curves obtained on heating the samples of Whatman, modern and old newsprint are given in Figures 4.12 and 4.13. These indicated a significant difference in DSC parameters of the untreated cellulose and modern and old newsprint samples.

The calculated values of onset temperature (T_o), peak height (P) of untreated samples and calculated ratios of peak heights (P_r), and peak area (A_r) of the second and first exothermic peaks are given Table 4.7.

Heating rate (40°C/m)	$T_{o\,(1)}$	P_1	A_1	$T_{o\,(2)}$	P_2	A_2	A_r	P_r
Whatman No.1	350.4	49.9	2100	481.0	37.9	1729	0.82	0.76
Modern newsprint	317.8	22.6	1643	463.9	57.9	2275	1.38	2.56
Old newsprint	305.2	14.8	1163	422.9	19.9	1356	1.16	1.34
Heating rate (40°C/m)								
Lignin	207.9	2.9	1497	469.0	27.9	6795	4.50	9.60

A_1 - peak area of the first exotherm A_2 - peak area of the second exotherm A_r - area ratio P_1 - peak height of the first exotherm P_2 - peak height of the second exotherm P_r - peak ratio $T_{o\,(1)}$ - onset temperature of the first exotherm $T_{o\,(2)}$ - onset temperature of the second exotherm

TABLE 4.7: DSC parameters of untreated Whatman No.1, modern and old newsprint samples

Calculated values of DSC parameters of modern newsprint treated with ethylene oxide at 20°C and 70°C are given in Tables 4.8 and 4.9 respectively. The DSC parameters of the same are given in Figure 4.14. It indicated that there was an increase in the magnitude of the first exotherm with increased exposure to ethylene oxide, which reached a maximum value at 94 hours at 20°C. A decrease in the calculated area ratio was also observed in this case (Tables 4.8 and 4.9).

Heating rate (40°C/m)	Time (hrs)	P_1	A_1	A_2	Ar
	0	23.5	1722	2412	1.4
	5	35.1	2010	2412	1.2
	30	43.9	2476	2972	1.2
	94	64.7	3240	2592	0.8

A_1 - peak area of the first exotherm A_2 - peak area of the second exotherm
A_r - area ratio P_1 - peak height of the first exotherm

TABLE 4.8: DSC parameters of a modern newsprint treated with ethylene oxide at 20°C

Heating rate (40°C/m)	Time (hrs)	P_1	A_1	A_2	Ar
	0	23.5	1722	2412	1.40
	3	23.9	1568	2227	1.42
	5	24.1	1670	2204	1.32
	7	28.4	1794	2296	1.28

A_1 - peak area of the first exotherm A_2 - peak area of the second exotherm
A_r - area ratio P_1 - peak height of the first exotherm

TABLE 4.9: DSC parameters of a modern newsprint treated with ethylene oxide at 70°C

The DSC parameters of the old newsprint treated with ethylene oxide are given in Figure 4.15 and the calculated values are given in Table 4.10.

Time (hrs)	$T_{o\,(1)}$	P_1	A_1	$T_{o\,(2)}$	P_2	A_2	A_r	P_r
Temperature 70°C								
0	279.3	6.9	1880	398.6	6.5	1781	0.95	0.94
5	281.3	8.1	1963	392.5	5.2	1538	0.78	0.64
7	283.3	8.4	1777	383.9	5.9	1716	0.96	0.70
9	271.4	5.3	1749	396.6	5.9	1646	0.94	1.10
Temperature 20°C								
94 hrs	284.3	8.2	1957	394.2	6.0	1590	0.81	0.70

A_1 - peak area of the first exotherm A_2 - peak area of the second exotherm
A_r - area ratio P_1 - peak height of the first exotherm P_2 - peak height of the second exotherm P_r - peak ratio $T_{o\,(1)}$ - onset temperature of the first exotherm $T_{o\,(2)}$ - onset temperature of the second exotherm

TABLE 4.10: DSC parameters of an old newsprint treated with ethylene oxide at 70°C and 20°C

Figure 4.15 showed a shift in onset temperature (T_o) to higher values for both exothermic reactions of the old newsprint sample treated for 7 hours at 70°C. In this case a reduction in area ratio (A_r) was observed for the sample treated for 5 hours at 70°C.

The increase of onset temperature for both the exothermic reactions in the treated samples indicated an improvement in thermal stability.

4.3.3.3.6 Elemental analysis

The carbon and hydrogen content of untreated Whatman, and old and modern newsprint is given in Table 4.11, whereas those for ethylene oxide treated samples are given in Table 4.12

Sample No.	C%	H%	O%
Whatman No.1	42.40	6.25	51.35
Modern newsprint	49.61	6.44	46.65
Old newsprint	33.55	4.82	61.36
Lignin	58.11	5.45	36.44

TABLE 4.11: Elemental analysis of untreated samples

Old newsprint contains a significantly lower carbon content and a higher oxygen content as compared to modern newsprint andWhatman No.1 (Table 4.11). This is partly due to the higher content of carboxylic acids resulting from degradation.

An increase in the carbon content (about 3%) was observed in old newsprint exposed to ethylene oxide for 9 hours at 70°C.

Temperature 70°C Time (hours)	% C	% H	% O
0	33.55	4.82	61.36
3	35.16	4.96	59.88
5	34.26	4.90	60.84
5 (+ 30 min. NH_3)	34.44	4.84	60.72
7	35.78	5.16	59.06
9	36.73	5.30	57.97
Temperature 20°C			
94 hours	35.11	5.04	59.85

TABLE 4.12: Elemental analysis of old newsprint treated with ethylene oxide

4.3.3.3.7 DETA

Figure 4.16 shows the tan-δ peak at 45°C at three different frequencies for untreated old newsprint. Figures 4.17 and 4.18 show that a new tan-δ peak appeares at a higher temperature, i.e. 55.5°C for the sample treated for 94 hours at 20°C, and 56.5°C for the sample treated for 9 hours at 70°C.

4.3.3.4 Discussion and Conclusions

The treatment was carried out at room temperature for different periods of time, as it is always preferable to do any chemical treatment to archival materials at room temperature. Later it was tried at 70°C, after pre-exposing to ammonia, as the lignin and ethylene oxide reaction was reported as having been carried out at 70°C, in presence of a base (Nikitin and Rudneva, 1935, Malinovskii, 1965). Since the ammonia pre-exposure makes the modern newsprints which contain mechanical wood yellowish, the rest of the treatments were carried out without exposing to ammonia.

When paper samples are exposed to ethylene oxide, three possibilities likely to occur can be listed as follows:

a. ethylene oxide reacts with cellulose
b. ethylene oxide reacts with lignin
c. formation of poly ethylene glycol and deposition on the paper, or involved in the reaction, or both.

Ethylene oxide reacts with alkaline cellulose to form hydroxyl ethyl cellulose (Heuser, 1944) and according to Nikitin and Rudneva (1935), ethylene oxide reacts with pure cellulose very slowly which can be accelerated in the presence of alkali, forming a product containing three hydroxyl groups which is capable of adding further ethylene oxide.

Since each variety of lignin contains a basic unit carrying a phenylpropane ring with a carbon-carbon double bond, and an aliphatic hydroxyl group in the propane unit and a phenolic hydroxyl group, ethylene oxide might react with one or more reactive groups at one or more positions. Under normal conditions and even in the gas phase, ethylene oxide does not react with alcohols (Malinovskii, 1965). The addition of ethylene oxide to phenol at 70°C in the presence of sodium phenate takes place in two steps and yields the ion of monoglycol phenyl ether (Eq. 4.5 - 4.7).

$$C_6H_5O^- + C_2H_4O \rightarrow C_6H_5OCH_2CH_2O^- \qquad \text{---- 4.5}$$

$$C_6H_5OCH_2CH_2O^- + C_6H_5OH \rightarrow C_6H_5O^- + C_6H_5OCH_2CH_2OH \qquad \text{---- 4.6}$$

$$C_6H_5OCH_2CH_2O^- + C_2H_4O \rightarrow C_6H_5OCH_2CH_2OCH_2CH_2O^- \qquad \text{---- 4.7}$$

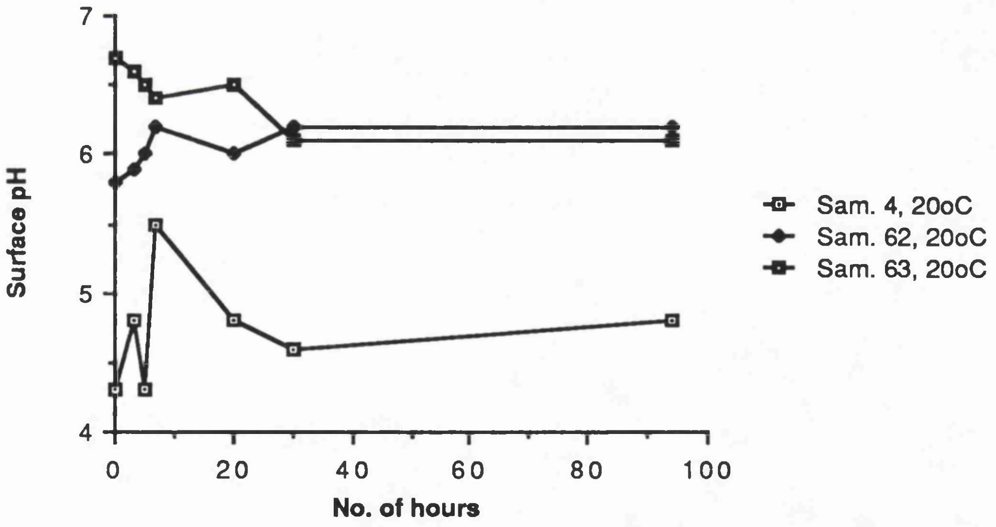
When ethylene oxide reacts with lignin it is likely that, at least at 70°C, the functional groups mentioned above react in a similar manner. It is also stated that ethylene oxide probably reacts with the phenolic (or enolic) rather than the aliphatic hydroxyl groups because of the much greater nucleophilicity of the phenoxide anions. Nevertheless, it need not follow that all the phenolic hydroxyls are easily hydroxyethylated and it is unlikely that polyethyleneoxy chains originating from a phenolic (or enolic) group could be propagated, because of the presence of water (Furukawa and Saegusa, 1963). Thus, Ishikawa, Oki and Fujita (1961) have observed that phenolic hydroxyl groups which are non-conjugated through the benzene ring with carbonyl or unsaturated moieties in the surface chain react with ethylene oxide and phenyl hydroxyl groups which are so conjugated, and are resistant to hydroxyethylation.

4.3.3.4.1 Weight

Weight gain or loss obtained is not significant except in the cases of the treatment for 7 and 9 hours at 70°C in all types of sample. Since humidity in the atmosphere and the moisture content in the sample could effect the results, the change in weight may not be reliable in indicating a chemical change.

4.3.3.4.2 Surface pH

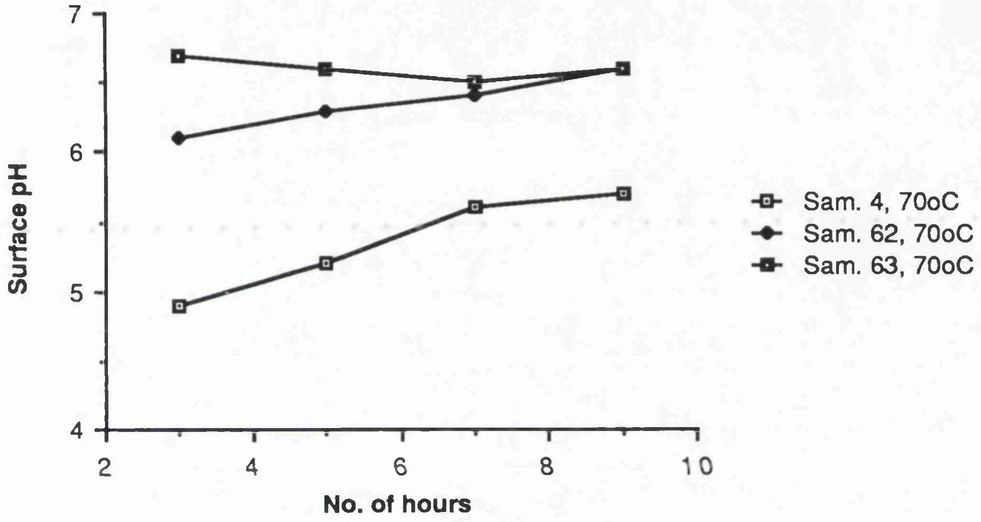
Surface pH of Whatman No.1 samples treated at 20°C decreased with the increase in the duration of the treatment. It also followed the same pattern at 70°C, displaying a clearer trend in it (Graph 4.2 and 4.3). The reason for this decrease in pH is unclear.



GRAPH 4.2: Change in surface pH on ethylene oxide treatment at 20°C

It is stated that the treatment of cellulose with ethylene oxide strongly increases its ability to hydrolyse (Nikitin and Rudnev, 1935). The decrease of surface pH which was observed may be due to the formation of hydrolysed products which are acidic in nature.

The surface pH of the samples containing lignin showed an increase with the increase in duration of treatment at 20°C and 70°C, and showed a direct correlation at the latter temperature (Graph 4.2 and 4.3). Ethylene oxide or a reaction product of ethylene oxide and lignin may have reacted with acidic compounds in paper samples containing lignin . Hence considering that assumption, the increase of pH in newsprints can be explained.



GRAPH 4.3: Change in surface pH on ethylene oxide treatment at 70°C

4.3.3.4.3 Physical appearance

With artificial ageing, it was observed that newsprint became yellow even after the ethylene oxide treatment, hence it is obvious that ethylene oxide under these conditions did not react or only partly reacted with the groups in lignin which cause discolouration on ageing.

4.3.3.4.4 FTIR

It is likely that if a reaction took place, one of the resultant products would be an ether. If this is so, there should be a strong peak at 1110 cm^{-1} due to C-O stretch in non aromatic ethers (Pouchert, 1970) in spectra of the treated samples. Since the spectra of Whatman paper samples showed a decrease in intensity of the peaks at 1092 cm^{-1} (which has been assigned to C-OH deformation in cellulose and C-O-C deformation in aliphatic ethers), and 1043 cm^{-1} and 1003 cm^{-1} (assigned to C-O stretching in cellulose), it was obvious that ethylene oxide had reacted with cellulose at 70°C for 9 hours. These changes may have occurred due to the formation of an ether although there was no indication at 1110 cm^{-1} where the C-O stretch in non aromatic ethers is expected.

In FTIR spectra of the samples of old and modern newsprints there was no evidence of the formation of aromatic ethers, as there was no new peak at 1250 cm^{-1} and there was no change in intensities of the peaks at 1235 cm^{-1} and 1245 cm^{-1}. There is a strong peak at 1250 cm^{-1} in aromatic ethers due to C-O vibrations (Pouchert, 1970). It is possible that the reaction occurred on a small scale but FTIR could not detect it. Spectra of some of the samples of old and modern newsprints treated for a long period at 20°C, and all those treated at 70°C, showed a decrease in intensity of the peak at 1456 cm^{-1}, and it might be that this change can be seen as a result of a chemical reaction. Various sources mention that peaks at 1460 cm^{-1} and in the region of 1480-1350 cm^{-1} and 1462-1452 cm^{-1} are due to C-H deformation and bending and methoxy groups in lignin (Appendix 4). Hence, a chemical reaction had occurred in the samples containing lignin treated under specific conditions, although its identity is not certain. As mentioned earlier, an intensity decrease of the peak at 1086/1092 cm^{-1} may have occurred, perhaps as the result of a rection of ethylene oxide with lignin or cellulose which leads to the formation of an ether. Old newsprint showed no change, probably because the reacting groups have already deteriorated and hence there was no reaction or a reaction had occurred to a very small extent but was not identifiable through FTIR.

The colourless ethylene oxide compound formed at 70°C may be polyethylene glycol. The deposition or actual reaction was not identified in the spectra of any of the samples.

4.3.3.3.5 DSC

An interesting trend was observed in the ratio of peak area in the DSC data. It showed that Whatman No.1 which consists of more or less pure cellulose had an area ratio which was less than 1, while milled wood lignin from pine had a ratio much larger than 1. Modern newsprint (Sample 62) gave a ratio much lower than the pine lignin sample, but higher than the Whatman No.1. Old newsprint (sample 4) gave a lower value than that of modern newsprint. Hence it was obvious that the area or peak ratio in DSC parameters could indicate a change in lignin content, if any.

In the case of modern newsprint, DSC showed that there was a definite decrease in area ratio with prolonged exposure to ethylene oxide, directed towards the Whatman No.1. Although the old newsprint showed a trend in that direction, it was not clearly defined. The DSC curve of modern newsprint was very similar to that of unbleached refined mechanical pulp (Figure 4.19). According to Lee et.al. (1989) unbleached refined pulp generally contains 4.4% lignin. Elemental analysis showed that there was a difference of 4.5% in carbon content between Whatman No.1 and modern newsprint. It indicated that the modern newsprint investigated contained about 4.5% lignin, which is a small amount, thus the observed changes due to ethylene oxide treatement were small, although larger than those in the Whatman No.1. Hence the latter indicates that the ethylene oxide is reacting with the ligneous component in the paper.

It was found that the long exposure (94 hours) at 20°C showed similar results to the 7 hours at 70°C, hence the author would recomend either of these two conditions, out of the various conditions under which the experiment was carried out, at least for partial stabilizing of lignin, although FTIR showed no change at room temperature. For the practical treatment of archival material the lower temperature is obviously preferable.

4.3.3.4 Conclusions

The results of reactions due to the ethylene oxide treatment were too small to be detected with FTIR. With DSC analysis it was obvious that a reaction with lignin had taken place on ethylene oxide treatment, and as a result the thermal stability was improved and hence to some extent partial stabilization of lignin-containing papers had occurred under the conditions specified above.

4.3.4 Diazomethane treatment

4.3.4.1 Reasons for the choice

As described in section 1.2.2.3, groundwood papers become yellowish as a result of the formation of quinone compounds due to a free-radical reaction initiated at phenolic hydroxyl groups in lignin. In order to retard the yellowing effect, blocking of these functional groups could be done with a reagent capable of making stable compound(s). Diazomethane is an effective reagent, which can be obtained in gas phase at room temperature and it can be used for the methylation of acids, phenols and enols (Fieser and Fieser, 1961). Groundwood papers contain organic acids, and diazomethane can methylate the carboxylic acids in paper, resulting in methylated product(s). As diazomethane is a gas, this treatment can be used even on fragile documents, and also it can block the functional groups which are responsible for the yellow colouration and simultaneously deacidify the documents.

4.3.4.2 Experimental method

Preparation of diazomethane (CH_2N_2)

Dry nitrogen gas was passed through the first tube of the methylation apparatus (Plate 4.2) which contained diethyl ether, at the rate of 6 ml per minute. The gas, saturated with ether vapour, then passed into the second tube containing equal volumes of diethyl ether, ethyl digol and aqueous potassium hydroxide solution, where the generation of diazomethane occured on adding N-methyl-N-nitroso paratoluene sulphonamide. The generated diazomethane was passed into the reaction vessel containing the paper samples. This process was carried out according to Schelenk and Gellerman (1960).

Treatment

Materials

Paper samples with and without lignin including Whatman No.1, artificially aged papers containing acid, Whatman No.1 treated with an indicator compound (i.e. Alizarin red S; sodium alizarin-sulphonate), methanol (AnalaR).

Procedure

Paper samples were treated with diazomethane for 3 hours and another batch of similar samples were treated with diazomethane in the presence of methanol. The weight of the samples was recorded before and after the treatment. The surface pH of the treated and untreated samples was also recorded.

Some of the treated and untreated samples were artificially aged by exposing them in the fadeometer for 96 hours. The intensity of colour was measured by recording the relative reflectance of the surface of each sample using a microscope fitted with a photometer head.

4.3.4.3 Results and observations

Sample No.	Year of publ. and type	Wt.ch. %	Surface pH	Rel. refl. wh. li.
1/st./-	1796, B, E	0.2	6.0	8.3
1/DM/1		0.2	6.1	8.5
1/DM/3		0.6	6.1	8.9
3/St/-	1899, B, E	-0.2	6.5	9.6
3/DM/1		0.3	6.6	9.6
3/DM/3		0.7	6.6	9.7
4/St/-	1910, M, E, G.W	0.0	4.1	8.2
4/DM/1		0.0	4.7	8.4
4/DM/3		0.3	5.1	8.6
5/St/-	1924, B, E	0.1	5.8	9.0
5/DM/1		0.3	6.0	9.2
5/DM/3		0.8	5.6	9.2
6/St/-	1930, B, A	0.1	5.3	8.8
6/DM/1		0.2	5.8	9.0
6/DM/3		0.7	5.8	9.1
7/St/-	1933, B, E	0.0	4.9	9.0
7/DM/1		0.1	5.6	9.0
7/DM/3		0.6	5.6	9.2
57/St/-	1989, N, E, G.W	-0.3	5.7	7.9
57/DM/1		0.4	6.2	8.3
57/DM/3		1.2	6.5	8.8
62/St/-	1989, N, E, G.W	0.0	5.5	8.6
62/DM/1		0.5	6.0	8.8
62/DM/3		1.4	6.0	8.9
63/St/-	1988, Wh.1, E	0.0	5.9	9.0
63/DM/1		0.4	6.4	9.1
63/DM/3		1.3	6.3	9.1
82/St/-	1979, B, E, G.W	-0.3	5.4	7.0
82/DM/1		0.1	5.8	8.0
82/DM/3		1.5	5.6	8.2
86/St/-	1989, N, S , G.W	-0.1	5.9	8.2
86/DM/1		0.5	6.1	8.6
86/DM/3		0.8	6.7	9.0
87/St/-	1989, N, E, G.W	-0.1	6.1	8.1
87/DM/1		0.2	6.4	8.4
87/DM/3		0.8	6.3	8.5
88/St/-	1989, N, S, G.W	-0.1	6.2	8.2
88/DM/1		0.2	6.5	8.3
88/DM/3		0.8	6.4	8.8
89/St/-	1961, N, E, G.W	0.5	4.7	8.4
89/DM/1		0.1	5.3	8.6
89/DM/3		1.2	4.9	9.0
90/St/-	1893, N, E, G.W	-0.2	4.2	8.2
90/DM/1		-0.3	4.5	8.3
90/DM/3		0.4	4.5	8.5
62U54				3.0
62U54/DM/1				3.3
62U54/DM/3				3.5
63U54				4.4
63U54/DM/1				5.0
63U54/DM/3				5.5

wt. ch. -weight change (- loss) publ. - publication Rel. refl. -relative reflectance
wh.li. -white light N - newsprint E - European G.W -groundwood

TABLE 4.13 Changes in weight surface pH and relative reflectance of light on diazomethane treatment

4.3.4.3.1 Weight

Weight changes observed are given in Table 4.13

4.3.4.3.2 Surface pH

Recorded surface pH is given in Table 4.13

4.3.4.3.3 Physical appearance

No colour change was observed due to the treatment. On artificial ageing colour became very slightly lighter.

4.3.4.3.4 FTIR

A number of samples treated with diazomethane, either in the presence or in the absence of methanol, showed some changes in peak intensities. With Whatman paper there was no indication of the appearance of new peak(s) although there was an indication of a decrease the intensity or disappearance of the peak at 1724 cm^{-1} (Figure 4.20).

In the case of lignin-containing papers, either an appearance of a new peak, or a shoulder, or an intensity increase of the peak at 2948 cm^{-1} was observed in FTIR spectra of almost all samples regardless of the presence or the absence of methanol. The intensity of the peak at 1173 cm^{-1} (1177, 1180, 1182 and 1184 being shifted in some of the samples according to the characteristic of the sample), showed an increase in FTIR spectra of many samples (88, 86, 57, 5, 3, 7, 6 and 1) and a decrease in a few samples (4, 62 and 82) with the treatment (Figure 4. 21), but methanol did not contribute in any special respect to the change in the intensity of this peak.

In FTIR spectra of some of the samples, the intensity of the peak at 1132/1128 cm^{-1} changed in both directions with the treatment, out of which some (62, 88 and 87) showed a decrease in intensity in the presence of methanol. The intensity decrease was greater in samples 62 and 88, while sample 87 did not show much difference due to the presence of methanol. The peak intensity increased in some of the samples (86, 57,5,4, $62U_{54}$, and 1) with the treatment, and in the presence of methanol the intensity increase was higher in samples 5,4, $62U_{54}$ and 1, while the intensity increase was not affected due to the presence of methanol in the other two samples.

With the treatment, in the FTIR spectra of some of the samples the peak at 1086/1092 cm^{-1} decreased in intensity (62, 88, 62 U54, 86 and 87) , while an increase in intensity (5, 3, 1 and 57) occurred in some of the other samples. The intensity decrease of the samples 62, 88, 62 U_{54} and 86 was greater in the presence of methanol while sample 87 did not show any difference in the presence of methanol. The intensity increase was higher in the samples 3, 1 and 57 when they were treated with diazomethane in the absence of methanol.

4.3.4.4 Discussion and Conclusions

When paper is treated with diazomethane, methylation of some of the functional groups present in the lignin components occurs. Schmid (1925) has observed no reaction in cellulose on attempted methylation using diazomthane (Heuser, 1944). It is reported that phenolic groups in lignin may be deactivated by methylation with diazomethane exclusively at the side chain sites (Allan, 1971), and according to Finar (1964), phenolic methyl ethers may be obtained in excellent yield by the action of diazomethane on phenol, as shown in equation 4.8.

$$ArOH + CH_2N_2 \text{ ------> } Ar.O.CH_3 + N_2 \qquad \text{--------} \ 4.8$$

Hence the reaction was tried under two different conditions, i.e. with diazomethane alone, and with diazomethane in the presence of methanol. To methylate high molecular weight organic acids efficiently, the presence of methanol is necessary (R. White, pers. comm.).

4.3.4.4.1 Weight

Weight gain was observed in all the treated samples, except in sample 90 which is a highly degraded old newspaper. This indicated that a reaction had taken place, even in Whatman samples; obviously the reaction must have been more complete in the presence of methanol as the weight gain was greater. The decrease in weight of sample 90 with the treatment may be accounted for by the lack of any reaction with phenolic groups, which were probably absent due to oxidation of the lignin of the deteriorated paper, and possibly also as a result of loss of water or other volatile reaction products.

4.3.4.3.2 pH

It was observed that in all cases the surface pH increased during the treatment, and it may be accounted for by the fact that the diazomethane could have methylated free carboxylic acids. The mechanism can be explained as follows.

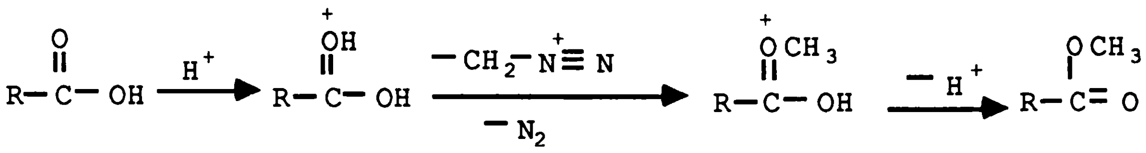


FIGURE 4.22: Mechanism of the methylation of free carboxylic acids with diazomethane

According to Browning (1967) diazomethane is effective in alkylating chiefly the phenolic, enolic and carboxylic groups which possess distinctly acidic properties.

4.3.4.3.3 Physical appearance

When the two Whatman samples were treated with a coloured acidic dye Alizarine red S, it was observed that in the presence of methanol, the colour loss was rapid. Hence in the presence of methanol the reaction occurs faster as the colour loss was more rapid in the presence of methanol.

4.3.4.3.4 FTIR

With the FTIR results, the disappearance or a decrease in intensity of the peak at 1724 cm^{-1} was observed, which has been assigned for free carboxylic acid groups resulting from the treatment under both conditions. Hence it is certain that acidic groups can be destroyed using diazomethane. This must be due to the methylation of carboxylic acids to methyl esters. From the FTIR results, it was not possible to distinguish between the reactions carried out in the presence of methanol or in its absence, even in the intensity of the peak at 1724 cm^{-1}. The peaks at 1173, 1132, 1096 cm^{-1} and 2906 cm^{-1} were affected due to the treatment in either way only in mechanical wood papers. Hence the change had occurred due to lignin. The peak at 1173 cm^{-1} is due to anti-symmetric C-O-C bridge stretching in cellulose and lignin and/or C=O vibration in lignin (Appendix 4). The C=O vibration can be changed, due to the methylation of ketone groups or aldehyde groups which can exist in lignin, and in lignin by-products such as vanillin, due to deterioration. The C=O vibration can also be changed as a result of methylation of phenol hydroxy groups. It is stated that many ketones react with diazomethane (Black, 1983). The intensity variation in both directions implies the fact that there would have been another chemical change, which the author has not yet identified.

The OH vibration in-plane bending in lignin is one of the assignments (Appendix 4) for the peak at 1132 cm^{-1}. Had methylation of phenolic hydroxyl groups taken place, obviously there should have been a decrease in intensity in this peak. It may be that the increase of this peak occurred with formation of additional ether links due to the stabilization of deterioration products as a result of methylation, as the 1132 cm^{-1} peak has also been assigned for aromatic and aliphatic ether links (Appendix 4).

The peak at 1092 cm^{-1} has been assigned for C-O-H deformation in cellulose and hydroxyl vibration in lignin (Appendix 4). The intensity decrease of the peak at 1092 cm^{-1}, may be due to the methylation of hydroxyl groups in lignin. As mentioned earlier, an increase in the intensity of this peak was also detected, which may be due to another chemical change which the author is as yet unable to explain.

The appearance or very slight increase of the peak at 2948 cm^{-1} may be due to the addition of CH_3 groups due to the methylation. This peak has been assigned for C-H stretching (Appendix 4).

4.3.4.3.5 Light measurements

With the measurement of relative reflectance of the fadeometer-exposed samples using white light, it was observed that the amount of absorbed light had increased with the treatment. When the colour is darker, the absorption is greater. Hence , it is obvious that due to the treatment, the intensity of colour on ageing has decreased, although, not by very much. Thus this diazomethane treatment can retard the yellowing of paper to some extent. Therefore this treatment must have achieved some success in partially capping lignin.

4.3.5 **Conclusions**

With the partial capping of lignin and deacidification, the diazomethane treatment has proved to be a possibly viable process for the stabilization of paper, especially mechanical wood papers.

It is encouraging that not only is there some demonstrated stabilization of lignin occuring during this treatment, but also, carboxylic acid groups causing acidity in different types of aged paper are destroyed.

There is obviously present the basis of a potentially useful treatment for stabilizing not only papers containing mechanical wood, but also partially deteriorated papers of different kinds.

Further long term experiments are required involving the treatment and natural ageing of a range of papers in order to evaluate the effectiveness of such a process.

PLATE 4.1 (a)

PLATE 4.1 (b)

PLATE 4.1: Scanning electron microscope photographs of (a) Whatman No.1 paper and (b) of that treated with $Mg(OH)_2$/IMS colloidal suspension

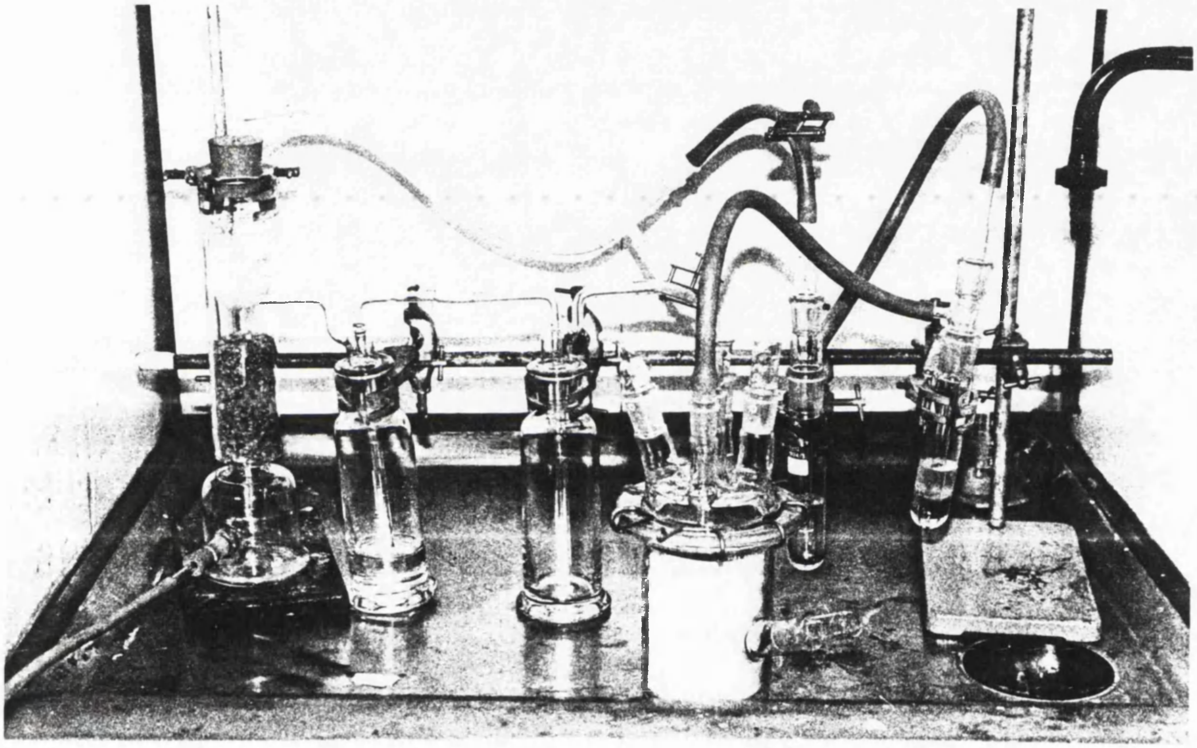


PLATE 4.2: Apparatus for the preparation of diazomethane and treatment of paper samples

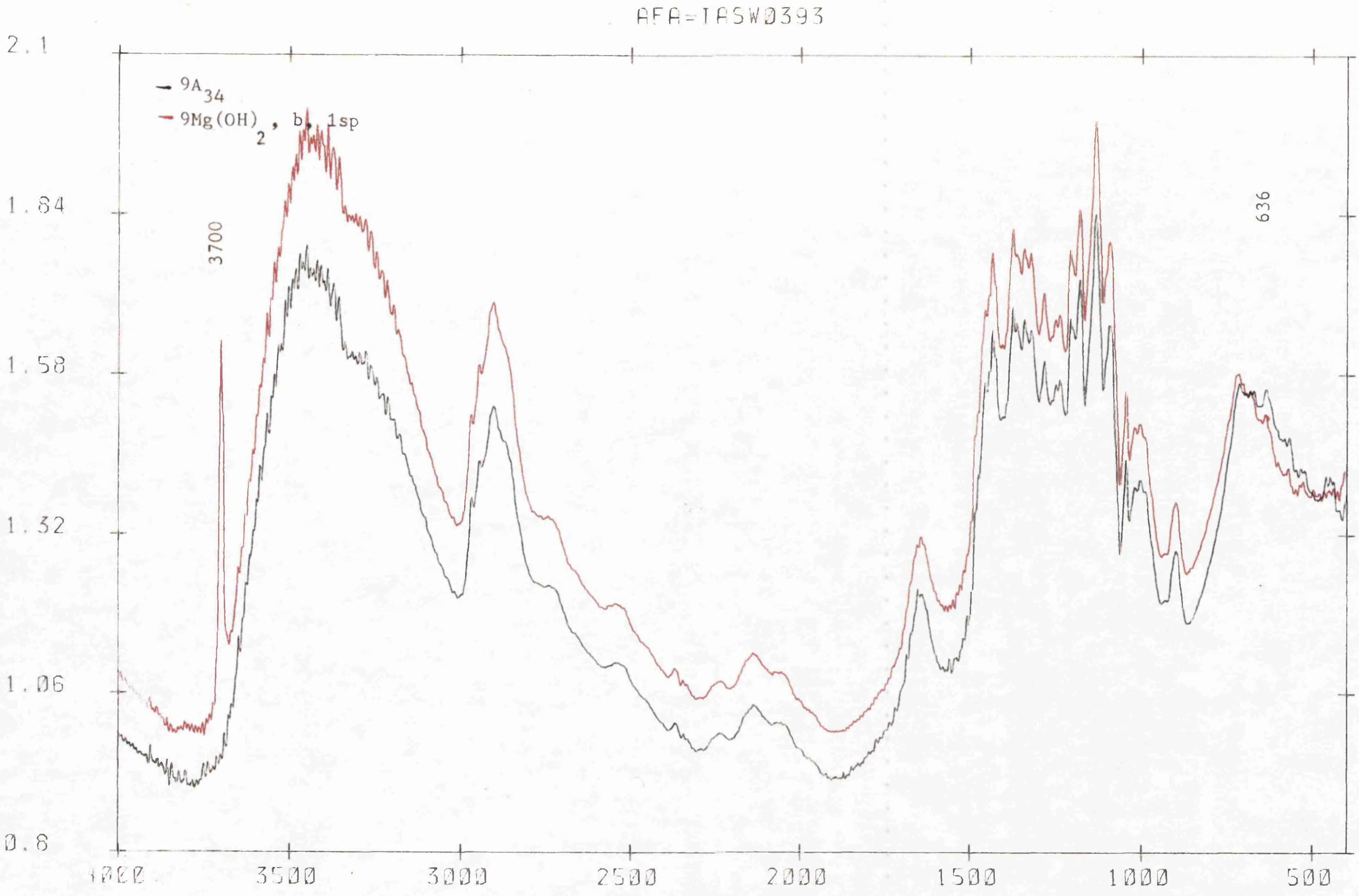

AFA=IASW0393
— 9A$_{34}$
— 9Mg(OH)$_2$, b, 1sp
3700
636
2.1
1.84
1.58
1.32
1.06
0.8
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.1

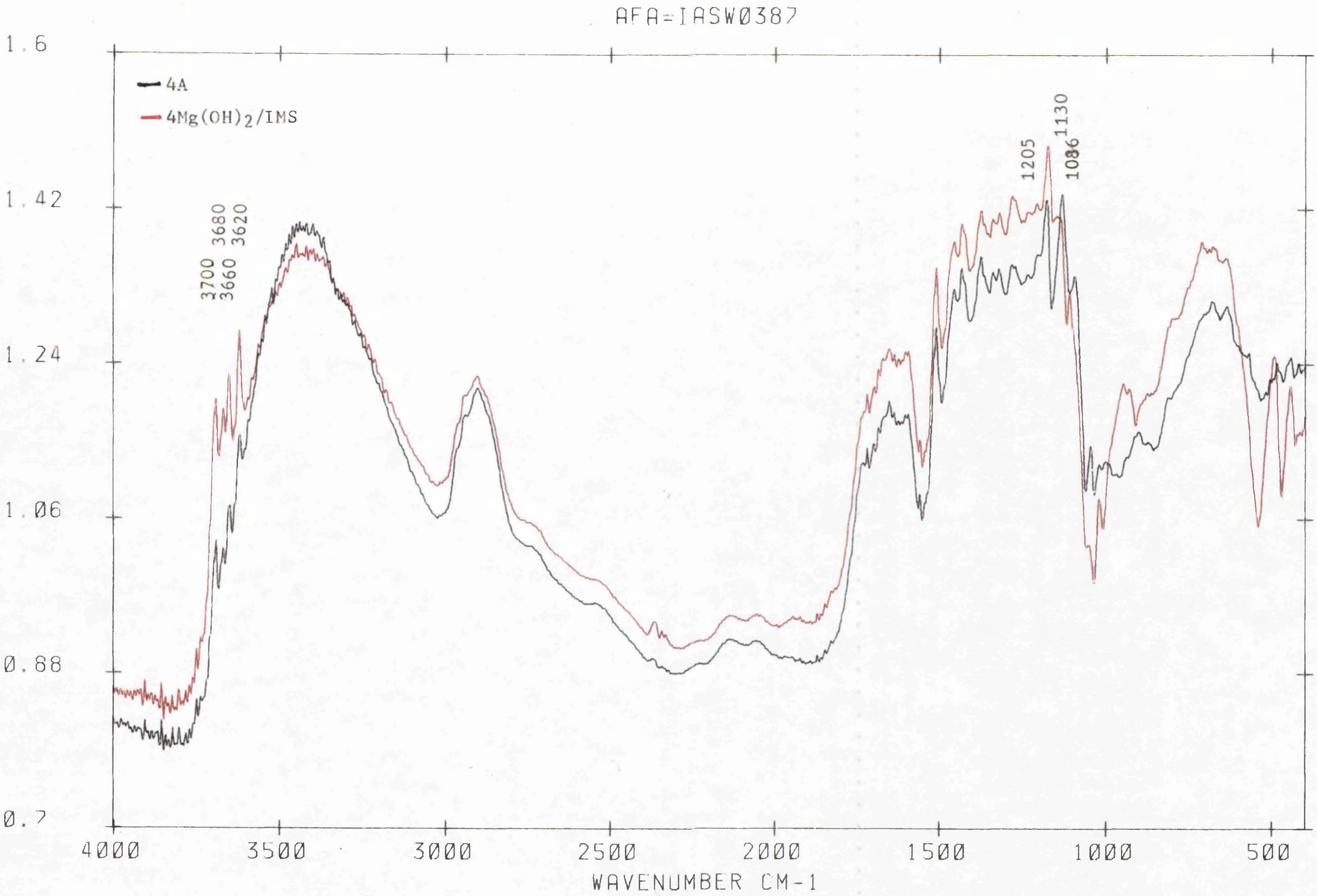

AFA=IASW0387
4A
4Mg(OH)$_2$/IMS
3700
3660
3680
3620
1205
1086
1130
1.6
1.42
1.24
1.06
0.88
0.7
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.2

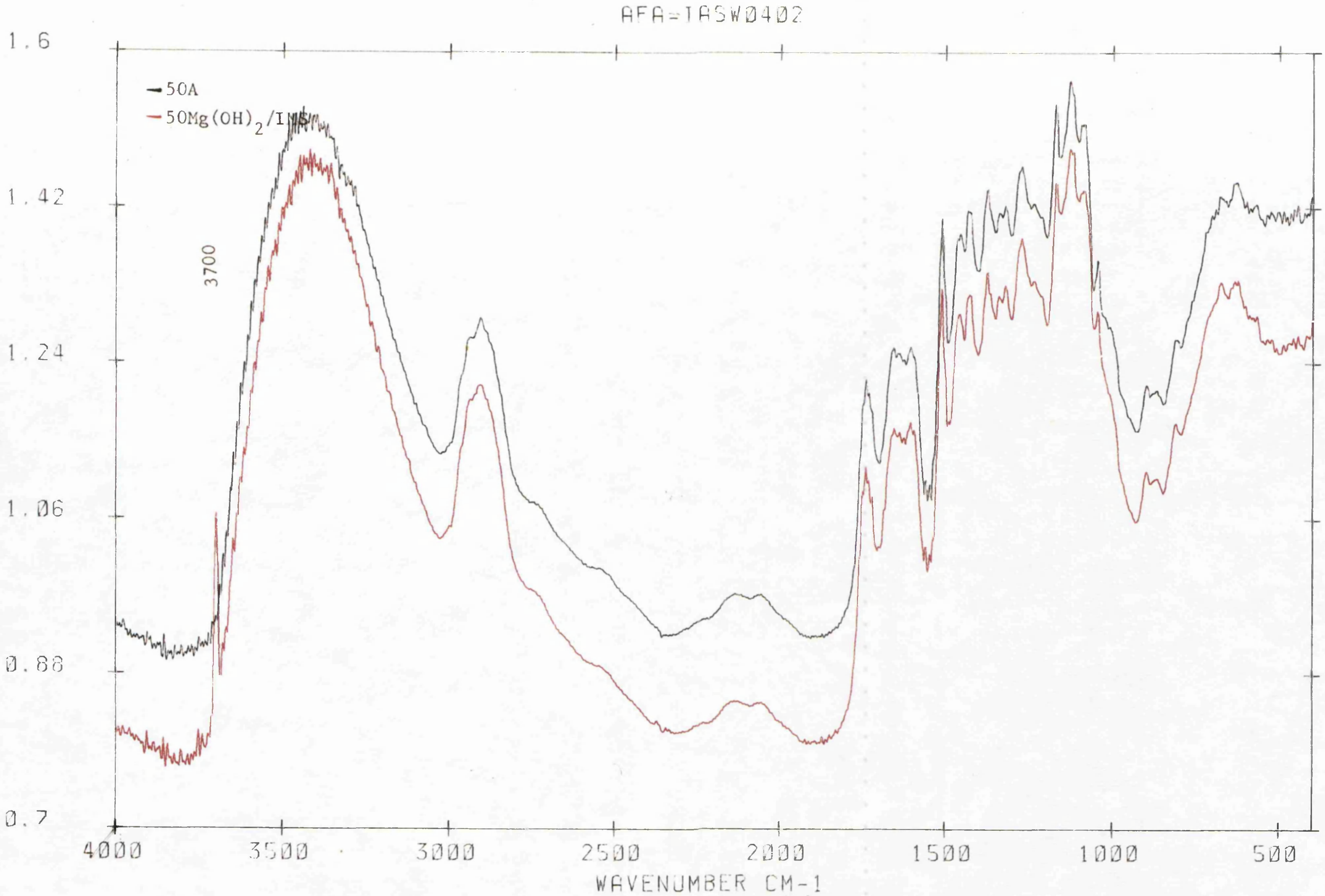

AFA=IASW0402
50A
50Mg(OH)2/IMS
3700
1.6
1.42
1.24
1.06
0.88
0.7
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.3

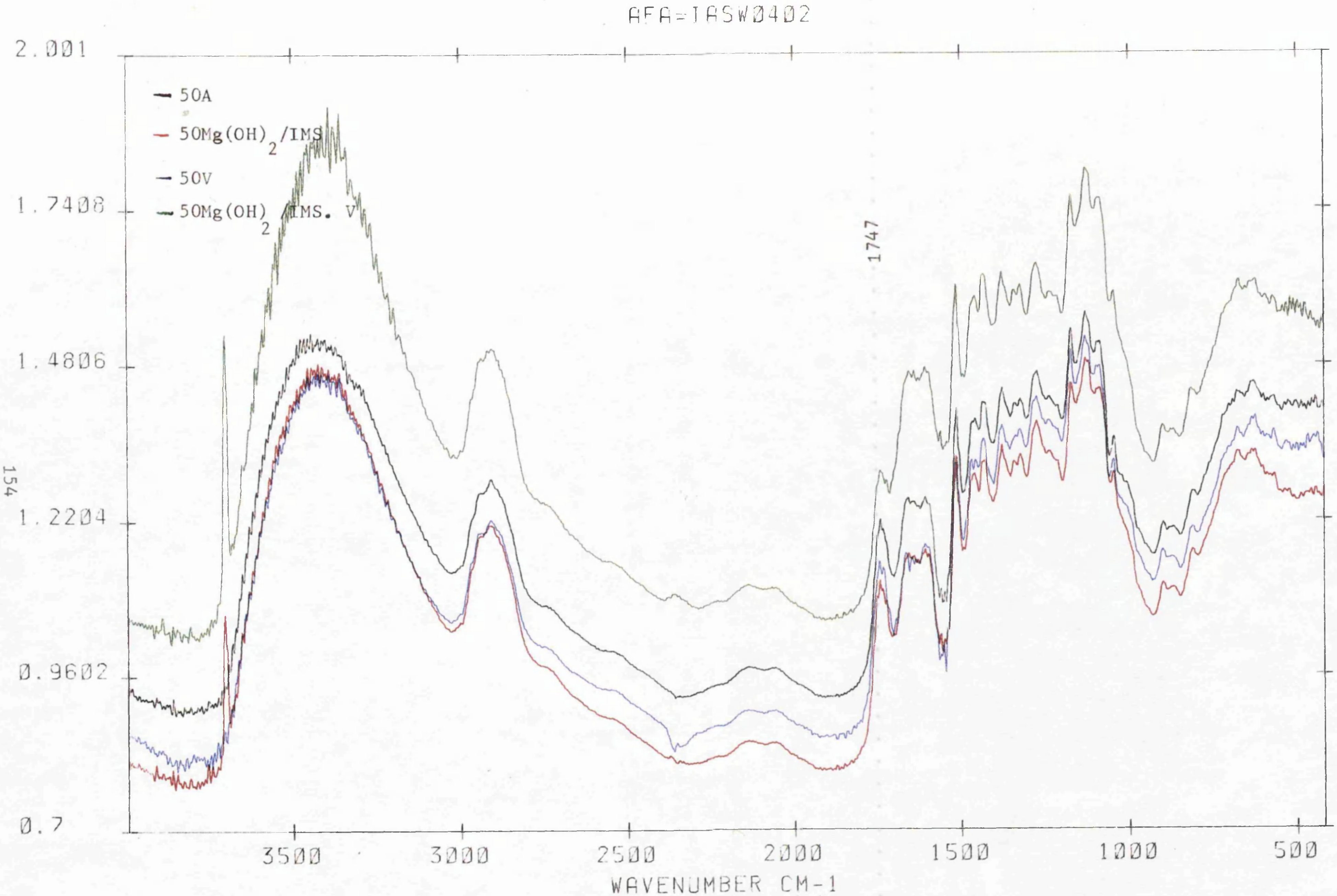

AFA=IASW0402
50A
50Mg(OH)$_2$/IMS
50V
50Mg(OH)$_2$/IMS. V
1747
2.001
1.7408
1.4806
1.2204
0.9602
0.7
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.4

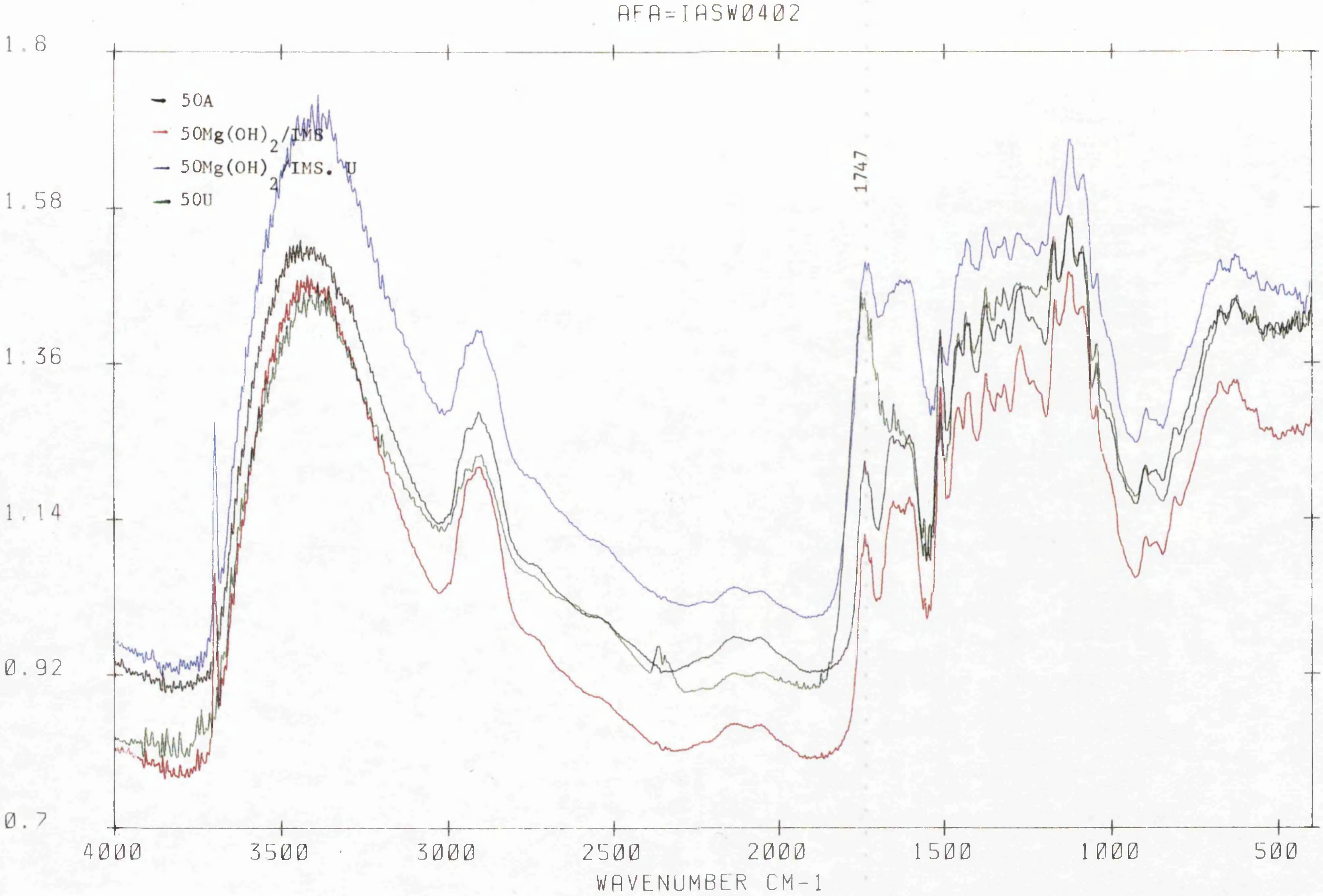

AFA=IASW0402
50A
50Mg(OH)$_2$/IMS
50Mg(OH)$_2$/IMS. U
50U
1747
1.8
1.58
1.36
1.14
0.92
0.7
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.5

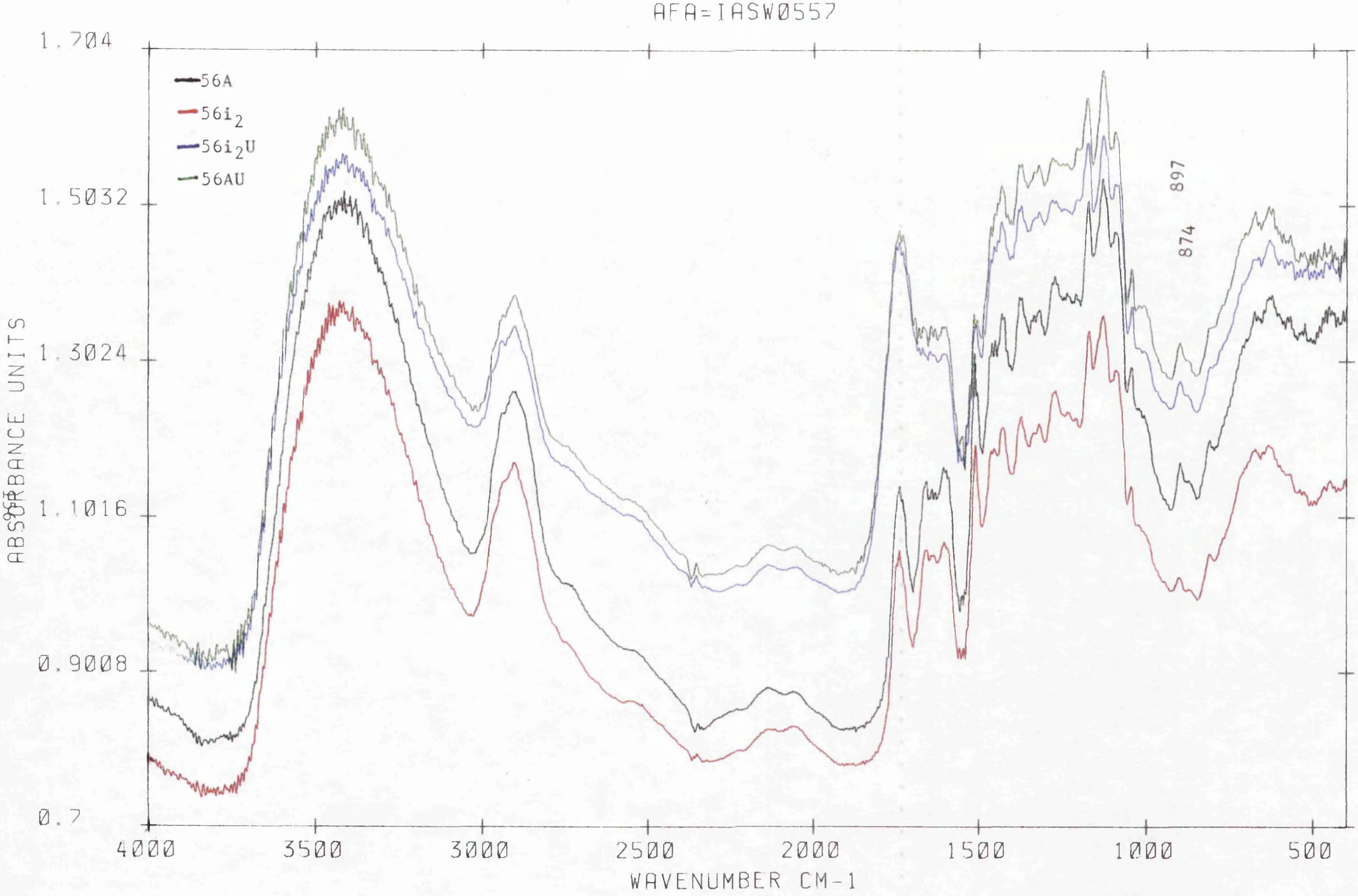

AFA=IASW0557
56A
56i2
56i2U
56AU
897
874
ABSORBANCE UNITS
1.704
1.5032
1.3024
1.1016
0.9008
0.7
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.6

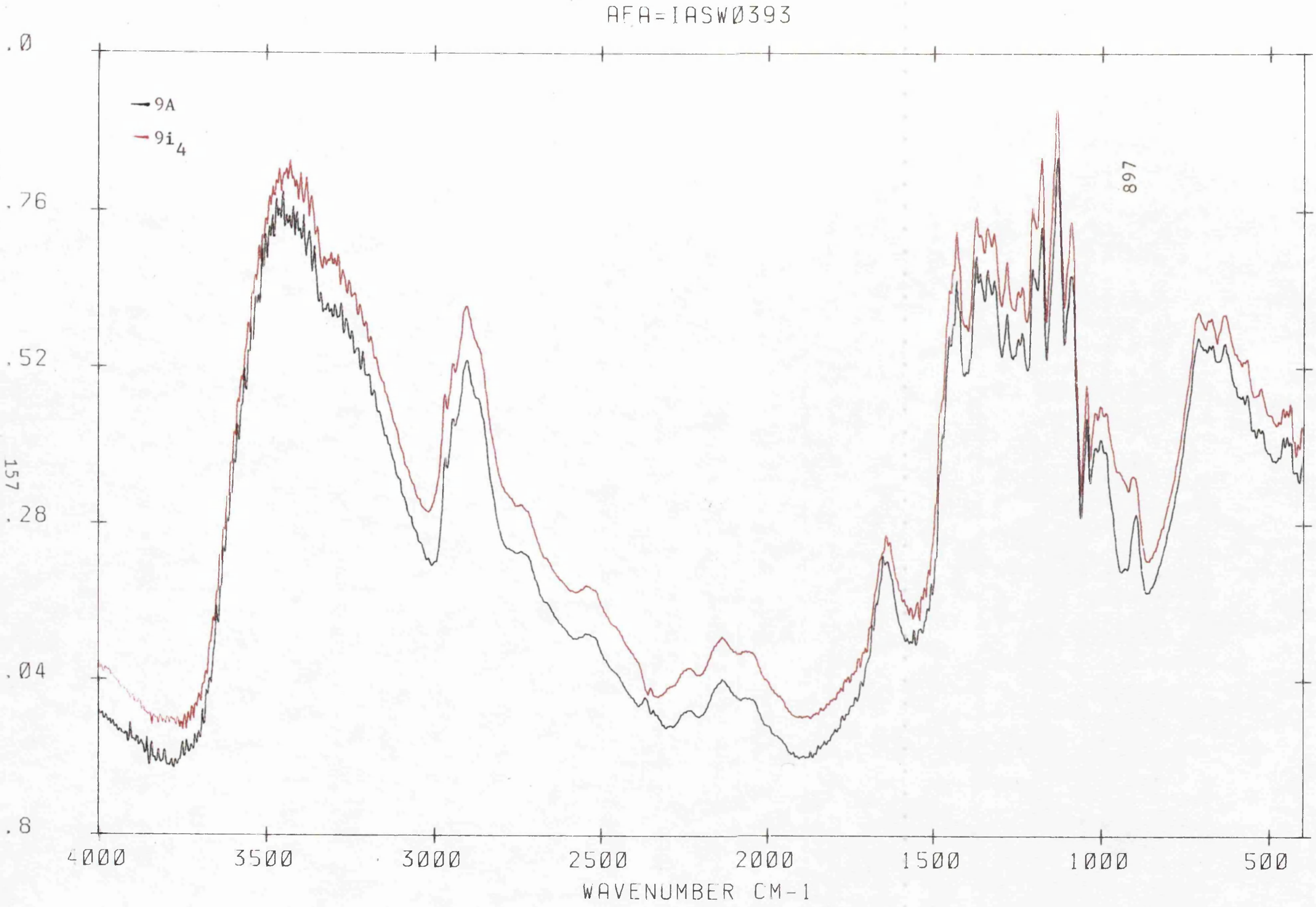

AFA=IASW0393
.0
.76
.52
.28
.04
.8
9A
9i$_4$
897
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.7

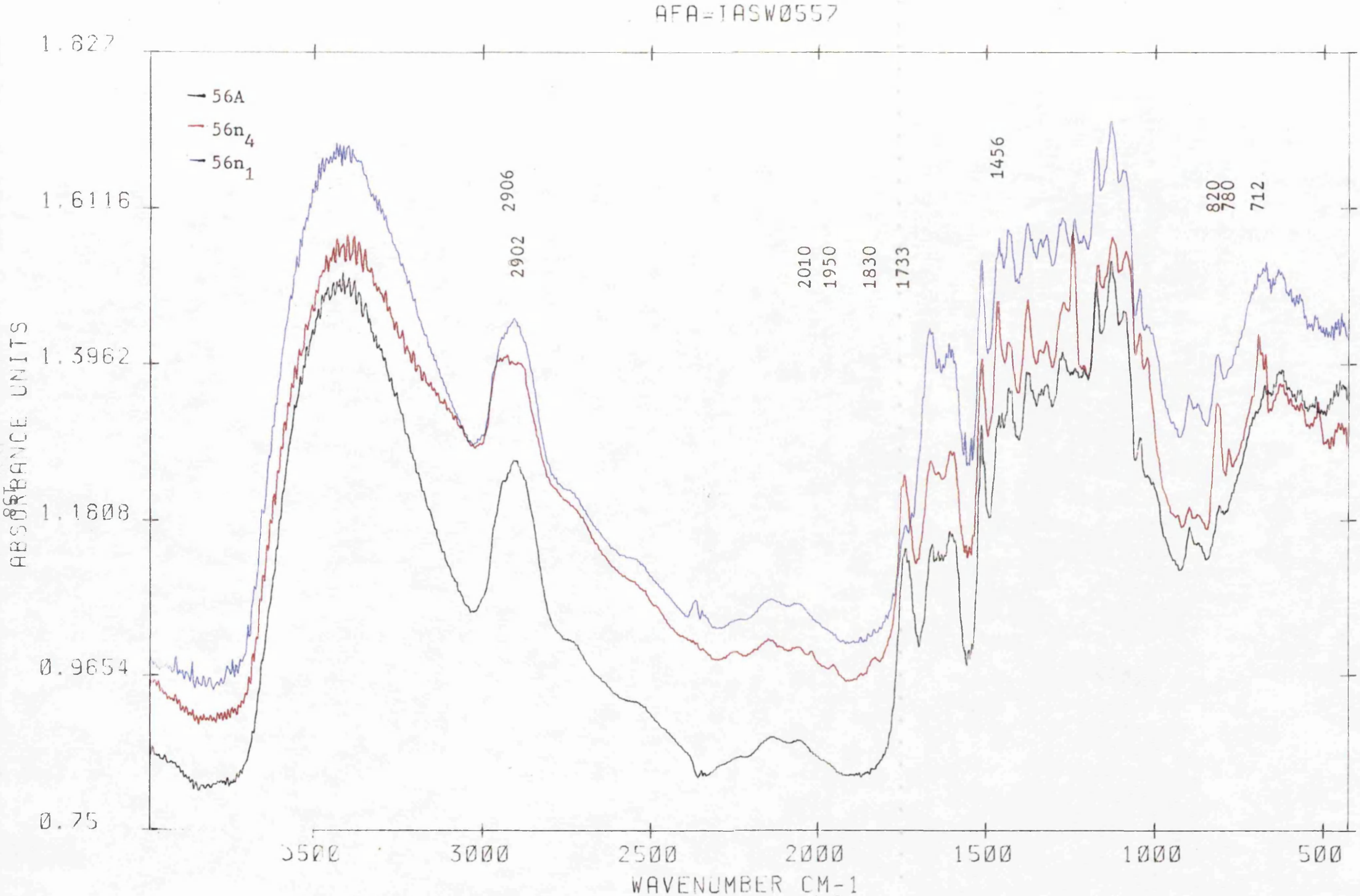

AFA=IASW0557
56A
56n4
56n1
1.827
1.6116
1.3962
1.1808
0.9654
0.75
ABSORBANCE UNITS
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1
2906
2902
2010
1950
1830
1733
1456
820
780
712

Figure 4.8

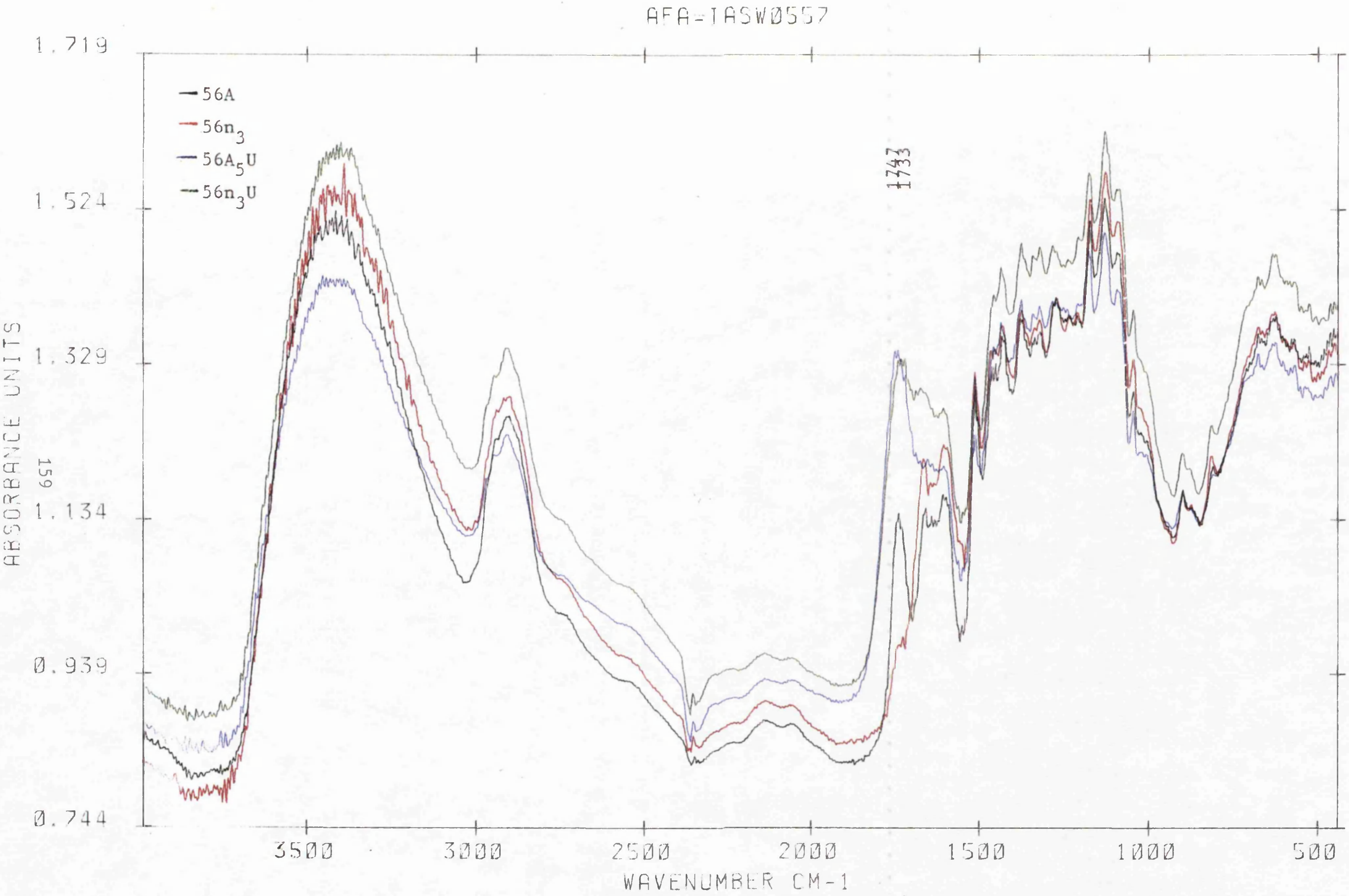

AFA-IASW0557
1.719
1.524
1.329
1.134
0.939
0.744
ABSORBANCE UNITS
56A
56n$_3$
56A$_5$U
56n$_3$U
1747
1733
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.9

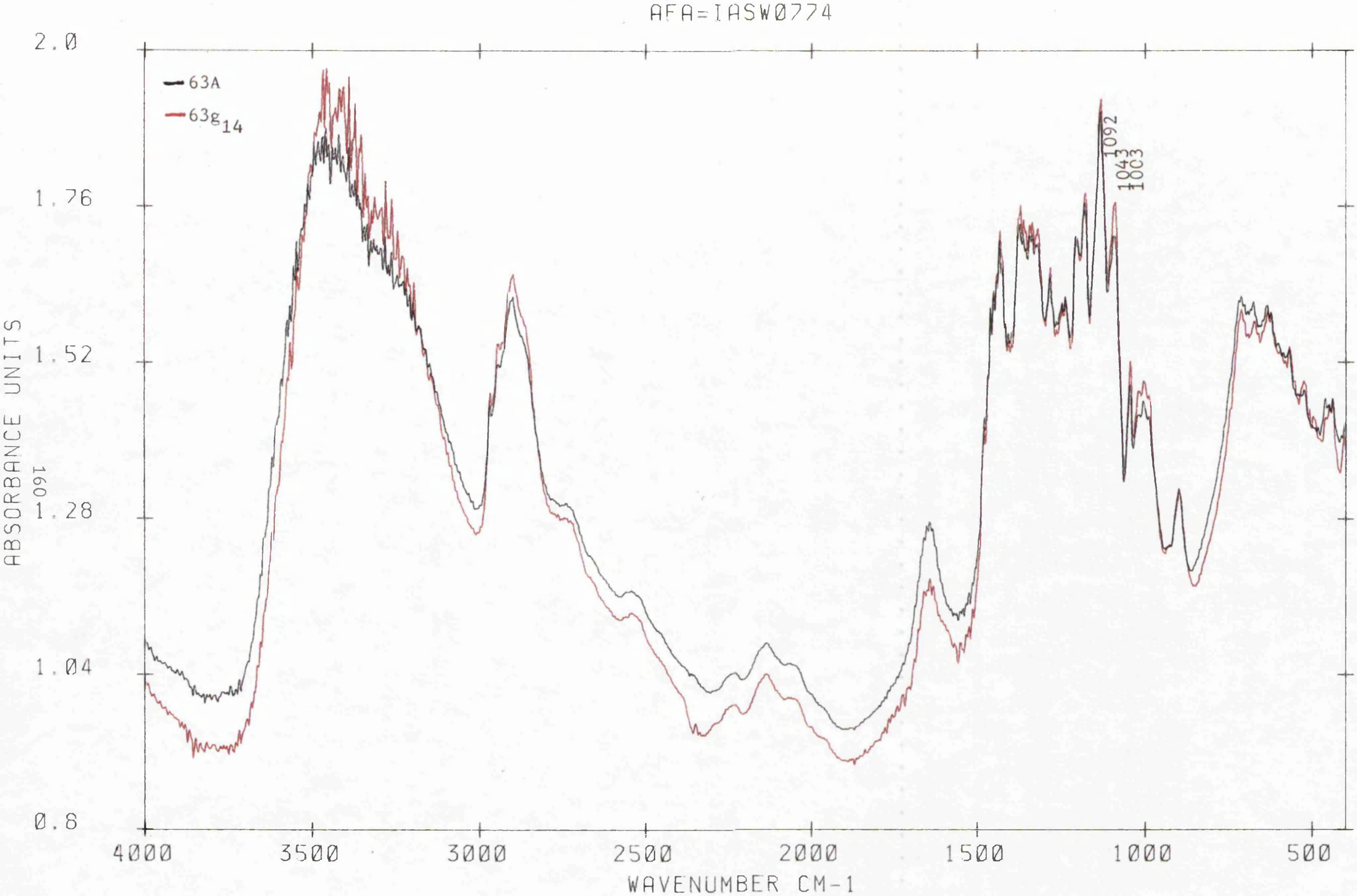

AFA=IASW0774
63A
$63g_{14}$
1092
1043
1003
2.0
1.76
1.52
1.28
1.04
0.8
ABSORBANCE UNITS
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.10

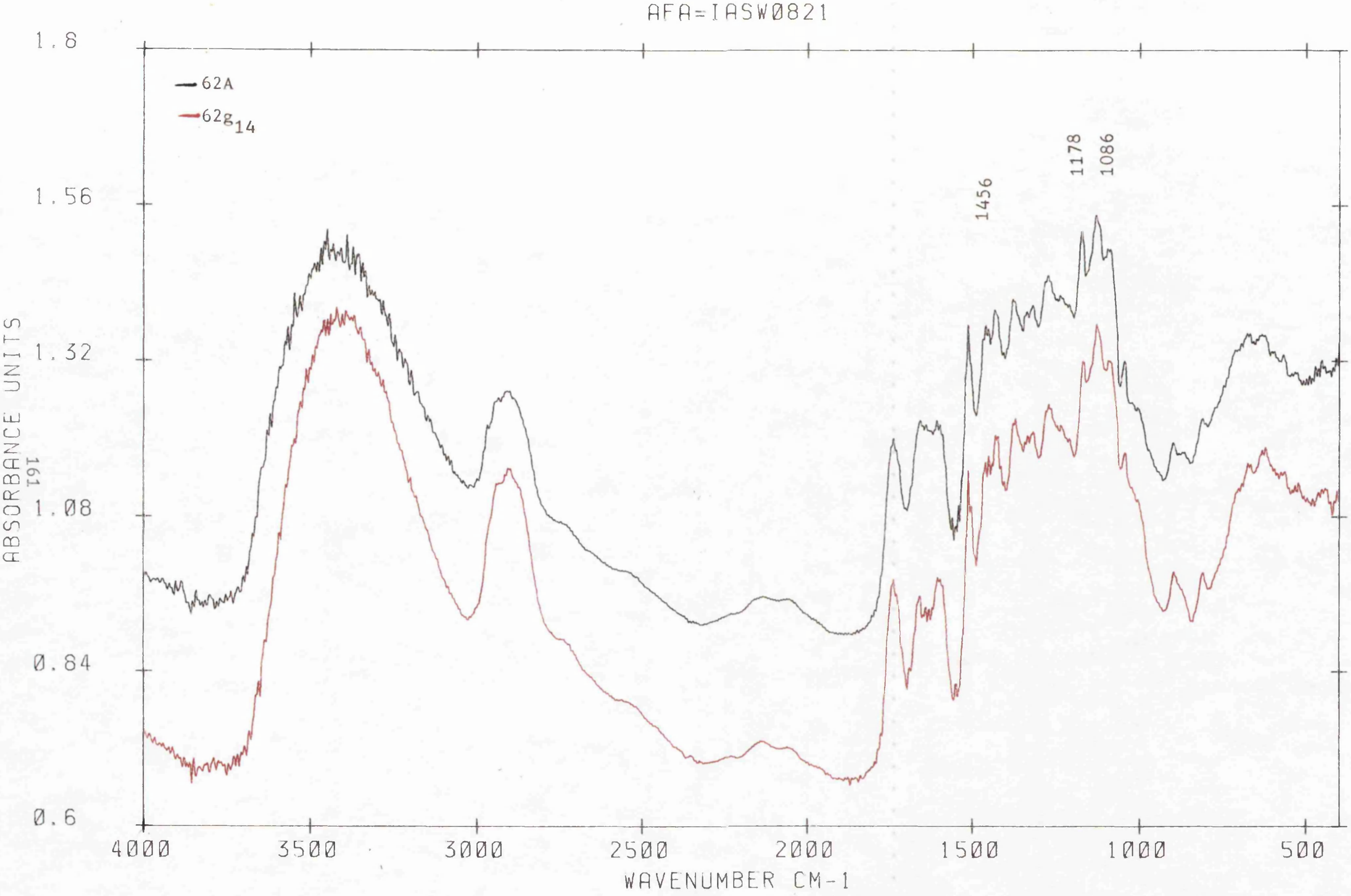

AFA=IASW0821
62A
$62g_{14}$
1456
1178
1086
1.8
1.56
1.32
1.08
0.84
0.6
ABSORBANCE UNITS
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.11

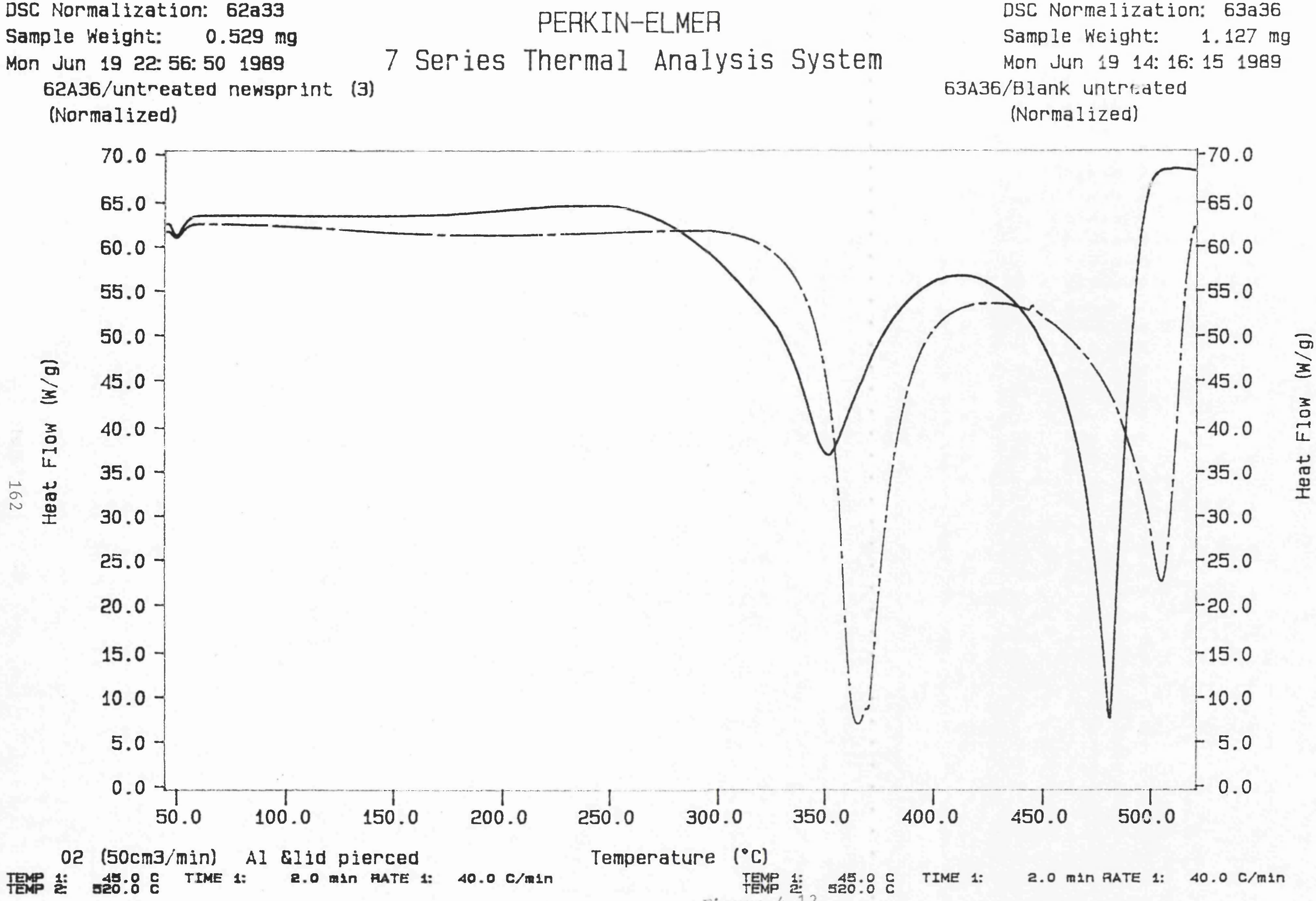

DSC Normalization: 62a33
Sample Weight: 0.529 mg
Mon Jun 19 22:56:50 1989
62A36/untreated newsprint (3)
(Normalized)
PERKIN-ELMER
7 Series Thermal Analysis System
DSC Normalization: 63a36
Sample Weight: 1.127 mg
Mon Jun 19 14:16:15 1989
63A36/Blank untreated
(Normalized)
Heat Flow (W/g)
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
450.0
500.0
Temperature (°C)
02 (50cm3/min) Al &lid pierced
TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 40.0 C/min
TEMP 2: 520.0 C
TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 40.0 C/min
TEMP 2: 520.0 C

Figure 4.12

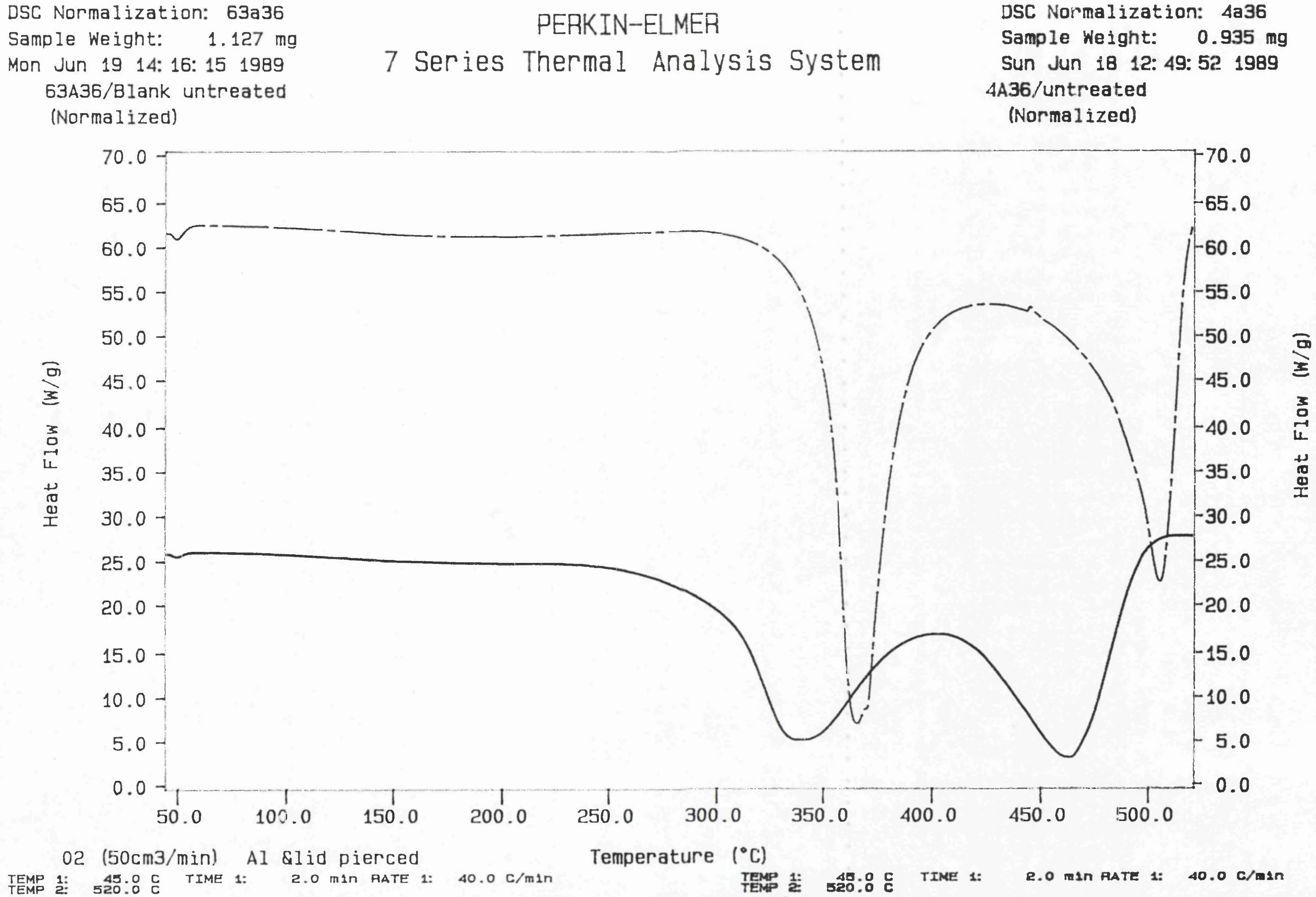
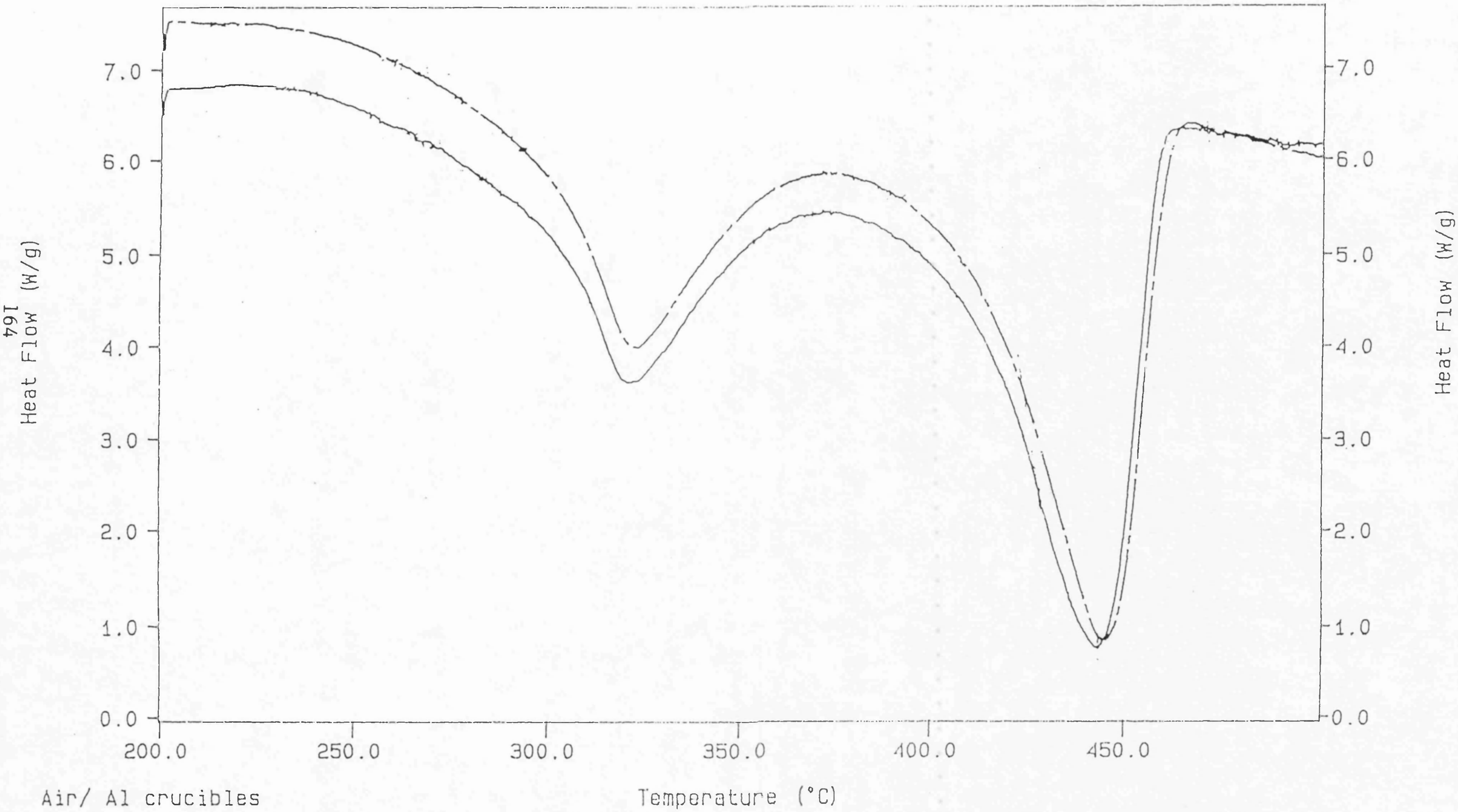

DSC Normalization: 63a36
Sample Weight: 1.127 mg
Mon Jun 19 14: 16: 15 1989
63A36/Blank untreated
(Normalized)
PERKIN-ELMER
7 Series Thermal Analysis System
DSC Normalization: 4a36
Sample Weight: 0.935 mg
Sun Jun 18 12: 49: 52 1989
4A36/untreated
(Normalized)
Heat Flow (W/g)
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
Heat Flow (W/g)
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
450.0
500.0
Temperature (°C)
02 (50cm3/min) Al &lid pierced
TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 40.0 C/min
TEMP 2: 520.0 C
TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 40.0 C/min
TEMP 2: 520.0 C

Figure 4.13

DSC Normalization: 6227a
Sample Weight: 0.527 mg
Sat Jun 24 16:35:03 1989
62g7a /5C/min in air
(Normalized)

PERKIN-ELMER
7 Series Thermal Analysis System

DSC Normalization: 62361
Sample Weight: 0.607 mg
Fri Jun 23 22:58:46 1989
62A36 in air /5C/min
(Normalized)



Air/ Al crucibles

TEMP 1: 200.0 C TIME 1: 2.0 min RATE 1: 5.0 C/min
TEMP 2: 500.0 C

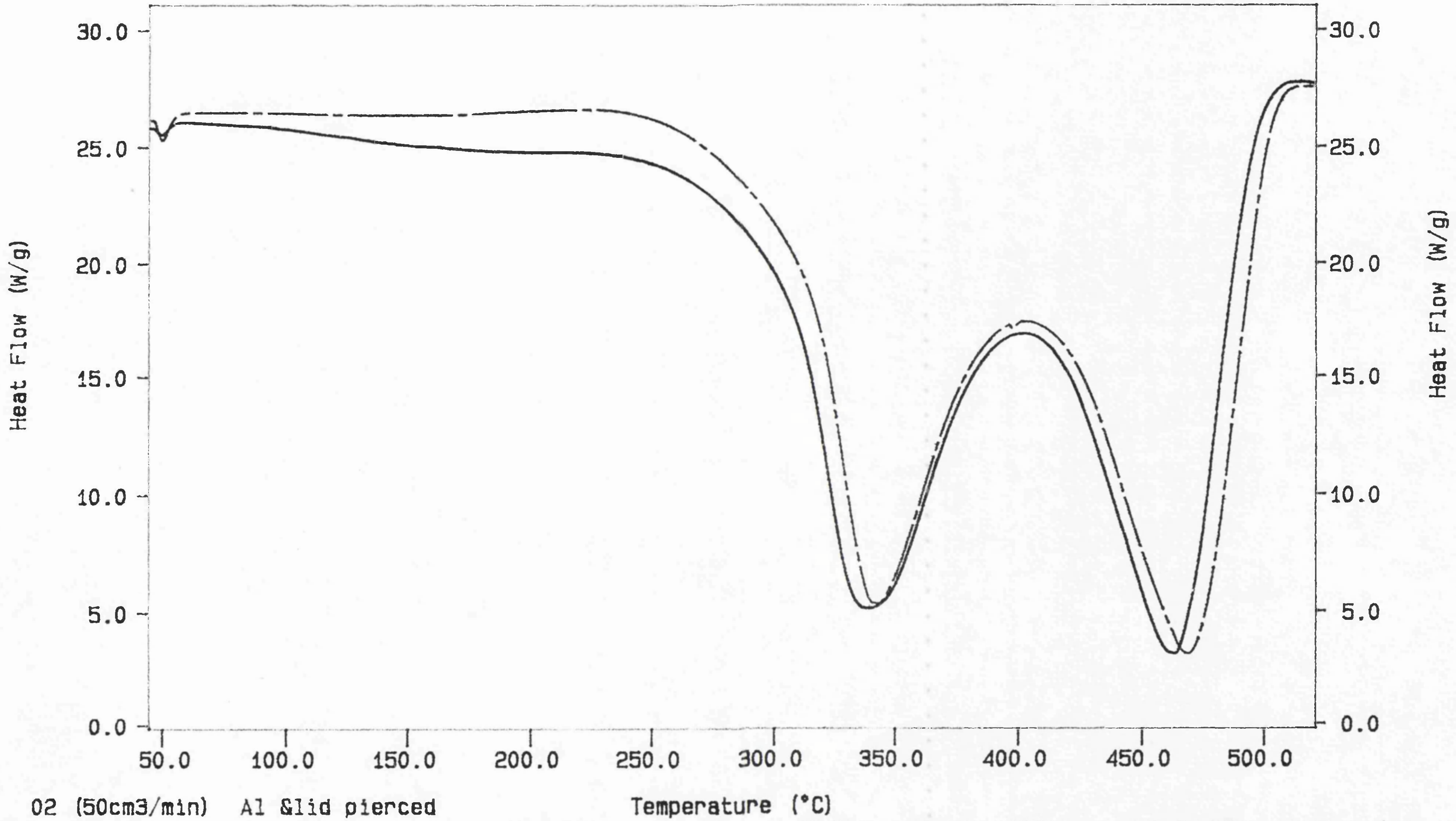
TEMP 1: 200.0 C TIME 1: 2.0 min RATE 1: 5.0 C/min
TEMP 2: 500.0 C

Figure 4.14

DSC Normalization: 4a36
Sample Weight: 0.935 mg
Sun Jun 18 12:49:52 1989
4A36/untreated
(Normalized)

PERKIN-ELMER
7 Series Thermal Analysis System

DSC Normalization: 4g7a
Sample Weight: 0.865 mg
Sun Jun 18 02:52:52 1989
4g7a/C2H40 7 hrs at 70C
(Normalized)



02 (50cm3/min) Al &lid pierced

TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 40.0 C/min
TEMP 2: 520.0 C

TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 40.0 C/min
TEMP 2: 520.0 C

Figure 4.15

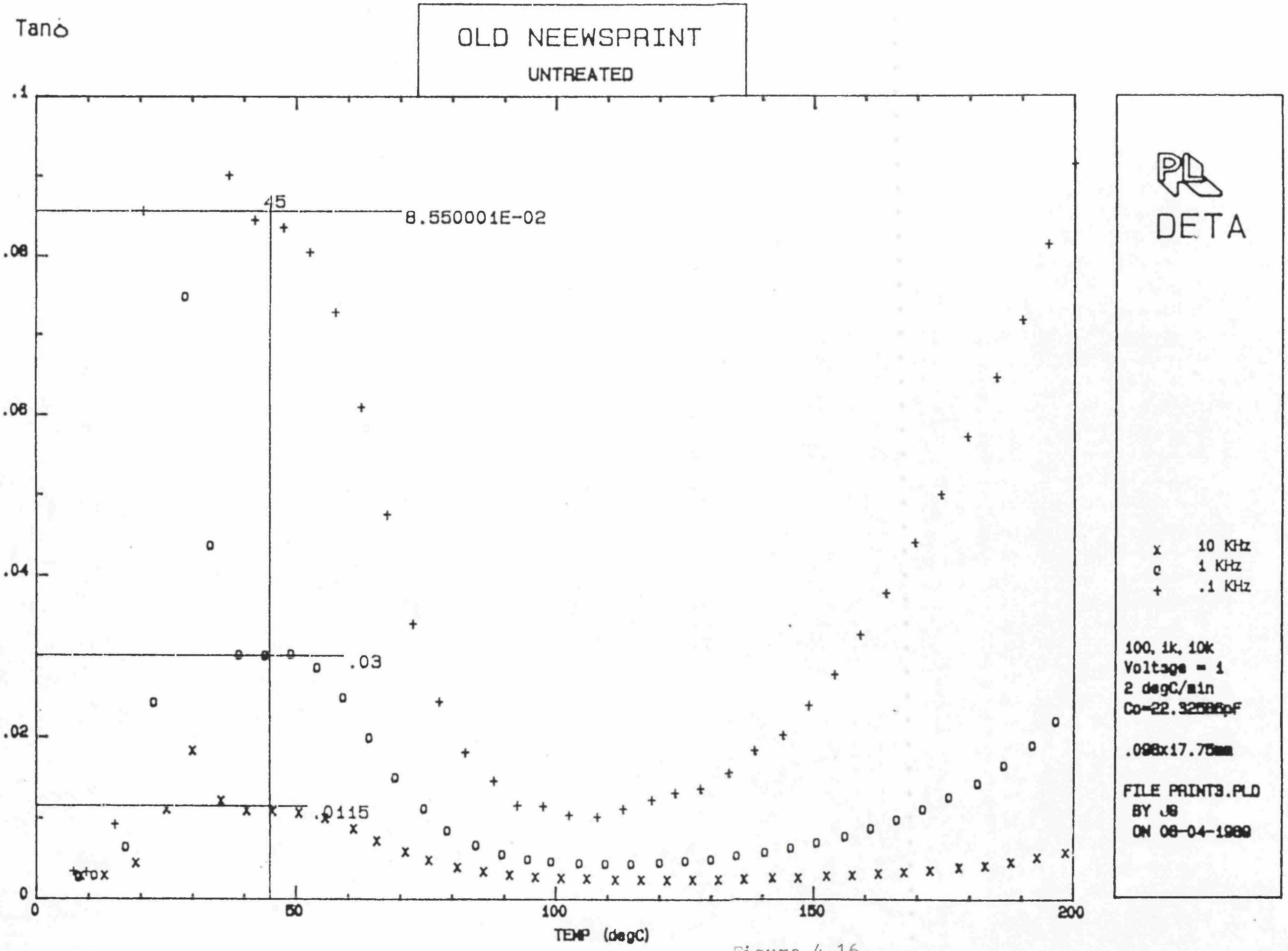

Tanδ
OLD NEEWSPRINT
UNTREATED
.1
.08
.06
.04
.02
0
0
50
100
150
200
TEMP (degC)
45
8.550001E-02
.03
.0115
DETA
x 10 KHz
o 1 KHz
+ .1 KHz
100, 1k, 10k
Voltage = 1
2 degC/min
Co=22.32586pF
.098x17.75mm
FILE PRINT3.PLD
BY JB
ON 08-04-1989

Figure 4.16

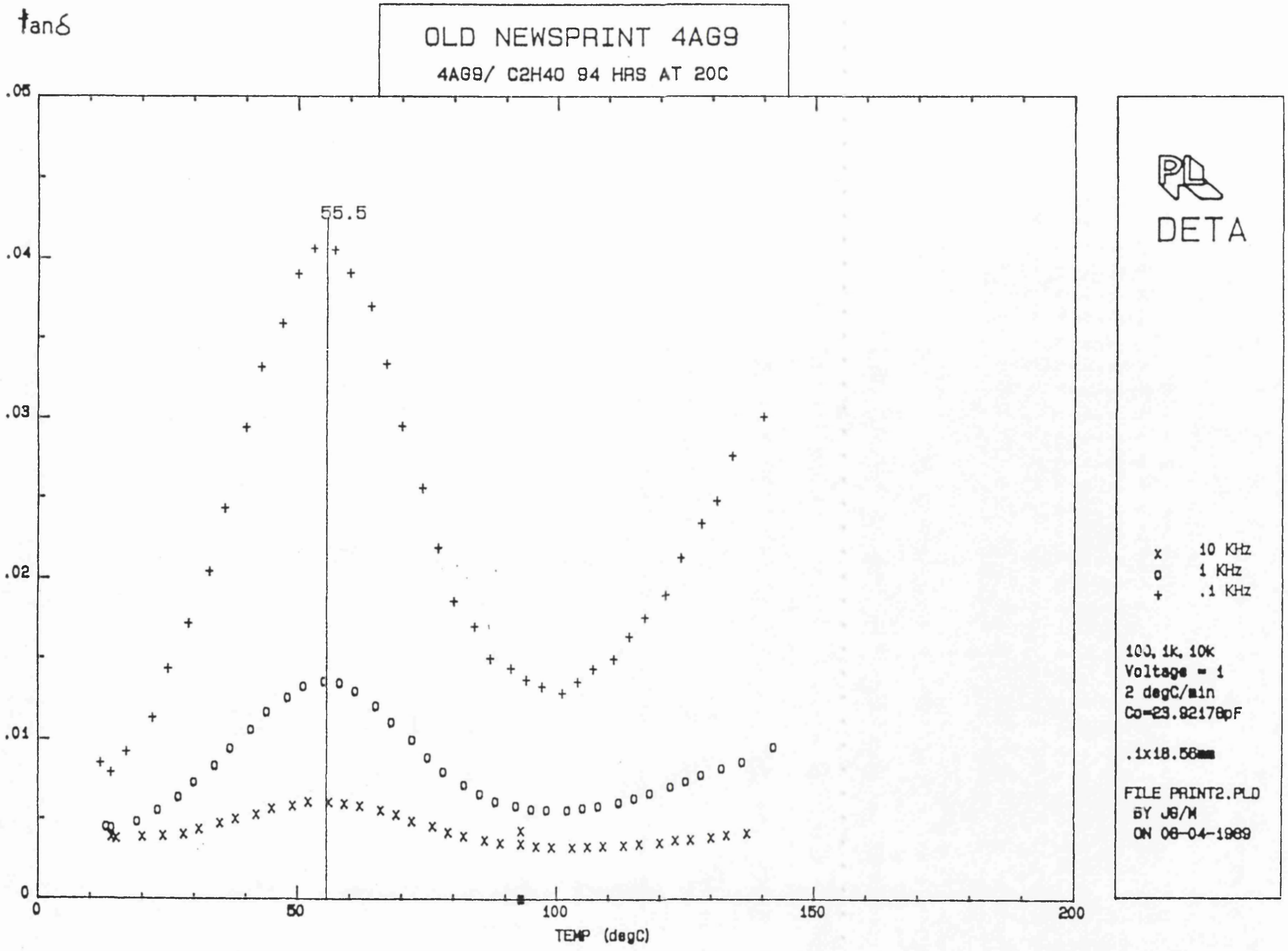

OLD NEWSPRINT 4AG9
4AG9/ C2H40 94 HRS AT 20C
tanδ
.05
.04
.03
.02
.01
0
0
50
100
150
200
TEMP (degC)
55.5
DETA
x 10 KHz
o 1 KHz
+ .1 KHz
100, 1k, 10k
Voltage = 1
2 degC/min
Co=23.92178pF
.1x18.58mm
FILE PRINT2.PLD
BY JG/M
ON 08-04-1989

Figure 4.17

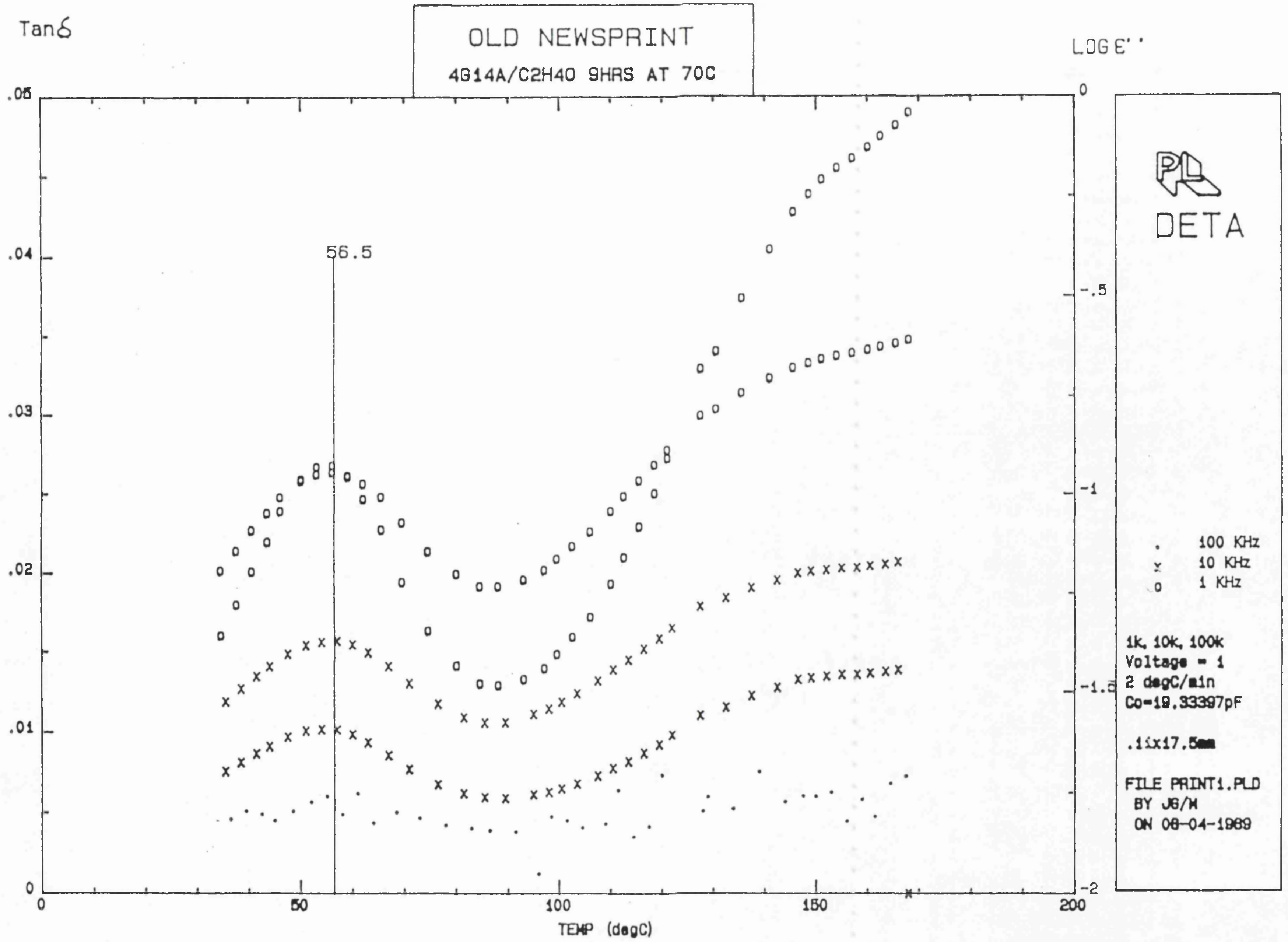

Tanδ
OLD NEWSPRINT
4G14A/C2H40 9HRS AT 70C
LOG ε''
.05
.04
.03
.02
.01
0
0
-.5
-1
-1.5
-2
56.5
0
50
100
150
200
TEMP (degC)
PL
DETA
• 100 KHz
x 10 KHz
o 1 KHz
1k, 10k, 100k
Voltage = 1
2 degC/min
Co=19.33397pF
.11x17.5mm
FILE PRINT1.PLD
BY JG/M
ON 08-04-1989

Figure 4.18

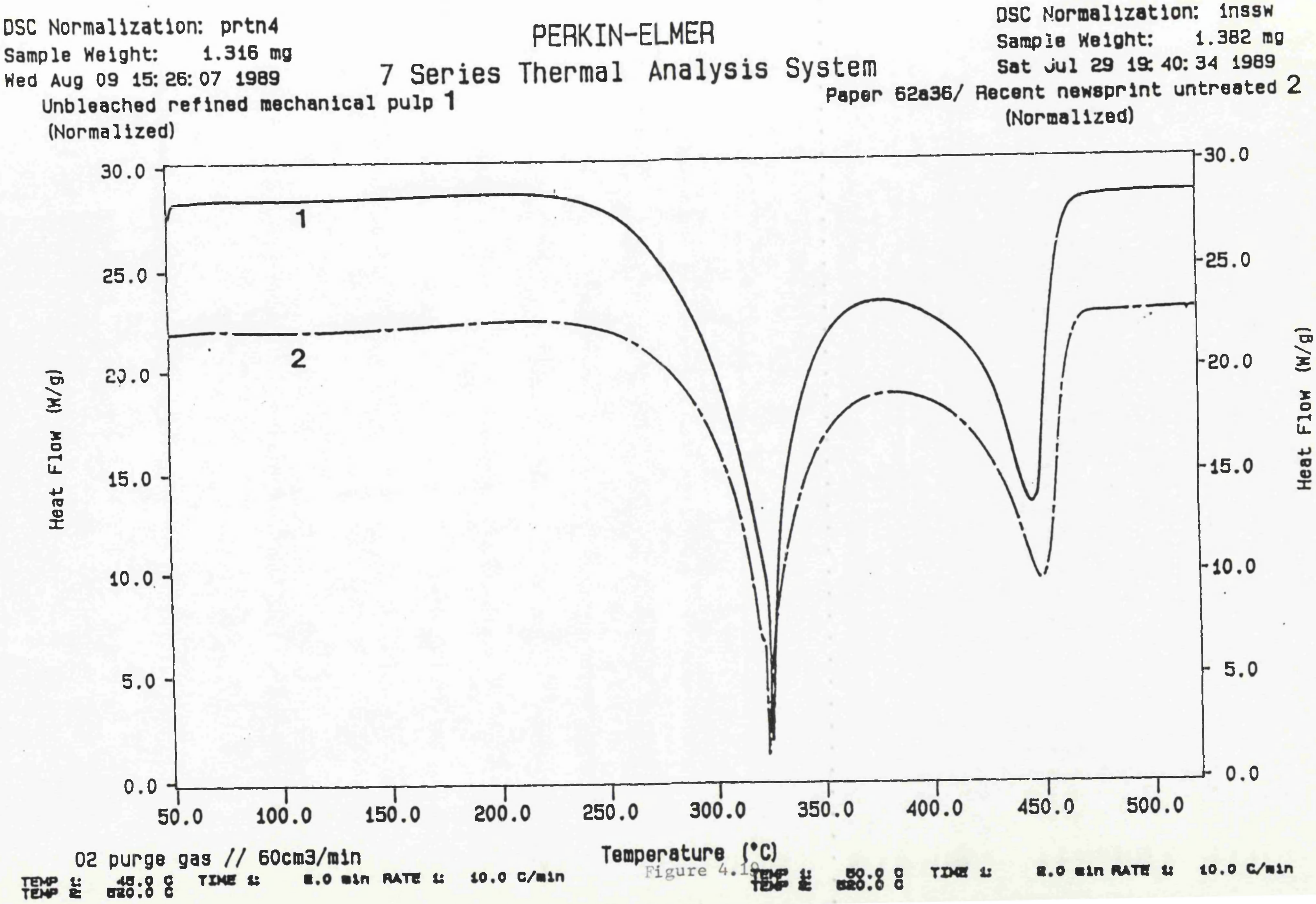

DSC Normalization: prtn4
Sample Weight: 1.316 mg
Wed Aug 09 15:26:07 1989
Unbleached refined mechanical pulp 1
(Normalized)
PERKIN-ELMER
7 Series Thermal Analysis System
DSC Normalization: inssw
Sample Weight: 1.382 mg
Sat Jul 29 19:40:34 1989
Paper 62a36/ Recent newsprint untreated 2
(Normalized)
1
2
Heat Flow (W/g)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
450.0
500.0
Temperature (°C)
O2 purge gas // 60cm3/min
TEMP 1: 45.0 C TIME 1: 2.0 min RATE 1: 10.0 C/min
TEMP 2: 520.0 C
TEMP 1: 50.0 C TIME 1: 2.0 min RATE 1: 10.0 C/min
TEMP 2: 520.0 C

Figure 4.10

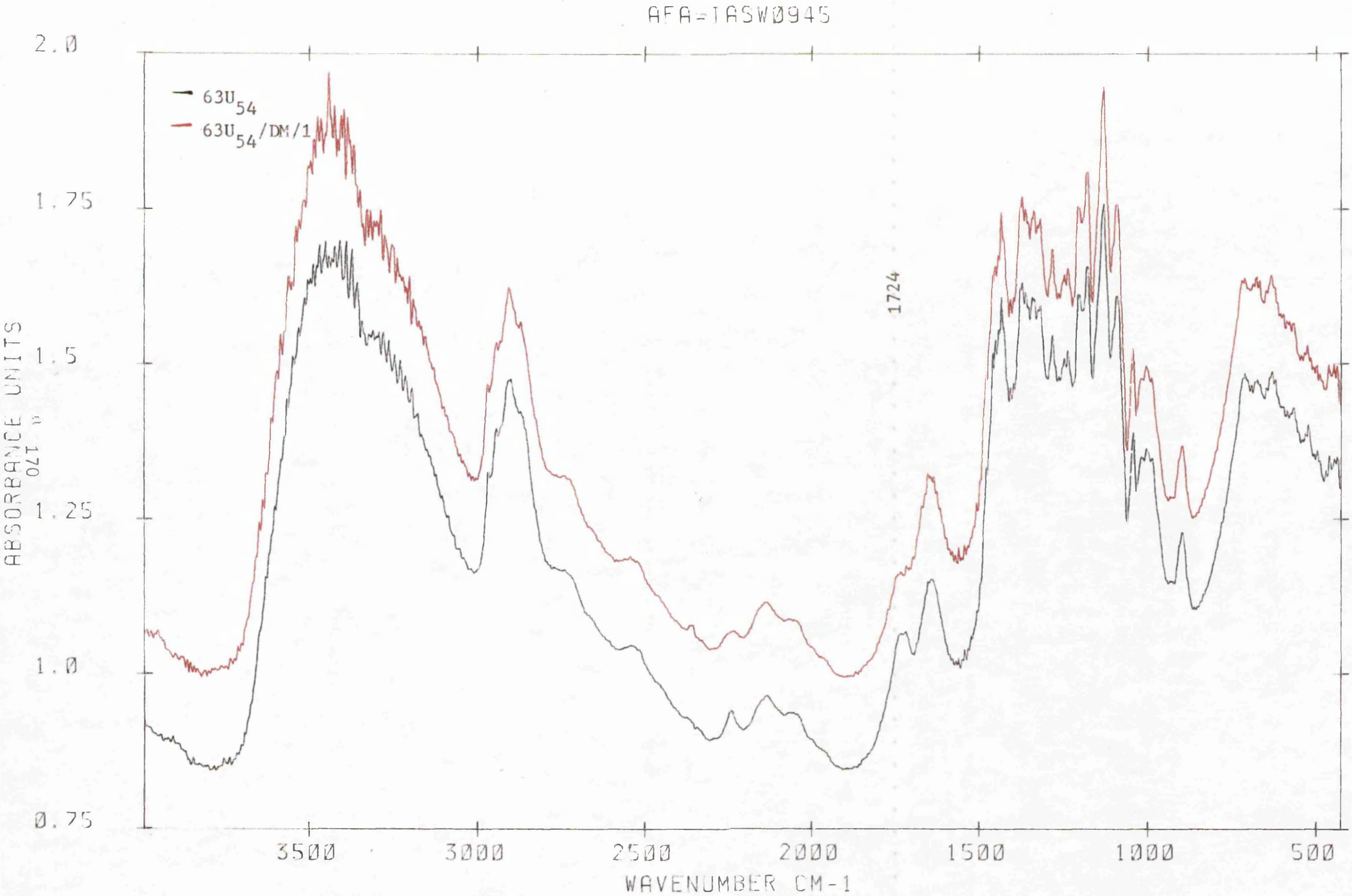

AFA-IASW0945
2.0
1.75
1.5
1.25
1.0
0.75
ABSORBANCE UNITS
63U54
63U54/DM/1
1724
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.20

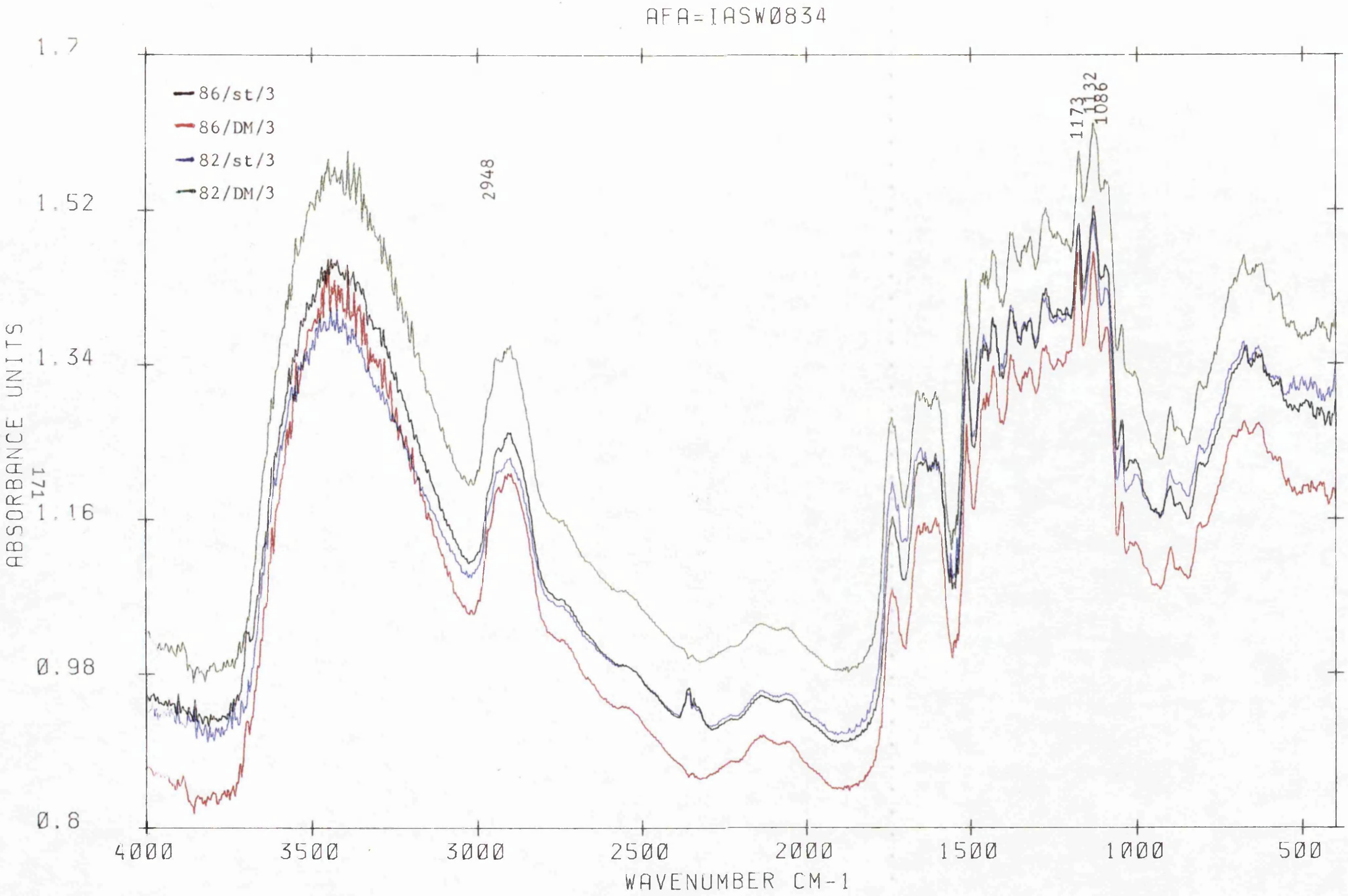

AFA=IASW0834
86/st/3
86/DM/3
82/st/3
82/DM/3
2948
1173
1132
1086
1.7
1.52
1.34
1.16
0.98
0.8
ABSORBANCE UNITS
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 4.21

Chapter 5

STRENGTHENING

5.1 INTRODUCTION

With handling, any paper artefact is subject to wear and tear, and to withstand this and the chemical deterioration described in chapters 1 and 3, paper should possess both permanence and durability. When newly manufactured, paper possesses a degree of strength which decreases with time due to deterioration and handling. Hence, to overcome the deterioration, strengthening has been identified as one of the most vital aspects of paper conservation in addition to stabilization. Graft copolymerisation is the only accepted chemical technique available so far for the strengthening of paper, although it is not yet fully developed as a large scale treatment. In practice, ethyl acrylate, methyl methacrylate and mixtures of these monomers have been used in graft copolymerisation processes. In this chapter the possibilities of strengthening paper using monomers are explored, and the analysis of monomer treated samples using FTIR, folding endurance and tensile strength measurements and pH measurements are discussed.

5.2 CONSOLIDATION WITH VOLATILE SILANES

5.2.1 Reasons for the choice

Cellulose in many ways resembles silica in that it has a hydroxylated surface having an isoelectric point of approximately 2, hence the applications of silanes on silica should be adaptable to paper, cotton and wood (Plueddemann, 1982).

Organo-silanes have been used as consolidants for the last 10-15 years in the field of conservation, and of these trimethoxymethyl silane is the most commonly used. Trimethoxymethyl silane can adhere to the surface and hydrolyse to form a polymer (silanol), which can increase the mechanical strength of the material. In practice, it is grafted onto labile hydroxyl groups and forms a polymeric coating. Being a volatile consolidant, it is very convenient to use in the vapour phase, even on materials such as fragile paper. Hence, in order to attempt the strengthening of paper, trimethoxymethyl silane vapour was used in this treatment.

5.2.2 Experimental method

Samples were suspended from a stainless steel rod, and placed in an airtight desiccator containing trimethoxymethyl silane in an evaporating dish for different periods, i.e. 1, 3, 6, and 10 days, at room temperature (20°C). One batch of samples was exposed to trimethoxymethyl silane in the presence of water for 10 days and another batch for 15 days, following the same procedure. Weight gain and/or loss was recorded. Some of the samples were artificially aged by exposing them in the fadeometer for 96 hours. Samples were analysed using FTIR, and the surface pH and tensile strength were measured for selected samples.

No. of days of the treatment	1	3	6	10	15
Batch No.	q_2	q_1	q_5	$^{o}q_3$, q_4	$^{o}q_6$

o in presence of water   Temperature 20°C

5.2.3 Results and observations

Sample No.	Wt. gain (%)	Surface pH	Tensile strength (kg)
4A	0.0	4.9	0.2
$4q_5$	70.0 ?		4.8 -
$4q_5U$			3.8
$4q_6$	1.6		0.8
$4q_6U$			1.0
9A	0.0	6.5	1.8
$9q_1$	-0.4	6.5	1.7
$9q_2$		6.4	2.0
$9q_3$	3.4	6.5	1.8
$9q_3U$			1.7
$9q_4$	0.2	6.2	2.6
$9q_4U$			2.0
56A	0.0	6.4	2.9
$56q_1$	0.4	6.5	2.0
$56q_2$		6.8	2.4
$56q_3$	6.0	6.7	1.6
$56q_3U$			1.6
$56q_4$	1.7	6.6	1.6
$56q_6$	5.0		2.6
$56q_6U$			2.8

A -blank   q -exposed to trimethoxymethyl silane   U -fadeometer ageing

TABLE 5.1: Changes in weight, surface pH and tensile strength on trimethoxymethyl silane monomer treatment

5.2.3.1 Weight

Weight recorded is given in Table 5.1

5.2.3.2 Surface pH

Surface pH recorded is given in Table 5.1

5.2.3.3 Tensile strength

Tensile strength recorded is given in Table 5.1

5.2.3.4 Physical appearance

The increase in stiffness was observed in old newsprint treated for 6 days although there was no difference in stiffness and colour in other treated samples.

5.2.3.5 FTIR

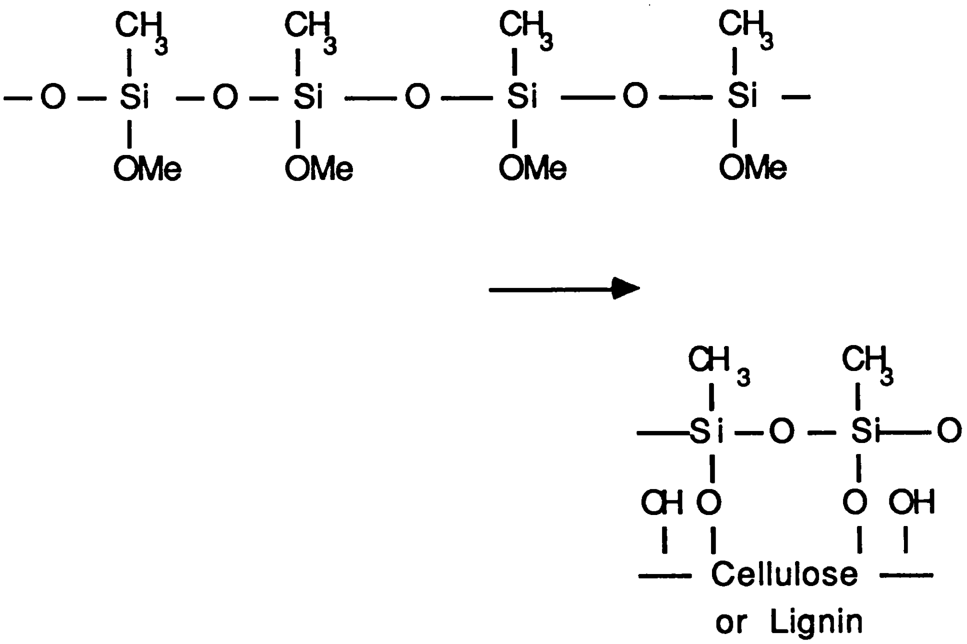
The Whatman No.1 paper samples did not show any changes in the FTIR spectra with the treatment under any conditions. The FTIR spectra of sample $4q_5$ which had an exceptionally heavy deposit of polymer showed a completely different pattern, indicating that a new compound was present. Two locations on the same sample showed different results in the FTIR spectra (Figure 5.1). The spectra of another sample of old newsprint treated for 15 days showed a decrease in intensity of the peaks at 3700, 3680, 3660 cm^{-1} and 3620 cm^{-1}, and an increase in intensity of the peaks at, 1178 cm^{-1}, and 1092 cm^{-1} and a shape difference in the range 1050 to 750 cm^{-1} (Figure 5.2).

An increase in the intensity of the peak at 1173 cm^{-1} was observed in the spectra of modern newsprints treated with trimethoxymethyl silane, under all conditions. A small peak or a shoulder was observed at 2940 cm^{-1} in spectra of modern newsprint samples subjected to the treatment for 1 day (q_2), 3 days (q_1) and 10 days (q_3, q_4) ; in the absence as well as in the presence of water. Also, the spectra of modern newsprint samples treated for 1 day and 10 days in the presence of water, showed a broad peak from 2920 to 2902 cm^{-1}. Modern newsprints treated for 10 days also indicated the appearance of a shoulder at 790 cm^{-1}. Modern newsprint samples treated for 15 days in the presence of water showed an increase in intensity of the peaks at 1092, 1128, 1273 cm^{-1} and 1373 cm^{-1}, in addition to 1173 cm^{-1}, the shoulders at 1209 cm^{-1} and 1236 cm^{-1} becoming small peaks and the appearance of a new peak at 790 cm^{-1} (Figure 5.3).

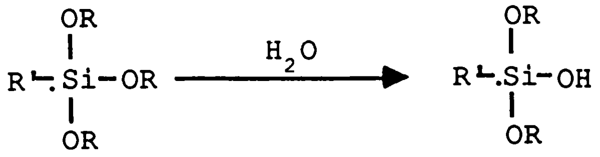
5.2.4 Discussion and conclusions

Trimethoxymethyl silanes should produce methyl silicone polymer, which deposit on paper in this treatment (Equation 5.1). It is stated that trialkoxy silanes undergo hydrolysis stepwise to give the corresponding silanols, which condense to siloxanes (Plueddemann, 1982).

According to Spry (1983) the alkoxy groups hydrolyse and then condense to give a silicone type (alkyl polysiloxane) network as a resin. The reaction is given in equation 5.2.

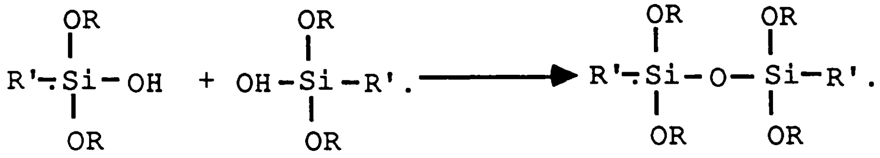


5.1



$$R'\text{-}\underset{OR}{\overset{OR}{Si}}\text{-}OR \xrightarrow{H_2O} R'\text{-}\underset{OR}{\overset{OR}{Si}}\text{-}OH$$

5.2a



$$R'\text{-}\underset{OR}{\overset{OR}{Si}}\text{-}OH + OH\text{-}\underset{OR}{\overset{OR}{Si}}\text{-}R'. \longrightarrow R'\text{-}\underset{OR}{\overset{OR}{Si}}\text{-}O\text{-}\underset{OR}{\overset{OR}{Si}}\text{-}R'.$$

5.2b

It is stated that coupling through organo-functional silanes often shows a well-aligned monolayer of silane, forming a covalent bridge between polymer and substrate. Although this coupling representation appears to be simple, the actual picture is much more complex (Plueddemann, 1982). Although it is clear that there is a formation of a resinous compound, it is difficult to be specific about its structure (i.e. linear or cross-linked) and the extent of coupling.

5.2.4.1 Weight and physical appearance

The weight gain in all the samples, except the Whatman paper treated for 3 days ($9q_1$), indicated the formation or deposition of a material resulting from the treatment. The formation of a polymer was particularly obvious in the old newsprint treated for 6 days, since a maximum weight gain was observed and also an increase in the stiffness. It could have been due to the longer duration of this treatment that these changes were observed, and hence the experiment was repeated to verify the findings. In contrast, as no change in the physical appearance was observed after 6 days, the treatment was continued for 15 days. Even so there was no appreciable difference in the physical appearance in comparison to the untreated samples. Hence the duration of the treatment is not the determining factor, in the observed weight gain. Except in the case of old newsprint treated for 6 days, the maximum weight gain was observed in the Whatman and modern newsprints, with treatment carried out for 10 days in the presence of water. This suggests that water is essential to the progress of the reaction and the formation of polymer. The deposition of polymer must therefore have occurred due to the formation of a silanol polymer as in the Equation 5.1.

5.2.4.2 Surface pH

After the treatment Whatman samples did not show a change in pH, except in the case of 1 day and 10 days exposure in the presence of water which showed a very slight decrease . This may have been due to experimental error in the measurement. All modern newsprints showed an increase in pH, indicating that the compound formed must have reacted with some of the acidic products in the paper or acidic groups in lignin, or possibly acid within the paper could not be detected at the surface due to coating of a resin on the paper.

5.2.4.3 Tensile strength

It was observed that the tensile strength increased in some instances and in others decreased due to the treatment. As a result of resin formation absorption of water becomes less, leading to loss in flexibility, and consequent early breakage. With decrease of water content embrittlement occurs, with concomitant decrease in tensile strength.

5.2.4.4 FTIR

Since Whatman papers did not show any changes in the FTIR spectra due to the treatment, it is possible that trimethoxymethyl silane did not react with pure cellulose, or that, the reaction had occurred on a very small scale as to be undetectable by FTIR.

The decrease in intensity of the peaks at 3700, 3680, 3660 cm^{-1} and 3620 cm^{-1}, assigned to hydroxyl groups (Appendix 4) was observed in old newsprints, which is almost certainly due to the loss of hydroxyl groups as a result of coupling with the resin. The intensity increase of the peak at 1128/1132 cm^{-1}, assigned to aromatic aliphatic ether linkage and/or OH in-plane bonding (Appendix 4) may also occur due to the condensation of siloxane (equation 5.1). The intensity increase of the peak at 1086/1094 cm^{-1} may be due to the formation of Si-O-Si and Si-O-C as the frequencies of those lies at 1090 -1020 cm^{-1} (Appendix 4). Although the peak at 1178 cm^{-1}, assigned to anti symmetric bridge C-O-C (Appendix 4), increased in intensity at some occasions with the treatment, this cannot be explained for certain, as there is no possibility of changing C-O-C stretching due to the treatment unless a reaction of methyl silanol with cellulose occurred when the keto form of cellulose existed, or with lignin when rearranged to give a carbonyl group in a side chain. On the other hand C-O stretching can change as a result of the formation of Si-O-C , further the frequency due to C-O-C might not be very different from the Si-O-C and hence the intensity increase of the peak at 1178 cm^{-1} may be explained in that respect. The intensity increase of the peaks at 1273 cm^{-1} and 1373 cm^{-1}, may be due to the formation of siloxane as both the peaks are assigned to CH deformation and bending vibrations (Appendix 4). The shoulder at 1209 cm^{-1} changing to a peak could have occurred as the deposition of resin, i.e. siloxane, could increase the OH in-plane bending which lies at 1205 cm^{-1} (Appendix 4), as siloxane may retain some OH groups. Intensity increase of the peak at 1236 cm^{-1} and an appearance of the peak at 790 cm^{-1} should be due to the $Si\text{-}CH_3$ as the frequency of $Si\text{-}CH_3$ lies at 1259 cm^{-1} and near 800 cm^{-1} (Appendix 4). With the FTIR evidence, condensation product formation could have occurred according to the mechanism in equation 5.1.

5.2.5 Conclusions

Although there were indications of polymer formation and increase in pH of the paper on many occasions as a result of the treatment, changes on the surface of the paper and decrease in tensile strength were observed at the same time. Hence, treatment with trimethoxymethyl silane does not significantly increase the durability of the paper when used under these conditions, and although initially promising, reactions with other monomers may be more effective and are subsequently investigated.

5.3 CYANOACRYLATE MONOMER TREATMENT

5.3.1 Reasons for the choice

Cyanoacrylate monomers are very volatile, the ethyl monomer having a vapour pressure of 2.2 mm/Hg. Curing occurs at room temperature on a wide range of substrates without the use of catalyst or of ionising radiation (Cagle, 1968). Their ageing properties are generally good (Landrock, 1985), and relevant data is given in Appendix 3. The ethyl and methyl monomers are those most commonly encountered commercially, but a wide range of grades is available offering different viscosities and degrees of monomer linkage. After preliminary experiments, most of the work was carried out using ethyl monomer.

5.3.2 Experimental method

Procedure

Samples of paper were exposed to ethyl cyanoacrylate monomer for periods upto fifteen days (1, 3,7, 10 and 15 days), some of them being exposed in the presence of water (p_3, p_4,p_5 and p_6).

Number of days	1	3	7	10	15
Batch No.	p_2	p_1 , $^{o}p_3$	$^{o}p_4$	$^{o}p_5$	$^{o}p_6$, $^{o}p_{6\text{-wt}}$

o -in presence of water Temperature 20°C

Cyanoacrylate monomers (ethyl, methyl, and high molecular weight) [Appendix 3] were poured into separate disposable aluminium dishes and placed in separate sealed plastic boxes containing paper samples suspended from steel rods, for 5 days. Weights and tensile strengths were recorded before and after treatment.

The monomer, which was found to give a reasonable weight gain and a reasonable increase in tensile strength was identified (ethyl), and samples were exposed to it for 3 $^{1}/_{2}$ days.

The same experiment was carried out both in daylight and in darkness to investigate the effect of light.

Because cyanoacrylate polymerisation is base - catalysed, and many of the paper samples to be consolidated were acidic, temporary deacidification was first carried out. A batch of samples was exposed to ammonia vapour for an hour in a closed plastic box, and exposed to the air for a further 10 minutes to remove excess ammonia vapour. The samples were then placed in a closed glass tank containing a small quantity of monomer for 3 $^{1}/_{2}$ days. The weight gain and/or loss was recorded, and the tensile strength measured. Some of the samples treated were exposed in the fadeometer for 96 hours for artificial ageing. The ammonia vapour treatment was found to cause a pronounced yellowing of the modern mechanical wood papers, and other deacidification techniques were therefore investigated. Other batches of samples were pre-treated separately, by exposing to cyclohexaylamine vapour; dilute ammonia vapour for 30 minutes; spraying with calcium hydroxide and magnesium hydroxide; and exposing all of them to the monomer under the same conditions for 3 $^{1}/_{2}$ days.

Samples were exposed to mixtures of ethyl and methyl cyanoacrylate monomers in the ratio of 1:1, 3:1 and 1:3 for 3 $^{1}/_{2}$ days. Whatman No.1 and modern newsprint were exposed to ethyl cyanoacrylate monomer for periods from 3 $^{1}/_{2}$ days to 15 days to check the effect of time on the treatment. Some of the samples of Whatman No.1 and both old and modern newsprint were exposed to ethyl cyanoacrylate monomer under different humidity conditions

Different types of Whatman papers, i.e. Whatman no. 44, 113, 114, 540 were exposed to ethyl cyanoacrylate monomer for 3 $^{1}/_{2}$ days under the same condition to investigate the effects of sizing.

One batch of Whatman No.1 paper and both old and modern newsprint samples was exposed to ethyl cyanoacrylate monomer at room temperature (20°C), and another batch was exposed at 40°C, in an airtight heated cabinet, to evaluate the effect of temperature on the treatment.

The initial experiments were designed to optimise the process, following which, treatment of a wide range of paper samples were carried out using ethyl cyanoacrylate monomer in an airtight chamber with a fan to provide circulation of the vapour, for a period of 3 $^{1}/_{2}$ days. Deacidification was not carried out.

In all the experiments described above, weight gain or loss was recorded, and analysis carried out using FTIR. In most of the cases, surface pH, folding endurance and tensile strength were also recorded. A selection of samples was artificially aged by exposure in the fadeometer for 96 hours, and some were examined under the scanning electron microscope.

Several samples with a weight gain of about 20% were selected, washed with acetone and toluene, and the weight difference recorded. Similar samples were extracted with acetone and toluene for 2$^{1}/_{2}$ hours using a soxhlet extractor, to investigate whether or not grafting of the monomer had occurred.

5.3.3 Results and observations

5.3.3.1 <u>Weight change</u>

Recorded weight changes are given in table 5.2 and most of the tables below.

5.3.3.2 <u>Physical appearance</u>

The samples treated with cyanoacrylate monomer did not show any colour change, except in the case of modern newsprints pre-exposed to ammonia vapour. Even on artificial ageing, the treated samples showed no difference in physical appearance to that untreated.

5.3.3.4 <u>FTIR</u>

The spectra of all Whatman samples treated with cyanoacrylate showed a new strong peak at 1747/1759 cm^{-1}, which was particularly intense in the spectra of samples treated in the presence of water (9p$_3$, 9p$_4$, 9p$_5$ and 9p$_6$). Also a small peak at 2247 cm^{-1} appeared in spectra of Whatman samples treated in the presence of water. In the spectra of Whatman paper, a peak at 854 cm^{-1} appeared as a kink in spectra of the sample treated for a day, as a very small peak in samples treated for 3 days, as a small peak in samples treated for 3 days in the presence of water and as a medium peak in samples treated for 7, 10 and 15 days in the presence of water. All Whatman samples treated in the presence of water showed a shape difference as the peaks at 1235 cm^{-1}, and 1245 cm^{-1} had merged into the peak at 1280 cm^{-1}, which gradually ended up as a branch of the peak at 1340 cm^{-1}. There was also an increase in intensity of the peak at 1280 cm^{-1} (Figure 5.4).

Sample No.	Wt. gain (%)
$9p_1$	3
$9p_2$	1
$9p_3$	14
$9p_4$	17
$9p_5$	22
$9p_6$	17
$56p_1$	14
$56p_2$	10
$56p_3$	24
$56p_4$	23
$56p_5$	24
$56p_6$	27
$56p_{6\text{-wt}\cdot}$	39
$4p_4$	7
$4p_5$	25
$4p_6$	12

p-cyanoacrylate treatment

TABLE 5.2: Weight gain with the cyanoacrylate treatment

Old newsprints treated in the presence of water for 7 days ($4p_4$) showed a strong peak, and samples treated for 10 ($4p_5$) and 15 ($4p_6$) days showed very strong peaks, at 1759/1747 cm^{-1} in all spectra. A small peak at 2247 cm^{-1}, and a medium peak at 854 cm^{-1} which masks the shoulder at 874 cm^{-1}, were observed only in the spectra of samples treated for 10 and 15 days in presence of water (Figure 5.5).

In spectra of some of the treated old newsprint samples (p_2, p_3 and p_4) the peak at 1086 cm^{-1} decreased or became a shoulder (p_3, p_5), and an intensity decrease in the peak at 1456 cm^{-1} (p_4, p_3 and p_2) was observed (Figures 5.5 and 5.6).

Sample No.	Wt. gain (%)	Tensile strength
4/0/1	0.3	0.8
4/0/1/U		0.3
4/1/1	0.5	0.9
4/1/1/U		0.6
4/2/1	0.4	1.3
4/2/1/U		0.3
4/3/1	0.4	1.0
4/3/1/U		0.2
4/4/1	0.3	1.0
4/4/1/U		0.4
4/5/1	0.3	1.4
4/5/1/U		0.7
4/6/1	0.4	0.7
4/7/1	0.7	0.5
4/8/1	0.6	0.7
4/9/1	0.4	0.5
4/10/1	0.9	0.8
62/0/1	0.0	2.9
62/0/1/U		2.2
62/1/1	9.7	3.9
62/1/1/U		3.4
62/2/1	9.6	3.4
62/2/1/U		3.1
62/3/1	8.6	3.3
62/3/1/U		2.2
62/4/1	8.4	3.0
62/4/1/U		3.3
62/5/1	3.7	3.0
62/5/1/U		2.6
62/6/1	2.2	2.9
62/7/1	10.2	3.6
62/8/1	8.1	3.5
62/9/1	10.0	3.2
62/10/1	10.4	3.2
63/0/1	0.2	2.9
63/0/1/U		2.7
63/1/1	2.3	2.9
63/1/1/U		2.2
63/2/1	1.9	3.6
63/2/1/U		3.4
63/3/1	1.7	3.4
63/3/1/U		3.3
63/4/1	1.6	3.2
63/4/1/U		3.2
63/5/1	1.6	3.2
63/5/1/U		3.2
63/6/1	1.1	3.2
63/7/1	2.8	3.6
63/8/1	2.1	3.4
63/9/1	3.4	3.9
63/10/1	1.5	3.8

TABLE 5.3: Changes in weight and tensile strength of the samples due to different cyanoacrylate monomer treatments

Modern newsprint treated with cyanoacrylate also showed an increase in intensity of the peak at 1749/1757 cm^{-1}, appearance of a peak at 854 cm^{-1} with a higher intensity masking the peak at 874 cm^{-1}, and appearance of a peak at 2247 cm^{-1}. It was observed that there was an intensity increase in the peak at 1269 cm^{-1} in spectra of the samples treated for 7, 10 and 15 days in presence of water. In addition to these changes, a shape difference was observed in the 2902 cm^{-1} peak with a small peak appearing at 2920 cm^{-1} in spectra of the

Sample No.	Wt. gain (%)	Tensile strength (kg)
4/0/6-9	0.1	0.2
4/9/ 6	0.2	0.7
4/9/ 7	5.3	1.3
4/9/ 8	0.7	0.3
4/9/ 9	0.1	0.2
4/0/ 6	0.0	
4/0/ 7	0.1	
4/0/ 8	0.3	
4/0/ 9	0.0	
62/0/6-9	-0.8	2.9
62/9/ 6	0.5	2.9
62/9/ 7	6.0	3.6
62/9/ 8	11.5	3.1
62/9/ 9	13.9	4.6
62/0/ 6	0.1	
62/0/ 7	-0.1	
62/0/ 8	0.6	
62/0/ 9	0.1	
63/0/6-9	0.3	3.4
63/9/ 6	0.4	3.2
63/9/ 7	1.3	3.4
63/9/ 8	5.2	4.1
63/9/ 9	5.4	3.6
63/0/ 6	0.0	
63/0/ 7	0.3	
63/0/ 8	0.3	
63/0/ 9	1.4	

No. of treatment:
4/0/6-9 - blank
/9/6 - exposure for 3 1/2 days followed by pre cyclo hexayl amine for 30 minutes
/9/7 - exposure for 3 1/2 days followed by pre dil. NH_3 (5%) for 30 minutes
/8/8 -exposure for 3 1/2 days followed by $Mg(OH)_2$ spray and drying
/9/9 - exposure for 3 1/2 days followed by $Ca(OH)_2$ spray and drying
/0/6-9 ; blank samples w.r.t treatments 6,7,8 and 9
/0/6 - cyclo hexayl amine exposure for 30 minutes
/0/7 - dil. NH_3 exposure for 30 minutes
/0/8 - $Mg(OH_2$ spray and drying
/0/9 - $Ca(OH)_2$ spray and drying

TABLE 5.4: The effect of alkalinity on the treatment

sample treated for 10 days in presence of water. When the cyanoacrylate treated samples were subjected to fadeometer ageing there was no change in the peak at 1759 cm^{-1}, although an intensity decrease was observed in the peaks at 1510 cm^{-1} and 2247 cm^{-1}. (Figure 5.7).

Spectrum of free cyanoacrylate polymer showed characteristic peaks, i.e. strong peaks at 1769/1761, 854 , 2247, 2934 cm^{-1} and 2856 cm^{-1} (Figure 5.8).

Sample No.	Wt. gain (%)	Tensile strength (kg)
4/7/3	0.2	1.2
4/7/4	0.2	1.0
62/7/3	9.3	3.9
62/7/4	16.2	4.4
63/7/3	4.4	4.0
63/7/4	4.7	4.2

Sample No./ Monomer No./ Treatment No.
Treatment No
3 - treated in the dark for 4 days
4 - treated in daylight for 4 days

TABLE 5.5: The effect of light on the cyanoacrylate polymer.

Sample No.	Monomer ratio ethyl : methyl	Wt. gain (%)	Increase in fold. end. (%)	Increase in tens. str. (%)
4/0/10-12	-	0.0	-	-
4/9&10/10	1 : 1	1.5	0	200
4/9&10/11	1 : 3	1.2	0	350
4/9&10/12	3 : 1	0.5	0	150
4/9/1	1 : 0	0.4	0	200
4/10/ 1	0 : 1	0.9	0	100
62/0/10-12	-	0.8	-	-
62/9&10/10	1 : 1	16.8	67	54
62/9&10/11	1 : 3	19.3	106	46
62/9&10/12	3 : 1	11.6	170	39
62/9/1	1 : 0	10.0	170	29
62/10/1	0 : 1	10.4	15	21
63/0/10-12	-	0.0	-	-
63/9&10/10	1 : 1	3.5	-18	-35
63/9&10/11	1 : 3	2.7	-27	-32
63/9&10/12	3 : 1	1.4	-55	-46
63/9/1	1 : 0	3.4	73	26
63/10/1	0 : 1	1.5	18	16

fold. end. -folding endurance tens. str. -tensile strength

TABLE 5.6: The effect on weight and strength in using different ratios of ethyl and methyl monomers on cyanoacrylate monomer treatment.

No. of days	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Wt. gain %	15	24	31	37	38	42	42	43	43	44	45	44	44	44

TABLE 5.7: Weight gain of sample p6-wt. on different days

Sample No.	No. of days of treatment	Wt. gain (%)	Increase in fold. end. (%)	Increase in tens. str. (%)
62/9/18	3½	6.0	127	46
62/9/19	5	10.4	18	61
62/9/20	7	11.8	76	61
62/9/21	11	24.3	27	82
62/9/22	15	29.4	18	93
63/9/18	3½	1.5	27	16
63/9/19	5	2.2	18	16
63/9/20	7	2.4	27	26
63/9/21	11	5.5	73	48
63/9/22	15	6.5	82	48

fold. end. -folding endurance tens. str. -tensile strength Wt. -weight

Table 5.8 The effect of the length of time on the cyanoacrylate treatment

Sample No.	Condition	Wt. gain %
4/0/-		0.0
4/9/ 36	moist	3.8
4/9/ 37	80% RH	0.9
4/9/ 38	53% RH	1.8
4/9/ 24	50-60% RH	0.3
62/0/-		0.0
62/9/32	dried	9.0
62/9/36	moist	19.8
62/9/37	80% RH	16.1
62/9/38	53% RH	14.2
62/9/24	50-60% RH	8.0
63/0/-		0.0
63/9/32	dried	2.2
63/9/36	moist	8.8
63/9/37	80% RH	11.1
63/9/38	53% RH	9.8
63/9/24	50-60% RH	2.3

RH -relative humidity

TABLE 5.9: The effect of humidity on the treatment

Sample No.	Whatman No.	Char.	% ash	Thick. (mm)	Wt. (g/2)	Lo. cap.	WetB (Kpa)	Dry B (Kpa)	Oth. com	Wt. gain(%)
63/9/17	1	Quali.	0.06; hi.al. cotton	0.18	87	N	1.7	97	-	4.8
70/9/17	44	Ashl. quan.	0.01; hi. al. cotton	0.18	80	N	2.0	117	-	1.3
71/9/17	540	Hard. ashl.	0.008; hi. al. cotton	0.16	85	N	48.3	186	hi.W.st ac. ha.	0.2
72/9/17	113	G.P and wet str.	NA; bl. sul. w.	0.42	125	VH	62.1	200	ex. s. cre.sur., ins. re., ni. pre.	4.5
73/9/17	114	G.P. and wet str.	NA; bl. sul. w	0.19	75	N	55.2	138	ex. s., sm. sur., ins. re., ni. pre.	4.6

ac. ha. - acid hardened Ashl. quan.- ashless quantitative bl. sul.w. - bleached sulphite wood Char. -characteristics co. -contains cre. sur. -creeped surface Dry B. - dry burst ex. s. -extremely strong G.P. -general purpose Hard. ashl. -hardened ashless hi. al.-high α hi. W. st. -high wet strength ins. re. -insoluble resin Lo. cap. -loading capacity N -normal NA -not analysed ni. pre. -nitrogen present Oth. com. -other comments Quali. -qualitative sm. sur. -smooth surface sul. -sulphite Thick. -thickness VH -very high w -wood Wet B. -wet burst wet str. -wet strengthened Wt. -weight

TABLE 5.10: Weight gain due to the treatment of different Whatman samples with/without wet strengthening

Sample No.	Temperature (°C)	Wt. gain (%)	Increase in fold. end. (%)	Increase in tens.str.(%)
4/9/24	20	0.3	0	50
4/9/34	40	0.5	0	71
62/9/24	20	8.0	58	25
62/9/34	40	11.5	94	29
63/9/24	20	2.7	18	16
63/9/34	40	3.5	27	16

fold. end. - folding endurance tens. str. - tensile strength Wt.- weight gain

TABLE 5.11 : The effect of temperature on the cyanoacrylate treatment

Sample No.	Year	Wt. change (%)	Change in fold. end. (%)	Change in tens. str. (%)
1/9/ 23	1796	5.6	58	74
2/9/ 23	1845	3.6	0	26
3/9/ 23	1899	7.7	150	57
4/9/ 23	1910	0.2	0	50
5/9/ 23	1924	2.3	-13	-18
6/9/ 23	1930	4.7	0	112
7/9/ 23	1933	1.2	0	107
8/9/ 23	1938	0.9	0	41
10/9/ 23	1605	4.0	100	100
54/9/ 23	1839	3.2	20	12
55/9/23	1900	0.8	-50	9
57/9/23	1988	14.1	176	69
62/9/23	1989	11.8	94	57
62/9/23 c.d	1989	10.4	100	83
63/9/23	1988	4.2	46	36
69/9/23	1963	3.0	100	29
74/9/23	1910	0.4	-50	-22
75/9/23	1949	22.7	-55	63
76/9/23	1909	3.4	0	15
77/9/23	1905	1.2	100	31
78/9/23	1920	3.5	0	32
79/9/23	1937	0.7	0	6
80/9/23	1966	3.4	38	24
81/9/23	1848	5.7	18	36
82/9/23	1979	11.4	100	80
83/9/23	1984	5.3	40	19
84/9/23	1843	5.4	50	69
85/9/23	1809	3.1	33	72
86/9/23	1989	7.7	29	17
86/9/23 c.d	1989	10.2	50	40
87/9/23	1989	10.7	40	50
88/9/23	1989	13.2	225	28
89/9/23	1961	7.7	-60	61
90/9/23	1893	1.7	0	-23

c.d. -cross direction   fold. end. -folding endurance   tens. str. -tensile strength

TABLE 5.12: Changes in weight, folding endurance and tensile strength in different samples due to the cyanoacrylate treatment

Sample No.	Wt. gain after treatment (%)	Wt. gain after f.m., h., amine exposure (%)	Conditions of amine, f.m., h exposure	Wt. gain after acetone extraction (%)
62/9/33 U	2.4	1.9	f.m.-1hr	0.4
63/9/33 U	1.1	1.0	f.m.-1hr	1.4
62/9/33 V	2.7	2.0	50°C; dry;-4 hr	0.2
63/9/33 V	1.3	0.9	50°C; dry;-4 hr	1.5
62/9/33 am.	1.9	2.1	CHA, -30 min.	0.0
63/9/33 am	1.1	1.2	CHA, -30 min.	1.8
62/9/33	3.0	-	-	-0.8
63/9/33	1	-	-	1.6
17A	-	-	-	-1.0
17R	20			19.5

am. -amine CHA -cyclo hexayl amine f.m. -fadeometer h. -heat

TABLE 5.13: Weight changes on extraction of the cyanoacrylate treated samples with acetone

Sample No.	Wt. gain due to the treatment (%)	Solvent used	Wt. gain after washing
4p_6-ac	12	acetone	10.3
9p_6 -ac	17	acetone	13.6
56p_6 -ac	27	acetone	26.5
4p_6-tol	12	toluene	12.0
9p_6 -tol	17	toluene	16.6
56p_6 -tol	27	toluene	23.8

ac. -acetone p -cyanoacrylate treatment tol -toluene Wt. -weight

TABLE 5.14: Changes in weight on washing the cyanoacrylate treated samples with acetone and toluene

5.3.3.3 Mechanical strength

Recorded tensile strength and folding endurance are given in Tables 5.12.

5.3.3.5 Scanning electron microscopic analysis

SEM photographs of Whatman No. 1 and a modern newsprint and those treated with cyanoacrylate monomer are given in Plate 5.1 and 5.2 .

5.3.3.6 Elemental Analysis

The percentage of C, H and N in the treated and untreated samples were as follows.

Sample No.	C	H	N
$56A_6$	46.97	6.68	0.00
$56p_3$	49.57	6.14	2.37

Table 5.15: Percentage of carbon, hydrogen and nitrogen in a modern newsprint and of that treated with cyanoacrylate monomer

5.3.3.6 Surface pH

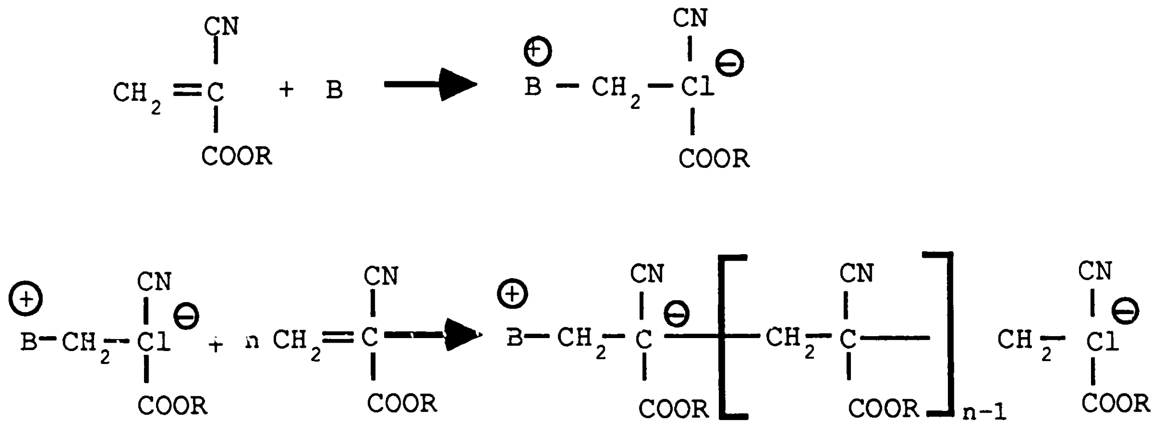
Recorded pH is given in Table 5.16

Sample No.	Wt. gain (%)	Surface pH (untreated)	Surface pH (treated)
1/9/14	3.6	6.2	6.2
3/9/14	7.9	7.0	6.6
4/9/14	0.2	5.0	5.1
6/9/14	2.4	5.6	5.8
10/9/14	1.5	5.2	5.3
17A/9/14	0.4	4.9	5.2
17R/9/14	4.6	4.8	5.5
34/9/14	1.4	5.0	5.3
50/9/14	3.0	5.9	6.2
62/9/14	9.5	5.9	6.4
64/9/14	2.0	5.3	6.2
65/9/14	2.7	4.9	5.4
66/9/14	1.0	5.1	5.5
67/9/14	2.3	5.8	6.4

TABLE 5.16: The effect of pH and the change in pH on cyanoacrylate treatment

5.3.4 Discussion and conclusions

Addition polymerisation occurs through the reaction of monomer containing double bonds of the general formula $CH_2 = CR_1R_2$ (Kinloch,1987), typical of which is the cyanoacrylate monomers CH2 = C(CN)COOR. It is reported that polymerization of cyanoacrylate is ionic (Landrock, 1985) and it undergoes an anionic mechanism, which is catalyzed by traces of moisture and weak bases (Parker and Taylor, 1966, Cagle, 1968; Rayner, 1972) , where as other "ethylenes" undergo polymerization only with strongly basic catalysis. The strong electron-attracting nitrile and ester groups situated in very close proximity to the ethylinic double bond may have probably enhanced polymerization (Parker and Taylor, 1966). Polymerization of ethyl cyanoacrylate can be represented as follows.



B = Lewis-base, eg.Water

5.3.4.1 *Evaluation of the treatment*

5.3.4.1.1 Weight gain:

It was observed that with the treatment there was an increase in weight in all the samples (Whatman, old and modern newsprints), under all conditions (Tables 5.2 and 5.3). Hence, deposition of polymer on the paper is inferred.

5.3.4.1.2 Physical appearance:

Since this treatment does not change the colour, it can be used for treating paper.

5.3.4.1.4 FTIR

With FTIR analysis it was assumed that the appearance of a peak at 1759 cm^{-1}, which is being assigned to C=O stretching in esters (Appendix 4), or the intensity increase of the existing peak at 1732 cm^{-1}, is due to the acrylate group in treated samples. The peak at 2247 cm^{-1} in spectra of treated samples is due to the CN group (Appendix 4). As well as these two, the peaks at 2934, 2856, 1267 and 854 cm^{-1} are characteristic peaks in the spectrum of the polymer. Hence, the appearance and/or increase of these peaks in the spectra of treated samples indicates the deposition of polymer. It was evident that with the increase in length of the treatment, the intensity increased especially in the peaks at 1757, 2247 and 854 cm^{-1}, which supports the observation that the weight gain increases with the length of treatment.

5.3.4.1.5 Mechanical strength

With the initial experiments it was clear that the cyanoacrylate monomer treatment had promise as a technique for strengthening paper. Although the artificially aged samples showed a decrease in tensile strength, it was always greater in the treated than the untreated samples (Table 5.3). Hence, it is obvious that on ageing, the papers treated with cyanoacrylate monomer do not completely lose the strength gained in treatment.

Many samples increased in folding endurance and tensile strength, some by more than a 100% after the treatment (Table 5.12). Hence, it is quite clear that, in general, the cyanoacrylate treatment strengthens paper.

5.3.4.1.6 Scanning electron microscopic analysis

The SEM photographs did not show any surface material or any fibre-linking due to the treatment. Paper treated by the British Library / University of Surrey graft copolymerization process has been reported to show linking of individual fibres with polymer (Burstall, Butler and Mollett, 1986). This was not, however, apparent in the sample of paper treated by that process which was examined in the course of this work, although a deposit on the surface was observed. In the cyanoacrylate process, no such surface deposit was visible. Hence it is clear that the monomer has been absorbed into the fibre, which is quite encouraging as it helps to avoid distortion of the colour and transparency of the paper. The polymer loadings in each case were similar.

5.3.4.1.7 Elemental analysis

The elemental analysis (Table 5.15) clearly showed that treated paper had gained nitrogen, which was not present in untreated papers, and the 2.37 % N present indicated that a reasonable amount of cyanoacrylate polymer, i.e. 21%, had been absorbed into the paper.

From the gravimetric results, the polymer content was 19%. The difference, 2%, must be due to the loss of moisture.

5.3.4.1.8 pH

The measurement of pH values (Table 5.16), indicated that the treatment increases the surface pH of paper, except in samples 1 and 3. Some of the increases in pH are very small, and the lack of change in sample 1 is not significant. Sample 3, however, was the only neutral paper, and was known to be buffered with calcium carbonate. This indicated a decrease in pH, implying that the paper had become acidic. Since the cyanoacrylate monomer was neutral, and as no other treatment had been applied, it should be impossible for the paper to become acidic. Hence, it is most likely that due to the treatment the coating of buffer particles occurred, so that it could not contribute to the pH and, as a result, the paper gave a lower pH after treatment. This will probably have no long term effect on the efficiency of the buffer. In general, cyanoacrylate monomer treatment increases the pH of paper. Similarly, increase in pH of acid papers on treatment with cyanoacrylates is probably due to the reduction in mobility of the acidic components of the paper. It may be argued that this would make deacidification more difficult after the treatment has taken place, but would on the other hand offer the paper some protection against atmospheric pollution.

5.3.3.2 *Selection of the Reaction Conditions*

5.3.3.2.1 Monomer

When a number of different monomers were tried out for Whatman and old and modern newsprints, monomers 7, 9 and 10 gave a reasonable weight gain (Table 5.3). Hence ethyl monomers 7 and 9, and methyl monomer 10 (Appendix 3) favour the treatment in respect of gaining weight, compared to others. This is probably due to the fact that the amount of free monomer in different products varies considerably, and the low viscosity cyanoacrylates are monomer rich, and hence more volatile, and therefore work correspondingly more rapidly. Considering the overall weight increase for all types of paper, ethyl cyanoacrylate (No. 9) was selected for future experiments.

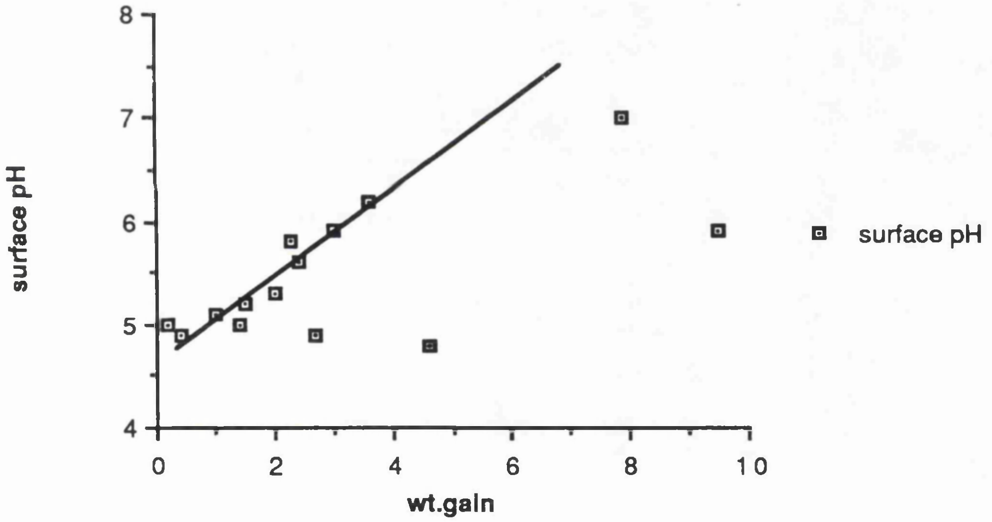
Mixtures of different monomer in varying proportions were investigated to determine that which gave optimum results in the treatment of paper. From the results (Table 5.6) , it was clear that a mixture of ethyl and methyl monomers in equal amounts gave a higher weight gain in old newsprint and Whatman papers, while a mixture of ethyl and methyl in a 1:3 ratio gave the maximum weight gain for modern newsprints. On mechanical testing it was observed that the Whatman samples treated with mixtures decreased in strength. Although mixtures gave better results in respect of tensile strength in old newsprint and modern newsprint, ethyl monomer alone gave fairly similar results, although the values obtained were less than some of those observed with treatments using mixtures. Folding endurance measurements did not show any change on treatment in the case of old newsprint, probably because of the strength of the individual fibres does not in this case contribute significantly to the folding endurance of the paper. Folding endurance in modern newsprint showed a change of the same order as the tensile strength. Hence, it appears that this treatment is not equally effective for all types of paper, a disadvantage showed by the graft copolymerization process as well. The reported moisture resistance of methyl cyanoacrylate is only fair, and ethyl cyanoacrylate has been shown to form stronger bonds than methyl between several different types of plastic surfaces. The higher homologues generally do not form bonds as strong as the methyl form (Landrock, 1985). Hence, taking all of these points into consideration, the treatment with ethyl monomer alone was then carried out.

5.3.3.2.2 Light

From the observations contained in Table 5.5 it was obvious that daylight favours the reaction, as the weight-gain and tensile strength were higher under daylight conditions in the case of modern newsprint and Whatman, while old newsprint did not show any difference in weight although the tensile strength increased in darkness. This seems to suggest that the polymerization process may also be light induced, but that the rate of reaction or its own in which the polymer is laid down affect the strength of various papers in different ways.

5.3.3.2.3 pH: alkalinity and acidity

It was found that pH alone does not affect polymer deposition (Table 5.16), as papers having the same pH did not gain monomer in equal amounts. However, out of 14 samples, 11 samples indicated a trend to a straight line relationship (Graph 5.1). The three samples (17R, 65 and 62), which did not come within this trend could be non-typical papers. Sample no. 17R is a pre-grafted paper, which was subjected to γ radiation treatment and hence must have gained more polymer. Sample no. 65 is a blue glazed paper, and probably due to the heavy gelatin component added for glazing, has gained more weight. Sample no. 62 which is a newsprint showed the maximum weight gain, which may be due to a sizing agent or to some other component added in the manufacturing process. It is stated, however that newspapers have no sizing (manufacturing literature) or hardly any sizing (D. Priest, pers. comm.).



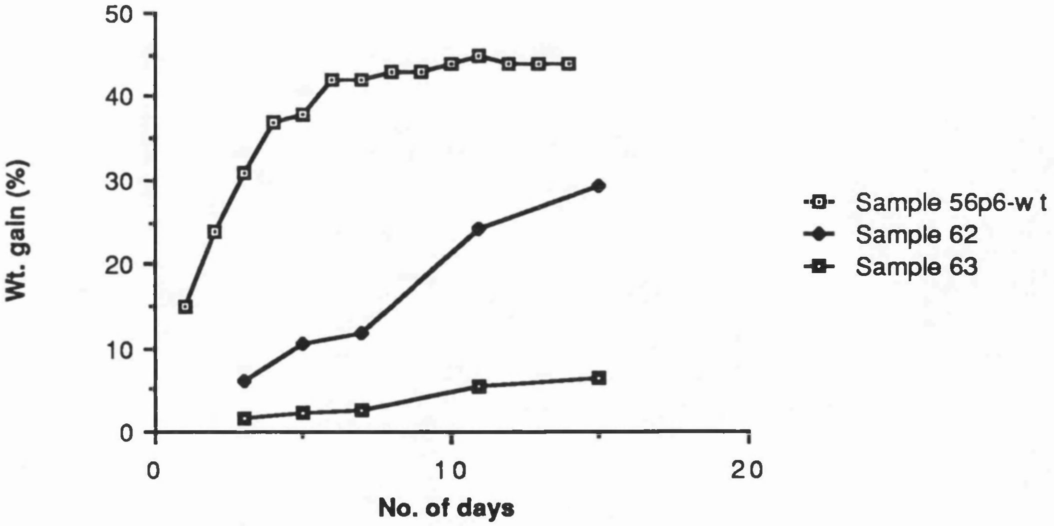
Graph 5.1: Effect of pH on cyanoacrylate treatment

It is possible that monomer is absorbed into the resinous component of fresh mechanical wood pulps, and that in the case of aged newsprints these components are absent or altered, and less monomer is therefore absorbed. From the results it was indicated that in general, polymer deposition increases with higher pH, i.e. in alkaline conditions, although it was reported that acid increases the rate of radiation copolymerisation (Garnett and Major, nd). It is stated that cyanoacrylate monomers cure faster on alkaline surface (Manufacturing literature).

When the effect of alkalinity on treatment was investigated, the sample of old newsprint which had been exposed to ammonia vapour was found to posses the maximum weight gain and increase in tensile strength. Although Whatman and modern newsprint pre-exposed to ammonia vapour gave moderate weight gain and tensile strength, in the case of modern newsprint a greater weight gain and tensile strength increase was observed in that which has previously de-acidified with calcium hydroxide solution . In case of Whatman, magnesium hydroxide pre-treatment has given the highest tensile strength, although maximum weight gain was observed in the calcium hydroxide pre-treated sample (Table 5.4). It was obvious that these pre treatments behave in different ways on different papers. Thus it is not possible to recommend an ideal pre-treatment in conjunction with the monomer treatment, and also, without any de-acidification treatment, all samples showed a reasonable weight gain and tensile strength increase. Hence, the remainder of the experiments were carried out without any de-acidification treatment.

5.3.3.2.4 Duration

Tables 5.7 and 5.8 indicated that with the increase in length of the treatment, the weight gain also increased (Graph 5.2). Hence if a higher weight gain is required, it is possible to prolong the process and check the subsequent properties for many samples, although different papers gain different amount of monomer in a specific time. The relationship between weight gain and exposure time had been demonstrated for three samples, but extended experiments involving a larger number of samples are required in order to decide on an optimum treatment time under given conditions. These additional experiments could not be performed within the time available for the project.



GRAPH 5.2: Correlation of the weight gain and the length of time on cyanoacrylate treatment

5.3.3.2.5 Moisture

Modern and old newsprints indicated a maximum weight gain when the treatment was carried out in the presence of moisture. It may be due to absorption of moisture into the paper enhancing the movement of monomer within the fibres, which allowed a more even distribution. At 80% RH Whatman showed the maximum weight gain, and even modern newsprint showed a reasonably high weight gain, while old newsprint showed a comparatively moderate weight gain (Table 5.9). Since different papers absorbed the maximum amount of monomer under different humidity conditions, it was impossible to define an optimum level of humidity.

5.3.3.2.6 Sizing

The Whatman samples which were both sized and unsized gave a reasonable weight gain, except for sample 70 and 71 (Table 5.10). Hence sizing did not have any significant effect upon the treatment.

5.3.3.2.7 Temperature

According to the observations (Table 5.11) of the weight gain measurements, 40°C was found to be favourable for the treatment. The tensile strength of sample 62 increased very slightly and Whatman showed the same values, while old newsprint, sample 4, showed a remarkable increase at 40°C. In the case of folding endurance sample no. 4 did not show any increase, Whatman showed a slight increase while modern newsprint showed a reasonable increase at 40°C. Although the weight gain was always greater at 40°C, a difference between that and at 20°C was not always large. At 40°C there was an additional improvement of the mechanical properties in only some of the paper. It was concluded that therefore has the process occurs reasonably well at the ambient temperatures, even if there is some slight improvement at 40°C it is nevertheless preferable to work at the lower temperature for practical reasons.

5.3.3.2.8 Type of the substrate

The results indicated (Table 5.12) that the papers consisting of mechanical wood could absorb higher amounts of monomer and also increased in folding endurance and tensile strength, with the exception of certain samples such as 90 and 89. Sample 90, which is a very old newsprint, did not show any change in folding endurance and tensile strength, and sample 4 which was a moderately old newsprint, followed the same pattern in respect of folding endurance, while the tensile strength was increased. The decrease or lack of change in folding endurance probably results from an increase in rigidity of the sheet without a corresponding gain in strength of individual fibres. Samples 5, 55, 74 and 75 also decreased in folding endurance and tensile strength. Sample no. 75, a loaded paper, gained a very large amount of monomer, and hence its rigidity may have lead to ease of breaking.

5.3.3.3 *Type of polymerization*

The cyanoacrylate polymerization onto paper could have occurred due to grafting and/ or consolidation. Originally the author was under the impression that graft copolymerisation had occurred, although with the SEM analysis it did not show any linkings between fibres on the surface. Since there was no specific method or technique to confirm the presence of grafting, the treated samples were extracted using acetone for 2 $^1/_2$ hours. From the observations (Table 5.13) it was clear that all the absorbed polymer resulting from the cyanoacrylate treatment could be solvent extracted. Where true grafting has taken place, and paper containing acrylate monomers been exposed to γ radiation, extraction with acetone did not lead to a significant weight change (sample 17R). Hence, it is clear that the present cyanoacrylate treatment is not a grafting process. It was found nevertheless, that the polymer was reasonably strongly bound to the paper, as washing with acetone and toluene at room temperature did not show a significant decrease in weight (Table 5.14)

5.3.4 **Conclusions**

It is found that the ethyl cyanoacrylate treatment can strengthen paper, enhancing strength in groundwood papers to a greater extent. The treatment can be carried out at room temperature, and it does not need sophisticated equipment, a reaction chamber being sufficient unless it is being carried out on a mass scale. The great advantage shared by both this process and the graft copolymerisation method, is that unlike the use of consolidants applied as polymers in solution, blocking does not occur upto concentrations of at least 20%. The other advantage of this process is that the polymer is completely absorbed into the fibres, and hence even a slightest colour change was not visible in treated samples, which is not so, in the case of British Library / Surrey University graft copolymerisation process as these samples showed a very slight colour change.

PLATE 5.1 (a)

PLATE 5.1 (b)

PLATE 5.1: Scanning electron microscope photographs of (a) Whatman No. 1 paper, and (b) of that treated with cyanoacrylate monomer

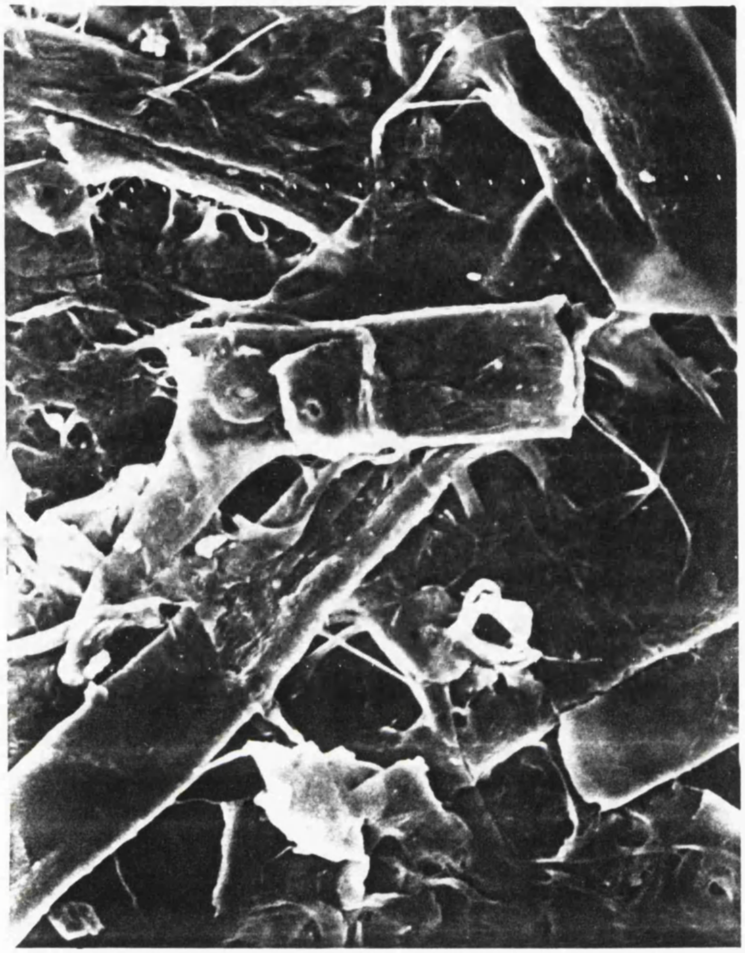


PLATE 5.2 (a)

PLATE 5.2 (b)

PLATE 5.2: Scanning electron microscope photographs of (a) modern newsprint and (b) of that treated with cyanoacrylate monomer

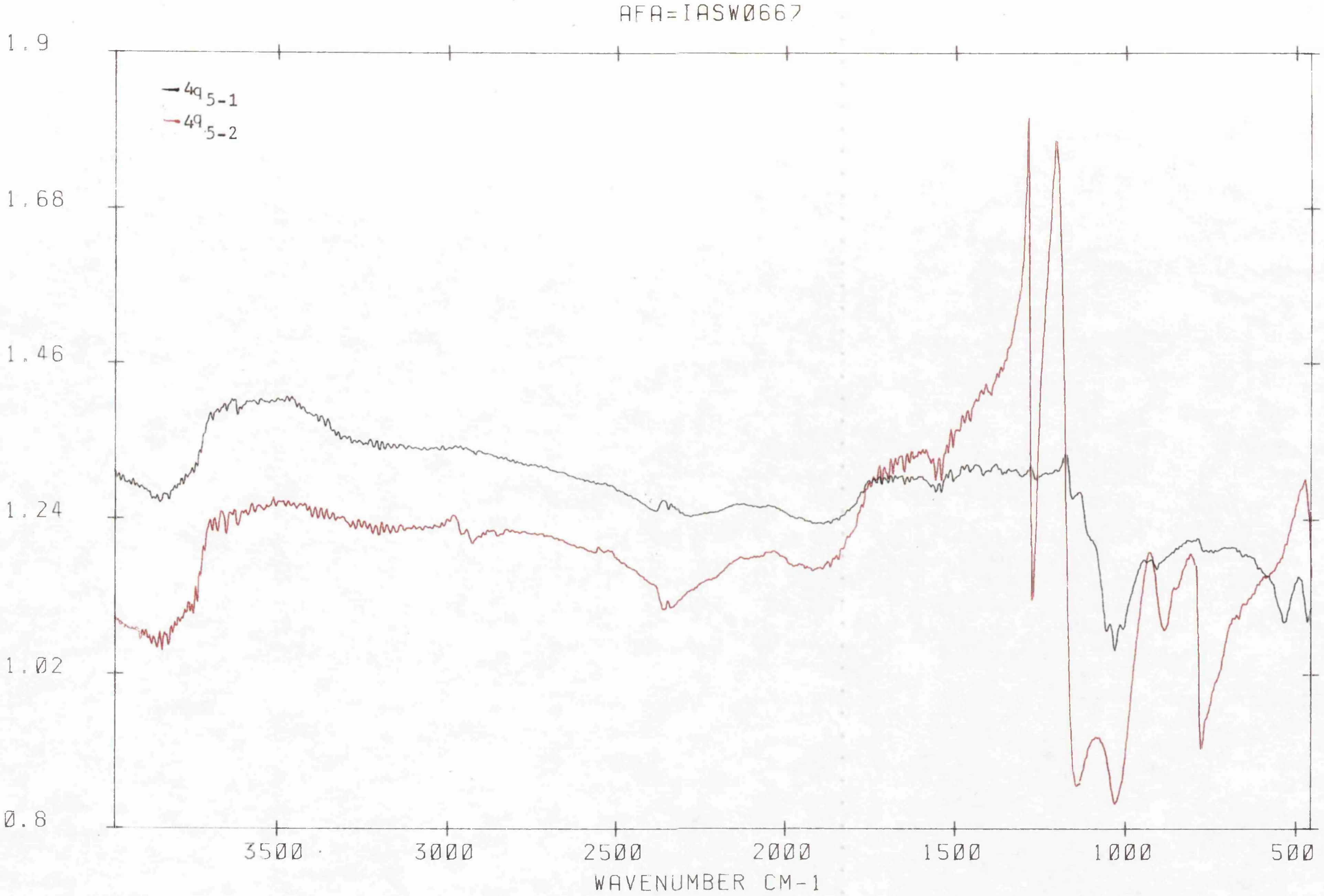

AFA=IASW0667
4q 5-1
4q 5-2
1.9
1.68
1.46
1.24
1.02
0.8
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.1

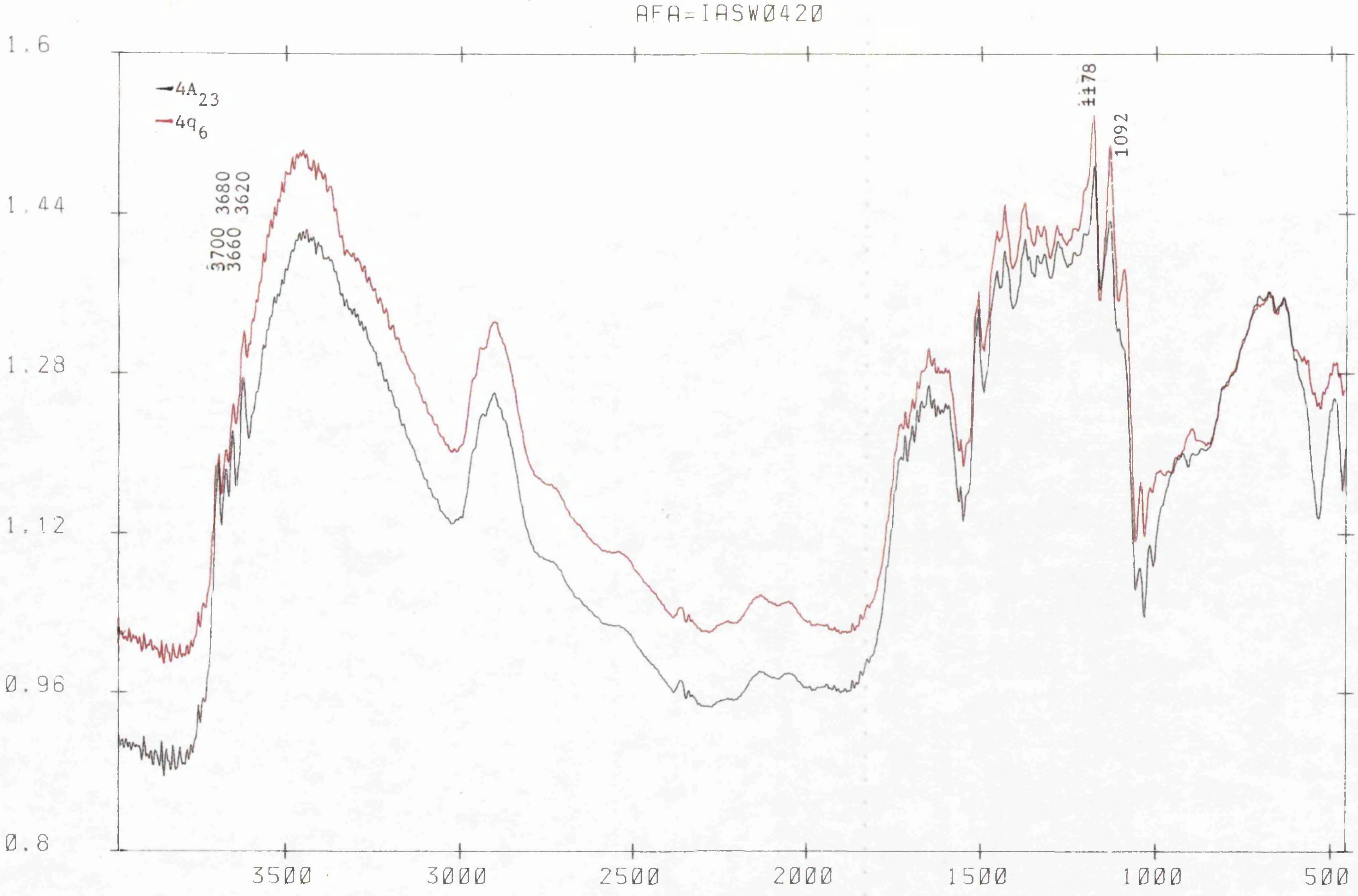
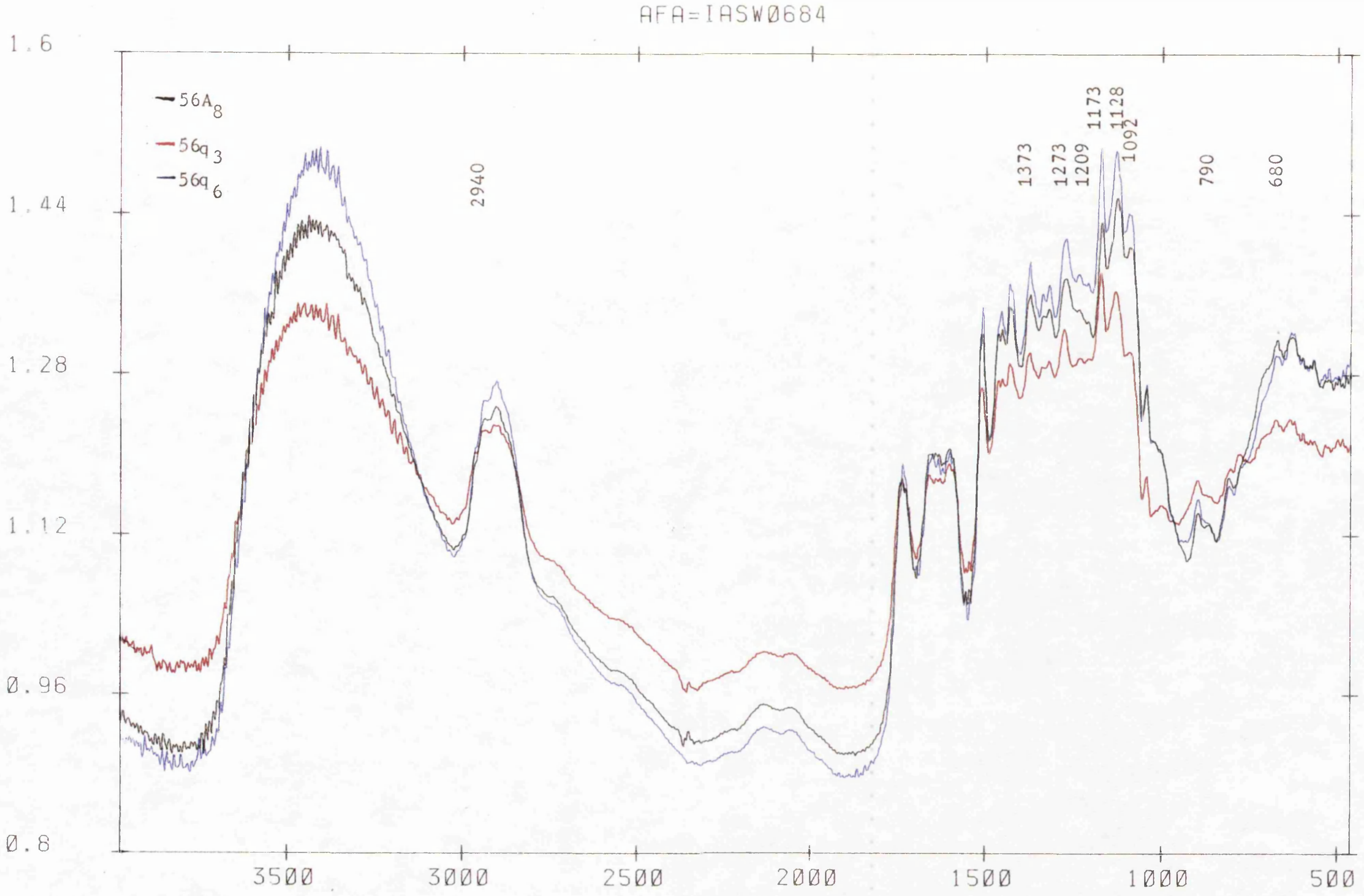

AFA=IASW0420
4A23
4q6
3700 3680
3660 3620
1178
1092
1.6
1.44
1.28
1.12
0.96
0.8
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.2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56q 3
56q 6
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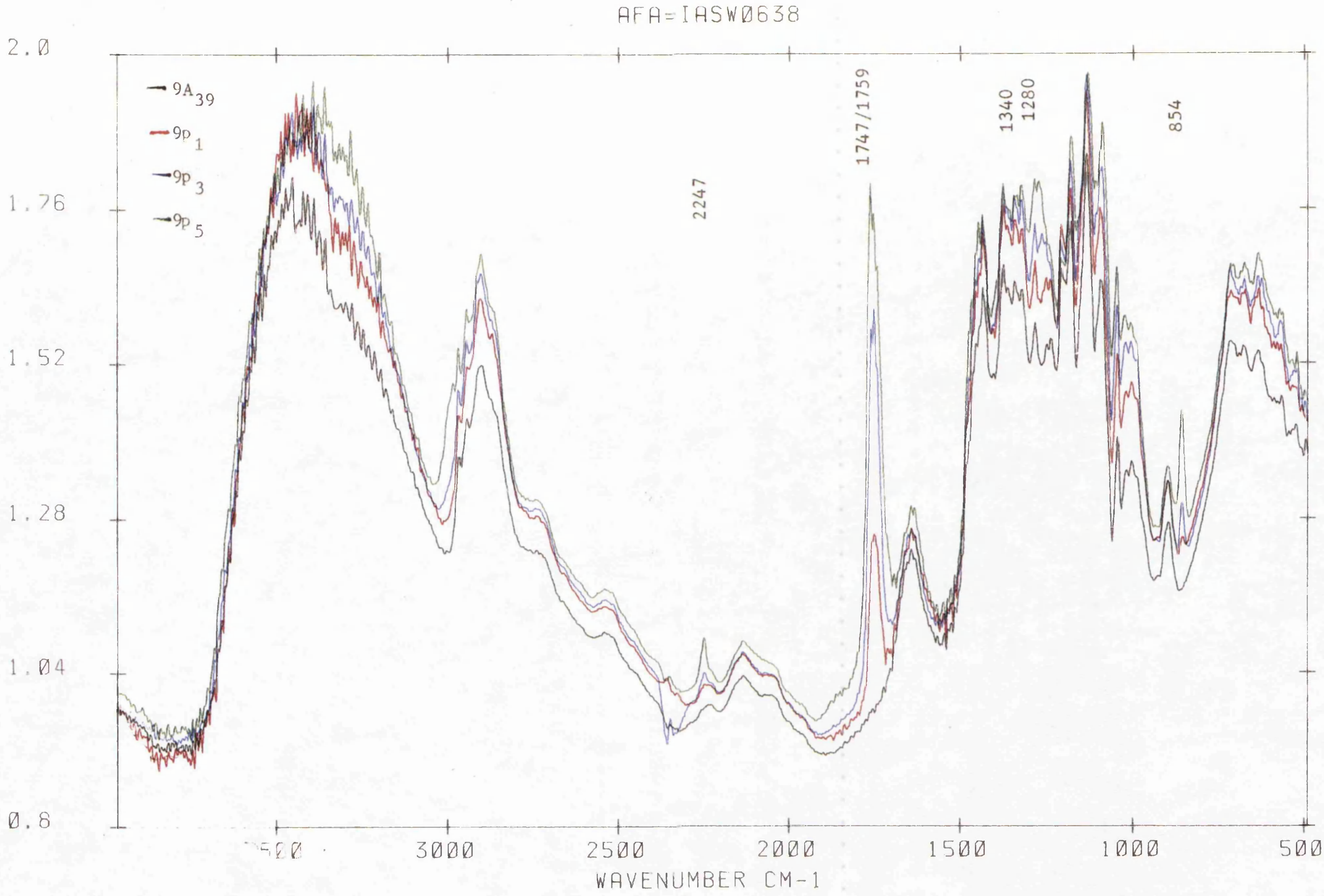
1373
1273
1209
1173
1128
1092
790
680
1.6
1.44
1.28
1.12
0.96
0.8
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.3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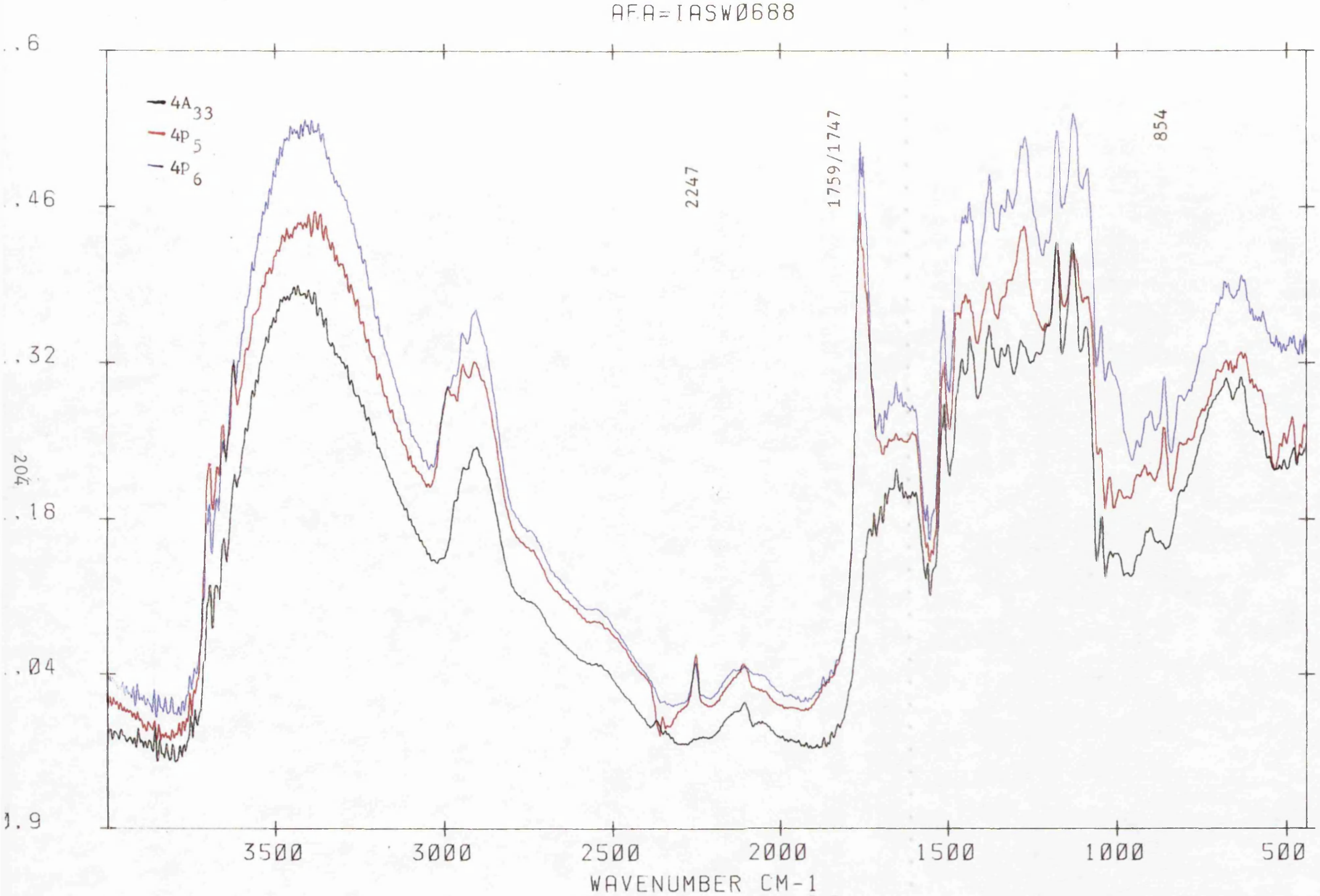
1.52
1.28
1.04
0.8
9A39
9P1
9P3
9P5
2247
1747/1759
1340
1280
854
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.4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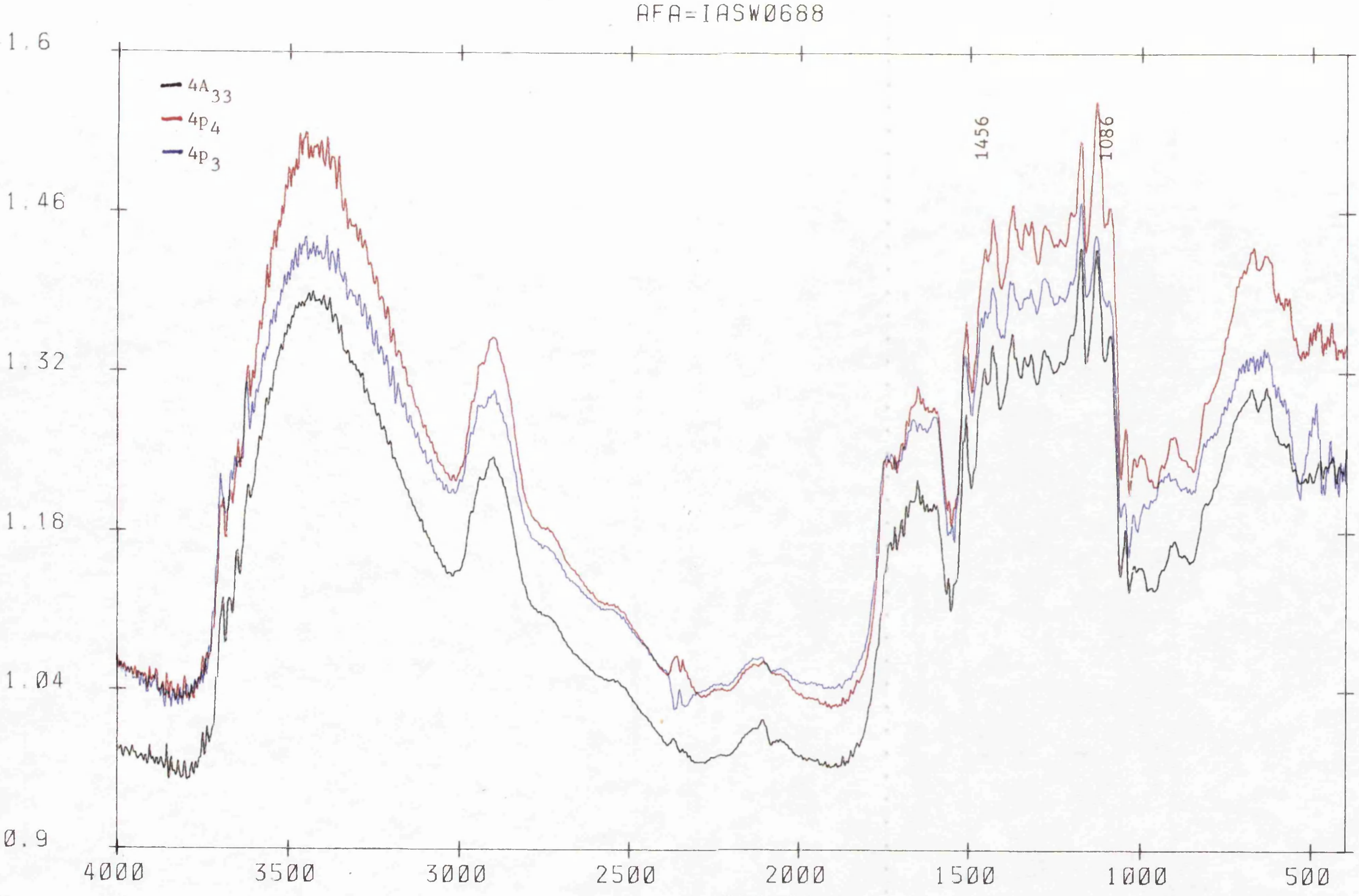
4P5
4P6
2247
1759/1747
854
.6
.46
.32
.18
.04
.9
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.5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4p4
4p3
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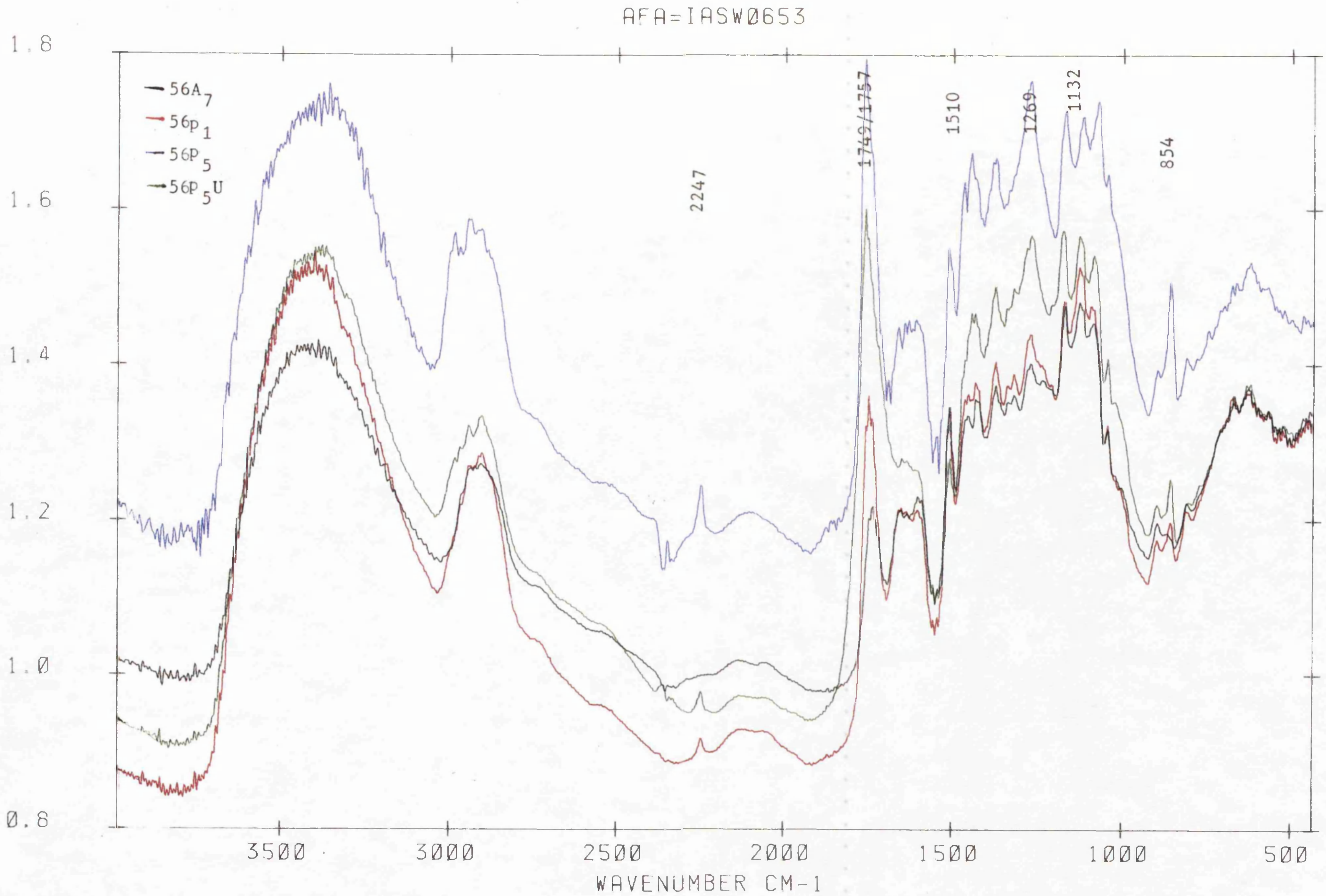
1086
1.6
1.46
1.32
1.18
1.04
0.9
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.6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56p1
56P5
56P5U
2247
1749/1757
1510
1269
1132
854
1.8
1.6
1.4
1.2
1.0
0.8
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.7

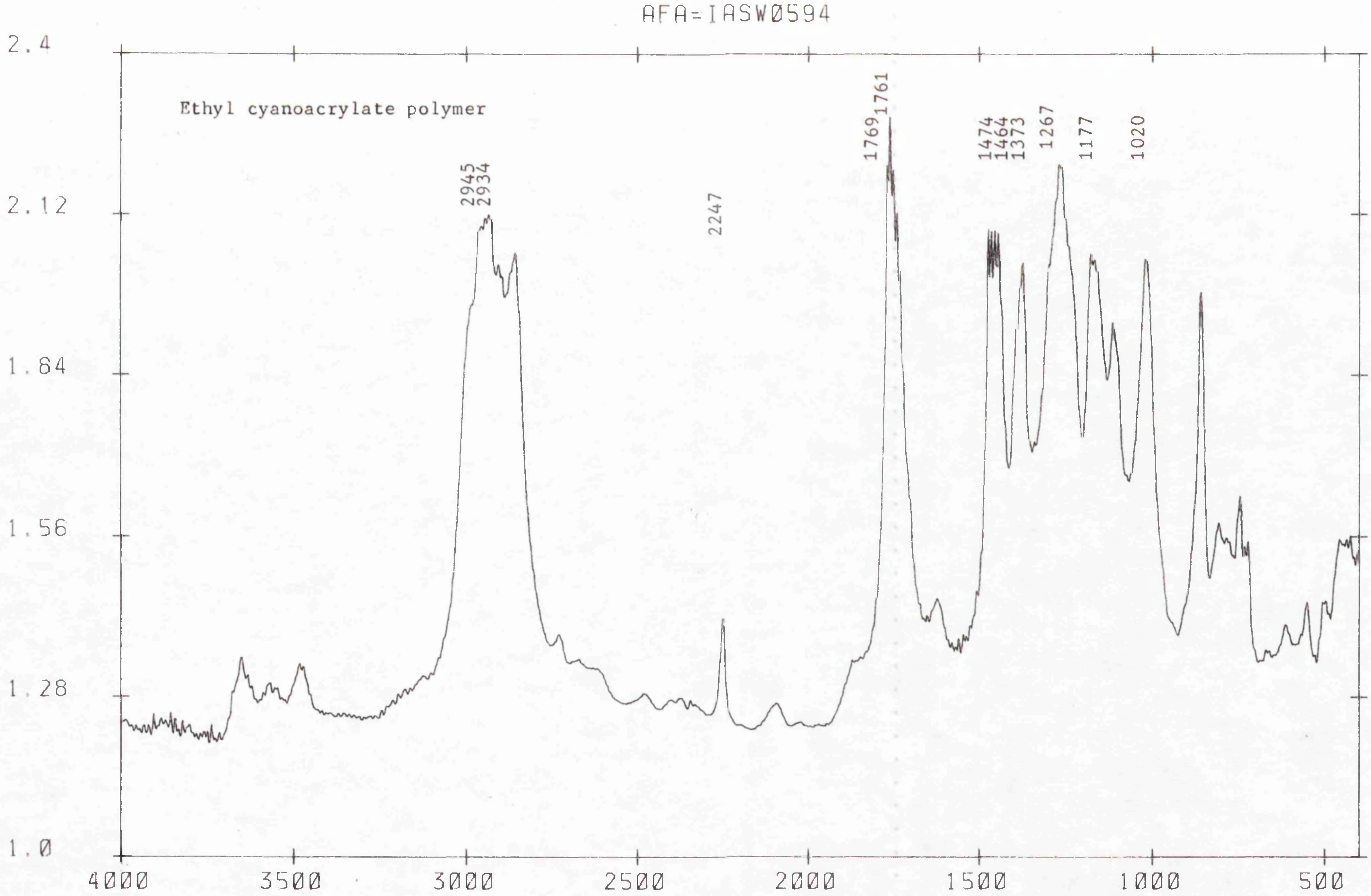

AFA=IASW0594
Ethyl cyanoacrylate polymer
2.4
2.12
1.84
1.56
1.28
1.0
2945
2934
2247
1769
1761
1474
1464
1373
1267
1177
1020
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER CM-1

Figure 5.8

Chapter 6

DISCUSSION AND CONCLUSIONS

This thesis pertains to the chemical deterioration and conservation of paper. These two interrelated subjects have been described in three chapters, together with experimental results. Two new inventions and one modification of an existing technique are the highlights, and it was possible to achieve conclusions in four aspects of this project. These are:

- a. paper deterioration
- b. FTIR as an analytical technique in paper analysis
- c. stabilization of paper
- d. strengthening of paper

6.1 Paper deterioration

Papers found in archives and libraries have been subjected to deterioration, and hence for experimental purposes it is rather difficult to find a sample that has not at least partially deteriorated. Even modern papers, eg. newsprint one week old, are in the process of deterioration. Whatman No.1, which consists of high α-cellulose was taken as the reference material, as pure cellulose does not undergo changes easily and it is accepted that Whatman is one of the most pure and stable papers which exist at present.

When artificial ageing was carried out in order to understand the deterioration process, it was apparent that deterioration varies in different types of paper, i.e., papers comprising pure cellulose and papers containing lignin (mechanical wood papers). It was very clear that papers containing pure cellulose, i.e. Whatman No.1, did not undergo visible change. However they showed some chemical changes with a longer period of deterioration due to photochemical degradation, which is principally oxidation. This indicates that cellulose undergoes photochemical changes in the presence of light, and as a result, almost all papers will produce uronic acid, as each and every paper contains cellulose, although its quantity varies in different types of paper.

Mechanical wood papers which contain hemicellulose and lignin in addition to cellulose, have a tendency to get discoloured in the presence of light. It is reported that discolouration occurs due to the formation of quinonone as a result of lignin degradation (Tschirner and Dence, 1988). The experimental observations indicated that the predominant changes occur due to light and fadeometer ageing and also the changes occur only in the IR peaks assigned for lignin. Hence, it is quite clear that the discolouration and changes which occur are due to lignin, although hemicellulose is also present in these papers. There is no possibility of forming a colour change due to hemicellulose, as it cannot form a radical or chromophoric group which could impart colouration. A likely reaction for deterioration of lignin due to light (visible and U.V.) is given in Figure 6.1.

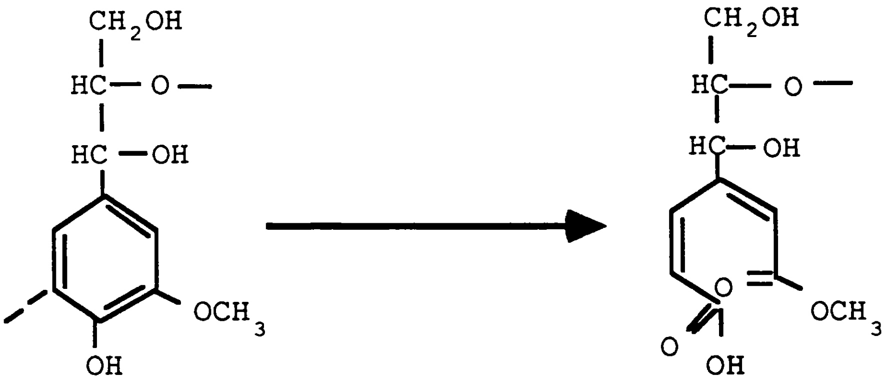


FIGURE 6.1: A possible reaction for the deterioration of lignin due to light

Old mechanical wood papers showed similar changes to modern mechanical wood papers except for the rate of deterioration. Paper artificially aged over a long period of time showed similar changes on both fadeometer and sunlight ageing. Thus it is probable that normal daylight and fadeometer exposure leads to the same product at the end although fadeometer exposure enhances the reaction.

Deterioration may occur not only with the major components of paper, but additives such as sizes, loadings, fillers and coatings also contribute to it. It is known that rosin-sized papers accelerate deterioration due to the addition of alum as a mordant in the process, as it increases the acidity which is a major cause of deterioration. From the results of the present work, it is clear that acidity can also arise due to the degradation of lignin in mechanical wood papers. Hence the major contribution to acidity in mechanical wood papers is the acidic by-products produced in lignin degradation, and not the sulphuric acid formed as a result of the addition of alum or of exposure to atmospheric sulphur dioxide.

In the literature, only Browning (1977) has mentioned insoluble and soluble acids. It was found that each and every aged paper, unless it was buffered, contains soluble and insoluble acids, and the insoluble acid content was always less compared with the soluble acid. Hence, measuring surface pH does not help in assessing the acid content other than approximately. Thus, aqueous deacidification processes will not be able to remove or neutralise all of the acid in paper unless the deacidification agent makes a complex or a stable salt.

6.2 FTIR as an analytical technique in paper analysis

The technique of FTIR spectroscopy had not been investigated in depth previously in relation to paper , although Hon (1986) identified it as a promising approach. An attempt was made to identify changes in the deterioration of different paper samples, of different origins, belonging to different periods. FTIR spectroscopy was found to be useful in studying different chemical changes including deterioration in mechanical wood papers, although it could not easily detect the deterioration of other papers. It has certain drawbacks, such as the failure to identify minute changes and the inability to recognise changes caused by some chemical reactions. However, some of the additions and changes were recognised as described in this study.

6.2.1 Interpretation of spectra

At the initial stage, it was tempting to assume that two paper samples were identical because they gave very similar spectra. Obtaining similar types of spectra from two samples of different physical appearance leads to two possible assumptions. Either these two samples are chemically identical, or FTIR is not capable of identifying all the differences. Since a softwood sample and a mechanical wood paper sample gave similar spectra (Figure 6.2), the latter assumption appears to be the more valid. It is stated that even a slight difference in spectra, i.e. intensity, shape and even small shoulders are significant (Hergert, 1971). It was difficult to evaluate all the chemical treatments carried out in this study as they were limited in addition by the inhomogenity and varying degrees of deterioration within the same sample, which lead to two different spectra although both were from the same sample, and the inability to detect minute changes occurring using FTIR.

While interpreting the spectra correct assignment of the peaks is very important. The literature cites different assignments for the same peak, and hence the author has attempted to identify the appropriate assignment from the published literature, using the experimental results to resolve choices where these occur.

6.2.2 Peak assignment

Detailed IR peak assignments are given in Appendix 2, and the more important functional group assignments are discussed below.

6.2.2.1 *Hydroxyl groups*

Three types of hydroxyl groups exist in paper samples, aliphatic OH, aromatic OH and hydroxyl in water. Hydroxyl absorption lies mainly between 3700 - 3000 cm^{-1} in the FTIR spectrum. The aliphatic OH peaks have been assigned mainly to the above region, although they absorb at 660, 1340 and 1088/1092 cm^{-1} in addition to the 3700- 3000 cm^{-1} band. Aromatic OH lies at a longer wavelength than aliphatic (Hergert, 1971), although the peak at 1205 cm^{-1} is a contribution of both types. The author has identified the peak at at 1510 cm^{-1} as being contributed by phenolic OH groups as described in Chapter 3.

6.2.2.2 *Carboxylic acid groups*:

It is known that aromatic and aliphatic carboxyl groups lie about 45 cm^{-1} apart, and that the aromatic carboxylic acid frequency lies at a longer wavelength than the aliphatic hydroxyl group. In spectra of paper samples, the peak due to the carboxylic acid group is not easy to detect under normal circumstances. From the observations made during this work, it is certain that the aliphatic carboxyl group lies at 1720/1724 cm^{-1}. In the case of mechanical wood papers, it is not possible to identify the aliphatic carboxylic acid group, as the carbonyl group in esters also lies in the same region, and thus it would mask the carboxylic acid peak if present.

It is reported that the aromatic COOH group lies in the 1695 - 1665 cm^{-1} region, and hence the peak at 1680 cm^{-1} which was visible only in lignin-containing papers must be due to C=O in aromatic acids. Since this peak was present even in modern newsprint, the author concludes that in the process of making paper, lignin had been subjected to certain changes (even in the mechanical pulping process) to give a compound that contains carboxylic acid groups, and which increases in quantity with ageing.

6.2.2.3 *Ester group*

The C=O in the ester group lies between 1724-1770 cm^{-1}. The peak at 1735 cm^{-1} has been assigned to the ester group. Since with aqueous sodium borohydride this particular group was reduced, it must be due to C=O in unconjugated ketones and aldehydes (Hergert, 1971). Surprisingly, with aqueous sodium hydroxide this peak also disappeared. Hence this particular group must have hydrolysed during alkaline treatment, and thus the group might be C=O in esters formed with an aromatic acid. Since aqueous sodium borohydride reduced this peak, it cannot be due to C=O in aliphatic carboxyl or aryl or $\alpha-\beta$ unsaturated esters, as it is stated (Hergert, 1971) that C=O in such esters is non-reducible by aqueous sodium borohydride.

The carbonyl stretch frequency in the ester group can vary due to aromatic or aliphatic character, and conjugation, such as in the vinyl non-aromatic group. The C=O stretch in unconjugated esters lies at around 1740 cm^{-1} (Pouchert, 1970), while in the conjugated aromatic esters the C=O stretch frequency lies between 1725 - 1659 cm^{-1}.

The phenolic esters have their carbonyl absorptions shifted to 1755 cm^{-1} (Hergert, 1971). With light ageing, it was observed that the peak at 1733 cm^{-1} increased and became

1747/1760 cm^{-1}, and hence the peak observed at lower frequency must be due to an ester group, which is probably aromatic.

It is stated that the C-O stretch peak of non-aromatic ethyl and higher esters is at 1030 cm^{-1}. From the present observations, no evidence could be found for this peak in the spectra.

6.2.2.4 *Carbonyl groups*:

Carbonyl group frequencies can arise due to esters, acids, ketones and aldehydes. In paper analysis, carbonyl groups are found mainly in ester groups and acid groups, which are important in deterioration and conservation studies. The group frequencies of carbonyl groups in esters and carboxylic acids have already been discussed in sections 6.2.2.2 and 6.2.2.3.

6.2.2.5 *Methyl and methylene groups*:

Aliphatic C-H, CH_2 and CH_3 stretching and bending frequencies have been assigned to the regions between 2940 - 2840 cm^{-1}, 1470-1460 cm^{-1} and 1370-1365 cm^{-1} (Hergert, 1971). The peaks reported in the present work at 2966 cm^{-1}, 2945 cm^{-1}, 2902 cm^{-1}, 1433 cm^{-1}, 1355 cm^{-1}, 1319 cm^{-1}, 1278 cm^{-1} and 720 cm^{-1} are due to C-H stretching, deformation and rocking in CH_2 and CH_3 groups in cellulose, and the peaks at 856 cm^{-1}, 1454 cm^{-1}, 2960 cm^{-1} are due to C-H stretching, bending and deformation in lignin, while the shoulder at 2860 cm^{-1} and the peak at 1373 cm^{-1} are due to C-H stretching, deformation and vibration of both cellulose and lignin.

6.2.2.6 *Ethylinic double bond*

The ethylinic double bond is normally only available in mechanical wood papers, as lignin contains an α, β double bond conjugated with an aromatic ring. The C=C stretching vibration of aromatic conjugated *trans* double bonds occur in the range of 1626 - 1608 cm^{-1} and the C-H out of plane deformation appears at 990 - 960 cm^{-1} (Hergert, 1960; 1971). On spectroscopic analysis of the experimented samples, no peak was observed in the region of 990 - 960 cm^{-1}. The peak observed at 1606 cm^{-1} in lignin samples may be due either to a C=C stretch, or to the C=O stretch in the carboxylate group which lies in the region of 1550 cm^{-1} and which has been shifted due to other structural changes, or to the aromatic skeletal peak which lies in the region 1605 -1595 cm^{-1} (Pearl, 1959) . On artificial ageing the peak at 1606 cm^{-1} increases, and hence it might be due to a carboxylate group in lignin compounds, which might arise as a result of degradation. If the peak is due to the ethylinic group, it is difficult to rationalise its increase in ageing. The peak in the region of 1605 - 1595 cm^{-1}, which has been allocated to skeletal vibration, may be strongly associated with aromatic C-O stretching according to Pearl (1959). Taking that fact into consideration, the intensity increase in the 1606 cm^{-1} peak on ageing could be explained as the aromatic C-O present in esters formed with aromatic acids in lignin degradation, which increases at a rapid rate in the process of degradation.

6.2.2.7 *Aromatic skeletal peaks*

The aromatic C=C absorption peak appears at 1605 - 1595 cm^{-1}, 1515 - 1505 cm^{-1} and 1450 - 1420 cm^{-1} (Sarkanen, Chang and Ericsson, 1967; Sundholm, 1968). From the experimental results it was observed that with aqueous sodium borohydride and sodium hydroxide the peak at 1510 cm^{-1} completely or partially disappeared, and on washing it reappeared, and hence the peak at 1510 cm^{-1} is not entirely due to the aromatic C=C group. It might be due to the aromatic C=C and phenolic hydroxyl group, because hydrogen in phenolic hydroxyl group could have been substituted by sodium in the treatment, and was regenerated on washing. The intensity of the peak at 1606 cm^{-1} increased very slightly, while that of the peak at 1757 cm^{-1} increased greatly. As mentioned in section 6.2.2.6, it is possible that the peak at 1606 cm^{-1} is due to aromatic skeletal vibrations, and it must have been associated with aromatic C-O stretching as it is stated that the peak at 1605 -1595 cm^{-1} may be strongly associated with the aromatic C-O stretching mode (Pearl, 1959).

It was not possible to confirm the identity of a peak at 1450 - 1420 cm^{-1} stated to be due to aromatic skeletal vibrations.

6.2.3 Substance identification and their deterioration

Papers mainly consist of cellulose, hemicellulose and in mechanical wood papers, lignin. In addition to these three major components sizing agents, additives and fillers are present in papers, although they vary from one another at some point.

6.2.3.1 *Cellulose*

Although many functional groups in cellulose have been identified by the appearance of peaks in spectra, these peaks are being contributed by other substances or other groups of the same substance, in the case of some of the peaks. The variation in relative intensity of certain peaks representing cellulose in different papers was an encouragement, although this change may be due to hydration of the paper.

However, the degradation of cellulose should manifest itself in the spectrum in the form of new peaks and modifications to existing peaks. The changes observed were very slight except for the appearance of free carboxylic acid groups in the spectrum of the sample aged in the fadeometer for 3 months. It is difficult to estimate the extent of deterioration of the cellulose molecule except in the case of the appearance of the peak at 1724 cm^{-1}, which is due to the formation of uronic acid and other acidic products.

6.2.3.2 *Lignin*:

Peaks at 1733 cm^{-1}, 1680 cm^{-1}, 1606 cm^{-1} and 1510 cm^{-1} have been observed in mechanical wood papers. The most characteristic peak is at 1510 cm^{-1}, which is relatively strong. This was found to decrease in intensity in samples subjected to optical degradation such as fadeometer ageing and daylight ageing. It also disappeared with aqueous sodium borohydride and sodium hydroxide treatments, and reappeared on washing. It was observed that the relative intensity of the peak at 1733 cm^{-1} increased and shifted to 1747 cm^{-1}, with a decrease in relative intensity of the peak at 1510 cm^{-1}, on ageing.

6.2.3.3 *Sizes*

Gelatin

Gelatin which is a protein, belongs to the category of non-cyclic secondary amides. It indicated weak peaks at 1541 cm^{-1} and 1552 cm^{-1} and an intensity increase of the peak at 1639 cm^{-1} which shifted to 1649 cm^{-1} in spectra of gelatin-treated samples. It is stated that there are peaks in the region of 1680-1630 cm^{-1} due to C-O absorption and in the region of 1570-1515 cm^{-1} due to NH_2 deformation of secondary non-cyclic amides (Bellamy, 1975). Hence with FTIR, papers containing gelatin could be identified if they had a certain minimum concentration (about 2% or more).

Rosin

With the treated papers, it was difficult to identify the peaks due to rosin.

6.2.3.4 *Buffering agents*:

$CaCO_3$

A strong peak at 1430 cm^{-1} and a medium peak at 874 cm^{-1} have been assigned for calcium carbonate in the literature (Browning, 1977). A weak peak or a shoulder at 874 cm^{-1} was observed in spectra of calcium carbonate treated samples, although there was no change in the peak at 1430 cm^{-1}, as it might have been masked by the peak which already exists at 1433 cm^{-1} which is due to C-H deformation of CH_2 groups in cellulose. If there is a reasonable amount of calcium carbonate; i.e. about 2% or more, FTIR can detect it. The identification of calcium carbonate in mechanical wood papers may be confused, as the mechanical wood papers contain a peak due to glucomannan at the same frequency.

Barium carbonate

The presence of barium carbonate was identified by the presence of a peak at 860 cm^{-1} and a shape difference of the region at 1650-1600 cm^{-1}.

Magnesium hydroxide

Magnesium hydroxide treated samples indicated a strong peak at 3700 cm^{-1}, which could be assigned to free hydroxyl groups, and since this peak is very sharp it might also be due to the hydroxyl group in magnesium hydroxide. It is stated that the O-H stretching frequency of magnesium hydroxide lies at 3698 cm^{-1} (Nakamoto, 1970). Hence, it is possible to identify the presence of magnesium hydroxide in papers using FTIR.

Sulphate ions

Sulphate ions absorb at 1130-1080 cm^{-1} (s) and 680-610 cm^{-1} (w) (Bellamy, 1968). Sulphate ions may be available in papers as a result of the pulping process, the addition of alum, and/or the formation of sulphuric acid due to atmospheric pollution.

Whatman paper treated with the dilute sulphuric acid showed an increase of the peak at 636 cm^{-1}, although there was no appearance of a new peak in the region of 1130-1080 cm^{-1} or an increase of the peak at 1092 cm^{-1} which is available in all cellulose papers.

Carboxylate ions

Carboxylate ions could be detected with difficulty by the presence of very weak peaks or shoulders at 1402 cm^{-1} and at 1550 cm^{-1}, as the peaks at 1400 cm^{-1} and 1550 cm^{-1} have been allocated for the symmetric and assymetric carboxylate ions respectively (Bellamy, 1975).

6.2.3.5 *Type of the paper*

From the observations it was observed that FTIR can be used to distinguish pure cellulose papers and mechanical wood papers, although it was difficult to identify the manufacturing process.

The other characteristic feature observed was that the difference in FTIR spectra of soft wood and hard wood due to the appearance of the peak at 820 cm^{-1} in the spectra of samples containing soft wood.

Hence, the author concludes that FTIR is useful in identifying mechanical wood papers and papers made out of soft-wood fibres.

6.2.3.6 *pH / acidity measurements*

The appearance of the peaks at 1724 cm^{-1} and 1680 cm^{-1} indicates the acidity of paper as described in this study. Also, quantitative measurements of FTIR spectra in the region of the hydroxyl groups indicate a trend in relation to the surface pH of the particular sample.

The author concludes that FTIR is a useful technique in determining the acidity of paper. Hence there is a possibility of discovering more, in a deeper study of this particular region, which could not undertake by the author because of the limited time and scope of the project.

6.2.4 Conclusions

FTIR is not a very sensitive method for determining the extent of degradation of paper, except in mechanical wood papers, but it is a powerful tool for the identification of the type of paper from a chemical standpoint, and also, it is almost non-destructive. FTIR can detect the presence of mechanical wood, along with the lignin degradation products, sizes, buffering agents, polymers and organic acids. The quantitative measurements also help in identifying the chemical reactions and the extent of the deterioration within certain limits.

6.3 Stabilizing paper

In respect of stabilizing paper, two aspects were considered in this project, namely deacidification and, in case of the mechanical wood papers, the capping of lignin.

6.3.1 Deacidification

The existing deacidification techniques at present can be categorised into aqueous, non aqueous and vapour phase processes. Aqueous treatments can remove all water-soluble acids, although the difficulties in disbinding and impossibility of deacidifying fragile documents arise in the process. Non aqueous techniques have advantages over the aqueous treatments, as in not being necessary to disbind the material, and easier use for more fragile materials. Vapour phase treatments are the best of all, as they possess the qualities mentioned for non aqueous techniques, and in addition they can overcome some of the drawbacks, such as fading of ink, and other adverse effects which result from non aqueous processes.

Out of the existing processes, the well known vapour phase methods are diethyl zinc, ammonia and morpholine. Due to dissociation, ammonium salts do not last long in the paper to neutralise the regenerated acids and also ammonia does not give any buffering action. Diethyl zinc is known to be a hazardous substance and also it is suggested that zinc salts help in accelerating deterioration (Whitmore and Bogaard, 1989). Morpholine is also identified as a health hazard, and it is not much more effective than ammonia in its action.

Among non-aqueous treatments, Wei' To i.e. methyl magnesium carbonate in trifluoro-trichloro ethane is one of the processes long established and which is still in practice.

When the author was exploring the possible compounds and new ideas, the possibility of using a colloidal suspension of magnesium hydroxide in IMS came into focus. Being a basic compound it could neutralise the acid, and it was also capable of forming a buffer; i.e. magnesium carbonate on exposure to carbon dioxide in the atmosphere. Moreover, this process can be applied to bound as well as unbound materials by spraying.

From the experimental observations, it was very clear that the treatment could increase the pH and it did not pertain only to the treated side, because some magnesium compounds migrated through the fibres, thus it could increase the pH on the reverse side also. Since this process can be applied by spraying, it can be used in deacidifying bound materials as well as fragile documents, in addition to the unbound and strong materials. Also, it was observed that although the pH lowers with artificial ageing, treated samples were always giving higher pH values to those of untreated. Thus it proves that this treatment is stable to a certain extent, even on ageing.

FTIR analysis indicated a sharp peak at 3700 cm^{-1}, which is due to the hydroxyl group from magnesium hydroxide (as it is sharp), in addition to the broad hydroxyl peak observed in cellulose. The detection of the presence of magnesium on the reverse side six months after the treatment, which was not present immediately after the treatment, indicated that the substance which migrates slowly with time is the magnesium compound, not the acid. Hence this modified process satisfies the necessary requirements such as neutralisation. From a chemical standpoint, magnesium hydroxide should form magnesium carbonate with the atmospheric carbon dioxide on storage, although there was no indication of forming magnesium carbonate over the period during which analysis were carried out. The time period for which the samples were exposed might not have been either long enough to form magnesium carbonate, or the amount of magnesium carbonate formed was minute. Hence the FTIR or SEM analysis could not detect it.

It should be stated that although the author started this process thinking that this method of using the colloidal suspension technique was new, later on it was discovered that Kopper had also tried the same process, mainly dipping the paper or book in the suspension, in 1986. He initiated it as a commercial process and it is stated that this was terminated, but no reason was given. The author recommends the process as it has the advantages of being able to be used on bound materials, and is simple to use and of very low toxicity.

6.3.2 Capping lignin

In the process of degradation, oxidation of lignin was observed. The active functional groups which are subject to oxidation must be blocked to retard or resist oxidation, in order to prevent degradation.

As mentioned earlier, vapour phase treatments are preferred in the conservation of archival and library materials, as they do not cause damage resulting from wetting.

6.3.2.1 *Formaldehyde treatment*

Formaldehyde forms a resin with phenols, and hence the author thought it possible that the phenolic group in lignin might react with formaldehyde and produce a stable resinous compound.

The experimental observations revealed that although under some conditions a compound formed due to the formaldehyde treatment, it tends to destabilize with heat and light. Moreover, the treated samples were usually acidic. Under some conditions, no change was observed. Further more, the treatment did not prevent the yellowing of paper on light exposure under any conditions. Thus, formaldehyde alone does not have a significant effect on the stabilization of paper.

6.3.2.2 *Formaldehyde and ammonia treatment*

In the presence of ammonia, the formaldehyde treatment indicated limited stabilization on treatment at 35°C for 3 days, as it showed a decrease in intensity of the peak at 1510 cm^{-1} and the disappearance of the peak at 1733 cm^{-1}, which indicated a reaction of the formaldehyde and ammonia with phenolic hydroxyl groups and removal of the oxidisable groups which give ester groups in ageing.

This treatment showed at least a partial stabilization, and no tendency to make the paper acidic. Yet because of the colour change taking place in paper due to the treatment it is not possible to reccomend this technique for stabilizing paper in the form of books and documents.

6.3.3.3 *Ethylene oxide treatment*

Ethylene oxide reacts with lignin at 70°C according to Nikitin and Rudneva (1935) and hence the treatment was carried out at 70°C in addition to room temperature. Papers containing lignin showed an increase in pH with the length of the reaction. Hence, it proves that this treatment can deacidify some papers containing lignin, as the aromatic acids can react with the ethylene oxide and form esters (Malinovoskii, 1965). From DSC results, it was indicated that ethylene oxide can stabilize lignin to a smaller extent, although FTIR results did not show any indication as such. The author concludes that the longer exposure at room temperature and about 7 hours at 70°C are equally effective in the process of stabilization of lignin, although it is only a partial solution to the problem.

6.3.3.4 *Diazomethane treatment*

Diazomethane can react with phenolic OH and carboxylic acids to give methylated products. Hence the diazomethane treatment was evaluated for stabilizing paper.

Due to the disappearance of the free carboxylic acids with the treatment, as indicated by increase of the surface pH and the FTIR results, the diazomethane treatment can deacidify the paper in respect of organic acids, which is not specific only to mechanical wood papers.

From the FTIR observations it was observed that changes occurred to some of the peaks responsible for hydroxyl vibrations due to chemical changes, and also from the light reflectance measurements it was obvious that the discolouration of paper in ageing was reduced.

Hence, the diazomethane treatment stabilizes paper at least partially, in addition to the deacidification of paper, and it seems to be a viable process for the treatment of archival materials in conservation.

6.4 Strengthening of paper

Monomer treatments were considered for strengthening paper, as these have already shown some success in the field of conservation. Out of these, graft copolymerisation is one of the most modern developments in paper conservation, and it contributes effectively towards the strengthening of paper.

6.4.1 Trimethoxymethyl silane treatment

Trimethoxymethyl silane hydrolyses and forms a polymer film on the surface, which should also help in resisting further damage. Hence experiments were carried out with trimethoxymethyl silane and it was discovered that it is not compatible with materials like paper, as it forms a hard thin film which is highly resistant to water. It also makes the paper too stiff, which enables the paper to break easily. It was also observed that the treatment was not at all uniform, as it indicated two types of spectra in the same sample at two different locations.

Taking all these factors into consideration, the author concludes that there is no positive evidence in favour of trimethoxymethyl silane treatment in the strengthening paper, although it is stated that the silane treatments can be applied to materials such as cellulose and wood. Thus trimethoxymethyl silane cannot strengthen paper; rather it makes the paper more brittle on many occasions.

6.4.2 Cyanoacrylate treatment

Another attempt in strengthening paper was made with a cyanoacrylate monomer which can polymerise easily.

The cyanoacrylate polymer deposition on the paper was observed with the weight gain and FTIR observations. Since the polymer deposition was not visible on the surface with SEM photographs it is clear that the polymer absorbs into the fibre, which prevents many problems such as water repellency, transparency and the colour changes. It was also noticeable that the decrease in surface pH had not occurred, unless the papers were likely to have been buffered.

Mechanical testing, i.e. tensile strength and folding endurance measurements, indicated that the papers, mainly ground wood papers which are not highly deteriorated, became stronger with this treatment.

This treatment can be carried out at room temperature in the presence of daylight using ethyl cyanoacrylate monomer. Unfortunately this treatment acts in different ways on different types of paper such as Whatman, old and modern newsprints.

Although this treatment can deposit the polymer onto paper, it is not being grafted and hence the treatment is reversible. Nevertheless, it can be concluded that cyanoacrylate treatment strengthens paper, and it is feasible in its application to conservation work.

6.5 Future prospects for research

The results observed in stabilizing and strengthening paper indicated possible directions for carrying out further research.

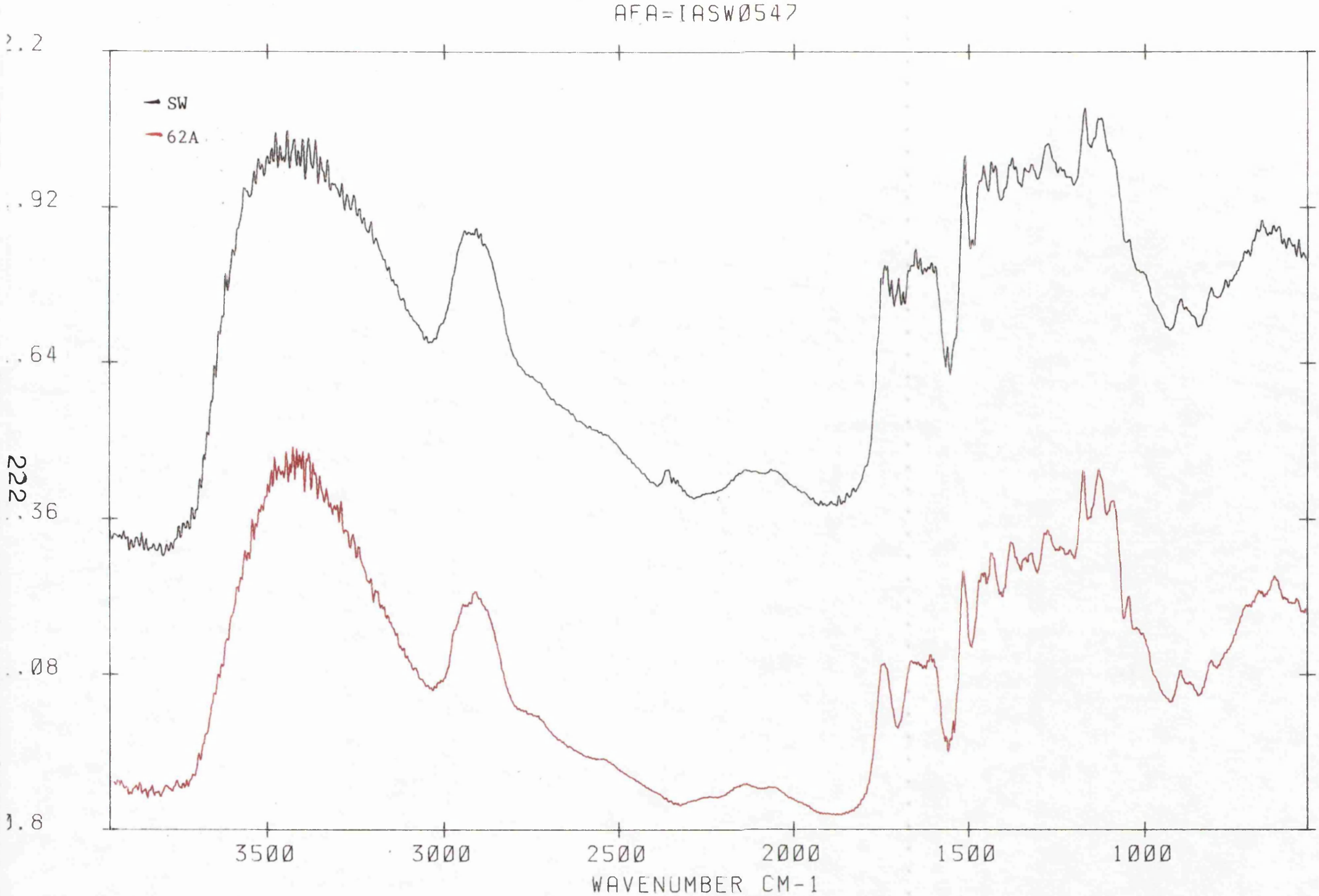
It was realised that ethylene oxide can manifest partial stabilization, with the limited experiments carried out under very few specific conditions. There are possibilities in exploring the reaction and the process further using DSC and other analytical techniques, trying out different temperatures and time periods to check whether there are better methods of employing ethylene oxide as a stabilizing agent for paper.

Among all the treatments carried out, the diazomethane treatment indicated the best possibilities from a chemical point of view, as it is already apparent that chemical changes take place towards stabilization as it deacidifies cellulose papers, chemically treated wood papers and mechanical wood papers in addition to the methylation of active functional groups in lignin to some extent.

Since the author carried out this set of experiments at the last stage of the work, it was not possible to carry out different options such as variation of time, pre-treatments and changing the amount of reagent reaching the paper. It is very likely that if one could carry on further research, there might be a possibility of operating a mass treatment process using diazomethane for stabilizing books and newspapers.

It was known that the cyanoacrylate treatment acted variably on different type of papers. It may be possible to identify the reasons for the variation of changes in paper due to the cyanoacrylate treatment, by further experiments. This treatment could also be adapted on a mass scale in order to strengthen paper. It is a possibility that one can make paper samples with known quantities of each component and vary one component at a time, and carry out the cyanoacrylate treatment under ideal conditions. Thus it may help in identifying the pattern of absorption and the material/s responsible for the rate of the reaction.

It is even possible that a combination of the above techniques, perhaps with others as yet untried, might lead to a satisfactory process for stabilizing and deacidifying mechanical wood papers.


AFA=IASW0547
SW
62A
.2
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.36
.08
.8
3500
3000
2500
2000
1500
1000
WAVENUMBER CM-1

FIGURE 6.2

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APPENDIX 1: List of samples

S. No.	Year	Name(B/N/M)	Origin	Traits			Cond	Other Com.
				G.W	Col.	Cal.		
1	1796	Elements of Chemistry (B)	E.	-	o.w.		n.g	rag paper,ge. sized, h.m.
2	1845	Arc. or Mis. tr. r.to Antiquity Vol. XXX1 (B)	E	-	o.w		g	rag paper
3	1899	Arc. or Mis. tr. r.to Antiquity Vol. LV1 (p.B)	E	-	o.w	-, co.	g	rag paper, m.m.
4	1910	The Aero Vol. 11 (J)	E	g.w	y.	-	v.b	mixed fib.
5	1924	Economics of Iron and Steel, 2nd ed. (B)	E	-	l.y.		g	mixed fib.
6	1930	The Manufacture of Steel Sheets (B)	E	-	o.w		g	mixed fib. m.m.
7	1933	Modern Steel Work (B)	E	-	l.y		g	mixed fib.
8	1938	A practical guide on Basic Open- Hearth Melting Practice (B)	E	-	l.y.	-, co	g	mixed fib. m.m.
9	1987	Whatman filter paper no.1	U.K	-	p.w.		g	rag fibre
10	1605 (m)	- (B)	E	-	y.	-	n.g	rag fibre. ge. sized, h.m.
11	19th C (m)	- (B)	E	-	o.w.	- co	n.g	mixed fib. (bl.)
12	1892 (m)		E	-	bl.		g	rag fib., highly sized with ge.
13	18th C (m)	- (sh.)	E	-	l.y.		b	rag fib., ge. sized, h.m.
14	1980	Sent from Coventry (B)	E	-	w		g	
15		The Lodger (B)	E	g.w.	y		n.g	S.W pres.
16	4/1987	Daily Telegraph (N)	U.K.	g.w	o.w.		g	

S. No.	Year	Name (B/N/M)	Origin	Traits			Cond.	Other Com
				G.W	Col.	Cal.		
17	1964	Richer the Dust (B)	E	g.w	br.		b	mixed fib., S.W. pre., m.m.
18	A1	Silver safe 40	U.K.	-	w.v.g.		no S	
18	A2	Silver safe 120	U.K.		w.		v.g	no S
19	1915	Letter to Fort St. George Vol. 25 (M)	India ?	-	y.		v.b	insect damage
20	1987	Whatman Chromato. grade 1	U.K.	-	p.w.		v.g	rag fib.
21	1924	Ceylon Annual General Report for 1923	E.		l.br.		b.	m.m.
22	1925	Circular; Colo. Sec. Office	E	-	br.		v.b	m.m.
23	1890	The Household Register	E.		d.br.		v.b.	m.m,laminated, paper is been crumpled.
24	1914	The Colonial Journal (J)	E.	-	y.		b.	insect damage m.m.
25	1921	Circular, Colo. Sec. Office	E.	-	l.br.		b.	brown patches m.m.
26	1957	Parliament of Ceylon	S.L	g.w.	d.br.		v.b.	brown dots, S.W. pre., m.m.
27	1952	Ceylon Adm. Reports (B)	S.L.	-	l.y.		n.g.	
28	1947	Ann. est. for the year 1946-1947 (B)	E	g.w.	d.br.		v.b.	S.W. pre. m.m.
29	-	- (pl.sh.)	E	-	y.		b.	S.W. ind., bl.
30	1931	- (B)	E	-	y.		b.	repaired,inserting a tissue m.m.
31	1914	Report of the Board of Education 1912-1913 (B)	E	-	y.		b	foxing, m.m.
32	1930	- (wri. doc.)	E.	-	y.		v.b.	ink is faded m.m.

S.. No	Year	Name (B/N/M)	Origin	Traits			Cond	Other Com
				G.W	Col.	Cal.		
33	1918	- (wri. reg.)	E	-	br.		v.b.	brown & black patches, ink must have contributed to det. h.m.
34	1987	Halfsheets	S.L.	-	o.w.	-	g	m.m.
35	1987	Envelope paper	S.L.		br.		g	m.m.
36		Laminated tissue	J.		tr.		b.	removed from sample 23
37	19thC	Whatman	U.K	-	o.w.		n.g.	sized with ge.
38	-	- (sh.)		-	w		g	S.W. pre., ac. pre., bl., m.m.
39	-	- (sh.)		-	o.w.	cal.	n.g.	S.W. pre.,ac. pre., m.m.,bl. transparent
40	-	- (sh.)		-	o.w	cal.	n.g.	S.W. pre., ac. pre., bl., m.m.
41	-	- (sh)		-	o.w.	cal.	n.g.	S.W. pre., ac. pre., bl., m.m
42	-	Familiar Wild Flowers (B)	E		o.w.		n.b.	translucent
43	1986	Reparing tissue	E.		w.		g	
44	1986	Reparing tissue	E		p.w.		g	
45	1986	Reparing tissue	E		p.w.		g	
46	1983	Report sheet	E		p.w	- co.	g	printed in bl.
47	1983	Conservation sheet	E		w	- co.	g	printed in g.
48	1983	Index card	E		w	- co	g	printed in g.
49	5/1989	Sunday Times (N)	E	g.w.	w		g	m.m.
50	5/1988	The Guardian (N)	E	g.w.	w.		g	m.m.
51	5/1988	Sunday Telegraph (N)	E	g.w.	w		g	m.m.
52	5/1988	The Independent (N)	E	g.w.	w		g	m.m.
53	5/1988	Financial Times (N)	E	g.w.	br.		g	m.m.

S.. No	Year	Name (B/N/M)	Origin	Trait G.W	Col.	Cal.	Cond.	Other Com
54	1839	Memoirs of Charles Mathews (B)	E	-	o.w.		n.g.	m.m, mixed fib.
55	1900	The early anals of the English Bengal (B)	E	-	o.w.		g	m.m, mixed fib.
56	7/1988	The Times	E	g.w.	o.w.		g.	m.m.
57	7/1989	The Guardian (N)	E	g.w.	o.w.		g	m.m.
57A	1988	- (w. bo.)	S.L.		w		g	m.m
58	1988	- (w. ma.fo. sh.)	S.L.		w		g	m.m
59	1988	- (w. offset sh.)	S.L.		o.w.		g	m.m
60	1988	- (w. printing sh.)	S.L.		o.w.		g	m.m
61	1988	- (w. printing sh.)	S.L.		o.w.		g	m.m.
62	1/1989	The Times	E	g.w.	o.w.		g	m.m., S.w. pre.
63	1988	Whatman No.1(sh.)		-	p.w.		g	rag fib.
64	1970	- (B)			w.		g	m.m.
65	1880	- (paper)			bl		g	
66	1920	- (pri. B)			y	-, co	n.g.	m.m
67	1988	- (com. pri. mat.)	E		w		g	m.m., bad qu
68	1963	A Dictionary of Geography (B)			y			
69	1963	Corpus Reformatorum Vol. C (B)	E	-	o.w.			m.m, acid pre.
70	1988	Whatman No. 44	U.K.	-	p.w	-	g	high α cotton
71	1988	Whatman No 540	U.K.	-	p.w.	-	g	high α cotton
72	1988	Whatman No. 113	U.K.	-	p.w		g	bl. sulphite W.
73	1988	Whatman No. 114	U.k.	-	p.w		g	bl. sulphite W.
74	6/1910	Univ. of Birm. Engi. and Min. J. (M)	E		o.w	cal		m.m
75	6/1949	J.of the Min. and Met. Soc.; R.S.Mines, L. (M)	E		o.w			m.m

S. No.	Year	Name (B/N/M)	Origin	Traits			Cond.	Other Com
				G.W	Col.	Cal.		
76	3/1909	Univ. of Birm. Engi. J. Vol.V11 no.4 (M)	E		o.w.			m.m
77	1/1905	Univ. of Birm. Engi. J. Vol.111 no.3 (M)	E	-	o.w.			m.m
78	1920	Technology, The J.of the Manch. Muni. Coll. of Technology Vol. X (M)	E	-	o.w.			m.m
79	1937	The J. of the R. Tech. Coll. Vol.1V pt.1 (M)	E	-	o.w.			m.m
80	1966	North East Coast Inst. of Engi. & Shipbuild.; Transactions Vol. 82 pt.7 (M)	E	-	o.w			m.m
81	1848	Archaeologia	E	-	o.w.			m.m
82	1979	Telephone Directory (L. Area) (B)	E	g.w.	y			m.m
83	1984	Graduate Opportunities (B)	E	g.w.	o.w.			m.m, S.W.pre
84	1843	Asie Centrale; chains De Montagnes (B)	E	-	w.			F.m.m.
85	1809		E	-	o.w.			e.m.m, ge. sized
86	2/1989	Divayina (N)	S.L.	g.w.	o.w.		g	m.m
87	6/1989	The Guardian (N)	S.L.	g.w.	o.w.		g	m.m
88	2/1989	Sri Lankadeepa (N)	S.L.	g.w.	o.w.		g	m.m
89	3/1961	Daily Sketch (N)	E	g.w.	y		b	m.m, S.W.pre
90	8/1893	LLOYD'S weekly Newspaper (N)	E		br.		v.b.	m.m, S.W.
91	1873	J.of the Liver. polytec. Soc. (M)	E		o.w.			m.m
92		Japanese tissue	J		w		n.g.	exp. to acid atm.
93		Box board	E		br.		b	exp. to acid atm.
94		Box board	E		br.		b	exp. to acid atm.
95	4/1969	Bri. Arch. Abs. (J)	E		w			m.m.

S. No.	Year	Name (B/N/M)	Origin	Traits			Cond.	Other Com
				G.W	Col.	Cal.		
96	1989	Univ. of L. Reg. for M.A ...M.S (B)	E		w		g	m.m
97		Univ. of L. Reg. for M.A ... AT (B?	E		w		g	m.m
98	1961	Science Monitor (N)	U.S.A.		y			
99	1959	Toronto Globe & Mail (N)	Canada	g.w.	y			
100	1969	Daily Glance (N)	Jamaica	g.w.	l.br.			
101	1954	Daily Glance (N)	Jamaica	g.w.	y			S.W. pre.
102	1951		Canada (Vic. B.C.)	g.w.	l.br.			
103	1949	The West Indian Sportsman (monthly) (N)	Jamaica		y			
104	1897	Vanity Fair (N)	E	-	l.br.			
105	1953	Daily Mirror (N)	E	g.w	l.br.			S.W. pre.
106	1962	Vic., Bri. Colum. (N)	Canada	g.w.	l.br.			S.W. pre.
107	1955	The Weekly News (N)	New Z.	g.w.	l.br.			S.W. pre.
108	1953	The Daily Telegraph (N)	E	g.w.	l.br.			S.W. pre.

Arc. - Archaeological
bri - British

Colours

bl. - blue   br. -brown   d. - dark   l. - light   o.w. - off white   p.w. -pale white
w. - white   y. - yellow

Origin

E - Europian   New Z. - New Zealand   S.L. - Sri Lankan
U.K. - United Kingdom

Miscallaneous

atm. - atmosphere   B - book   cal. - calandered   co - coated
com. - computer   e - early   exp. - exposed   fib. - fibre
g.w. - groundwood   ge. - gelatin   h.m - hand made   J. - Journal
m. - manufacture   ma. fo. - manifold   mat. - material   m.m. - machine made
N. - newspaper   no. - number   pre. - present   pri. - printed
qua - quality   sh. - sheet   S.W. soft wood

Pulps

S.W. bleached sulphate (Lumini pine)
S.W. unbleached sulphite
S.W. unbleached sulphate
H.W. bleached sulphate (Eucalyptus)
H.W. bleached magnafite sulphite
H.W. sulphate (Botnia)
Cotton linters
Cotton linters, bleached
Flax
Mechanical pulp, unbleached refined
Chemi thermo mechanical pulp (TMP)

APPENDIX 2: List of treatments

Symbol/Number	Treatments
A	blank
B	washed with water
C	washed with water containing few drops of Synperonic N
D	washed with hot water
E	washed with calcium hydroxide
F	washed with calcium hydroxide and calcium bicarbonate
G	washed with barium hydroxide
H	fiber analysis
I	qualitative analysis, tests for starch, gelatin, rosin, protein and ground wood
J	qualitative analysis for casein.
K	treatment with 2% gelatin solution
L	sizing: treatment with rosin, Alum and washing
M	treatment with 2% sodium hydroxide solution
N	treatment with 4% Alum solution
O	treatment with 2% sodium hydroxide for 2 minutes and 4% Alum for 2 minutes
P	treatment with 2% sodium hydroxide for 2 minutes, 4% Alum for 2 minutes and washing
Q	bleaching with chlorene: used sodium hypochlorite solution
R	Graft co-polymerized
S	washed with 0.001N sulphuric acid
S_1	washed with 0.05% sulphuric acid for $^1/_2$ an hour.
T	washed with 0.05% sulphuric acid for $^1/_2$ an hour and rinsed with water
U	exposed in fadeometer
V	oven ageing
W	sized with parchment
X	rinsed with 5% sulphuric acid and oven aged at 60°C
Y	washed with dil. ammonia
Z	washed with dil. hydrochloric acid
a	treated with Schiff's reagent for checking aldehyde group
b	treated with 2,4 dinitrophenyl hydrazene for checking aldehyde and ketone groups and washed with alcohol to remove excess reagent
c	treated with sodium sulphate: c_1 - 1N, c_2 - .1N, c_3-.01N, c_4 - .001N
d	treated with 2% aluminium sulphate [$Al_2(SO_4)_3.16H_2O$]
e	treated with 2% aluminium chloride [$AlCl_3.6H_2O$]
f	treated with 2% magnesium hydroxide and IMS colloidal suspension
g	treated with ethylene oxide
h	exposed to daylight
i	exposed to formaldehyde vapour
j	treated with 100 vols. hydrogen peroxide for $^1/_2$ an hour
k	treated with chloramine T
l	treated with chloramine T and washed with 2% sodium sulphite
m	treated with deuterated water
n	exposed to formaldehyde and ammonia vapour
o	exposed to ozone
p	exposed to methyl cyanoacrylate monomer

Symbol/Number	**Treatments**
q	exposed to trimethoxymethyl silane monomer
Oz	exposed to ozone

Diazomethane treatment

/St/	blank
/DM/	diazomethane

Treatment No.

1 - exposed to diazomethane for 3 hours
2 - exposed to diazomethane in the presence of methanol for 3 hours

Cyanoacrylate monomer treatment

Sample No./ Monomer No./ Treatment No.

Monomer No.	
0	blank
1	RS cyanoacrylate adhesive stock no. 555-459
2	Anglo superstick 31
3	Anglo superstick 32
4	Anglo superstick 34
5	Loctite prism 401
6	Loctite prism 460
7	Eurecryl cyanacrylat 2460
8	Eurecryl cyanacrylat 2464
9	Permabond cyanoacrylate adhesive grade C1
10	Permabond cyanoacrylate adhesive grade C3

Treatment No.	
1	exposed to different monomers (1-10) for 5 days
2	exposed to monomer (1) for $3^1/_2$ days after exposing to ammonia vapour for 1 hour
3	exposed to monomer (7) vapour in the dark for 4 days
4	exposed to monomer (7) vapour in the daylight for 4 days
5	exposed to monomer (7) vapour in the daylight for $3^1/_2$ days
6	exposed to cyclohexayl amine for 30 minutes and then exposed to ethyl monomer (9) for $3^1/_2$ days
7	exposed to dilute ammonia for 30 minutes and then exposed to monomer (9) for $3^1/_2$ days
8	sprayed magnesium hydroxide and dried, then exposed to monomer (9) for $3^1/_2$ days
9	sprayed calcium hydroxide and dried, then exposed to monomer (9) for $3^1/_2$ days
/0/6	exposed to cyclohexayl amine for 30 minutes
/0/7	exposed to dilute ammonia (5%) for 30 minutes
/0/8	sprayed magnesium hydroxide and dried
/0/9	sprayed calcium hydroxide and dried
10	exposed to a mixture of ethyl and methyl monomers (1:1) for $3^1/_2$ days
11	exposed to a mixture of ethyl and methyl monomers (1:3) for $3^1/_2$ days
12	exposed to a mixture of ethyl and methyl monomers (3:1) for $3^1/_2$ days
13	exposed to ethyl monomer (9) for $3^1/_2$ days
14	exposed to ethyl monomer (9) for $3^1/_2$ days
15	exposed a book to ethyl monomer (9) for $3^1/_2$ days
16	exposed to ethyl monomer (9) for $3^1/_2$ days
17	exposed to ethyl monomer (9) for $3^1/_2$ days

Treatment No.	
18	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days
19	exposed to ethyl monomer (9) for 5 days
20	exposed to ethyl monomer (9) for 7 days
21	exposed to ethyl monomer (9) for 10 days
22	exposed to ethyl monomer (9) for 15 days
23	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days
24	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days
24-ext.	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and extracted in acetone for $2^{1}/_{2}$ hours
25	exposed to ethyl monomer (9) for 5 days
26	exposed to ethyl monomer (9) for 7 days
27	exposed to ethyl monomer (9) for 10 days
28	exposed to ethyl monomer (9) for 15 days
29	exposed to ethyl monomer (9) for 20 days
30	exposed to ethyl monomer (9) for 25 days
31	exposed to ethyl monomer (9) for 30 days
32	dried for 2 days and exposed to ethyl monomer (9) for $3^{1}/_{2}$ days, under dried condition
33	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days
33-amine	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and to hexayl amine for $^{1}/_{2}$ an hour
33-amine; ext.	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and to hexayl amine for $^{1}/_{2}$ an hour and extracted in acetone for $2^{1}/_{2}$ hours
33U	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and in the fadeometer for 1 hour
33U; ext.	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and in the fadeometer for 1 hour and extracted in acetone for $2^{1}/_{2}$ hours
33h	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and oven aged for 4 hours at 50°C
33h; ext.	exposed to ethyl monomer (9) for $3^{1}/_{2}$ days and oven aged for 4 hours at 50°C and extracted in acetone for $2^{1}/_{2}$ hours
/0/ext.	extracted in acetone for $2^{1}/_{2}$ hours
34	exposed to monomer (9) for $3^{1}/_{2}$ days at 40°C
35	exposed to monomer (9) for $3^{1}/_{2}$ days at room temperature (20°C)
36	exposed to monomer (9) for $3^{1}/_{2}$ days under moist condition
37	exposed to monomer (9) for $3^{1}/_{2}$ days at 80% RH
38	exposed to monomer (9) for $3^{1}/_{2}$ days at 50% RH
39	exposed to monomer (9) for 1 hour
40	exposed to monomer (9) for 3 hours
41	exposed to monomer (9) for 5 hours
42	exposed to monomer (9) for 8 hours
43	exposed to monomer (9) for 24 hours
44	exposed to monomer (9) for 2 days
45	exposed to monomer (9) for 3 days
46	exposed to monomer (9) for $3^{1}/_{2}$ hours

APPENDIX 3: Technical data of cyanoacrylate monomers

Monomer No.	Name of the monomer ←	Technical Information monomer	Manufacturer
1	RS cyanoacrylate adhesive stock no. 555-459	main constitute:- ethyl cyanoacrylate storage:- +30 C ? colour:- colourless	RS components Ltd.
2	Anglo superstick 3i	main constitute:- ethyl cyanoacrylate storage:- dark,dry place, $5\text{-}150^{0}$ C ? viscosity:- Ns/m2 0.002 specific gravity:- 1.10 refractive index:- similar to glass (1.3) acid and alkali resistance:- generally good. alkalis can affect the adhesive strength water resistance:- good. after few weeks the shear strength decreases gradually. temperature resistance:- -200 C to 800 C shelf life:- 1 year chemical toxicity:- low	Chamtek Anglo adhesives division
3	Anglo superstick 32	viscosity:- 0.1 Ns/m^2 all other properties are similar to Anglo super stick 31	-do-

Monomer No.	Name of the	Technical Information monomer	Manufacturer
4	Anglo superstick 34	viscosity:- 1.5 Ns/m^2 all other properties are similar to anglo super stick 31	Chamtek Anglo adhesives division
5	Loctite prism 401	main constitute:- ethyl cyanoacrylate colour:- colourless viscosity:- 120 mPa.s maximum operating temperature:- +800 C shelf life:- 6 mths sp. gravity:- 1.05 temperature resistance:- -500 C to +1200C humidity resistance:- high humidity can affect physical properties	Loctite UK
6	Loctite prism 460	main constitute:- high molecular wt. cyanoacrylte colour:- colourless viscosity:- 50 mPa.s sp. gravity:- 1.1 other properties are similar to Loctite prism 401.	Loctite UK

Monomer No.	Name of the	Technical Information monomer	Manufacturer
7	Eurecryl cyano acrylat 2460	main constitute:- ethyl cyanoacrylate colour:- colourless viscosity:- 40-70 m Pa.s sp. gravity:- 1.06 re. index:- 1.3 temperature resistance:- -30 to +1000C water resistance:- polymer state is resistant to water and moisture.	Schering Industrial Chemicals
8	Eurecryl cyano acrylat 2464	main constituent:- ethyl cyanoacrylate colour:- colourless viscosity:- 300-400 m Pa.s sp. gravity:- 1.07 all other properties are similar to eurecryl 2460	-do-

Monomer No.	Name of the	Technical Information monomer	Manufacturer
9	Permabond cyano acrylate adhesive grade C1	main constitute:- Ethyl cyanoacrylate viscosity:- 1-5 MPa S vapour pressure:- 2.2 mm Hg thermal conductivity:- 7.2x10-4 Cal/cm. sec. oC temperature range:- -30 to +850 C shelf life(at 5-250C):- 6 months - 1 year boiling point:- 48-540C (2 mm Hg) storage:- 1-40C bond durability:- good. but can be attacked by both caustic and acid soln.s together with Ketone solvents of the acetone type. other characteristics:- can be dissolved easily with acetone, ethyl acetate, trichloroethane or M.E.K.	Permabond Adhesives Ltd.
10	Permabond cyano acrylate adhesive grade C3.	main constituents:- Methyl cyanoacrylate viscosity:- 50-120 MPa.S. temperature range:- -30 to +950C. other properties are similar to permabond cyanoacrylate grade C1.	Permabond Adhesives Ltd. Permabond Adhesives Ltd.

APPENDIX 4: Infrared frequencies

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
3725-3740 D, w		**OH vib., Mg salts**		
3700 w, m, s		**str. vib. OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
3688 m		**str. vib. OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
3668 w		**str. vib. OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3670-3590	str. vib. free OH, (C)	..	..
3651 m		**str. vib. OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3670-3590	str. vib. free OH, (C)	..	..
	3640 m	free OH, pri. alcohol	27	208
3618 m		**str. vib. OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3670-3590	str. vib. free OH, (C)	..	..
	3640-3610 m	str. vib. free OH	27	208
	3615-3600	str. vib. free OH, (Ph)	..	..
	3623	free OH, sec. alc.	27	208
3580 v w		**str. vib. OH, (C)**		
	3700-2500	str. vib. OH, (C)	27	208
	3570	OH, (S)	9	210
3557 w		**OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-3500	free OH, carboxy. ac.	27	208
3539 w		**OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-3500	free OH, carboxy. ac.	27	208
	3550-2500 s	H bonding in OH, (C)	16	7

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
3512 v w		**OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-3500	free OH, carboxy. ac.	27	208
	3550-2500 s	H bonding in OH, (C)	16	7
3503 v w		**OH, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-3500	free OH, carboxy. ac.	27	208
	3550-2500 s	H bonding in OH, (C)	16	7
3485		**H bond. in O-H--O, (C)**		
	3700-2500	str. vib. OH, (C)	16	7
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-2500 s	H bonding in OH, (C)	16	7
	3490	H bond. in O-H--O, (aG)	9	210
	3488 s	OH str. (intra H bond., (C)	23	74
	3484	H bond. in O-H--O, (C)	9	210
	3480	H bond. in O-H--O, .intra & inter,	..	..
3450 w		**free OH & bonded OH, (C)**		
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-2500	H bond. in OH, (C)	16	7
	3450	str. vib. OH, (gL; sL)	5	272
	3447 v s	OH str.,(intra H bond.)	23	74
3396 w		**str. vib. OH, (C)**		
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-2500	H bond. in OH, (C)	16	7
	3400-3300	str. vib.-H bond. in OH, (L)	10	750
	3400-3230 s	bonded OH, inter mol.; polymeric	27	208
	3405 sh	str. vib.-H bond. (inter) OH,	15	66
	3400	str. vib. OH	10	489
	3390	str. vib. OH	7	1022

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
3385		**H bonded OH str., (C, L)**		
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-2500	H bond. in OH, (C)	16	7
	3400-3300	H bonded OH str. vib. , (L)	10	750
	3400-3230 s	bonded OH, inter mol.; polymeric	27	208
	3390	str. vib. OH	7	1022
	..	.. .. .., (C, X, L, W)	19	58
	3384	H bond.-OH--O, (aG)	9	210
3371		**str. vib. in OH, (C)**		
	3700-3300	str. vib. in OH,	5	273
	3571-3125	free OH & bonded OH, (C)	17	450
	3550-2500 s	H bond. in OH, (C)	16	7
	3400-3300	H bonded OH str. vib, (L)	10	750
	3400-3230 s	bonded OH, inter mol.; polymeric	27	208
2966 w		**str. vib.,-CH, (C)**		
	3550-2500	H bond. in OH, (C)	16	7
	3200-2900	str. vib., CH, (L)	10	750
	2975 w	str. vib.-CH, (4-MGX)	15	88
	2970 sh	str. vib.-CH, (w)	15	65
	2968 w	str. vib.-CH, (C)	..	..
	.. ..	.. .. ..	23	74
	2967	ali. CH vib.,-asym. CH$_3$, (L)	22	306
	2966 w	C-H str., (C)	25	211
2945 w		**str. vib.,-CH, (C)**		
	3550-2500 s	H bond. in OH, (C)	16	7
	3200-2900	str. vib.-CH, (L)	10	750
	2940-2820	str. & bend.-aliphatic CH,	5	274
	2955 w	str. vib.-CH	15	68
			23	74
	2942 w	anti sym. str.,CH$_2$ str., (C)	25	211
	2941	C-H str., -CH & CH$_2$, (C)	17	450
	2941	C-H str., Cotton	26	1005
	2940	CH str., (PU)	8	221
	..	str. vib.-CH$_3$, CH$_2$, (gL & sL)	5	272
	2938	ali. CH vib.,-asym. CH$_2$, (L)	22	306
	2935 sh	anti sym. str.-CH$_2$	15	88
	2933 m	.. .. . , (C)	..	68
			23	74

Observed frequency	**Allocated frequency**	**Allocated group**	**Reference No.**	**Pg**
2920 w sh		**CH str., (L)**		
	2920	CH str., (L)	19	58
	2911 v.w.	CH str., (C)	25	211
2902 s		**CH str., (C)**		
	3550-2500 s	H bond. in OH, (C)	16	8
	2940-2820	str. & bend.-ali. CH	5	274
	2914-2870 st	CH str., (W)	15	76
	2904 s	CH str., (C)	15	68
			23	74
	2900	.. .. , (X)	19	58
	2890	CH str.,	7	1022
	..	.. .. , (W)	19	58
	.. sh	tert. CH, (L)	10	750
	2880	.. .. , (C)	..	..
2860 k		**C-H str., (C) &, ...-CH$_3$, (L)**		
	3550-2500 s	H bond. in OH, (C)	16	7
	2940-2820	str. & bend.-ali. CH,	5	274
	2899-2817	C-H str.,-CH$_3$	17	450
	2875-2850	OH str.-CH$_3$, CH$_2$, (gL)	5	272
	2860-2850	methoxyl, (L)	10	750
	2874 sh	CH str, (C)	15	68
	2873 m	CH str., (4 MGX)	..	88
	2853 w	CH$_2$ sym. str., (4 MGX)	..	..
	.. ..	CH$_2$ sym. str., (C)	25	211
	2850 w	CH$_2$ str., (C)	15	68
			23	74
2750 k				
	3550-2500 st	H bond., -OH, (C)	16	7
2637 s		**O-D str.**		
2692	2780-2400	O-D str.	27	208
	2530	OD	19	505
2540 sh				
	3550-2500 st	H bond.-OH, (C)	16	7
2360-2330		**CO$_2$**		
		CO$_2$		
2240 m		**CN str.**		
	2247	CN str., (mod. cot.)	17	451
		.. .. ..	26	1000
2125 m				
2050 sh				

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1800 m				
	1795	C=O str.,-anhydr.	17	451
	1792	.. , substitute anhydr.	17	451
	..	C=O str.	26	1005
1765-1760 D, s		**C-O str.**		
	1765-1760	C-O str.-Ac, (P)	5	273
	1761	C=O str,-est.	26	1001
1747 s		**C=O,-est. (L)**		
	1750-1710	C=O, -est, ketone	4	857
	1750	C=O,-est, (Ac. C)	10	488
1733 v s		**C=O, un conj. ketone, .. , acetyl &uronic ester**		
	1750-1710	C=O, -est, ketone	4	857
	1740-1735	Acetyl & Uronic ester	5	277
	1740	C=O, (C)	16	65
	..	C=O, (L)	22	306
	1739 w	CO str.	7	1022
	..	.. , ester, (C)	17	452
	1735	C=O-un conj. ket.	(NaBH4. tre.)	
	..	poly (vinyl alcohol	20	117
	..	acrylic co-polymers	..	..
	1732	RCHO str., (W)	19	58
	1730	C=O str., -COOH & $COOCH_3$, (HC)	6	1020
	1730	pri. HC,(H.W)	5	277
	..	xylan	6	1020
1724 w		**C=O,-COOH &ester**		
	1750-1710	C=O, -est, ketone	4	857
	1730-1725 st	C=O str.-Acetyl or COOH,	15	76
	1720-1715	carboxyl-Uronic acid	5	27
		un conj. carboxyl, (kraft L)	..	289
	1727	p-ethyrified Vanilic acid	..	281
	1725	C=O,-acid or ester, (L)	10	750
	1724	C=O str,-ac.	26	1005
	1720	C=O in Valrez 248 (finishing agent)	8	224
	1715 st.	C=O.-Carbamate	11	137

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1702 v w		**C=O str., (L)**		
	1725-1650	C=O str., (L)	10	750
	1715-1700	C=O str.,-sat. open chain ketones	5	275
	.. ..	conj. aldehydes	..	..
	1712-1705	C=O,-non conj. keto.	10	750
	1710-1705	.. ..	12	220
	1704	C=O str.-	7	1022
	1700	C=O, ArCOR & ArCHO str., (L)	19	58
	1694	ester grp., (L)	12	203
1680 v w		**C=O, Van. ac.**		
	1725-1650	C=O str., (L)	10	750
	1686	C=O,-Actyl van. ac.	5	275
	1677	C=O,-Van. ac.	5	275
	.. w	lignin, (w)	15	76
	1668	C=O,-ald. or keto. (L)	10	750
1651 sh		**C=O, (L) & CO (Ge)**		
1659	1725-1650	C=O, (L)	10	750
	1680-1630	CO, sec. amide	1	233
	1668-1666	C=O, conj. ald.	12	220
	1668	C=O,-ald. or keto. (L)	10	750
	1664	C=O, hydroxy propiovanilline	5	276
	1663 w	C=O,	12	220
	1660	C=O,-p-subst. aryl keto., (sL & gL)	5	272
	..	C=O,-keto. at a to arom. ring, (L)	10	750
	..	conj. C=O & COOH	..	764
	..	C=C, (L)	22	306
	1658	C=O,-ald. or keto.	12	203
	..	ester grp., (L)	..	..
	1653	C=O,-acetoguaiacone	5	276
1625-1640 D,s		**adsorbed H_2O, (C), C=C str.,-alip. (L)**		
	1640 m	hydrated H_2O	15	88
	..	Casein	20	117
	1639	CO,-Sodium phenate (Acetoguaiaacone)	5	276
	1635	adsorbed H_2O, (C)	15	68
			23	74
	..	.. .. , (W)	15	76
	1630	.. .. , (C,X,W)	19	58
	1626 w	ethylene vib	7	1022
	..	C=C str.,-alip.	26	1005

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1600		**C=C str. & skeletal vib.,-arom. ring, (L)**		
	1626-1608	C=C str.,-aro. conj. trans double bonds	5	277
	1605-1595	aro. skelet. vib., (g & s L model com.)	..	..
	1603-1595	aro. str., (L)	10	750
	1600-1550	asym. str., -COO^-	28	6
	1600-1510	C=C skelet. vib., -aro. ring, (L)	..	..
	1605	C=C, COO, (X)	19	58
	1600 s	COO-, (W)	15	76
	1600 sh	COO- a. sym. str., (4,O-MGX)	..	88
	1600	C=C str., aro. ring	26	1005
	..	.. ..	4	857
	1595 m	lignin, (W)	15	76
	..	.. ,	6	1019
	1592	C=C, COO, (L)	19	58
	..	COO^- str.	26	1005
	1591	.. .. , (W)	..	..
1578 v w		**C=C skelet. vib., (L)**		
1583	1600-1510	C=C skelet. vib., -aro. ring (L)	10	750
	1585-1580	ring vib.,-conj. with a C=O	..	..
	1582	C=C str., aro. ring conj. with C=O	26	1003
1552 w		**NH_2 def., (Ge)**		
1541	1600-1510	C=C skelet. vib.,(L)	10	750
	1610-1550	COO^- anti sym. vib.	1	198
	1570-1115	NH_2 def.,-sec. non cyclic amine	..	233
1525-1530 D,v.w	1600-1510	C=C skelet. vib.,(L)	10	750
1520 v.w				
	1600-1510	C=C skelet. vib.,(L)	10	750
	1520	Casein	20	117
	1515	arom. ring	10	764

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1510 m		**arom. str. & skelet. vib., (L) ; phenolic group (L)**		
	1600-1510	C=C skelet. vib., -arom. ring, (L)	10	750
	1515-1510	aro. skelet. vib., (gL)	5	272
	.. ..	aro. str. vib.,-un conj gL, (L)	10	750
	1515-1505	aro. skelet. vib., (s & g model comp)	5	277
	1515	aro. ring	10	764
	1510	ring str. coupled by C-H,-plane def.	5	278
	1505	benzene ring vib.	30	68
	1498	benzene ring, (W)	19	58
	1495	.. .. , (L)	..	..
1454 1456		**C-H bend. & def. vib, including OCH_3, (L)**		
	1480-1350	C-H def.,-(L)	10	750
	1470-1460	alip. C-H str & bend.,	5	274
	1470-1420	C_H def. vib.,-CH_2 (C)	16	8
	1462-1452	C-H bend. vib., (L)	10	750
	1455-1400 m	OH plane bend., (W)	15	76
	1470 sh	OH plane bend., (C)	..	68
	1465	CH_2, (xylan)	6	1023
1454	1465	CH_3 def., (L)	..	..
1456	1460	asym. C-H def., (gL)	5	272
	..	C-H bonds, including OCH_3 grp., (soft & hard wood L)	..	278
	..	(pri. HC in hard wood)	5	284
	1460 m	(L) & CH_2 sym. bend on pyran ring, (W)	15	76
	1460	asym. vib.,-CH_3, CH_2 scissoring, (L)	22	306
	1455	CH_3 scissoring, (X)	19	58
	..	C-O-H def., (C)	25	211
	1454	.. .. , (W)	..	..
	1450	.. .. , (L)	..	..
	..	OH def. vib., (C)	16	45

Observed frequency	**Allocated frequency**	**Allocated group**	**Reference No.**	**Pg**
1433 s 1429 w		**int. def. of C-H, -CH_2,(C)**		
	1480-1350	C-H def., (L)	10	750
	1470-1420	int. def.,-CH, CH_2, (C)	16	8
	1450-1420	aro. skelet. vib.	4	857
	1435	$CaCO_3$	20	117
	1434	CH_2 absorbance	1	24
	1430	aro. skelet. vib.,(gL)	5	272
	1430	CH_2 bend., (C)	8	224
	..	Cellulose	6	1020
	..	CH_2 sissor motion, (C)	..	..
	..	alip. grps, (L)	10	750
	.. m	CH_2 sym. bend.	15	65
	.. s	CH_2 sym. bend.,-hydroxymethyl, (W)	..	76
	..	int. def. of CH_2, CH_2OH, (C)	16	60
	..	CH_3 scissoring, (L)	19	58
	1427	OH vib.,-in plane,	22	306
	1426	.. .. , (C)	..	..
	..	CH_2 def., (C)	25	211
	1425	aro. skelet. vib., (g & s L)	5	272
	.. w	COO- & carboxylic acid, (W)	15	76
	.. w	COO- sym. str., (4 O-MGX)	..	88
	..	CH2 def. vib.	18	83
	..	.. ..	30	68
	1419	CH_3 scissoring, (W)	19	58
	1416 w	CH_2 bend. vib., (C)	23	74
	1412	.. .. , (X)	..	..
1402 v w		**sym. vib., COO^-**		
	1480-1350	C-H def., (L)	10	750
	1400-1300	sym. vib., COO^-	1	198
	1405 w	C-O-H, C-C-H def., (C)	25	211
	1390 m	CH bend., (4 O-MGX)	15	88
1373 m		**CH def. & bend. vib, (C, L)**		
	1480-1350	CH def., (L)	10	750
	1385-1370	sym. def. of H,-CH_3,	1	22
	1370-1365	alip. CH str. & bend.	5	274
	1380 s	CH bend., (W)	15	76
	1379	C-H def., (C)	26	1005
	1375 m	CH bend., (C)	15	68
			23	74
	1370	sym. CH def.,(gL)	5	272
	..	phenolic OH,	..	273
	..	CH bend., (C & HC)	6	1023

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1355 v w		**CH bend., (C)**		
	1480-1350	CH def., (L)	10	750
	1366	CH bend., (W)	19	58
	1365 m	CH bend., (C)	..	..
	1365	.. ..	15	68
	1360	.. ..	19	58
	1358	C_1H bending, (C)	15	64
	1357	C-C-H def., (C)	25	211
	1350 w	OH plane bend., (4 O-MGX)	15	88
1340 w		**OH vib., (C)**		
	1350	OH def. vib., (C)	16	45
	1335 w	OH plane bend., (C)	15	68
	..	.. ..	23	74
	..	ring breathing with CO str.,-S der.,	5	279
	1334 m	CH_2 and C-O-H def., (C)	25	211
	1334	CH_2 def.	..	213
	1333	OH vib. or C=O vib,- carbonyl, (L)	22	306
1319 w		**CH_2 wagging, (C)**		
	1335-1315 w	CH_2 wagging, (W)	15	76
	1330-1325	ring breathing with CO str., (sL)	5	272
	1320	CH_2 wagging, (W)	19	58
	1317	Cellulose	6	1020
	..	CH_2 wagging, (C & probably HC)	..	1023
	.. w	OH plane bend.	15	88
	1315 w	CH_2 wagging, (C)	..	68
	.. ..	.. ..	23	74
	1311	.. ..	19	58
1278 m		**CH bend., (C) & CO str., -arom. OCH_3 (L)**		
	1300-1100	C-O-C, ether bond	13	4
	1270-1268	CO str.,-aro. OCH_3 (L)	10	750
	1282	CH bend., (C)	6	1023
	1280 m	CH_2-O-H def.,(C)	25	211
	..	CH_2 def.,	..	213
	1277 m	CH bend., (C)	15	68
	1277	.. .. ..		
	1276	.. .. ..	19	58
	1275	ring breathing with CO str., (gL)	5	272
	.. v w	CH bend., (4 O-MGX)	15	88
	1270	ring breathing with CO str., (gL)	5	279
	.. sh	lignin, (W)	15	76
	1269	C_2H_4O ring	13	4

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1278 m	1265	soft wood lignin	6	1020
	1265	asym. vib. =C-O-C of ethers like OCH_3, (L)	22	306
	1260	guaiacyl nucleus, (L)	19	58
1234-1250 D, w		**CO str., (C, L)** **Si-CH_3**		
1236 m	1300-1100	C-O-C, ether bond	13	4
	1245-1205	CO bond, (V, Phenyl OH)	2	494
	1245-1205	CO bond, (V, Phenyl OH)	30	67
	1235-1267	CO str. vib., (aldo pyranosides)	16	37
	1235-1230	ring breathing with CO str., (sL)	5	272
	1230-1215	CO str.,-aro. phenyl (L)	10	750
	1259	Si-CH_3	1	375
	1249 w	C-C-H def., (C)	25	211
	1245 w	OH plane bend., (4 O-MGX)	15	88
	1242	OH in plane bend., (X)	19	58
	1240	.. .. , (W)	..	..
	1240	CO str., -O=C=O, (X)	6	1024
	.. m	CO str.,-Acetyl, (W)	15	76
	1235	.. , ester	17	426
		ring breathing with CO str., (sL)	5	279
	..	(pri. H,-hard wood)	5	284
	..	C=O vib. in plane, (L)	22	306
	1230	ring breathing with CO str., (gL)	5	272 279
	1230	ester, (C)	11	137
	.. b	lignin, -HW	6	1020
	1224	syringyl nucleus, (W)	19	58
1205 w		**OH plane bend., (C)** **& phenolic OH (L)**		
	1300-1100	C-O-C, ether bond	13	4
	1245-1205	C-O bond., -phenyl OH, (L)	30	67
	1210-1200 w sh	phenolic OH	5	273
	1210-1190 s b	sulphonic acid or sulphonate grps., (Lignosulphonate)	..	290
	1205	CH_2 def.	25	213
	1203	syringyl nucleus, (L)	19	58
	1200 m	OH plane bend., (C)	15 23	68 74

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1178-1169 m		**anti sym. bridge COC str., (C, L) ; CO vib. (L)**		
	1300-1100	C-O-C, ether bond	13	4
	1180	C-O vib., (L)	22	306
	1165 s	anti sym. bridge COC str., (4 O-MGX)	15	88
	1163	C-O and/or C-OH def. (C)	26	1002
	1162 s	anti sym. bridge COC str., (W)	15	76
	1160	asym. C-O-C bridge str., (C)	6	1020
	..	anti sym. bridge COC, (X)	19	58
	1155	anti sym. bridge COC, (C, L)	19	58
	1150	1,3,4-substituted aro. ring, (L)	10	750
	..	anti sym. bridge COC, (W)	19	58
1132		**aro. ali. ether link**		
1128		**OH in plane bend. (C, L)**		
1126	1300-1100	C-O-C, ether bond	13	4
	1150-1125	aro. ali. ether link	5	286
	1145-1125	tertiary alcohol	..	274
	1140-1130	C-H,-aro. ring	..	..
	1125-895 s	CO & ring str., (W)	15	76
	1140	dialkyl ether link, (L)	10	750
	1130	aro. CH plane def., (sL)	5	272
	..	ring breathing with CO str., (gL)	5	279
	.. s	anti sym. plane ring str., (4 O-MGX)	15	88
	1125	O-H in plane bend.,(L)	19	58
	..	C-O vib., (L)	22	306
	1120	.. .. ,(W)	..	..

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1084/1092 m		**C-OH def (L), OH def. (L)** **C-O-C def., ali. ether** **Si-O-Si & Si-O-C**		
	1125-1085 s	C-O-C def.,-ali. ethers,	5	274
	1120-1075	secondary alcohol	5	274
	1100-1005	C-O vib.,-alcoholic OH, (L)	30	67
	1100-1005	C-O vib.,-alcoholic OH, (L)	2	494
	1092-1076	ali. ether link & secondary OH, (L)	10	750
	1090-1020	Si-O-Si & Si-O-C	1	375
	1065-1025 w	C-O-C def.,-ali. ethers	5	274
	1110	=C-OH, (X, W)	19	58
	1100	ring str.,	8	144
	1090 v.w	C-O-H def., (C)	25	211
	1087	OH vib., (L)	10	750
	1086	C-O vib.,-sec. alco., (L)	22	306
	1085	C-O def.,-sec. alco. & ali. ether	5	272
	1065	C-C str.,	8	144
1043 m		**CO str., -CH_2OH, (C)**		
	1125-1085 s	C-O-C def.,-ali. ether	5	274
	1100-1005	CO vib.,-alcoholic OH, (L)	2	494
	.. ..	CO vib.,-alcoholic OH, (L)	30	67
	1070-1020	C-O & C-C str.	8	144
	1070-1010 two sharp	CO str.,-pri. alco.	5	274
	1065-1025 w	C-O-C def.,-ali. ether	5	274
	1040-1030	aro. ring C-H,	..	..
	1035-1030	C-O def.,-OCH_3, (L)	10	750
	1055	(pri. H,-hard wood)	5	284
	1050	C-O str.,-CH_2OH, (C)	19	58
	..	.. .. , (W)	..	..
	1048	C-O vib., pri. alco.,(L)	22	306
	1045 s	skelet. vib. involving C-O str., (4 O-MGX)	15	88
	.. i rel. 1730		8	219
	1043	OH vib., (L)	10	750
	1042	rock. fre. of CH_3 attached to aro. ring	1	27
	1040	dialkyl ether link, (L)	10	750
	1038	pri. alco.,-beta hydr. conif. alco. & coni. alco.	5	274
	1037	ring vib., (X)	19	58
	1035 s	skelet. vib. involving C-O str., (C)	15	64
	.. s	C-O str., (C)	23	74

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
1043 m	1035 v s	C-O-H def., (C)	25	211
	1032	ring vib., (W)	19	58
	1030	.. , (L)	..	..
	..	(pri. H,-hard wood)	5	284
	..	=C-O-C sym. str., (L)	22	306
1020		**CO str., ester**		
	1100-1005	CO vib.,-alcoholic OH, (L)	2	494
	.. ..	CO vib.,-alcoholic OH, (L)	30	67
	1030	CO str., ethyl & higher esters	14	273
	1025	ring vib., (C)	19	58
	1020	CO str., (C)	23	74
	1015	CO str., methyl ester	14	273
1003 T, m		**C-O str., (C)**		
	1010	pri. alcohol	5	274
	1005 s	skelet. vib. involving CO str., (C)	15	68
	.. ..	CO str., (C)	23	74
	1000	China clay	20	117
	..	pri. benzylic alco.,-vanillyl alco.,	5	274
	996 s	C=O str., (C)	23	74
	990	(pri. H,-hard wood)	5	284
	985	C-O str., (W)	19	58
	984	.. , (C)	..	..
	975	.. , (X)		
931 v w k				
897 m		**anti sym. out of plane or/and C_1 group frequency, (C)**		
	897 m	anti sym. out of plane ring str., (4 O-MGX)	15	88
	895	(pri. HC)	5	284
	..	C1 grp. fre. or a G ring str. fre., (b linked P)	6	1024
897 m	895	C1H bend. for b linked P	24	171
	.. w	b link ring str., (W)	15	76
	..	CH_2 def.,	25	213
	893 v w	Cl-H, CH_2 & C-O-H def., (C)	25	211

Observed frequency	Allocated frequency	Allocated group	Reference No.	Pg
897 m	892 m	anti sym. out of plane ring str., (C)	15	68
	..	b linked glucose, (C)	19	58
	892 m	C1 group freq., (C)	23	74
	890	.. .. , (X, W)	..	..
874 sh or w		**$CaCO_3$ & glucomanan**		
	875 sh	glucomanan, (W)	15	77
	879	$CaCO_3$	21	98
	873	..	3	2
856 sh		**C-H out of plane in S.W., (L)**		
	860	ortho subst. phenol	5	288
	.. sh	aro. C-H out of plane def., (g & s L)	..	272
	858	mono H out of plane def.,-1,3,4, subst. aro. ring	10	750
	855	aro. C-H out of plane def., (gL) ; char. of soft wood	5	280
	844 8	C_1H equit. posit. w.r.t. plane of pyran. ring, (C)	16	56
854 w-m		**acrylate**		
	854	acrylate	29	174
820 w		**tri subst. arom. ring (S.W. L)**		
	840	3,6 anhydro ring, (C)	16	56
	835	aro. C-H out of plane def., (s & g L)	5	272
	..	tri subst. aro. ring, (L)	10	750
	..	epoxy ring vib.	14	97
	817	H out of plane def. of two adjs. ring,- 1,3,4 subst. aro. ring, (L)	10	750
	815	aro. C-H out of plane def., (gL)	5	272
	..	s.w. L	5	280
790		**$Si-CH_3$**		
	800	$Si-CH_3$	1	375

Observed frequency	**Allocated frequency**	**Allocated group**	**Reference No.**	**Pg**
720		**rocking CH$_2$ & OH**		
714		**out of plane vib., (C)**		
712	700-650 m	OH out of plane bend.,	15	77
	725 sh	OH out of plane bend.,-(4 O-MGX)	15	85
	720	rock.,-CH$_2$,	1	29
	700 sh	OH out of plane, (C)	15	68
660		**OH out of plane bend. (C)**		
	700-650	OH out of plane bend.	6	1024
		(C & other com.,- W)	15	77
	655 m	sulfonic acid, (Ligno sulfonic acid) ?	5	270
	.. m b	sulfonic acid or sulfonate grp., Ligno sulfonate)	5	290
	650 s	OH out of plane bend., (C)	15	68
	.. ..	OH out of plane bend., (4 O-MGX)	..	88
636 w		**SO$_4^{-2}$**		
	632	BaSO$_4$	20	117
	630 w	C-S vib., (thio L)	5	270
	605	BaSO$_4$	20	117
575 v w k				
560 v w				
520 v w				
	540-520 w b	sulfonic acid or sulfonate grp., (ligno sulfonate)	5	290
500 v w k				

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APPENDIX 5

Scanning electron microscopic analysis of $Mg(OH)_2$/IMS treated samples

Ref. No.	Sample No.	time gap, be. treat. and analysis	Observations photograph	X-ray analysis elem. present
SEM 1	9 A_{19} -T		l. thin f.	-
SEM 2	9 A_{19} -R		l. thin f.	-
SEM 3	2 A_5 -T		l. thin f.	Al, S
SEM 4	2 A_5 -R		l. thin f.	Al
SEM 5	4 A_5 -T		fat f.	Al, Si
SEM 6	4 A_5 -R		fat f., broken	Al, Si, S, K, Fe
SEM 7	9 f, s, 1sp (2) -T	3 months		Mg
SEM 8	9 f, s, 1sp (2) -R	3 months		-
SEM 9	9 f, s, 2sp (2) -T	3 months		Mg
SEM 10	9 f, s, 2sp (2) -R	3 months		-
SEM 13	2 f, s, 2sp (2) -T	3 months		Mg, Al, Si, S
SEM 14	2 f, s, 2sp (2) -R	3 months		Al, S
SEM 15	4 f, s, 1sp (2) -T	3 months		Mg, Al, Si, Fe
SEM 16	4 f, s, 1sp (2) -R	3 months		Al, Si
SEM 17	4 f, s, 2sp (2) -T	3 months		Mg, Al, Si, Fe, K
SEM 18	4 f, s, 2sp (2) -R	3 months		Al, Si
SEM 19	9 f, s, 1sp (3) -T	1 month	thin f., sm. & m. part.	Mg
SEM 20	9 f, s, 1sp (3) -R	1 month		-
SEM 21	9 f, s, 2sp (3) -T	1 month	thin f., m. part.	Mg
SEM 22	9 f, s, 2sp (3) -R	1 month		-
SEM 23	2 f, s, 1sp (3) -T	1 day		Mg, Al, Si, S
SEM 24	2 f, s, 1sp (3) -R	1 day		Al, Si
SEM 25	2 f, s, 2sp (3) -T	1 day	thin f.,sm. part.	Mg, Al, Si, S, Ca

Ref. No.	Sample No.	time gap, be. treat. and analysis	Observations	
			photograph	X-ray analysis elem. present
SEM 26	2 f, s, 2sp (3) -R	1 day		Si, Al, S, Ca
SEM 27	4 f, s, 1sp (3) -T	1 month		Si, Al, Mg, S
SEM 28	4 f, s, 1sp (3) -R	1 month		Al, Si, S
SEM 29	4 f, s, 2sp (3) -T	1 month		Mg, Al, Si, S, Fe
SEM 30	4 f, s, 2sp (3) -R	1 month		Si, Al, Fe
SEM 31	2 f, s, 1sp (3) -T	3 months		Mg, Al, Si, S
SEM 32	2 f, s, 1sp (3) -R	3 months		Al, Ca
SEM 33	$3Mg(OH)_2$/IMS -T	6 months	thin f., not clear	Mg, Al, Si, Ca
SEM 34	$3Mg(OH)_2$/IMS -R	6 months	thin f., sm. part.	Mg, Al, Si, S
SEM 35	3A -T		not clear	Al, Si, S
SEM 36	3A -R		thin cotton f.	Si, Al, S
SEM 37	$9Mg(OH)_2$/IMS -T	6 months	thin f., not clear	Mg, Cl
SEM 38	$9Mg(OH)_2$/IMS -R	6 months	thin f., sm. part.	Mg, Cl, K, Si
SEM 39	$4Mg(OH)_2$/IMS -T	6 months	fat f., not v. clear. sm. part.	Mg, Al, Si, S, K
SEM 40	$4Mg(OH)_2$/IMS -R	6 months	not clear	Si, Al, Mg, K
SEM 41	$4A_3$ -T			Al, Si, K
SEM 42	$4A_3$ -R			Al, Si, S, Fe
SEM 43	9A -T			-
SEM 44	9A -R			-

be. - between f - $Mg(OH)_2$/IMS treatment treat. - treatment