An Investigation of the Factors Affecting the Degradation of Cellulose Acetate Artefacts in Museum Collections

by

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"The curve that sets most things straight is a smile."

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ABSTRACT

Plastics have had an increasing influence on human activity since the early years of the 20th century and as such are becoming an increasingly important part of museum collections. These plastics are already exhibiting signs of degradation, which raises the question of how they should be stored and treated. However, little is known about the specific degradation processes which occur. Further research is required because the lack of information is hindering the correct approach to plastic conservation.

Current interest concerns the degradation of cellulose acetate artefacts; the work carried out and reported here examines this problem by studying artefacts of various ages and degrees of degradation using accelerated ageing and comparing these results to those for naturally aged samples. Initial work has been carried out to investigate the plastic each artefact is made from and also its chemical composition. Various analytical techniques have been used to investigate the additives, impurities and degradation products that may be present. The results from these techniques and further work are discussed.

Micro-Fourier Transform Infrared (FTIR) Spectroscopy has been found to be an excellent technique for the identification of the base polymer in a plastic artefact, as minute samples are used. It has also been used to monitor changes in the base polymer of the plastic artefacts. Ion chromatography has been used to study levels of water-extractable acetate and oxalate as well as other significant anions. The presence of oxalate in degraded samples indicates chain scission occurring and high levels of acetate indicate deacetylation is occurring. Non-destructive and destructive sampling for ion chromatography have been used to explore if this is a viable screening process to identify artefacts in the early stages of degradation. Chain scission has been investigated further using gel permeation chromatography. X-ray fluorescence spectroscopy results indicate that trace levels of Se may be important in preventing the initiation of degradation, as so far it has only been detected in undegraded artefacts.

Results indicate that deacetylation is the predominant process; while chain scission is secondary or a possible surface reaction. Another factor is plasticiser loss.

ABBREVIATIONS

3-D – Three dimensional

ATR – Attenuated Total Reflectance

DTGS – Deuterium Triglycine Sulphate

DVB – Divinylbenzene

FID – Flame Ionisation Detector

FTIR – Fourier Transform Infrared Spectroscopy

GC – Gas Chromatography

GC-MS – Gas Chromatography – Mass Spectrometry

GPC – Gel Permeation Chromatography

HPLC – High Pressure Liquid Chromatography

IC – Ion Chromatography

IR – Infrared

LACMA – Los Angeles County Museum of Art

MCT – Mercury Cadmium Telluride

MCTA – Mercury Cadmium Telluride Analytical

NMR – Nuclear Magnetic Resonance

PS – Polystyrene

PVC – Polyvinyl Chloride

RAPRA – Rubber And Plastics Research Association

RH – Relative Humidity

RSD – Relative Standard Deviation

SCER – Smithsonian Centre for Environmental Research

SCMRE – Smithsonian Centre for Materials Research and Education

SRS – Self-regenerating Suppressor

TGA – Thermogravimetric Analysis

TGA-FTIR - Thermogravimetric Analysis - Fourier Transform Infrared Spectroscopy

THF - Tetrahydrofuran

UV – Ultraviolet

XRF – X-ray Fluorescence Spectroscopy

ZPD – Zero Path Difference

Table of Contents

CHAPTER 1

INTRODUCTION

1 Introduction

Plastic materials have had a great influence on life since their introduction in the mid 19th century. Worldwide production in the 1990's was approximately 100 million tonnes per year[1]. However, plastics today have an image of being cheap and mass-produced. This was not always the case as plastics in the 1920's and 1930's were considered chic and collectable. Therefore, they have become an increasingly important part of museum collections. From 'Industry and Technology' to 'Fashion and Design' plastics are in every part of life and have been for the past century.

Unfortunately museums have discovered that plastics do not last forever as a large number of artefacts in these collections are exhibiting various degrees of degradation. The deterioration can range from slight discoloration to warping and cracking which totally destroys the artefact. The early cellulose based man made plastics, cellulose nitrate and cellulose acetate, are especially sensitive to these problems[2,3]. Investigation into the causes of degradation is essential to allow museum conservators and curators to develop proper storage conditions and treatment strategies to help preserve artefacts made from these materials. This project has concentrated on one of these early plastics, cellulose acetate, which unfortunately has been unable to live up to the claim, in 1929, that it was "practically everlasting"[4]. It is important to remember that many of these early plastics are based on biorenumerable polymer systems and hence would have been seen as almost as durable as the natural polymer, e.g. cotton or wood.

This project was necessary to allow a better insight into the degradation of three-dimensional cellulose acetate artefacts to be established. There was a need for this as the majority of studies have been carried out on film samples and therefore, very little knowledge of the degradation of three-dimensional cellulose acetate was available. It was also necessary to develop a full understanding of the processes involved in degradation of cellulose acetate.

1.1 History and Uses of Cellulose Acetate

Cellulose acetate was first discovered in 1865 by a German scientist called Schützenberger, by simply heating cotton and acetic acid to 140 °C in a sealed tube[5,6]. Franchimont improved on the

acetylation reaction in 1879 by adding sulphuric acid to the reaction mixture as a catalyst[6]. The reason for these experiments was an attempt to find an alternative to potentially flammable cellulose nitrate[7-9]. However, the commercial replacement of cellulose nitrate with cellulose acetate was held back due to the high costs[9] and the need to use toxic solvents such as chloroform[10] in manufacture, as cellulose acetate must be in solution to allow plastic artefacts to be moulded.

The beginning of the commercial production of cellulose acetate is credited to Cross and Brevan, who used zinc chloride, instead of sulphuric acid, as a catalyst[11]. The main advantage of zinc chloride over sulphuric acid is that higher temperatures can be used without degradation of the cellulose[12]. Zinc chloride, as well as many other catalysts, were tried both commercially and experimentally during the early years of production. However, because sulphuric acid is cheaper and the production time is shorter[12] it became commercially favoured[13]. The interest in cellulose acetate was greatly helped by the discovery, by Milnes, in 1903 that cellulose acetate became soluble in acetone, if acetylation was controlled by the addition of water to the completed reaction mixture[6,11,14]. This was later discovered to be because diacetate was produced rather than the fully esterified triacetate. The outbreak of World War I brought about the commercial success of cellulose acetate because a non-flammable 'dope' for the fabric of the aircraft wings was needed[8]. The Dreyfus brothers were responsible for setting up plants in both Britain and America to supply the Allies with cellulose acetate 'dope'[10]. However, the end of hostilities left the brothers looking for new outlets for cellulose acetate, especially as the American factory was only half-finished[10,11].

The main use for cellulose acetate from 1919 to the 1930's was as an artificial silk, with the bulk plastic needing much more research to allow a commercially viable product to be found[9,11]. The use of new plasticisers was investigated and eventually in 1927 the combination of alkyl phthalates and/or triphenyl phosphate was found to overcome problems of warping and weathering[11]. This coincided with the introduction of the modern plastics injection moulding machine by Eckert and Ziegler in 1926[10] which signalled the beginning of cellulose acetate plastics taking over from cellulose nitrate for manufacture of a range of artefacts.

The uses of cellulose acetate expanded dramatically from 'dope' and artificial silk to film and three dimensional (3-D) plastic objects, such as, windshields, steering wheels and other car parts,

aircraft parts, electrical devices, vacuum cleaner parts, telephones, pens, pencils, transparent fountain pen barrels, spectacle frames, visors, safety glasses, combs, buttons and buckles, costume jewellery, vanity cases, toys, lamp shades, desk accessories, film cores, playing cards, containers, phonograph and gramophone records and many more products[7,15-20]. The success of cellulose acetate increased until maximum production was reached in 1947, when 131,000,000 lb. was estimated to have been produced in America[11].

While the main use of cellulose acetate today is in cigarette filters, it is still used as a mouldable plastic to produce toothbrush handles, screwdrivers and spectacle frames. The continued use of cellulose acetate, which is relatively expensive, is helped by the fact that it tends to make skin sweat less than other plastics, and is therefore a more attractive option for a handle.

1.2 Chemistry and Manufacture of Cellulose Acetate

Cellulose acetate is a derivative of cellulose[21] and its solid structure retains a lot of the character of the cellulose from which it is derived. Therefore, the chemistry of cellulose itself must be appreciated before the chemistry of manufacture of cellulose acetate can be fully understood.

1.2.1 Cellulose

Cellulose is found in all terrestrial plants and is made up of long polysaccharide chains, which are arranged to form a fibrous structure (figure 1.1). The molecular structure of cellulose (figure 1.2) indicates that it is comprised of linear, unbranched chains of 1-4 linked β-D-glucopyranose residues[8,14]. It also shows that three sites are available for reaction with an acetylating agent. However the reactivity of each of these hydroxyl groups is different, due to basic organic chemistry and stereochemistry[22]. There are two types of hydroxyl group in the cellulose as those at C_2 and C_3 are secondary and the one at C_6 is primary. Therefore, the reactivity and stability of each is different, C_2 and C_3 should be similar and C_6 would be more reactive.

The fibrous structure of cellulose (figure 1.1) is formed through intermolecular interactions, which mean the chain adopts a helical character. These helical chains wrap around each other to form the elementary fibril. These then group together to produce micro-fibrils, which in turn

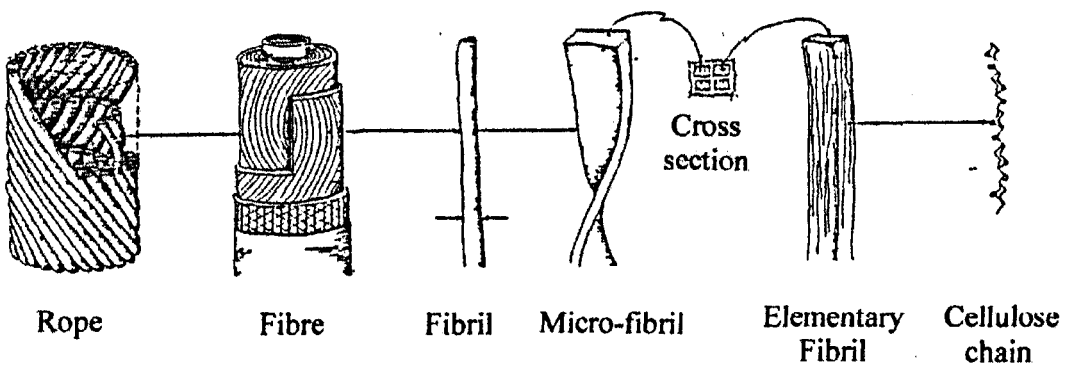


Figure 1.1 Fibrous structure of cellulose[22]

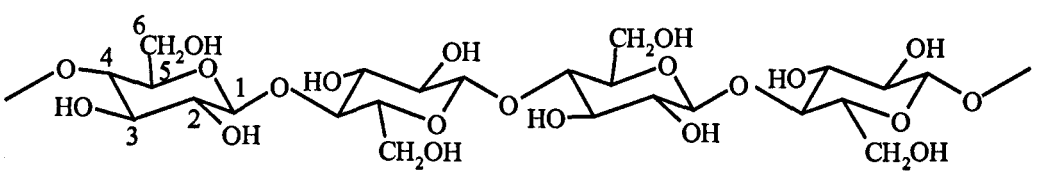


Figure 1.2 Chemical structure of cellulose

entwine to construct fibrils and finally the fibre[23]. The fibre structure also has a major effect on the reactivity of each of the three sites as some are hidden within the helix so cannot be reached by reactants.

Cellulose must be derivatised before plastics can be produced, as it is impossible to plasticise it directly. This is due to the high percentage of crystalline structure, which is maintained by inter-molecular and intra-molecular hydrogen bonding between hydroxyl groups. These interactions are strong enough to render cellulose insoluble and, therefore, impermeable to plasticiser, which is essentially a solvent retained within the plastic mass[24].

1.2.2 Acetylation

The acetylation of cellulose to cellulose acetate has been carried out using the same basic reaction since the 1890's[6], (figure 1.3).

$$C_6H_{10}O_5 + 3(CH_3CO)_2O \longrightarrow C_6H_7O_5(CH_3CO)_3 + 3CH_3COOH$$

Cellulose Acetic anhydride Cellulose triacetate Acetic acid

Figure 1.3 Esterification reaction of cellulose to cellulose acetate

This reaction, which is an esterification, has been modified for commercial manufacture. The current manufacturing method involves the addition of acetic anhydride (ethanoic anhydride), acetic acid (ethanoic acid) and sulphuric acid to cellulose in controlled amounts and conditions. The basic manufacture scheme is shown in figure 1.4. However, many variations of this have been used since 1894 when Cross and Brevan first started commercially producing cellulose acetate[6].

The pre-treatment of cellulose, first introduced by Brayer and Co. in 1898[6], is necessary to achieve a more easily controlled and rapid reaction. This process has two main effects, to purify the raw material and to open the fibrous cellulosic structure to allow the acetic anhydride to penetrate throughout the fibre. This allows for a more uniform product, as all three sites are available for esterification. The method involves addition of glacial acetic acid with a small amount of inorganic acid (usually sulphuric acid) to initiate slight acetylation, usually at no more than 50 °C, thus ensuring the main acetylation is less exothermic[8]. The original source of

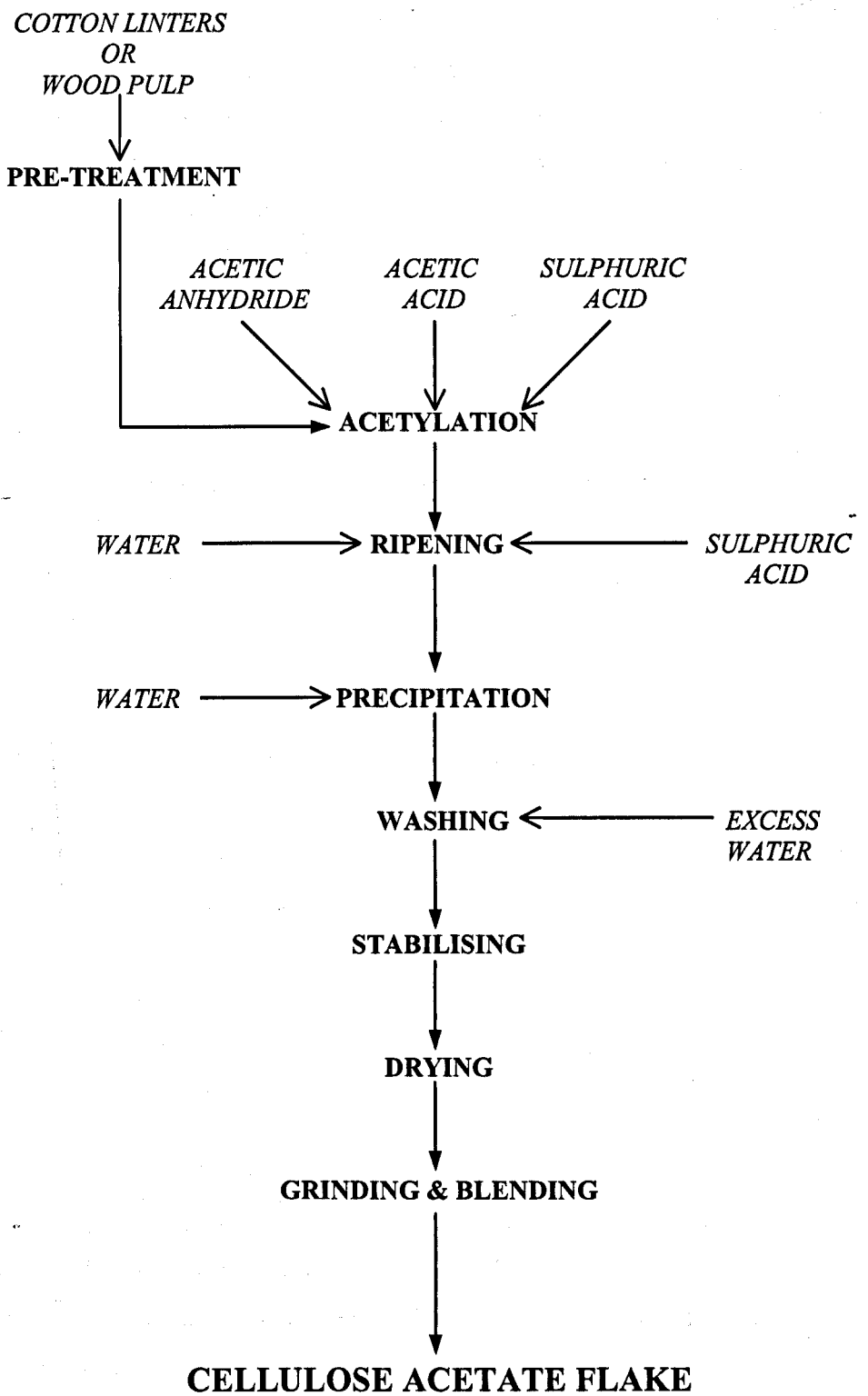


Figure 1.4 **Scheme for manufacture of cellulose acetate**[8,11,13,14,23,24]

cellulose was cotton linters, however, these were expensive and greatly contributed to the increased cost of cellulose acetate plastic compared with that of cellulose nitrate. Wood pulp, a cheaper source of cellulose, was not a viable option as it gave a final product of poor colour and clarity[11] and required extreme conditions to clean up the cellulose[14]. This is one area that has been improved in modern production. It is now possible to use wood pulp as the cellulose raw material, due to improved clean-up procedures, and still be able to produce a transparent product while reducing costs[13].

Once pre-treated the cellulose is then mixed with a slurry of acetic acid, acetic anhydride and sulphuric acid, which must be pre-cooled to allow the temperature rise during acetylation to be controllable[8]. Using glacial acetic acid as a diluent/solvent further controls this temperature increase. Glacial acetic acid is the most common solvent used as it is easily recovered and reused, as acetic anhydride is converted to acetic acid during the reaction[11]. The cellulose acetate product also passes into the glacial acetic acid solution as it is formed, so progression of the reaction can be followed visually, as the white cotton linters slowly become soluble[8].

A second method is also available using methylene chloride as a diluent/solvent. This is used in the Dormagen Process, which was the first continuous reaction process to be developed. It was reported[8] that no temperature rise was apparent during the acetylation reaction. Maintaining the temperature at below 50 °C removed the possibility of a reduction in the molecular weight of the cellulose chains and therefore, minimised the degradation of the cellulose acetate product. The Dormagen Process used sealed, pressurised vessels to reduce the reaction time. The use of pressurised vessels has been continued into modern production, for both the acetic acid and methylene chloride methods.

After acetylation is complete the solution is transferred to the ripening vessel where it is hydrolysed back to the diacetate from the triacetate. The terms diacetate and triacetate are commonly used to describe the level of acetylation in the cellulose acetate. However, degree of substitution or percentage substitution should be used, as these are more accurate. Degree of substitution describes the amount of acetylation by the number of hydroxyl groups which have been replaced per glucose ring. Theoretically, fully acetylated cellulose acetate has a degree of substitution of 3.0, however, this is not experimentally possible and triacetate has a degree of substitution of 2.8 – 2.9 and diacetate has a degree of substitution of 2.2 – 2.5. A second way of

defining the level of acetylation is by using percentage substitution, which is calculated using the following equation:

$$\frac{\text{No. Acetylated groups}}{\text{Total No. available for reaction}} \times 100$$

Equation 1.1

Using this system diacetate is considered to be 54.5 % substituted and triacetate is 62.5 %[13]. Changes in degree of substitution have a dramatic effect on both solubility and physical properties. Triacetate is easily soluble in chloroform but diacetate is soluble in acetone[8]. The physical properties also change, making cellulose acetates with different degrees of substitution suitable for certain applications[13].

It is necessary to hydrolyse back (ripen) rather than acetylate directly to diacetate to ensure a uniform distribution of acetate groups throughout the final product[14]. Ripening is carried out by slowly adding water with 10 % sulphuric acid to the cellulose acetate solution and monitoring the solubility; a reasonable amount of water was suggested as 22.5 % (by weight) of the cellulose used[14]. Once the cellulose acetate becomes soluble in acetone, indicating diacetate had been reached, sodium acetate or a chloride salt, usually magnesium chloride, is added to stop the hydrolysis[13]. The ripening reaction took 65 – 75 h to transform the cellulose acetate from a chloroform soluble triacetate to the acetone soluble diacetate, therefore, sampling and solubility testing was only necessary from about 54 h until completion[8]. The use of dilute acetic acid[21] replaced water in later manufacturing, as it is less reactive and reduced the deterioration of cellulose acetate caused by reduction in molecular weight. With the use of pressurised vessels the ripening process has been reduced to a few hours in modern manufacture[13].

Once the required acetate value is reached, tested by solubility changes, the cellulose acetate has to be precipitated from solution. This is simply done by the addition of copious volumes of water with continuous stirring. Care has to be taken to ensure the cellulose acetate was not in too large lumps or too fine dust[11] as this would have a detrimental effect on further processing (section 1.2.3). The cellulose acetate is then centrifuged and washed with water to remove any free acetic or sulphuric acid. However, some aceto-sulphate esters still remain attached to the cellulose backbone and these are mostly removed in the stabilisation step[8]. The aceto-sulphate

esters are present because sulphuric acid does not act as a true catalyst but takes part in the reaction. A proposed reaction mechanism is shown in figure 1.5.

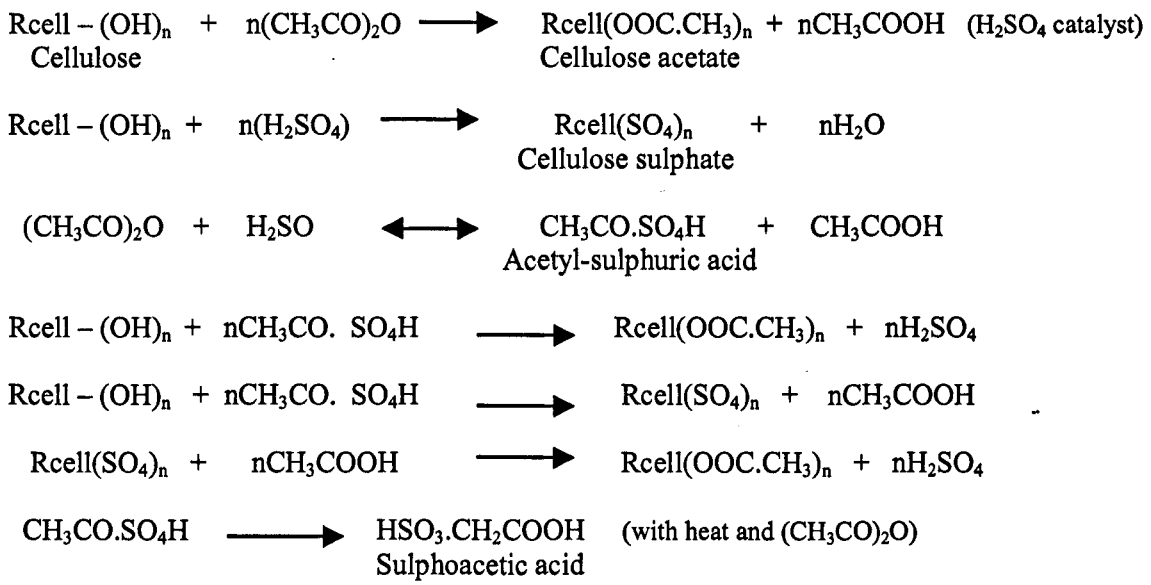


Figure 1.5 Reaction mechanism for sulphuric acid catalyst[25,26]

The cellulose acetate was then stabilised by boiling the water using 'live steam' and adding sulphuric acid to give a maximum total concentration of 0.02 % (V:V). The level of acidity was closely monitored to ensure the final product was of a high standard and acid free. After the mixture had been boiled for 1.5 – 2 h, it was treated with excess cold water. It was then washed until free of any acid[8,14].

Two methods of drying were used, a) on large trays and b) by passing hot air through the cellulose acetate. Care had to be taken not to exceed 100 °C as degradation occurred above this temperature. The final moisture content was usually 2 – 3 %[8,14]. In modern manufacturing the cellulose acetate is dried using the second process.

The final process in producing cellulose acetate flake was to grind and blend the cellulose acetate powder to give a consistent product with the correct flake size and percentage acetate content. As batch-to-batch variation could not be avoided, it was common to blend together up

to 5 tonnes of powder to ensure continuity of cellulose acetate flake quality[8]; this is still common practice today[13]. The whole process can now be carried out within a day due to computer control of pressurised vessels and the use of a continuous flow reaction. However, it is only changes in manufacturing equipment and not the reaction which has improved production time.

1.2.3 Further Processing

The cellulose acetate flake can be further processed in many ways, shown in figure 1.6, to produce a wide range of products. This project will focus on the 3-D objects, which were prepared from moulding powder by means of compression or injection moulding. Unplasticised cellulose acetate is not sufficiently thermoplastic to be manipulated[11]. Hence, the main priority in fabricating moulding powder is the addition of plasticiser, as this transforms the cellulose acetate flake into a workable plastic[16]. Modern cellulose acetate is plasticised with diethyl phthalate[13]. However, in the past, many plasticisers were tried, especially phthalates and phosphates. The use of different plasticisers meant that cellulose acetate with different properties could be produced[21,27,28]. For example, tributyl phosphate produces a tough, solvent-resistant, non-flammable product where as diethyl phthalate produces a water-resistant product.

The second most important part of plastic processing was the introduction of colour. Cellulose acetate offered a wide range of colour in both transparent and opaque effects; this meant that product range could be extended and greatly helped the popularity of the plastic. In general, dyestuffs were used for transparent objects while pigments, often with additional fillers, were used for opaque articles[28]. The range of colours used was almost as varied as the range of plasticisers, with a mixture of organic and inorganic colorants used [29,30]. The colorants had to be added along with a solvent and heating to ensure homogeneity in the final product.

Cellulose acetate can be moulded into 3-D objects by two techniques:

a) compression moulding and
b) injection moulding.

Compression moulding is the older of the two procedures and requires a heating cycle as the mould must be a) heated, to allow the powder to flow into the desired shape, and then b) chilled, before the finished article can be removed. This leads to two main disadvantages: longer production time and products require 'finishing' to give the necessary surface quality[28].

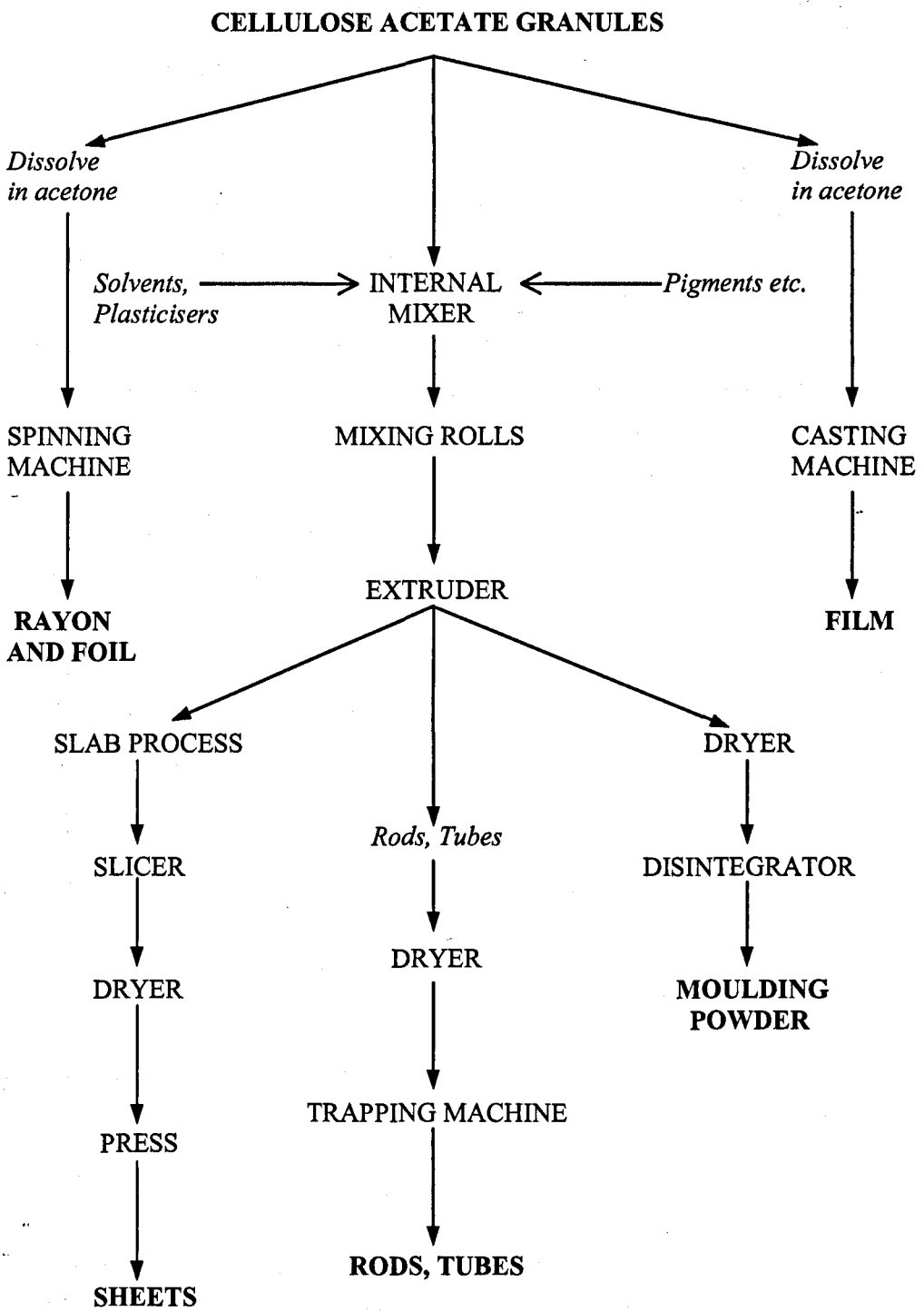


Figure 1.6 **Scheme for manufacture of cellulose acetate plastic products**[8,11,13,14,23,24]

Polishing is necessary to give a uniform surface as the heating and then chilling of the cellulose acetate causes 'flashing' of the surface.

When injection moulding became commercially available in 1926[10], it rapidly replaced compression moulding as the processing technique for cellulose acetate. In this procedure, moulding powder is simply heated in an adjoining cylinder and is injected, once it is free flowing, into the mould through a small nozzle. A new mould is then placed next to the nozzle and the process continues with no change in temperature. The speed of production is greatly increased due to removal of the heating cycle; 120 injection moulding cycles could be achieved per hour[20]. The moulds are also lower cost and lighter than those used for compression moulding, so easier to use. Furthermore, the only finishing required is the removal of the small stalk formed in the nozzle[11,28]. This caused a large reduction in production costs making cellulose acetate a more viable product and replacement for cellulose nitrate.

Cellulose acetate moulding powder with different degrees of substitution were used for certain applications because of the desirable physical properties. Film grade cellulose acetate is 60.5 – 61.5 % acetylated, plastic grade is 52.5 – 56.5 % acetylated and fibre grade is 54.5 % acetylated[13].

1.3 Degradation Processes of Cellulose Acetate

The majority of studies carried out on the degradation processes of cellulose acetate artefacts have been on films[31-39] rather than 3-D objects. However, the few studies on 3-D objects show that the processes are very similar, that is, deacetylation, hydrolysis and plasticiser loss.

1.3.1 Deacetylation

Deacetylation of cellulose triacetate film and 3-D objects have been studied using thermal analysis[31], NMR spectroscopy[40], Raman spectroscopy[41] and GC-MS[42] which show reduced acetate levels in degraded samples. Deacetylation results in acetic acid vapours being present in and around the artefacts (known as the 'vinegar syndrome'[38,43]).

This loss of acetate groups from the polymer has many implications in the degradation of cellulose acetate. It is proposed that the acid vapours released to the atmosphere can cause the 'spread' of what is commonly known as 'Doll's Disease'[41,42], as the acid will catalyse the deacetylation of another as yet undegraded cellulose acetate artefact. It was concluded that the acid-catalysed reaction could also be started by moisture ingress, which reacts with residual sulphuric acid, from manufacturing, trapped within the plastic matrix. Although sulphuric acid is used as a catalyst it actually reacts with the cellulose to form aceto-sulphate esters[8,11,14,44] (figure 1.5) which may not be converted to cellulose acetate during manufacture. The deacetylation reaction then becomes autocatalytic[11], (figure 1.7), because the acetic acid released remains trapped within the plastic matrix as migration to the surface is slow[11]. The trapped acetic acid leads to further problems, as it catalyses hydrolysis of C-O bonds[45] (discussed in section 1.3.2) as well as deacetylation.

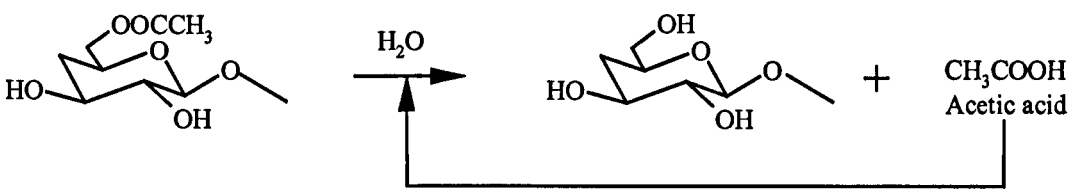


Figure 1.7 Autocatalytic deacetylation of cellulose acetate

NMR studies[40] have shown that the loss of acetate is not random but follows a distinct reactivity order of C_2 then C_6 then C_3, (figure 1.8). This is not expected from basic organic chemistry principles as C_2 and C_3 should have similar reaction rates as both are secondary alcohols and C_6 is primary. This shows that the predominant effect in cellulose acetate chemistry, and especially degradation, is stereochemistry. The stereochemistry of cellulose acetate is linked to the structure of the original cellulose from which it is manufactured. The fibrous structure of cellulose (figure 1.1) means that reactive sites in some areas of the polymer are accessible, whereas others are buried within the fibre structure and, therefore, less available for reaction, hence there is the need for pre-treatment (figure 1.4). The relative reactivity of each of the acetate groups has been studied and defined by Goodlett et al.[46] and was also shown to be C_2, then C_6 and then C_3, however in this study the reaction of C_2 and C_6 was found to be very similar.

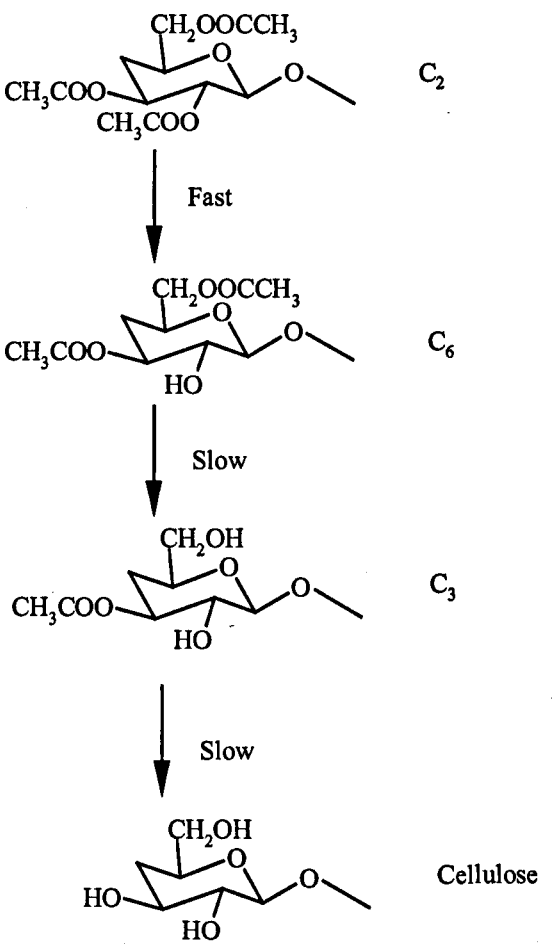
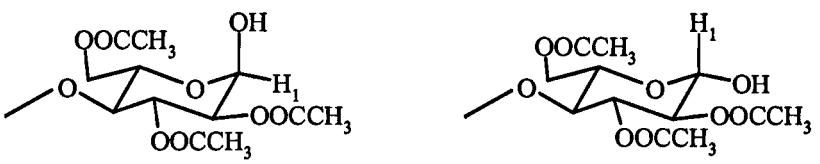


Figure 1.8 **Sequence of acetate loss from cellulose acetate**[40]

1.3.2 Hydrolysis

Hydrolysis causes a reduction in polymer chain length, known as chain scission, with subsequent reduction in polymer strength[45] and rupturing of the object. Chain scission has been observed using spin echo NMR spectroscopy[40]. An alternative technique, gel permeation chromatography (GPC), can be used to observe changes in molecular weight distribution due to shortening of the polymer chain as chain scissioning occurs. However, spin echo NMR spectroscopy detects the α and β anomers of the end groups of the polymer chains, (figure 1.9). As the polymer breaks down more chains are formed and the intensity of these peaks increases proportionally with degradation[40].

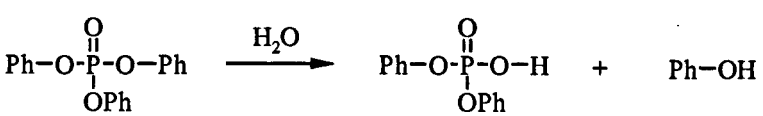


α end group β end group

Figure 1.9 α and β anomers of polymer chain end groups

This is the same as degradation of the original cellulose, which undergoes chain scission in acid environments at the glycosidic link between C_1 and O[45]. It is believed that ultra-violet and possibly visible light can provide the activation energy for chain scissioning[47], although little work has been done on the effect of light on cellulose acetate[48]. Once started, the chain scissioning is catalysed by trapped acetic acid.

It is also believed that the decomposition of plasticiser, especially triphenyl phosphate, accelerates hydrolytic degradation due to the formation of diphenyl phosphate, a strong acid[39] (figure 1.10). This acid also catalyses deacetylation in the same way as acetic acid (figure 1.7). The presence of a second acid increases the rate of hydrolysis and subsequently the rate of degradation.



Diphenyl Phosphate Phenol

Figure 1.10 Decomposition of triphenyl phosphate[42]

The chain scissioning is also not random and tends to occur at the lactone ring. The ring undergoes acid catalysed ring opening between d5 and d6, (figure 1.11), leaving the cellulose acetate backbone prone to chain scissioning.

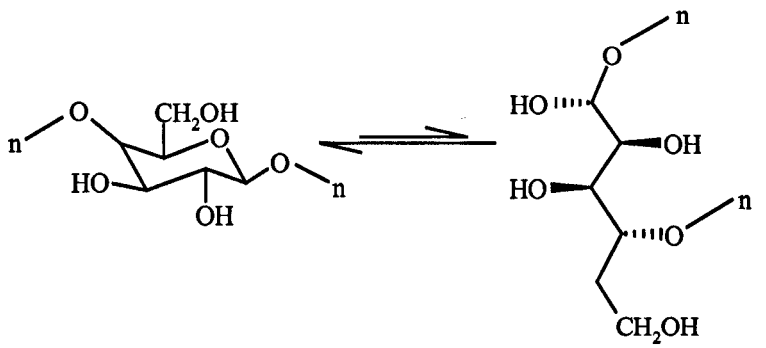


Figure 1.11 Lactone ring opening[49]

The occurrence of chain scissioning then leads to the presence of oxalate in degraded samples, although the mechanism for the formation of oxalic acid is not clear, as was seen in a previous study on cellulose nitrate[50] and also in studies on cellulose acetate film degradation[31,34-37]. The oxalate can be detected by ion chromatography and is a very good indication that degradation via chain scissioning is occurring. .

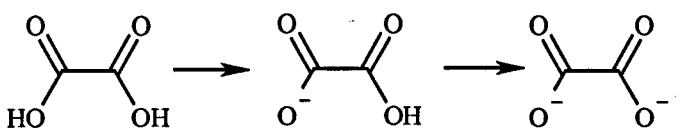


Figure 1.12 Ionic structure of oxalic acid

1.3.3 Plasticiser Loss

Plasticiser loss is a major factor in the degradation of cellulose acetate artefacts, even although the polymer is not directly affected. This is due to the fact that to enable cellulose acetate to be used as a mouldable plastic, 20 – 40 % plasticiser by weight must be added[42]. Therefore, when it is lost, the plastic artefact changes dramatically.

Plasticiser loss has two major effects.

a) The surface becomes sticky and unpleasant to touch[38]. This is especially detrimental as many cellulose acetate artefacts are meant to be held and touched, e.g. steering wheels and tool handles[13,15].
b) The loss of plasticiser causes the plastic to become brittle and more susceptible to physical damage[41].

It is thought that plasticiser loss occurs after deacetylation of the polymer. This is because plasticiser will become insoluble in the polymer, as changes due to degradation occur, and will migrate to the surface of the artefact[41]. It is, therefore, assumed to be a final stage of degradation. This was shown in a study of a Gabo sculpture[47] when it was noticed that a vinegar odour, i.e. deacetylation, was detected five years before an oily substance, i.e. plasticiser, appeared on the surface.

In general, plasticiser loss can be considered an indication that degradation has started and most probably is well advanced. Therefore, it is important to find an 'early warning system' to allow conservators to identify problematic artefacts before visible signs of degradation appear. This will allow the artefacts to be preserved and degradation to be minimised by keeping susceptible ones in a closely monitored, isolated environment.

1.4 Recent work

The majority of recent work on cellulose acetate degradation has been to try to encourage biodegradation by the use of enzymes and composting. This is an attempt to find a solution to the solid-waste problem being encountered in many areas of the world[51]. In theory, secondary cellulose acetate (53 – 56 % acetyl groups) should be biodegradable although very slowly, so ways of speeding up this mechanism have been investigated. One such study by Ach[52] showed that the replacement of traditional plasticisers with specific esters and other low molecular weight components quickened biodegradation to only a few years, which is comparable to oak leaves. Another study[53] looked at 'normal' cellulose acetate films added to *in vitro* enrichments or suspended in a wastewater treatment system. It was shown that > 80 % of the cellulose acetate degraded in 4 – 5 days. Other studies have used radiolabelled cellulose acetate to study biodegradation[54] and citrate esters as plasticisers to enhance biodegradation[55]. Further studies

established a link between the degree of substitution and biodegradability, with lower degrees of substitution showing far easier and quicker biodegradation[51,56]. The future of cellulose acetate as a working plastic for both films and 3-D objects is bright as it was shown to be one of the best plastics for biodegradation[57,58] and with increased thought for environmental issues the interest in eco-friendly plastics will increase.

The nuclear industry[59] is also interested in the degradation products of cellulose acetate as it is thought that these short chain acids can form complex radionuclides with nuclear waste products. Therefore, a study was carried out using capillary electrophoresis as this technique can separate compounds without prior knowledge of the chemical structure.

Another major area of interest is in the storage and degradation of cellulose acetate motion picture films which are waiting for copying to more stable media. C. Tumosa at the Smithsonian Institute, Washington D. C., has carried out a study of the use of deep freeze storage[60]. It was found that storage in freezers had no ill effects on the samples, even after 500 cycles of freezing and defrosting. A separate study by Jacobsen[38] investigated many factors involved in storage such as the use of bags, scavengers, temperature and relative humidity. There has also been work carried out on early warning systems to detect degradation such as the acid indicator developed by Harthan et al.[36]. Work by Allen et al.[37,61] has investigated the causes of degradation and also how to predict the stability of the films. They discovered that there was a link between moisture regain, acidity and degradation in both natural and accelerated ageing conditions. It was shown that plasticiser helped to stabilise the films and that metal storage containers, usually iron, accelerated degradation. A lifetime of 35 years was predicted for the majority of films, allowing time for copying.

Many reviews of cellulose acetate and other plastic artefacts have been carried out in museums to try to assess the best course of action for future preservation. Three overviews by Quye[62], Williamson[1] and Fenn[63] all concluded that constant monitoring was required as no exact predictions of stability could be made; the need for further knowledge and understanding was also voiced. E. Then[64] and Y. Shashoua[2] suggest an in-depth survey for the continual observation of plastic artefacts and the grading of the condition of individual pieces. Song et al.[65] have carried out a review of prediction methods and concluded that different techniques were required for crystalline, amorphous and rubbery polymers. Allen et al.[66] have produced an

overview of ageing and stabilisation of filled polymers which studies all aspects of interactions within the polymer matrix and shows various connections between additives and relative stability.

There have been other studies on the effect of plasticisers used in cellulose acetate production. These included looking at the type and level of plasticiser used and a direct link was observed between plasticiser levels and water adsorption and the resultant effect on degradation in cellulose acetate plastics[67,68]. Both studies showed that plasticiser helped to prevent water ingress and subsequent degradation. A separate study at the University of Derby[42] showed a link between phosphate plasticiser and autocatalytic degradation.

Two groups, one on films[69] and one on dolls[41], have also studied 'The Vinegar Syndrome'. These studies both showed that the acetic acid released by degrading cellulose acetate had a detrimental effect on other artefacts in close proximity. This leads to degradation rapidly spreading throughout an entire collection. The study on films also investigated the use of molecular sieves to help prevent the acid induced degradation, this was found to improve the stability of films. It was also shown that the sieves would have a lifetime of 30 – 40 years, which is comparable to the lifetime of the cellulose acetate film[61].

There is also work being carried out to improve the synthesis of cellulose acetate as it will hopefully become an important biodegradable plastic of the future. These studies have been investigating homogeneous solutions[70], different starting materials[71] and the use of NMR to evaluate three synthesis routes[72].

The final part of recent work has been involved in raising the image of not only cellulose acetate but plastics in general and disseminating information about plastics conservation and treatment, within research circles and to the general public. The "Classic Plastics Clinic" which was held at The Royal Museum, Edinburgh, from 2nd – 3rd April 1997, and the book (Plastics Collecting and Conserving)[73] published after the event helped to reach a wide range of people. This event allowed members of the public to bring along their plastic objects and have them identified and subsequently be given information on the appropriate care of the objects. The triennial ICOM conferences also help to spread the knowledge and understanding of modern materials and the past two conferences have had papers presented on many plastics and their conservation[74,75].

The book "Saving the 20th Century"[76] also deals with modern materials and helps to spread information on many topics between scientists and also to the general public.

1.5 Aims

The aims of this project can be divided into three main areas.

a) To investigate the degradation procedures and pathways that are occurring in 3-D cellulose acetate artefacts.
b) To identify important features of the chemical composition of the plastic, which hinder or accelerate degradation. Sulphate levels and zinc oxide were found to be important in a previous study of cellulose nitrate[50].
c) To find the best conditions for storage and display of cellulose acetate artefacts.

The degradation of cellulose acetate has been monitored using various analytical techniques. Micro-Fourier Transform Infrared (FTIR) spectroscopy was used to identify the plastic as well as monitoring the loss of acetate groups and plasticiser from degrading artefacts.

Ion chromatography was used to investigate the presence of acetate, formate, chloride, nitrate, sulphate and oxalate in the plastic. An increase in acetate levels indicates that deacetylation is occurring, oxalate shows chain scission is involved in ageing and formate is produced by oxidative degradation. Chloride and sulphate are anions present due to residual chemicals from the manufacturing process, as chloride salts are often used to stop acetylation, while sulphuric acid is the most common catalyst used. Higher nitrate concentrations may indicate the use of a cellulose acetate – cellulose nitrate mixture[12] to give desired colour effects.

The presence of metals was investigated using X-ray fluorescence spectroscopy as a previous study on cellulose nitrate[50] showed that zinc oxide fillers acted as a buffer and helped to slow down or prevent degradation. Gel permeation chromatography has been used to study any change in molecular weight distribution of the polymer, indicating that chain scissioning is occurring. Thermogravimetric analysis has been used as a stand-alone technique and also coupled to FTIR to investigate what is lost to the atmosphere on heating of both degraded and undegraded samples. Headspace gas chromatography has been used to further investigate the atmosphere around the samples as degradation occurs. It is thought that the most common vapours released from the samples will be acetate and plasticiser, probably phthalates.

In this study naturally aged samples have been studied as well as accelerated aged samples. The samples were aged by using elevated temperatures and various relative humidities. The samples were aged for extended periods of time and samples were regularly taken for analysis.

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CHAPTER 2

TECHNIQUES AND PROCEDURES

2 Techniques and Procedures

2.1 Fourier Transform Infrared (FTIR) Spectroscopy

Micro-FTIR spectroscopy is a very useful technique for identifying the components of the base polymer of any plastic artefact. It has found many applications in industry and research in recent years, as an efficient tool for studying the chemical ageing of polymers[1,2], but is especially useful with museum collections as the microscopic sample removed means there is minimal damage to the artefact. The sample can be as small as 100 μm^2,[3] so with careful sampling this will be difficult to notice even on close inspection of the artefact.

In this study, micro-FTIR spectroscopy proved to be a useful technique for monitoring the ratio of acetate to hydroxyl groups present on the cellulose backbone structure of plastic cellulose acetate artefacts.

2.1.1 Principles of FTIR Spectroscopy[4-8]

The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to the microwave region. The wavelengths of infrared radiation fall in the range 0.1 to 500 μm or 14000 to 20 cm^{-1}. For infrared spectroscopic applications the mid infrared region from 4000 to 200 cm^{-1} is generally used.

Molecules absorb radiation when the natural molecular vibration has the same frequency as the incident radiation energy. The vibration of the molecule must have associated with it an alternating electric field, i.e. the vibration must have a changing dipole moment coupled with its motion. The atoms comprising a molecule can vibrate in several ways. Infrared spectrometry involves examination of the stretching, twisting, bending and rotational motions in a molecule. The possible vibrational modes of a methylene group are shown in figure 2.1. The rate at which these component atoms vibrate is quantised and can only take place at a well defined frequency. As a wide range of vibrations occur simultaneously, a highly complex absorption spectrum that is uniquely characteristic of a molecule is produced. The infrared spectrum of a compound is,

therefore, the superposition of absorption bands of specific functional groups which interact with the surrounding atoms of the molecule.

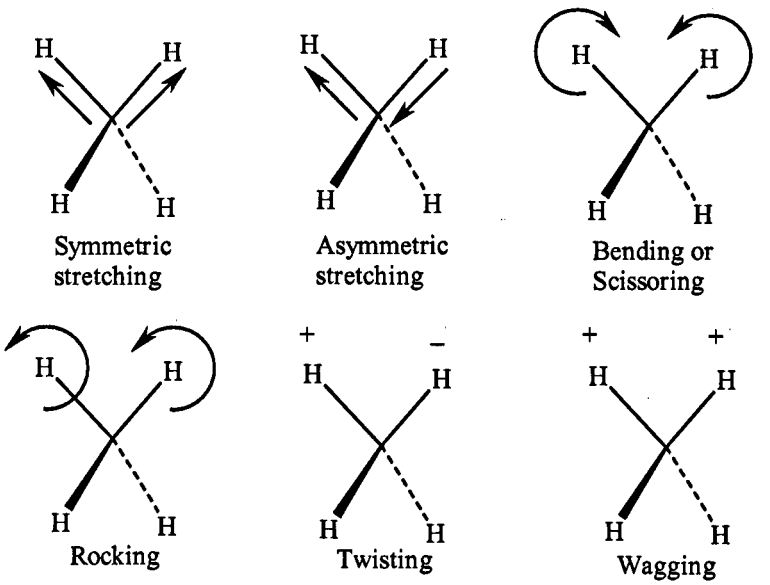

Figure 2.1 Localised vibrations of a methylene group

The goal of infrared spectroscopic applications is to determine the chemical functional groups contained in a particular material. Each functional group absorbs uniquely characteristic frequencies of infrared radiation. Thus, a plot of radiation intensity versus frequency (the infrared spectrum) fingerprints the identifiable chemical groups in the sample.

The FTIR spectrometer consists of three basic components

a) a source,
b) a Michelson interferometer and
c) a detector.

The Michelson interferometer consists of a beamsplitter, a fixed mirror and a moving mirror. Figure 2.2 shows a simplified schematic diagram of the FTIR spectrometer.

Collimated radiation from the broadband infrared source, A, is directed into the interferometer and impinges on the beamsplitter, B (e.g. a very thin film of germanium). The beamsplitter splits the incoming beam into two beams of equal energy. Approximately 50 % of the light is

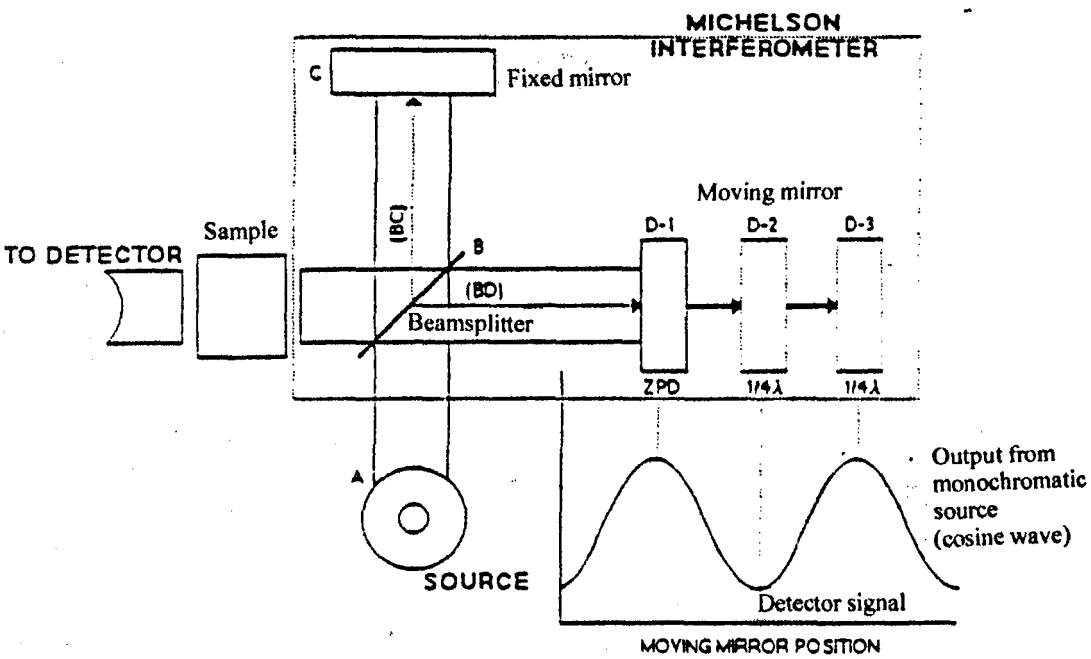

Figure 2.2 **Schematic diagram of an FTIR spectrometer**

transmitted through the film and is directed onto the moving mirror, D. The other 50 % is directed to the fixed mirror, C. The beams reflect off the surfaces of the two mirrors and recombine at the beamsplitter. Here constructive and destructive interference occur, depending on the position of the moving mirror relative to the fixed mirror. The resulting beam passes through the sample where selective absorption takes place, and then continues to the detector.

When the position of the moving mirror, D, is such that the distance between the beamsplitter and the mirror, BD, is exactly the same as the distance between the beamsplitter and the fixed mirror, BC, the two reflected beams pass through exactly the same path length and consequently, are totally in phase with each other. As a result, the two beams interfere constructively and the detector observes a maximum signal intensity. The position of the moving mirror is called the Zero Path Difference, or ZPD.

As the mirror moves away from the ZPD, the distance BD increases relative to the fixed distance BC. When the distance between the beamsplitter and the moving mirror, BD, is ¼ of the wavelength of light, being observed, longer than the distance BC, the total optical path (beamsplitter-mirror-beamsplitter) difference between the two beams is ½ wavelength. The two beams are now 180 degrees out of phase with each other and, at this point in the scan, interfere with each other destructively, causing a minimum in the detector response. With each ¼ wavelength displacement, this pattern of constructive and destructive interference repeats itself. Since data sampling occurs continuously, a cosine wave results.

The detector signal is sampled at precise intervals during the mirror scan. Both the sampling rate and the mirror velocity are controlled by the reference signal which is produced by modulation of the beam from the helium-neon (HeNe) laser. The resulting signal is known as an interferogram and contains all the information required to reconstruct the spectrum via the mathematical process known as the Fourier transformation.

FTIR is a slightly more advanced method of recording an infrared spectrum compared with conventional dispersive spectrometers. FTIR spectrometers have a number of inherent features which lead to this advantage over dispersive instruments. They are mechanically simple and have only one moving component (the moving mirror) which results in little system wear and high reliability. All frequencies are viewed simultaneously (Felgett's advantage), producing a

spectrum in as little as one second. Combining many scans, therefore, also increases the sensitivity, as signal-to-noise ratio is directly proportional to the square root of the number of scans taken. There is greater optical throughput (Jaquinot's advantage), as there are no slits in the interferometer to define resolution or limit the amount of energy reaching the detector. The use of an internal HeNe laser to monitor the position of the moving mirror within the scan provides an internal wavelength calibration standard since the wavelength of the HeNe laser is accurately known (Conne's advantage). Finally, as the data is in digital form, software packages can be used to manipulate and examine spectra.

The two most common detectors used for FTIR spectroscopy are deuterium triglycine sulphate (DTGS) and mercury cadmium telluride (MCT). The DTGS detector is a pyroelectric detector which uses ferroelectric materials operating below their Curie point temperatures. When the infrared radiation is incident on the detector, there is a change in polarisation which can be employed to produce an electric signal. MCT detectors are more sensitive and rely on quantum interactions between the incident photons and semiconductor. The detector generates a small voltage when exposed to radiation that can be electronically processed. DTGS detectors operate at room temperature while MCT detectors are cooled to liquid nitrogen temperatures.

2.1.2 Instrumentation

Infrared analysis of very small samples poses considerable difficulties, yet there is a common requirement for the analysis of samples as small as 25 μm in diameter, such as fibres or contaminants in heterogeneous mixtures. This problem can be overcome by the use of a microscope attachment to an FTIR spectrometer. As very small sample sizes can be used, this technique is very applicable to conservation work, where only limited sample is often available.

A schematic diagram of a typical FTIR microscope is shown in figure 2.3. Most IR microscopes are based on conventional optical microscopes but with the addition of a high quality reflection (Cassegrainian) objective lens capable of imaging both the IR beam and an optical source. The transfer optics takes the IR beam from the interferometer to a sensitive detector (usually MCT).

The measured area of the sample must be strictly delimited so that the IR beam is only focused on the area of interest. The limit on sample size that can be analysed by micro-FTIR

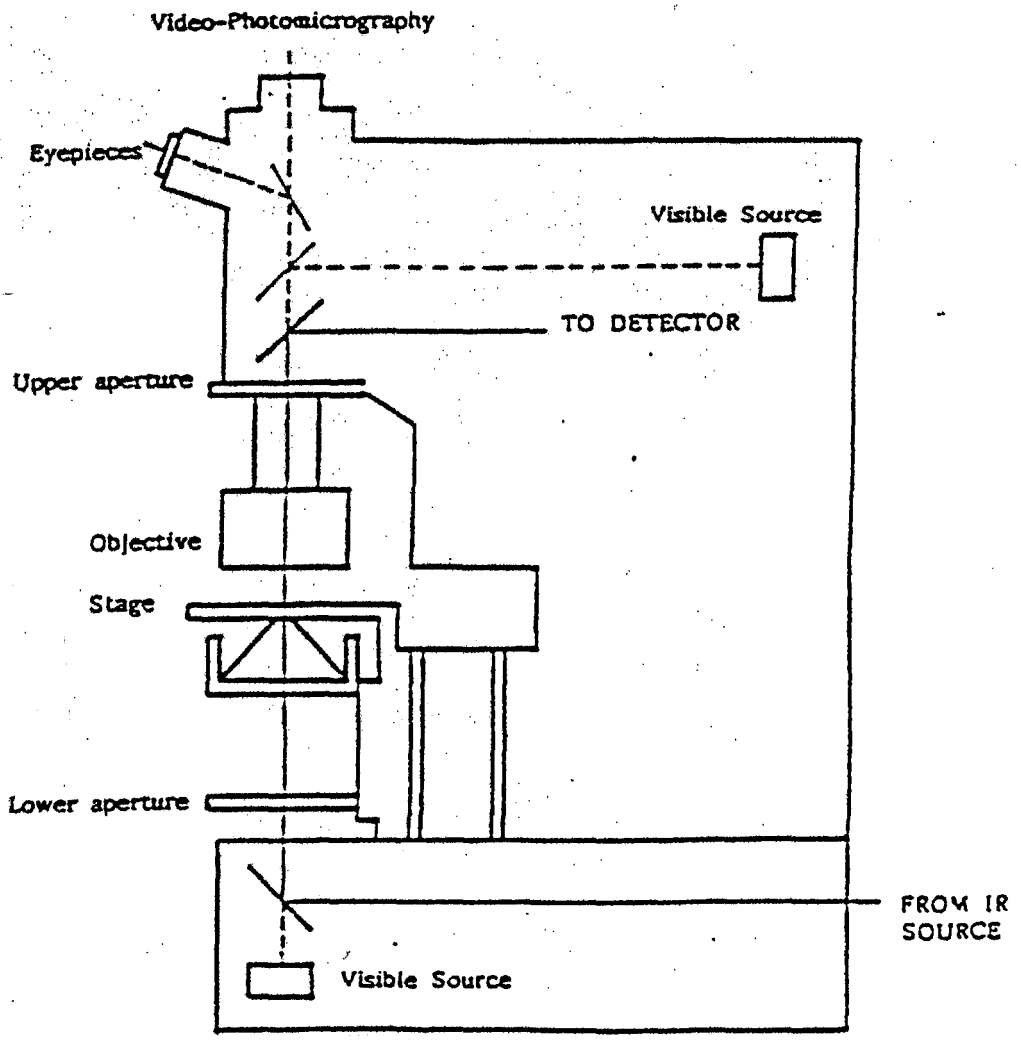

Figure 2.3 Schematic diagram of an FTIR microscope in transmission mode[1]

spectroscopy is essentially that of the diffraction of IR radiation. As the size of the sample approaches the radiation wavelength, some of the IR energy is bent around the defined area, resulting in a blurring of the image and the detector receiving spectral information from outside the area of interest. This results in flat-bottomed peaks which cannot be used for further analysis.

As well as the analysis of small samples, microscope attachments present other advantages. Relatively simple sample preparation is needed, the sample needs only to be crushed or microtomed so that the thickness is around 25 – 30 μm, then placed on the microscope stage. The surface of a sample can also be scanned using eyepieces so that specific areas of interest can be analysed.

In this study, an MCTA Nic-Plan microscope was used, coupled to a Nicolet 510P spectrometer. The microscope was fitted with three objective lenses; the first is a 10X optical objective which is used initially to focus and centre the sample. The other two lenses are the infrared objectives, one is for transmission and one for reflectance. A Cassegrainian Reflechromat objective lens (SpectraTech) with 15X magnification is used for transmission or reflectance spectra and a zinc selenide (ZnSe) ATR (attenuated total reflection) objective lens (SpectraTech) with 25X magnification is used for reflectance spectra only. Each spectrum was collected with 128 scans over the wavenumber range 4000 – 650 cm^{-1} with a resolution of 4 cm^{-1}, for both modes.

Attenuation total reflection (ATR) or internal reflection is an established method for infrared analysis, which is useful in studying the surface degradation of polymers[9]. Fahrenfort invented the ATR method in 1961. Light or infrared radiation exiting from a transparent medium such as ZnSe is partially reflected back into the medium, if the angle of incidence is sufficiently large, where it will be totally internally reflected. However, when a sample is placed in contact with the ZnSe the totally internally reflected radiation will be partially absorbed by the substance. This occurs because the radiation passes a short distance into the less dense substance as an 'evanescent wave'. Since the passage through the sample is small, the absorption is much less than for a transmittance measurement through even a thin film[10].

2.1.3 Sample Preparation

For measurement of a transmission spectrum, < 1 mg was removed from the artefact of interest using a scalpel and flattened between two diamond windows (SpectraTech μ-sample plan, figure 2.4). The ideal thickness of a sample was considered to be 25 – 30 μm by literature[3], however this was impossible to measure. One diamond window was removed leaving the sample in place on the second window, which was then placed on the microscope stage.

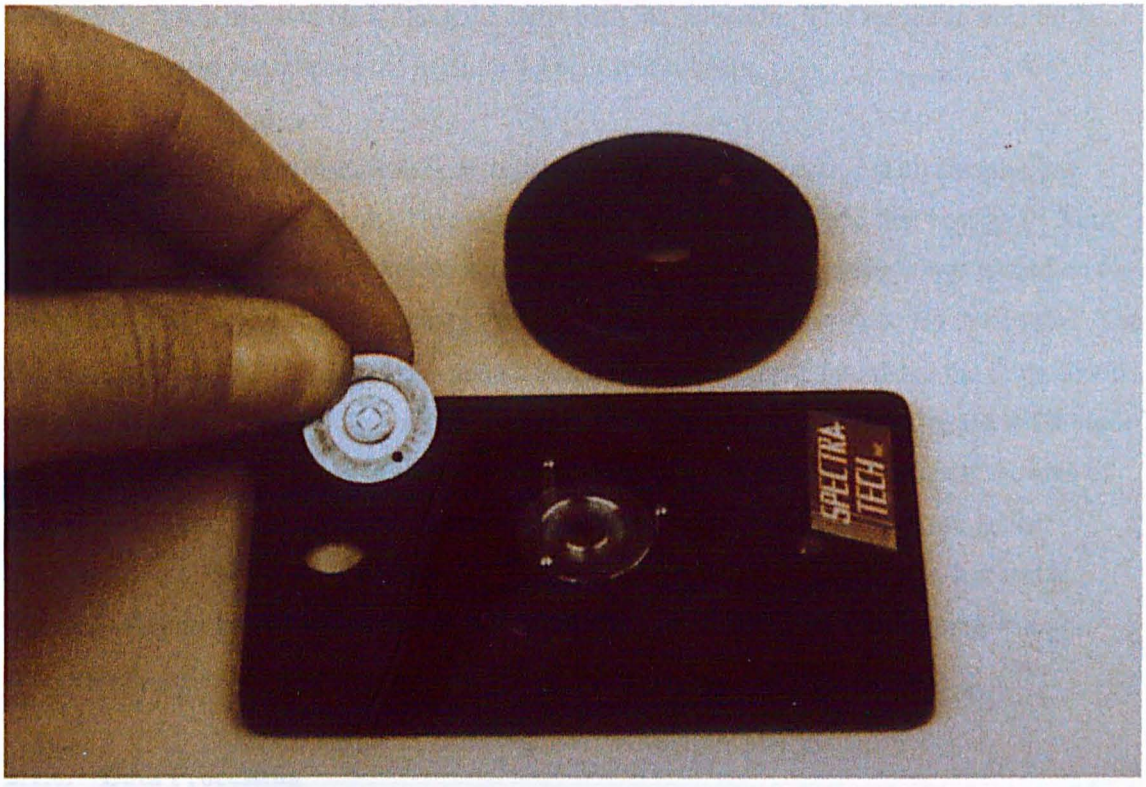

Figure 2.4 Photograph of SpectraTech μ-sample plan diamond windows

The sample image was brought into focus using the optical 10X objective lens and centred using the cross-wires. The objective lens was then switched to the Cassegrainian lens and either pinhole (1.5 mm) or adjustable knife-edge apertures were used to focus the beam onto the condenser by delimiting the area of interest to between 100 μm^2 and 40 μm^2. The visible beam was switched to an IR beam and the spectrum were recorded.

The reflectance mode was used to identify the plasticiser present in the artefacts. A dichloromethane swab was wiped across the surface of the sample (area 2 cm X 2 cm approximately) until the entire residue had been removed. The swab was then extracted into 2 mL of dichloromethane and this was blown down with nitrogen to a concentrated drop. The drop was transferred to a clean gold reflectance mirror and allowed to evaporate. The gold reflectance mirror was then placed on the microscope stage and the procedure followed as for the transmission mode (only one pinhole aperture (2.5 mm) was necessary as the condenser is redundant in reflectance mode). A larger aperture was used than for transmission IR due to the need for the beam to travel back along the same path for detection. This results in only 50 % of the detection power and hence the need for a larger initial beam.

No sample preparation is required for measurements by ATR, however, not all samples are suitable for this type of analysis. The sample must be reasonably flat and thin enough (< 3 cm thick) to fit between the objective lens and the microscope stage. The sample was placed on the microscope stage and brought up, using the coarse focus, until it almost touched the crystal. The objective lens was then placed in the contact mode and contact made by raising the stage slowly, using the fine focus, until an 'oil effect' was observed. The lens was switched to the ATR mode and the spectrum recorded. A pinhole aperture (2.5 mm) was again used to delimit the area of interest to 100 μm^2; a larger aperture was used than for transmission IR due to the greater magnification of the ATR objective. The stage was lowered so that contact was lost and a background spectrum recorded. When necessary the crystal was cleaned by wiping with the ATR cleaning cloth (SpectraTech).

2.1.4 Data Processing

The initial data from the FTIR output is in the form of a single beam spectrum. In order to obtain the standard transmittance spectrum for the sample, this single beam spectrum is ratioed against a background spectrum. The background is usually a single beam spectrum collected with no sample in the holder. Transmittance (T) is defined as:

$$T = \left(\frac{I_s}{I_o}\right)_\nu$$

Equation 2.1

where I_s is the instrument response function (single beam spectrum) with the sample,

I_o is the instrument response function without the sample, and

ν is frequency.

If the instrument response is identical with and without the sample, the transmittance value will be one. If the sample absorbs light, less energy reaches the detector and the transmittance value is less then one. If the sample is totally absorbing, no energy passes to the detector and the transmittance value is zero. Most systems multiply the transmittance value by 100, defining percentage transmittance.

For quantitative analysis it is necessary to convert from percentage transmittance spectrum to absorbance, where the Beer-Lambert law (equation 2.2) states that a linear relationship exists between the measured absorbance (A) and the concentration of a sample.

$$A = \log_{10}\left(\frac{1}{T}\right) = abc$$

Equation 2.2

Where a is the absorptivity of the sample,

b is the internal path length of the sample cell, and

c is the concentration of the analyte.

As a and b are constant, A is proportional to c.

When a compound has a strong, well-defined absorption band, the magnitude of the absorbance of the peak can be calculated. By comparison with the absorbance of a standard or series of standards of known concentrations, it is possible to calculate the unknown concentration of the compound under investigation.

Often with IR spectroscopy it is not desirable to create a calibration curve from known standards, internal or external, as high errors are introduced. Quantitative analysis can be improved by establishing the blank or background absorbance in the vicinity of the band of interest and constructing a baseline for all samples (figure 2.5). The baseline absorbance is measured at the point where a perpendicular line from the peak maximum intersects the baseline. This absorbance is subtracted from the peak absorbance. Using the baseline correction method,

all measurements are made at points defined by the spectrum itself, i.e. there is no dependence on wavelength. Changes in the instrument sensitivity or optical set-up are also eliminated.

2.1.5 Sampling and Analysis Errors

The errors involved in FTIR analysis can be split into two areas, instrumental error and sampling error. Sampling error can be further sub-divided: choosing a spot for measurement of a spectrum; and physically sampling with the scalpel from the specimen. Errors from each were calculated through a set of experiments.

Experiment A involved recording ten spectra from the same spot on a sample, after it had been flattened between two diamond windows and analysed on one window only, refocusing the microscope between each spectral collection to give the instrumental error. Experiment B involved the recording of ten spectra from different areas of the same sample on a single diamond window (after flattening), giving the first sampling error. Experiment C involved the recording of ten spectra from different samples from the same specimen, giving the second sampling error.

Using equation 2.3 – 2.5 each individual error can be calculated.

$$S_A^2 = S_I^2$$

Equation 2.3

$$S_B^2 = S_I^2 + S_{Spot}^2$$

Equation 2.4

$$S_C^2 = S_I^2 + S_{Spot}^2 + S_{Scalpel}^2$$

Equation 2.5

Where s^2_A is the standard deviation from experiment A

s^2_B is the standard deviation form experiment B

s^2_C is the standard deviation from experiment C

s^2_I is the instrumental error

s^2_{spot} is the sampling error due to selection of area for analysis

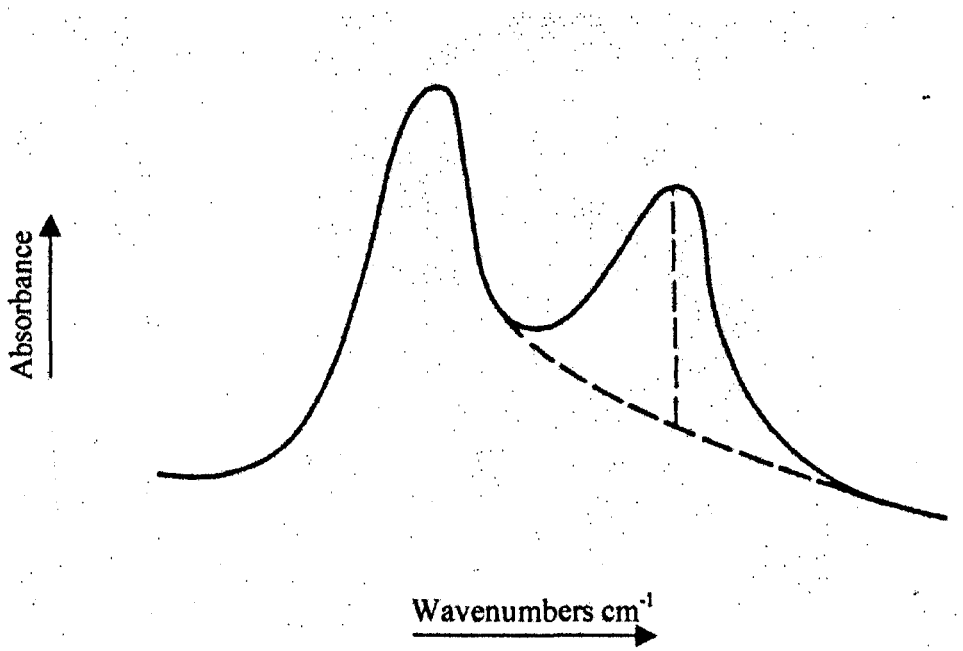

Figure 2.5 **Construction of baseline correction for quantitative analysis**

$s^2_{scalpel}$ is the sampling error due to physical sampling

Therefore, instrumental error is given by equation 2.3, sampling error due to choosing the exact spot for spectra recording is given by equation 2.6 and sampling error due to physical removal of the sample with the scalpel is give by equation 2.7.

$$\text{Spot error} = \sqrt{\left(s_B^2 - s_A^2\right)}$$

Equation 2.6

$$\text{Scalpel error} = \sqrt{\left(s_C^2 - s_B^2\right)}$$

Equation 2.7

These errors were calculated for each of the five spectral features studied and the results are shown in table 2.1. It can be seen that the greatest error was found in the cm^{-1} position of the O-H peak; this is probably due to the broad nature of this peak leading to no distinct maximum. The instrumental error was in general very small showing that the spectrometer was stable. The error associated with the selection of the sampling spot was also small even although this was heavily reliant on the operator. Physical removal of the sample from the specimen introduced the largest error, but in general the errors are very small and show that the sampling technique used can be considered an accurate method for analysing cellulose acetate artefacts.

Table 2.1 %RSD errors calculated for measurement of spectra of samples by FTIR Spectrometry

Parameter	Instrumental error	Spot error	Scalpel error
O-H peak position	0.36	1.06	0.74
C=O peak position	0.09	0.06	0.05
C-H peak position	0.04	0.008	0.28
O-H:C-H	3.14	4.78	31.9
C=O:C-H	0.72	1.38	5.6

The precision of this technique was greatly helped by careful sampling. It was very important to be sure that an area, which was representative of the degradation of the whole sample, was chosen.

2.2 Ion Chromatography (IC)

Ion chromatography was used to investigate if any anions were present on the surface or within the matrix of the cellulose acetate artefacts. The presence of acetate, formate, chloride, nitrate, sulphate and oxalate in the plastic was investigated. An increase in acetate levels indicates that deacetylation is occurring, oxalate shows chain scission is involved in ageing and formate is produced by oxidative degradation. Chloride and sulphate are present due to residual chemicals from the manufacturing process, as chloride salts are often used to stop acetylation, while sulphuric acid is the most common catalyst used[11]. Higher nitrate concentrations may indicate the use of a cellulose acetate – cellulose nitrate mixture to give desired colour effects[12].

2.2.1 Principles of Ion Chromatography[13-16]

Ion chromatography is a term used to describe the analysis of dissolved ions by ion exchange chromatography, using HPLC equipment. The technique, therefore, follows the principles of ion exchange chromatography. Separation of ionic materials is achieved by passage of a solution through a column consisting of an ion exchanger or stationary phase. This stationary phase consists of porous resinous material containing fixed charge-bearing functional groups and oppositely charged mobile counter ions. Transport of analytes through the column is performed by an eluent. The analytes are separated due to variation in affinity for the stationary phase, with components of lowest affinity eluted first.

The primary process of ion exchange chromatography involves interaction of charged ionic materials in the sample, in the mobile phase, with permanently charged counter ions on the stationary phase. This interaction between the sample and the stationary phase is an equilibrium process. For example, the exchange between a resin initially with acidic hydrogen attached and a solution containing K^+ ions, can be written as:

$$\text{Resin-}H^+ + K^+ \leftrightarrow \text{Resin-}K^+ + H^+$$

If the affinity of the resin for K^+ is greater than for H^+ then exchange will take place.

The equilibrium constant or selectivity coefficient $K_{K/H}$ can also be determined:

$$K_{K/H} = \frac{[K^+]_R[H^+]}{[H^+]_R[K^+]}$$

Equation 2.8

where $[K^+]_R$ and $[H^+]_R$ are the equilibrium concentrations of the ions within the resin structure and $[K^+]$ and $[H^+]$ are the equilibrium concentrations in the mobile phase. The ion exchange constant is taken as being a quantitative characterisation of the possibility of exchange between the ion exchanger and certain ions contained in the sample. If $K_{K/H} > 1$ then H^+ ions present in the solution have a greater affinity for the stationary phase than K^+. If $K_{K/H}$ is equal to 1 then both ions have identical affinities for the stationary phase.

The affinity of ions for the stationary phase determines the retention times of the analytes and is governed by the physical properties of the ions. The stationary phase has a greater affinity, (hence longer retention time) for

a) an ion with higher charge or valency,
b) an ion with a smaller ionic radius in the hydrated state and
c) the ion with the greater polarisability.

The partitioning of each ion between the stationary and mobile phase can be defined by the concentration distribution ratio, D_C:

$$(D_C)_K = \frac{[K^+]_R}{[K^+]}$$

Equation 2.9

by combining equation 2.8 and equation 2.9 we get:

$$(D_C)_K = K_{K/H}\frac{[H^+]_R}{[H^+]}$$

Equation 2.10

The larger the value of D_C, the slower the progress of the solute through the system and hence, analytes in a solution will elute from the column in order of increasing values of D_C.

2.2.2 Chromatographic Parameters

A number of quantitative measurements can be made to describe the quality of a chromatographic separation. As well as being able to state where on chromatograms solute peaks are eluted, it is necessary to determine whether or not solutes are separated from one another and if so, how efficiently.

Figure 2.6 shows a typical chromatogram for a solution containing three components and the parameters used to characterise the peaks. The total retention time of an ion is related to its distribution coefficient by the retention volume, equation 2.11.

$$V_R = D_C V_S + V_O$$

Equation 2.11

Where V_R = the eluent volume required for the total removal of a component from the column

D_C = the distribution coefficient

V_S = the volume of the ion exchanger

V_O = the dead volume of the chromatographic system

2.2.2.1 Selectivity

Although a peak in a chromatogram can be identified by its retention time, this varies with column length and mobile phase flow rate. Peaks are commonly identified using the capacity factor, k' which is directly proportional to D_C but takes account of the volume of each component. For component A in figure 2.6,

$$k'_A = \frac{t_{RA} - t_O}{t_O} = \frac{V_A - V_O}{V_O}$$

Equation 2.12

If k' = 0, then the solute is eluted without being retained by the stationary phase. To achieve separation of analytes during chromatography it is necessary that the resin takes them up in

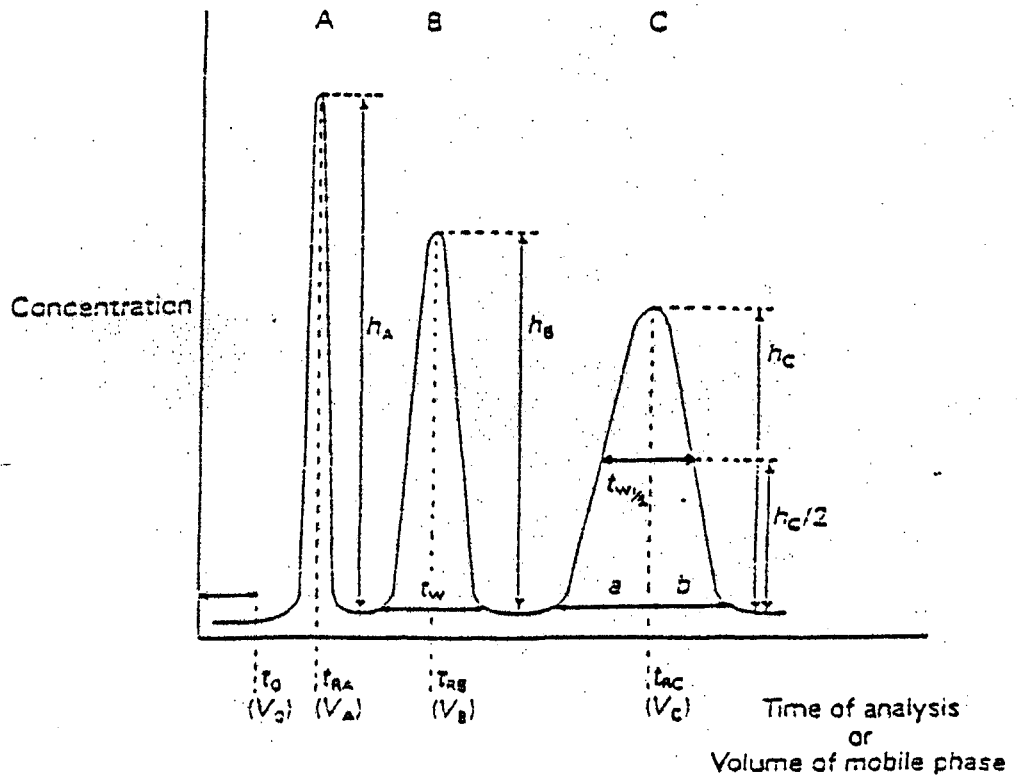

Figure 2.6 Typical chromatographic separation[18]

t_o = time for solvent or mobile phase to pass through the system

t_{RA} = retention time of component A, that is the time for A to pass through the system; V_A is the retention volume

t_{RB} = retention time of B, V_B = retention volume

t_{RC} = retention time of C, V_C = retention volume

h = peak height, h_A for component A, h_B for B, h_C for C

t_w = width at the base of peak

$t_{w½}$ = width of peak at half height

distinct preferences. Selectivity describes the separation of two peaks relative to each other in a chromatogram and is defined by the selectivity or separation factor ($\alpha_{A/B}$).

$$\alpha_{A/B} = \frac{k'_B}{k'_A} = \frac{(D_C)_B}{(D_C)_A}$$

Equation 2.13

2.2.2.2 Resolution

The resolution, R_S, is a measure of the degree to which peaks in a chromatogram are resolved or separated. R_S for component A in figure 2.6 is defined by equation 2.14:

$$R_S = \frac{t_{RB} - t_{RA}}{0.5(t_{WA} + t_{WB})}$$

Equation 2.14

For peaks to be completely resolved at the baseline, a value of $R_S \geq 1.5$ is required. If the resolution is significantly greater than 1.5, the longer elution time would be undesirable due to longer run times, and in practice a compromise is obtained.

2.2.2.3 Efficiency

The efficiency of a chromatographic column is a measure of the narrowness of a peak. To separate the components, it is necessary that they do not spread out in the column and overlap one another. The unit in which the efficiency of a chromatographic column is expressed is the theoretical plate, N. The total number for a column is calculated using one of the alternate equations:

$$N = 16\left(\frac{t_R}{w}\right)^2$$

Equation 2.15

$$N = 5.54\left(\frac{t_R}{w_{1/2}}\right)^2$$

Equation 2.16

where w is the width of the peak at baseline

$w_{½}$ is the width of the peak at half height and

t_R is the retention time

In figure 2.6 it can be seen that the chromatographic peaks are often rounded, and it is therefore, usual to extrapolate the peak height, h (as shown by the dotted line).

Generally the efficiency of a column increases as the particle size of the resin decreases. In practice, values of $N > 1000$ are desired.

For a good separation of components in a mixture, three conditions have to be met:

a) the peaks must be retained on the column ($k' > 0$),
b) the peaks must be separated from one another ($\alpha > 1$), and
c) the column must have a minimum number of theoretical plates ($N > 1000$).

2.2.3 Instrumentation[17]

Two Dionex instruments were used during the experiments carried out in Glasgow to cover the range of anions of interest and a third was used at the SCER, Smithsonian Institute, Edgewater, Washington D.C.. General details will be discussed in this section with instrument specific details given in sections 2.2.3.1 – 2.2.3.3 and the eluents will be discussed in section 0.

The components of the Dionex instruments are shown in figure 2.7. The samples were introduced into the system via the sample injector. This has two purposes; to direct the flow of liquid; and to allow sample introduction. A loop injector was used so that an exact volume was injected each time. When the valve is in the load position, the eluent washes through a side loop and into the column and when it is switched to the inject position, the eluent flows through the sample loop, allowing mixing, and onto the column.

The next part of the instrument is the guard and separator column. The separator columns are prepared by polymerising styrene (PS) and divinylbenzene (DVB). The copolymerisation of PS/DVB contains significant crosslinking, which makes the resin more mechanically stable. In

anion exchange columns, the resin is sulphonated to provide an intermediate layer of 10 – 25 μm. In addition a thin layer of latex particles are incorporated around this core which are usually aminated. These particles employ both electrostatic and van der Waals interactions. The size of the latex particle is considerably smaller than those in the core allowing rapid and efficient anion exchange. Column specific details will be given in sections 2.2.3.1 – 2.2.3.3.

Guard columns are smaller versions of the separator columns; they contain very similar resin matrices and help to prolong the life of the separator column by retaining possible contaminants.

The exchange of Y^- ions in a sodium bicarbonate eluent will be as follows:

$$\text{Resin-}NR_3^+OH^- + Y^- \longrightarrow \text{Resin-}NR_3^+Y^- + OH^-$$

$$Y^- + Na^+ \longrightarrow Na^+Y^-$$

The eluent converts the anions to dissolved sodium salts.

The final part of the instrument is the detector, which comprises of the suppressor column and the conductivity cell. The conductivity cell measures the conductivity after the sample has passed through the suppressor column. Conductivity is the most common method to detect ionic compounds in ion chromatography. However, the eluents used in IC have a high conductivity, resulting in greatly reduced sensitivity due to the low signal-to-noise ratio.

A conductivity detector, therefore, is most effective when coupled with a suppressor column. Chemical suppression in IC greatly enhances signal-to-noise ratios by

a) decreasing the background eluent conductivity and
b) increasing the analyte conductivity.

There are three types of suppressor available (column suppressors, membrane suppressors and self-regenerating suppressors), however, the self-regenerating suppressor (SRS) is the one used in all three instruments.

The SRS was introduced from 1992 and consists of alternating layers of high capacity ion exchange membranes separating a cathode and anode. The screens create a low volume flow path for the eluent and provide an ion transport path for the ion exchange process. The chemical

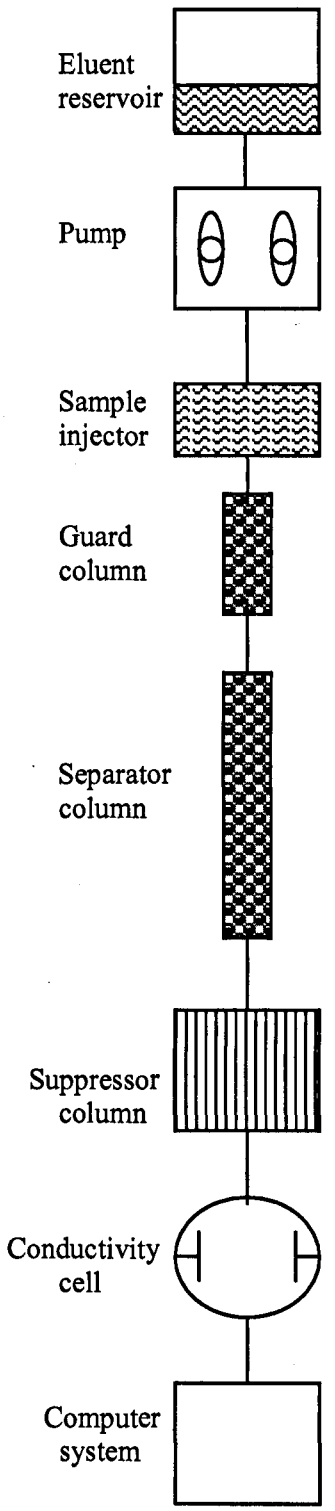

Figure 2.7 Schematic diagram of Dionex instruments

regenerant ions are generated inside the SRS by electrolysis, where hydronium ions are formed by oxidation of water (anode), and water is reduced to form the hydroxide ion (cathode) (figure 2.8).

The suppression process can be split into three main parts; an expended region where the eluent enters the suppressor column (in sodium ion form), a region of dynamic equilibrium in which the suppression reactions occur and a regenerated region where the eluent exits the suppressor column (in hydrogen ion form). Figure 2.8 shows the method of suppression in the Dionex 4000i and DX-500 instruments. The principles are the same for the DX-100 instrument, with sodium carbonate – sodium bicarbonate replacing di-sodium tetraborate as the eluent.

In an SRS, the chemistry involves two different reactions. The sodium ions are substituted by protons, and borate ions are converted to boric acid. By converting the borate ions to weakly dissociated boric acid, the background conductivity is significantly reduced. By substituting protons for sodium, the conductance of the solution per ion is raised about tenfold – proportional to the ratio of molar conductances. This increase in conductance lowers the limit of detection and improves the sensitivity. The two processes are carried out simultaneously in the following way. On either side of the flow path are membranes that have covalently bound negative ion charges on them, the presence of these charges has the effect of making the membranes permeable only to positive ions. In the leftmost compartment an electrochemical anode oxidises a flowing water solution to generate oxygen and protons. These protons pass through the membrane into the flowing eluent and neutralise the borate ions to boric acid, and supply protons as counterions to the A^- ions. At the same time, sodium ions are passing through the membrane on the rightmost side and into a basic solution that is generated by the reduction of water at the cathode. The sodium ions are removed to waste by the water regenerant flow.

After suppression the analyte solution passes into the conductivity cell, which contains a pair of fixed position platinum electrodes. When a potential is applied to the two electrodes, immersed in a solution of electrolytes, an electric current begins to flow through the solution which has a certain electrical conductance. The resistance of the cell is measured using a Wheatstone bridge. The precise area of the electrodes and their distance apart is required, but as this is often difficult to measure conductivity cells are calibrated using a standard solution of potassium chloride.

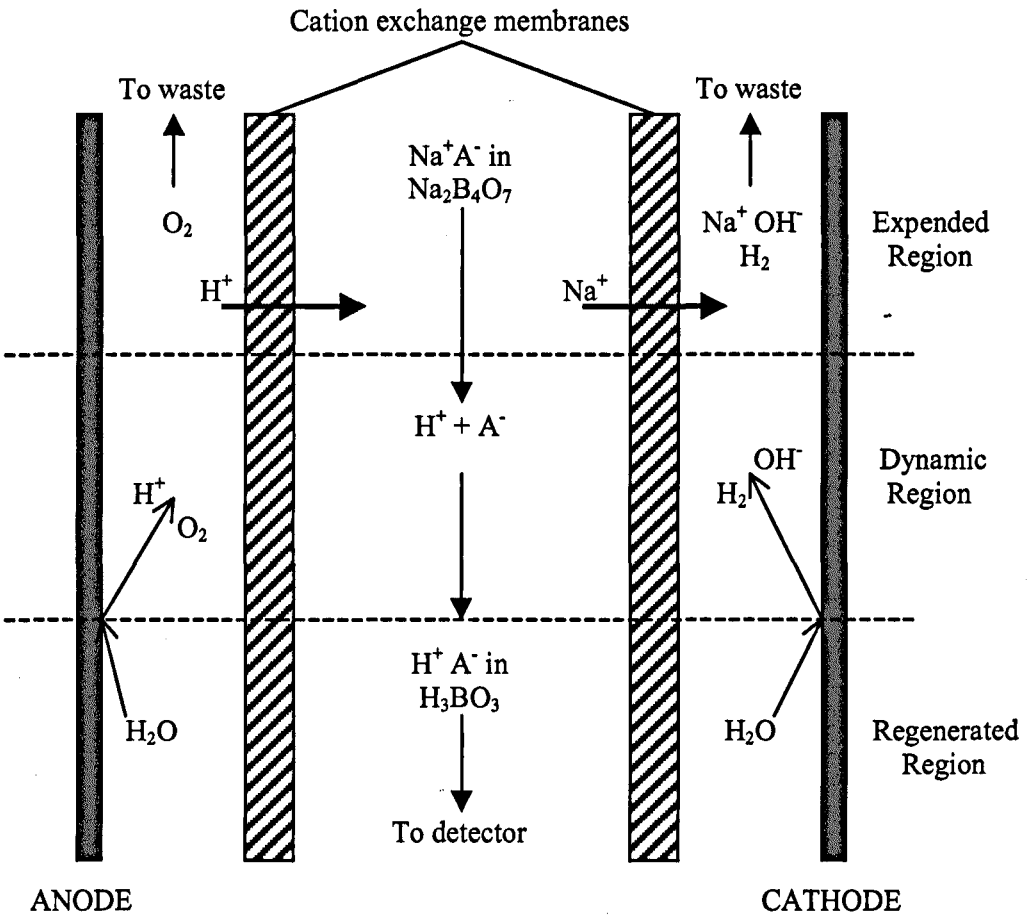

Figure 2.8 **Schematic diagram of a suppressor column in 4000i and DX-500 instruments**

Modern conductivity detectors are designed with wide signal suppression ranges, i.e., extensive zero offset capability.

Detectors are equipped with temperature compensators as an increase of 1 °C will cause the electrical conductance to increase by approximately 2 %. Normally a platinum resistance thermometer will automatically correct conductivities measured over a range of temperatures to a value at 25 °C.

The data collected by the conductivity cell is transformed using a digital to analogue converter and sent to the Dionex AI-450 Chromatography Workstation. This system provides automation of the complete chromatographic analysis. The chromatograms are integrated and reports generated.

2.2.3.1 Dionex 4000i

The main differences between the systems used are in the pump, separator column and eluent. The pump in the 4000i is a double reciprocating pump to ensure a pulse-free flow. At the time of operation the 4000i was fitted with an AS4 separator column and AG4 guard column (both Dionex). These columns contain an alkanol quaternary ammonium group attached to a support material of polystyrene-divinylbenzene, with sulphonated layer (latex anion exchange resin). The AS4 column has packing material with a particle size of 15 μm, 3.5 % crosslinking of divinylbenzene and small latex particles.

An isocratic elution method was employed with this system using a flow rate of 2 mL per minute. The eluent used was di-sodium tetraborate (borax) at a concentration of 6 mM. The combination of separator column and eluent allowed the anions acetate, formate and chloride to be detected in a reasonable retention time, with sufficient separation.

2.2.3.2 Dionex DX-100

The pump in this instrument is a single piston pump and therefore must be used in conjunction with a pulse dampner to smooth the flow to the columns. At the time of operation the DX-100 was fitted with an AS5 separator column and AG5 guard column (both Dionex). These columns

contain the same stationary phase as the AS4, however, the crosslinking is only 0.5 % and it has larger latex particles resulting in less efficient separation.

An isocratic elution method was also used, this time with a flow rate of 1 mL per minute and the eluent used was sodium carbonate : sodium bicarbonate (2.2 mM : 2.8 mM) eluent. The combination of separator column and eluent allowed the anions chloride, nitrate, sulphate and oxalate to be detected in a reasonable retention time, with sufficient separation.

2.2.3.3 Dionex DX-500

The DX-500 is the modern version of the 4000i and as such uses the same pump, separator column and eluent. However, a gradient elution method was used on this instrument. The gradient method consisted of an initial 2 minute rinse with distilled water followed by 11.5 minutes at 4.2 mM borax. The eluent strength was then increased linearly to 22.75 mM over 7 minutes and held for a further 7 minutes before a final 2 minute rinse with 4.2 mM borax. This allowed all six anions (acetate, formate, chloride, nitrate, sulphate and oxalate) to be determined in one analysis.

2.2.4 Sample Preparation

2.2.4.1 Destructive Sampling

Approximately 50 mg of plastic was removed from the artefact of interest, using a scalpel or nail-clippers. The sample was then accurately weighed and placed in a Sterilin plastic container (Ross Lab., Macclesfield, England). 5 mL of distilled water was added and the sample allowed to soak at room temperature for 24 h. The extract was then analysed by ion chromatography.

2.2.4.2 Non-destructive Sampling

A damp cotton wool bud was swabbed twenty times over the area of interest (approximately 2 cm X 2 cm). The cotton bud was then placed in a Sterilin plastic container with 5 mL distilled water for 10 minutes. The extract was then analysed by ion chromatography.

2.2.5 Calibration Solutions

Stock solutions of the six anions were prepared using sodium acetate, sodium formate (Fisions Scientific Equipment, Loughborough, England), sodium chloride, sodium nitrate, sodium oxalate (Merke Laboratory Supplies, Poole, England) and sodium sulphate (Aldrich Chemical Co. Ltd., Gillingham, Dorset, England). 500 mL of each stock solution (1 g L^{-1}) was prepared by dissolving relevant amounts of each dried salt (table 2.2) in 400 mL distilled water in a 500 mL volumetric flask and making up to the mark with distilled water. These solutions were transferred to storage bottles and kept in a cool, dark place.

Table 2.2 Weights of salt used to prepare stock solutions in 500 mL

Sodium Salt	Weight used / g
Acetate	0.695
Formate	0.756
Chloride	0.824
Sulphate	0.686
Nitrate	0.740
Oxalate	0.761

The stock solutions were used to prepare mixed standard solutions with concentrations of

a) 1, 2, 3, 4 and 5 μg mL^{-1} of each ion for calibration of the 4000i,
b) 2, 3, 4 and 5 μg mL^{-1} of each ion for calibration of the DX-100 with the exception of nitrate, which was used at concentrations of 2, 4, 6 and 8 μg mL^{-1} and
c) 1, 2, 3, 4 and 5 μg mL^{-1} of each ion for calibration of the DX-500.

The calibration solutions were prepared each day of analysis, by pipetting 100, 200, 300, 400, 500, 600 or 800 μL of the appropriate stock solution into 100 mL volumetric flasks, using 50 – 200 μL and 200 – 1000 μL variable volume pipettes (Jencons Scientific Ltd., England) and making up to the mark with distilled water. The same supply of distilled water was used for the 0 μg mL^{-1} (blank) solution as was used to prepare the other mixed standards.

2.2.6 Eluent Preparation

The eluent used must have an affinity with the sample ion for the stationary phase for separation to be possible. It must also provide a low background conductivity, after suppression, to allow sensitive detection of the sample ions, ideally down to the $\mu g\ L^{-1}$ range.

The eluent used with both the Dionex 4000i and DX-500 was a solution of di-sodium tetraborate, $Na_2B_4O_7$ (borax). As this is a very weak eluent, it allows separation of acetate and formate anions at retention times sufficiently different from the signal caused by the water in the injected volume (water dip). Borax also has the advantage that after suppression it gives a very low background conductivity reading because H_3BO_3, the suppressor product, is only weakly dissociated[17].

The eluent was prepared by dissolving 19.068 g borax (Merke Laboratory Supplies, Poole, Dorset, England) in about 600 mL distilled water in a large beaker; slight heating was required to dissolve the salt. The solution was transferred to a 1000 mL volumetric flask and 200 mL distilled water added. After cooling the volume was made up to the mark with distilled water to give 50 mM stock solution diluted to 6 mM for use with the 4000i. Automatic dilution was carried out by the DX-500 system.

The eluent used with the DX-100 was a sodium carbonate-bicarbonate (Na_2CO_3-$NaHCO_3$) salt solution. This is a stronger eluent than that used for the 4000i and DX-500; it does not separate acetate, formate and chloride, but allows chloride, nitrate, sulphate and oxalate to be detected in a reasonable time (under 6 min). Detection of chloride is dependent on low levels of acetate and formate.

The eluent was prepared by dissolving 23.318 g of sodium carbonate and 23.523 g sodium bicarbonate in about 600 mL distilled water in a large beaker. Slight heating was necessary to dissolve the salt. The solution was transferred to a 1000 mL volumetric flask and 200 mL distilled water added. After cooling the volume was made up to the mark with distilled water to give a 0.22 M Na_2CO_3 – 0.28 M $NaHCO_3$ stock solution which is diluted to 2.2 mM – 2.8 mM for use.

2.2.7 Sampling and Analysis Errors

Errors for the IC results were calculated using standard deviations of the duplicate samples and injections and were found to be dependent on the number of dilutions which had to be carried out to allow concentrations to be within the linear range of 1 – 8 $\mu g\ mL^{-1}$. The standard deviations of the results were based on the calibration error. Detection limits were calculated on the basis of three times the signal-to-noise ratio at the appropriate retention time for the anion in question.

Care had to be taken during sampling to ensure a representative sample was obtained, this was more difficult for the destructive sampling procedure as samples had to be taken from the edge of the artefact in this case.

2.3 Gel Permeation Chromatography (GPC)

Chain scission is a common degradation process in polymers which involves the breaking of bonds at certain random or regular sites along the polymer backbone. If this occurs, then a reduction in the average molecular weight of the polymer occurs. The reduction in molecular weight can be investigated using gel permeation chromatography, or size exclusion chromatography, as this is a technique for separating materials according to their molecular size and shape by passing a solution through a column consisting of a polymeric gel.

2.3.1 Principles of Gel Permeation Chromatography[18,19]

The stationary phases used in GPC are porous particles with a closely controlled pore size. Depending on their size and shape, sample molecules may be able to enter the pores of the stationary phase particles. The pores of the gel exclude molecules greater than a certain critical size whilst smaller molecules can permeate the gel structure by diffusion. Excluded molecules pass through the system more rapidly than smaller ones that can diffuse into the gel. Diffusion within the gel also varies with molecular size and shape because pores of different dimensions are distributed throughout the gel structure in a random manner. These smaller molecules are eluted at rates dependent upon their degree of permeation into the gel, and components of a sample mixture therefore, elute in order of decreasing size or molecular weight. Unlike other

chromatographic processes, in GPC there is no interaction between the solute and the surface of the stationary phase.

Packings for GPC columns are semirigid, crosslinked macromolecular polymers. The gels can be hydrophilic, for separations in aqueous and other polar solvents, or hydrophobic, for use in non-polar or weakly polar solvents. The gels are chemically stable at pH values less than 10 and can be used routinely and indefinitely.

2.3.2 Instrumentation

2.3.2.1 In-house

The apparatus used was based on a standard chromatography system and consisted of a pump, controller, separation column, detector and integrator. A Pye Unicam PU 4003 pump was used in conjunction with a Pye Unicam PU 4003 controller. A tetrahydrofuran (HPLC grade) (THF) eluent was passed at a flow rate of 1 mL min^{-1} through two GPC columns (with 10^4 Å and 500 Å pore size), each 32 cm long and connected in series in the order 10^4 Å then 500 Å. This allows the separation of firstly high molecular weight samples then low molecular weight samples. The columns are packed with PL gel styrene with particle size of 5 μm diameter. The gel retards the smaller molecules, as they go in and out of more pores than the larger molecules and therefore, exit later. This ensures that fractionation is on the basis of molecular size in solution with the largest molecules leaving the columns first followed by the smaller molecules[20].

The separated components were detected with a Pye Unicam PU 4026 refractive index (RI) detector, set at a range of 0.05 X 10^{-3} and response time 5 s. The chromatogram was recorded on a Spectra Physics Chromjet integrator at chart speed 0.5 cm min^{-1}.

2.3.2.2 Rapra (Rubber and Plastics Research Association, Polymer Characterisation Unit, Shawbury, Shrewsbury, Shropshire)

The chromatographic conditions used at Rapra were:

Columns:	PL gel 2 x mixed bed-B, 30 cm, 10 μm
Solvent:	THF, with antioxidant

Flow-rate: 1.0 mL/min
Temperature: 30 °C
Detector: refractive index

2.3.3 Sample Preparation

2.3.3.1 In-house

A small sample, approximately 20 mg, was removed from an artefact using either a scalpel or nail-clippers. The material was weighed accurately into a 25 mL 'Quickfit' glass vessel, 20 mL THF (Merke Laboratory Supplies, Poole, England) was added and the stoppered vessel sonicated until the sample dissolved. The solution was left for 24 h to ensure complete dissolution. Toluene (Merke Laboratory Supplies, Poole, England) was added as an internal standard at a concentration of 0.5 % (V:V).

2.3.3.2 Rapra

A single solution of each sample was prepared by adding 10 mL of solvent to 20 mg of sample and leaving over night to dissolve. On the following day a small amount of 1,2-diclorobenzene, was added in the solvent as an internal marker and the solutions thoroughly mixed. The solutions were filtered through a 0.2 µm polyamide membrane prior to chromatography.

2.3.4 Calibration Preparation (In-house only)

Four polystyrene standards (Polymer Labs. Ltd., Church Stretton, U.K.) were chosen to cover a range of molecular weights from 1,500,000 – 4000. The calibration solutions were prepared by dissolving 0.2 g of each polystyrene standard in 90 mL THF in 100 mL volumetric flasks before making up to the mark with THF. A mixed standard was then prepared by mixing 5 mL of each standard solution, with 0.5 % (V:V) toluene added as an internal standard. The measured retention times are converted to relative retention times by dividing by the retention time of toluene. This was then plotted against ln molecular weight to give a calibration graph.

2.3.5 Data Processing

2.3.5.1 In-house

The chromatogram collected on the integrator was photocopied onto mm^2 graph paper to allow three points to be accurately marked before computer processing can begin. These points are

a) the origin of the chromatogram,
b) a deskewing point which is as far from the origin as possible but having the same y co-ordinate and
c) a second scaling point which is at a convenient point on the chromatogram.

These are then given accurate co-ordinates relating to the elution time and traced back on to the original chromatogram. This was then scanned into a computer and vectorised using "Un-graph" software to give a digital form. The digital form was imported into a computer program called "Origin". This program integrates the area under each peak on the chromatograms and uses the calibration graph to calculate the molecular weight distribution of each unknown peak. This was then converted from polystyrene molecular weight to cellulose acetate molecular weight using the Mark-Huwinck equation (equation 2.17).

$$[\eta] = kM^{\alpha+1}$$

Equation 2.17

Where k = 0.71 and $\alpha = 1.2 \times 10^{-4}$ for cellulose acetate in THF[21] and:

$$\text{Hydrodynamic volume} = [\eta]M$$

Equation 2.18

This means that M (molecular weight) can be calculated from a graph of $kM^{\alpha+1}$ vs. elution time for any given polymer and solvent.

2.3.5.2 Rapra

The data was acquired and processed using Viscotek Trisec 3.0 software. The GPC system used was calibrated with polystyrene and the results are, therefore, expressed as the "polystyrene equivalent" molecular weights.

2.3.6 Sampling and Analysis Errors

The main problem with sampling in the GPC analysis was the solubility of the samples. However, the samples which could be dissolved produced very reproducible data with % RSD on duplicate injections at < 3 %. Obtaining a representative sample from the artefact was difficult as samples had to be taken from the edges.

2.4 Thermogravimetric Analysis (TGA)

TGA is a useful technique for investigating the level of compounds which are generated as degradation occurs. Conventional TGA was used to investigate the differences in the weight loss on heating of samples showing different signs of degradation and TGA-FTIR was used to identify these compounds as degradation occurred. The gas released from the TGA was passed through an FTIR gas cell and analysed.

2.4.1 Principles of Thermogravimetric Analysis[22,23]

Thermogravimetry can be considered to be continuous or frequently repeated measurements of the weight or change in weight of a sample as it is subjected to a temperature programme. This technique is especially useful when studying dehydration and thermal decomposition both of which are associated with degradation. It can also be used coupled with FTIR to allow identification of the substances which are being formed at specific temperatures.

2.4.2 Instrumentation

A Perkin-Elmer TGS-2 Thermogravimetric Analyser, with a Perkin Elmer System 7/4 Controller and Thermal Analysis Data System was used for the TGA at the Smithsonian Institute, Washington D.C.. All samples were analysed in dry air flowing at 20 mL min^{-1}, over a temperature range of 30 °C – 335 °C with a heating rate of 20 °C min^{-1}. The instrument was calibrated daily using nickel and alumel (ideal transition temperatures are 354 °C and 163 °C respectively).

A Perkin-Elmer Model GX FTIR coupled to a Perkin-Elmer Pyris TGA7 was used for the TGA-FTIR at Perkin-Elmer, Atlanta. All samples were analysed in dry air flowing at 20 mL min^{-1}, over a temperature range of 20 °C – 470 °C. A scan rate of 20 °C min^{-1} was chosen as a compromise between resolution and sensitivity. The upper temperature was chosen as the sample had become a char by this point. FTIR spectra were collected over the range 4000 – 600 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

2.4.3 Sample Preparation

Samples were prepared for both techniques by the same method. The samples were cut up into small fragments using nail-clippers and approximately 30 mg was accurately weighed into the TGA pan. This was hung on the stirrups and the glass shield replaced around it. The instrument was then initiated, during this process the inert gas (nitrogen) started flowing and the sample pan was weighed and set at 100 %. The heating programme was then started and data collected.

2.4.4 Data Processing

For conventional TGA there is very little data processing as a plot of percentage weight loss against time or temperature is simply generated as the data is collected. These can be manipulated using the computer software.

For TGA-FTIR the TGA data is processed as for conventional TGA and the FTIR spectra are collected as described in sections 2.1.2 and 2.1.4. The spectra are then checked against a vast library to aid identification of the degradation products.

2.4.5 Sampling and Analysis Errors

The main source of error in this technique is the accurate weighing of the small amounts of sample that is used. However, the instrument also making an initial weight measurement overcame this. Also low temperature weight loss can be the loss of moisture from the sample surface or highly volatile degradation products, such as acetic acid.

Again care had to be taken in obtaining a representative sample from the artefact as the sample had to be taken from the edge.

2.5 X-ray Fluorescence Spectroscopy (XRF)[6,13,24,25]

XRF is an excellent technique to investigate metal ions present in museum artefacts as it is a surface technique. Modification of the instrument allowed non-destructive analysis of the artefact, which is required when dealing with museum collections. A previous study on cellulose nitrate artefacts showed that metal additives or impurities could have a catalytic or protective effect on the degradation process[26]. It was hoped that a link could be established between metal content and extent of degradation of cellulose acetate.

2.5.1 Principles of X-ray Fluorescence Spectroscopy

When a sample is placed in a beam of high energy photons, such as X-rays or fast moving electrons, the energy is transferred to the sample atoms. If the X-ray has sufficient energy, the absorbing atoms become excited and electrons are lost from the inner shell, K, and the atom becomes ionised. The K^+ state is very unstable and is partially stabilised if an electron from a higher shell (L, M, N, etc.) undergoes a transition to the K^+, figure 2.9, this causes a change in energy. This difference in energy is released as an X-ray; the energy or wavelength of the emitted X-ray is characteristic of the element being bombarded and can be used to identify it.

The energy of the released radiation is given by:

$$\Delta E = \frac{hc}{\lambda}$$

Equation 2.19

Where h is Planck's constant,
c is the velocity of light and
λ is the wavelength of the X-ray.

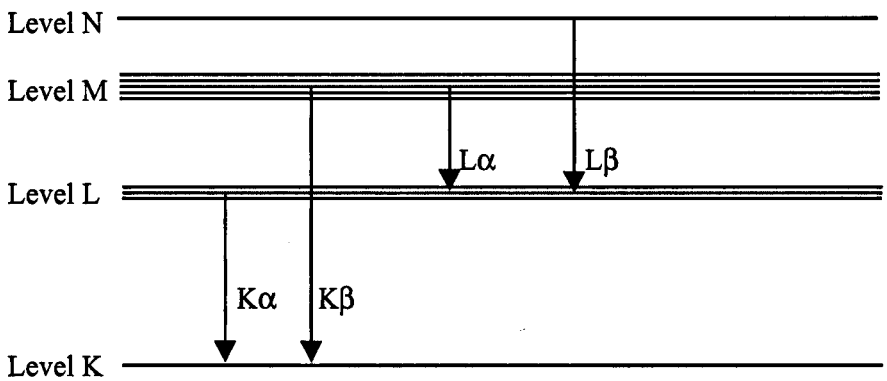

Figure 2.9 Schematic of spectral levels produced on release of X-rays

The fluorescent X-rays emitted can be analysed by passing them onto a crystal, which diffracts the X-rays into individual wavelengths according to Bragg's law:

$$n\lambda = 2d\sin\theta$$

Equation 2.20

Where d is the interplanar spacing,

n is an integer (order of dispersion), and

θ is the angle of dispersion.

The resolved X-rays are then detected by an appropriate system such as a scintillation counter. Such a system is referred to as a "wavelength dispersive system" (WDXRF), and has good resolution for multi-element analysis.

For "energy dispersive X-ray fluorescence" (EDXRF) systems, as opposed to WDXRF systems, the crystal analyser is eliminated and the undispersed X-rays are sorted into energy groups by means of a semiconductor detector coupled to a multichannel analyser.

2.5.2 Instrumentation

EDXRF is used instead of WDXRF because multi-element analysis is rapid with this system. Qualitative analysis is also possible in very quick times with EDXRF, as low as 5 $\mu g\ g^{-1}$. However, the sensitivity for low atomic weight elements, i.e. Ca and below, is not good because of lower fluorescent yields and transmission efficiencies.

An Oxford ED 2000 instrument had been adapted to allow direct analysis of artefacts in air rather than vacuum, to avoid the need for sampling, (figure 2.10). This was coupled to a Canberra Energy Dispersive XRF system with a rhodium source to analyse the samples.

Excitation is achieved by the use of an X-ray tube (figure 2.11). The tube uses a hot cathode, typically a tungsten filament, which emits electrons by thermionic emission. The electrons are accelerated by a potential onto a target anode made or plated with an element of choice, in this case rhodium. The collisions convert kinetic energy mainly into heat but a small amount of X-rays are also produced. The generated X-rays pass through a window of beryllium and onto the sample.

The fluorescent X-rays from the sample are detected by means of a semiconductor detector, e.g. lithium "drifted" silicon, cooled in liquid nitrogen to reduce detector noise. Semiconductor detectors are fabricated with the semiconductor material deposited on glass in a sealed, evacuated envelope. When radiation, such as X-rays, falls on the semiconductor material, it becomes a conductor and hence, a very rapid change in electrical resistance can be detected.

The response time for a semiconductor is the time required to change from an insulator to a conductor and can be as short as 1 nanosecond. The X-rays entering the detector produce voltage pulses proportional to their energies. These pulses are then amplified and sorted according to energy by means of a multichannel analyser. A spectrum showing the elemental composition of the sample is then produced.

2.5.3 Spectra Recording

Sampling was not necessary as the artefact was brought into direct contact with the interface of the detector and the spectra recorded. The rhodium source was operated at 0.3 mA and 46 kV potential, and spectra were recorded over 100 s.

2.5.4 Sampling and Analysis Errors

Reproducibility of spectra from the same spot on the artefact were found to be < 5 % RSD. However, large differences between different areas of the surface were found, with the relative

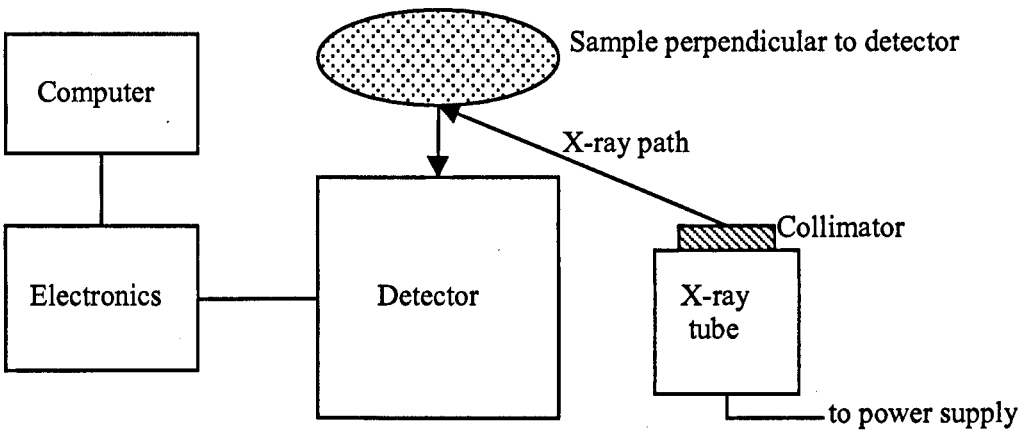

Figure 2.10 Schematic diagram of adapted XRF instrument

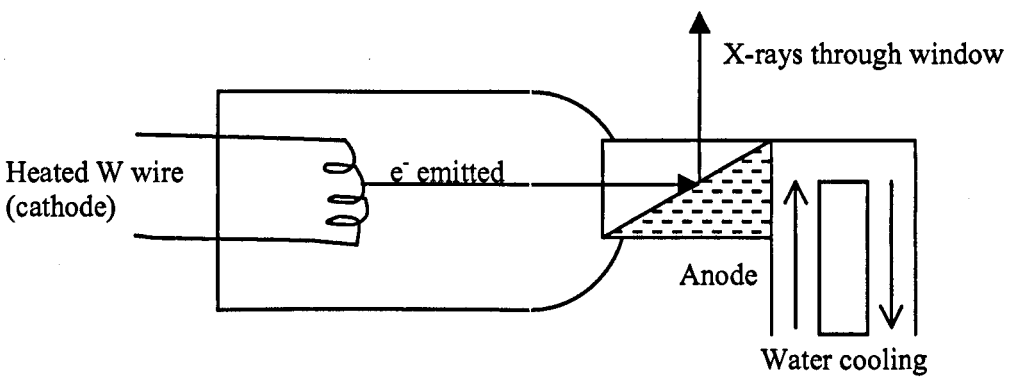

Figure 2.11 Schematic diagram of a high vacuum X-ray tube

amounts of the metals changing across the surface. To overcome the problems of the changing relative amounts of metal across the sample surface, spectra were taken from numerous areas and compared. Also as this is a surface technique there is no data found for the bulk of the plastics.

2.6 Headspace Gas Chromatography (GC)

Headspace gas chromatography was used to investigate the atmosphere surrounding the samples after accelerated ageing had finished. The presence of high levels of acetic acid would indicate that deacetylation was occurring, while the presence of phthalate would indicate that plasticiser was lost.

2.6.1 Principles of Headspace GC[27,28,29]

GC is an important analytical technique as it offers rapid and very high resolution separations of a wide range of compounds, with the only restriction that analytes should be volatile. Headspace GC is a technique used to analysis gases surrounding samples by the use of a gas syringe and normal GC equipment.

Separation of the analytes is achieved by passage of the sample and mobile phase through a column consisting of a stationary phase. The stationary phase is different depending on the type of column used; with capillary columns it is coated onto the walls of the column, however, with packed columns it is coated onto the particles in the column. The mobile phase is the carrier gas which carries the analytes through the column. Partitioning between the stationary and mobile phases separates the analytes.

The technique, therefore, follows the principles of standard chromatography which have been discussed in section 2.2.2.

2.6.2 Instrumentation

There are three main parts of a GC instrument, the injection port, column and detector. Each of these parts will be discussed in turn. The injection port is where the sample is introduced to the

system and also where it is vaporised. It then moves onto the column where it is separated into the component parts and finally passes into the detector.

A Pye Unicam PU 4550 capillary chromatograph was used with a BP1 column, 12m length X 0.2 mm id and 0.25 μm film thickness. The detector used was a flame ionisation detector (FID). The chromatograms were recorded on a Spectra Physics Chromjet integrator at chart speed 1.0 cm min^{-1} and attenuation 64.

The FID is a perfect detector for this type of analysis, when the exact composition of the sample is unknown, as it is a universal detector which detects most organic compounds. The gas leaving the column is mixed with hydrogen and air which is ignited to produce a continuous flame. As the compounds from the column enter the flame they undergo combustion, a small percentage of carbon atoms undergo ionisation during this process. The electrons are collected by an electrode, polarized with respect to the flame, resulting in an electrical current which is amplified to provide the chromatographic signal.

The carrier gas was nitrogen at a flowrate of 2 mL min^{-1}. The injector port temperature was 250 °C and the detector was set at 350 °C. The oven temperature programme was optimised as 45 °C for 3 mins then ramping to 200 °C at 10 °C min^{-1} and holding for 2 mins.

2.6.3 Sample Preparation

Approximately 1 g of sample was weighed into a 10 mL glass vial, the vial was then sealed using an airtight septum cap. The samples, including a blank, were then placed in an oven at the temperature of accelerating ageing for one week. The samples were then removed and a 1 μL gas sample was obtained using a gastight syringe through the rubber septum. The gas sample was then injected into the GC and the temperature programme started.

The chromatograms obtained were compared visually and by using tables showing the occurrence of peaks and their intensities.

2.6.4 Sampling and Analysis Errors

There were no problems with choosing a representative sample in this technique as a large sample, 1 g, was used and this analysis was carried out at the end of the experimental work so the artefact samples could be totally destroyed and pieces from all areas (edges and middle) included in the headspace GC sample. Duplicate injections were run, however, a suitable internal standard could not be found due to the large intensity of peaks in the more degraded samples.

2.7 Elemental Analysis[4,30]

Elemental analysis was used to obtain data on the relative percentages of carbon, hydrogen, nitrogen and oxygen within the cellulose acetate samples. It was hoped this technique would be able to identify any samples which were a mixture of both cellulose acetate and cellulose nitrate. Also, it was hoped that an indication of the effect of different percentages of elements present, e.g. high oxygen content, on the degradation of cellulose acetate would be found.

2.7.1 Principles of Elemental Analysis

Instrumentation for carbon, hydrogen and nitrogen (CHN) analysers is based on one of two general procedures. One involves the separation of the combustion products, carbon dioxide, nitrogen and water using specific absorbents, with the resulting change in the composition of the gas mixture being measured. The other involves separation by gas chromatography. Thermal conductivity is the detection method in both cases.

2.7.2 Instrumentation

The sample (< 3 mg) is combusted in pure oxygen at temperatures of up to 1800 °C. Carbon in the sample is converted to carbon dioxide and carbon monoxide, hydrogen is converted to water. Nitrogen is released as the free gas along with some oxides. A schematic diagram of an elemental analyser is shown in figure 2.12. The combustion gases are carried by a stream of helium gas into a secondary furnace where simultaneous reduction and oxidation of the gases occurs. Nitrogen oxides are reduced to nitrogen, carbon monoxides are converted to carbon

dioxide and oxygen is removed. Any interferences are also removed from the gases if needed, e.g. a magnesium oxide layer in the furnace to remove fluorine or a silver wool plug to remove chlorine, bromine and iodine.

For this study, separation of the gases was achieved by means of specific adsorbents for carbon dioxide and water. Three pairs of thermal conductivity cells (glass coated platinum filaments) are used in series for detection: one pair each for water, carbon dioxide and nitrogen. A magnesium perchlorate trap between the first pair of cells absorbs any water from the gas mixture before it enters the second pair of cells. The differential signal, measured before and after the trap, is proportional to the amount of hydrogen (measured as water removed) in the sample. A soda-asbestos trap between the second and third pair of cells results in a signal proportional to the carbon (measured as carbon dioxide removed) in the sample. The last pair of cells measures nitrogen by comparing the helium-nitrogen mixture with pure helium.

Results are reported as a percentage for each element and are calculated by analysing standard samples and occasional blanks.

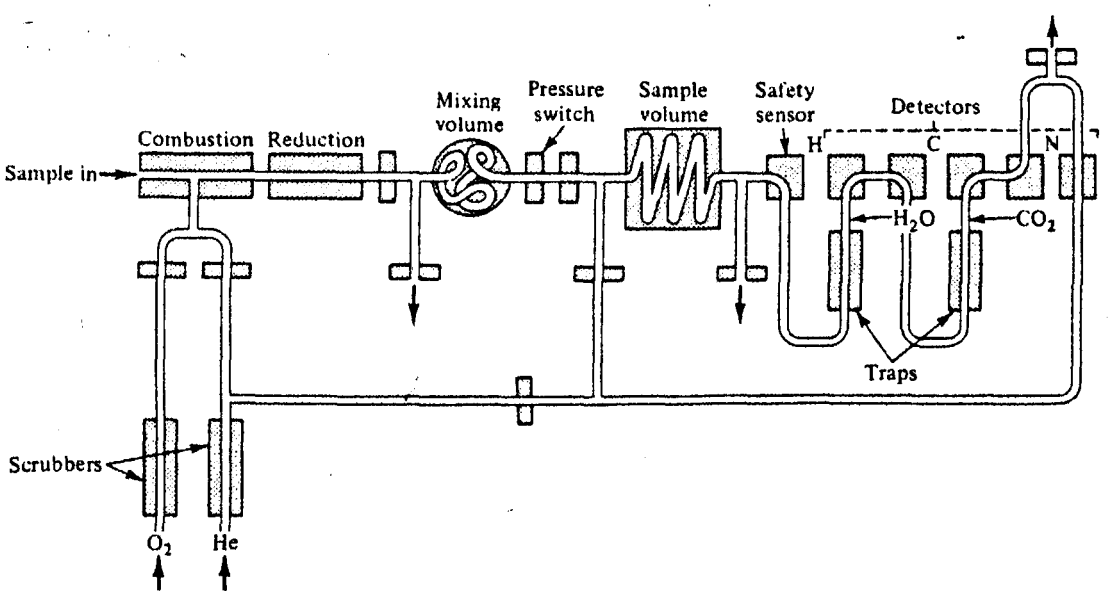

Figure 2.12 Schematic diagram of an elemental analyser

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CHAPTER 3

STUDY OF THE NATURAL AGEING OF CELLULOSE ACETATE

3 Study of Naturally Aged Artefacts

3.1 Introduction

The samples for this section have been collected from various sources, although the majority have been stored in museum conditions for the greater part of the artefact's lifetime. The samples cover a wide range of age and degradation; the known history and a description of condition are given for each artefact. Each artefact was examined visually to assess the degradation, then analysed by Fourier transform infrared (FTIR) spectroscopy, ion chromatography (IC), X-ray fluorescence (XRF) spectroscopy and elemental analysis. The results for each artefact are discussed in turn, with overall conclusions given on the usefulness of the techniques in assessing the extent of degradation.

3.2 Visual Observations

3.2.1 1996 Cellulose Acetate

This material was supplied by Courtaulds Chemicals, (Spondon, Derby) and was used as a test sample. The samples were in two shapes, a circular slab (diameter 49 mm, height 4 mm) and a stepwise piece (length 59 mm, width 38 mm, step 1 height 8 mm, step 2 height 4 mm, step 3 height 1 mm) as shown in figure 3.1. The specimens used for the study were transparent, colourless and in excellent condition, as they were collected immediately after manufacture.

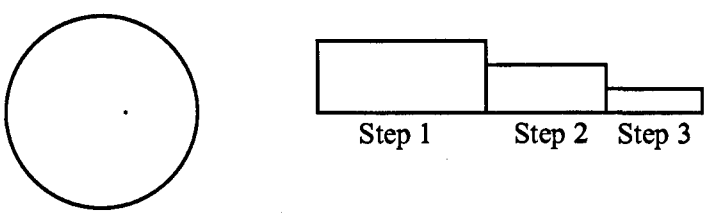

Figure 3.1 Schematic diagram of 1996 cellulose acetate

3.2.2 1967 Tortoiseshell Hairslide

This sample was one of a set of six, 3 each of two designs, supplied by Robert Bollé, Musee d'Oyonnax, France and was in excellent condition with no visual signs of degradation. It was part of a collection kept in storage at the Musee d'Oyonnax. No other history was known about the sample. A photograph is shown in figure 3.2.

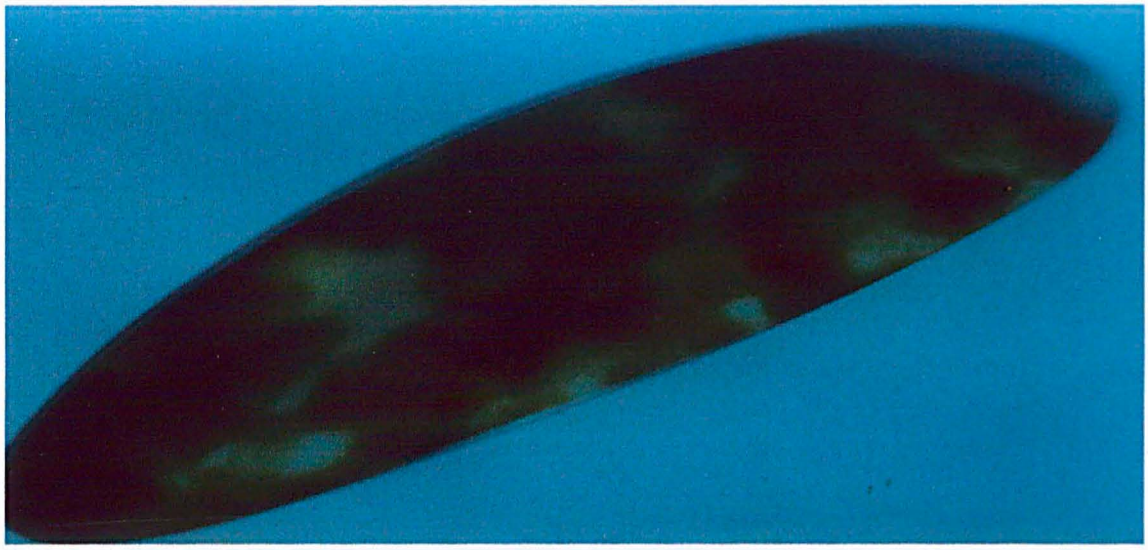

Figure 3.2 Photograph of 1967 Tortoiseshell Hair Slide

3.2.3 1967 Tortoiseshell Comb

As for the hairslides, this sample was one of a set of seven supplied by Robert Bollé and again was in excellent condition showing no signs of degradation. A photograph is shown in figure 3.3.

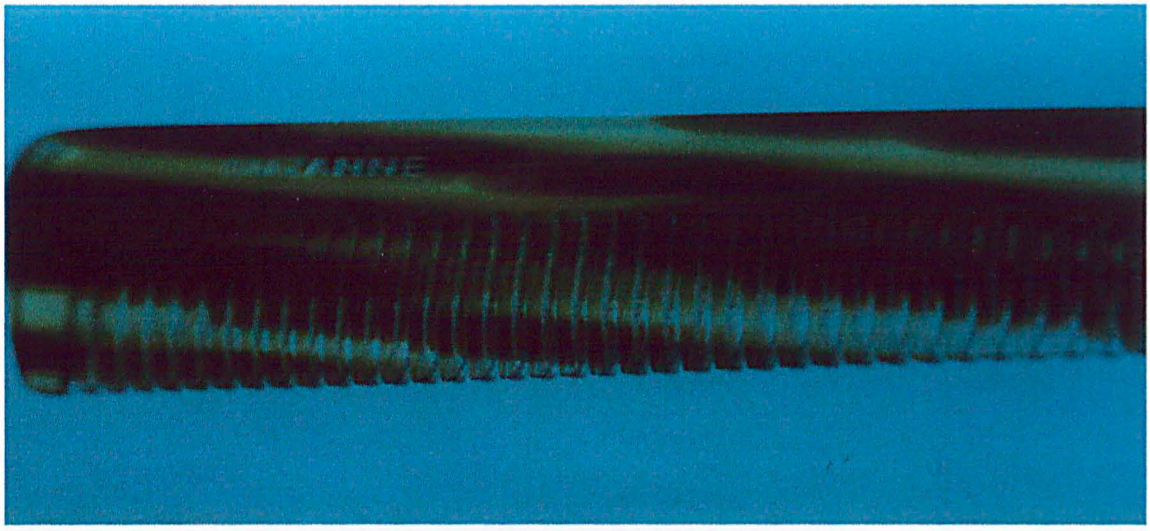

Figure 3.3 Photograph of 1967 Tortoiseshell Comb

3.2.4 1946 Tortoiseshell Comb

Robert Bollé as part of a set again supplied this sample; however, it was in a slightly worse condition with a few small areas of crazing. A photograph is shown in figure 3.4.

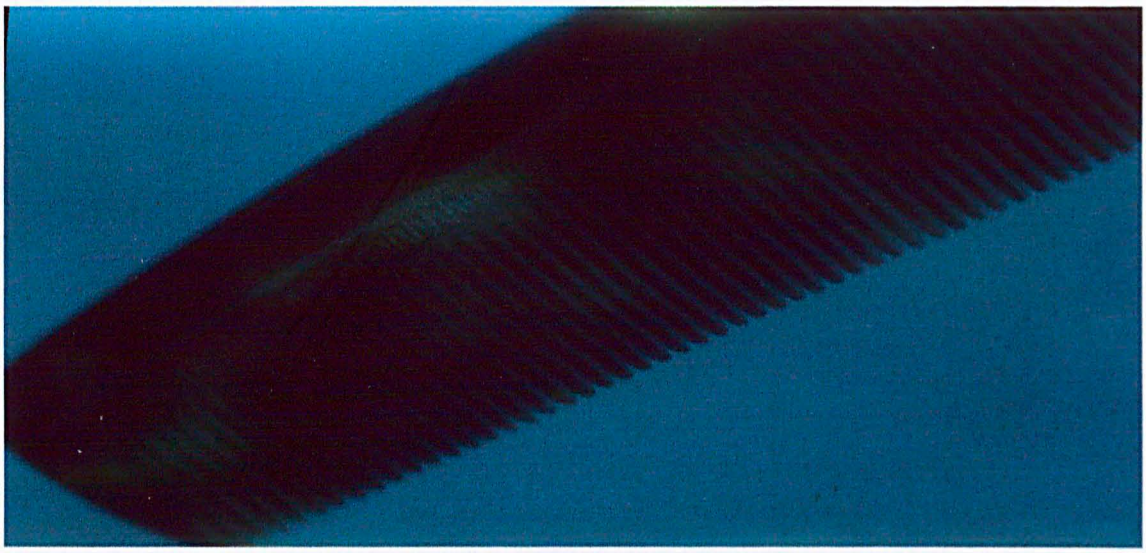

Figure 3.4 Photograph of 1946 Tortoiseshell Comb

3.2.5 1940's Doll

A member of the public donated this sample to the Department of Conservation and Analytical Research, National Museum of Scotland, Edinburgh, after learning about historical plastic degradation through the press. It had been kept sitting on a bed, fully clothed (figure 3.5) for the majority of its lifetime. However, it had spent the last six months, before donation, wrapped up in a plastic bag and placed in a box in the attic. During the time in the attic the doll underwent severe degradation, of which there had been no signs before it was wrapped and placed in the attic.

Figure 3.5 Photograph of 1940's doll being unpacked

This sample has been split into many different parts as the different areas of the doll have been affected differently by degradation. The body and face were in excellent condition, the right leg was in good condition, but the arms and left leg were very badly degraded. This variation could have been due to the type of storage used in the attic, however, the doll was repackaged before being transported to the museum and therefore, no precise information is available.

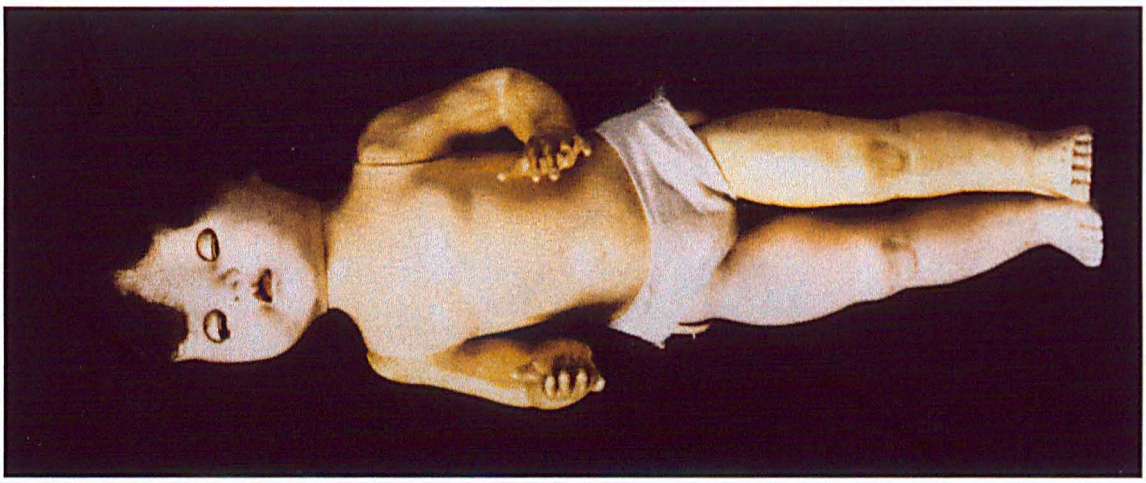

Figure 3.6 Photograph of undressed 1940's doll

As can be seen in figure 3.6, the body was still flesh pink and had no signs of cracks, crazing or blisters. It was completely smooth and not sticky. The face had some slight discoloration compared with the body, probably due to bleaching by sunlight. The degraded arms were badly cracked, crazed and covered in blisters, and there were also areas of discoloration where the flesh pink had turned to orange or white patches and strips (figure 3.7). This could not have been due to sunlight as the doll wore a long sleeved dress and coat (figure 3.5) while on display. The differences between the two legs were quite dramatic, the left leg had similar degradation to the arms although not as severe. However, the right leg only had a small patch of discoloration (flesh pink to orange) at the thigh area. Due to these differences in degradation from place to place many parts of the doll were analysed separately.

Figure 3.7 Photograph of close-up of 1940's doll's arm

3.2.6 Knife Handle

A member of staff at the National Museum of Scotland, Edinburgh, donated a set of knives with marble affect handles, as shown in figure 3.8, received as a gift in the early 1960's. These appeared to be in excellent condition, with no blistering, discoloration or softness.

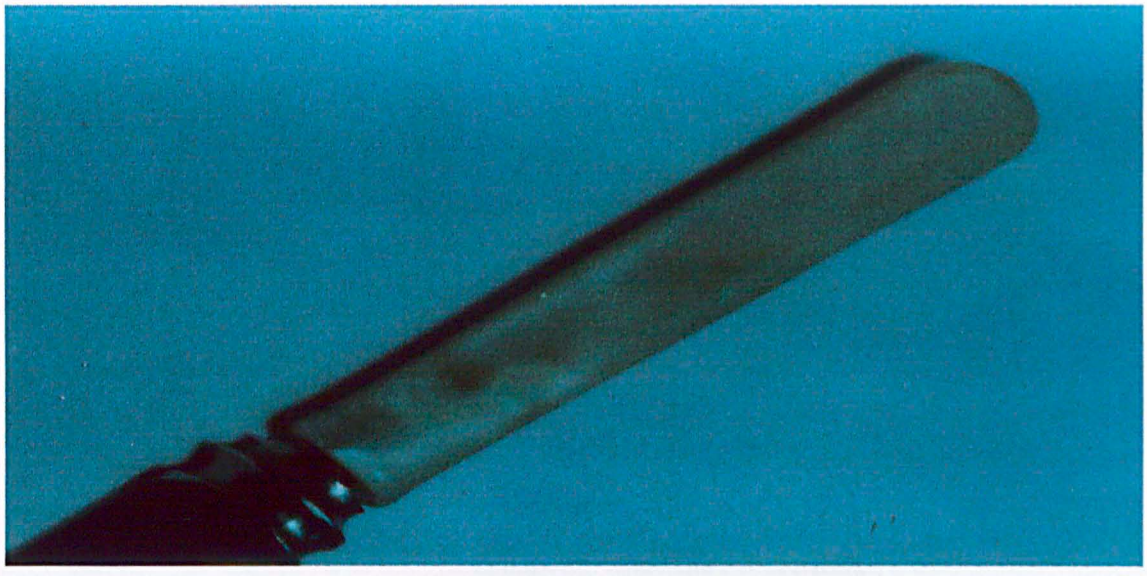

Figure 3.8 Photograph of knife handle

3.2.7 Cellulose Acetate Test Square

This sample was found in storage in the National Museums of Scotland, Edinburgh. The square had originally been green but had degraded badly from the centre outwards. The middle had turned totally brown and the colour gradually changed from brown to green from the inside to the outside. Therefore, this piece had areas in bad condition and good condition.

3.2.8 Artemide Lamp

Access to this sample was granted by the Metropolitan Museum of Fine Art, New York. The only signs of degradation were fine cracks at the edges (figure 3.9). Unfortunately very little history is known about the storage or display of this artefact prior to it being acquired by the museum in 1988. It was designed by Gruppo Architetti and manufactured by Artemide in 1967 and has been displayed since 1996. It was 34 cm high and 54 cm wide, the circumference of the shade was 170 cm and was approximately 2 mm thick. Samples were taken, using cotton wool swabs, from six places: the cracked edges; an area with no cracks; inside the well; the base; the underside edge; and near the middle of the lamp on the underside.

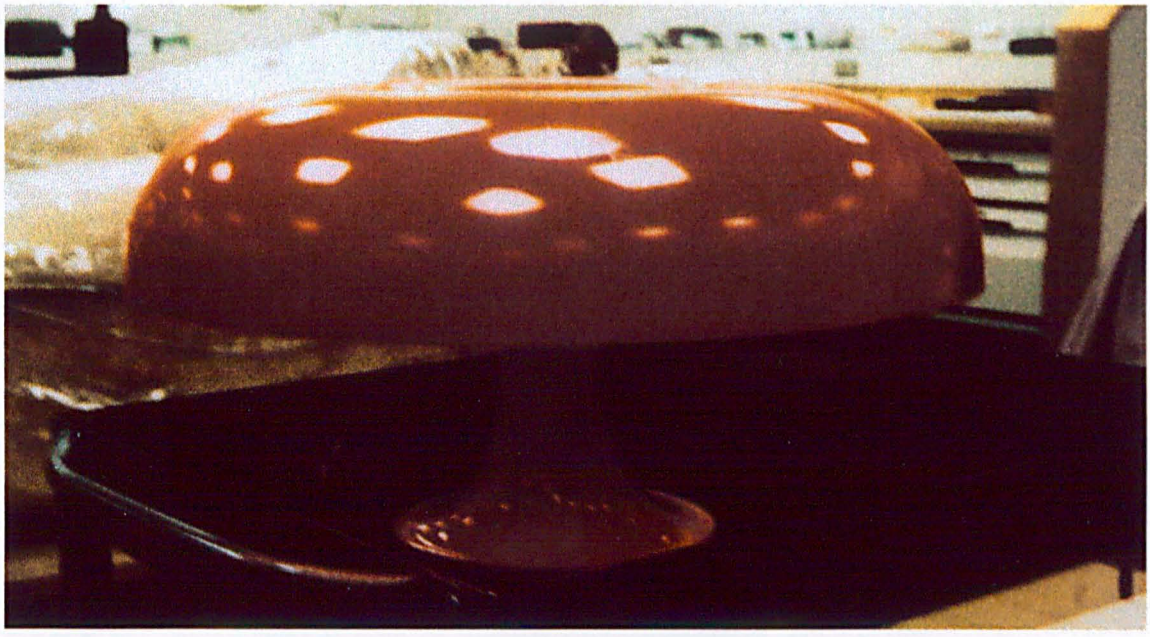

Figure 3.9 Photograph of Artemide Lamp

3.2.9 Inguis Box

René Jules Lalique designed this box in 1924 and Seicoid manufactured it, although, the date of manufacture is uncertain. It was showing blistering, cracks and had fine white crystals in places. Again, access to the piece was granted by the Metropolitan Museum of Fine Art, New York. A photograph is shown in figure 3.10. Very little history is known about the box prior to it being acquired by the museum in 1978. It has been on display since 1996. The box was a dark orange colour with dimensions of 8 cm X 8 cm X 3 cm, and was marked as being made in France. Swabs were taken from blistering on the top, an indented area on the top (containing crystals), the side and the base. No samples were taken internally as the top and base had become stuck together, probably due to plasticiser loss and swelling.

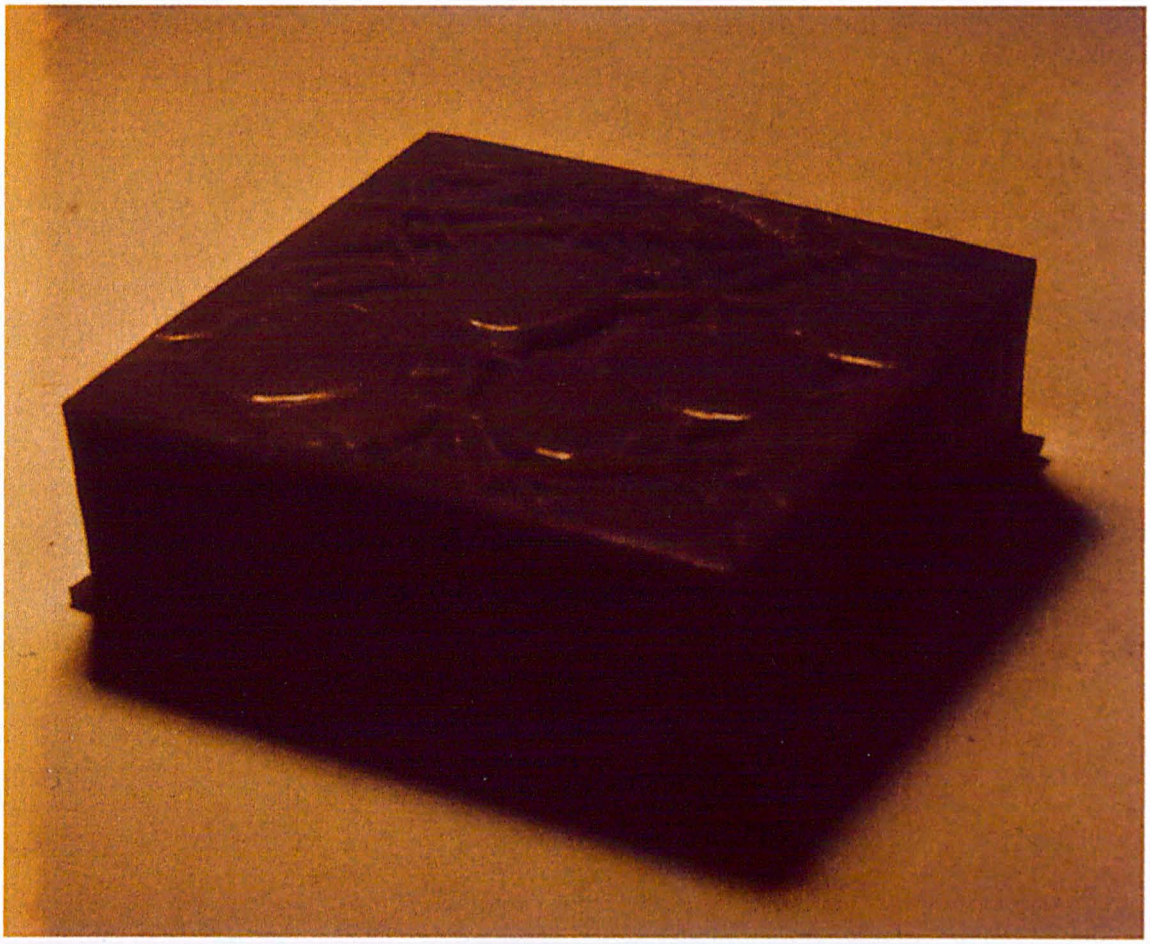

Figure 3.10 Photograph of Inguis Box

3.2.10 Moholy-Nagy Painting

Conservators at the Los Angeles County Museum of Art (LACMA) took samples from this artefact which were sent to the Smithsonian Institute for analysis. It was described as '"Composition, 1938" by Laszlo Moholy-Nagy, oil and incisions on rhodoid, Los Angeles County Museum of Art, gift of Eugene Bielawski[1]'. It was displayed at the artist's home during the 1940's, when the sheet was clamped in brackets (one at each corner) which held it a few inches out from the wall. An angled spotlight was then used in order to cast a shadow of the painted and incised elements on the wall behind the sheet. The sheet was 82.5 cm X 59.3 cm. It was said to smell strongly of acetic acid, be badly warped and have areas that exhibit cracks and crazing. Again this sample was divided into different areas, which were analysed separately. The artwork was acquired by LACMA in 1997 when it arrived in a clear plastic box with only 2 sets of 5 holes, approximately 3 mm, for ventilation. It had been stored in this way since being on display in 1991. Therefore, it would have been exposed to high relative humidity and temperature before being placed in the controlled museum conditions.

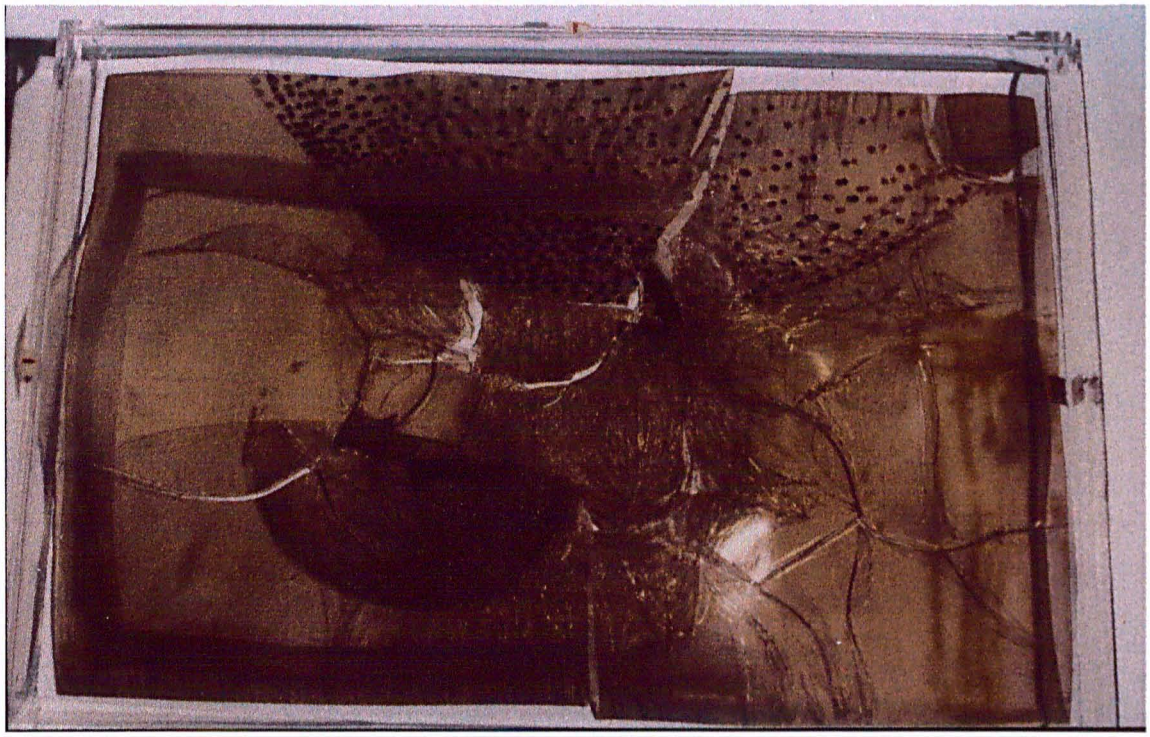

Figure 3.11 Photograph of Moholy-Nagy composition[1]

3.2.11 Storage Folder

This sample was donated by the Peabody Museum, Cambridge, Boston. It had been used to house fabric since 1956, and was beginning to warp and release acetic acid. The fabric samples were being rehoused to avoid acid related degradation from the release of acetic acid vapours, thus an empty folder could be taken for analysis.

3.2.12 Various Combs

The Philadelphia Museum of Modern Art allowed access to a drawer full of plastic combs of unknown class. Samples were taken from those which had the appearance and smell of cellulose acetate, a selection are shown in figure 3.12. In total, 11 combs were sampled and analysed. The combs had been placed in the drawer from various sources and were awaiting proper identification and storage.

Figure 3.12 Photograph of a selection of combs

3.2.13 Duchamp Painted Acetate

This Duchamp painted acetate was an image of a large glass sculpture; it was showing slight warping and a faint acetic acid odour. The Head of Paper Conservation at the Philadelphia Museum of Art carried out the swabbing under my supervision. It has been at the museum since 1972 and has alternated between storage and display as part of the museum's exhibition rota.

Table 3.1 Summary of Degradation and Sampling

Sample Name	Year	Location	Degradation	Mode of Sampling
Cellulose Acetate	1996	Derby	None	Destructive
Tortoiseshell Hairslide	1967	France	None	Destructive
Tortoiseshell Comb	1967	France	None	Destructive
Tortoiseshell Comb	1946	France	Minor	Destructive
Artemide Lamp	1967	New York	Minor	Non-destructive
Storage Folder	1956	Boston	Minor	Destructive
Duchamp Painted Acetate	pre-1972	Philadelphia	Minor	Non-destructive
Inguis Box	late 1920's	New York	Intermediate	Non-destructive
Knife Handle	Unknown	Scotland	Severe	Destructive
Moholy-Nagy Painting	1938	Los Angeles	Severe	Non-destructive
Test Square	Unknown	Scotland	Varied	Destructive
Various Combs	Unknown	Philadelphia	Varied	Non-destructive
Doll	1940's	Scotland	Varied	Destructive

3.3 Solubility Tests

The generic term of 'cellulose acetate' has been used as the commercial name for four cellulose esters: cellulose diacetate, cellulose triacetate, cellulose acetate butyrate and cellulose acetate propionate. These four polymers all emit acetic acid on degradation and produce similar, though distinguishable, FTIR spectra. However, the solubility of each is very distinct: cellulose diacetate is readily soluble in acetone, cellulose triacetate in dichloromethane and cellulose acetate butyrate does not dissolve in either solvent. Cellulose acetate propionate was only produced as a speciality polymer and was not commonly used. The difference in solubility of the acetates was actually utilized by manufacturers to determine when the correct degree of acetylation had been reached[2-5]. Therefore, solubility was used in this study as a means of identifying the exact form of 'cellulose acetate' found in each sample. Unfortunately these tests

were not possible on any of the museum artefacts, as pieces could not be removed for solubility testing.

Tests were conducted by placing approximately 0.5 g of each sample in 5 mL acetone or 5 mL dichloromethane. The samples were then left for 24 h and the solubility of each sample was noted.

The solubility tests, carried out on artefacts referred to as destructively sampled in table 3.1, showed that all of the samples used were readily soluble in acetone and therefore, can be positively identified as cellulose diacetate (referred to as cellulose acetate throughout). A small amount of insoluble white powder was left in the acetone solution for both the doll's body and leg, indicating that a small amount of the original material was not cellulose acetate; this is most likely to be a metal oxide filler used to produce an opaque plastic.

3.4 Fourier Transform Infrared (FTIR) Spectroscopy

Instrumentation used is described in section 2.1.2 and sampling procedures are described in section 2.1.3 and 2.1.4. It was found in practise that very few samples were suitable for analysis with the ATR objective lens due to the limits on artefact thickness and shape; therefore, all discussions are based on spectra recorded by the transmission mode.

FTIR data could only be collected from samples which were donated for destructive analysis. Spectra were measured for the following items:

a) 1996 cellulose acetate,
b) 1967 tortoiseshell hairslide,
c) 1967 tortoiseshell comb,
d) 1946 tortoiseshell comb,
e) 1940's doll, various areas,
f) knife handle,
g) test square,
h) storage folder and
i) Moholy-Nagy painting.

Two very small pieces of the Moholy-Nagy painting which had fallen off the artefact were analysed by FTIR but unfortunately were too small for any other destructive analysis to be carried out. The items were confirmed as cellulose acetate by comparing spectra to those of known standards and spectral libraries.

It is important to be able to differentiate between cellulose acetate, cellulose nitrate and urea formaldehyde because the look and use of these plastics are very similar; they have a good depth of finish and were often used to imitate natural products such as tortoiseshell, horn and ivory. Typical spectra of these three plastics and cellulose are shown in, figures 3.13 – 3.16. It can be seen from these figures that there are clear differences between the spectra of the three plastics.

The peaks of interest in the cellulose acetate spectra were those of O-H, C=O and C-H, as they can be used to indicate degradation. As the cellulose acetate degrades there is a loss of acetate groups and hence a loss of C=O and these are replaced by O-H peaks as the polymer reverts back to the original cellulose. The peaks of interest in the cellulose acetate spectra (figure 3.13) are O-H at 3488 cm^{-1}, C=O at 1752 cm^{-1} and C-H at 1372 cm^{-1}. The corresponding peaks in cellulose nitrate (figure 3.14) are O-H at 3495 cm^{-1}, C=O from plasticiser at 1734 cm^{-1}, NO_3 at 1660 cm^{-1} and C-H at 1372 cm^{-1}. Urea formaldehyde (figure 3.16) has a totally different spectra with the main peaks of O-H at 3340 cm^{-1} and 1383 cm^{-1}, C=O at 1638 cm^{-1} and N-H at 1542 cm^{-1}. The cellulose spectra (figure 3.15) has fewer peaks than the others due to the relative simplicity of this compound, with the two main peaks being O-H at 3340 cm^{-1} and C-H at 1317 cm^{-1}.[6]

The intensities of the C=O (ca. 1750 cm^{-1}) and O-H (ca. 3480 cm^{-1}) peaks in the spectra of samples were ratioed against the C-H (1370 cm^{-1}) to allow an assessment of degradation to be made. The results are shown in table 3.2. The position of the C-H peak in the spectrum remains constant (1369 – 1372 cm^{-1}) as it is the same for cellulose and cellulose acetate and it can therefore be used as the comparison peak for the calculation of intensity ratios. As the cellulose acetate degrades there is loss of C=O which is replaced with O-H as the acetate is lost and the polymer reverts to the original cellulose. This means that as degradation occurs the C=O to C-H ratio will decrease as the peak intensity decreases with loss of C=O groups and the O-H to C-H ratio will show an opposite increase as the C=O groups are replaced by O-H groups.

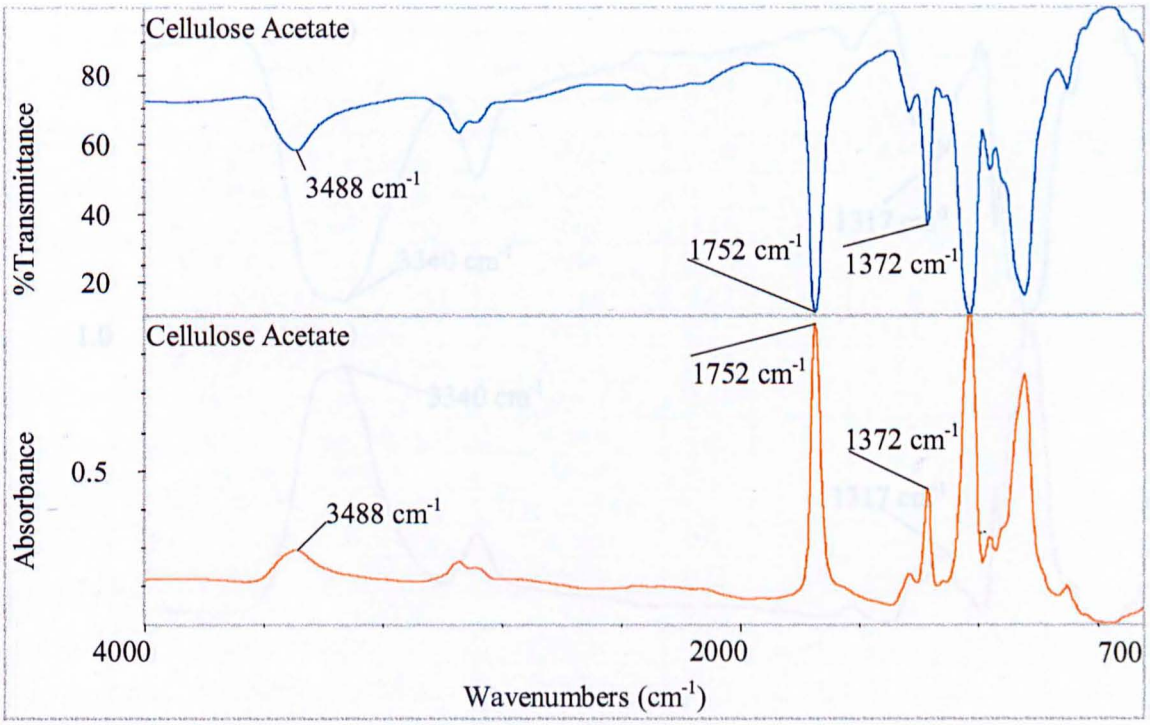

Figure 3.13 Typical FTIR spectra of cellulose acetate

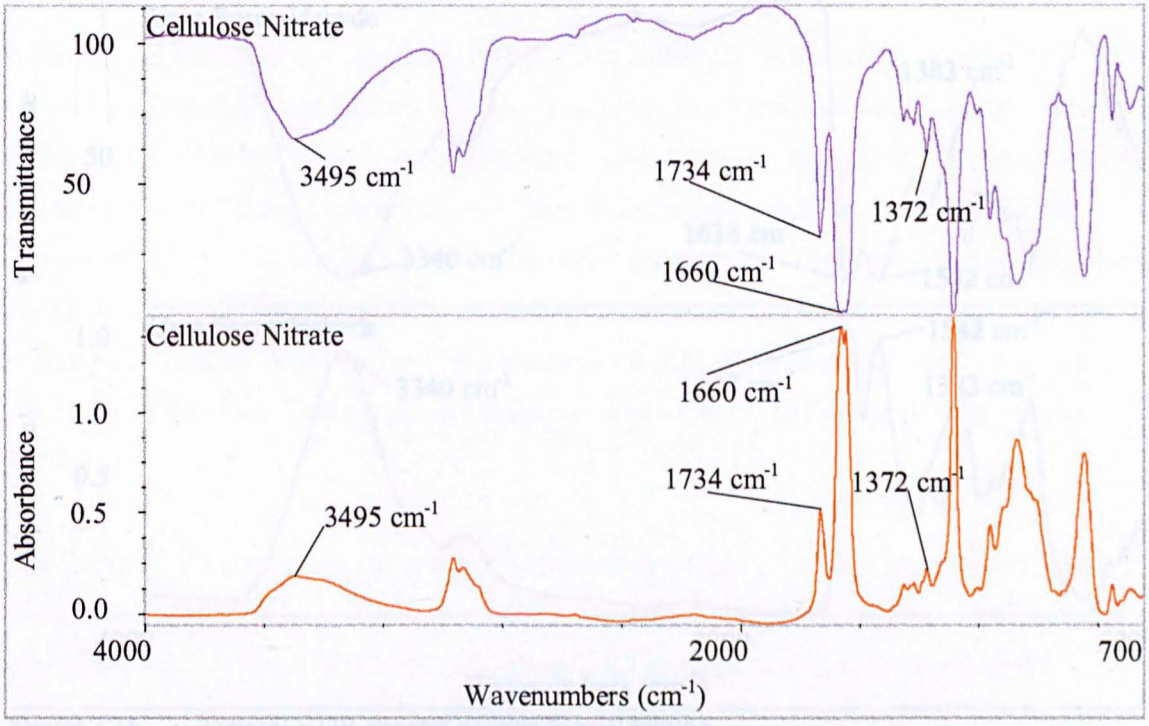

Figure 3.14 Typical FTIR spectra of cellulose nitrate

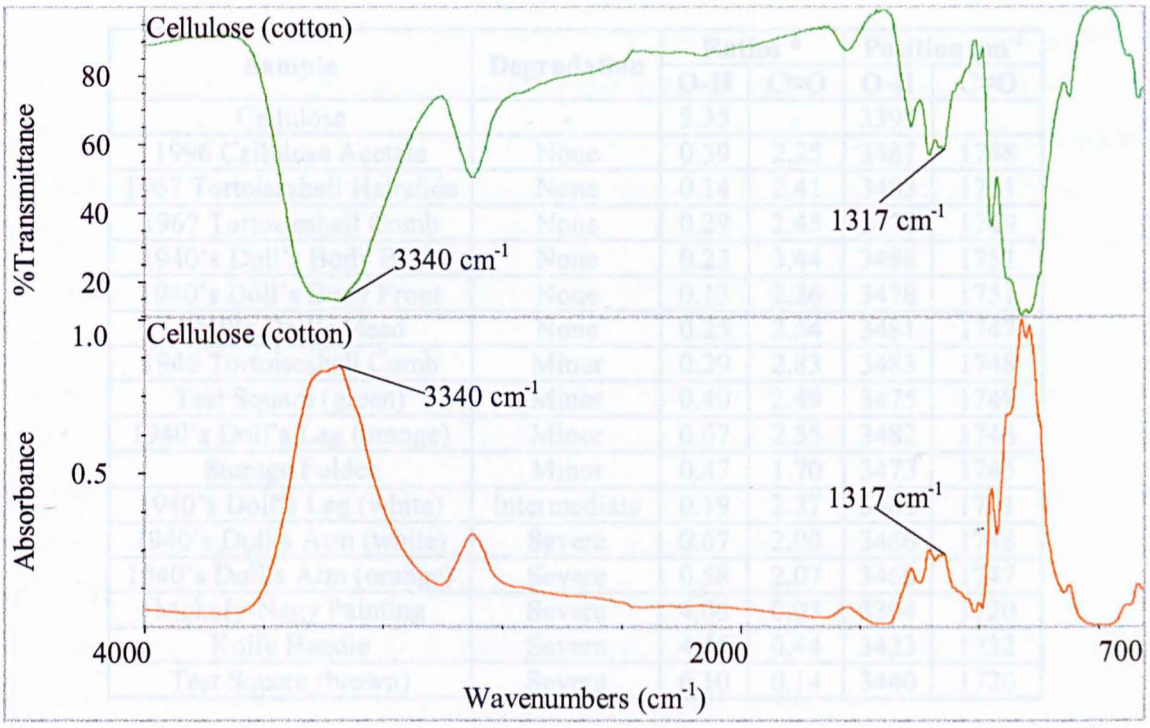

Figure 3.15 Typical FTIR spectra of cellulose

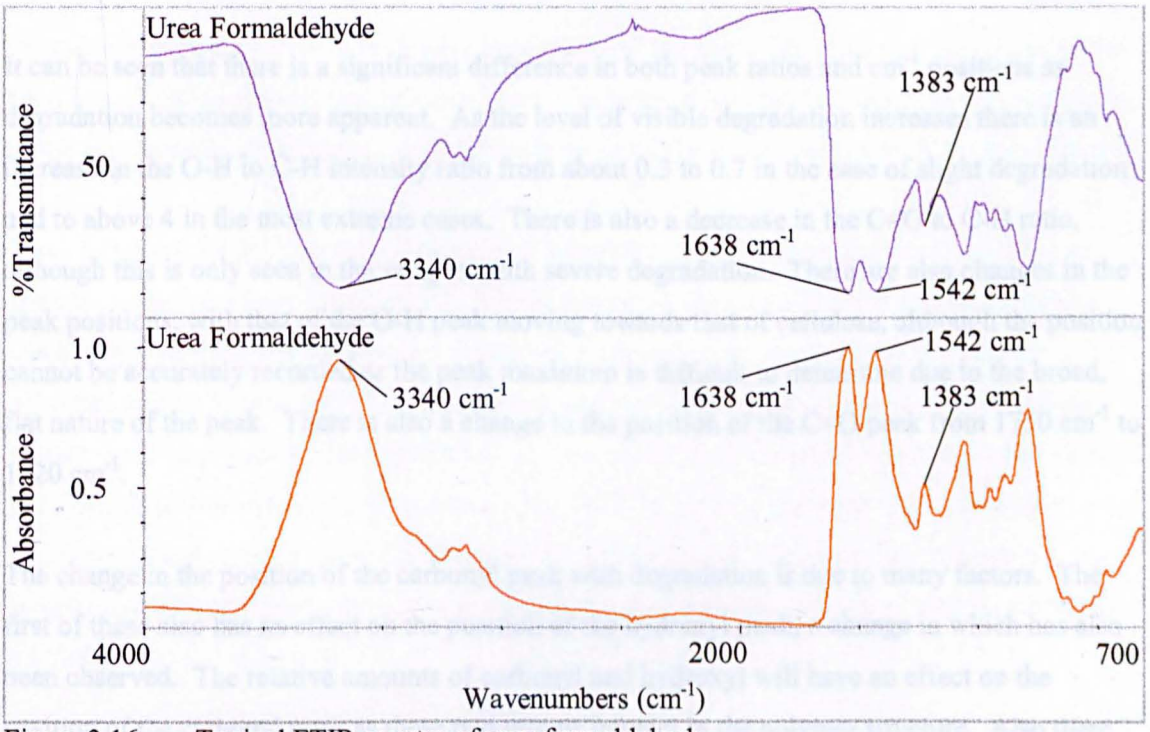

Figure 3.16 Typical FTIR spectra of urea formaldehyde

Table 3.2 FTIR results of naturally aged samples

Sample	Degradation	Ratios *		Position cm^{-1}	
		O-H	C=O	O-H	C=O
Cellulose	-	3.35	-	3397	-
1996 Cellulose Acetate	None	0.39	2.25	3487	1748
1967 Tortoiseshell Hairslide	None	0.14	2.41	3483	1751
1967 Tortoiseshell Comb	None	0.29	2.45	3478	1749
1940's Doll's Body Back	None	0.23	3.44	3488	1751
1940's Doll's Body Front	None	0.13	2.26	3478	1751
1940's Doll's Head	None	0.25	2.54	3481	1747
1946 Tortoiseshell Comb	Minor	0.29	2.83	3483	1748
Test Square (green)	Minor	0.40	2.49	3475	1749
1940's Doll's Leg (orange)	Minor	0.67	2.55	3482	1748
Storage Folder	Minor	0.47	1.70	3473	1745
1940's Doll's Leg (white)	Intermediate	0.19	2.27	3483	1751
1940's Doll's Arm (white)	Severe	0.67	2.00	3466	1748
1940's Doll's Arm (orange)	Severe	0.58	2.07	3460	1747
Moholy-Nagy Painting	Severe	4.06	0.03	3394	1720
Knife Handle	Severe	4.45	0.44	3423	1732
Test Square (brown)	Severe	6.10	0.14	3440	1720

* - Intensity ratio of O-H (1750 cm^{-1}) or C=O (1750 cm^{-1}) to C-H (1370 cm^{-1})

It can be seen that there is a significant difference in both peak ratios and cm^{-1} positions as degradation becomes more apparent. As the level of visible degradation increases there is an increase in the O-H to C-H intensity ratio from about 0.3 to 0.7 in the case of slight degradation and to above 4 in the most extreme cases. There is also a decrease in the C=O to C-H ratio, although this is only seen in the samples with severe degradation. There are also changes in the peak positions, with that of the O-H peak moving towards that of cellulose, although the position cannot be accurately recorded as the peak maximum is difficult to determine due to the broad, flat nature of the peak. There is also a change in the position of the C=O peak from 1750 cm^{-1} to 1720 cm^{-1}.

The change in the position of the carbonyl peak with degradation is due to many factors. The first of these also has an effect on the position of the hydroxyl peak, a change in which has also been observed. The relative amounts of carbonyl and hydroxyl will have an effect on the position of the carbonyl peak as these two groups interact in the polymer structure. Also there are two types of carbonyl present in the cellulose acetate (figure 1.2 and sections 1.2.1 and 1.2.2)

as the C_6 and ring carbonyl groups will interact differently with the rest of the polymer structure. It has been shown that the carbonyl groups are lost in a precise manner (figure 1.8)[7] resulting in the same changes in position from sample to sample as deacetylation progresses. Also as degradation advances there will be changes in the β-linking of the O-H and C=O and changes in the hydrogen bonding as the helix unwraps and repositions. Finally differences in the density and morphology of the cellulose acetate will have an effect on the peak position of the C=O peak as the interactions within the polymer will be affected by these factors.

The results are best displayed as scatter plots of ratio against reduced time (year of analysis (1999) – year of manufacture). For the knife handle this was estimated as 1963, however, this is not precise and will only be used for the purposes of these graphs. It can be seen from the plot of O-H:C-H (figure 3.17) that the older samples are generally more degraded, also the more visually degraded samples have higher ratios. The plot of the C=O:C-H ratio also shows the samples which are oldest as the most degraded, however, in this case the ratio decreases with increasing degradation (figure 3.18). The exception to this is the knife handle, although this could be older than was estimated, following discussions with the owner on the introduction of this type of knife and also the date of purchase. However, the knife handle does show greater degradation than expected by the visual appearance of the handle and this may be related to the need to soak the handles in warm water in order to remove the metal blades, this was necessary as the accelerated ageing experiments (chapter 4) could not be carried out with the knives intact.

It can be seen from the two sets of ratios that, generally, older samples are more degraded as acetate groups have been replaced with hydroxyl groups. This is indicative of deacetylation which has been shown to be the main degradation process in the degradation of cellulose triacetate motion picture films[8-10]. This shows that the degree of substitution of the cellulose acetate is not important to the degradation process as all of the samples studied have been shown to be cellulose diacetate and not cellulose triacetate[11]. This fact, that degree of substitution is not important, is also backed up by the observation by Brown et al[12] that cellulose triacetate is not compatible with plasticiser and hence is not suitable for "thermoplastication" and injection moulding.

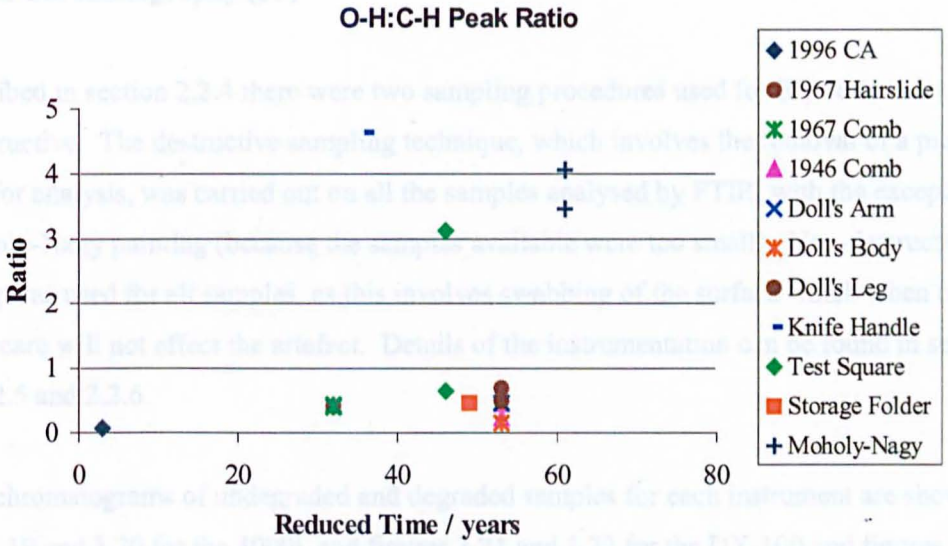

Figure 3.17 Scatter plot of O-H:C-H ratio vs. reduced time

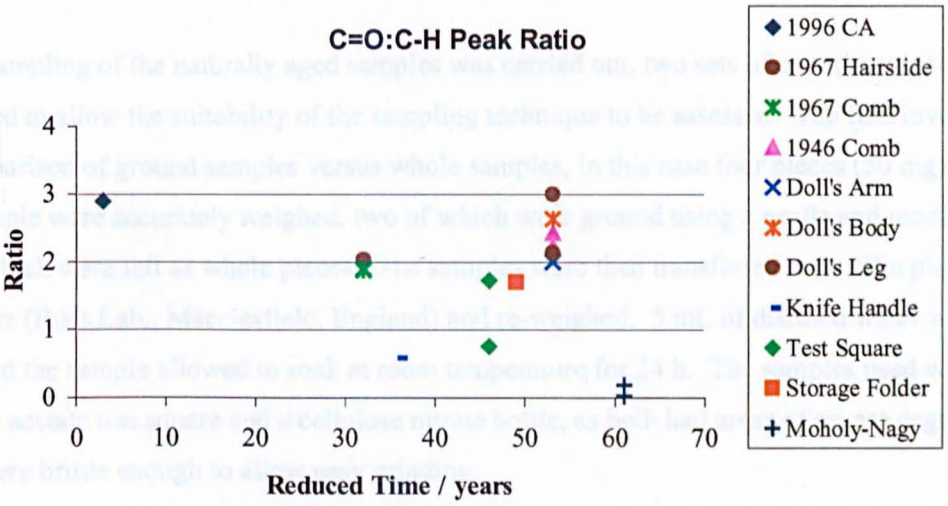

Figure 3.18 Scatter plot of C=O:C-H ratio vs. reduced time

3.5 Ion Chromatography (IC)

As described in section 2.2.4 there were two sampling procedures used for IC, destructive and non-destructive. The destructive sampling technique, which involves the removal of a piece of artefact for analysis, was carried out on all the samples analysed by FTIR, with the exception of the Moholy-Nagy painting (because the samples available were too small). Non-destructive sampling was used for all samples, as this involves swabbing of the surface which when carried out with care will not effect the artefact. Details of the instrumentation can be found in sections 2.2.3, 2.2.5 and 2.2.6.

Typical chromatograms of undegraded and degraded samples for each instrument are shown in figures 3.19 and 3.20 for the 4000i, and figures 3.21 and 3.22 for the DX-100 and figures 3.23 and 3.24 for the DX-500.

3.5.1 Destructive Sampling

Before sampling of the naturally aged samples was carried out, two sets of experiments were performed to allow the suitability of the sampling technique to be assessed. The first involved the comparison of ground samples versus whole samples, in this case four pieces (50 mg) of each sample were accurately weighed, two of which were ground using a pestle and mortar and two of which were left as whole pieces. The samples were then transferred to Sterilin plastic containers (Ross Lab., Macclesfield, England) and re-weighed. 5 mL of distilled water was added and the sample allowed to soak at room temperature for 24 h. The samples used were the cellulose acetate test square and a cellulose nitrate bottle, as both had areas of severe degradation which were brittle enough to allow easy grinding.

The results (table 3.3) showed that there was no difference in the concentration of the ions detected for the ground and whole samples except for the concentration of oxalate in the cellulose acetate sample which was much higher for the whole sample. This is most probably due to chain scission initially occurring at the surface and not being prevalent throughout the bulk of the sample which would result in a higher concentration at the surface and hence a greater extractable concentration from the whole sample than the ground sample.

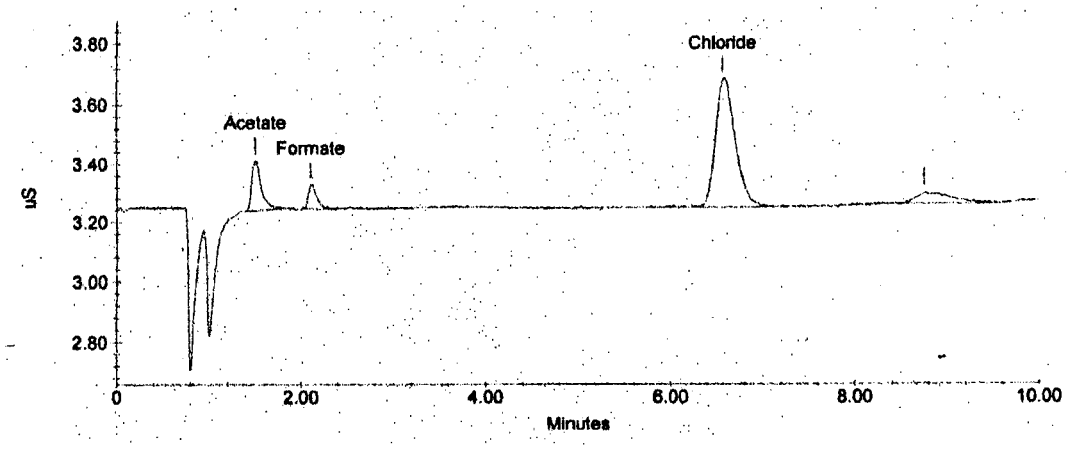

Figure 3.19 **Typical chromatogram of an undegraded sample (1996 cellulose acetate, after natural ageing) using 4000i**

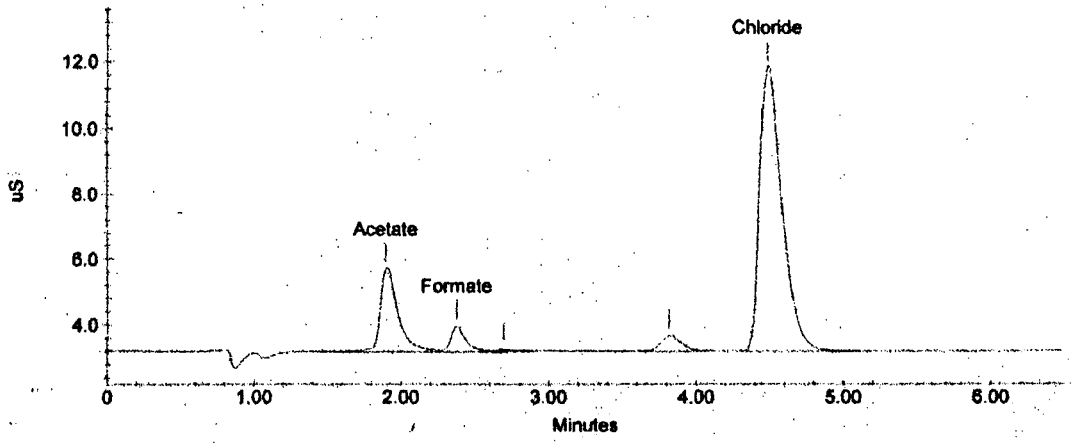

Figure 3.20 **Typical chromatogram of a degraded sample (doll's leg, after ageing at 50 °C and 75 % relative humidity for 117 days) using 4000i**

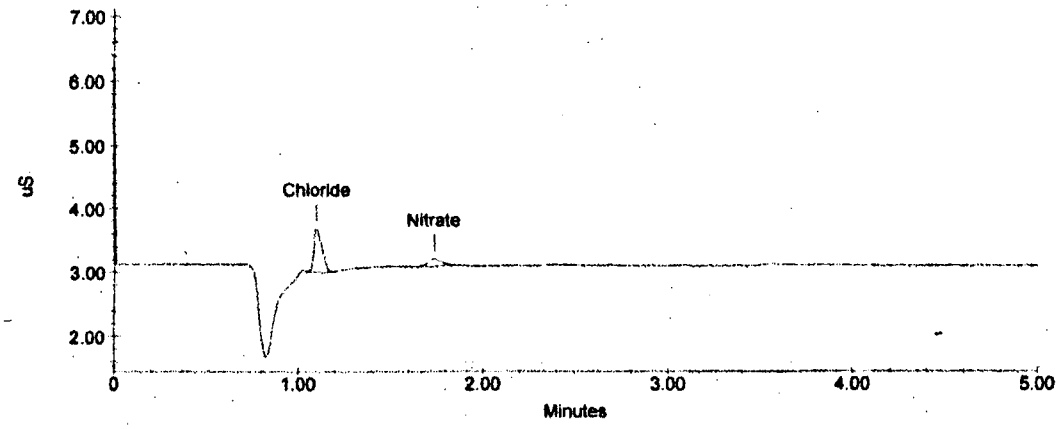

Figure 3.21 **Typical chromatogram of an undegraded sample (1967 hairslide after ageing at 50 °C and 75 % relative humidity for 102 days) using DX-100**

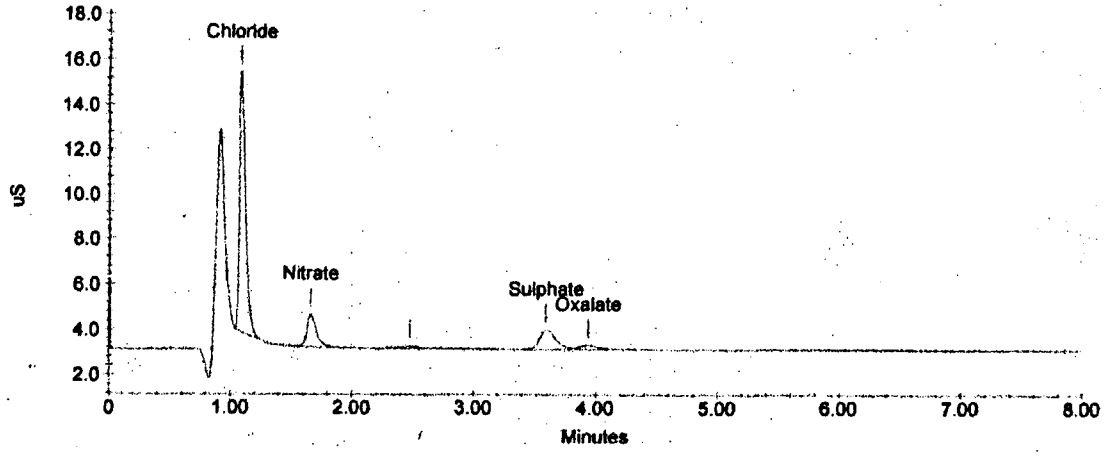

Figure 3.22 **Typical chromatogram of a degraded sample (1967 hairslide after ageing at 50 °C and 12 % relative humidity for 480 days) using DX-100**

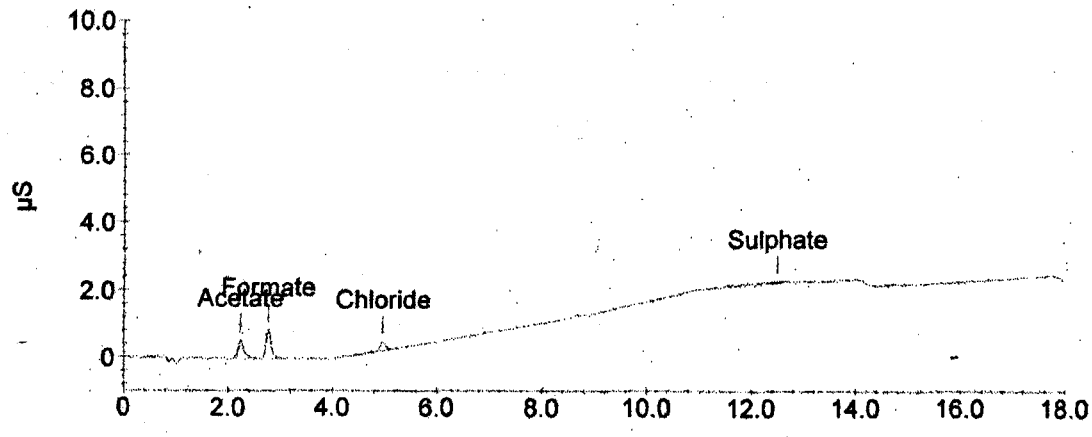

Figure 3.23 **Typical chromatogram of an undegraded sample (Artemide lamp after natural ageing) using DX-500**

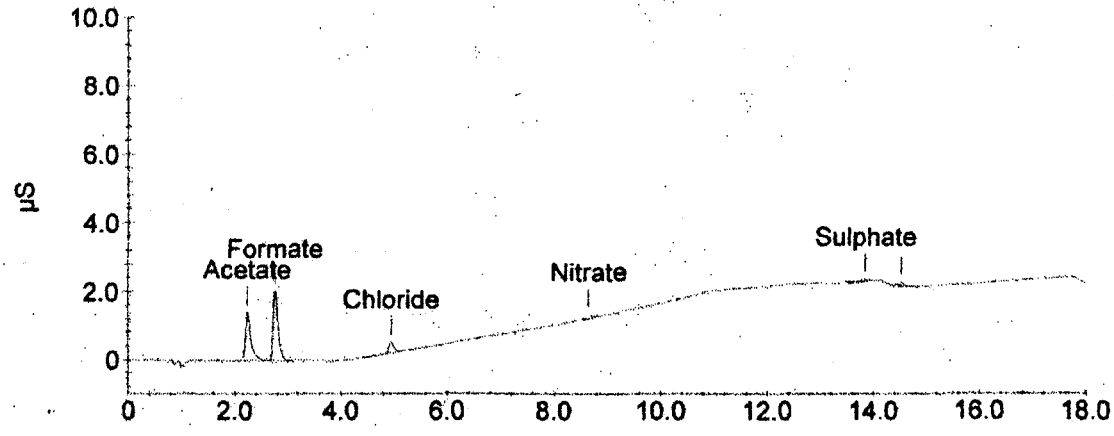

Figure 3.24 **Typical chromatogram of a degraded sample (Moholy-Nagy Painting after natural ageing) using DX-500**

It can also be seen from these results that there is a very distinct difference between the anion profiles of cellulose acetate and cellulose nitrate. This would allow this technique to be used to identify plastics as well as assess the degradation of the samples. The use of the non-destructive sampling procedure would be most useful in this process.

In practise it was found that it was not possible to grind the less degraded samples as these were too pliable. Therefore, it was decided to use whole samples when carrying out the destructive sampling technique.

The second experiment, which was carried out, was to determine the amount of time that the sample needed to soak in distilled water in order to allow all of the water extractable anions to be taken into solution. In this case the cellulose nitrate bottle was used as the cellulose acetate test square was the only cellulose acetate sample available for destructive analysis, at this point, and this was rather small and was required to be kept for further analysis. Four samples were prepared, two samples were allowed to soak for 72 h and two were sampled after 24, 45, 68 and 72 h. The water removed from the samples for the daily analysis was replaced each time.

The results (table 3.4) show that the vast majority of the water extractable anions have been extracted after 24 h, therefore, this time was chosen for the sampling technique to allow speedy analysis of the samples throughout this study. This was especially significant when the accelerated ageing study was being carried out.

The destructive sampling procedure was then used to assess the ion concentrations for other naturally aged samples as shown in table 3.5.

Acetate levels are higher for samples which show visual signs of degradation. However, the concentration for the knife handle is also high, although it appeared in perfect condition on initial inspection. Removal of the handles from the metal knife blades meant soaking them in hot water and this could have had a detrimental effect accelerating the degradation. The handles had to be separated from the blades to allow these to be included in the accelerated ageing studies (chapter 4). The only samples with detectable concentrations of oxalate were the extremely degraded areas of the doll's arm and leg. This would suggest that deacetylation is the first and main degradation process with chain scission being a secondary reaction which occurs

Table 3.3 Bulk concentrations of ions ground vs. whole samples – from IC analysis of extracts (destructive)

Sample	Cellulose Type	Concentration / µg g^{-1}					
		Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
Bottle Whole	Nitrate	263.3 ± 35.7	152.0 ± 45.0	16.9 ± 1.4	2432.4 ± 52.9	16.3 ± 20.0	1059.3 ± 16.8
Bottle Ground	Nitrate	262.6 ± 35.7	151.2 ± 44.9	20.5 ± 1.2	2708.3 ± 77.0	26.3 ± 28.9	1173.4 ± 25.9
Test Square Whole	Acetate	521.7 ± 35.6	46.1 ± 7.7	142.2 ± 9.5	249.1 ± 58.1	117.6 ± 20.1	38.9 ± 0.6
Test Square Ground	Acetate	509.8 ± 34.8	45.1 ± 6.7	142.3 ± 8.5	286.2 ± 56.5	140.7 ± 19.6	12.9 ± 0.3

Standard deviations obtained from calibration error, n = 4

Table 3.4 Bulk concentrations of ions over time, cellulose nitrate bottle – from IC analysis of extracts (destructive)

Sample	Concentration / µg g^{-1}					
	Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
24 h A1	235.4 ± 54.2	104.8 ± 41.2	12.2 ± 3.6	886.4 ± 99.2	341.3 ± 36.0	1087.9 ± 39.7
45 h A1	24.8 ± 9.7	8.0 ± 5.2	1.9 ± 1.3	27.1 ± 3.4	12.9 ± 1.8	80.8 ± 1.4
68 h A1	0.9 ± 1.8	4.8 ± 3.2	1.1 ± 0.4	3.5 ± 1.6	1.6 ± 1.7	20.6 ± 1.6
72 h A1	0.5 ± 1.6	3.6 ± 1.4	0.6 ± 0.9	2.4 ± 0.8	0.9 ± 0.7	5.3 ± 0.7
Total	261.6 ± 55.1	121.2 ± 41.7	15.8 ± 4.0	919.4 ± 99.3	356.7 ±36.1	1194.6 ± 39.8
72 h A2	218.9 ± 33.5	71.5 ± 6.9	29.8 ± 4.3	678.1 ± 26.8	306.7 ± 23.5	854.9 ± 28.1
24 h B1	520.7 ± 79.1	203.0 ± 61.2	112.2 ± 9.4	4545.2 ± 271.2	9.4 ± 2.1	1466.6 ± 45.0
45 h B1	27.0 ± 2.2	10.2 ± 5.8	3.7 ± 0.7	132.9 ± 3.8	ND	56.0 ± 1.5
68 h B1	1.5 ± 2.1	4.6 ± 3.6	2.8 ± 0.8	21.0 ± 1.8	ND	12.8 ± 1.9
72 h B1	0.7 ± 1.4	1.5 ±2.1	0.9 ± 0.5	9.4 ± 1.5	ND	5.3 ± 0.9
Total	549.9 ± 79.2	219.1 ± 61.6	119.6 ± 9.5	4708.5 ± 271.2	9.4 ± 2.1	1540.7 ± 45.1
72 h B2	488.4 ± 49.0	222.6 ± 35.6	101.7 ± 6.5	5527.8 ± 83.8	11.7 ± 0.9	1422.6 ± 50.6

Standard deviations obtained from calibration error, n = 4
ND – not detected
Detection limit - sulphate 0.55 µg g^{-1}

Table 3.5 Bulk concentrations of ions from naturally aged samples – from IC analysis of extracts (destructive)

Sample	Degradation	Concentration / μg g^{-1}					
		Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
1996 CA	None	9.5 ± 1.3	1.3 ± 2.1	4.0 ± 1.5	8.3 ± 1.3	1.0 ± 0.7	ND
1967 hairslide	None	13.1 ± 1.0	0.8 ± 1.7	5.8 ± 1.1	9.7 ± 1.0	1.0 ± 0.5	ND
1967 comb	None	6.8 ± 1.9	ND	4.6 ± 1.8	2.3 ± 3.1	1.4 ± 0.3	ND
1946 comb	None	50.7 ± 1.0	0.6 ± 1.3	7.1 ± 2.3	5.9 ± 1.3	2.0 ± 0.7	ND
Doll's Chest	None	9.3 ± 0.5	1.0 ± 0.6	5.8 ± 1.2	3.1 ± 0.7	2.4 ± 0.3	ND
Doll's Back	None	11.6 ± 0.6	0.9 ± 0.7	7.7 ± 1.2	4.3 ± 0.7	3.5 ± 0.4	0.3 ± 1.1
Doll's Arm	Severe	279.7 ± 8.4	11.8 ± 1.2	21.7 ± 8.9	14.9 ± 1.8	104.2 ± 5.2	73.7 ± 15.6
Doll's Leg	Intermediate	248.1 ± 7.5	5.8 ± 1.9	13.6 ± 1.7	6.6 ± 8.3	39.3 ± 4.1	24.4 ± 12.4
Knife Handle	None	69.1 ± 0.8	ND	68.8 ± 19.9	31.2 ± 1.4	0.6 ± 0.5	ND
Storage Folder	Minor	103.8 ± 2.9	ND	14.9 ± 2.1	5.3 ± 0.6	10.4 ± 0.8	0.7 ± 1.0

Standard deviations obtained from calibration error, n = 4

ND – not detected

Detection limits – formate 0.35 μg g^{-1}, oxalate 0.33 μg g^{-1}

after degradation has reached a certain level. This conclusion has also been drawn by Cardamone et al.[13], Bryk[14], Allen et al. (with regard to motion picture film)[15] and Ram et al.[16].

Chloride levels also appear to increase as degradation increases. This is likely to be due to more chloride impurity in the plastic being dissolved as the polymer matrix becomes more open due to deacetylation and consequent loss of hydrogen bonding. The chloride is present in the matrix because magnesium chloride (or another chloride salt) is commonly used to stop the ripening or deacetylation step of manufacture, when cellulose triacetate is back-acetylated to cellulose diacetate[17]. Sulphate concentrations in the steeping water were high only for more degraded samples and this could be due to the fact that the trapped sulphuric acid (the most common catalyst[3,17,18]) can be present as part of the polymer in the form of aceto-sulphate esters. As these are physically part of the polymer and not just within the matrix, the degradation of the artefact would have to be more severe to allow the release of the sulphate (figure 1.5).

In all cases nitrate was detected and this is most probably due to air contamination as elemental analysis results showed that nitrogen was only present at trace levels in two samples and not present at all in the others. This indicated that a cellulose acetate – cellulose nitrate mixture has not been used. Finally the levels of formate, an indicator of oxidative degradation, are low or not detected except for the most degraded samples, suggesting some oxidative degradation in these artefacts. Although again this would show that deacetylation is the initial degradation process with chain scission and/or oxidative degradation occurring later in the breakdown of the artefact[8-10,13-16].

3.5.2 Non-destructive Sampling

The results for the non-destructive sampling, table 3.6, showed similar trends to those for destructive sampling even although the results themselves were different, as acetate was higher in degraded samples compared with those that were not degraded. However, it is important to remember that the concentrations cannot be compared directly and that it is only possible to see if the same conclusions can be drawn for both sampling procedures. Also oxalate was only present in the samples which were showing greater signs of degradation. The levels of chloride, nitrate and sulphate were low although higher levels of all three were found in the more

Table 3.6 Surface concentrations of ions from naturally aged samples – from IC analysis of swabs (non-destructive).

Sample	Degradation	Concentration / μg cm^{-2}					
		Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
1996 Cellulose Acetate	None	ND	0.1 ± 0.05	ND	ND	ND	ND
1967 Tortoiseshell Hairslide	None	0.9 ± 0.03	0.1 ± 0.05	ND	0.9 ± 0.03	0.2 ± 0.04	ND
1967 Tortoiseshell Comb	None	6.9 ± 0.03	2.1 ± 0.04	2.5 ± 0.02	1.3 ± 0.01	1.6 ± 0.06	ND
1946 Tortoiseshell Comb	None	2.4 ± 0.03	0.5 ± 0.05	0.9 ± 0.03	0.4 ± 0.06	0.8 ± 0.03	ND
Knife Handle	None	23.9 ± 0.5	0.6 ± 0.05	1.2 ± 0.03	ND	0.2 ± 0.06	ND
Storage Folder	Minor	83.7 ± 0.2	ND	22.3 ± 1.7	2.2 ± 0.02	1.0 ± 0.2	0.4 ± 0.02
Moholy-Nagy	Intermediate	314.8 ± 23.7	13.5 ± 9.5	ND	ND	ND	1.7 ± 0.8
Artemide Lamp	Minor	228.1 ± 30.6	ND	ND	ND	6.4 ± 2.7	1.0 ± 0.7
Inguis Box	Intermediate	143.0 ± 16.5	47.7 ± 24.1	14.8 ± 2.6	2.3 ± 0.7	6.8 ± 3.6	2.8 ± 1.6
Duchamp Painted Acetate	Minor	243.3 ± 21.8	38.0 ± 15.1	40.8 ± 19.7	ND	7.2 ± 4.7	2.7 ± 1.3

Standard deviations obtained from calibration error, n = 4

ND – not detected

Detection limits – formate 0.42 μg cm^{-2}, chloride 0.38 μg cm^{-2}, nitrate 0.29 μg cm^{-2}, sulphate 0.42 μg cm^{-2}, oxalate 0.28 μg cm^{-2}

degraded samples. In addition, the formate levels were only significant in samples which were older.

Higher chloride levels are only seen in three samples, these were older but not necessarily more degraded than the other samples. This could have been due to less efficient washing of the cellulose acetate during early manufacture which would lead to greater levels of impurities and contamination[19,20]. Sulphate levels were higher in the more degraded samples although it was not detected at all in the Moholy-Nagy which was a severely degraded sample. Nitrate concentrations did not follow a pattern connected to the extent of degradation. Finally, formate concentrations were higher in those samples which were degraded indicating that oxidative degradation may have occurred on the surface of those artefacts.

The significantly higher concentrations of ions for the storage folder, Moholy-Nagy, Artemide lamp, Inguis box and Duchamp are most probably due to these pieces being handled far less than the other samples. This would be due to these artefacts being museum pieces where as the others have been handled throughout their lifetimes. The lack of handling would result in any ions present on the surface being left and perhaps even increased by additional migration to the surface, whereas with the readily handled artefacts the ions would be removed.

Swabs were taken from many areas of the doll both inside and out. This was to allow comparison of the two surfaces of the doll in anticipation that an indication of the initiator of degradation may be found. If UV light, indoor pollutants or handling were factors in the onset of degradation then the outer surface would show greater degradation, whereas, if the main factors were temperature or relative humidity then both surfaces would be similar. If the metal fixtures within the doll had an effect, as was seen by Edge et al.[9] and Allen et al.[15] then the inside surface, near these parts, would show greatest degradation. Therefore, an investigation of many areas was carried out.

The results are shown in table 3.7 and 3.8. The inside surface of the doll has higher levels of degradation indicated by the high concentrations of acetate present in both the arm and leg of the doll (average of 6.6 $\mu g\ mL^{-1}$ and 4.3 $\mu g\ mL^{-1}$ respectively). This could be due to the influence of the metal fixtures[9,15] or the enclosed nature of these parts, which would lead to a build up of acetate levels on the surface, whereas on the outer surface the acetate would volatilise and be

Table 3.7 **Surface concentrations of ions on outside surface of doll – from IC analysis of swabs (non-destructive).**

Sample	Degradation	Concentration / μg cm^{-2}					
		Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
Left Arm	Severe	0.7 ± 0.03	ND	1.0 ± 0.05	0.5 ± 0.04	0.5 ± 0.01	0.9 ± 0.2
Right Arm	Severe	1.5 ± 0.04	ND	1.5 ± 0.6	0.4 ± 0.04	0.4 ± 0.01	0.2 ± 0.2
Left Leg	Minor	2.1 ± 0.02	ND	1.4 ± 0.06	0.7 ± 0.03	0.7 ± 0.02	ND
Right Leg	None	0.9 ± 0.06	ND	0.7 ± 0.06	0.5 ± 0.05	ND	ND
Foot	Minor	0.4 ± 0.02	ND	0.5 ± 0.03	0.4 ± 0.03	0.2 ± 0.2	ND
Body Front	None	1.2 ± 0.06	ND	0.7 ± 0.07	0.3 ± 0.04	0.1 ± 0.02	ND
Body Back	None	1.0 ± 0.05	ND	0.8 ± 0.06	ND	0.4 ± 0.03	ND
Forehead	Minor	0.1 ± 0.04	ND	0.7 ± 0.07	0.1 ± 0.06	1.6 ± 0.01	ND
Nose	Minor	0.2 ± 0.06	ND	0.2 ± 0.05	0.1 ± 0.04	0.8 ± 0.07	ND
Cheek	Minor	0.9 ± 0.07	ND	0.8 ± 0.02	0.4 ± 0.04	0.6 ± 0.4	ND

Standard deviations obtained from calibration error, n = 4

ND – not detected

Detection limits – formate 0.42 μg cm^{-2}, nitrate 0.29 μg cm^{-2}, sulphate 0.42 μg cm^{-2}, oxalate 0.28 μg cm^{-2}

Table 3.8 **Surface concentrations of ions on inside surface of doll – from IC analysis of swabs (non-destructive)**

Sample	Degradation	Concentration / μg cm^{-2}					
		Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
Right Hand	Severe	4.0 ± 0.02	ND	1.2 ± 0.03	0.8 ± 0.06	3.6 ± 0.01	0.9 ± 0.01
Right Elbow	Severe	12.6 ± 0.03	ND	2.8 ± 0.06	1.4 ± 0.1	3.8 ± 0.01	2.4 ± 0.03
Right Arm	Severe	3.1 ± 0.03	0.2 ± 0.02	ND	ND	1.7 ± 0.07	5.1 ± 0.06
Left Ankle	Minor	3.9 ± 0.03	ND	0.3 ± 0.03	ND	1.0 ± 0.04	6.6 ± 0.06
Left Knee	None	4.3 ± 0.02	ND	0.8 ± 0.06	ND	0.5 ± 0.02	6.5 ± 0.06
Left Thigh	Minor	4.7 ± 0.01	ND	2.7 ± 0.3	1.3 ± 0.09	1.6 ± 0.07	8.2 ± 0.06
Body Front	None	ND	ND	0.2 ± 0.05	ND	0.9 ± 0.04	0.1 ±0.4
Body Back	None	1.7 ± 0.04	ND	1.4 ± 0.04	0.2 ± 0.02	1.5 ± 0.06	0.1 ± 0.4

Standard deviations obtained from calibration error, n = 4

ND – not detected

Detection limits – acetate 0.96 μgcm^{-2}, formate 0.42 μgcm^{-2}, chloride 0.38 μgcm^{-2}, nitrate 0.29 μgcm^{-2}, sulphate 0.42 μgcm^{-2}, oxalate 0.28 μgcm^{-2}

removed by handling and/or cleaning. There is also a far higher concentration of oxalate on the inside of the doll (average of 3.7 $\mu g\ mL^{-1}$), for the same reasons as for acetate, although oxalic acid is less volatile than acetic acid and would therefore, show less difference, as observed. Visual inspection of the doll showed that degradation looked similar on both surfaces, the exception was around the metal fixtures, where the plastic was blackened but not blistered or cracked as expected. However, these areas did not have increased levels of acetate or oxalate when compared with the other inside surfaces.

The levels of chloride and nitrate were generally slightly higher on the inside than the outside, probably due to less handling e.g. doll's leg average 2.7 $\mu g\ cm^{-2}$ inside vs. 1.4 $\mu g\ cm^{-2}$ outside for chloride and 1.3 $\mu g\ cm^{-2}$ inside vs. 0.7 $\mu g\ cm^{-2}$ outside. However, there was an unexpected increase in sulphate levels on the inside surface, probably due to leaching of the 'mobile' salt to the surface of the artefact as a consequence of the action of moisture. The ions will dissolve in any moisture present and will then move to the surface where the moisture will evaporate and leave a residue of ions. On the inside surface this will remain intact and gradually be added to with further migration. On the outside surface handling and/or cleaning will remove this residue of ions. Formate is very low in both cases, showing very little oxidative degradation, however, if it did occur, it would be expected that formate would be higher on the outside as oxidative degradation would be more prevalent on this surface.

The results for the various combs analysed (table 3.9) show that not all of the combs were cellulose acetate. Although it is not possible to make a positive identification by IC alone, it would be reasonable to conclude that 1 – 6, 9 and 11 were cellulose acetate with 7 and 8 being cellulose nitrate. Number 10 was possibly urea formaldehyde or casein because these are all very similar plastics with a depth of finish and feel that can be easily mistaken. The differences in the ion profile for the different plastic types shows that IC, with non-destructive sampling, could be a useful technique for indicating the identity of plastics if FTIR is not available.

For further discussions, only the combs that appeared to be cellulose acetate will be considered. It can be seen that acetate and oxalate levels are generally high. This could suggest that degradation is quite advanced. There could be a build up of short chain organic acids and aldehydes from the drawer material itself, as wood[21-24], adhesives and varnishes[25] and paint[26] are known to emit potentially dangerous levels of these volatiles. The levels could also be caused

Table 3.9 **Surface concentrations of ions on various combs – from IC analysis of swabs (non-destructive).**

Sample	Degradation	Concentration / μg cm^{-2}					
		Acetate	Formate	Chloride	Nitrate	Sulphate	Oxalate
Comb 1	Minor	285.3 ± 23.6	ND	ND	5.5 ± 1.3	2.6 ± 0.8	2.4 ± 1.4
Comb 2	Intermediate	339.8 ± 31.8	ND	ND	ND	ND	13.4 ± 3.5
Comb 3	Minor	254.3 ± 19.5	ND	ND	57.4 ± 12.4	ND	6.1 ± 2.8
Comb 4	Minor	356.8 ± 36.4	ND	ND	9.0 ± 2.8	8.2 ± 2.3	8.4 ± 3.7
Comb 5	None	412.1 ± 37.9	ND	ND	10.0 ± 3.4	4.5 ± 2.1	3.6 ± 0.9
Comb 6	Severe	133.4 ± 18.2	ND	ND	39.7 ± 1.4	14.0 ± 5.6	4.8 ± 1.6
Comb 7	Minor	22.6 ± 4.2	ND	3.3 ± 1.9	286.9 ± 35.4	40.9 ± 19.2	4.1 ± 1.8
Comb 8	None	17.4 ± 2.8	ND	7.4 ± 1.8	140.6 ± 21.5	ND	ND
Comb 9	None	281.0 ± 26.7	ND	ND	13.5 ± 1.2	ND	ND
Comb 10	None	15.6 ± 3.8	ND	ND	14.9 ± 1.7	ND	ND
Comb 11	Minor	255.2 ± 34.6	ND	5.7 ± 2.4	30.7 ± 2.9	ND	ND

Standard deviations obtained from calibration error, n = 4

ND – not detected

Detection limits – formate 0.42 μg cm^{-2}, chloride 0.38 μg cm^{-2}, nitrate 0.29 μg cm^{-2}, sulphate 0.42 μg cm^{-2}, oxalate 0.28 μg cm^{-2}

by a build up of acetic and oxalic acid in the drawer, from one or two badly degraded combs affecting the others. This is possible due to the enclosed environment of the drawer; this phenomenon was seen in the accelerated ageing study (chapter 4) where the samples in close proximity to degraded samples were negatively effected by the degraded sample; this has been reported as 'Doll's Disease' and 'The Vinegar Syndrome'[12,16,27]. This theory is also indicated by the higher than expected levels of nitrate found on all the combs, coming from off-gassing of the nitric acid and nitrogen oxide gases produced when cellulose nitrate degrades[28-30]. Levels of residual chloride and sulphate from manufacture are not a factor in degradation of cellulose acetate as the varying levels show no correlation with the degree of degradation of the combs. Formate was not detected on any of the combs indicating that oxidative degradation of these artefacts was not occurring, most probably due to the enclosed, airless nature of the storage area.

3.5.3 Comparison of Sampling Procedures

Although the absolute values are different between the two sampling procedures, it can be seen that the general trends in the two main ions, acetate and oxalate, are very similar, with levels rising for degraded samples. When considering the relative extents of degradation, it is apparent that, for the artefacts studied, an increase in acetate occurs before any increase in oxalate, indicating that deacetylation occurs initially with chain scission as a secondary reaction after degradation has progressed relatively far[13-16].

Nitrate levels are consistent from artefact to artefact throughout both swabbing and destructive sampling procedures. The concentrations are low and do not seem to be connected to degradation as undegraded samples and badly degraded samples have similar levels. This nitrate contamination must be from the atmosphere and possibly the close proximity of degrading cellulose nitrate artefacts in some cases.

When the ratio of concentrations of chloride and sulphate to acetate are calculated it shows that there is a difference in the distribution of these ions between the degraded and undegraded samples. In the undegraded artefacts the higher concentrations of chloride and sulphate are found within the bulk of the samples, but in the degraded samples higher concentrations of chloride and sulphate are found at the surface. This is explained by the degradation process, as deacetylation occurs the aceto-sulphate esters[5,31,43]which attach the sulphate to the polymer are

broken, making the sulphate mobile, which allows it to migrate to the surface. The chloride left over from manufacture will also be migrating to the surface in the degraded artefacts because the solubility of the chloride in the polymer matrix changes as degradation occurs. These ions are still present in the undegraded artefacts but are trapped within the matrix, however, when the water impregnates into the polymer this will release these ions for extraction, therefore the concentrations of chloride and sulphate are higher in the bulk of the undegraded samples.

3.6 X-ray Fluorescence (XRF) Spectroscopy

Instrumentation and sampling details can be found in sections 2.5.2 and 2.5.3, respectively. XRF was used to help to establish if there was a link between metals present and degradation; as a previous study by Stewart et al.[33] showed, zinc oxide filler was able to scavenge acid and slow down or prevent degradation. If a similar link was established for cellulose acetate then XRF would be a potentially important tool for assessing artefacts, especially as this is a non-destructive technique.

XRF analysis was carried out on the samples chosen for accelerated ageing,

a) 1996 cellulose acetate,
b) 1967 tortoiseshell hairslide,
c) 1967 tortoiseshell comb,
d) 1946 tortoiseshell comb and
e) 1940's doll, various areas.

The results are shown in table 3.10.

The data shows one very interesting result. Selenium is present in undegraded areas of the doll but is not present in degraded parts, spectra are shown in figures 3.25 and 3.26. Selenium has been used as a heat-resistant red pigment in plastics[32] and may have been used in combination with white pigments to produce a fleshy pink colour. However, this would not have been common as the separation of selenium and tellurium is complicated and it would not have been economically viable to isolate selenium from the mineral. If a selenium pigment had been used, then the reason for it only being present in some areas of the doll is unclear. It would suggest that the different parts of the doll were made from different batches of cellulose acetate, possibly

even from different manufacturers. This is also indicated by the different levels and forms of degradation seen, however, the reasons for this are unclear.

Table 3.10 Metals present in naturally aged artefacts – XRF analysis

Sample	Degradation	Elements Present
1996 Cellulose Acetate	None	None
1967 Tortoiseshell Hairslide	None	Zn, Cu, Fe
1967 Tortoiseshell Comb	None	Zn, Cu, Fe
1946 Tortoiseshell Comb	None	Zn, Cu, Pb
1940's Doll's Belly	None	Ti, Zn, Se
1940's Doll's Chest	None	Ti, Fe, Zn, Se
1940's Doll's Left Leg	Minor	Ti, Fe, Zn
1940's Doll's Right Leg	None	Ti, Fe, Se
1940's Doll's Left Arm	Severe	Ti, Fe, Zn
1940's Doll's Right Arm	Severe	Ti, Fe, Zn
1940's Doll's Head	Minor	Ti, Se

The other metals present within the samples are expected, the presence of titanium and/or zinc throughout the doll is due to the use of filler (as indicated by the solubility tests, section 3.3) to make the cellulose acetate opaque. The iron, copper and lead in the samples are from the pigments used in the artefacts to create the desired colour effect. These are the same trace metals as were found in cellulose nitrate samples studied by Stewart et al. in a previous study[33]and this is expected, as the same or similar pigments were used to colour both cellulose nitrate and cellulose acetate.

3.7 Elemental Analysis

Elemental analysis was carried out on the samples chosen for accelerated ageing, and the results are shown in table 3.11. Oxygen values were calculated by subtracting the carbon, hydrogen and nitrogen values from 100, therefore these are only estimates, as sulphate, chloride and trace elements are not accounted for. The elemental analysis was carried out in order to discover if any mixing of cellulose acetate and cellulose nitrate had taken place in these samples as was indicated by some of the high nitrate ion levels found in the artefacts (section 3.5).

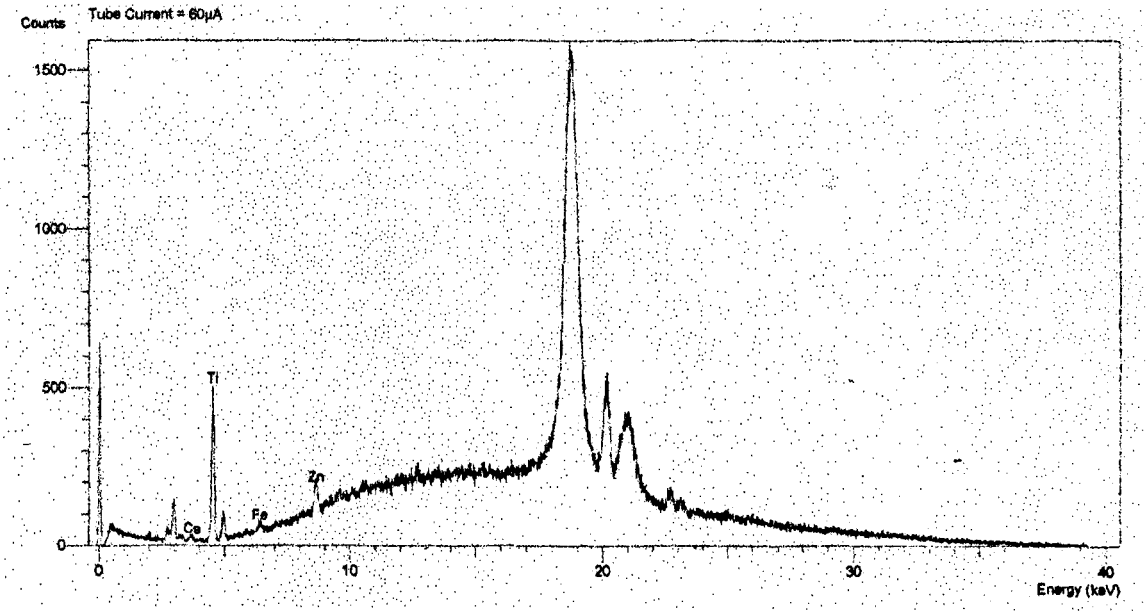

Figure 3.25 XRF spectrum of 1940's doll's left arm (degraded), no selenium

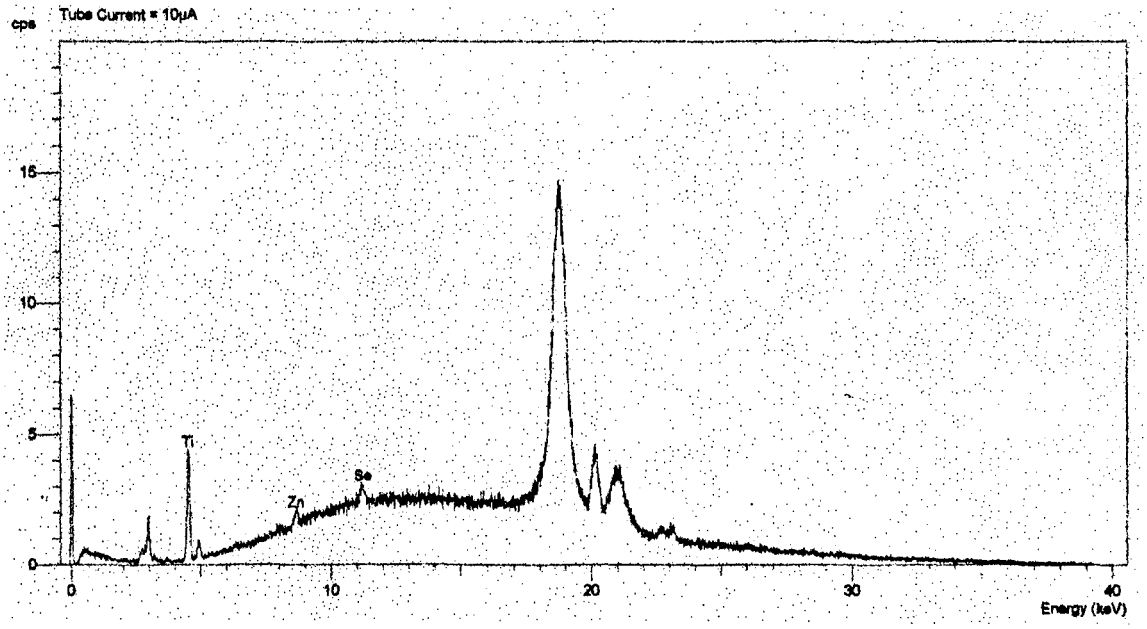

Figure 3.26 XRF spectrum of 1940's doll's chest (undegraded), selenium present

The results show that none of the samples were cellulose acetate – cellulose nitrate mixtures as levels of nitrogen were extremely low and generally not detectable. Levels of nitrogen found in cellulose nitrate samples were typically 7 – 9 % for artefacts in good condition[33]. The carbon, hydrogen and oxygen levels are generally very similar and differences in concentrations between artefacts do not seem to relate to visible signs of degradation.

Both diacetate and triacetate have similar percentage carbon (theoretical 46 – 47 %), hydrogen (theoretical 5 – 6 %) and oxygen (theoretical 47 – 48 %) levels, therefore it is impossible to discriminate between the types of cellulose acetate using this technique. The differences between the theoretical values and those found in this study are due to the plasticiser which is present at 20 – 40 % in samples of cellulose acetate. It would be expected that plasticiser loss would have an effect on the relative percentages of carbon, hydrogen and oxygen, however, this was not observed due to the samples only being analysed by elemental analysis after natural ageing when plasticiser loss would not have been widespread.

Table 3.11 Percentage carbon, hydrogen, nitrogen and oxygen present in naturally aged samples - Elemental analysis

Sample	Degradation	Percentage Element Present (%)			
		Carbon	Hydrogen	Nitrogen	Oxygen
1996 Cellulose Acetate	None	48.8	6.0	ND	45.3
1967 Tortoiseshell Hairslide	None	52.1	5.8	ND	42.1
1967 Tortoiseshell Comb	None	50.5	5.7	ND	43.8
1946 Tortoiseshell Comb	None	49.8	5.6	< 0.2	44.7
1940's Doll's Body	None	52.0	5.8	ND	42.2
1940's Doll's Left Leg	Minor	49.4	6.0	ND	44.6
1940's Doll's Right Arm	Severe	49.6	5.8	< 0.3	44.6

ND- not detected

3.8 Overall Conclusions From Study of Naturally Aged Artefacts

The results from the analysis of the naturally aged samples indicate that the main process of degradation is deacetylation with chain scission as a secondary process after degradation has reached an advanced stage. Oxidative degradation resulting in formate is not a major factor in the degradation of most artefacts as very little evidence of this has been found. This conclusion

is supported by the intensity ratios and peak positions in the FTIR spectra, the higher acetate ion concentrations found in the IC results along with the low oxalate concentrations. However, changes to the polymer matrix are indicated by the presence of plasticiser on the surface of some samples and the levels of chloride and/or sulphate found by IC.

The main factor for the level of degradation seems to be the age of the artefacts as the older samples show more signs of degradation. However, use and storage are also significant factors as the pieces which have been displayed in non-museum conditions are more degraded than those which have spent their lives in museum storage. This would be expected as a piece which has been held in museum storage during its lifetime will have experienced fewer fluctuations in temperature and relative humidity than one kept by a private owner/collector, as museum environments are monitored and controlled. It is generally believed that fluctuations in temperature and relative humidity are more detrimental than constant high or low temperatures or relative humidities[34].

Also, museum storage areas are generally windowless and any light sources are UV filtered, therefore, exposure to light, especially UV radiation, will be minimal which would not necessarily be the case for the property of a private owner/collector. Furthermore, museum storage areas, which have been designed for this purpose, will be properly ventilated to avoid dangerous levels of indoor pollutants such as organic acids, aldehydes, sulphur dioxide or ozone building up. Although levels of these in a private household will be low, there is no way of knowing the exposure that an artefact may have suffered.

Finally, there is the question of selenium in the undegraded parts of the doll. This would indicate that there is possibly a connection between selenium levels and lack of degradation. However, as the majority of samples could not be tested by XRF there is no data to prove if this is simply a one-off or a wider issue. There is a great need for more samples, especially doll's with flesh coloured appearance, to be found to enable this phenomenon to be investigated further.

It can be seen from the different ion profiles that have been identified, that with a little more study, the non-destructive swabbing of artefacts for analysis by IC could be a valuable identification tool when FTIR is not available. The initial use of all of the techniques show that

FTIR and non-destructive sampling with IC both have a great potential for helping in the identification of plastic artefacts in museums and assessing the degree of degradation.

XRF would also be a good technique for metal content analysis that may prove to be significant especially for plastics in which the filler can act as a buffer to scavenge degradation products and help to slow down or prevent degradation worsening.

Finally, the analysis of the combs indicated that doll's disease, as has been found by other studies, can be a major problem as all of the combs studied were contaminated with either acetic or nitric acid vapours.

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CHAPTER 4

STUDY OF THE DEGRADATION OF CELLULOSE ACETATE USING ACCELERATED AGEING

4 Study of Selected Artefacts by Accelerated Ageing

4.1 Introduction

Ageing is defined in the dictionary[1] as a) the fact or process of growing old, or b) becoming or appearing older. In the case of museum artefacts ageing generally implies degradation and deterioration caused by irreversible chemical and physical changes that occur slowly over time. One of the basic functions of museums and galleries is the preservation of collections to reduce, minimise or eliminate the effects of long-term ageing. In order to do this the process of ageing must be understood, as must the factors which affect it. Accelerated ageing by means of increasing temperature, humidity, light exposure or any other factors that could prove detrimental to a material or composite is often used to model effects, that might otherwise occur after years, decades or even centuries.

The three main objectives of accelerated ageing are to

a) establish the relative ranking of materials with respect to their chemical and/or physical stability,
b) estimate the potential long term serviceability of materials and,
c) quicken degradation[2], to help identify the processes involved within a reasonable timescale.

Many environmental factors can be controlled during accelerated ageing including light, humidity, temperature and pollutant gases. These are all important factors in the degradation of artefacts in museums and as such are routinely monitored and, where possible, controlled. Damage of organic materials in artefacts by UV radiation can be limited using filters and specialised glass. Indoor pollutants such as formaldehyde, acetic acid, sulphur dioxide and ozone are generally removed using scavengers and/or air flow systems. However, monitoring and controlling the museum environment can be expensive and often a compromise setting has to be used, as the optimum conditions for each material are often not known nor can be individually achieved.

An important consideration in accelerated ageing studies of polymers is water absorption. A previous study on cellulose nitrate[3] showed that water absorption initiated hydrolysis, and therefore degradation, in the plastic artefacts. It is also generally accepted that the presence

of moisture can speed up degradation, although 'the chemical role of water in weathering is far from being completely understood'[2].

Water can have at least three kinds of effects which are important in the degradation of polymers,

a) the hydrolysis of ester or amide bonds,
b) the loss of the bond between polymer and substrate or pigment and
c) the generation of hydroxyl radicals or other reactive chemical species.

Water is especially harmful when condensation reactions have been used in the formation of polymers, as these can be reversed[2]. Therefore, it is expected that degradation will increase with increasing relative humidity. Oxidation can also be a major factor, especially when the generation of hydroxyl radicals is concerned.

In this study, humidity and temperature effects on three dimensional cellulose acetate objects were investigated to predict their stability during storage and display in typical museum environments. As pollutants and UV content in light are normally controllable, these factors were of less importance to study and model compared to relative humidity and temperature. However, it is impossible to know how much exposure an object has had in the past to UV and pollutants, especially if the object has had a useable life before being added to a collection.

Erhardt et al.[4] have shown that the most important factor to remember when using accelerated ageing to study degradation is that comparison of different accelerated ageing conditions and the evaluation of changes occurring at specific conditions must be treated separately. This is a crucial distinction when trying to determine if a certain set of conditions accurately represent natural ageing conditions. Therefore, extreme conditions should be avoided.

It is also important to choose the correct parameter for measurement, as the measured property needs to be suitably sensitive to reveal either;

a) a marked change at a very early stage
b) a dramatic change near the time of failure
c) or a predictable change throughout[2]

It must also demonstrate the relationship between chemical and physical changes.

In the experiments conducted in this study, higher than normal temperatures and various relative humidity (RH) values were used to induce changes in a material over a shorter time scale than would occur naturally. However, there can be problems relating the results from such tests to what happens to real samples in normal museum conditions of room temperature and relative humidity[4] for many years. For results to be comparable to natural ageing it must be presumed that thermally activated processes are occurring. To help overcome problems in this study, accelerated ageing results are compared to results of long-term natural ageing of museum pieces.

Conservation Issues

Ultimately, the aim of conservation is to develop techniques which can

a) assess the extent of degradation,
b) monitor the rate of degradation and any changes or trigger points and
c) identify artefacts with the potential for degradation so that these can be isolated.

It is important to observe the overall pattern of deterioration. There are three ways which this can proceed:

i) (auto)acceleration with time,
ii) an induction period before deterioration begins or
iii) different changes or processes in discreet stages[4].

The conservation approach to preserving an object depends on which process or combination of processes is likely to occur. For example, in case (ii) if conditions can be found to prolong the induction period, then artefacts can be stabilised and should remain in its present condition for much longer than if left. In case (iii), it may be possible to stop one stage thus preventing the next stage beginning and, again, stabilising the object. However, case (i) is the most serious as it is difficult to control once it is started. For plastics, and in fact most materials, passive conservation rather than active is the preferred approach for museum and gallery collections.

Observations from the conservation survey of a Gabo sculpture at the Tate Gallery, London, demonstrate that scenario (iii) is occurring in cellulose acetate degradation[5]. Firstly an acetic acid or vinegar odour was observed, then the surface became sticky and oily and eventually cracks appeared and the plastic became very brittle. A further problem with this item, however, is that Gabo used polyvinyl chloride (PVC) and cellulose acetate in the same

objects which can confuse the issue of degradation as PVC degrades to produce hydrochloric acid which can catalyse the cellulose acetate degradation. He also recycled old cellulose acetate with new plastic in the construction of the artefacts, this would lead to degrading pieces which were emitting acetic acid being mixed with undegraded cellulose acetate and the degradation being spread as is seen with "Pedigree Doll's Disease" or the "Vinegar Syndrome"[6-10].

4.2 Relative Humidity (RH)[11]

Changes in humidity can be potentially damaging to many types of artefacts and can be especially detrimental when linked with changes in temperature. It is vital, therefore, that humidity is understood and its effects studied. There are two measurements of air humidity, absolute humidity and relative humidity.

Absolute humidity is a measure of the amount of water contained in a certain volume of air. However, this does not take into account the temperature of the air, which can have a dramatic effect on the 'dampness' of the air. For example, hot air with 10 g m^{-3} of water vapour will have a drying effect, where as cold air with the same level of water vapour will cause moisture condensation. Therefore, a measure of humidity which is not affected by temperature, called relative humidity, is more commonly used.

Relative humidity is expressed as a percentage and defined as follows:

$$RH = \frac{\text{amount of water in a given quantity of air}}{\text{maximum amount of water which the air can hold at that temperature}} \times 100$$

Equation 4.1

Museums and galleries use a range of methods to control and monitor % relative humidity and temperature conditions in both display and storage areas. Conditioned silica gel is commonly used to adjust the relative humidity of small air volumes (e.g. sealed cases) although other materials are available[11]. Telemetric electronic systems and hygrometers are typical monitors.

In experiments monitoring controlled % relative humidity in the laboratory, saturated salt solutions are useful[12]. Different concentrations of salts, such as magnesium nitrate and

sodium chloride in aqueous solutions provide a relatively easy way of maintaining a known % relative humidity at a specified temperature.

4.3 Sample Preparation

Samples for the accelerated ageing study were selected from the artefacts under study to represent a range of ages and degrees of visible degradation. The samples used were:

a) 1996 cellulose acetate slab as manufactured (Courtaulds Chemicals, Spondon, Derby),
b) 1967 tortoiseshell hairslide,
c) 1967 tortoiseshell comb,
d) 1946 tortoiseshell comb,
e) 1940's doll, i) body, ii) left leg and
f) knife handle of unknown age (aged under conditions at 70 °C only).

Samples were cut into pieces approximately 4 cm x 5 cm (thickness ranged from 2 – 5 mm), weighed and suspended from the lid of a small desiccator (volume about 950 mL, no dessicant), using polypropylene strips and small pieces of 'blu-tac'. A saturated salt solution, as illustrated in figure 4.1, was placed in the well of the desiccator to control relative humidity (RH). For these experiments, three relative humidity values were chosen to include a 'wet', 'normal' and 'dry' atmosphere. These were 75 % RH controlled by sodium chloride solution, 55 % RH controlled by magnesium nitrate solution and 12 % RH controlled by lithium chloride solution. The salts were produced by Sigma Chemical Co., St. Louis, USA. The desiccators were then exposed to temperatures of 35 °C (figure 4.2), 50 °C or 70 °C in thermostatically controlled ovens.

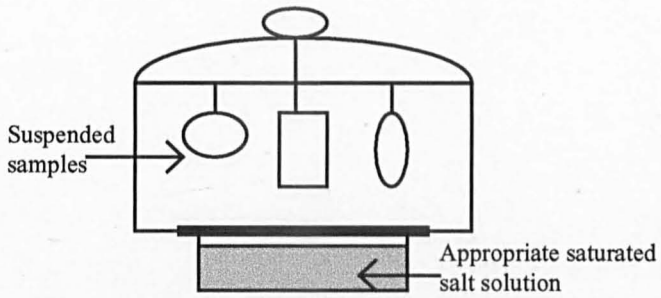

Figure 4.1: Illustration of accelerated ageing apparatus

A piece of each artefact was placed in each desiccator, ensuring that none touched each other and that they were suspended well above the solution. This allowed samples of each artefact, six samples per desiccator, seven for 70 °C to be exposed to all temperatures and relative humidities under investigation. The knife handle was only aged at 70 °C, as it was very awkward to manipulate and sample as it disintegrated into a fine powder after ageing. It was also very difficult to remove the metal blade and drilling a hole proved impossible, therefore suspending the sample in the desiccator was difficult.

Figure 4.2 Photograph of desiccators *in-situ* at 35 °C

The experiments at 70 °C were stopped after 62 days exposure, due to the extreme degradation of the samples. The experiments at 50 °C and 35 °C were allowed to continue until the experimental period of this study ended (approximately 600 days). Control samples of only cellulose acetate made in 1996 were set up at 55 % RH and 12 % RH at 50 °C to determine if the presence of other artefacts affected the rate of degradation. This could have occurred due to excessive build up of acetic acid or other volatiles as degradation progressed. This has been seen in 'Pedigree Doll's Disease'[9] when cellulose acetate degradation was observed to apparently spread from one artefact to the next like a 'disease'.

4.4 Analysis

The samples were monitored for changes in their visual appearance, colour, size, flexibility, mass, chemical composition and release of odorous volatiles detectable by smell. Chemical analysis was carried out using micro-FTIR spectroscopy and ion chromatography (sections 2.1 & 2.2). Changes in visual appearance and smell were noted during sampling, in order that the observations could be related to results from the analytical techniques used. Weighing the samples at regular intervals and plotting the weights and percentage total weight against time monitored variations in their mass during the experiment.

4.5 Results and Discussion

4.5.1 Visual Observations

Changes in colour, size and flexibility were observed during accelerated ageing. At 70 °C and 75 % RH or 55 % RH a strong smell of acetic acid was noted within 24 hours and the surface of most artefacts became sticky and oily within 6 days. The same was seen at 12 % RH, although, the timescale was slightly longer with the strong acetic acid smell occurring after 2 – 3 days and an oily substance appearing after 10 – 15 days. The amount of oily substance on the surface, later identified by reflectance FTIR as most probably dimethyl phthalate plasticiser (section 4.5.3), fluctuated as ageing progressed and after 42 days disappeared from the surface of the samples. The samples then became very brittle and disintegrated when touched (figure 4.3).

Samples yellowed at 70 °C after 3 – 13 days, most predominantly at 55 % RH. Although this discolouring could be connected to the use of a nitrate salt to control relative humidity, as the results from analysis by ion chromatography also showed increased nitrate levels (1996 cellulose acetate 8.3 $\mu g\ g^{-1}$, 1967 hairslide 5.7 $\mu g\ g^{-1}$, 1967 comb 3.5 $\mu g\ g^{-1}$, 1946 comb 5.4 $\mu g\ g^{-1}$, doll's body 3.4 $\mu g\ g^{-1}$, doll's leg 7.9 $\mu g\ g^{-1}$ and knife handle 14.9 $\mu g\ g^{-1}$ after 13 days, the doll's leg then rose to a maximum of 216.2 $\mu g\ g^{-1}$ after 35 days) in the samples aged at 55 % RH, suggesting that the nitrate salt could be contributing to the colouring observed. All of the samples aged at 70 °C visibly shrank after exposure for 62 days (figure 4.4).

Degradation, especially embrittlement, was fastest at a high relative humidity, indicating that high moisture content in the air accelerates processes which lead to plasticiser migration.

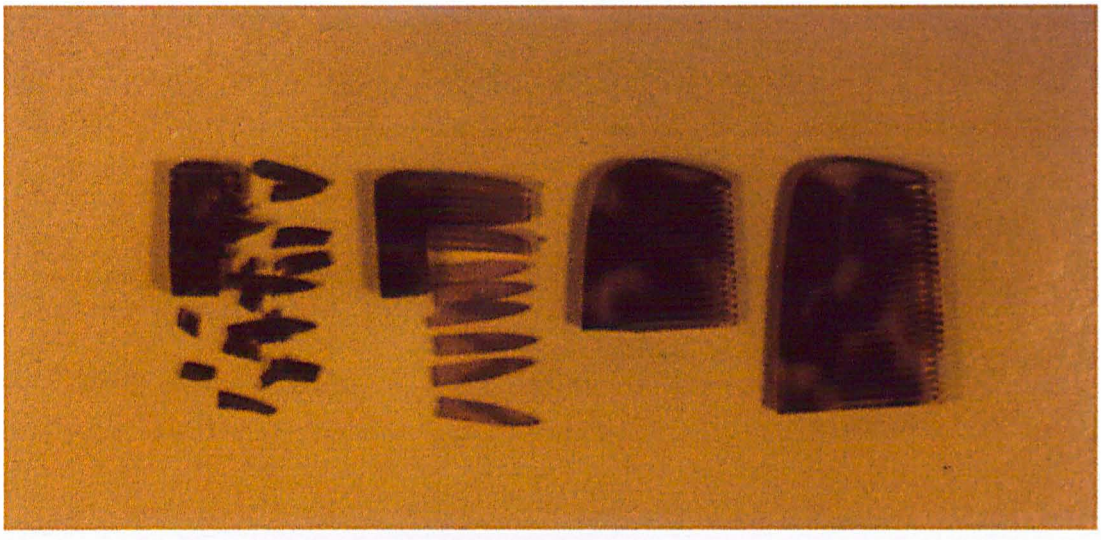

Figure 4.3 Photograph of embrittlement leading to disintegration of 1967 comb aged at 70 °C

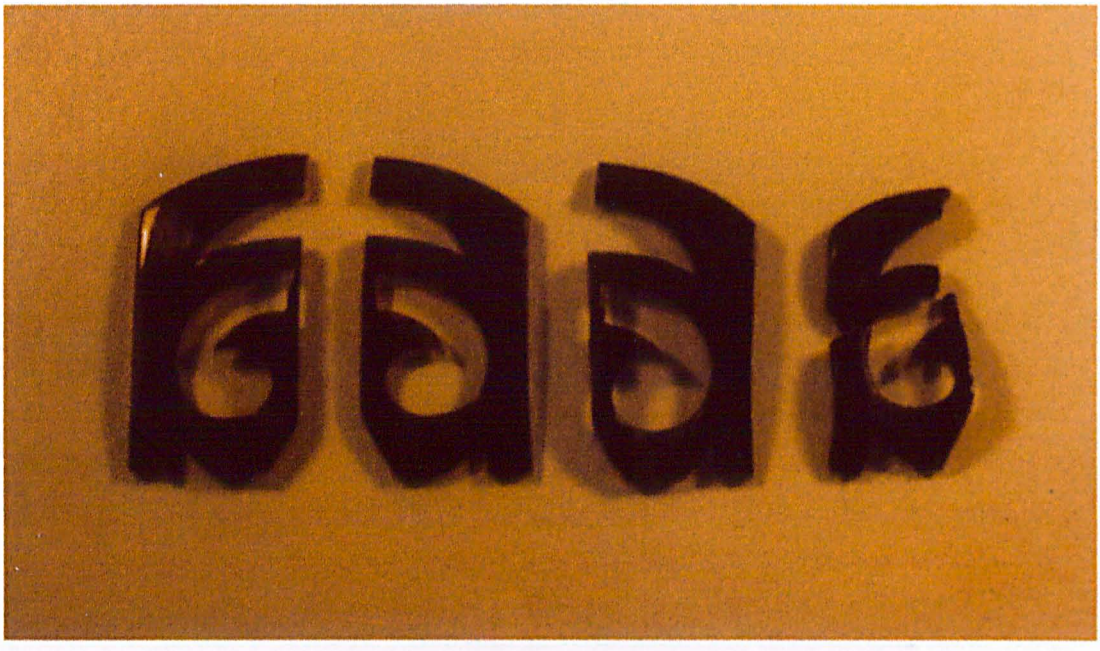

Figure 4.4 Photograph of shrinkage of 1967 hairslide aged at 70 °C

The samples aged at 50 °C (594 days) showed similar signs of degradation to those at 70 °C after 40 – 60 days, although the transformation was slower, allowing individual stages to be

identified. A slight vinegar smell was present before ageing began and this strengthened to a powerful smell of acetic acid in the early stages of the ageing process, around 100 days. This was followed by slight discoloration and a sticky surface after approximately 200 days. The samples then progressed to become severely discoloured and brittle. When the samples were measured, slight shrinkage had occurred (2 – 3 mm in each case) after 594 days. The doll's leg and doll's body samples became swollen and had surface liquid after 50 days. This was most probably due to absorption of salt solution, as an increase in nitrate concentrations on the surface of the artefact (doll's body 401.9 $\mu g\ g^{-1}$, doll's leg 45127.4 $\mu g\ g^{-1}$) was detected by ion chromatography and the liquid was not sticky like the plasticiser.

At 35 °C, only the samples aged at 75 % RH for 554 days showed the same signs of degradation as those aged at 50 °C, with the surface becoming sticky and discoloured. Only a very slight odour of acetic acid was detected in the three desiccators, with plasticiser only observed after 470 days in the samples aged at 75 % RH. This confirmed the expectation that degradation is slower at lower temperatures and relative humidities.

In all cases the smell of acetic acid preceded any plasticiser appearing on the surface, indicating that deacetylation is detectable before plasticiser loss occurs. This is due to the plasticiser becoming insoluble in the changing polymer matrix. It was well documented[13] that plasticisers were specific to the types of cellulose acetate i.e. triacetate, diacetate and monoacetate, therefore as the polymer undergoes deacetylation the original plasticiser will become insoluble and migrate to the surface of the artefact.

The 1996 cellulose acetate aged separately, at 55 % RH and 12 % RH, showed very little change visually, only slightly discolouring (yellowing) at 55 % RH. There was no loss of flexibility and no shrinkage. However, there was a smell of acetic acid detectable after 98 days at both relative humidities and the surface became sticky with plasticiser after 126 days at 55 % RH and 317 days at 12 % RH. These observations were in stark contrast to those of the 1996 cellulose acetate aged with the other five artefacts at 50 °C and 55 % RH or 12 % RH.

It was decided to age the six artefacts together as this would best represent a museum situation, where separation of artefacts may be desirable but not practical. From a practical point of view lack of time and space meant that the six artefacts had to be aged in one desiccator for each relative humidity. This experimental design is limited and it was

therefore felt that one artefact should be studied singularly to be able to assess any affect the off-gassing of acids from other artefacts would have. However, the mixed artefacts are realistic of museum storage.

The limitations of this experimental design are not a problem when assessing these results and identifying the factors which affect degradation as this situation will only accelerate the ageing and not change how it progresses or the factors which initiate it. In my opinion the artefact, which has had the greatest effect on the other samples, is the doll's leg as it was the most degraded before the accelerated ageing study began.

4.5.2 Weight Changes

The percentage weight losses for all accelerated aged samples are shown in table 4.1. A significant weight loss was observed in all samples aged at 70 °C and 50 °C while those aged at 35 °C showed little change in weight. The weight loss was suspected to be due to two processes, loss of acetate and/or plasticiser to the atmosphere, and these processes were studied in more detail by FTIR, IC, TGA, TGA-FTIR and GPC, described below and in chapter 5.

The different plasticiser in each artefact (section 4.5.3) would have an effect on the vapour pressure and hence the magnitude of volatilisation of the plasticiser. This would therefore, have an effect on the weight loss of each sample.

The older samples generally showed a greater weight loss than the newer cellulose acetate, suggesting a faster rate of degradation. The greatest weight loss was shown by the doll's leg, which showed signs of degradation at the start of the experiments, (55.1 %, over 62 days at 70 °C and 75 % RH, initial weight 2.699 g) which also exhibited the greatest level of visible degradation. In contrast the doll's body, which was not visually degraded initially, had a large weight loss at 70 °C and 75 % RH (52.9 %, over 62 days, initial weight 2.326 g) but showed relatively little visual degradation. Over 594 days at 50 °C and 75 % RH, all samples exhibited a weight loss of between 7.0 % and 28.7 %, the only exception being the doll's leg which gained weight. At 35 °C samples of the doll's leg exhibited significant weight loss at all relative humidities and at 55 % RH, the 1946 comb showed significant weight loss (5.1 %, after 554 days at 35 °C and 55 % RH, initial weight 2.903 g).

Table 4.1: Percentage weight loss of samples after ageing

Sample	Initial Degradation	Final Degradation	Weight loss / %								
			70 °C (62)			50 °C (594)			35 °C (554)		
			75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH
1996 Cellulose Acetate	None	Intermediate	16.3	13.9	8.3	13.0	17.5	5.5	-1.3	-0.7	1.9
1967 Tortoiseshell Hairslide	None	Severe	16.1	9.3	6.9	7.0	2.0	2.8	-2.9	-2.2	1.5
1967 Tortoiseshell Comb	None	Severe	28.8	22.8	14.3	26.5	7.5	3.0	1.7	-0.7	1.3
1946 Tortoiseshell Comb	Minor	Severe	35.1	15.4	0.7	28.7	11.9	8.1	-1.3	5.1	2.1
1940's Doll's Body	None	Intermediate	52.9	21.5	22.6	8.6	1.7	2.7	1.9	-1.0	1.2
1940's Doll's Leg	Minor	Destroyed	55.1	40.2	42.0	10.7	-4.9	1.5	7.8	4.0	3.7
Knife Handle	None	Destroyed	11.4	17.1*	16.8*	NA	NA	NA	NA	NA	NA

( ) – number of days exposure

* – 42 days exposure

NA – not available

At 70 °C weight loss was relatively slow up to 35 days, but after this point there was a dramatic increase in the rate of weight loss in all samples. Figure 4.5 exemplifies this with the doll's leg. In all the samples the greatest weight loss was observed at 75 % RH, then 55 % RH and finally 12 % RH.

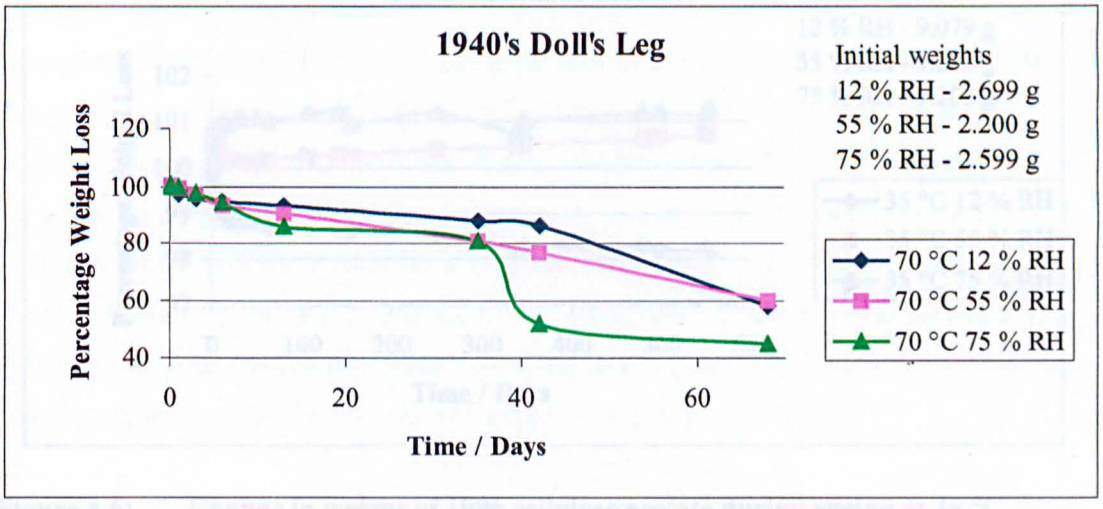

Figure 4.5: Change in weight of doll's leg during ageing at 70 °C.

At 50 °C the situation is more complicated as different samples show different trends. As a general trend there is an initial period of gradual weight loss until 241 days, followed by more rapid degradation. Both combs show greatest weight loss at 75 % RH and least at 12 % RH, whereas the 1967 hairslide and doll's body have greater weight loss at 12 % RH than 55 % RH. The modern 1996 cellulose acetate showed greatest weight loss at 55 % RH, then 75 % RH and least at 12 % RH. An initial weight gain in the doll's leg sample at 55 % RH coincides with an increase in nitrate concentrations as detected by ion chromatography (table 4.10) and is explained by absorption of salt solution from the desiccator reservoir as the sample was visibly damp and may have been splashed when the desiccator had been replaced in the oven.

At 35 °C it can be clearly seen (figure 4.6) that at both 75 % RH and 55 % RH, there is an initial increase in weight due to equilibration in the desiccator. The samples, which have been placed in the desiccator, must adjust (equilibrate) to the higher relative humidity of the atmosphere and must, therefore, take up moisture from the environment to achieve this. In contrast, there is a comparable decrease in weight for the samples at 12 % RH as samples lose moisture to adjust to the lower relative humidity. The effect of equilibration was seen for all samples at 35 °C. At higher temperatures equilibration will take place in minutes or

hours rather than days and so the weight gain is not observed as losses of volatiles, such as plasticiser and acetic acid, have occurred by the time of the first weighings.

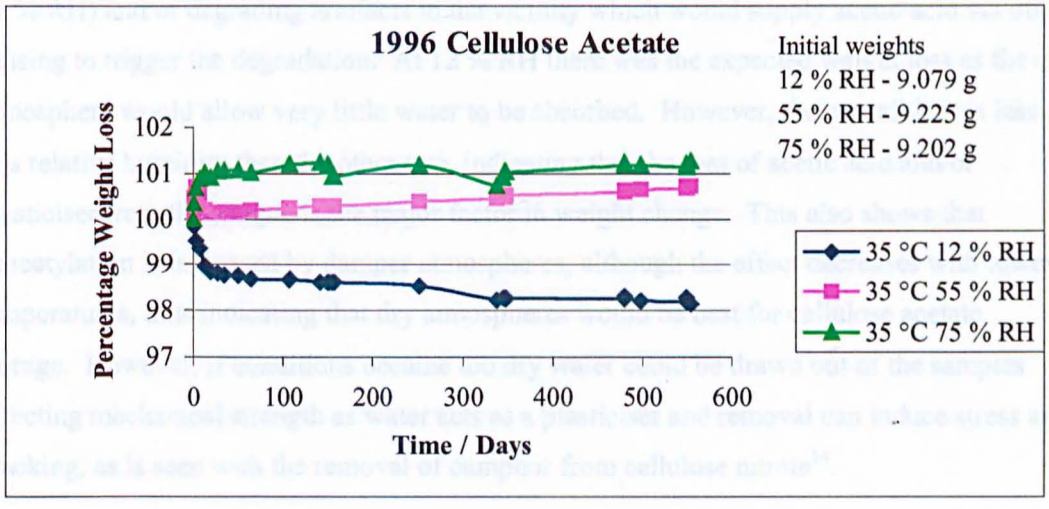

Figure 4.6: Change in weight of 1996 cellulose acetate during ageing at 35 °C

In general there is very little change in the weight of samples at 35 °C, due to the slower rate of degradation at this temperature. This slower rate allows water absorption, especially at 75 % RH and 55 % RH, to replace any weight which is lost by acetic acid and/or plasticiser evaporation. In the dryer atmosphere of 12 % RH there is an overall weight loss as less moisture is available for ingress, so total replacement is not possible. There is very little difference between the rates of degradation at different relative humidities at this temperature. This has implications for low temperature storage and display, as it would mean that the control of relative humidity in these environments would not be necessary and would make this a more practical option for museums.

The results generally indicate that relative humidity becomes a less important controlling factor in degradation as temperature decreases. However, for most of the test pieces, degradation was worst at 75 % RH.

The weight change results are not what were expected. Based on prior knowledge it was predicted that at 75 % RH and 55 % RH the samples would have a large initial weight gain as water absorption would be required to initiate deacetylation and then the weight would rapidly decrease by loss of acetic acid and/or plasticiser by evaporation. However the results

show that weight loss is far greater than any gain by water absorption, except at 35 °C where the slow rate of degradation allows any weight loss by acetic acid and/or plasticiser to be replaced by water intake. This shows that deacetylation can occur without a large influx of water into the system and could be easily triggered by a moderately damp environment (e.g. 55 % RH) and/or degrading artefacts in the vicinity which would supply acetic acid via off-gassing to trigger the degradation. At 12 % RH there was the expected weight loss as the dry atmosphere would allow very little water to be absorbed. However, the overall loss is less at this relative humidity than the other two, indicating that the loss of acetic acid and/or plasticiser from the sample is the major factor in weight change. This also shows that deacetylation is increased by damper atmospheres, although the effect decreases with lower temperatures, thus indicating that dry atmospheres would be best for cellulose acetate storage. However, if conditions became too dry water could be drawn out of the samples affecting mechanical strength as water acts as a plasticiser and removal can induce stress and cracking, as is seen with the removal of camphor from cellulose nitrate[14].

After these observations it would be sensible to suggest that cellulose acetate artefacts have to be monitored carefully and should be kept individually as much as possible. Although individual storage is not practical it would be important for samples which are known or suspected to be degrading to be kept separately from those which are in good condition, as these experiments show that acetic acid can easily encourage degradation in previously unaffected artefacts.

4.5.3 Fourier Transform Infrared (FTIR) Spectroscopy

The instrumentation used is described in section 2.1.2 and sampling procedures are described in sections 2.1.3 and 2.1.4. It was found in practice that very few objects could by analysed with the ATR objective on the FTIR microscope because the artefact thickness and shape was restricted by the distance from the stage to the objective lens. Hence, all spectra were recorded using the transmission mode after sampling with a scalpel.

4.5.3.1 Peak Positions

Changes in peak position and ratio of intensity of O-H or C=O to C-H intensity were monitored over time at the three temperatures and three relative humidities studied as degradation occurred. Typical spectra of an undegraded and degraded cellulose acetate are

shown in figure 4.7 and 4.8. O-H was used as a measure of the number of hydroxyl groups on the cellulose acetate polymer backbone and C=O was used to monitor the removal of acetate groups as the cellulose acetate degraded.

The peak position, measured in wavenumbers (cm^{-1}), of the C-H reference peak (table 4.2) was shown not to significantly change for any of the seven samples studied at any of the temperatures or relative humidities investigated. With the exception of the doll's leg at 50 °C and 55 % RH, however, the IC results show that at the time this change was seen the sample had absorbed a large amount of nitrate and it also appeared damp. This meant that sampling and spectral collection was extremely difficult and this may explain the change in peak position. Of the other three samples that showed a change greater than the 4 cm^{-1} (resolution of the instrument), two were within instrumental error and the other showed a maximum 1 cm^{-1} change when repeatability error is considered, therefore these can be said to be insignificant.

The C=O peak showed significant change in the peak position for all of the samples at 70 °C and 75 % RH, with the doll's leg and knife handle showing change at all three relative humidities and all samples aged at 50 °C at all relative humidity values (table 4.3). The doll's body also showed a shift in position at 55 % RH. The shift in the C=O peak position was from 1750 cm^{-1} towards 1720 cm^{-1}, in all cases.

The change in the position of the carbonyl peak with degradation is due to many factors. The first also has an effect on the position of the hydroxyl peak, a change in which has also been observed. The relative amounts of carbonyl and hydroxyl will have an effect on the position of the peak as these two groups interact in the polymer structure. Also there are two types of carbonyl present in the cellulose acetate (figure 1.2 and sections 1.2.1 and 1.2.2) as the C_6 and ring carbonyl groups will interact differently with the rest of the polymer structure. It has been shown that the carbonyl groups are lost in a precise manner (figure 1.8)[15] resulting in the same changes in position from sample to sample as the deacetylation occurs. Also as degradation occurs there will be changes in the β-linking of the O-H and C=O and changes in the hydrogen bonding as the helix unwraps and repositions. In addition changes in density will have an effect as well as the morphology of the polymer. As the deacetylation is systematic[15] the effects on density and morphology will be systematic and lead to the similar changes in position, which are seen in the samples.

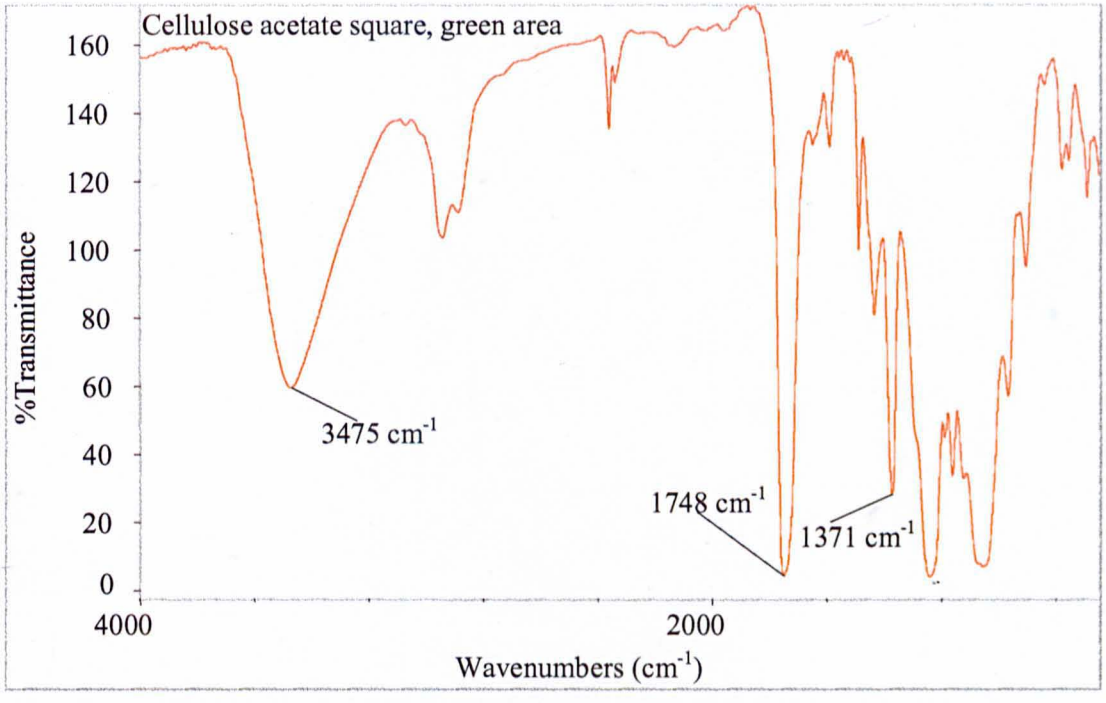

Figure 4.7 **Typical FTIR spectrum of undegraded cellulose acetate, cellulose acetate test square (green area)**

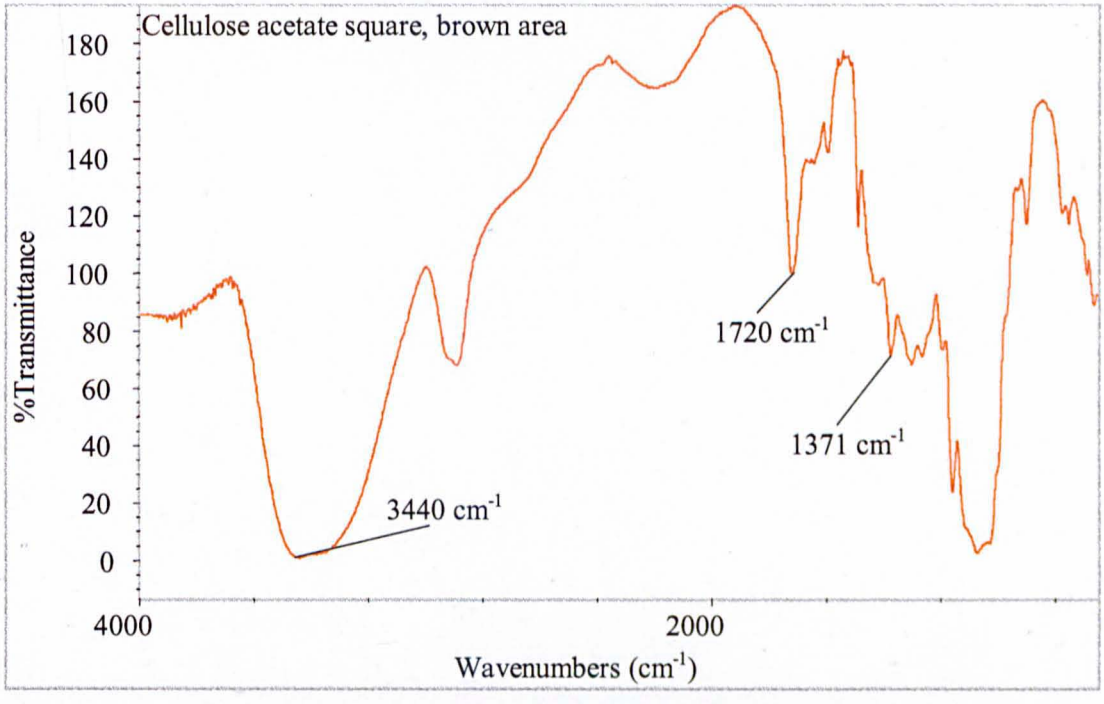

Figure 4.8 **Typical spectrum of degraded cellulose acetate, cellulose acetate test square (brown area)**

Table 4.2 Maximum change in peak position of C-H peak from 1370 cm^{-1}

Sample	Initial Degradation	Final Degradation	Maximum Change in C-H Peak Position / cm^{-1}								
			70 °C (62)			50 °C (594)			35 °C (554)		
			75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH
1996 Cellulose Acetate	None	Intermediate	3.1	1.6	0.8	2.3	2.2	1.7	1.3	1.9	1.3
1967 Tortoiseshell Hairslide	None	Severe	4.4	1.9	1.3	2.4	2.1	2.9	0.7	0.5	4.8
1967 Tortoiseshell Comb	None	Severe	0.9	0.5	0.3	1.0	1.7	1.4	2.0	1.8	2.3
1946 Tortoiseshell Comb	Minor	Severe	2.3	1.6	0.5	2.1	1.8	1.3	1.4	2.7	3.0
1940's Doll's Body	None	Intermediate	1.9	2.7	0.7	8.5	2.9	2.3	0.8	0.9	0.9
1940's Doll's Leg	Minor	Destroyed	2.2	2.3	1.8	2.7	26.0	2.3	3.1	0.4	0.9
Knife Handle	None	Destroyed	1.5	0.9*	3.1*	NA	NA	NA	NA	NA	NA

( ) – number of days exposure

* – 42 days exposure

NA – not available

Table 4.3 Maximum change in peak position of C=O peak from 1750 cm^{-1} towards 1720 cm^{-1}

Sample	Initial Degradation	Final Degradation	Maximum Change in C-H Peak Position / cm^{-1}								
			70 °C (62)			50 °C (594)			35 °C (554)		
			75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH
1996 Cellulose Acetate	None	Intermediate	9.5	NC	NC	21.8	23.8	25.7	NC	NC	NC
1967 Tortoiseshell Hairslide	None	Severe	15.0	NC	NC	33.0	31.0	21.4	NC	NC	NC
1967 Tortoiseshell Comb	None	Severe	36.6	NC	NC	25.3	30.7	19.1	NC	NC	NC
1946 Tortoiseshell Comb	Minor	Severe	33.9	NC	NC	25.8	33.9	18.1	NC	NC	NC
1940's Doll's Body	None	Intermediate	22.8	9.4	NC	17.6	29.0	29.1	NC	NC	NC
1940's Doll's Leg	Minor	Destroyed	35.7	28.8	22.9	29.0	21.3	17.4	21.2	NC	NC
Knife Handle	None	Destroyed	19.4	10.2*	11.2*	NA	NA	NA	NA	NA	NA

( ) – number of days exposure

* – 42 days exposure

NA – not available

NC – no change (< 4 cm^{-1})

However, many of these factors would result in a change in peak shape as well as position as shoulders of new peaks would appear adding to the width of the C=O peak. This is not observed as the peak remains the same width throughout ageing and no shoulders are formed. Therefore, it can be said that the environment of the carbonyl group is changing as deacetylation occurs resulting in changes in electron density around the group and hence a change in shift.

The O-H peak position showed the most variation out of the three peaks, (table 4.4), which is probably due to the width of the peak. The C-H and C=O peaks are sharp peaks whereas the O-H peak is broad and will therefore have a wider range of possible maxima; which can be seen in the typical spectra shown in figures 4.7 and 4.8.

At 70 °C only four samples showed no change in the peak position of the O-H peak, these were the 1967 hairslide at 55 % RH and 12 % RH, the 1946 comb at 12 % RH and the knife handle at 75 % RH.

At 50 °C the situation was slightly different, as there was a change seen in all samples for both the O-H and C=O peaks. This greater change is most probably due to the longer accelerated ageing period, also the IC results (section 4.5.4) show that contamination from the saturated salt solutions used to control relative humidity was a problem and would have resulted in extra moisture being present in the samples which would have had an effect on the O-H peak. By far the largest change was seen in the doll's body aged at 75 % RH and 50 °C with a change of 379 cm^{-1}, this change occurred in the middle of the ageing experiment and then gradually moved back to a higher position. It was visually observed that at this time the sample appeared very soft and pliable as though a lot of moisture had been drawn from the atmosphere (maximum of 12807.5 $\mu g\ g^{-1}$ for chloride after 197 days). The doll's leg showed a very similar change in position at all three relative humidities, this also followed the visual degradation as the three samples showed similar levels of degradation after ageing. Samples, which showed the greatest O-H peak change, had the most degradation visually.

Finally, at 35 °C there was no change in the C=O peak at any relative humidity. However, the O-H peak again showed some very significant changes. The largest change was observed in the doll's leg at 75 % RH with the 1946 comb also showing large changes at 55

Table 4.4 Maximum change in peak position of O-H peak from 3180 cm^{-1} towards 3000 cm^{-1}

Sample	Initial Degradation	Final Degradation	Maximum Change in O-H Peak Position / cm^{-1}								
			70 °C (62)			50 °C (594)			35 °C (554)		
			75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH	75 % RH	55 % RH	12 % RH
1996 Cellulose Acetate	None	Intermediate	65.7	11.9	11.5	14.8	6.3	9.3	NC	NC	NC
1967 Tortoiseshell Hairslide	None	Severe	61.7	NC	NC	6.6	8.2	6.4	5.1	NC	6.8
1967 Tortoiseshell Comb	None	Severe	35.7	11.6	5.3	42.6	8.0	10.0	4.8	6.0	NC
1946 Tortoiseshell Comb	Minor	Severe	118.1	37.6	NC	86.9	134.7	11.0	5.3	57.5	70.1
1940's Doll's Body	None	Intermediate	17.0	16.8	6.8	348.6	10.6	6.6	7.9	5.9	7.6
1940's Doll's Leg	Minor	Destroyed	55.5	63.9	60.7	87.4	85.2	84.5	101.9	22.2	5.2
Knife Handle	None	Destroyed	NC	73.1*	33.6*	NA	NA	NA	NA	NA	NA

( ) – number of days exposure

* – 42 days exposure

NA – not available

NC – no change (< 4 cm^{-1})

% RH and 12 % RH. In general the other samples had small, < 8 cm^{-1}, or no changes with the 1996 cellulose acetate showing no change in any sample.

4.5.3.2 Peak Intensity Ratios

The next set of data to be studied was the ratio of the magnitude of the peaks O-H or C=O to the reference C-H peak as there was a direct correlation between the O-H:C-H ratio and the C=O:C-H ratio. Where the O-H:C-H ratio increased then the C=O:C-H ratio decreased. These ratios showed a great possibility for use in the evaluation of cellulose acetate artefact degradation because these changes could be seen in the spectra before any visual evidence of degradation had become apparent. There also appeared to be a critical value of the two ratios, which indicated that degradation had begun: when the ratio of O-H:C-H went above 0.5 degradation had begun; if above 1.0 then it was well advanced. This was reflected in the C=O:C-H ratio: below 2.0 then degradation had been initiated (figure 4.9 and 4.10). The 1996 cellulose acetate which was aged on its own showed no change in the peak ratios except at the very end of the ageing, at 55 % RH when the OH:CH ratio increased and the CO:CH ratio decreased, however, neither of these went above/below the critical values.

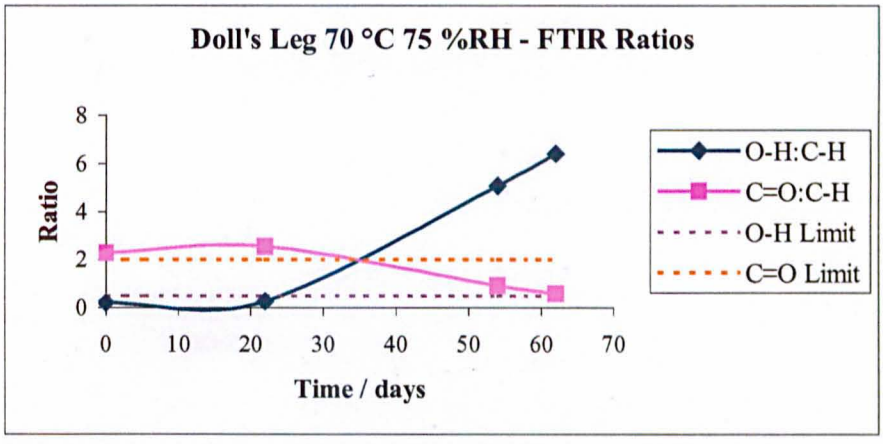

Figure 4.9 Graph of peak intensity ratios (degrading sample) – doll's leg

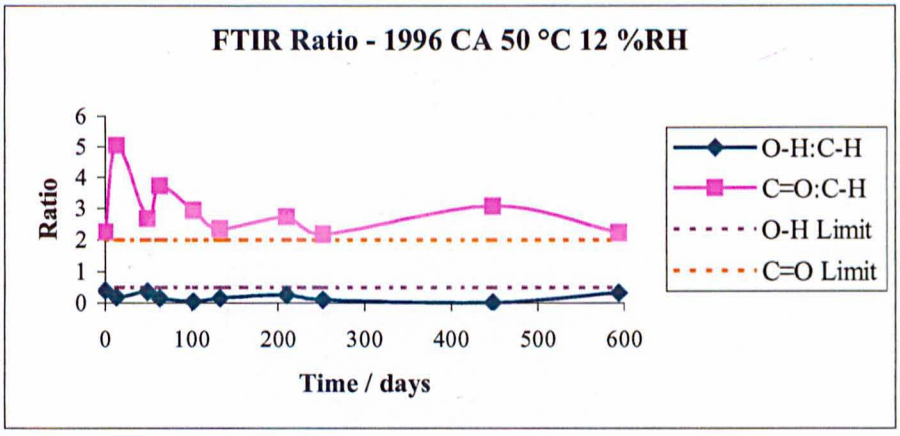

Figure 4.10 Graph of peak intensity ratios (undegrading sample) – 1996 cellulose acetate

4.5.3.3 Plasticiser Identification

The final analysis carried out by reflectance FTIR was the identification of the substance that was migrating to the surface during degradation. This was suspected to be plasticiser and, as the artefacts under study were all from the 1940's or later, it was presumed that a phthalate plasticiser had been used. The method for sampling is described in section 2.1.3.

The samples collected were compared with standard phthalate samples prepared by dipping the cotton wool swab in the phthalate and then extracting with dichloromethane as for the samples. The results were not entirely conclusive, as the spectra did not match well. This could be due to a variety of reasons, the first being that it is very difficult to obtain pure phthalate standards, as these will always contain a slight mixture of compounds. The second reason would be that the surface swab would not only contain plasticiser but also traces of other material, such as acetic or oxalic acid, which would cause differences in the spectra. Also it was difficult to locate the sample area after solvent evaporation. Finally it was extremely difficult to obtain good quality reflectance spectrum from the gold mirror, because solvent evaporated as the spectra were collected causing changes in the spectrum. In general it was not an easy procedure to perform.

The FTIR spectrum of the extract taken from the surface of the 1946 comb is shown in figure 4.11, along with the spectra for dioctyl and dimethyl phthalate. These spectra appear to indicate that the extract is predominately dioctyl phthalate. However, plasticisers do not stay blended easily with cellulose diacetate and only those with relatively low molecular weight

can be used. Therefore, it is unlikely that dioctyl phthalate was the original plasticiser. It is known from the manufacturers that diethyl phthalate is the plasticiser used in modern manufacture and it is most likely that this or dimethyl phthalate would be the plasticisers used throughout the samples.

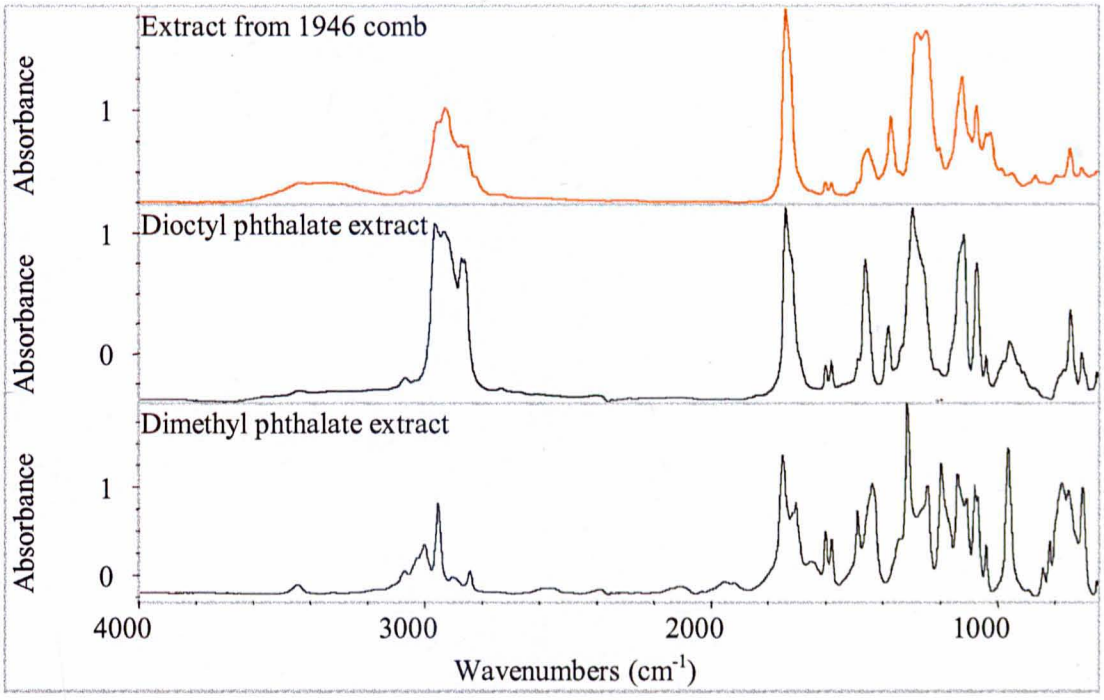

Figure 4.11 FTIR spectra of plasticiser extracts and standards

4.5.4 Ion chromatography (IC)

As described in section 2.2.4 there were two sampling techniques used for IC, destructive and non-destructive. Details of instrumentation can be found in sections 2.2.3, 2.2.5 and 2.2.6.

It was attempted in this part of the study to carry out a simple kinetic study on the data by plotting the results against $t^{½}$ where t is length of time of accelerated ageing study in days. The kinetic study was attempted on the IC data, as this data was available for both the bulk and the surface of the artefact. It was hoped that one of these areas would represent a simple kinetic reaction and yield an equation which could be adapted to allow prediction of the lifetime of an artefact. However, it proved very difficult to interpret this data owing to the complex situation occurring within the artefact matrix. There are three processes occurring;

a) diffusion of water into the cellulose acetate

b) reaction of acid catalyst [HA] with ester to evolve acetic acid

c) diffusion of acetic acid out of the cellulose acetate

However, the relationship of one to another is not fully understood and therefore complicates the kinetic situation.

Moreover the situation is further complicated in filled artefacts as there will be adsorption of the acetic acid by the filler (usually zinc oxide), which reduces the systems capacity for auto-catalysis of deacetylation and hence reduces the rate of degradation. All of these factors would have an effect on the rate of reaction and the kinetics; however, it is impossible to say from these experiments what the effect of each would be. Therefore it is not possible to produce an equation for the rate of reaction or kinetic order. Such an equation would be most helpful in predicting the lifetime and degradation pattern of cellulose acetate pieces.

For first order kinetics to apply it needs to be assumed that a reaction takes place immediately. However, studies of degradation of cellulose acetate have shown that the reaction does not occur instantly[8,16] and cellulose acetate can appear stable for many years after water ingress and before acetic acid evolution.

The true kinetics order is found by the following equation:

$$k = [water][acetate][catalyst]$$

Equation 4.2

4.5.4.1 Destructive Sampling

Destructive sampling (section 2.2.4.1) involved the removal of a small piece of sample (50 mg) which was then soaked in distilled water for 24 h. The water was then analysed to reveal the levels of acetate, formate, chloride, nitrate, sulphate and oxalate within the bulk of the polymer matrix. The results for each artefact are discussed in turn and then general trends for each anion will be discussed at the end.

1996 Cellulose Acetate

The 1996 cellulose acetate was aged with the other artefacts and on its own to allow the effect of degrading samples on an undegraded sample to be assessed. The results from the two sets of samples (figures 4.12 and 4.13, respectively) show that the pieces on their own had far less degradation than those, which were aged with the older and more degraded

pieces. This indicates that it is advisable to remove degrading artefacts from the storage or display of ones which appear stable to reduce the rate of deterioration in collections.

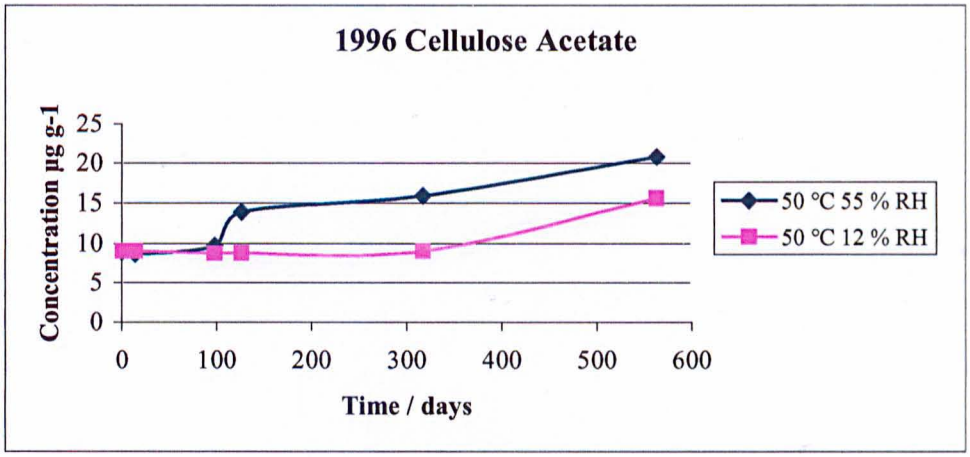

Figure 4.12 **Graph of changes in concentration of leached ions over time of the 1996 cellulose acetate sample aged alone at 50 °C and 55 % RH**

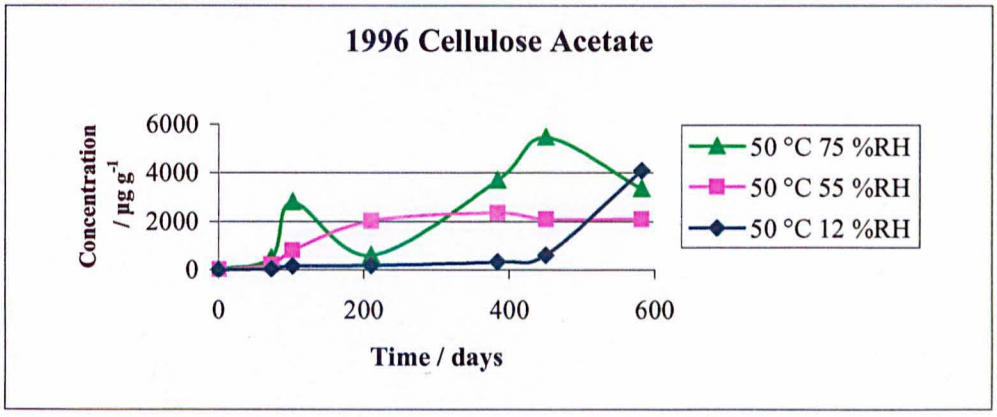

Figure 4.13 **Graph of changes in concentration of extracted acetate over time of the 1996 cellulose acetate sample aged with degrading samples at 50 °C and 55 % RH**

In the case of the 1996 cellulose acetate sample aged alone very little change was seen in the concentration of any of the extractable ions for any of the samples at either 55 % RH or 12 % RH. These samples were only studied at 50 °C and 55 % RH or 12 % RH due to equipment constraints. When these results were compared to those at the same temperature and relative humidity but with other artefacts present (table 4.5) then it was clear that the other degrading pieces were having a detrimental effect on this sample. Samples of the 1996 cellulose acetate aged with degrading cellulose acetate had higher levels for acetate, oxalate and sulphate, the three ions which indicate that degradation is occurring. This was also observed when sampling was being carried out as the sample on its own was visually undegraded

Table 4.5 **Bulk concentrations of ions, initial and final concentrations of 1996 cellulose acetate aged alone and with other samples – from IC analysis of extracts (destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Intermediate	9.5	9832.3	1.3	1.1	4.0	452.1	8.3	5.2	1.0	19.1	ND	ND
70 °C 55 % RH	None	Minor	9.0	5126.8	1.8	2.1	3.5	21.3	7.9	5.4	0.9	7.9	ND	ND
70 °C 12 % RH	None	Minor	9.3	3518.6	1.6	1.7	3.7	36.4	8.1	6.2	0.8	0.7	ND	ND
50 °C 75 % RH	None	Intermediate	8.9	3331.6	1.0	ND	3.5	72.6	7.3	6.2	1.0	15.3	ND	9.7
50 °C 55 % RH	None	Intermediate	8.6	2078.1	0.8	ND	3.3	19.7	6.8	104.2	0.9	14.3	ND	60.3
50 °C 12 % RH	None	None	7.8	4081.9	ND	47.1	3.7	13510.0	7.0	11.9	0.7	18.4	ND	84.2
35 °C 75 % RH	None	None	7.9	24.2	0.8	ND	5.6	2.9	6.4	2.6	0.9	0.6	ND	1.7
35 °C 55 % RH	None	Minor	2.6	26.5	0.7	4.0	4.6	5.3	0.2	146.2	0.6	1.2	ND	2.1
35 °C 12 % RH	None	None	4.5	57.3	0.1	ND	5.2	22.4	0.4	2.3	1.6	1.2	ND	2.2
50 °C 55 % RH*	None	None	8.9	20.8	1.2	0.4	3.4	7.2	4.3	0.9	0.6	0.5	ND	0.1
50 °C 12 % RH*	None	None	9.0	15.6	0.7	0.9	2.5	4.0	6.6	0.9	1.0	1.4	ND	0.1

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}, oxalate 0.33 µg g^{-1}

* – sample aged alone

whereas the sample aged with the others was visibly degraded at 50 °C. In general the sample on its own changed very little during ageing and could be said to be very stable.

This problem was probably encountered by all samples except for the initiator of the degradation, which I believe to be the doll's leg. However, due to the lack of space and time it was not practical to study each artefact separately, therefore the extent of the affect on the other artefacts cannot be said. However, this situation as mentioned previously is realistic of museum display and storage conditions.

The 1996 cellulose acetate, aged with the other samples showed an increase in acetate levels over time at all three temperatures. This increase could have been adsorbed from other artefacts or produced from this sample, it is most likely that the acetate was initially adsorbed and then produced by the sample, this is indicated by the visual observations where degradation clearly occurs and also the FTIR results (section 4.4) where degradation is also observed. At 70 °C there was no change in the sample until 40 days, after which there was a dramatic increase in the levels of acetate, chloride and sulphate. The increase in acetate indicates that degradation via deacetylation had occurred and this was seen in the visual appearance of the sample as it shrank and became brittle. This was also seen in the weight loss, which was gradual until 35 days then dramatically increased. The increase in chloride levels only occurred in the sample at 75 % RH and this was probably due to contamination from the saturated salt solution (sodium chloride) as the increase is greater than could be expected even from a very poorly manufactured cellulose acetate sample. The increase in sulphate, however, mirrors the increase in acetate and would indicate that as deacetylation occurs the trapped acid catalyst from manufacture is made available for extraction during sampling as this technique only measures the water extractable ions. It is expected that sulphate would become more available for extraction when acetate groups are lost because the sulphate is thought to be attached to the polymer via aceto-sulphate esters[13,17-19]. When these become detached from the polymer backbone the sulphate would become available for extraction into the water.

The levels of the other ions, nitrate, formate and oxalate remained constant in the 1996 cellulose acetate samples throughout the ageing study. Formate levels would only increase if oxidative degradation was occurring and this is not likely as manufacturers now add UV stabilisers to cellulose acetate products[5] and these would reduce the effect of UV light and, therefore, oxidative degradation. The low levels of the oxalate concentrations indicate that

chain scission has not occurred which would mean that this is a secondary degradation process as the acetate concentrations show that deacetylation has taken place. The nitrate levels do not change throughout the analysis but are relatively high, as these were expected to be zero due to no nitrate being involved in the preparation of cellulose acetate. Therefore the only possible reason for nitrate being present is contamination from the atmosphere or handling as this sample was not in contact with a nitrate salt solution.

At 50 °C contamination from the saturated salt solutions was a serious problem as can be seen in the large increase in the levels of chloride at 12 % RH and nitrate at 55 % RH (graphs 4.14 and 4.15). This shows a need for a change in the design of the experiments for any future work, controlling relative humidity in a way which did not involve the risks of contamination. Acetate, sulphate and oxalate results were interesting. The acetate and sulphate graphs again show very similar shapes, indicating that there is a direct relationship between them. The acetate levels increase from 100 days onwards, but oxalate levels increase after 500 days. This shows that deacetylation occurs firstly followed by chain scission as a later process. I believe that deacetylation would occur to a large extent very rapidly at 70 °C, resulting in loss of the majority of acetate groups from the cellulose acetate. This would result in large changes in the hydrogen bonding and therefore, polymer strength and stability, thus handling destroys the artefact before chain scission reactions can occur to a detectable level. However, at the lower temperatures deacetylation is less severe, with the loss of fewer acetate groups and therefore, less effect on hydrogen bonding resulting in the polymer remaining strong and intact, which allows the secondary chain scission of the backbone to occur.

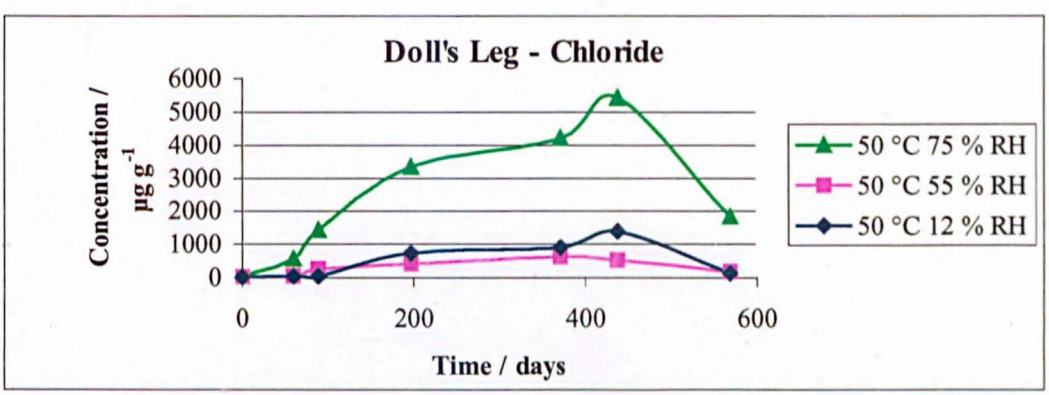

Figure 4.14 **Graph of typical IC profile showing chloride saturated salt solution contamination – doll's leg aged at 50 °C**

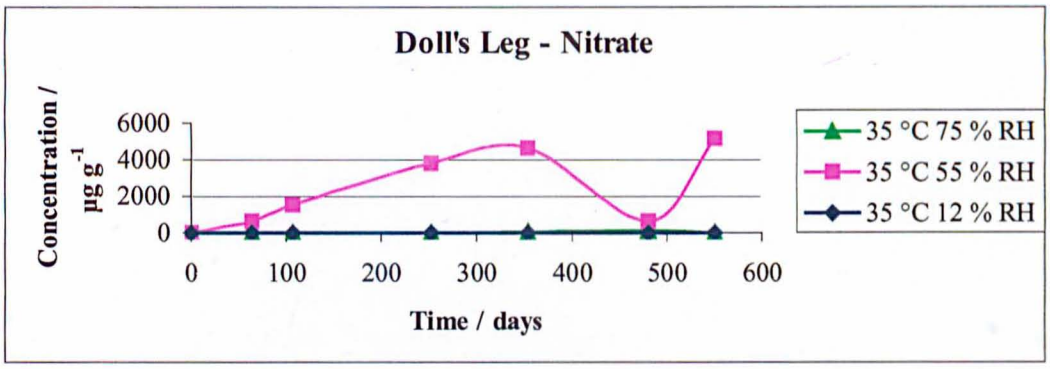

Figure 4.15 Graph of typical IC profile showing nitrate saturated salt solution contamination – doll's leg aged at 35 °C

At 35 °C the trends in the results are different as there is no apparent correlation between acetate and sulphate. Only acetate and oxalate showed any real change over the 580 days whereas sulphate and formate do not change over the ageing period. Again there is contamination from the nitrate salt solution. Chloride gradually increased from the beginning in all samples, peaking at 350 days then decreasing. This could have been due to contamination from magnesium chloride (or similar salt) used to stop the deacetylation reaction during manufacture rather than from the salt solutions used to control relative humidity as the effect is not only seen in the 75 % RH and 12 % RH samples but also in the 55 % RH sample which was controlled by a magnesium nitrate salt solution. Any salt left within the cellulose acetate could slowly leach out and be extracted because the solubility of the chloride within the polymer matrix would change as the matrix degraded. This is similar to the process resulting in plasticiser migration.

As for the other samples at 50 °C and 70 °C, acetate levels only increased at 35 °C and 75 % RH. After 100 days levels rise slightly, increasing slowly until 350 days when it dramatically increased before levels dropped (figure 4.16). At the two lower relative humidities acetate levels increase at the very end of the ageing period and it is not possible to predict if these would have followed a similar pattern to that at 75 % RH if ageing had continued. At 55 % RH oxalate levels increased after 350 days and then also fell back to initial levels, as did acetate levels at 75 % RH, with the results obtained at the other two relative humidities showing slight rises at the end of the experiment.

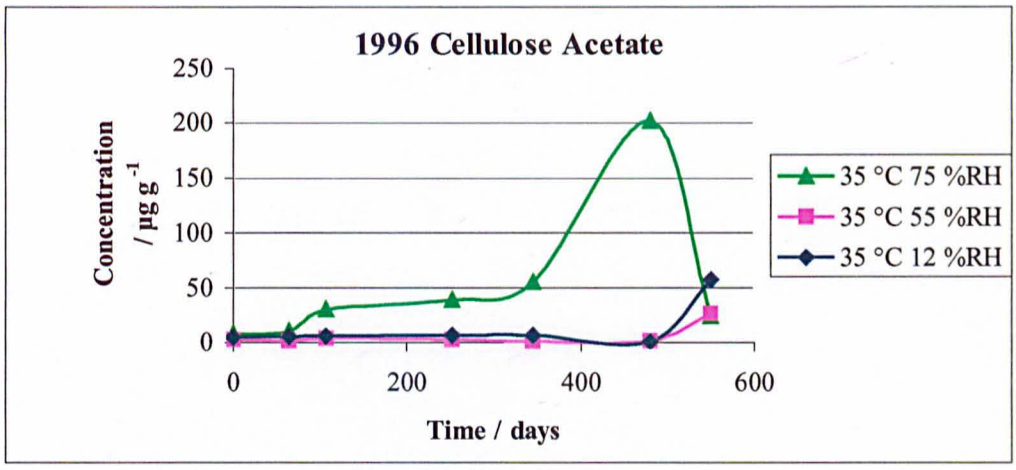

Figure 4.16 **Graph of changes in extractable acetate concentration of 1996 cellulose acetate aged at 35 °C**

1967 Tortoiseshell Hairslide (table 4.6)

The 1967 hairslide aged at 70 °C shows very similar results to the 1996 cellulose acetate aged at the same temperature. The acetate and sulphate concentrations increased in very similar patterns after 14 days, with chloride levels following a similar trend. The greatest increase was seen in the acetate, especially at 75 % RH, then the sulphate and chloride both increased to relatively high concentrations. This could also be explained by possible contaminant ions from manufacture becoming extractable after deacetylation has begun. The nitrate and formate levels showed similar trends to these ions in 1996 cellulose acetate with both fluctuating during the ageing but showing no significant change. Again the starting levels for the nitrate are high. A cellulose acetate – cellulose nitrate mixture for this artefact was discounted after elemental analysis (section 3.7) and no obvious explanation can be given for this observation.

The main difference between this sample and the 1996 sample is the increase in oxalate concentration which is seen here at 75 % RH after 35 days. There is also a very slight increase in oxalate for the samples at 55 % RH and 12 % RH. As deacetylation occurred relatively early in ageing, as shown by an early increase in acetate levels it appears that even with aggressive ageing, there was time for this sample to begin the second phase of degradation (chain scission) before it was totally destroyed.

Table 4.6 **Bulk concentrations of ions, initial and final concentrations of 1967 tortoiseshell hairslide – from IC analysis of extracts (destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Intermediate	13.1	9695.1	0.8	ND	5.8	41.1	9.7	12.7	1.0	30.5	ND	5.2
70 °C 55 % RH	None	Minor	13.5	2147.3	0.9	ND	6.0	6.9	9.2	2.3	0.9	3.4	ND	0.8
70 °C 12 % RH	None	Minor	13.0	956.8	1.0	0.9	6.1	21.2	9.9	3.2	0.7	2.2	ND	1.2
50 °C 75 % RH	None	Minor	12.1	3300.4	ND	ND	3.4	34.8	1.0	4.6	ND	11.2	ND	2.9
50 °C 55 % RH	None	Minor	11.7	1184.1	0.2	ND	3.6	30.1	0.9	1665.5	0.2	9.2	ND	73.4
50 °C 12 % RH	None	None	12.6	35.9	ND	3.7	2.8	91.3	0.8	3.7	0.3	1.8	ND	0.9
35 °C 75 % RH	None	Intermediate	6.4	27.5	ND	3.5	20.2	26.5	2.1	3.0	2.4	1.3	ND	4.4
35 °C 55 % RH	None	Intermediate	1.4	33.6	0.8	3.0	17.6	8.1	ND	387.3	1.4	1.2	ND	2.0
35 °C 12 % RH	None	Minor	0.4	13.7	0.8	ND	13.4	11.4	0.6	1.8	0.2	2.0	ND	3.0

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}, nitrate 0.298.3 µg g^{-1}, oxalate 0.33 µg g^{-1}

At 50 °C deacetylation occurred in this sample at a later stage of ageing compared to 1996 cellulose acetate sample, as acetate levels increased after 450 days compared to 100 days. This would indicate that the degradation in this piece was slower than the newer piece. Interestingly in this case there is a very similar type of increase in the nitrate and oxalate at 55 % RH. Although the large increase in the nitrate level could be attributed to salt contamination during the experiment, the oxalate results suggest that the large moisture intake has started a chain scission reaction. By comparing these results and the weight change results it is indicated that a low moisture intake is required to initiate deacetylation which has then autocatalysed, however, water intake can also initiate chain scission. However, in this case there is a large weight gain in the samples indicating that a large water intake is required for this initiation, and in these samples this is achieved by the salt solution contamination.

The sulphate levels increased but did not reflect acetate levels as observed with the other samples. The chloride levels of all three samples aged at 50 °C rose and fell at the same times, possibly due to leaching of chloride salt residues from the manufacturing process as discussed above. The fluctuation in levels could have been due to the salt migrating towards the surface, as it becomes mobile due to changes in the polymer structure, this would then be removed by handling and sampling; the process is then repeated as degradation progresses. Formate levels similarly fluctuated, but were not significant amounts.

At 35 °C the 75 % RH acetate increases after 350 days, with the lower two relative humidities showing a slight increase in the very last analysis, similar to the trends for the 1996 cellulose acetate. The difference is that in this case, the trend in the oxalate levels mirror the acetate results, although at a much lower concentration. Again this would be due to the increased water uptake when the contamination from the salt solutions occurred. Again a problem was encountered with contamination from the nitrate salt solution used to control the 55 % RH atmosphere. However, this time there was also a problem with salt contamination from the sodium chloride salt solution in the 75 % RH.

1967 Tortoiseshell Comb (table 4.7)

The 1967 comb at 70 °C shows the same increase in acetate and sulphate levels after 35 days as both the 1996 cellulose acetate and the 1967 hairslide. In this case there was no change in the nitrate levels observed showing no problem with salt solution contamination. There was,

Table 4.7 **Bulk concentrations of ions, initial and final concentrations of 1967 tortoiseshell comb – from IC analysis of extracts (destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Destroyed	6.8	9527.6	ND	ND	4.6	44.2	2.3	7.7	1.4	24.1	ND	ND
70 °C 55 % RH	None	Intermediate	6.2	4126.4	0.2	0.7	4.4	ND	2.1	1.4	1.5	20.1	ND	0.2
70 °C 12 % RH	None	Minor	5.9	1247.3	ND	8.1	4.2	12.6	2.5	1.8	0.8	0.9	ND	ND
50 °C 75 % RH	None	Minor	5.9	2024.2	ND	ND	4.8	286.3	8.4	0.8	0.8	37.2	ND	5.7
50 °C 55 % RH	None	Intermediate	5.2	1253.2	ND	ND	4.1	20.1	ND	85.9	0.7	13.1	ND	24.7
50 °C 12 % RH	None	Minor	6.1	2.5	ND	3.1	4.9	18.2	6.4	1.1	ND	1.1	ND	ND
35 °C 75 % RH	None	Minor	3.5	4.8	0.7	ND	4.4	1.7	2.4	2.0	1.7	0.8	ND	0.2
35 °C 55 % RH	None	Minor	4.9	18.5	ND	2.5	4.4	3.5	0.8	160.7	2.0	1.5	ND	1.0
35 °C 12 % RH	None	None	4.2	26.8	ND	ND	5.6	5.7	ND	0.7	0.9	0.7	ND	1.1

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}, nitrate 0.298.3 µg g^{-1}, oxalate 0.33 µg g^{-1}

however, an increase in the chloride of both relative humidities controlled by chloride salts and no change in that controlled by the nitrate salt, implying that the samples were most probably contaminated by the salt solutions rather than trapped chloride, from manufacture, being released. Formate and oxalate levels only changed in one sample each, the formate at 12 % RH and the oxalate at 55 % RH. The rise in oxalate, indicating chain scission, is most likely due to increased moisture intake from the chlroide salt solution contamination initiating this secondary reaction.

The problems with the contamination from the salt solutions have caused difficulties with interpreting the results, as changes in chloride cannot be definitely attributed to either salt solution contamination or residues from manufacture. The problem has been less significant for nitrate as there is no other source for the nitrate ion. However, in a positive way it has been able to give some more information on the effect of moisture in direct contact with the cellulose acetate artefacts.

At 50 °C the samples again showed an increase in acetate after 450 days, with oxalate levels increasing more slowly at the same time. Again contamination from the controlling salt solutions was a problem at both 55 % RH and 75 % RH. Although in this case there was an increase in the chloride levels at both other relative humidities which would be due to release of trapped chloride from manufacture. There was no significant change in formate levels. The most unusual result in this case was the sulphate which rose before the acetate at 375 days, all three samples showed a similar rise although to different extents.

The results for acetate at 35 °C were nearly identical to those for the 1996 cellulose acetate and 1967 hairslide, with a rise then fall in the concentration after 350 days. The two lower relative humidities both showed an increase in the last sample at 550 days. In this case formate, sulphate and oxalate all showed no significant change. The nitrate concentrations indicate that contamination was again a problem. Finally the chloride levels of all three samples aged at 35 °C fluctuate with all samples showing increases and decreases, indicating that chloride which had not been properly removed during manufacture was becoming insoluble in the polymer matrix and available for extraction, because if it was from salt solution contamination then it would not be apparent at 55 % RH which used a nitrate salt solution.

1946 Tortoiseshell Comb (table 4.8)

The 1946 comb showed similar trends, in the results obtained, as for the other samples, with a sharp increase in acetate concentration after 35 days. There was, however, a change in the oxalate values for this artefact, with the sample at 12 % RH showing an increase in oxalate concentration after 10 days. Oxalate also increased in the 75 % RH sample after a longer period of time. There was a large increase in sulphate at 75 % RH but no change at the other two relative humidities. This would be because the degradation at 75 % RH was severe and therefore, more sulphate would have been released by degradation of the aceto-sulphate esters than in the other samples. Chloride results indicated contamination at both 75 % RH and 12 % RH, and nitrate and formate showed no change in concentration over the ageing period.

At 50 °C, the acetate results were completely different from the other samples with the 55 % RH sample showing a vast increase, while 12 % RH showed little or no change and the 75 % RH sample showed similar rises as the other artefacts. The large increase at 55 % RH was mirrored in the oxalate and sulphate results, with all three showing large increases over the same period of ageing. The formate levels at 55 % RH also increased although this fell again by the time the other anion levels increased. Again there seems to be chloride contamination. However, the large increase in nitrate at 55 % RH was also seen in the sample at 75 % RH which would suggest that contamination may not be the only factor involved. The increased degradation is most probably linked to the increased moisture uptake caused by the salt solution contamination.

The results for the 1946 comb at 35 °C were also different from those of the other artefacts. The greatest increase for all the anions was at 55 % RH not 75 % RH as would normally be expected. However, there was significant contamination from the nitrate salt solution and this additional moisture uptake would explain the advanced degradation. Acetate concentrations at 75 % RH and 12 % RH increased very slightly when compared to the massive increase at 55 % RH. This increase paralleled an increase in nitrate and sulphate. In all cases the 75 % RH and 12 % RH samples showed similar slight increases in concentrations of the other anions, although far less than for the 55 % RH sample.

Table 4.8 **Bulk concentrations of ions, initial and final concentrations of 1946 tortoiseshell comb – from IC analysis of extracts (destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	Minor	Destroyed	50.7	6234.3	0.6	ND	7.1	6.6	5.9	9.2	2.0	37.4	ND	3.4
70 °C 55 % RH	Minor	Intermediate	45.6	4010.9	ND	1.8	7.0	ND	6.2	3.2	1.9	4.8	ND	0.4
70 °C 12 % RH	Minor	Minor	49.8	3947.4	ND	2.1	7.3	52.3	6.0	4.6	1.5	1.2	ND	5.2
50 °C 75 % RH	Minor	Destroyed	40.2	1736.4	0.6	2.1	3.6	410.3	2.1	2.9	0.9	41.8	ND	13.2
50 °C 55 % RH*	Minor	Destroyed	39.5	8083.3	0.5	ND	3.7	116.4	1.9	27.6	0.2	47.6	ND	20.3
50 °C 12 % RH	Minor	Minor	42.3	108.8	0.6	4.6	4.0	254.8	ND	4.1	0.7	1.4	ND	ND
35 °C 75 % RH	Minor	Intermediate	1.2	5.6	ND	ND	2.1	3.7	6.1	2.6	4.1	0.9	ND	3.9
35 °C 55 % RH	Minor	Minor	2.1	703.3	ND	34.7	10.2	171.8	ND	44.3	4.4	28.8	0.1	11.7
35 °C 12 % RH	Minor	Minor	2.8	66.3	0.9	ND	9.6	5.8	1.8	1.2	3.2	1.1	ND	10.5

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}, nitrate 0.30 µg g^{-1}, oxalate 0.33 µg g^{-1}

* – 210 days ageing

1940's Doll's Body (table 4.9)

The doll's body at 70 °C reacted in the same way as the other samples, with an increase in acetate, sulphate and oxalate after 35 days. In the previous samples discussed an increase in acetate concentration indicating deacetylation has been seen before an increase in oxalate concentration indicating chain scission. However, in this sample there was a simultaneous increase in both acetate and oxalate which indicates that deacetylation and chain scission are occurring at the same time. This was most probably due to greater deacetylation having occurred prior to the start of the experiments, indicated by the higher initial acetate levels. There was also an increase in the formate levels of this artefact which was not seen in the other samples. Only the sample at 75 % RH showed an increase in the sulphate concentration which indicates that degradation at the highest relative humidity is greatest and releases the most sulphate for extraction. There appeared to be chloride contamination at 75 % RH which could also effect the degradation and increase the rate at which it proceeded.

At 50 °C there was a large increase in acetate concentration at 75 % RH which may have been caused by chloride salt solution contamination of the sample as the increase in acetate happened immediately after the increase in chloride. This would be due to the increased moisture content as the chloride salt would have been absorbed along with water which is known to initiate deacetylation[2]. There was also an increase in the oxalate and sulphate levels of the sample at 75 % RH after the increase in acetate concentration. The oxalate concentration changes paralleled those of acetate, indicating that chain scission may have been occurring at the same time as deacetylation due to increased moisture. The samples at the other two relative humidities showed an increase in acetate after 450 days ageing, with the oxalate levels in the sample at 55 % RH increasing. However the other anions remained constant, except for nitrate at 55 % RH indicating contamination from the saturated salt solution.

At 35 °C there was again evidence of contamination by the chloride salt solution initiating degradation as there was a significantly rapid increase in chloride followed closely by an increase in acetate and oxalate at 75 % RH. However, this time there was no change in the sulphate concentration. Indeed none of the samples aged at 35 °C showed a change in sulphate or formate concentrations over time. Again nitrate contamination was a problem. Both 55 % RH and 12 % RH samples showed an increase in oxalate and acetate in the last 100 days of ageing.

Table 4.9 Bulk concentrations of ions, initial and final concentrations of 1940's doll's body – from IC analysis of extracts (destructive)

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Severe	10.5	6240.6	1.0	9.5	6.8	883.5	3.7	17.1	3.0	72.9	0.2	27.8
70 °C 55 % RH	None	Intermediate	11.2	3529.3	0.8	8.1	6.2	9.2	2.8	1.4	2.8	1.4	0.1	21.4
70 °C 12 % RH	None	Minor	10.8	2563.3	0.6	20.2	6.6	47.8	3.2	10.3	3.3	2.8	0.1	10.8
50 °C 75 % RH	None	Severe	9.2	3246.5	1.0	ND	6.8	237.1	3.5	10.4	ND	10.3	ND	24.3
50 °C 55 % RH	None	Minor	8.7	1514.5	1.1	ND	6.2	60.2	1.8	1323.9	ND	6.6	0.3	16.8
50 °C 12 % RH	None	Minor	9.0	199.6	0.8	2.4	7.1	283.8	1.7	11.1	0.3	3.0	0.1	2.5
35 °C 75 % RH	None	Intermediate	9.8	38.2	1.1	ND	3.2	24.8	0.2	3.5	3.8	2.2	ND	4.2
35 °C 55 % RH	None	Minor	8.7	31.4	0.4	3.5	4.6	6.9	1.4	114.2	2.7	3.2	ND	6.4
35 °C 12 % RH	None	Minor	7.6	36.5	1.2	ND	5.2	16.2	0.6	2.6	1.8	2.4	ND	7.4

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}, sulphate 0.42 µg g^{-1}, oxalate 0.33 µg g^{-1}

1940's Doll's Leg and Knife Handle (tables 4.10 and 4.11 respectively)

The doll's leg and knife handle at 70 °C showed very similar results for acetate, with levels immediately increasing at 75 % RH, then reducing after 35 days (when all the other artefacts showed an increase). The other two relative humidities were very similar to the other artefacts in that they increased after 35 days. All levels for the other anions for the doll's leg increased at each relative humidity. However, it is very interesting to note that the sample aged at 75 % RH did not show an increase for oxalate, where the other two samples aged at 55 % RH and 12 % RH increase before any increase in acetate was noticed. This can be explained by the initial state of degradation seen on the doll's leg. The degradation was more advanced in this sample prior to the start of the experiments which would have allowed scission of the cellulose acetate chain to have occurred before these ageing experiments were started. All three relative humidities showed an increase in chloride from the release of trapped residual salt from manufacture, rather than contamination as it was seen in the sample aged using a nitrate salt as well. There was also a rise in the nitrate levels in all samples in the middle of the ageing period although these had all returned to the original levels by the end of the ageing experiment. The sulphate levels were high to begin with in this sample, due to the advanced state of degradation, and rose in the samples aged at 55 % RH and 12 % RH but not 75 % RH.

At 50 °C there was a substantial increase in acetate levels at 55 % RH after 100 days, after contamination by the controlling salt solution, indicated by a peak in nitrate concentration from 0 – 200 days. This would be caused by the increased moisture uptake inducing degradation. There was a parallel increase in oxalate at this relative humidity and formate levels after this contamination, at 200 days. There appeared to be chloride contamination at 75 % RH but no corresponding increase in acetate and/or oxalate. The samples aged at the other two relative humidities showed an increase in acetate and oxalate after 100 days although this is very gradual compared to 55 % RH. The chloride concentration also increased for the samples aged at the other two relative humidities indicating that release of salt from manufacture was occurring. Nitrate levels for the chloride-controlled relative humidities did not change over the ageing period. In all cases there was an increase in sulphate levels showing that degradation was occurring as ageing progresses.

Again at 35 °C results for the doll's leg are different from those of the other five artefacts. Acetate concentrations only increased at 75 % RH, but actually decreased at 55 % RH and

Table 4.10 Bulk concentrations of ions, initial and final concentrations of 1940's doll's leg – from IC analysis of extracts (destructive)

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	Intermediate	Destroyed	248.1	52.0	5.8	11.5	13.6	101.0	6.6	0.4	39.3	36.1	24.4	6.3
70 °C 55 % RH	Intermediate	Severe	213.5	4291.8	4.6	9.3	12.9	22.4	6.4	0.6	38.9	105.6	21.3	52.1
70 °C 12 % RH	Intermediate	Severe	222.5	3841.8	5.1	17.8	13.0	225.4	6.1	4.8	35.1	26.5	22.5	48.2
50 °C 75 % RH	Intermediate	Severe	198.5	2102.4	2.5	ND	12.2	182.7	4.6	2.2	28.7	69.5	19.6	153.9
50 °C 55 % RH	Intermediate	Severe	220.3	1349.5	2.9	101.6	11.8	164.8	3.2	24929.6	20.2	60.3	22.4	346.2
50 °C 12 % RH	Intermediate	Intermediate	184.6	512.9	2.0	ND	11.2	130.7	4.0	6.2	19.8	89.5	23.8	92.8
35 °C 75 % RH	Intermediate	Intermediate	298.4	207.0	2.1	101.8	17.9	3591.1	4.2	2.9	24.8	67.2	19.7	12.2
35 °C 55 % RH	Intermediate	Intermediate	245.6	117.6	ND	63.9	12.4	67.9	3.6	5160.1	21.0	103.9	20.2	475.7
35 °C 12 % RH	Intermediate	Minor	278.1	96.7	ND	ND	15.6	34.7	1.4	5.9	24.1	21.5	22.8	46.3

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}

Table 4.11 Knife Handle

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg g^{-1}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Destroyed	69.1	126.4	ND	2.1	68.8	25.0	31.2	0.6	0.6	13.8	ND	0.9
70 °C 55 % RH	None	Destroyed	60.7	1048.2	0.1	7.8	60.4	1.9	28.4	3.3	0.5	22.5	ND	ND
70 °C 12 % RH	None	Destroyed	61.3	500.2	ND	19.7	65.1	35.9	30.3	7.0	0.7	2.6	ND	ND

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 42 days (70 °C), 594 days (50 °C), 554 days (35 °C)

ND – not detected

Detection limits – formate 0.35 µg g^{-1}, oxalate 0.33 µg g^{-1}

12 % RH. This could perhaps indicate that the lower temperature and relative humidities are helping to slow ageing. In all cases the starting concentration was high (184.6 – 298.4 μg g^{-1}) due to the advanced state of degradation at the start of the experiment. Again there was definite contamination of the sample by the chloride salt at 75 % RH and this could have enhanced the deacetylation of this sample. However, the nitrate contamination did not encourage deacetylation in the sample at 55 % RH but did seem to cause an increase in oxalate which could mean that chain scission occurred preferentially in this sample, possibly due to deacetylation prior to accelerated ageing. Sulphate levels rose then returned to the original concentrations, as was seen at 50 °C. In all cases, the formate levels rose at the end of the ageing experiment, indicating that oxidative degradation is a third and final step in the overall degradation processes.

The acetate results for the knife handle are very similar to those for the doll's leg. However, in this case there is no significant increase in oxalate concentration. The three samples all showed a reduction in nitrate concentrations during ageing and a rise in sulphate concentrations after 35 days. The nitrate would have been from air contamination collected during use and would be gradually removed during sampling. There were very high initial concentrations of chloride, probably due to the high level of handling during use before donation. At both 75 % RH and 55 % RH the levels of chloride decreased during ageing but the 12 % RH sample showed an increase. In all cases, formate rose after 35 days although at 55 % RH the anion concentration fell again to insignificant levels.

Conclusions for Bulk Sampling

In general, it can be concluded that acetate levels rise before oxalate. This indicates that deacetylation is the first degradation process and is followed by chain scission. Interestingly, at high temperatures oxalate levels do not increase dramatically although there is severe degradation of the cellulose acetate artefacts. This suggests that deacetylation alone maybe more detrimental to an artefact than deacetylation and chain scission together, and could be explained by the rate at which deacetylation occurs at 70 °C. When the deacetylation occurs at a reduced rate there is a chance that the polymer will simply shrink and the hydrogen bonding will shift. This would result in loss of plasticiser and embrittlement but not destruction of the artefact, because it will be able to maintain mechanical strength as it slowly changes from triacetate to diacetate and ultimately to monoacetate. Also if the deacetylation occurs quickly, there is less chance for chain scission reactions to occur

because rapid degradation destroys the integrity of the artefact, via loss of strength due to loss of acetate groups and subsequent changing hydrogen bonding, before the polymer backbone begins to degraded. When deacetylation is slower the artefact integrity remains intact as degradation progresses and chain scission is involved in the breakdown of the polymer backbone.

There was a large problem with contamination from the saturated salt solutions used to control the relative humidity throughout these experiments. Results from these samples show that although there is an insignificant contribution of relative humidity to the degradation of cellulose acetate at lower temperatures, there is a detrimental effect if an aqueous solution is in contact with cellulose acetate even for a short period of time. Therefore, it would be best to note that washing of these plastics with any sort of aqueous solution would probably be detrimental to the artefact if proper drying was not carried out afterwards.

Sulphate and chloride were both released concurrently or after acetate, indicating that changes in the polymer matrix from deacetylation released these anions for extraction. Chloride becomes insoluble in the changing polymer matrix, as does plasticiser, and can be extracted from the bulk sample, as it is now mobile. Sulphate can also become insoluble but in addition is produced by the breakdown of aceto-sulphate esters when the polymer degrades which means that degradation would have to be worse to release sulphate than chloride.

Low levels of formate indicate that oxidative degradation is not significant in the degradation of cellulose acetate. Nitrate concentrations are also insignificant, as it appears to be simply contamination.

In general it can be said that higher relative humidity has a worse effect on cellulose acetate degradation, although, the difference between the relative humidity and degree of degradation decreases with decreasing temperature. This would show that the effect of relative humidity becomes less important at lower temperatures and, therefore, indicate that temperature control and ventilation are more important than relative humidity in the preservation of cellulose acetate artefacts.

4.5.4.2 Non-destructive Sampling

Non-destructive sampling (section 2.2.4.2) involved swabbing an area of the surface of the artefact (2 cm X 2 cm) with a cotton wool swab moistened with distilled water, and extracting this distilled water (5 mL) for 24 h before analysis by IC. This gave an indication of acetate, formate, chloride, nitrate, sulphate and oxalate levels on the artefact surface. The results for each artefact are discussed in turn followed by discussion of general trends for each anion.

1996 Cellulose Acetate (table 4.12)

The 1996 cellulose acetate aged on its own showed little change visually in the samples with ageing. This was also seen in the IC results with no ion showing a significant change except for the acetate which showed a slight increase after 317 days at 55 % RH and 563 days at 12 % RH. The results for the samples aged with the other artefacts, however, show increases in acetate levels for all samples after a similar length of time as was observed in the destructive sampling results. The chloride concentrations in the samples aged at all three relative humidities increased from low levels, especially after 40 days, which was also seen in the trends of the destructively sampled results. This would indicate that chloride is becoming mobile with deacetylation and is migrating to the surface. The other anions showed no change in the surface concentration during the ageing at 70 °C. Significantly there was very little difference between the samples aged at the different relative humidities indicating that this has less influence on the surface reactions than the bulk.

At 50 °C the trends in the changes in acetate concentrations were also similar to the trends found for the destructive sampling as the samples aged at all three relative humidities showed an increased concentration after 150 days. Again the difference in the relative humidities was not so prevalent in these samples. There was evidence of contamination in the samples at 55 % RH and 12 % RH indicated by the large increases in nitrate and chloride respectively, this trend was also seen in the destructively sampled results. Formate and sulphate levels showed no overall change over the ageing period. Oxalate concentration increased in the 55 % RH sample most noticeably, probably due to excess moisture, but all three samples showed a slight increase in overall oxalate concentration.

Table 4.12 **Bulk concentrations of ions, initial and final concentrations of 1996 cellulose acetate aged alone and with other samples – from IC analysis of swabs (non-destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Intermediate	ND	18.3	0.1	ND	ND	3.9	ND	2.5	ND	0.9	ND	1.0
70 °C 55 % RH	None	Minor	0.2	15.4	ND	1.4	ND	2.2	ND	2.1	ND	ND	ND	ND
70 °C 12 % RH	None	Minor	0.3	12.2	0.1	0.9	ND	2.4	0.3	0.9	ND	ND	ND	ND
50 °C 75 % RH	None	Intermediate	ND	21.6	0.2	ND	ND	5.0	0.1	0.6	ND	0.6	ND	1.4
50 °C 55 % RH	None	Intermediate	ND	21.0	0.1	4.3	0.4	8.7	ND	1.4	0.4	1.0	ND	5.7
50 °C 12 % RH	None	None	ND	92.0	0.3	4.6	ND	77.9	0.3	1.4	0.5	1.5	ND	2.4
35 °C 75 % RH	None	None	0.5	29.1	ND	2.0	0.4	9.6	0.4	2.1	ND	1.4	ND	0.4
35 °C 55 % RH	None	Minor	0.3	15.8	0.2	1.1	0.4	7.8	ND	5.0	0.1	1.5	ND	0.7
35 °C 12 % RH	None	None	0.6	27.2	0.3	0.2	0.2	9.4	0.3	1.6	ND	0.5	ND	0.4
50 °C 55 % RH*	None	None	1.5	6.0	ND	ND	0.5	2.6	0.7	0.3	ND	0.4	ND	ND
50 °C 12 % RH*	None	None	0.2	3.9	ND	0.6	0.1	2.2	0.2	0.2	ND	0.1	ND	ND

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – acetate 0.96 µg cm^{-2}, formate 0.42 µg cm^{-2}, chloride 0.38 µg cm^{-2}, nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

* – sample aged alone

The sample aged at 35 °C showed very little evidence of ageing during the experiments. There was an increase in the acetate concentrations of the samples at all three relative humidities, although these did not follow the order of highest to lowest. There was also an increase in formate levels for this sample at all relative humidities. Oxalate and sulphate concentrations did not change over the ageing period. Samples aged at both 75 % RH and 55 % RH had signs of contamination with increases in chloride and nitrate respectively. In all cases trends seen in the non-destructive sampling results could also be seen in the destructive sampling results.

1967 Tortoiseshell Hairslide (table 4.13)

The 1967 hairslide aged at 70 °C revealed comparable trends to the destructive sampling results for acetate with increases in both after 40 days, and for sulphate which increased after 35 days. However there is a difference in the results between the two techniques for the other anions. Formate levels showed no change with destructive sampling but a significant change in all samples with swabbing. Formate is an indicator of oxidative degradation, which would occur at the surface, hence explaining the swabbing results.

Conversely the chloride concentrations were less for the surface than the bulk, probably due to residual chloride from manufacture being present throughout the sample, therefore, more in the bulk than at the surface. There was no change in the nitrate levels or oxalate concentrations, the nitrate levels were high throughout and the oxalate levels were low.

At 50 °C the acetate concentrations, for the samples aged at each relative humidity, increased but not at the same rate as for the results for the steeping samples where levels only rose at the end of the study period. In this case there was a gradual increase throughout at 55 % RH and 12 % RH and maximum levels reached in the middle of the ageing period at 75 % RH. Contamination by nitrate was not evident in these results. Again the chloride levels fluctuated in these samples, showing that the surface levels are more changeable than the bulk due to removal of ions by handling and sampling. Formate levels were again higher for the surface technique and sulphate levels did not change over time. There was an increase in oxalate levels for 55 % RH only, although this could be linked to the effect of the nitrate salt solution contamination postulated from the destructive sampling results.

Table 4.13 **Bulk concentrations of ions, initial and final concentrations of 1967 tortoiseshell hairslide – from IC analysis of swabs (non-destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Intermediate	0.9	30.7	0.1	8.8	ND	5.0	0.9	2.2	0.2	1.9	ND	0.6
70 °C 55 % RH	None	Minor	0.8	16.3	0.1	2.4	ND	0.5	0.7	0.4	ND	0.4	ND	0.2
70 °C 12 % RH	None	Minor	1.2	16.6	ND	4.3	0.7	1.4	0.9	1.6	0.3	0.4	ND	ND
50 °C 75 % RH	None	Minor	0.8	19.0	0.1	2.1	ND	2.9	0.8	ND	0.2	0.5	ND	0.3
50 °C 55 % RH	None	Minor	0.7	8.0	ND	9.7	ND	22.6	0.7	2.8	ND	1.4	ND	6.6
50 °C 12 % RH	None	None	0.5	13.1	0.2	2.8	0.6	6.2	ND	0.9	ND	0.9	ND	0.6
35 °C 75 % RH	None	Intermediate	1.0	42.4	ND	6.7	0.3	87.8	1.0	ND	0.1	0.2	ND	2.8
35 °C 55 % RH	None	Intermediate	0.9	23.9	ND	7.5	ND	6.7	0.8	55.5	ND	0.4	ND	1.2
35 °C 12 % RH	None	Minor	1.4	23.0	ND	4.1	1.1	9.4	1.0	1.1	0.4	0.2	ND	0.2

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – formate 0.42 µg cm^{-2}, chloride 0.38 µg cm^{-2}, nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

At 35 °C the trends in the results are very different from those of the destructive technique. The 75 % RH sample shows the largest increase in acetate levels with both sampling procedures, after 100 days at the surface and after 350 days for the bulk. Acetic acid, being volatile and mobile would be expected to migrate to the surface leading to high concentrations which will not be sustained throughout the artefact. Formate again showed an increase in all samples which was not seen in the bulk samples. All samples showed increased chloride levels, indicating that chloride from manufacture and handling can be extracted. Chloride contamination was evident in the 75 % RH sample and nitrate contamination was problematic as for the destructive sampling procedure. There is no significant change in the concentration of the sulphate and oxalate anions over the ageing period.

1967 Tortoiseshell Comb (table 4.14)

The 1967 comb behaved differently from the other samples discussed so far. The acetate levels gradually increased from day 0, (the starting level was higher than the others), and the rate increased rapidly after 40 days. Formate levels were high throughout at the surface, which is opposite to the trend seen in the bulk results as it was low throughout in this case. This indicates that oxidative degradation occurs preferentially at the surface of the artefact. The other anions showed no significant changes.

Likewise at 50 °C, acetate levels increased from the beginning of ageing and formate levels were higher than for the bulk. Contamination from salt solutions could be seen in the samples at 12 % RH and 55 % RH with the appropriate increases seen in the concentration of the chloride and nitrate salts, respectively. The sulphate concentrations did not change during ageing, but oxalate concentration at 55 % RH increased significantly while remaining constant in the other samples aged at 50 °C. If the extra moisture from contamination by the saturated salt solutions was the only factor that caused the additional degradation then the sample at 12 % RH would also have shown a significant increase in oxalate.

At 35 °C, there was a large initial increase in acetate concentration which then reduced until the end of the study. This was not predicted, but indicated that the initial degradation rate slowed. This could have been due to the longer equilibration period which occurred at 35 °C, during this time moisture was being absorbed by the artefact samples to allow the relative humidity to be constant throughout, this increased water movement could have

Table 4.14 Bulk concentrations of ions, initial and final concentrations of 1967 tortoiseshell comb – from IC analysis of swabs (non-destructive)

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Destroyed	6.9	21.1	2.1	6.6	2.5	2.8	1.3	0.6	1.6	1.0	ND	0.5
70 °C 55 % RH	None	Intermediate	5.0	10.4	0.1	3.1	ND	4.6	0.7	ND	ND	ND	ND	ND
70 °C 12 % RH	None	Minor	4.6	11.2	ND	1.2	0.5	ND	1.5	0.7	ND	1.2	ND	0.4
50 °C 75 % RH	None	Minor	5.1	56.4	0.3	ND	0.9	7.5	1.1	0.5	1.0	3.8	ND	0.4
50 °C 55 % RH	None	Intermediate	4.2	38.8	0.4	3.8	0.6	5.6	ND	10.1	0.8	0.7	ND	7.5
50 °C 12 % RH	None	Minor	4.7	17.6	ND	1.0	0.8	28.6	0.8	1.8	0.7	0.3	ND	1.1
35 °C 75 % RH	None	Minor	7.1	11.0	0.1	1.5	2.1	2.5	1.4	0.3	1.4	0.2	ND	0.5
35 °C 55 % RH	None	Minor	6.2	20.4	0.5	ND	0.6	6.7	1.0	2.2	ND	0.2	ND	0.8
35 °C 12 % RH	None	None	5.1	10.9	0.6	10.4	0.6	3.6	1.4	1.0	1.0	ND	ND	0.1

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – formate 0.42 µg cm^{-2}, nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

caused initial degradation which then slowed. Another reason could have been degradation which had occurred prior to the start of the ageing experiments, this could have left acetate residues which were removed in the first samples and then degradation occurred at the same rate as for the other samples. Formate levels were again higher at the surface compared to the bulk of the sample. All samples showed an increase in chloride concentration, with evidence of slight nitrate contamination at 55 % RH. Both oxalate and sulphate showed no change over the study period.

1946 Tortoiseshell Comb (table 4.15)

At 70 °C the 1946 comb behaved like the 1967 comb with acetate concentrations gradually increasing from the beginning of the ageing and showing an incisive increase after 40 days. Unusually none of the other anions showed any changes with ageing.

At 50 °C there was a marked difference between the two sampling procedures. Acetate levels rose for all samples, obtained by non-destructive sampling, but there were marked differences between each relative humidity and the other samples. At 75 % RH there was an increase after 150 days which was maintained throughout the study. At 55 % RH there was an increase after 75 days which then declined after 200 days to return to the original level. At 12 % RH, the acetate concentration rose after 200 days and then fell at the very end. Formate levels again were higher for surface sampling compared to the bulk. Chloride and nitrate concentrations indicated contamination in all samples, although this was not mirrored in the oxalate concentrations which did not change. The sulphate results were very interesting as the 75 % RH sample had a large peak of sulphate at 200 days which mirrored the formate increase in this sample. The samples aged at the other two relative humidities showed no change in sulphate concentration.

At 35 °C there was a dramatic increase in acetate at 75 % RH which started after 75 days and rose to 350 days. After this the level reduced down to those of the other two relative humidities where acetate levels increased more gradually. This indicates that the 75 % RH sample was degrading when the others were not. Once more, formate concentrations are higher than those seen in the bulk samples. All three show an increase in chloride levels although the 75 % RH increase is very similar to that of acetate and it could be this additional moisture which caused the more significant degradation in this sample. Nitrate

Table 4.15 Bulk concentrations of ions, initial and final concentrations of 1946 tortoiseshell comb – from IC analysis of swabs (non-destructive)

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	Minor	Destroyed	2.4	20.3	0.5	4.8	0.9	4.8	0.4	2.1	0.8	1.4	ND	0.9
70 °C 55 % RH	Minor	Intermediate	2.1	9.6	ND	2.1	1.4	ND	0.6	1.2	0.6	1.8	ND	ND
70 °C 12 % RH	Minor	Minor	3.3	9.4	0.4	2.6	1.6	0.2	0.4	2.1	0.4	ND	ND	0.6
50 °C 75 % RH	Minor	Destroyed	0.9	70.8	0.3	2.1	0.7	33.5	0.3	ND	0.6	2.0	ND	0.5
50 °C 55 % RH*	Minor	Destroyed	0.7	30.2	ND	1.6	0.5	7.4	0.5	4.8	0.4	1.8	ND	2.1
50 °C 12 % RH	Minor	Minor	0.6	14.4	1.4	ND	0.7	0.6	ND	0.9	0.8	0.4	ND	0.8
35 °C 75 % RH	Minor	Intermediate	1.9	14.5	ND	10.5	0.8	4.0	0.5	0.7	0.7	0.9	ND	0.9
35 °C 55 % RH	Minor	Minor	1.7	27.0	ND	4.9	ND	5.6	ND	2.9	0.4	0.3	ND	0.9
35 °C 12 % RH	Minor	Minor	2.1	11.9	ND	5.5	ND	5.8	0.5	1.1	1.1	0.5	ND	0.3

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – formate 0.42 µg cm^{-2}, chloride 0.38 µg cm^{-2}, nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

* – 210 days ageing

levels indicated contamination while sulphate and oxalate did not change even with the increased moisture from contamination.

1940's Doll's Body (table 4.16)

The doll's body is different from previous samples as formate was higher in the bulk than the surface, although the levels of formate on the surface were still extremely high. Acetate behaved in the same way as others at 55 % RH and 12 % RH. At 75 % RH, there was a large initial increase then a reduction followed by another increase after 40 days. This could be due to removal of acetate from the surface which is then replaced with new acetate as degradation occurs. The four remaining anions showed no overall change in concentration over the period of ageing.

At 50 °C, there was a large increase in the acetate concentration at 12 % RH, there is a parallel increase in the chloride concentration due to saturated salt solution contamination. The nitrate concentration also shows an increase indicative of contamination from the saturated salt solution, at 55 % RH, in this case there is a similar rise in sulphate concentration which shows that the additional moisture has a detrimental effect on the artefacts. There is a large increase in the oxalate concentrations of the samples aged at all three relative humidities. Formate concentrations remain constant throughout and appear higher than the bulk concentrations.

Samples at 35 °C showed an increase in acetate levels at all relative humidity values, the greatest being at 75 % RH. In this case formate levels are higher for surface than bulk. Chloride levels increased in all samples indicating that this was either being released from the bulk as degradation occurred or was there as surface contamination. Nitrate showed contamination at 55 % RH, which was very similar to the conclusions based on the results of the destructive sampling. However, sulphate showed no overall change. Oxalate was unchanged overall, although increased at 75 % RH in the middle of the ageing period.

1940's Doll's Leg (table 4.17)

The doll's leg samples at 70 °C showed increased acetate levels after 40 days, as do the samples from the other artefacts. Formate was higher at the surface than the bulk in all cases except 12 % RH. There was a slight increase in chloride at 75 % RH, which was indicative

Table 4.16 Bulk concentrations of ions, initial and final concentrations of 1940's doll's body – from IC analysis of swabs (non-destructive)

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Severe	1.1	26.7	ND	16.8	0.7	4.0	0.1	0.4	0.7	1.5	ND	1.9
70 °C 55 % RH	None	Intermediate	0.9	13.4	ND	4.1	0.4	1.4	0.3	0.9	0.4	2.1	ND	0.7
70 °C 12 % RH	None	Minor	0.7	12.9	ND	9.4	0.3	2.6	0.1	0.1	ND	1.4	ND	0.5
50 °C 75 % RH	None	Severe	0.9	92.3	0.2	4.9	0.6	82.5	ND	0.3	0.8	2.6	ND	4.9
50 °C 55 % RH	None	Minor	1.2	368.5	0.1	11.9	0.8	38.5	0.3	235.2	ND	2.2	ND	31.0
50 °C 12 % RH	None	Minor	0.6	2767.5	0.3	30.6	0.1	1766.3	0.5	1.1	0.6	3.3	ND	17.1
35 °C 75 % RH	None	Intermediate	1.1	105.4	0.7	8.1	ND	35.5	0.7	ND	0.1	0.4	ND	2.1
35 °C 55 % RH	None	Minor	0.9	25.6	0.8	5.4	0.9	7.4	0.4	23.5	0.3	0.9	ND	1.4
35 °C 12 % RH	None	Minor	1.4	10.8	0.8	8.0	ND	18.8	0.3	3.0	0.2	0.6	ND	0.5

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – formate 0.42 µg cm^{-2}, chloride 0.38 µg cm^{-2}, nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

Table 4.17 **Bulk concentrations of ions, initial and final concentrations of 1940's doll's leg – from IC analysis of swabs (non-destructive)**

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	Intermediate	Destroyed	1.5	36.8	ND	32.9	1.8	8.3	2.6	1.4	1.5	1.1	0.6	0.7
70 °C 55 % RH	Intermediate	Severe	0.9	15.9	0.3	22.4	1.5	2.3	2.9	4.2	1.2	3.4	0.5	1.4
70 °C 12 % RH	Intermediate	Severe	1.4	13.4	0.7	19.8	1.6	1.3	2.8	0.8	1.4	0.8	0.7	1.6
50 °C 75 % RH	Intermediate	Severe	1.3	71.3	0.1	2.9	1.7	132.1	2.4	ND	1.4	2.1	1.0	3.4
50 °C 55 % RH	Intermediate	Severe	0.9	26.1	ND	ND	1.4	5.2	2.0	97.4	1.6	3.7	1.2	230.5
50 °C 12 % RH	Intermediate	Intermediate	1.5	60.9	ND	3.3	2.0	76.1	2.3	1.5	2.0	1.7	0.9	18.8
35 °C 75 % RH	Intermediate	Intermediate	2.0	99.8	ND	9.5	1.6	39.4	2.1	ND	1.4	6.2	0.7	1.6
35 °C 55 % RH	Intermediate	Intermediate	0.9	51.9	ND	23.1	1.4	12.5	2.3	405.7	1.2	2.9	0.9	19.3
35 °C 12 % RH	Intermediate	Minor	0.8	22.4	0.3	7.4	1.4	15.0	2.7	1.0	1.3	ND	0.5	0.7

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 62 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – formate 0.42 µg cm^{-2}, nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

of release as degradation occurred rather than contamination. The levels of nitrate, sulphate or oxalate did not change indicating no contamination.

At 50 °C the acetate levels fluctuated but all rose slightly by the end of ageing. However, there was no sign of the large increase in acetate which is seen in the bulk results. There was evidence of contamination in all samples, and an increase in sulphate concentration at 55 % RH appeared linked with nitrate contamination as both increased in the same way. Oxalate concentrations increased in all samples significantly, but the greatest increase was at 55 % RH which reflected the greatest level of contamination.

At 35 °C there was a similar increase in the acetate levels of the samples aged at all three relative humidity values. The concentrations of chloride and nitrate showed contamination in the samples from the saturated salt solutions, this trend was also seen in the destructive sampling results. The largest contamination was in the 75 % RH sample which also showed the greatest increase in sulphate and oxalate levels. The other two samples, at 55 % RH and 12 % RH also showed an increase in both oxalate and sulphate, indicative of the levels of contamination seen in these samples.

Knife Handle (table 4.18)

The knife handle results for the non-destructive sampling revealed similar trends to those for the destructive sampling, with the acetate concentrations starting very high then decreasing and rising again after 40 days. Formate concentrations were again lower at the surface than in the bulk, this trend was observed in the three filled samples and could have been due to the filler acting as a scavenger and therefore, decreasing the levels of oxidative degradation. None of the other anions showed any changes during ageing.

Conclusions for Surface Sampling

In general samples aged at 70 °C did not show any changes in the anion concentrations at the surface because they were not aged for long enough. Deacetylation was too aggressive and degradation too severe for the other effects seen in the bulk to be achieved at the surface, meaning that only acetate levels changed for these samples. The trends in the results obtained using the destructive sampling procedure showed that deacetylation releases chloride and sulphate for extraction. However, for this to be observed by the non-destructive

Table 4.18 Bulk concentrations of ions, initial and final concentrations of knife handle – from IC analysis of swabs (non-destructive)

Sample	Initial Degradation	Final Degradation	Ion Concentration / µg cm^{-2}											
			Acetate		Formate		Chloride		Nitrate		Sulphate		Oxalate	
			Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
70 °C 75 % RH	None	Destroyed	23.9	22.7	0.6	6.8	1.2	7.2	ND	1.4	0.2	3.1	ND	1.1
70 °C 55 % RH	None	Destroyed	20.2	19.7	0.4	0.9	0.8	3.5	ND	0.7	ND	0.9	ND	0.6
70 °C 12 % RH	None	Destroyed	21.4	22.3	0.6	7.2	2.4	4.3	ND	3.2	0.1	0.9	ND	0.3

Standard deviations obtained from calibration error, n = 4

Initial – after natural ageing

Final – after 42 days (70 °C), 594 days (50 °C), 554 days (35 °C)

Detection limits – nitrate 0.29 µg cm^{-2}, sulphate 0.42 µg cm^{-2}, oxalate 0.28 µg cm^{-2}

sampling procedure the ions must also have time to migrate to the surface of the sample for extraction to be possible. At 70 °C the ageing period was too short for this to be achieved. As was seen in the bulk samples chain scission, shown by oxalate concentration increases, was not observed, again due to the severity of the deacetylation at this temperature.

Formate was higher at the surface than in the bulk of the sample for all of the transparent samples, however, the reverse was true for the filled samples. This would indicate that the fillers are impeding oxidative degradation of cellulose acetate at the surface of these samples.

As for destructive sampling, acetate increases always preceded oxalate increases, again showing that deacetylation is the initial degradation process and chain scission is secondary. The loss of sulphate and chloride was less prevalent from the surface, probably due to slow migration of these anions through the polymer matrix.

4.5.4.3 Comparison of Sampling Procedures

It can be clearly seen from the two sets of results that there was inconsistent correlation between ion concentration in the trends for the ion concentrations at the surface and in the bulk of the cellulose acetate and at other times there is no correlation. This is probably due to the choice of sampling area. For the destructive sampling technique, the samples were most conveniently removed from the edges of the sample, as it was impossible to remove pieces from the middle. By contrast, swabbing was taken from the middle outwards towards the edges to avoid contamination from handling. Also if the artefact was obviously wet or contaminated by salt solution this area was avoided if at all possible. This was easier with the swabbing than the destructive sampling as the salt contamination generally started at the sample edges.

It can be seen from the results that ion levels on the surface do not always represent what is happening within the bulk of the sample. Therefore if swabbing was used for assessing degradation of cellulose acetate samples, great care would have to be taken in choosing areas for analysis so that samples were as representative of the whole artefact as possible. It would be preferable to analyse several areas of the one artefact to obtain a more complete picture of the condition of the sample.

4.6 Overall Conclusions From Accelerated Ageing Study

The visual observations, and results obtained by FTIR and IC all clearly show that deacetylation is the primary degradation process. This was observed by the strong smell of acetic acid, increase in the extractable acetate concentrations and reduction in peak intensity of the C=O peak in the FTIR spectra and the consequential movement in peak position.

Several secondary degradation processes were observed in the ageing studies, namely plasticiser loss, chain scission and oxidative degradation. Plasticiser loss followed deacetylation as the smell of acetic acid occurred before surfaces became sticky. Extractable acetate concentrations increased at least a few days before oxalate concentrations increased, an indication of chain scission, as shown by the IC results. This even occurred when a large amount of water came into contact with the artefact due to contamination from saturated salt solutions used to control % relative humidity during ageing. Finally, oxidative degradation was evident through increasing levels of extractable formate concentrations on the surface of samples but not in the bulk samples indicating that this is a surface reaction only. Oxidative reactions can be slowed by fillers, where the zinc oxide or other fillers can act as an acid absorbent, thereby slowing or inhibiting degradation.

Temperature was found to have more effect on degradation than relative humidity as all of the samples at 70 °C were badly degraded whereas the samples at 75 % RH and lower temperature were not. The effect of relative humidity was found to decrease when temperature decreased. This has practical implications for museum store and display areas, i.e. % relative humidity may not need to be as controlled as temperature. Contact with aqueous solutions was seen to be devastating, as all of the samples, which were contaminated with salt solution showed increased degradation in one form or another. Cellulose acetate artefacts should therefore, not be immersed in aqueous solutions or water and the recommended form of cleaning would be gentle rubbing with a cloth. Liquids are not advisable as these will simply be absorbed with unknown consequences. However, another possibility would be the use of a hydrophobic alkaline to help to reduce acidity and repel water from being absorbed.

Loss of acetic acid and/or plasticiser from the degrading test samples was consistently greater than intake of water. This indicates that moisture is needed to initiate the reaction but once started it is auto-catalytic. This is confirmed by the difference in the 1996 pieces aged

alone and with the other items. This supports the view that prevention of degradation starting is the best way of preserving cellulose acetate artefacts. However, degradation can be slowed by reducing temperature as demonstrated when aged samples, were removed from the ovens and placed at ambient temperature and relative humidity degradation was significantly reduced. This compounds the conclusion that temperature has a very significant effect on the rate and extent of degradation.

It was also noted that even after severe degradation artefacts did not necessarily disintegrate completely. The slow rate of deacetylation at 50 °C did result in shrinkage of the artefact but these were still in relatively good condition and remained intact as long as they were carefully handled. Badly degraded samples should be removed from the vicinity of relatively more stable artefacts, as demonstrated in the experiments when the 1996 cellulose acetate which was aged alone compared to ageing with the other artefacts; the lone sample was in far better condition due to the lower levels of acetic acid in the atmosphere.

An important general point is that when assessing cellulose acetate artefacts, it should be remembered that the surface is not always representative of the bulk sample. Therefore, as much information should be collected as possible before any final decision or assessment is made. From these accelerated ageing studies, micro-FTIR is the best technique for assessing the condition of cellulose acetate as the least ambiguity was found in these results. The IC results were shown to be highly dependent on the area sampled, therefore, care must be taken if using this technique to make a condition assessment. However, if the limitations are known and considered then the non-destructive sampling with IC would be a valuable technique for assessing degradation as it is easy to do *in-situ*. This would be the best method if micro-FTIR were not available or feasible.

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CHAPTER 5

FURTHER INVESTIGATION OF THE DEGRADATION OF CELLULOSE ACETATE BY OTHER ANALYTICAL TECHNIQUES

5 Further Investigation

5.1 Introduction

Following the assessment of aged cellulose acetate by micro-FTIR and IC, it was decided that further investigation of the degradation processes was required. Therefore the following techniques were employed to develop a fuller understanding of the reactions and processes involved. Gel permeation chromatography (GPC) was used to further investigate the role of chain scission in the degradation process by monitoring changes in molecular weight distribution. Thermogravimetric analysis (TGA) both on its own and coupled to FTIR, was used to characterise volatile compounds lost from the surface of the artefacts; this was further enhanced by the use of headspace gas chromatography (GC). The headspace GC was used to monitor the environment around the artefact within the enclosed ageing chamber after ageing at different temperature and % relative humidity conditions to identify volatiles which could account for changes in the rate of degradation. Samples for this investigation were mainly those used for the accelerated ageing study as destructive analytical techniques were used.

5.2 Gel Permeation Chromatography (GPC)

GPC was used to investigate changes, if any, in polymer molecular weight distribution to assess degradation by chain scission. Experiments were carried out both in-house and at Rapra (Rubber and Plastics Research Association, Polymer Characterisation Unit, Shawbury, Shrewsbury, Shropshire).

Instrumentation is described in section 2.3.2 and sampling procedures are described in sections 2.3.3 to 2.3.5. It was found in practise that very few samples were suitable for GPC analysis as the aged samples very quickly became insoluble in the THF solvent, thus prohibiting analysis.

Analysis was carried out only on samples investigated by accelerated ageing and the cellulose acetate test square. The aim was to elucidate the stage of ageing where chain scission was occurring. However, due to the solubility problems, it was only possible to obtain results from the samples that were naturally or partially aged.

In-house GPC analysis was carried out on the accelerated aged samples (table 5.1), a typical chromatogram is shown in figure 5.1. In many cases, the sample became insoluble before any change in molecular weight or distribution of the polymer could be determined. This concurred with the observation that, deacetylation was occurring before chain scission, as the solubility of cellulose acetate is well documented to change with level of acetylation[1-4] (sections 1.2.2 and 3.3). The level of acetylation during degradation changes from diacetate, which is readily soluble in acetone and THF, to monoacetate, which is very insoluble.

Table 5.1 Samples analysed by GPC at Strathclyde

Sample	Ageing Conditions	Degradation	Mw	Mn
1996 cellulose acetate	Natural	None	149,000	54,700
1996 cellulose acetate	50 °C 75 % RH 102 days	Minor	151,000	54,900
1967 hairslide	Natural	None	170,000	59,600
1967 hairslide	50 °C 75 % RH 102 days	Slight	165,000	58,900
1967 comb	Natural	None	168,000	53,000
1967 comb	70 °C 12 % RH 13 days	Slight	161,000	52,500
1967 comb	70 °C 55 % RH 13 days	Intermediate	NA	NA
1967 comb	70 °C 12 % RH 42 days	Intermediate	163,000	52,700
1967 comb	70 °C 55 % RH 42 days	Severe	NA	NA
1967 comb	70 °C 75 % RH 42 days	Severe	NA	NA
1967 comb	50 °C 75 % RH 102 days	Intermediate	NA	NA
1946 comb	Natural	Minor	192,000	61,400
1946 comb	50 °C 75 % RH 102 days	Slight	195,000	62,700
Doll's body	Natural	Minor	186,000	54,100
Doll's body	70 °C 12 % RH 42 days	Intermediate	182,000	53,800
Doll's body	70 °C 55 % RH 42 days	Intermediate	179,000	53,600
Doll's body	70 °C 75 % RH 42 days	Intermediate	183,000	54,000
Doll's body	50 °C 75 % RH 89 days	Severe	NA	NA
Doll's leg	Natural	Severe	185,000	54,200
Doll's leg	50 °C 75 % RH 89 days	Extreme	NA	NA
Knife handle	Natural	Minor	NA	NA

NA – not available

Mw – molecular weight as defined by weight

Mn – molecular weight as defined by number

As seen from the results (table 5.1) after a certain stage of ageing samples can no longer be analysed by GPC due to the problems with solubility in THF. Various solvents (table 5.2) were

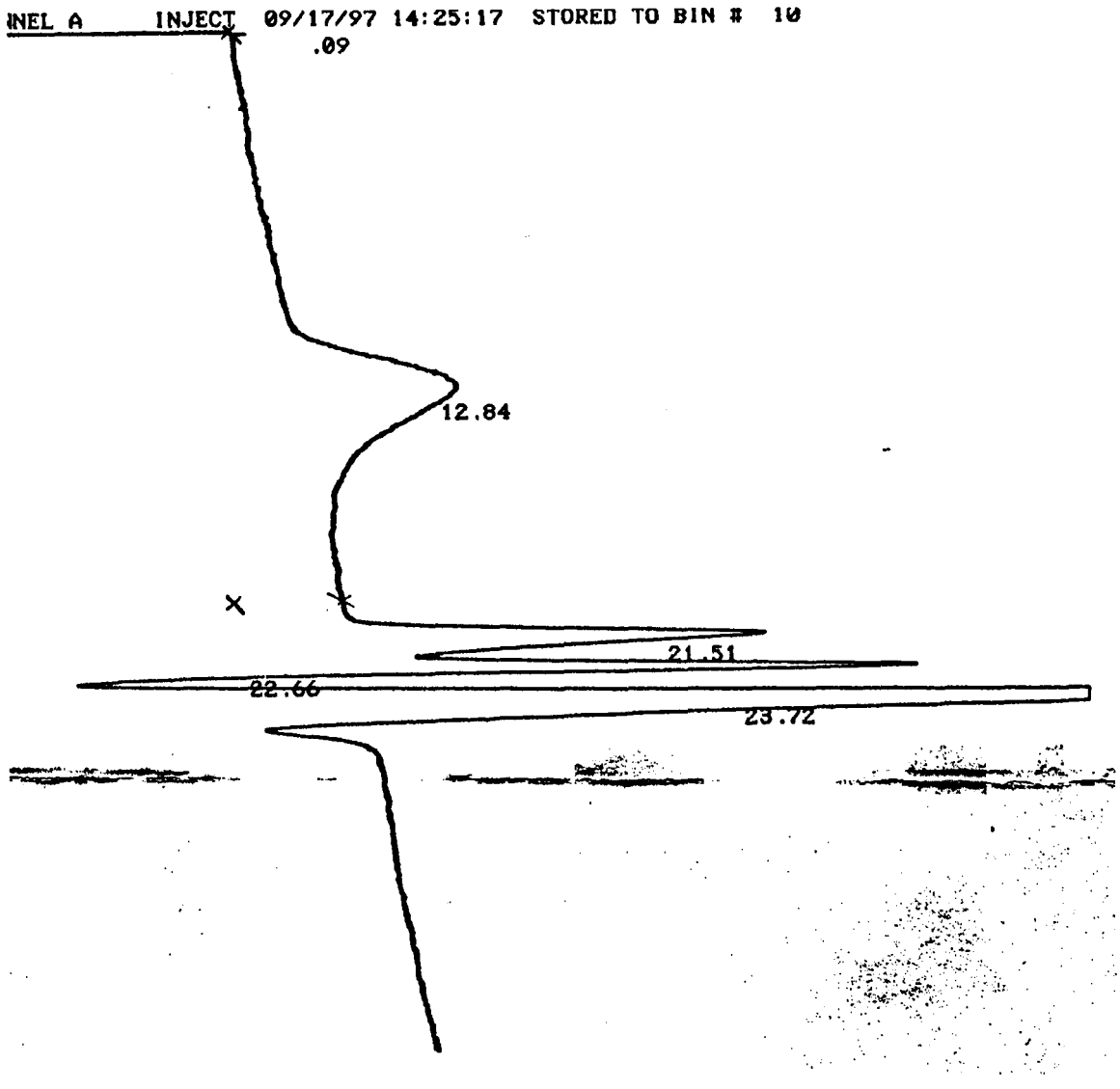

Figure 5.1 **Typical GPC chromatogram of cellulose acetate**

investigated to try to find a suitable mobile phase to allow the GPC work to continue, however, no suitable solvent or combination of solvents could be found.

Table 5.2 Solvents investigated as possible mobile phases for GPC

Solvent	Solubility		Suitability
	Natural	Accelerated	
THF	✓	✗ (slight)	✗
THF + heat	✓	✗ (slight)	✗
Methanol	✗	✗	✗
Acetone	✓	✗	✗
Hexane	✗ (slight)	✗	✗
DMF	✗ (slight)	✗	✗
DMF + heat	✓	✗ (slight)	✗
Dichloromethane	✗	✗	✗

A selection of samples were submitted for analysis by GPC at Rapra but the same solubility problems were encountered. The samples sent to Rapra are shown in table 5.3, although, only samples 1, 4, 5, 7 and 9 could be analysed.

Table 5.3 Samples sent to Rapra for analysis

Sample	Sample No.	Rapra No.	Ageing Conditions	Degradation
Doll's Leg	1	7217	Natural	Severe
Doll's Leg	2	7218	50 °C 12 % RH 435 days	Extreme
Doll's Leg	3	7219	70 °C 75 % RH 62 days	Extreme
Peabody Folder	4	7220	Natural	Slight
1996 CA	5	7221	Natural	None
1996 CA	6	7222	70 °C 75 % RH 62 days	Intermediate
1967 Comb	7	7223	Natural	None
1967 Comb	8	7224	70 °C 75 % RH 62 days	Severe
1967 Hairslide	9	7225	70 °C 12 % RH 62 days	Intermediate
1967 Hairslide	10	7226	70 °C 75 % RH 62 days	Severe

In all cases, both in-house and Rapra analysed (tables 5.1 and 5.4, respectively), little or no change was observed in any of the samples, which could be dissolved (figures 5.2 and 5.3). The IC results (section 4.5.4) indicate that deacetylation is the initial process in cellulose acetate degradation and these results would also show this as a change in solubility is seen before any evidence of chain scission has been observed. However, these solubility problems mean that no conclusive evidence is available regarding the occurrence of chain scissioning.

Table 5.4 Results of GPC carried out at Rapra

Sample	Run No.	Mw	Mn	Polydispersity
1	A2050	182,000	53,100	3.4
(7217)	A2056	187,000	53,300	3.5
4	A2052	170,000	66,800	2.6
(7220)	A2065	172,000	67,700	2.5
5	A2049	151,000	56,500	2.7
(7221)	A2060	151,000	55,300	2.7
7	A2051	166,000	52,600	3.2
(7223)	A2068	171,000	51,900	3.3
9	A2054	172,000	60,400	2.8
(7225)	A2061	173,000	60,600	2.9

Mw – molecular weight as defined by weight

Mn – molecular weight as defined by number

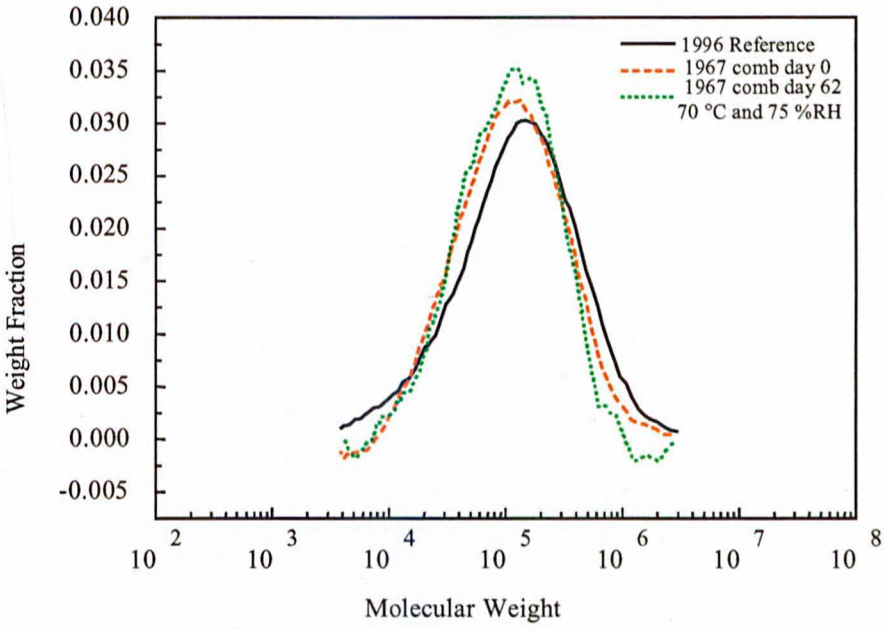

Figure 5.2 Molecular weight distribution of 1967 tortoiseshell comb unaged (--), aged at 70 °C and 75 %RH for 62 days (--) and 1996 cellulose acetate unaged (--), –analysed in-house

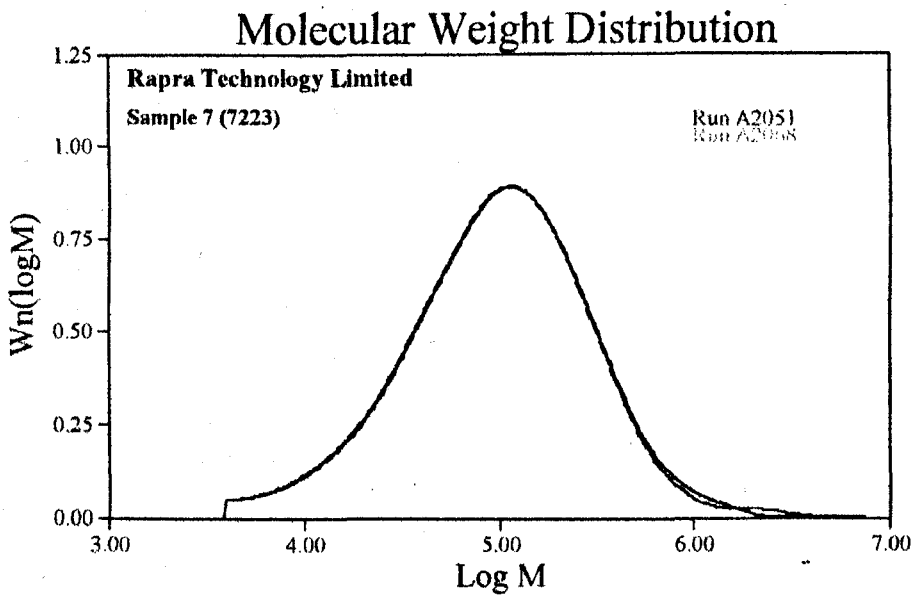

Figure 5.3 **Molecular weight distribution of 1967 tortoiseshell comb – analysed at Rapra**

5.3 Thermogravimetric Analysis (TGA)

TGA was used to investigate the weight change in the cellulose acetate samples due to loss of volatiles when samples were heated in an inert atmosphere. Instrumentation used is described in section 2.4.2 and sampling procedures are described in section 2.4.3 and 2.4.4. As for GPC, analysis was carried out on the samples investigated by accelerated ageing, the cellulose acetate test square and new cellulose acetate from a plastics identification kit (for comparison with the 1996 cellulose acetate). It was not possible to analyse all of the samples using this technique due to time constraints, therefore, samples were chosen to represent the range of degradation observed in each artefact after accelerated ageing.

Samples under test were each assigned a letter for identification purposes as follows;

A) Cellulose acetate from test kit,
B) 1996 cellulose acetate natural ageing
C) 1996 cellulose acetate 50 °C, 55 % RH, day 102
D) 1996 cellulose acetate 50 °C, 75 % RH, day 300
E) 1967 hairslide natural ageing

F) 1967 hairslide 50 °C, 75 % RH, day 210
G) 1967 hairslide 50 °C, 12 % RH, day 300
H) 1967 comb natural ageing
I) 1967 comb 70 °C, 12 % RH, day 62
J) 1967 comb 70 °C, 75 % RH, day 62
K) 1946 comb natural ageing
L) 1946 comb 50 °C, 55 % RH, day 210
M) 1946 comb 50 °C, 75 % RH, day 300
N) Doll's body natural ageing
O) Doll's body 50 °C, 55 % RH, day 200
P) Doll's body 50 °C, 75 % RH, day 197
Q) Doll's leg natural ageing
R) Doll's leg 50 °C, 55 % RH, day 200
S) Doll's leg 50 °C, 75 % RH, day 200
T) Cellulose acetate test square, green area (no degradation)
U) Cellulose acetate test square, brown area (badly degraded)
V) Knife handle, 70 °C 55 % RH, day 62 (badly degraded)

In the case of the artefacts, which were studied by accelerated ageing (chapter 4), three samples were chosen to represent the full range of degradation observed during these studies. Therefore, these artefacts had a naturally aged (least degraded), mildly degraded and badly degraded sample analysed by TGA.

The first point noted was that the naturally aged 1996 cellulose acetate (B) and the test kit cellulose acetate (A) were similar in their TGA patterns and only showed weight loss at the final carbonisation stage at 315 °C. This showed that the cellulose acetate used as a control sample throughout this study is very similar to cellulose acetate that is marketed as a control sample. The aged 1996 cellulose acetate samples (C and D) had an additional weight loss starting round 95 °C, due to loss of acetic acid. This acetic acid would have needed to have been from previous degradation, as the samples would not have had time to degrade during the analysis. Sample C lost less acetic acid than sample D as expected because sample C was less degraded than D so less acetic acid would have been available for volatilisation within the matrix.

The three 1967 hairslide samples (E – G) showed no acetic acid loss in any of the samples, regardless of state of degradation. While the naturally aged sample carbonised at 320 °C, this temperature reduced with severity of degradation with the most aged sample (G) showing very little carbonisation at 300 °C.

The first two 1967 comb samples (H and I) showed very similar degradation and both lost some acetic acid at 95 °C before carbonising at 310 °C. The third sample in this set (J) behaved differently. It lost more acetic acid than the other two as expected but at 270 °C there was a sharp loss of weight and total destruction of the sample. This would again be due to changing energy requirements for breaking bonds within the polymer.

The naturally aged 1946 comb sample (K) (figure 5.4) had a very similar profile to the other naturally aged samples, with some acetic acid loss and slight carbonisation at 315 °C. However, the two aged samples (L and M) (figure 5.5 and 5.6) showed the sharp transition, seen in sample (J), although earlier at 250 °C and 200 °C, respectively. The less degraded sample (L) lost some acetic acid whereas the more degraded sample (M) lost much more acetic acid due to trapped acetic acid within the matrix of the more deacetylated cellulose acetate being released.

The change in carbonisation temperature (illustrated in figures 5.4 – 5.6) would be due to the naturally aged sample needing more energy to carbonise, as the bonds within the polymer would be stronger in the undegraded sample. When degradation occurs there is a change in the polymer backbone with the loss of acetate groups, resulting in changes to hydrogen bonding and helical structure of the polymer (section 1.2.1 and figures 1.1 and 1.2). This would result in a change in the energy required to carbonise the sample and hence a reduction in the temperature required to do so. The other major difference in the thermograms is the amount of sample remaining after analysis, in the naturally aged sample a substantial amount of charred material is left at the end of analysis, however, in the aged samples the entire sample is lost and a reading of zero weight obtained. The reason for this is due to the levels of oxygen present around the samples, the more degraded samples will have more oxygen released, at lower temperatures due to weaker bonds, resulting in an atmosphere capable of complete combustion of the sample, however only partial combustion is possible in the more stable undegraded samples.

The naturally aged sample of the doll's body (N) and the first aged sample (O) show very similar signs of degradation both carbonising initially at 240 °C. The aged sample actually released less acetic acid than the naturally aged sample. The earlier carbonisation temperature, than seen in the previous samples, could be due to filler being present. However, the more badly degraded sample (P) lost the greatest amount of acetic acid with a sharp degradation transition at 280 °C. Like sample (J) this sample was completely destroyed.

The naturally aged doll's leg sample (Q) showed the fact that it was more degraded to begin with as it had a slight loss of acetic acid before a very sharp degradation transition at 290 °C, which the other naturally aged samples did not have. Sample (R), which had degraded further, released more acetic acid with a lower transition temperature of 260 °C. This sample was totally destroyed by this point unlike the naturally aged sample. Finally the most severely degraded sample (S) had a very large acetic acid loss with the same transition temperature of 260 °C, also leading to complete destruction.

The two samples from the cellulose acetate test square (T and U) showed marked differences between the degraded and undegraded samples. The green area of the square showed very little acetic acid loss and minimal weight loss at the carbonisation temperature of 270 °C. By contrast, the brown degraded area showed a very similar profile to that of sample R (the medium degraded doll's leg), with slight acetic acid loss, as was seen in the undegraded sample, but a sharp degradation transition at 290 °C.

Finally the knife handle sample (V) also had a typical degraded sample profile, with the sharp transition at the end of the analysis, in this case starting at 290 °C. It also had a significant acetic acid loss similar to sample S.

General observations for the samples are that there is a final carbonisation at approximately 315 °C for transparent samples and at < 300 °C for filled samples, typically between 200 °C to 290 °C (figure 5.7 and 5.8). This lower average temperature could be due to two factors, more oxygen would be present in the fillers, therefore the combustion of the samples would be easier and the fillers could have an affect on bonding and, hence, polymer stability. Acetic acid was lost around 95 °C in all samples except for the pristine condition cellulose acetate of the test kit and 1996 cellulose acetate sample.

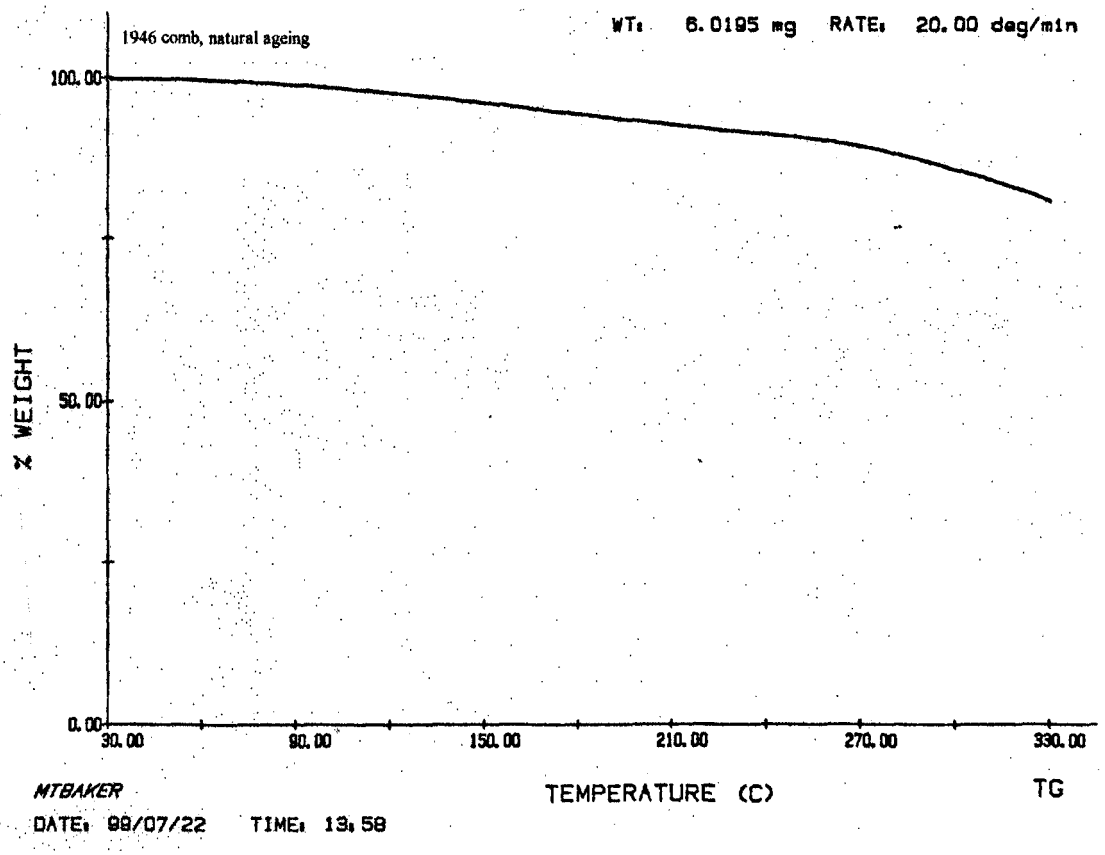

Figure 5.4 TGA trace of undegraded 1946 comb, sample K

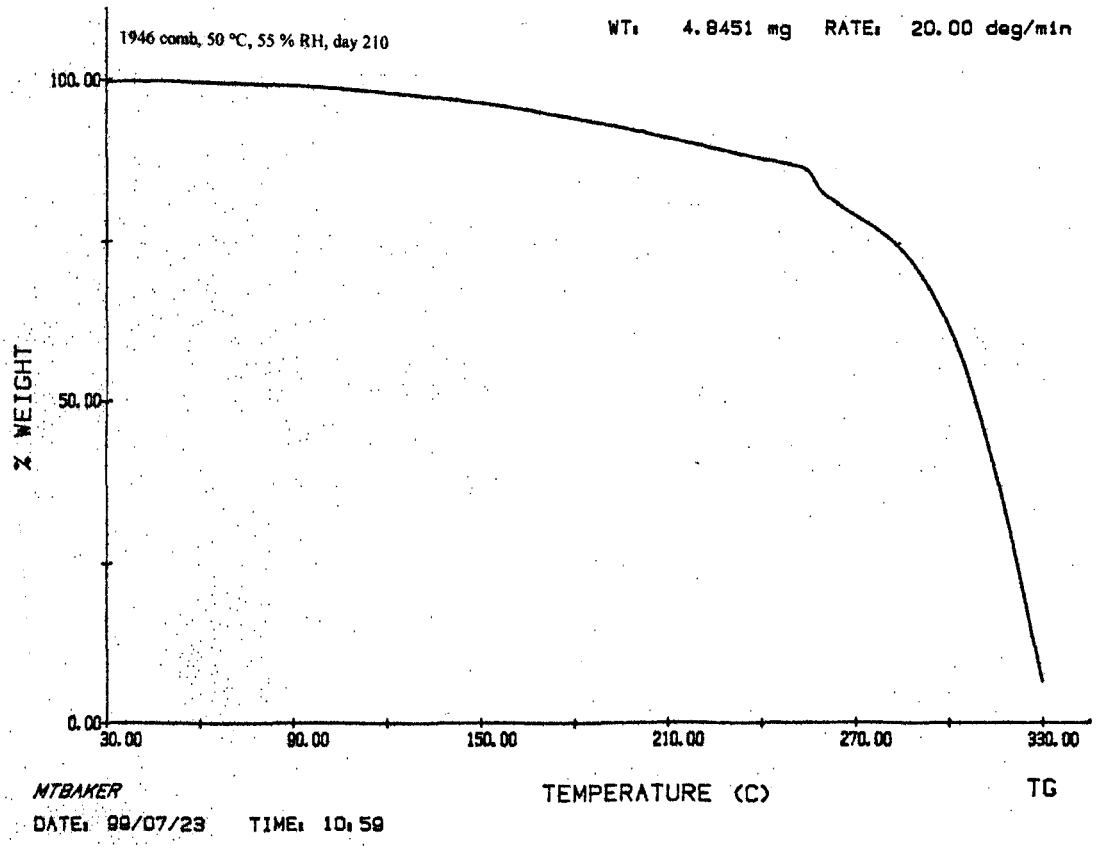

Figure 5.5 **TGA trace of degraded 1946 comb, aged at 50 °C and 55 % RH for 210 days, sample L**

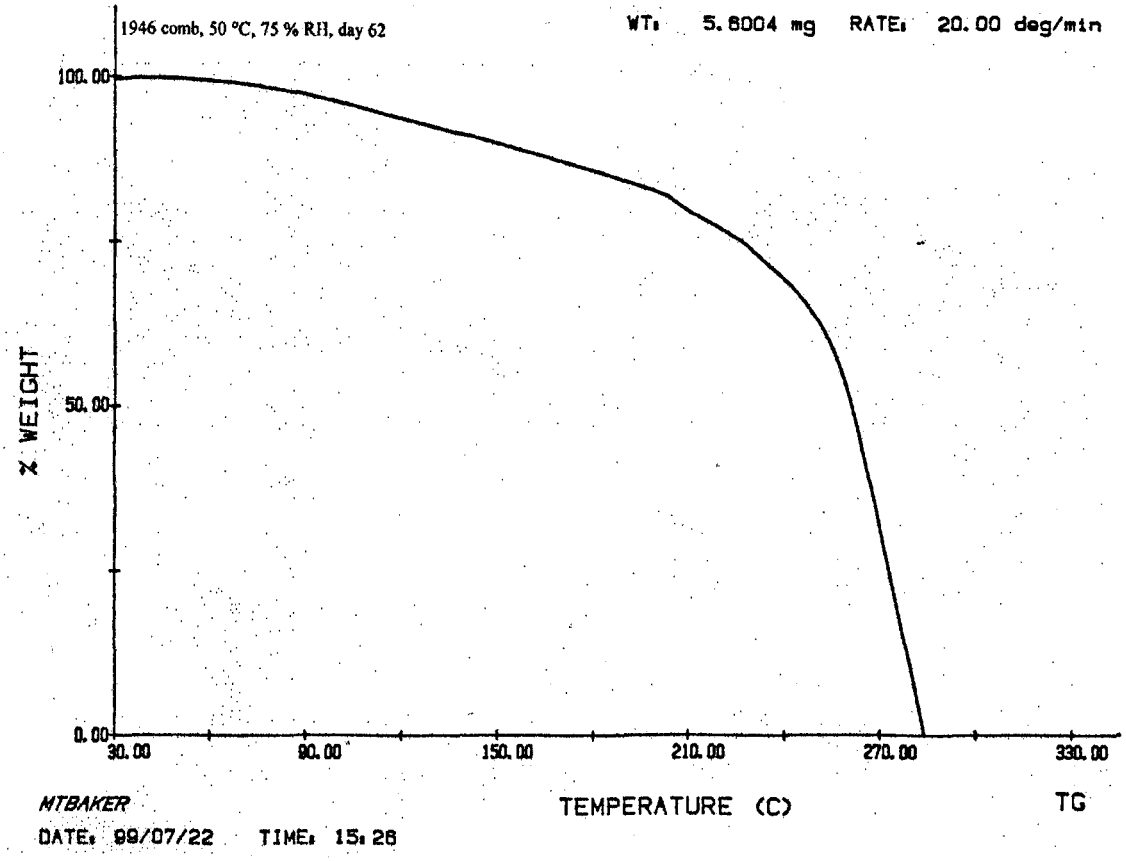

Figure 5.6 **TGA trace of extremely degraded 1946 comb, aged at 50 °C and 75 % RH for 300 days, sample M**

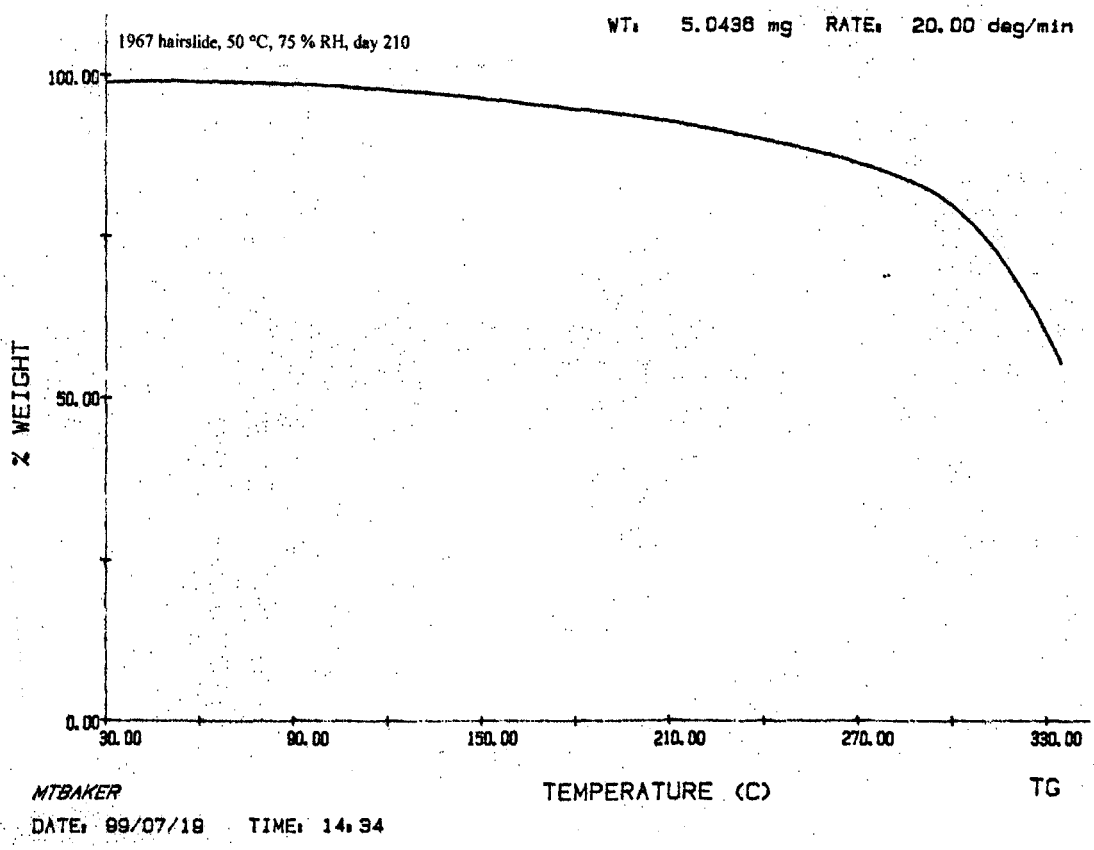

Figure 5.7 **TGA trace of unfilled cellulose acetate, 1967 hairslide aged at 50 °C and 75 % RH for 210 days, sample F**

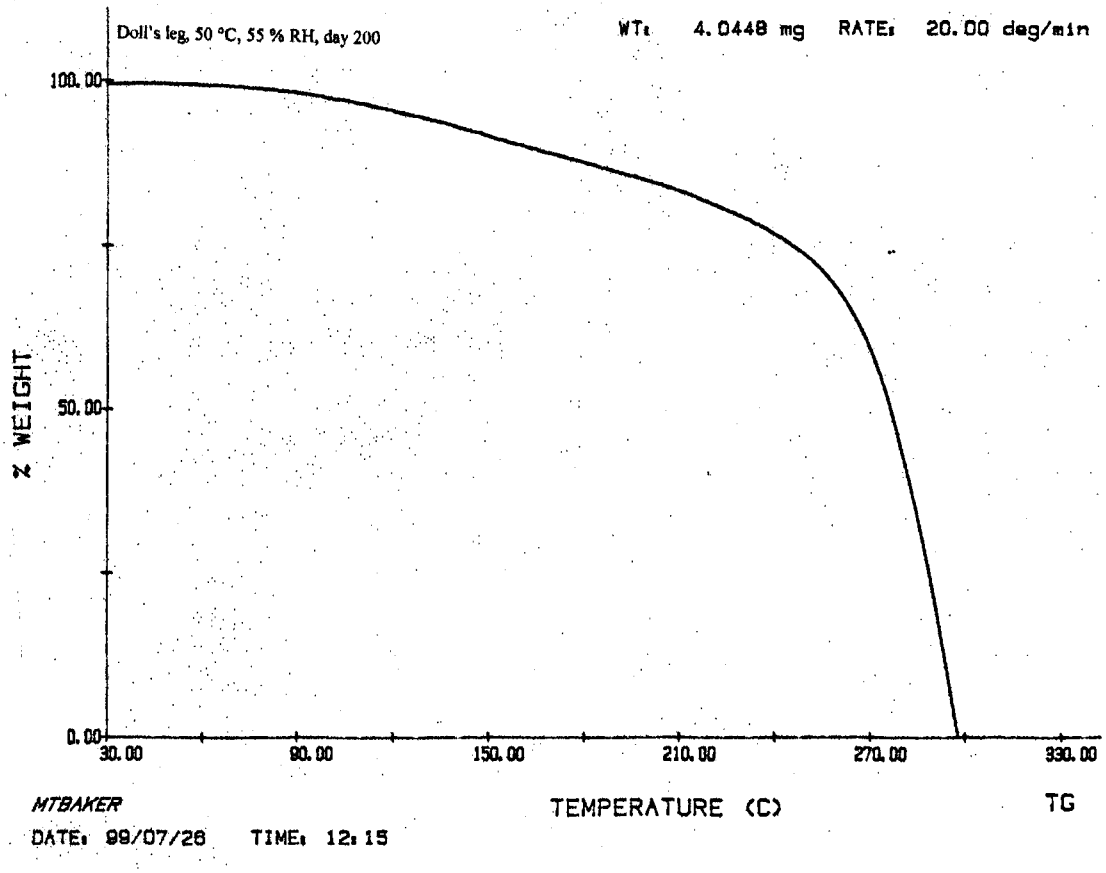

Figure 5.8 **TGA trace of filled cellulose acetate, doll's leg aged at 50 °C and 55 % RH for 200 days, sample R**

5.4 Thermogravimetric Analysis – Fourier Transform Infrared Spectroscopy (TGA-FTIR)

TGA-FTIR was used to identify the volatiles that were lost during weight loss in the cellulose acetate samples heated in an inert atmosphere. Instrumentation used is described in section 2.4.2 and sampling procedures are described in sections 2.4.3 and 2.4.4. Analysis was carried out on only three samples from the same artefact (1946 comb) by Perkin Elmer, Technology Park/Atlanta, 510 Guthridge Ct., Norcross, GA, USA. The three samples were chosen to cover a range of degradation as follows;

1) 1946 comb, naturally aged (cellac1)
2) 1946 comb, 50 °C, 55 % RH, day 210 (cellac2)
3) 1946 comb, 70 °C, 75 % RH, day 62 (cellac3)

Degradation increased from sample 1 to 3.

The TGA data (figure 5.9) showed a relative decrease in stability from the naturally aged sample to the badly degraded sample as expected. The naturally aged and 50 °C samples (1 and 2) showed no weight loss until above 200 °C, indicating no loss of acetic acid and therefore no previous degradation. However, the 70 °C sample (3) did lose weight before 200 °C indicating loss of acetic acid. Weight was rapidly lost from sample (3) at 250 °C, whereas 1 and 2 show rapid weight loss at 320 °C and 300 °C respectively. This indicated a gradual decrease in stability due to the changes in the hydrogen bonding and helical formation of the sample by the change in energy required to break these bonds. However, the FTIR results indicated that any weight loss below 200 °C was simply surface moisture.

It was thought that loss of acetate and plasticiser would account for weight loss in the samples. However, the FTIR spectra showed that various esters and acids including acetic acid, water and carbon dioxide were responsible for the majority of loss from the cellulose acetate samples. There was a small percentage of unidentified material lost in each sample showing that deacetylation occurs to a greater extent than plasticiser loss or chain scission.

The spectra for sample 1 showed nothing except water and carbon dioxide from 50 °C to 200 °C. Above this temperature a number of other IR bands started to form and between 334 °C and

370 °C, the spectra were identified as acetic acid with 71.3 % certainty from a library match (figure 5.10). All the spectra collected before and after this temperature range showed acetates, esters and short chain acids as well as carbon dioxide. At 440 °C, the spectra had reverted back to only bands for carbon dioxide and a small amount of water, due to the sample having carbonised.

Sample 2 showed very similar results to those of sample 1. Acetic acid was positively (88.9 % certainty) identified at the lower temperature of 290 °C and the spectra remained constant until 328 °C when it also begin to change to show a higher percentage of other acetates, esters and short chain acids (figure 5.11). The final spectrum at 432 °C contained bands for only water and carbon dioxide as the sample had carbonised and was decomposing to carbon dioxide. In this sample the acetic acid was released at a lower temperature than for sample 1 as the sample has degraded and the bonds within the polymer are, therefore, weaker which means that less energy is required to break these bonds and hence release the acetic acid.

Sample 3, the most degraded sample, was again very similar, although the loss of acetic acid was identified at the lower temperature of 173 °C (91.6 % certainty) (figure 5.12) and the spectra remained the same until 289 °C when other acetates and short chain acids formed. This change in temperature reflected lower energy to break fewer and less stable hydrogen bonds in the changing polymer structure.

In general it can be said that TGA-FTIR confirmed that deacetylation is the predominant degradation process in cellulose acetate as acetic acid was the compound lost in the highest proportion, followed by other acetates and then short chain acids. The loss of acetic acid also occurred at a lower temperature in the more degraded sample indicating that the polymer matrix becomes unstable as degradation occurs, opening up the polymeric matrix for analysis with the use of less energy, as was seen in the IC (section 4.5.4.1) and FTIR (section 4.5.3) results.

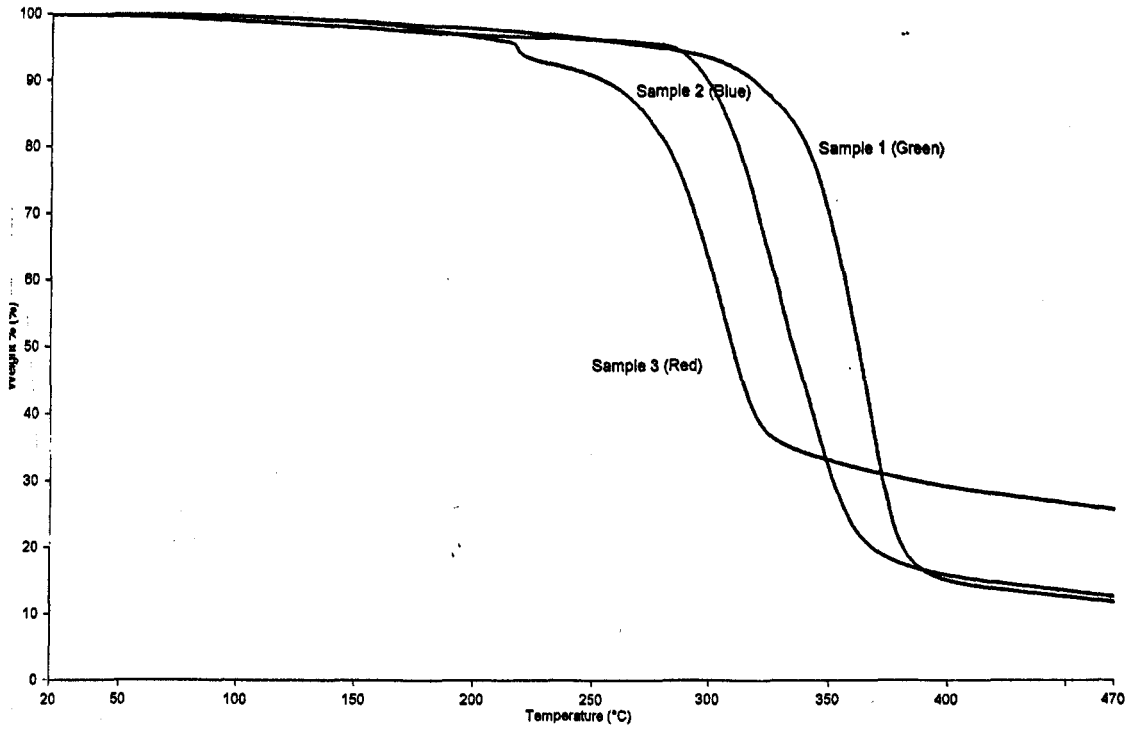

Figure 5.9 **TGA trace for all three samples analysed by TGA-FTIR; 1946 comb, naturally aged (sample 1); 1946 comb, aged at 50 °C and 55 % RH for 210 days (sample 2); 1946 comb, aged at 70 °C and 75 % RH for 62 days (sample 3)**

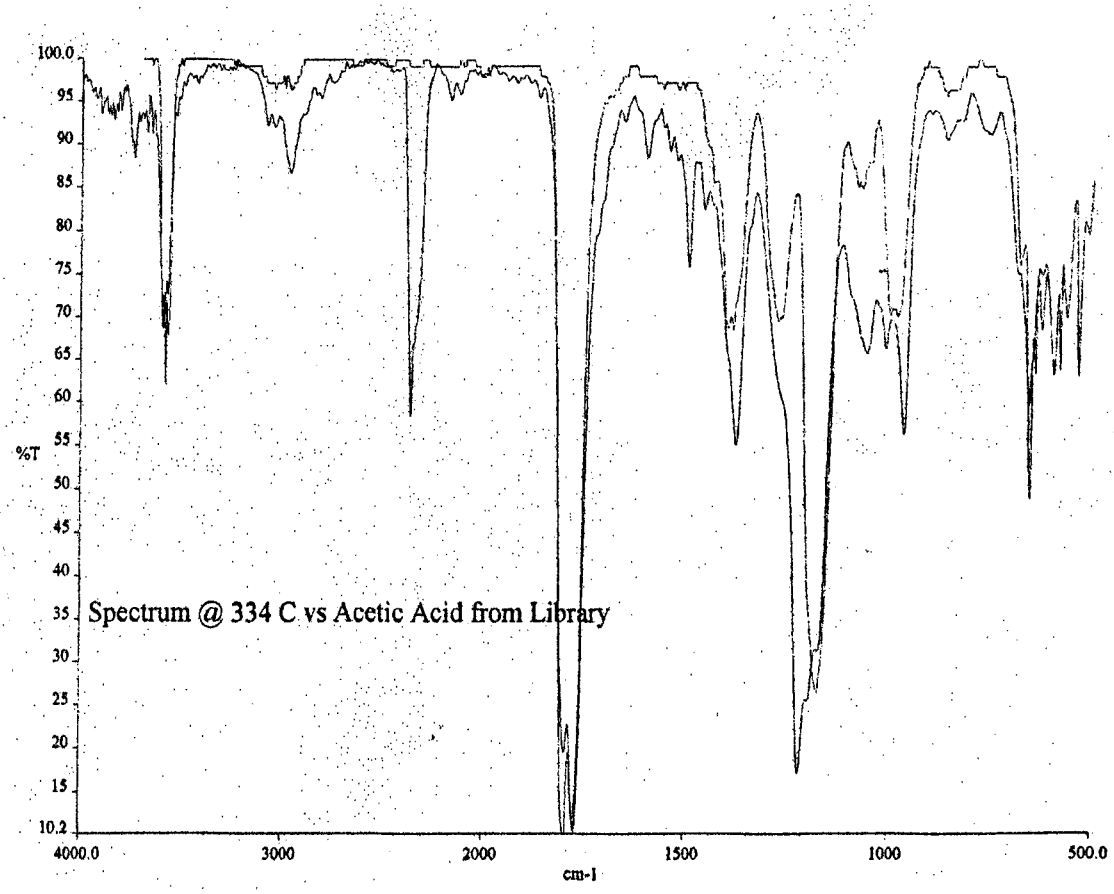

Figure 5.10 FTIR spectra of acetic acid vs. sample 1 (cellac1) at 334 °C

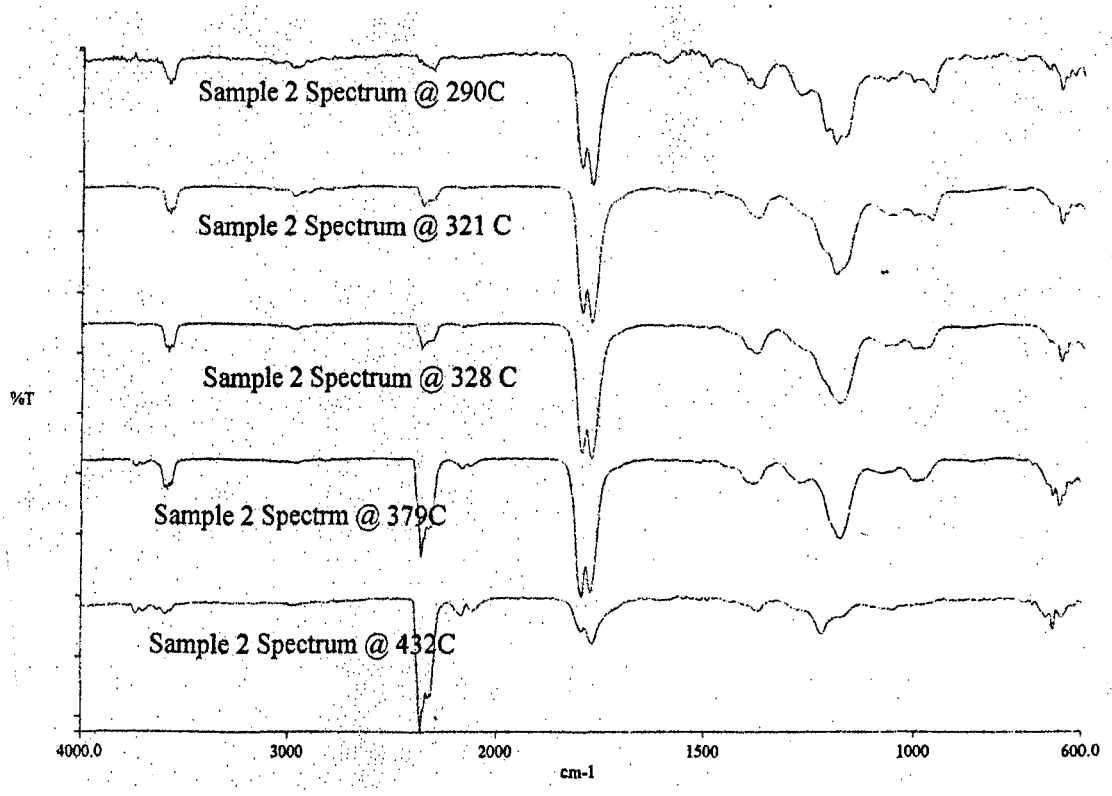

Figure 5.11 FTIR spectra of volatiles over temperature range 290 °C – 432 °C

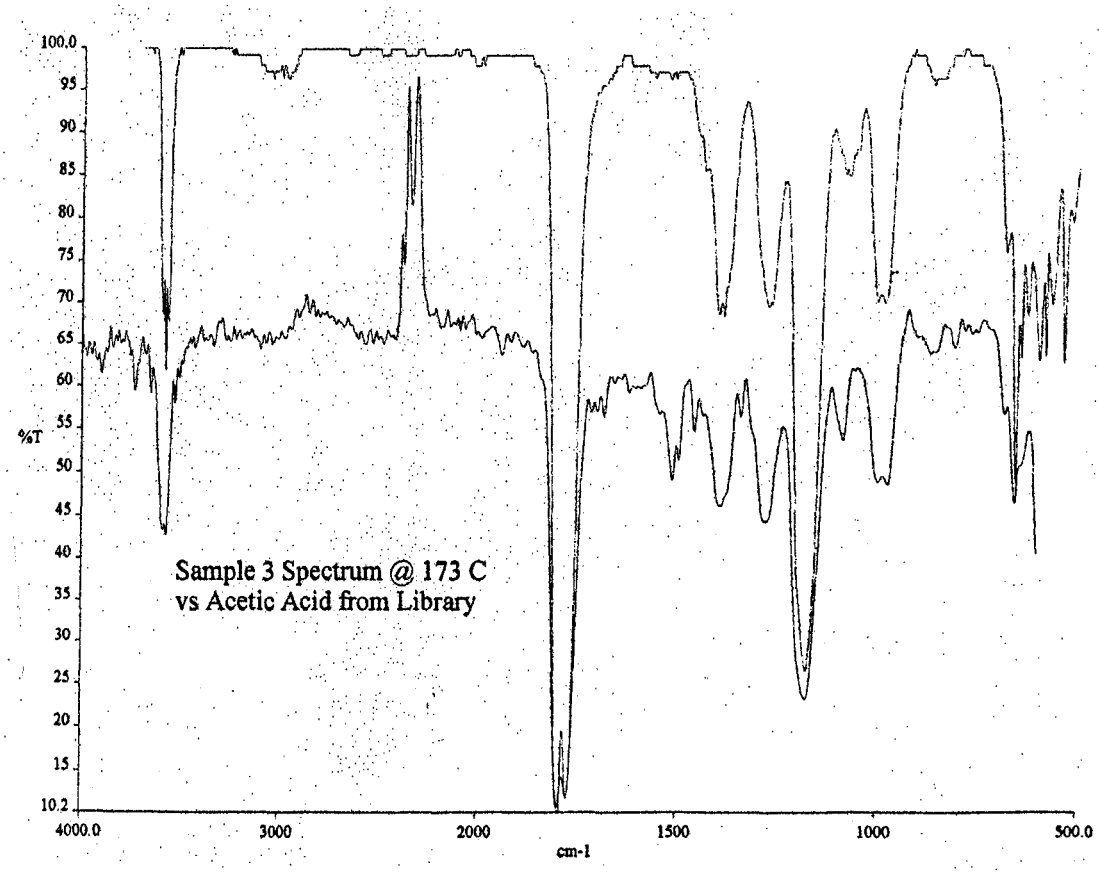

Figure 5.12 FTIR spectra of acetic acid vs. Cellac3 at 173 °C

5.5 Headspace Gas Chromatography (Headspace GC)

Headspace GC was used to investigate the atmosphere surrounding the samples after ageing had been completed. Instrumentation is described in section 2.6.2 and sampling procedures are described in section 2.6.3. Analysis was carried out on the samples from the accelerated ageing study, after the ageing study at each temperature had been completed, 1 g of each sample was weighed into individual glass vials and sealed with airtight septum caps. The samples were heated for 1 week at the temperature of ageing and the gas above the samples analysed.

In general, the samples aged at 70 °C had more degradation products present in the atmosphere surrounding the sample than those at 50 °C which had more than those at 35 °C. There was no clear distinction between different relative humidities at the same temperature, this would indicate that temperature is more important in the degradation of cellulose acetate than relative humidity. Also naturally aged sample chromatograms differed depending on the temperature these samples were heated at for accelerated ageing. This would indicate that some of the peaks are immediately released depending on the temperature of ageing, i.e. at 70 °C there is enough heat to volatilise more compounds from the surface than at 50 °C or 35 °C. Interpretation was carried out on a purely visual basis as identification of peaks from known acetic acid and phthalate standards proved impossible due to the high number of peaks in a short time period (0 – 4 minutes). Typical chromatograms for the phthalate standards and acetic acid are shown in figure 5.13.

1996 Cellulose Acetate (figure 5.14)

The 1996 cellulose acetate had the least number of chromatographic peaks representing the lowest level of degradation. The peak height of the peaks was also less for this sample than any of the others. The samples aged at 70 °C had many more components than those aged at 50 °C and 35 °C, with the 75 % RH sample having marginally more peaks than those at 55 % RH and 12 % RH which were almost identical. This implies that degradation at 70 °C was similar and relative humidity was irrelevant by the end of the ageing period, although % relative humidity can be a significant factor in ageing as discussed in chapter 4. At 50 °C the sample aged at 12 % RH showed the greatest deterioration at the end of the ageing period, indicating that relative

humidity has less influence on degradation at the lower temperature. At 35 °C there was very little difference between any of the samples, including the naturally aged sample.

1967 Tortoiseshell Hairslide (figure 5.15)

The 1967 hairslide showed very similar results to that of the 1996 cellulose acetate. More peaks (components) were present in the samples that had been accelerated aged. The naturally aged samples released fewer volatile compounds than the 1996 cellulose acetate. Again the sample aged at 70 °C and 75 % RH had the most components present, although only marginally over the 55 % RH and 12 % RH samples which were very similar. 12 % RH was worst at 50 °C as was seen in the 1996 cellulose acetate sample. At 35 °C the chromatogram for the sample aged at 75 % RH showed more components than the other samples, which were almost identical. For the naturally aged samples, more volatiles were released when the temperature of analysis increased.

1967 Tortoiseshell Comb (figure 5.16)

The 1967 comb behaved similarly to the 1967 hairslide, with the samples at 70 °C being much more degraded than those at 50 °C and 35 °C. As before, the 75 % RH sample was marginally worse than those at 55 % RH and 12 % RH. It is interesting to note that for this sample, the naturally aged samples did not have an increase in components as ageing temperature increased. Chromatograms from samples aged at 35 °C and 55 % RH and 12 % RH were comparable to those from the naturally aged sample at this temperature.

1946 Tortoiseshell Comb (figure 5.17)

The 1946 comb aged at 70 °C showed the greatest number of volatiles for all three relative humidities out of all the artefacts studied. The chromatograms for the three samples aged at 50 °C were all very similar. The same can be said for the samples aged at 35 °C. The naturally aged samples again showed the expected increase in volatile components as the temperature of analysis increased.

1940's Doll's Body (figure 5.18)

The doll's body samples behaved similarly with samples aged at 70 °C and 75 % RH realising more volatiles. Chromatograms for samples aged at 55 % RH and 12 % RH were very similar, with two additional peaks in the chromatogram for the 12 % RH sample. The sample at 50 °C and 35 °C were also very similar, with 12 % RH again having the most volatiles released at 50 °C. At 35 °C the samples behaved as predicted, correlating high humidity with most volatilisation. The naturally aged samples volatile levels increased with increasing temperature.

1940's Doll's Leg (figure 5.19)

Finally the doll's leg released less volatile compounds than expected, behaving much like the 1996 cellulose acetate even though the sample was visually the worst degraded. The greatest number of volatiles were released at 70 °C with results for all three relative humidities being similar. The 50 °C and 35 °C samples were also comparable to those of the other artefacts, with the 75 % RH sample producing the most volatiles. In this case, the naturally aged samples deteriorated only slightly as temperature increased.

Overall Conclusions from Headspace GC

Overall the results showed that ageing at 70 °C produced the greatest number of volatile degradation products. Degradation at 50 °C and 35 °C was similar in most cases.

Relative humidity at the end of the ageing period did not seem to have as much influence as it did during the long-term ageing period. This supports the observation that temperature is the most important factor in the degradation of cellulose acetate and while significant in some cases relative humidity is generally less important.

The results from the headspace analysis experiment where samples were enclosed in small vials indicates that pollutant scavenging is very important as levels of acetic acid and other volatiles dramatically increased degradation, for example samples at 70 °C in these enclosed atmospheres only survived for 62 days compared to over 500 days at 50 °C and 35 °C.

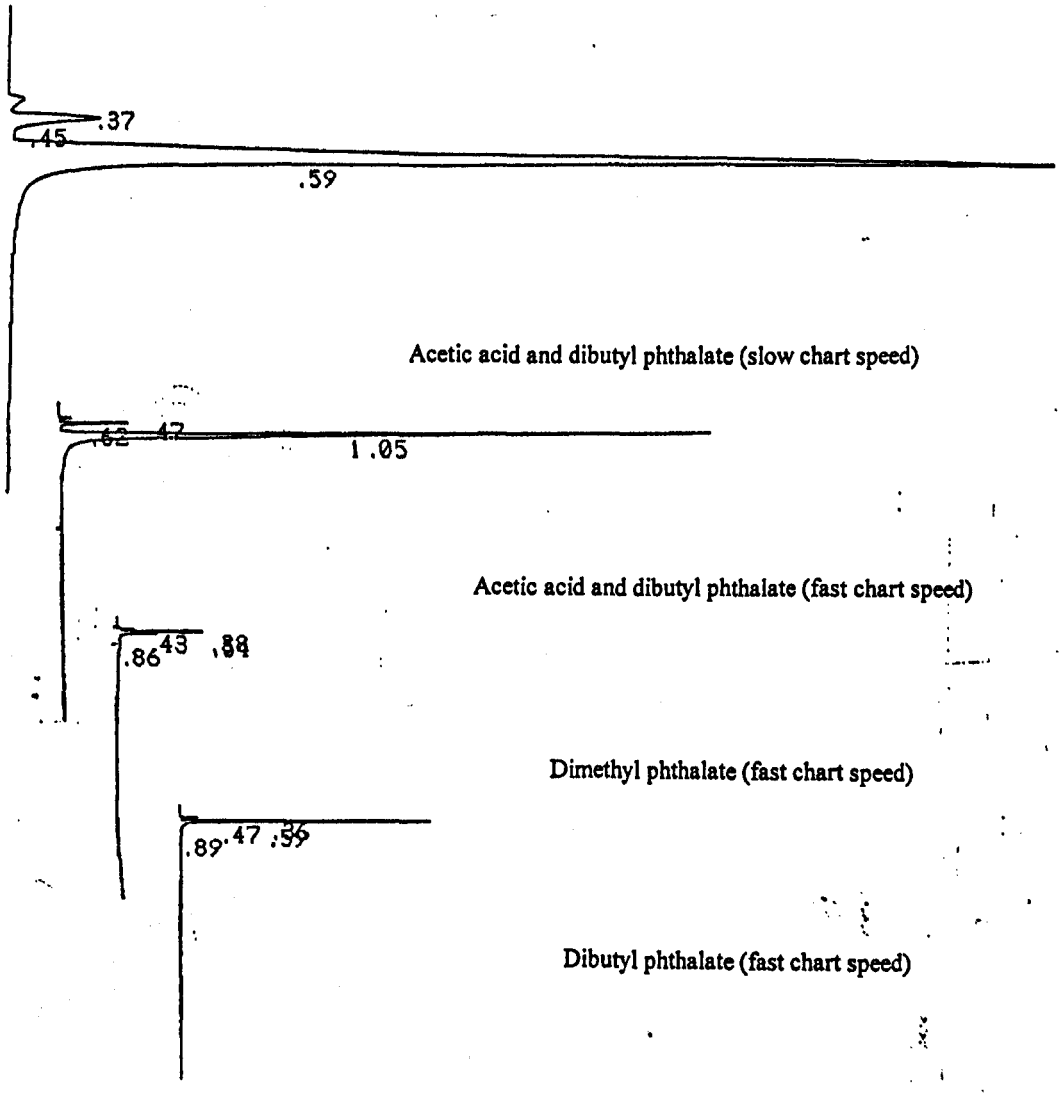

Figure 5.13 Headspace GC chromatograms of standards

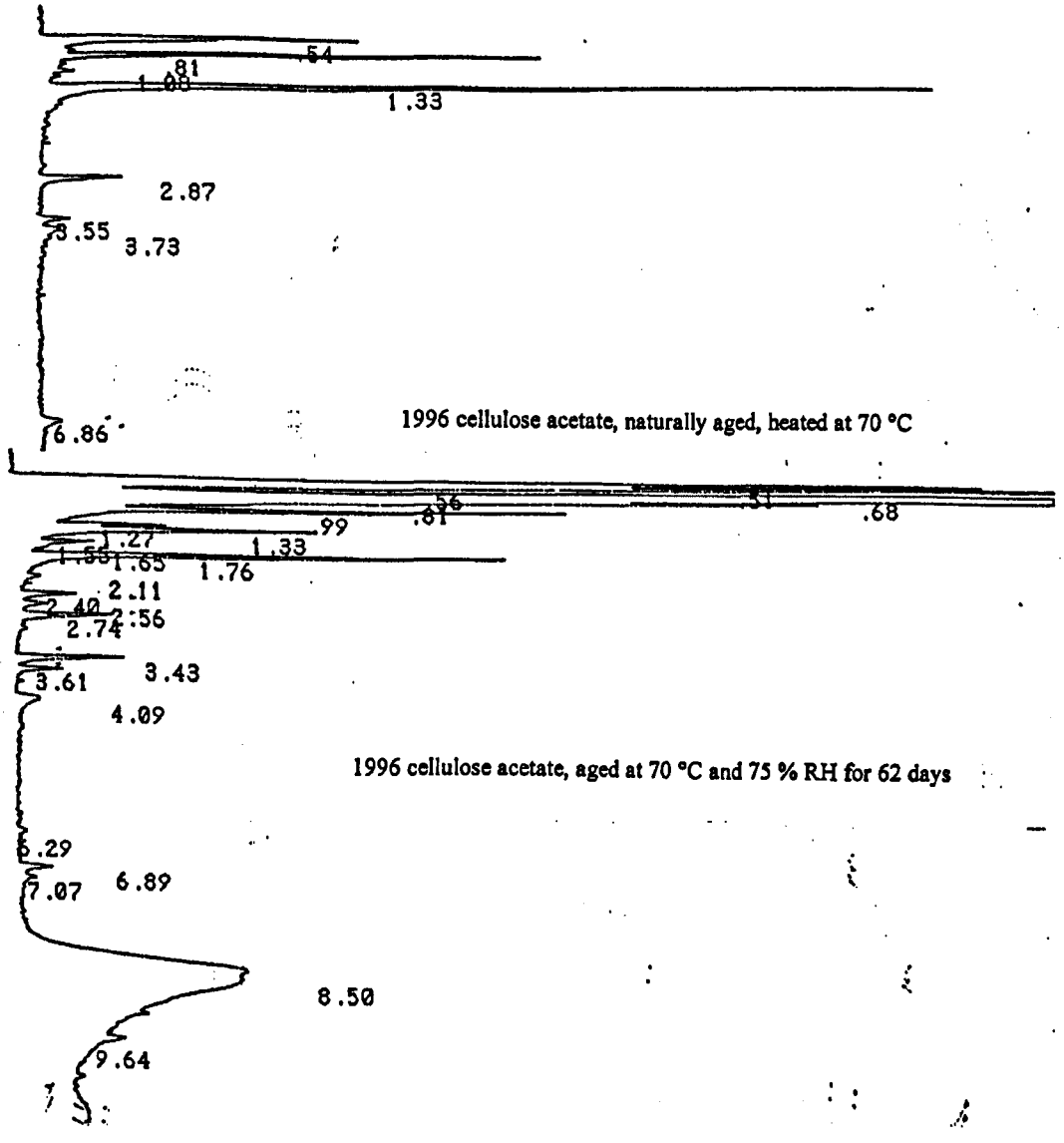

Figure 5.14 **Headspace GC chromatograms of 1996 cellulose acetate, naturally aged and aged at 70 °C and 75 % RH for 62 days**

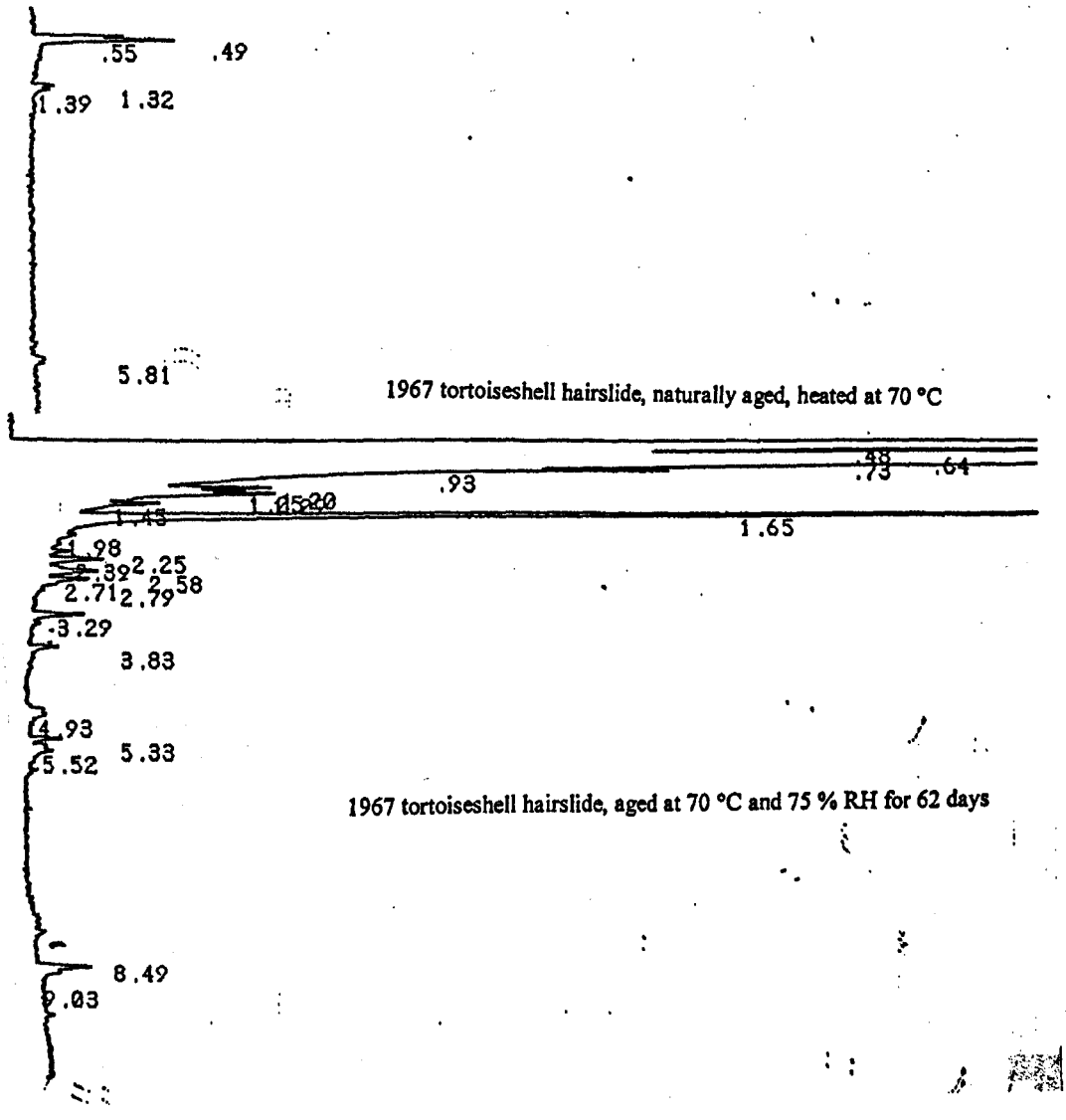

Figure 5.15 **Headspace GC chromatograms of 1967 tortoiseshell hairslide, naturally aged and aged at 70 °C and 75 % RH for 62 days**

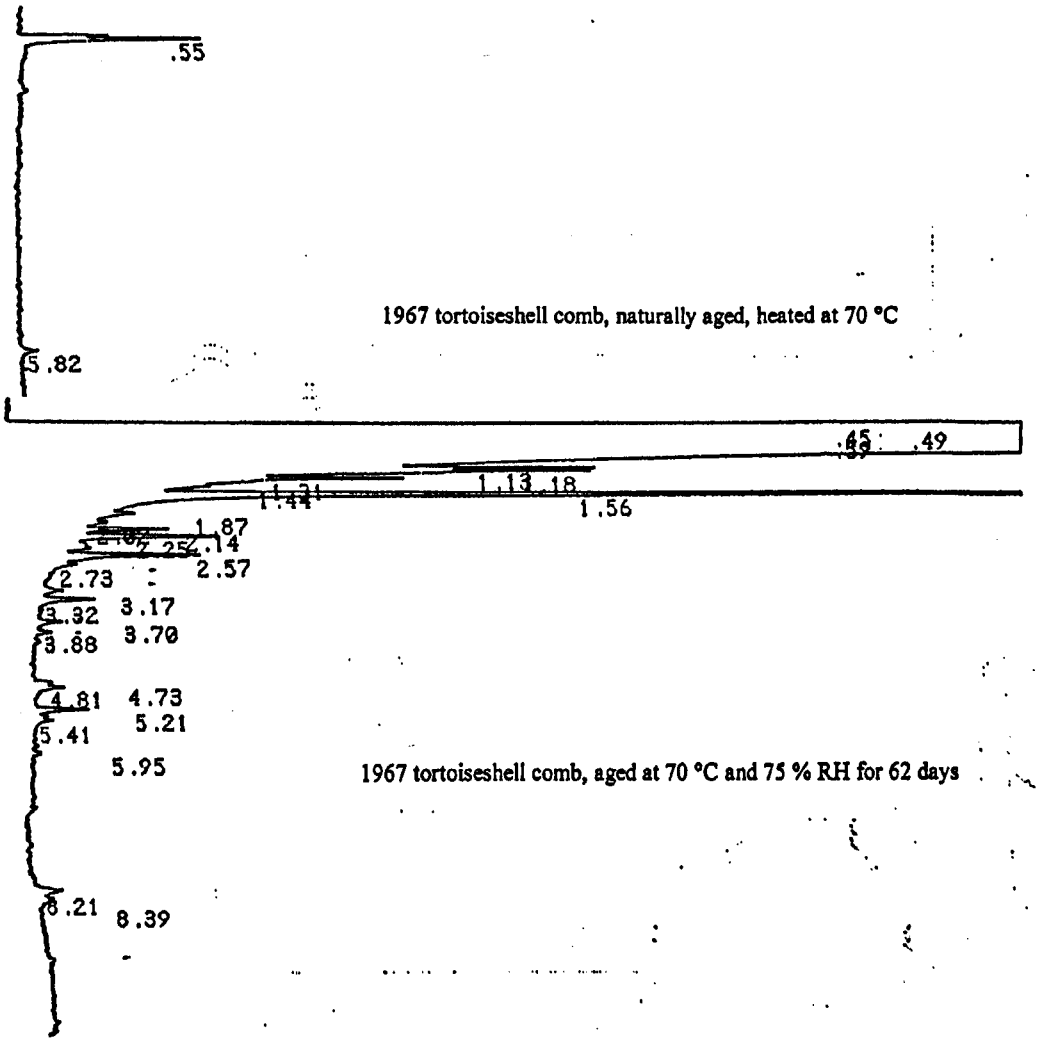

Figure 5.16 **Headspace GC chromatograms of 1967 tortoiseshell comb naturally aged and aged at 70 °C and 75 % RH for 62 days**

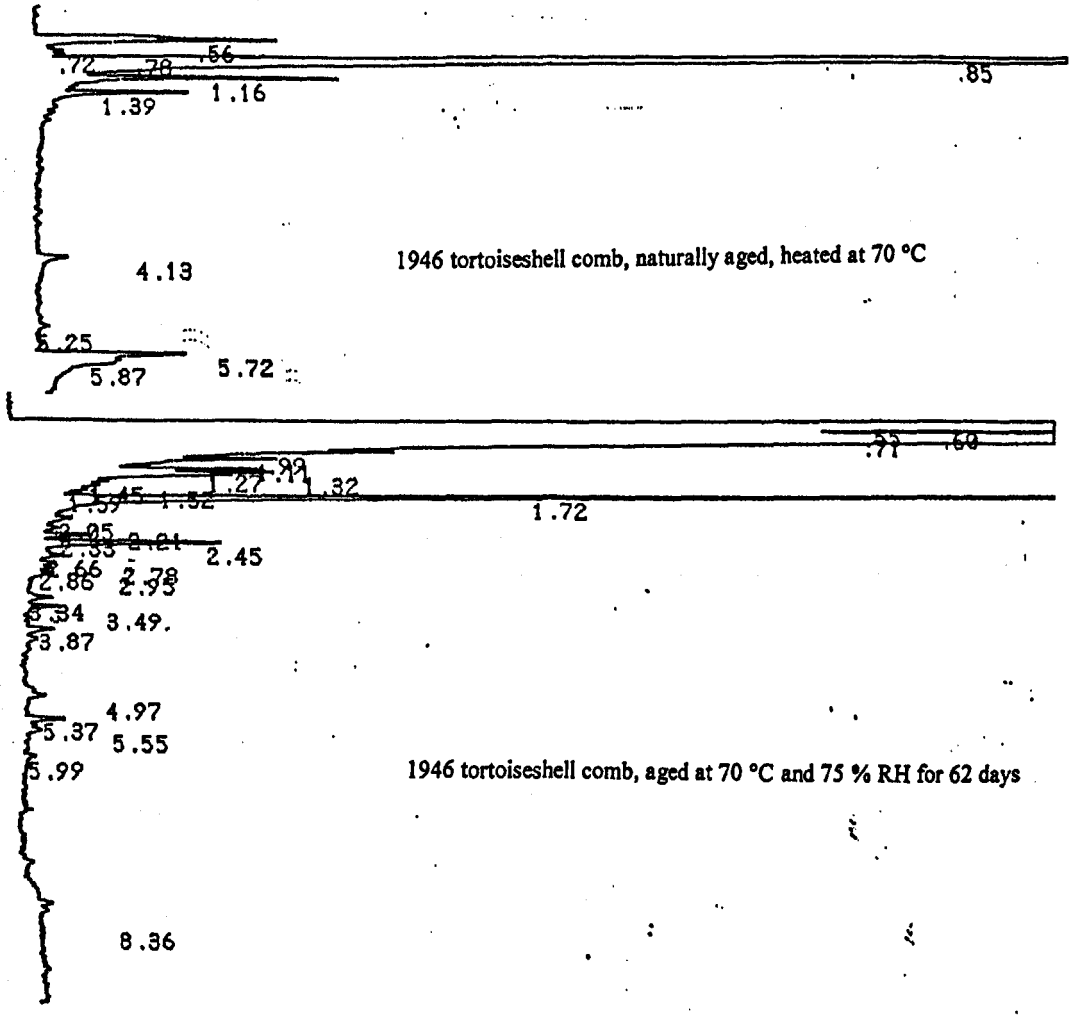

Figure 5.17 **Headspace GC chromatograms of 1946 tortoiseshell comb naturally aged and aged at 70 °C and 75 % RH for 62 days**

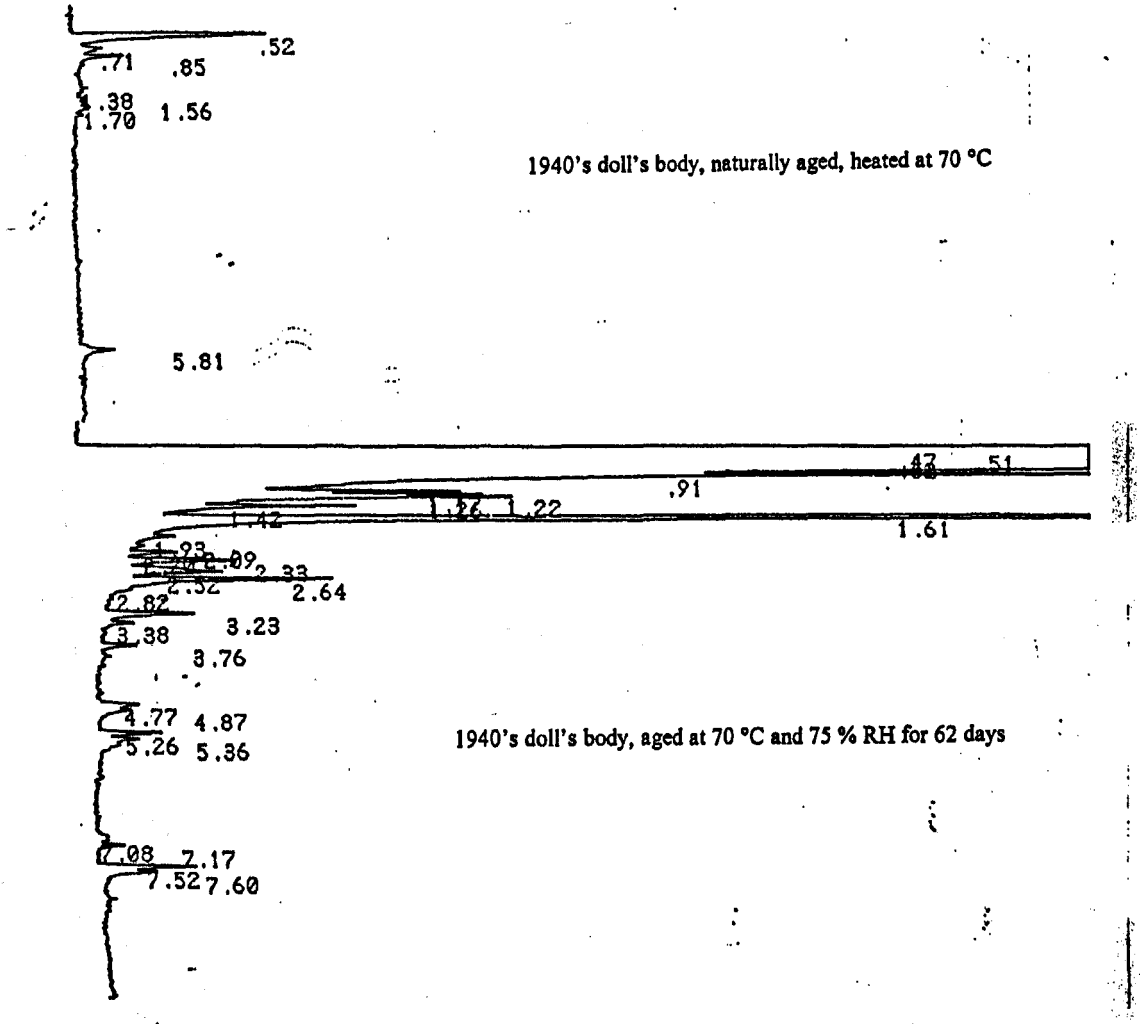

Figure 5.18 **Headspace GC chromatograms of 1940's doll's body naturally aged and aged at 70 °C and 75 % RH for 62 days**

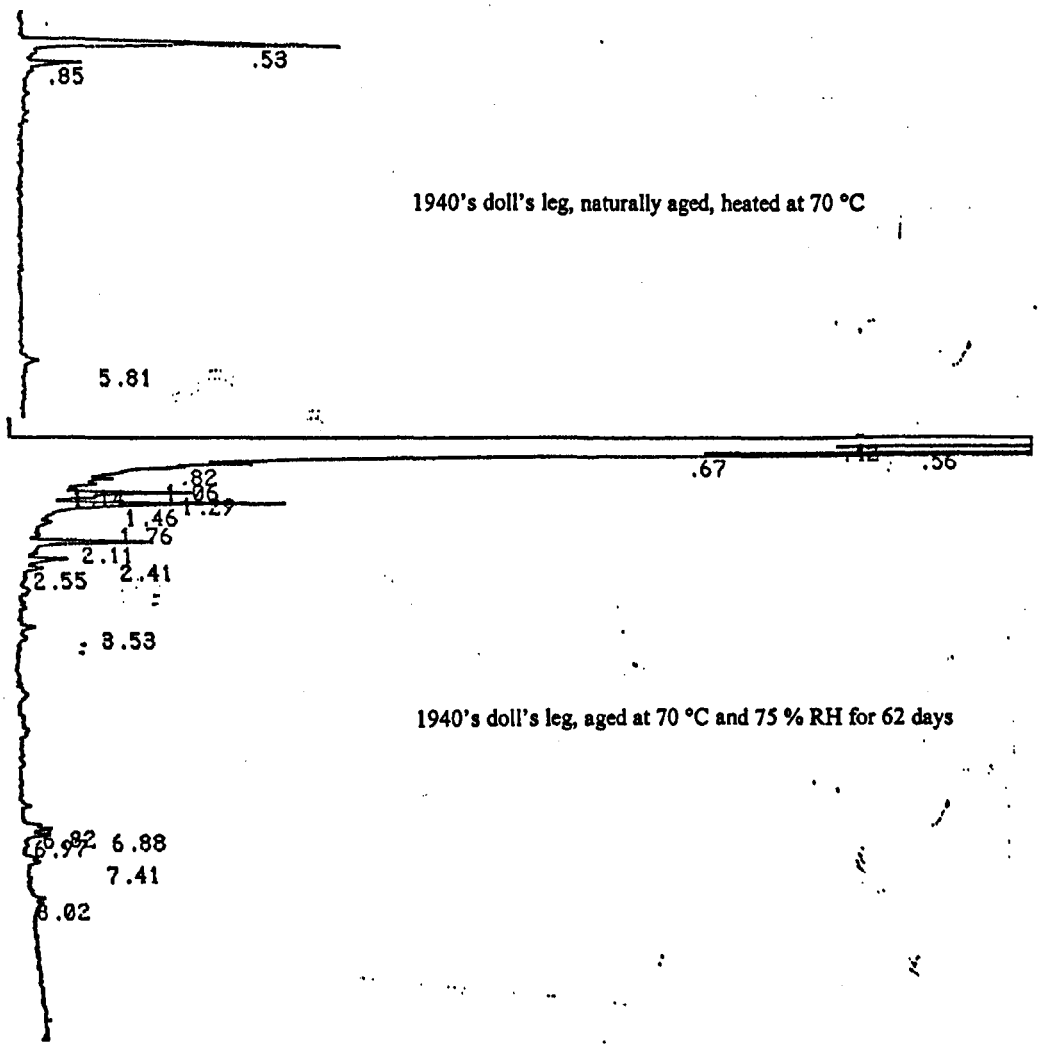

Figure 5.19 **Headspace GC chromatograms of 1940's doll's leg naturally aged and aged at 70 °C and 75 % RH for 62 days**

5.6 Overall Conclusions from Further Investigation

The overall conclusions from these further studies are that deacetylation can be confirmed as the major process of degradation in cellulose acetate. This was evident in the results from all of the analytical techniques used. Plasticiser loss occurs after deacetylation due to changes in the polymer structure and, hence, changes in solubility. Chain scission may be occurring, as indicated by the IC results (section 4.5.4), unfortunately this could not be confirmed by GPC because of the solvent solubility problems.

Headspace GC results show that high levels of volatile degradation products in an enclosed environment around a degrading sample has a detrimental effect on degradation. Acetic acid evolved by deteriorating cellulose acetate can autocatalyse the degradation reaction. Other volatiles, such as plasticiser, can affect the appearance of the artefact, leading to a sticky surface and accelerating discoloration. Therefore, monitoring and controlling, where necessary, of these volatiles is vital to help keep cellulose acetate artefacts in good condition.

The results obtained by TGA and TGA-FTIR indicate that acetic acid is the main volatile lost with only low levels of plasticiser, other acetates and short chain acids. This would indicate that deacetylation is the first and main degradation process with plasticiser loss and chain scission (indicated by the identification of short chain acids) being secondary processes.

The results in combination show that temperature is a more important factor than relative humidity in maintaining stability in cellulose acetate. The influence of relative humidity decreases with decreasing temperature, indicating that as long as temperature is controlled at room temperature or below then control of relative humidity is less important.

5.7 References

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6 Conclusions and Recommendations for Future Work

6.1 Conclusions

The results from the analytical studies of natural and accelerated aged 3-D cellulose acetate objects (chapters 3 – 5) all arrived at the same conclusions. Evidence for the primary degradation process deacetylation was shown by (i) the presence of the acetic acid smell, (ii) a change in position and intensity of the carbonyl peak in FTIR spectra, (iii) an increase in extractable acetate ions from IC results, (iv) the release and identification of acetic acid by TGA and TGA-FTIR results and (v) a change in solubility of the samples in the GPC analysis.

A secondary degradation process of plasticiser migration was shown by identification of phthalate compounds on the surface of nearly all samples by reflectance FTIR. Chain scission and oxidative degradation were also taking place, shown by an increase in extractable oxalate and formate, respectively, in the IC results and presence of short chain organic acids (indicating chain scission) by TGA-FTIR.

From the natural ageing study (chapter 3) it can be seen that the older samples exhibited greater signs of degradation than the newer samples. This could be due to improved manufacturing procedures and quality control, as well as age. The accelerated ageing study (chapter 4) gave greater insight into the degradation processes and also the factors which control degradation. It was found that higher temperature had a greater effect on increasing degradation than higher relative humidity. As the temperature was lowered the role of relative humidity became less significant. This was supported by results from further studies (chapter 5), as the headpsace GC analysis results show that the greatest degradation is found in the samples aged at 70 °C and not necessarily 75 % RH.

Differences were observed between filled and unfilled cellulose acetate. Accelerated ageing IC results showed that the zinc oxide (or other filler) reduces or inhibits oxidative degradation by acting as an acid scavenger and thereby reducing degradation damage. A variation was also seen in the TGA results where there was a distinct difference between the final transition

temperatures of the filled and unfilled samples, with the filled cellulose acetate samples having a lower transition temperature.

It was also noted during the accelerated ageing study that shrinkage of the artefact did not necessarily result in its destruction. If the ageing rate was slow, as at 50 °C and 35 °C, in the study the samples shrank but with careful handling could still be preserved. Volatile compounds, such as plasticiser, can affect the appearance of the artefact by leading to a sticky surface and accelerating discoloration. Embrittlement was fastest at a high relative humidity, indicating that high moisture content in the air accelerates processes leading to plasticiser migration, although this influence diminished with decreasing temperature.

Use and storage are also significant factors. The artefacts, that were displayed in non-museum conditions were more degraded than those that came from controlled museum environments. This would be expected as a piece kept in a museum environment will have experienced fewer fluctuations in temperature and relative humidity than one kept by a private owner/collector.

6.2 Conservation Issues

The most important controlling factor in cellulose acetate degradation to emerge from this study was that the role of relative humidity is reduced when temperature is lowered. This suggests that museums would only need to control temperature for the display and storage of cellulose acetate. Accelerated ageing also showed that separating degrading artefacts from artefacts in good condition is essential. This was concluded from the results obtained for the 1996 cellulose acetate aged when alone and with other samples, and from naturally aged comb samples analysed by non-destructive sampling and IC. These combs had all been stored in a drawer, which contained a mixture of plastics (probably cellulose acetate, cellulose nitrate, urea formaldehyde and casein) and the results (section 3.5.2) showed that cross-contamination by acetic acid (from cellulose acetate combs) and nitric acid (from cellulose nitrate combs) on the surface of the majority of combs analysed had occurred. This well-documented phenomenon is known as "Vinegar Syndrome"[1-3] or "Pedigree Doll's Disease"[4,5]. Although individual storage is not always practical, it would be important for samples that are known or suspected to be degrading to be kept separately from those which are in good condition, as this study has shown that acetic acid can easily encourage degradation in previously unaffected artefacts.

Therefore, it is vital to continually monitor and assess the condition of all cellulose acetate and other plastic artefacts, as the degrading artefacts must be isolated. Micro-FTIR and non-destructive sampling coupled to IC are both excellent techniques for monitoring and assessing the level of degradation in cellulose acetate artefacts. However, care must be taken when choosing an area for analysis, as the degradation levels can change from one area of the surface to another. It is recommended that more than one sample should be taken when trying to assess the condition of a cellulose acetate artefact. The non-destructive sampling procedure for IC analysis would be a valuable technique for assessing degradation, as it is easy to do *in-situ*. Non-destructive swabbing of artefacts for analysis by IC could be a valuable identification tool when micro-FTIR is not available and warrants further investigation.

The problem of contamination by the saturated salt solutions used to control relative humidity in the accelerated ageing study highlighted a key conservation issue. A large uptake of moisture clearly contributed to the degradation of the cellulose acetate and this would mean that cleaning with ionic aqueous solutions would be best avoided. For non-destructive sampling the sample was immediately dried after swabbing and there was no additional degradation, so, cleaning with pure aqueous products would be tolerable as long as careful drying was included in the procedure. A suggested alternative would be to use a hydrophobic alkaline solution to neutralise the acid on the polymer surface and also prevent moisture ingress.

It is vitally important for museums and private collectors to properly identify any plastic artefacts, as many samples donated to this study had been misidentified as cellulose acetate. Materials need to be identified so suitable storage and display conditions and conservation treatment can be applied. The best conditions for cellulose acetate can differ from those for cellulose nitrate or urea formaldehyde, for instance[6,7].

Storage and display areas for cellulose acetate (cellulose nitrate) should be kept well ventilated to avoid a build up of acids. Alternatively, scavengers such as activated charcoal, can be used to reduce levels of indoor pollutants which include the acids emitted by degrading cellulose acetate[8,9].

6.3 Future Work

The biggest problems encountered during this project was a lack of cellulose acetate artefacts available for destructive sampling and that the majority of the plastics artefacts donated and purchased were found to be cellulose nitrate or urea formaldehyde. Therefore, for future work to be carried out it is important to find more cellulose acetate artefacts to allow a larger database to be compiled. This is particularly important with regards to filled cellulose acetate, such as the 1940's doll, as this would allow the intriguing XRF result, where selenium was found in some areas of the 1940's doll and not others, to be investigated. In this case, selenium was found in the undegraded areas of the doll but was not present in the degrading areas. However, due to a lack of samples, this could not be fully investigated.

A further assessment of non-destructive sampling with IC and micro-FTIR for assessing the condition of cellulose acetate would be important. The major area which needs further research is how the results and degradation from the surface are related to the reactions occurring within the bulk of the artefact. It would also be helpful to have purpose-made accelerated ageing equipment to avoid the problems encountered with the saturated salt solutions used to control relative humidity.

Another major area of further study, that should be investigated, is the effect that degrading cellulose acetate has on other materials including fabrics, as well as the problem of composite plastic artefacts for example in sculptures by Gabo, Naum and Moholy-Nagy.

6.4 References

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