HERITAGE SMELLS:

NEW METHODS OF ANALYSES FOR THE ASSESSMENT OF PLASTICS IN HERITAGE COLLECTIONS

by

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This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

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Abstract

Collation and assessment of forty-one historical polymer fragments using ATR-FTIR spectroscopy has been conducted. The polymer fragments included natural, semi-synthetic and synthetic plastics which varied in age, composition, function, provenance and previous environmental exposure. The forty-one fragments belonged to nine different polymer types which included: cellulose acetate, cellulose nitrate, PVC, polyurethane, rubber, polyethylene, polypropylene, polystyrene and polycarbonate. As expected, the analysis of plastics by ATR-FTIR for polymer classification was shown to be a suitable technique. It was possible to identify additives and potential degradation of some plastic fragments. In addition, the efficacy of the data interpretation tool principal component analysis (PCA) for potential applications in polymer characterisation and polymer degradation was also examined.

Plastics in heritage collections were recently identified as an emissive source. As a result it was important to understand the chemical compounds they release and how they might affect the stability of other heritage objects. Therefore the usefulness of emission data as a non-invasive tool for the examination of forty-one historical polymer fragments was investigated. Tenax-TA sampling tubes were used to collect the volatile organic compounds emitted from forty-one historical polymer fragments which were previously characterised with ATR-FTIR spectroscopy. Thermal desorption-gas chromatography coupled with mass spectrometry (TD-GC/MS) was successfully used to separate and identify the emissions from the forty-one samples at 23 °C, after heating to 70 °C and after accelerated degradation.

It was recognised from the laboratory based study that there was no benefit in heating plastic samples prior to the collection of VOCs. To determine the utility of the developed TD-GC/MS method for plastic identification, or stability classification, a number of objects currently held in heritage collections were examined non-invasively and at room temperature using Tenax-TA sampling tubes.

Examination of the VOC emission profiles (both in laboratory work and in case studies) identified acetic acid as an important pollutant emitted from some plastic materials (most notably cellulose acetate and rubber). These vapours can further promote deterioration of the source object or cause cross-contamination of susceptible objects stored or displayed in close proximity to the emission source. Therefore a small scale investigation of the acidic emissions from selected plastic objects in heritage collections was conducted.

CHAPTER 1

INTRODUCTION

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1 Introduction

1.1 The history of plastic materials

Since natural rubber was discovered the composition of plastic materials has evolved with the introduction of semi-synthetic plastics then synthetic plastics. A key driver for the need for new materials came during the Second World War, and in the years to follow. For example, the outbreak of World War II and the restrictions that this placed on the import of raw materials meant that there was a need to develop new synthetic plastics which could be used to replace the materials in short supply, such as rubber. In addition, the war created the requirement for new plastic alternatives to traditional materials which would be light weight and durable, such as substituting glass for poly(methyl methacrylate). As a result of the war effort a wide range of plastics were subsequently developed including polystyrene, poly(methyl methacrylate), polyethylene, polyurethane and synthetic rubber. Much was learned about the chemistry of plastics during the war years and this enabled more specialised plastics to be introduced for specific purposes, such as polytetrafluoroethylene (PTFE) which is an excellent coating, resistant to most chemicals and has found use in industrial applications and domestic, principally non-stick frying pans. Moreover, the post-war years saw a reduction in the cost of raw materials which allowed the mass production of plastic objects. With so many different formulations available, plastics became cheap common replacements for traditional materials. In the years that followed, there was a slow but continued growth in the number of new plastic formulations due to the improved understanding of polymer chemistry. Scientists were, therefore, able to engineer plastics for a variety of specific applications.

1.1.1 Natural polymers

The earliest civilisations made use of natural polymers such as those from plants, animals and insects[1]. Brydson[2] discusses in detail the history of plastics from their natural form to synthetic materials and notes that the use of natural polymers was recorded in the Old Testament of the Bible. In the books of Genesis and Exodus it is written that ‘slime’ was used as mortar and a waterproof coating and that a number of ‘slimepits’ were to be found in the vale of Siddim[2]. Many scholars have likened slime to what is now known as bitumen or tar. Brydson[2] also notes the practise of soaking cloth in a mixture of bitumen and lavender oil in Ancient Egypt in the preparation of mummy wrappings. Amber (a fossilised tree resin) and shellac (a secretion from the female lac bug) were both used for many thousands of years as decorative objects[1-3]. Animal horns and hooves were moulded using heat for more practical applications, such as drinking receptacles[3].

Perhaps the most important natural polymer was rubber, a milky exudate which was obtained by tapping the trunk of the rubber tree commonly found in South America[4, 5]. In addition to natural rubber and water, the milky liquid contains a small amount of other components, such as fatty acids, carbohydrates and proteins[6, 7]. A wide variety of trees produce latex, although ‘hevea brasiliensis’ (also known as the rubber tree) is the principal source of latex for natural rubber production since it produces a high yield. The latex is contained within channels in the bark of the trees and is harvested by creating an incision in the bark which cuts through the latex channels. The latex is collected in buckets which are hung from the trunk of the tree. In South America, as early as 6 A.D., people would have used the latex to make waterproof coatings for fabrics, create soles for shoes and even make balls for games[5, 8]. Work independently conducted by Hancock and Goodyear resulted in the knowledge that rubber heated in the presence of sulfur created a cross-linked product which was flexible and elastic over a wide temperature range and more suited to climates which experienced a range of temperatures[3].

1.1.2 Semi-synthetic plastics

Semi-synthetic plastics are natural polymers which have been chemically modified to produce a product with more desirable properties (e.g. more stable and easily moulded). The chemist Christian Friedrich Schönbein is regarded as the first person to recognise the potential significance of the reaction between nitric acid and cellulose to produce comparatively pure nitrates, which he patented and began to manufacture in 1846[9]. However, the reaction involved in the production of cellulose trinitrate was not fully understood and the unstable nature of the product was not recognised, as a result there was a large explosion at the manufacturing facility in

Faversham killing many workers in 1847. It was later established that residual sulfuric acid was the cause of the instability and the amount of acid was roughly equal to the level of instability[10]. Efforts were subsequently made to ensure the stability of the product, making the manufacturing process safer and enabling the product, often known as guncotton, to be used by the military as an explosive[9].

Some years later, Alexander Parkes discovered that the addition of castor oil, and later camphor, to cellulose nitrate would allow the material to be moulded without shrinkage and in 1862 he showcased his work at The International Exhibition in London[1]. He marketed his products under the name Parkesine, but unfortunately his business did not succeed. Finally, in 1870 the American John Hyatt, as part of a competition, developed a substitute for ivory to be used in billiard balls. He discovered that the best method was to heat cellulose nitrate and camphor under pressure to produce a hard material, similar to ivory. Hyatt marketed the material, known as Celluloid, as a substitute for more expensive materials and celluloid gained popularity especially within the middle classes[11]. In the years that followed celluloid was developed for various applications including photographic and cinematic film bases which were manufactured by Eastman Kodak. However, the high flammability of cellulose nitrate made it unsuitable as a film base and alternatives were subsequently sought[12].

Cellulose acetate was first developed by Schützenberger in 1865 by heating acetic acid and cotton linters in a sealed tube[13]. It was originally used as dope applied to the wings of aircraft to stiffen and waterproof the fabric. It also found use a much cheaper alternative to materials such as mother-of-pearl, resulting in the plastic being used in jewellery and in decorative cutlery in the 1930s and 1940s[1]. However, it was the requirement for a more stable film base that led to extensive research into cellulose acetate. The process of manufacture has changed over the years to the commercial method used today which converts cellulose to cellulose acetate with a mixture of acetic acid and acetic anhydride in the presence of a small amount of sulfuric acid catalyst[14]. Phthalate esters and triphenyl phosphate are commonly used plasticisers which aid moulding, though over time these compounds tend to migrate to the surface of the plastic which can cause the plastic to shrink and weaken.

1.1.3 Synthetic plastics

In the early 1900’s phenol formaldehyde plastic, known as Bakelite, was developed and patented by Leo Baekeland. Bakelite, the first synthetic plastic, was the product of the condensation reaction between phenol and formaldehyde[3]. The syrupy product was oven cured in moulds over many hours and attempts to shorten the curing time resulted in a product which was brittle[3]. Baekeland experimented with additives and found that incorporation of wood flour produced a tough plastic. He stopped the reaction between formaldehyde and phenol before completion and the solid that was produced was then ground to a powder[3]. The powder was placed in a heated mould which melted the powder causing the material to flow and adopt the shape of the mould, the action of heat continues the polymerisation reaction to produce a heat resistant product which is a good electrical insulator[3]. Bakelite had many uses, but is most synonymous with the outer casing of old wireless radios and old telephones[1].

The next important plastic to be developed was poly(vinyl chloride) (PVC) in the 1920s[1]. At that time attempts to produce PVC on a large scale had failed, but the co-polymerisation of vinyl chloride and vinyl acetate and the application of plasticisers enabled the plastic to be produced at a lower processing temperature making it more commercially successful. Despite the initial delays, PVC was commercially produced from 1938 in Germany and a few years later in the USA[1]. PVC has been utilised in the rigid or plasticised form as window frames, electrical cable insulation, flooring and clothing, for example.

As noted earlier the outbreak of World War II drove the development of new plastics. During that time polyethylene, polyurethane, polyamides, poly(methyl methacrylate), polystyrene and synthetic rubber were developed[3]. In the years that followed there was mass production of synthetic plastics for use in disposable items such as drinks bottles and food packaging which has perhaps given plastics a cheap image. In recent years the concerns associated with the potential risk to human health and, indeed, the risk to the environment when the objects are disposed of at the end of their useful lifetime has generated a certain degree of dislike towards plastics. Conversely, in industrial and scientific contexts the image of plastics is much more positive. Since many plastics are specifically engineered for a particular purpose they are often considered to be cutting-edge. For example, Kevlar®, an incredibly strong plastic fibre, is used by steelworkers and welders in specialised clothing to protect the wearer from high heat and laceration[15]. Perhaps a more notable example is the use of Kevlar® in personal body armour which has played a vital role in protecting military and law enforcement personnel[16]. In addition, plastics have also become an integral part of medicine, with plastics routinely being used in hip replacements, prosthetics and surgical sutures[17, 18]. It is evident that plastics have many far reaching applications and it is therefore important to collect such artefacts not only to record their industrial function but also for their artistic design, plastic type and significance in terms of our social and cultural heritage.

1.2 Plastic objects in heritage environments

Plastic based materials are becoming increasingly common within heritage collections and reflect the ubiquitous nature of these materials in society. Plastic objects feature in collections in many forms from cinematic film and sculpture to household appliances. Many of the early semi-synthetic plastics were sought after as they were made as decorative objects which imitated more expensive materials such as tortoiseshell[11, 19] and ivory[1, 11]. In addition to synthetic and semi synthetic plastics there are also many examples of natural plastics within collections. Such examples include natural rubber, horn, shellac and gutta percha, some of which would have been heat moulded into a range of objects such as liquid receptacles, brooches and buttons[20]. In this research, 41 plastic objects were selected for study, as shown in Table 1.1, hereafter information regarding identification, degradation and formation of plastics will focus on this select group of materials.

Table 1.1. Plastic objects selected for examination within this study

Sample	Object	Description
Natural		
Rubber		
HS 268	Pipette bulb	Brown, opaque, cracked
HS 269	Dolls head	Brown, opaque, cracked
HS 103	Hot water bottle	Brown, opaque, pliable

Table 1.1 (*continued*). Plastic objects selected for examination within this study

Sample	Object	Description
Semi-synthetic		
Cellulose acetate		
HS 91	Crumb brush	Pink, opaque, rigid
HS 474	Thin film	Colourless, transparent
HS 475	Thin film	Colourless, transparent
HS 476	Thin film	Colourless, transparent
HS 477	Thin film	Colourless, transparent
Cellulose nitrate		
HS 270	Comb	White, opaque, rigid
HS 271	Cigarette case	Mock tortoiseshell, transparent, rigid
HS 248	Ruler	Orange, transparent, rigid
Synthetic		
Polycarbonate		
HS 52	ResinKit™	Colourless, transparent, rigid
HS 143	Dolls milk bottle	Green, transparent, curved, rigid
HS 413	Drinking glass	Colourless, transparent, curved, rigid
HS 466	Moulded shape	Colourless, transparent, rigid
HS 467	Raw polymer beads	Colourless, transparent, rigid
Polystyrene		
HS 36	ResinKit™	Colourless, transparent, rigid
HS 38	ResinKit™	White, opaque, rigid
HS 405	Stereo cassette player	White, opaque, rigid
HS 409	Cassette tape	Grey, opaque, rigid
HS 446	Moulded shape	Colourless, transparent, rigid
PVC		
HS 62	ResinKit™	Colourless, transparent, rigid
HS 415	Swim arm bands	Yellow, opaque, textured, pliable
HS 424	Record	Black, opaque, ridged, pliable
HS 430	Money wallet	Black, opaque, pliable
HS 468	Moulded shape	Grey, opaque, rigid
Polyurethane		
HS69	ResinKit™	Colourless, transparent, elastomer
HS 86	Packing material	White, foam
HS 458	Packing material	Pink, antistatic foam
HS 461	Packing material	Black, foam
HS 464	Packing material	Grey, foam
Polypropylene		
HS 77	ResinKit™	White, opaque, rigid
HS 400	Thermos® flask	Black, opaque, rigid
HS 403	Thermos® flask cup	White, opaque, rigid
HS 416	Tupperware® box	Brown, opaque, rigid
HS 444	Moulded object	Colourless, semi-transparent, rigid

Table 1.1 (*continued*). Plastic objects selected for examination within this study

Sample	Object	Description
Synthetic		
Polyethylene		
HS 80	ResinKit™	White, opaque, pliable
HS 404	Scalextric crash barrier	White, opaque, pliable
HS 417	Tupperware® lid	Colourless, semi-transparent, pliable
HS 459	Packing material	Black, crosslinked foam
HS 463	Packing material	White, non-crosslinked foam

1.3 Traditional methods used to identify plastics in heritage collections

The number of plastic objects held in museum collections is immense and at times it is difficult to identify polymer type based on visual observation alone. The identity of the materials used to create an object is of significant importance to curators who need to make informed choices with respect to preventative conservation[21]. Traditionally, conservators may have relied on their personal experience to identify the material. Initially, this would have involved non-destructive methods of identification and attributes such as appearance, feel, odour, patent numbers, trademarks, physical form and degradation would all have been examined[1, 3, 8].

Unfortunately, not all materials can be identified by these simple observational tests and often a combination of non-destructive and destructive tests are employed. The hot pin test, as one example, has been used to determine the identity of a plastic based on the pH of the generated emissions using pH paper. In this test a small sample of material would be removed rather than sampling the bulk material since that might produce a surface blemish or initiate or accelerate degradation. The test is non-selective and false positives are possible because additives can alter the pH of the emissions. Even without taking additives in to account PVC, cellulose nitrate and cellulose acetate all generate acidic vapours and cannot be discriminated with this test. Similarly, polystyrene and polyethylene generated neutral pH vapours and could not be selectively identified: in contrast however phenol formaldehyde would produce alkaline vapours[22]. The odours associated with the emitted vapours can also give information about the identity of a plastic. For example, vinegar odour is unique to cellulose acetate, camphor is unique to cellulose nitrate and candle wax is common to polyethylene and polypropylene[1, 3, 23, 24]. However odour recognition is a subjective practice and it can be difficult to describe, and perhaps most importantly, additives can alter the odour of a plastic.

The density of a plastic can also give clues to its identity. However, additives could once again confuse the results. In addition, this type of assessment is not suited to foams and a small sample would need to be removed from the bulk in order to conduct the test. Data tables can be consulted for a small range of specific plastics; in general a hydrocarbon based plastic, such as polyethylene, has the lowest density since carbon and hydrogen are of relatively low mass[1, 22]. The Beilstein test has been shown to be useful in determining the presence of halides and is therefore commonly used to identify PVC[8, 22]. In this test a length of copper wire is heated in a flame, to remove impurities and create a layer of copper oxide, then the hot wire is then held against the plastic under analysis for a few seconds before the wire is returned to the flame[25]. At this point the colour of the flame is observed. A bright green flame indicates that the plastic is likely to be PVC[25]. Once again, additives are known to create false positives. In addition, similar to the hot pin test, the application of a hot wire to the surface of a plastic object can initiate or accelerate degradation of the object under test. Spot tests can be used to identify plastics and involve spotting a small amount of a reagent on to a small fragment of unknown plastic. For example, Koob[26] reported a suitable spot test for cellulose nitrate which involved mixing 20 mg of diphenylamine with 1 cm^3 of concentrated sulfuric acid. A few drops of this mixture were then spotted on to a small amount of cellulose nitrate and after a few minutes a deep blue colour was generated.

1.4 Use of instrumental-based methods for the identification of plastics in heritage objects

Whilst the traditional methods of identification, described above, are useful and relatively simple, they can be invasive and the results have a degree of uncertainty. For this reason instrumental methods of analyses are recommended where possible. Less destructive instrumental techniques are often used within cultural heritage; for example, spectroscopic techniques are often used to analyse plastics. Fourier transform infra-red spectroscopy will be discussed in detail in Chapter 4 and therefore this section will focus on the use of other instruments used as tools for plastic identification.

As part of the POPART project (Preservation of Plastic ARTefacts) established by the European Commission from 2008-2012, researchers built a reference library of Raman spectra to be used for the identification of plastics[27]. Spectra were collected with a Perkin Elmer Raman Spectrometer 400F combined with a Raman Micro 300 Raman microscope, which was equipped with a CCD detector and a diode laser operating at 785 nm with a maximum power of 96 mW. Samples of approximately 0.5 mm^2 were placed on a glass slide for analysis. A small database comprising of 44 plastic samples was constructed and then tested by conducting a blind test on a sample previously identified in another project. The spectra from the blind test samples were compared with the newly built library and a match for poly(methyl methacrylate) was obtained. As a result of the POPART project it was concluded that bench top Raman spectrometers are more efficient than the portable instruments tested within the project; since the former successfully collected useable spectra and the portable instruments did not provide legible spectra for almost half of the samples that were assessed.

Pyrolysis gas chromatography mass spectrometry (Py-GCMS) may also be used to identify polymeric materials although the technique is invasive and destructive[28]. A small sample is heated to very high temperatures in an inert gas to pyrolyse the sample so that it may be analysed by GCMS[28]. For this reason characterisation of polymeric materials by spectroscopic means is normally undertaken in the first instance. Py-GCMS is best suited to situations where the object under study has previously been broken producing small samples which can be sacrificed for analysis. Although the pyrogram can be complicated and difficult to interpret, marker compound tables can be used to provide an accurate identification of the polymer[28].

1.5 Condition assessment of historical plastics in heritage environments

The terms ‘degradation’ and ‘useful lifetime’ can often be misinterpreted in a heritage context. The polymer industry regard a plastic as being degraded when it loses a particular percentage of the object's original weight, at which stage the plastic is considered to have reached the end of its useful lifetime as it is no longer fit for purpose. In a heritage context the definition is not as well defined and objects often have to be considered on a case by case basis. With regards to heritage objects the term 'useful lifetime' can often be misunderstood. Objects are not necessarily 'in-use' in a traditional sense, but rather are on display or in storage. In general, most heritage institutions would regard an object as being at the end of its useful lifetime when it shows significant loss of quality or when the original meaning of the object is no longer perceivable. In addition, an object may be considered at the end of its lifetime when its degradation causes an adverse impact on other collection items, at which point it will be removed from exhibition.

Standard terminology has been developed within the conservation field to describe the forms of degradation commonly encountered when dealing with plastic objects. Some key terms are given in Table 1.2, together with materials known to be affected by specific degradation forms. Upon acquisition of an object, the institution bears the responsibility for the storage and preservation of that object, it has a duty of care for the object and must choose the most appropriate method of preservation and storage in order to maximise its lifetime whilst maintaining the integrity of the object. This task in itself has many challenges since plastics are still relatively new additions to collections (with respect to more traditional materials) and standard procedures for their care have not yet been fully established. Condition assessment to identify plastic objects that might be degraded, or are at their useful lifetime, is therefore an essential part of preventive conservation. Museum surveys conducted in the 1990′s at the Victoria and Albert (V & A) Museum and the British Museum provided an indication of the condition of plastic objects in collections at the time of monitoring[29, 30]. The British Museum had over 3000 plastic or plastic containing objects within collections; however, due to limited time and resources only a small, but representative, part of the collection was examined. A range of plastics identified included cellulose acetate, Bakelite, cellulose nitrate, polyurethane, polypropylene, polyethylene, nylon, polystyrene, rubber and poly(vinyl chloride) (PVC). The objects were visually examined for signs of degradation and requirement for conservation work, these were noted together with the surrounding environmental conditions[30].

The study highlighted that 27.5 % of the collection required no treatment, demonstrating that these objects were in a good condition and stable. 60 % was deemed a low conservation priority which meant that the objects were in a stable condition but had slight damage such as dirt and surface abrasions. Unstable and damaged objects accounted for 12 % of the collection and actively degrading and unstable objects accounted for 0.6 % of the total number of objects surveyed. All of the unstable objects comprised of cellulose acetate, cellulose nitrate, polyurethane or PVC.

Table 1.2. Visual indicators of degradation

Degradation Form	**Appearance**	**Caused by**	**Plastics affected**
Discolouration	Colour fade or yellowing	Pigment fade or chemical breakdown of plastic by UV light	Cellulose acetate, cellulose nitrate, polyurethane, rubber & PVC
Crumbling	Crumbling	UV light	Polyurethane foam
Crazing	Micro-cracks, a network of small internal or external cracks	Stress by bending or plasticiser loss	Cellulose nitrate & poly (methyl methacrylate)
Weeping	Sticky surface, liquid droplets	Plasticiser migration	PVC, cellulose nitrate & cellulose acetate
Warping	Distortion	Plasticiser loss and heat	Cellulose acetate, cellulose nitrate, PVC, polystyrene, polyethylene & polypropylene
Bloom	Powder or crystal growth which can be rubbed off	Plastic additives migrating to the surface which are solids at room temperature	Cellulose acetate & cellulose nitrate

Table 1.2 (*continued*). Visual indicators of degradation

Degradation Form	**Appearance**	**Caused by**	**Plastics affected**
Cracking	Large cracks resulting in the disintegration of the object	Stress or damage	Hard plastics- such as Bakelite, polystyrene, cellulose acetate & cellulose nitrate

More recently, as part of the Popart project, a survey was conducted within the furniture collection of the V & A Museum[31]. The date of the objects ranged from the 1930's to modern day and included both historic plastics and modern recycled materials. Of the 200 objects surveyed 57 % were found to be in good condition, 28 % were recorded as being in a fair state (interpreted as having minor damage such as discolouration) and 12 % were in a poor condition (physical damage was present with brittleness and sweating of objects being a possibility). Only 3 % of the objects studied were classed as unacceptable and therefore chemically unstable; this time the most unstable objects contained polyurethane.

As the previous museum surveys have shown, the number of highly unstable and actively degrading plastic objects can vary between heritage institutions due to the type and age of the plastics. A collection which contains a high proportion of objects comprising of cellulose acetate, cellulose nitrate, rubber, PVC or polyurethane will be likely to have a high percentage of actively degrading objects since these are the plastic types which have been shown to be the most susceptible to deterioration[12-17, 35]. The type of damage observed can be classified into 4 categories: chemical, physical, mechanical and/ or biological damage [32]. Chemical damage tends to occur as a result of the effects of temperature, humidity, light, oxygen and gaseous pollutants on an object. Physical damage is produced by constant changes in temperature or humidity and loss of plasticisers or other important additives. Signs of physical damage include shrinkage or expansion (which in turn can cause the object to crack) and give a loss of flexibility. Mechanical damage is as a result of the object being used and manifests itself as minor surface scratches or signs of wear. Lastly biological damage is often as a result of pest damage or fungal growth.

1.6 Indicators of plastic degradation

Often, in addition to visual changes (brittleness, cracking, discolouration, surface bloom) objects experience during degradation, there can be other indicators of chemical damage such as the emission of volatile products. Conservators at the British Museum were alerted to a potential plastic degradation issue due to significant discolouration of tissue paper that was used to package a cellulose nitrate shadow puppet. On closer inspection, after the tissue was removed, it was clear that the puppet (Figure 1.1) had become increasingly yellow and brittle to the touch[33]. The object was degrading and had started to produce nitrogen dioxide which had reacted with moisture in the air to produce nitric acid. The nitric acid was responsible for the deterioration of the tissue paper and had initiated an autocatalytic breakdown cycle of the puppet itself.

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Figure 1.1. Degrading cellulose nitrate shadow puppet

Furthermore, the metal rivets which held the puppet together were corroded and the legs of the puppet had become severely crazed and detached from the puppet. Tests identified the plastic as cellulose nitrate and found a pH gradient across the object with the legs being highly acidic (pH 3.2 ± 0.2) and the body less so (pH 5 ± 0.2). Therefore, the object had been subjected to severe chemical damage.

In addition to cellulose nitrate, emissions (and odours) can also be used as indicators of cellulose acetate degradation[34-36]. The hydrolysis of cellulose acetate causes cellulose deacetylation and glycosidic bond cleavage to produce acetic acid (vinegar odour)[37], often referred to as the vinegar syndrome[38]. The acetic acid generated can be emitted as a vapour but it can also catalyse further deacetylation and encourage a continuous auto-catalytic degradation of the object until it reverts to the cellulose starting material. The acidic vapours emitted also have the potential to affect other objects in close proximity to the degrading object by cross contamination[38, 39]. “Pedigree Dolls disease” is one such example of the risk of cross contamination[40]. Between 1940 and 1958 the Pedigree Dolls and Toys Company produced a range of cellulose acetate based dolls. By the 1990’s a doll collector, who had a number of the dolls in various sizes, suspected that the dolls were degrading and that the ‘disease’ was capable of spreading from an infected doll to a healthy doll. At the time, degradation was noted as (i) a strong vinegar odour from the doll; (ii) a change in shape and colour of the limbs of the doll; (iii) a liquid film on the inner surfaces of the doll; (iv) surface cracking and (v) moveable parts of the doll, like the eyes for example, becoming sticky and immobile. The ‘disease’ was reported to spread more efficiently when the dolls were in close proximity and when the air exchange rate was restricted. Therefore, the generation of acids is of great concern to museum curators as not only could the plastic objects themselves be lost to degradation, but, as they degrade the volatiles they release can adversely affect other collection items (plastic or otherwise) in close proximity to the deteriorating item[41].

1.7 Aims and objectives

The research outlined within this thesis is part of the ‘Heritage Smells!’ project funded by the AHRC/EPSRC Science and Heritage Programme. The ‘Heritage Smells!’ project aims to understand more about the condition of heritage collections by using VOC pattern recognition. The project comprises of three challenge areas: paper, pest control treatments and modern materials (plastics). The latter of which will be the focus of this thesis.

To better understand polymer type and deterioration processes a literature review was first undertaken and, as reported in Chapter 2, includes information on polymer degradation. Further information on polymer synthesis has been included in Appendix A. Thereafter the key aims and objectives of this work were to critically evaluate a selection of forty-one polymer reference samples in order to gain a better understanding of the advantages and limitations of infra-red (IR) spectroscopy as a tool for the characterisation and identification of polymer type and degradation. The data is presented in Chapter 4 and includes a detailed examination of the main IR absorption bands from each of the forty-one reference samples which enables a high level of interpretation (such as the identification of degradation products or additives) which is not possible using spectroscopic databases alone. Such commercial databases often comprise of spectra obtained from pristine samples, however as a plastic sample degrades the search algorithm used by the database will become less effective and as a result plastic samples may be incorrectly characterised. Since many users rely on databases to characterise unknown samples it was important to understand whether the collected spectra were representative of a polymer type regardless of the age of the sample or the presence of additives. Therefore principal component analysis (PCA) was employed to interrogate the collected spectra. A further step was taken to investigate whether IR spectra could differentiate between samples at different stages of degradation. Therefore, one reference polymer was sub-sampled with each sub-sample being exposed to a differing degree of accelerated degradation. Spectra were first examined visually and then interrogated with PCA.

The ultimate aim of the research programme was to determine the usefulness of emission data as a non-invasive tool for the examination of polymeric objects in museum, or other heritage, collections. Here it was necessary to first interpret the small volatile products emitted by reference polymers and determine which, if any, could be used as VOC markers to aid their identification. Therefore a robust programme of VOC emission research was undertaken and included the following objectives, which are described in detail in Chapter 5.

- The examination of VOCs emitted by polymeric reference materials placed in a controlled environment. The VOC emissions were measured at 23 °C to reflect the temperature which would be used in field monitoring and also at 70 °C to reflect previous studies in the field which typically heated samples prior to VOC collection.

- Accelerated degradation of fragments prior to VOC collection by exposure to UV and visible light.
- Critical evaluation of the chromatograms allowed detailed interpretation of emission profiles and allowed assessment of polymer type, and in some cases, identification of polymer deterioration and the presence of additives.

In Chapter 6, a number of real life case studies are reported where VOC emission profiles surrounding objects held in different museums were assessed. Here VOCs from 7 plastic objects were measured non-invasively at room temperature to determine the utility of the developed method. The objects varied in formulation, age, physical size and state of deterioration. Once again, critical examination of the obtained chromatograms enabled identification of polymer type, and in some cases, indicators of degradation and the presence of additives.

In Chapter 7, a small scale investigation of the acetic acid emissions from selected plastic objects in heritage collections was conducted. Acetic acid was measured non-invasively at room temperature using Palmes diffusion tubes.

Finally, Chapter 8 discusses the overall conclusions and provides suggestions for further work.

1.8 References

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CHAPTER 2

POLYMER CHEMISTRY AND THE DEGRADATION OF PLASTIC OBJECTS IN HERITAGE COLLECTIONS

Contents of Chapter 2

2 Polymer chemistry and the degradation of plastic objects in heritage collections

2.1 Basic polymer chemistry

2.1.1 Terminology and polymer structures

The words ‘plastic’ and ‘polymer’ are often, incorrectly, used interchangeably. The word *polymer* literally means *many parts* and is essentially the joining together of small units (known as monomers) to form a high molecular weight macromolecule (polymer)[1, 2]. Plastic is the term used to describe a polymer which has been modified with additives to impart particular properties[3]. The completed product contains a base polymer structure which has been modified with additives such as plasticisers, fillers and stabilisers added during the manufacturing process[3].

Polymers can be produced with various structures, the simplest being a linear structure but branched, cross-linked and dendrimers are also common polymeric structures[1]. When more than one monomer unit is used in polymerisation, copolymers can be formed which can have one of four structures: alternating, block, statistical and graft[1]. An alternating copolymer has a structure in which the two different monomer units are in a regular pattern along the length of the polymer chain. A block copolymer has a structure in which the two different monomer units appear in defined blocks within the polymer chain. A statistical copolymer had a random arrangement of the two different monomer units along the length of the chain. Finally, a graft copolymer has a structure in which one of the monomers forms a backbone and the other monomer grafts on to the backbone forming branches. Polymer properties can be affected by a variety of factors, some of which are discussed below.

2.1.2 Stereoisomerism

The polymerisation of asymmetric vinyl monomers, such as styrene, vinyl chloride and propylene, creates the possibility for variations in spatial arrangement. The orientation of the monomer units being added to the growing polymer chain is called tacticity. Vinyl polymers produce three stereoisomers (Figure 2.1) the first of which is defined as isotactic, where the substituent groups are all situated on the same side of the polymer chain. The second is syndiotactic, where the substituent groups alternate from side to side along the length of the polymer chain. Finally, atactic describes polymers which have a random positioning of substituents along the length of the polymer chain[1].

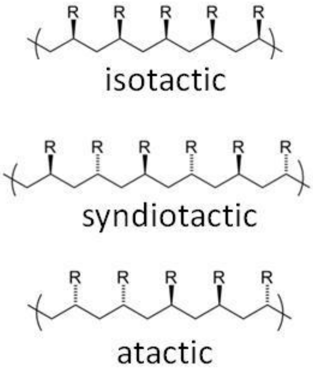

Figure 2.1. Stereoisomers of vinyl polymers

Since isotactic polymers have the substituent groups on the same side of the polymer chain, the chains can pack together in a crystalline structure to produce a polymer with good mechanical strength, an example being isotactic polypropylene[4].

2.1.3 Crystalline and amorphous polymers

Crystalline polymers can, with enough heat, melt to a liquid with a disordered structure[1]. On a molecular level the atoms in the polymer chains will vibrate slightly at ambient temperature and the weak secondary bonds formed between the polymer chains will be maintained[3]. However, when thermal energy (heat) is added, the vibrations of the atoms in the polymer chains increase to a point where the weak secondary bonds are no longer able to hold the chains together and a disordered structure is obtained[3]. A plot of the melting process of a crystalline polymer is shown in Figure 2.2 (line 1). It is characterised by a distinct volume change and the presence of latent heat of melting. Adding thermal energy to a crystalline polymer at a constant rate will increase the temperature of the polymer at a constant rate, until the melting point (T_m) is reached[5]. At the T_m the thermal energy being added to the polymer is used for melting rather than raising the temperature of the polymer, this is known as the latent heat of melting[5]. During this stage the temperature remains constant until the polymer has melted, after which the temperature of the polymer begins to rise once more. The increase in temperature is at a slower rate since the heat capacity of a polymer after melting is higher (indicated by the increase in the steepness of the slope). This means that the polymer can accept more thermal energy with a small increase in temperature. Since melting involves a change of state from solid to liquid it is therefore considered a first order transition[6].

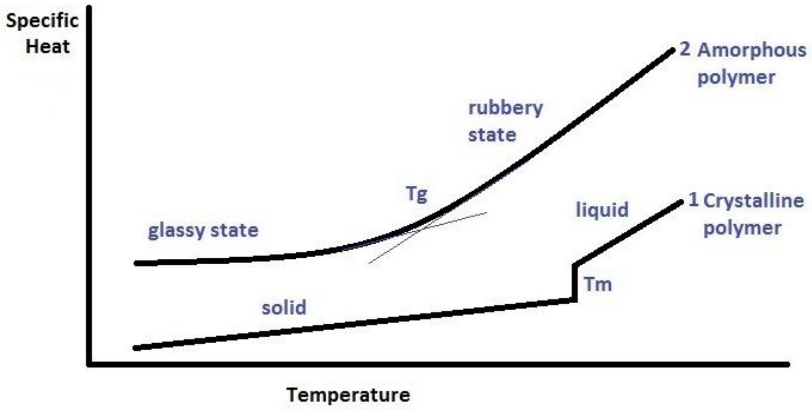

Figure 2.2. Specific heat against temperature plot for crystalline and amorphous polymers

Conversely, amorphous polymers do not have a melting point but they do have a glass transition temperature (T_g), as demonstrated in Figure 2.2 (line 2). The T_g is the temperature at which the polymer experiences a change in mechanical properties from the glass-like state to rubber-like state[1]. In amorphous polymers the chains are arranged in a completely random order. Below the T_g the polymer is hard and brittle since chain motion is restricted. The chains do not have sufficient thermal energy or the space to move freely and rotate in a crankshaft motion and so the polymer is brittle. When thermal energy is applied, the chains now have sufficient energy to move and due to thermal expansion (increase in free volume) the chains have the space to rotate freely giving a flexible polymer. Since there is no phase change (polymer remains solid above and below the T_g) the transition is considered to be second order[6]. It should be noted that crystalline polymers have small amorphous portions which will have an associated T_g[1]. It is only the amorphous portion which undergoes changes at the T_g. Upon heating, crystalline polymers will first pass through a T_g (amorphous portion only) and then through the melting point of the crystalline portion[6].

The amount of thermal energy required to keep polymer chains moving will affect the T_g. The ease of movement of the chains will depend on the flexibility of the polymer backbone, steric effects and branching[1]. Polymers with a flexible backbone will require less thermal energy to move the polymer chains and will, therefore, have a low T_g. Polyethylene has a T_g of -90 °C, which means that at room temperature the polymer is above its glass transition and consequently is soft and flexible[1]. The highly flexible backbone of polyethylene requires very little thermal energy to move the polymer chains and so the polymer has a very low T_g. When the backbone contains large functional groups (e.g. phenyl group) then the rotation of the polymer chains can be restricted[3], as is the case in poly(phenylene sulfone) which is so rigid it does not have a T_g[7].

Pendant groups which are large can hinder the rotation of the backbone and raise the T_g. However, in some case the reverse is true where large pendant groups may increase the flexibility of a polymer and reduce the T_g. In the polyacrylate series (methyl methacrylate to butyl methacrylate) there is a reduction in T_g from approximately 100 °C to 20 °C, shown in Figure 2.3[3].

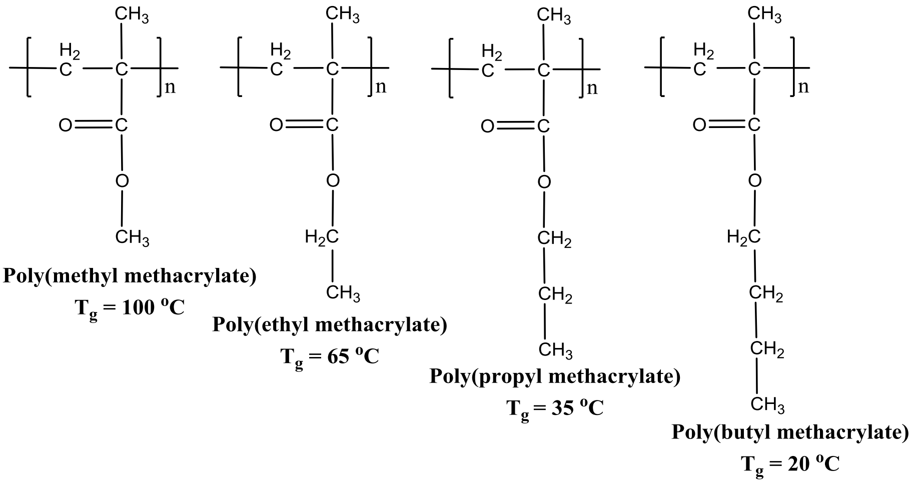

Figure 2.3. Polyacrylate series, where pendant groups reduce the T_g

Poly(butyl methacrylate) has a long and flexible pendant group which helps prevent the chains from packing together and become rigid[3]. The large pendant group, in this case, keeps the polymer chains apart and increases the free volume between the chains.

2.1.4 Classification of synthetic polymers

Polymers may be classified based on their properties, in particular their response to thermal treatments[6]. For instance the majority of synthetic polymers can be classified as thermoplastics or thermosets. Thermoplastics have the ability to melt upon heating and solidify again when cooled; this process is repeatable, which means that the polymer may be recycled. However, each time this cycle is repeated a small amount of chemical degradation will occur[8]. Thermoplastics tend to consist of linear or lightly branched chains with no cross-linking between the chains[1]. Polyethylene, polypropylene, polystyrene, polycarbonate and poly(vinyl chloride) are examples of thermoplastics. The classic model used to describe the polymer chains within a thermoplastic is likened to a bowl of spaghetti. On heating, the polymer chains (or strands of spaghetti) can move and reposition themselves relative to each which means that the polymer can be deformed and re-moulded. Conversely, thermosets do not have the ability to melt and reform after initial processing and are generally rigid and have good thermal stability[1]. During the manufacture of thermosets, the polymer chains react and cross-link to produce a network structure[8]. The network structure means that the polymer chains are interconnected and cannot move over each other, which prevents melting and reshaping. Polymers of this type must be produced in their final form during manufacture.

Polymers may also be categorised in terms of their polymerisation pathways. In the late 1920s W.H. Carothers suggested the terms ‘condensation’ and ‘addition’ polymerisation to describe the different pathways in which polymers are produced since polymers produced via condensation polymerisation loses a small molecule during the reaction and addition polymerisation involves the joining together of monomer units with no loss of small molecules[1, 2]. However, as new polymers were developed it became clear these terms may not be appropriate in all cases. In the 1950s P. J. Flory defined new terminology which better described the polymerisation reactions[1]. Addition polymerisation was replaced with the term chain-growth polymerisation[6]. Step-growth polymerisation replaced the term condensation polymerisation and better explained the reaction, especially for examples such as polyurethane which followed the kinetics of a condensation reaction but did not eliminate water or other small molecule during the reaction[6]. Further information on the preparation of natural, semi-synthetic and synthetic polymers can be found in Appendix A.

2.1.5 Chain-growth polymerisation mechanisms of synthetic polymers

Chain-growth (addition) polymerisation is the process in which a polymer is made by a single chain reaction using unsaturated monomer units (i.e. those that contain double bonds). Chain-growth polymerisation tends to have typical features such as initiation, propagation and termination steps[2]. Chain-growth polymerisation may proceed via various mechanisms, two of which are outlined below.

2.1.5.1 Free radical mechanism

Chain-growth polymerisation may proceed via the free-radical mechanism for the production of many polymers. Polymerisation tends to occur under high pressure (1000-3000 atm) and at temperatures between 80 – 300 °C and so this method of polymerisation is often referred to as high pressure polymerisation[4]. Initiation requires a 'free radical initiator' which is a material that can be forced to decompose to free-radicals by the action of heat, UV light or a promoter. Benzoyl peroxide is one such example of a free-radical initiator (Figure 2.4), it decomposes at approximately 80 °C to produce benzoyloxy radicals[1, 3, 9].

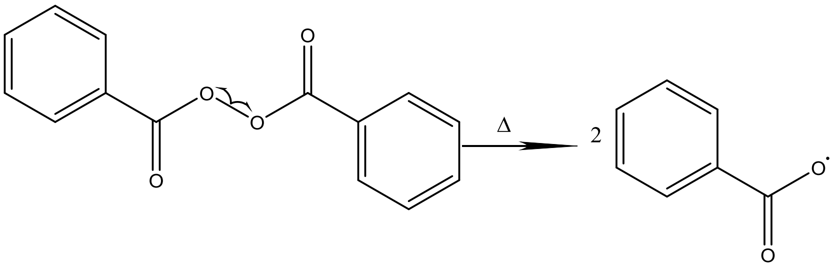

Figure 2.4. Benzyl peroxide decomposition to radicals

The rate of benzoyloxy radical production will depend on the concentration of the initiator, the temperature and the presence of other additives[4]. Therefore the rate at which the radicals are formed is the rate determining step. The benzoyloxy radical

($BzO^\bullet$) reacts with the monomer which produces more radicals (Figure 2.5) which go on to react with more monomer units and so the process is repeated.

Figure 2.5. Initiation step of free radical polymerisation

When the radical initiator reacts with the monomer it breaks the unsaturated bond which means that the bond can attach itself to another monomer and so on causing the polymer chain to grow. Propagation is the rapid continuation of monomers joining together to form increasingly long chains. It is reported that it takes only 0.01 to 0.10 s to generate a polymer chain of at least 1000 monomer units[1]. Polymerisation occurs under high temperature and pressure and the conversion from the unsaturated monomer to long-chained saturated polymer is usually highly exothermic and the excess heat must be dissipated or there is the risk of explosion. During the propagation stage it is possible for chain transfer to occur which involves the transfer of the free radical activity to another species which stops the growth of that current polymer chain. The newly formed radical can react with some monomer to begin a new polymer chain or it may abstract an atom from the backbone of a previously formed polymer chain[10]. The latter process is common when almost all the monomer has been consumed and the amount of polymer present is high. When this type of chain transfer happens it creates branched polymer chains.

Termination tends to occur via combination or disproportionation and both reactions destroy free radicals[1]. When two radical species react and form one product with a single bond, this is known as combination termination (Figure 2.6) and prevents continuation of the reaction[2, 4, 6].

$$\sim CH_2C^\bullet HX + \sim CH_2C^\bullet HX \longrightarrow \sim CH_2CHXCHXCH_2\sim$$

Figure 2.6. Combination termination

Disproportionation occurs when two radical species react with hydrogen extraction to form two products, one of which is unsaturated (Figure 2.7)[2, 6].

$$\sim CH_2C^{\bullet}HX + \sim CH_2C^{\bullet}HX \longrightarrow \sim CH_2CH_2X + \sim CH{=}CHX$$

Figure 2.7. Disproportionation

2.1.5.2 Ziegler-Natta catalysts

An alternative method to the free radical process (FRP) is the use of Ziegler-Natta catalysts, which are useful when polymerisation needs to be controlled. As has already been discussed, vinyl polymers may produce three stereoisomers (atactic, isotactic and syndiotactic), each of which have different properties. It is therefore favourable to be able to control the stereoregularity of a polymer to impart desirable properties. Since FRP generally produces atactic polymer, the development of Ziegler-Natta catalysts in the 1950s was a huge breakthrough in the field of polymer chemistry since they are capable of producing stereo-regular polymers[4, 9].

Ziegler-Natta catalysts are the general name given to organometallic complexes formed between main-group metal alkyls and metal halides[6]. For example, such catalysts are used in the production of isotactic polypropylene which is crystalline and used in the automobile industry and in plastic furniture[9]. Polyethylene may also by synthesised using these catalysts to produce a linear polymer, which has a crystalline structure and as a result is strong and can be used in pipes and bottles, for example[9]. Many combinations of components of Ziegler-Natta catalysts are possible, some of the common combinations are outlined in Table 2.1[1, 2].

Table 2.1 Common components of Ziegler-Natta catalysts

Metal alkyl	**Transition metal compound**
$(C_2H_5)_3Al$	$TiCl_4$ or $TiBr_3$
$(C_2H_5)_3AlCl$	$TiCl_3$ or VCl_3
$(C_4H_9)Li$	$MoCl_5$ or $CrCl_3$

The polymerisation mechanism is complex, however it is considered that the vacant coordination site on the transition metal is responsible for the catalytic activity[6, 11, 12].

In basic terms a monomer molecule may bond to a vacant coordination site on the transition metal. The monomer molecule then inserts itself in to the carbon-transition metal bond to extend the alky chain[6]. The process is repeated with another monomer molecule and the alkyl chain continues to grow. The stereochemistry of the linear polymer is controlled due to the spatial requirements of the transition metal coordination compound, producing an isotactic or syndiotactic polymer[6, 9]. In addition to polymers such as polyethylene and polypropylene, Ziegler-Natta catalysts are used in the synthesis of a material which is almost identical to natural rubber[9]. By treating the monomer isoprene (obtained from the thermal cracking of petroleum fractions) with a suitable Zeigler-Natta catalyst the polymer cis-1,4-polyisoprene is produced- which has the same geometry as natural rubber. Synthetic isoprene rubber has the added benefit of containing none of the natural rubber proteins which can contaminate a product.

2.1.6 Production of synthetic polymers via step-growth polymerisation

Step-growth (condensation) polymerisation is the process in which a polymer is produced by the reaction between two monomer units to form a dimer, which then reacts with more monomers to form a trimer and so on (Figure 2.8). This process is repeated many times to form oligomers and then to form long polymer chains.

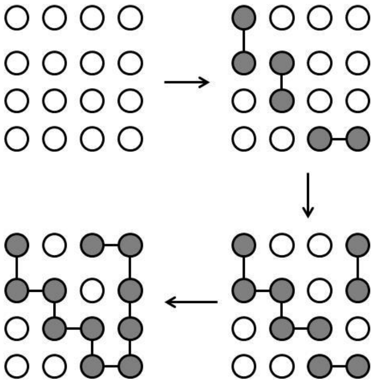

Figure 2.8. Representation of step-growth polymerisation

In step-growth polymerisation there is a gradual increase of high molecular weight product throughout the reaction after an initial rapid loss of monomer[6]. It is the same mechanism that occurs throughout the reaction with no initiator required- typically reactions occur between reactive starting materials. Polymers such as polyurethane, polycarbonate and nylon are synthesised this way. In some step-growth reaction mechanisms a small molecule (such as water) can be eliminated during the reaction, as such this is termed a polycondensation reaction. Alternatively, when the reaction proceeds without the elimination of a small molecule, such as in the polymerisation of polyurethane, the reaction is termed a polyaddition.

The main differences between chain-growth and step-growth polymerisation processes are summarised in Table 2.2.

Table 2.2. Characteristics of chain- and step-growth polymerisation

Chain-growth polymerisation	**Step-growth polymerisation**
Growth is by monomer addition at one end of the polymer chain	Growth occurs throughout the matrix
Stages of mechanism include initiation, propagation and termination	Repetition of similar steps throughout reaction
Initiator is required	Initiator not required
Termination renders chain ends inactive	Chain ends remain active
Some monomer remains in matrix, even after long reaction times	Rapid monomer loss at start of the reaction
Molecular weight of polymer chain increases rapidly at beginning of the reaction	Molecular weight increases slowly, with a more rapid increase towards the end of the reaction.

Figure 2.9, illustrates the difference between step-growth and chain-growth polymerisation[13]. In chain-growth polymerisation it is shown that the molecular weight of the polymer increases rapidly as high molecular weight polymer is formed immediately and continues to be formed throughout the reaction and long reactions times help increase the yield, but does not affect the molecular weight[6].

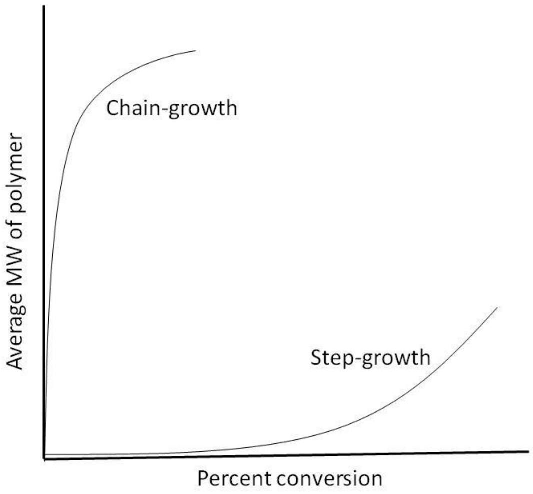

Figure 2.9. Molecular weight development in chain/step-growth polymerisations[13]

In step-growth polymerisation it is shown that there is a high conversion of monomer in the early stages of the reaction, with a slow increase in molecular weight of the polymer. This is due to the rapid formation of small molecules such as dimers, trimers and oligomers, of low molecular weight, throughout the matrix[13]. It is in the latter stages of the reaction when the monomers, dimers and trimers etc. join together to form a growing polymer chain, that the molecular weight begins to rise[14].

2.1.7 Polymerisation methods

Polymerisation can be conducted by one of four methods, namely, in bulk, in solution, in suspension or in emulsion. Bulk polymerisation tends to be the method which is considered to be most straightforward since it involves mainly pure monomer with only minor amounts of other starting materials (initiators and other additives)[6]. However, since polymerisation is exothermic and polymers have poor thermal conductivity, there is a risk that the reactants can overheat (causing charring or degradation) and the reaction becomes out of control[4]. The heat of the reaction may be dissipated somewhat by stirring the reactants, but still the technique is not used widely in industry[6]. Nicholson[6] reports that only three polymers are produced by bulk polymerisation: polystyrene, polyethylene and poly(methyl methacrylate).

A way of overcoming the problems associated with bulk polymerisation and the heat generated by polymerisation is to conduct the reaction in solution. An appropriate solvent is chosen in which the monomer can dissolve. The temperature of the solvent can be controlled to quell the heat of the reaction, but there is a limitation in that the reaction temperature is restricted by the boiling point of the solvent[6]. This limitation may consequently restrict the rate of reaction. In addition, it is important to remove all traces of solvent from the polymer which can be a difficult task.

Polymerisation by suspension involves rapid stirring of the monomer in water to produce minute droplets[4]. Therefore, the monomer is suspended rather than dissolved in the liquid, as is the case in solution polymerisation. Dispersion agents, such talc or gelatine, are added to prevent these small droplets from cohering[3, 4]. The polymerisation reaction occurs within each individual droplet to produce small polymer beads. Stirring must be vigorous in order to prevent the polymers agglomerating and the technique is not suitable for tacky polymers such as synthetic elastomers[6]. The method is commonly used in industry to produce poly(vinyl chloride).

Emulsion polymerisation is a further development from the suspension method. In this method the monomer, initiator, soap, water and other ingredients are stirred in a reaction vessel[4]. The monomer forms small droplets which are surrounded by soap molecules acting as an emulsifying agent to protect the monomers during polymerisation[6]. The polymer particles obtained from emulsion polymerisation are much smaller than those obtained in suspension polymerisation and may have a higher molecular weight[4].

2.1.8 Polymer additives

Additives are added to polymers in the final stages of manufacture to produce the final plastic product. The additives impart new chemical and physical properties to the material- which should then be referred to as a plastic rather than a polymer. A variety of additives can be used including plasticisers, antioxidants, stabilisers and fire retardants. In addition, colourants or fillers such as carbon black and calcium carbonate may be added to alter the appearance of plastics. Since additives can be expensive, manufacturers will use only what is required to produce a plastic for a given function[3]. For example, PVC window frames have an average useful lifetime of up to 50 y and so the plastic will require a sufficient quantity of light stabiliser that will not be exhausted within the lifetime of the product- which increases the cost of the final product. Conversely, plastic carrier bags which have a useful lifetime of up to 1 y, will require less additives since the product is not designed for long term use making the cost of the product substantially cheaper.

The most important additive is arguably plasticisers since some plastics can contain up to 50 % by weight of plasticiser. The flexibility of a plastic can be modified by the addition of plasticisers, examples of which include di(2-ethylhexyl) phthalate (DEHP), camphor and triphenyl phosphate. Increased flexibility allows the plastic to be processed at a lower temperature which reduces the likelihood of inducing degradation as a result of high processing temperatures. Furthermore, plasticisers reduce the brittleness of the final product at low temperature. The plasticiser (P) disperses itself between the polymer chains and is weakly held in place by Van der Waals interactions (Figure 2.10). The dispersion of plasticiser causes the polymer chains to be pushed apart increasing the free volume or intermolecular space. It is the increase in space (free volume) that allows the polymer chains to move more freely and reduce the glass transition temperature (T_g). The ease of movement of the polymer chains means that the polymer is flexible and can be easily shaped.

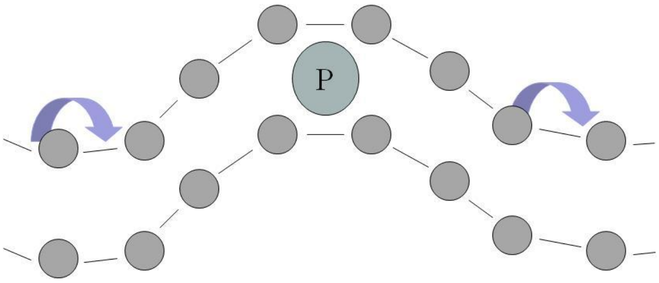

Figure 2.10. Dispersion of plasticiser between polymer chains

Fillers may also be added, but these are relatively cheap when compared to plasticisers or other additives. Fillers tend to be materials such as wood powder, calcium carbonate or glass beads and serve to alter the appearance of the plastic as well as to modify properties such as compression strength and resistance to abrasion. For example, wood powder was commonly used in the production of phenol-formaldehyde plastic, Bakelite. The wood powder reduced the amount of shrinkage of the plastic during moulding and strengthened the final product[3]. Impact modifiers improve the ability of a plastic to recover from the effects of impact and generally have a rubber like quality- typical examples include acrylonitrile butadiene styrene (ABS)[3]. Plastics such as polystyrene and PVC contain impact modifiers which absorb and dissipate the energy from shock without damaging the polymer. Finally, blowing agents can also be used to alter the physical properties of plastics by producing foams such as polyurethane and polystyrene. Gases or volatile liquids are dissolved in to the polymer during processing, the increase in temperature and pressure during manufacture causes the expansion of gas or the evaporation of liquid blowing agents to create cells within the plastic. The most commonly used gases are carbon dioxide and air. The liquids commonly used would have historically included CFCs such as trichlorofluoromethane (CCl_3F), however due to legislation this is no longer used and has been replaced with hydrocarbons such as pentane.

The chemical properties of polymers can be altered by the addition of antioxidants, stabilisers and fire retardants. Antioxidants inhibit oxidation by reacting with the free radicals that are produced by the action of heat and light during processing or they may prevent the formation of radicals[3, 4]. Butylated hydroxytoluene (BHT) is a commonly used antioxidant; however it is quite volatile and is therefore not suitable for products which require a long useful lifetime.

Stabilisers may include ultraviolet absorbers, which preferentially absorb in the ultraviolet range and not the visible range. A polymer which incorporates a stabiliser that absorbs in the visible range would colour (discolouration/yellow) significantly over time compared to an untreated polymer after prolonged exposure[4]. The general action of UV absorbers is to dissipate the absorbed energy in the form of radiation (fluorescence), or by converting the energy to heat or by chemical reaction to benign products[4]. Typical examples include 2-(2-hydroxyphenyl)-benzotriazole and 1,3,3-tris-(2-hydroxyphenyl)-triazine.

Fire retardants are important in polymers which are to be used in buildings and furniture, for example. In general, fire retardants work in a number of ways[4]. Firstly, the retardants can chemically interfere with the flame propagation process. The retardants may also generate large quantities of incombustible gas which will dilute the air supply and suppress burning. They may absorb heat by reacting or decomposing which reduces the ability to burn. Finally, retardants may form a surface coating on the polymer meaning that the oxygen required for burning is unable to penetrate the barrier. Examples of fire retardants include phosphates (such as tricresyl phosphate) and halogen containing compounds (such as tribromotoluene)[4].

2.1.9 Further processing

When polymers are produced they are generally made in to flakes or granules which are further processed in to films, sheets and 3 dimensional objects. Films and sheets are generally made by calendaring and extrusion. The former process involves a series of heated and rotating rollers, which have an ever decreasing gap between them to thin the sheet to the desired thickness. Extrusion involves heating the plastic to a melt and pushing it through a die (specialised manufacturing tool which can cut and shape plastics) to produce a continuous profile[3]. These methods of processing are commonly used to manufacture carrier bags and protective films[3].

Advances in technology in the 1920s enabled 3 dimensional objects to be created with a high throughput. Injection moulding is still the most commonly used technique to date and is used to create a vast range of objects from CDs and car dashboards, to furniture and packaging. The plastic flakes or granules are poured in to a hopper which directs the granules in to a cylinder which is heated until the plastic has low enough viscosity to permit flowing properties. The plastic is then injected under pressure in to a pre-cooled split mould which forces the plastic into the desired shape. The plastic is quickly cooled by the mould and is ejected when the mould opens.

Foams, such as polyurethane, are produced by adding water to the isocyanate and polyol during synthesis. The whole mixture can be added to a mould or moving trough and the water reacts with isocyanate to produce an amine and carbon dioxide[1, 3]. The carbon dioxide creates bubbles and expands within the polymer matrix to produce a foam in the shape of the mould or large blocks if produced in a moving trough. Alternatively, blowing agents such as trichlorofluoromethane (CCl_3F) may be used. Chlorofluorocarbons (CFCs) have since been banned due to their destructive effects on the ozone layer, but historically they were used until the 1970s.

2.2 Mechanisms of plastics degradation

Plastic objects can suffer from chemical, physical, mechanical and / or biological damage. The damage can manifest itself in many ways and can range in severity. Degradation is inevitable and with much of the degradation being initiated before an object joins a collection there is only so much that conservators can do to ensure that objects last as long as possible. When an object reaches a severe state of degradation implications of such deterioration must be considered. For instance, if the deteriorating object is on public display then the meaning or intention of that object must still be discernible despite the degradation. Perhaps most importantly (from the viewpoint of a curator or conservator), it should be determined whether the degrading object is putting the stability of other objects at risk.

Degradation can begin during the manufacturing of a plastic object as a result of high temperature processing or as a result of the function of the object before it joined a collection. Light, temperature, oxygen, moisture, pollutants and physical stress can all cause or exacerbate degradation processes. Since most objects have a prior history which is unknown, the best that heritage institutions can do is to try and manage the objects in collections so as to stabilise them and slow the degradation as much as possible in an ethical manner which can be a difficult task with so many objects in collections. However, it is important to be aware of the forms and causes of degradation experienced by different plastics so as to make informed decisions about the treatments and future storage of objects. Degradation of plastic heritage objects may involve a complex combination of thermal, oxidative and photolytic processes, creating a synergistic effect. In addition, the objects will likely contain a range of additives such as plasticisers and stabilisers which may complicate the process of degradation.

2.2.1 Thermal degradation

Temperature control is essential for objects which may already be in an active state of degradation and is strongly suggested for all other objects where possible. The importance of temperature control was reinforced by Michalski[15] who reported that increasing the storage or display temperature by 5 °C can halve the lifetime of an object. Heat degrades plastics by providing enough energy to break bonds along the backbone of the polymer, or from side groups. The action of heat in the degradation of plastics is known as thermolysis or thermal degradation. The breaking of bonds tends to occur at weak sites within the polymer chain. Weak sites can be a natural part of the polymer structure or they may have been inadvertently introduced during manufacturing in the form of impurities or may have been produced as a result of other degradation mechanisms, such as oxidation[3, 16].

Thermal degradation of the polymer backbone is termed depolymerisation and involves breaking the backbone into smaller molecules which causes a rapid decrease in the molecular weight of the polymer[16]. These small molecules (dimers, trimers etc.) can breakdown further to produce monomers, a process which is known as depropagation[16]. The action of breaking bonds to produce much shorter fragments causes a major loss of mechanical strength within the plastic which, for example, can manifest itself as brittleness and cracking.

Side group scission generally occurs more readily than backbone scission since it can occur at lower temperatures[3, 16, 17]. Side group scission involves the loss of small molecules, which may be volatile in nature. An example of this would be the side group scission of PVC where a molecule of HCl is lost per repeat unit in a process known as dehydrochlorination[18]. The action of losing a molecule of acid from one repeat unit and the creation of a double bond destabilises the next repeat unit and so on in an autocatalytic process along the length of the polymer chain[16, 18]. A further concern is that the generated HCl is acidic and will promote further degradation of the plastic itself and will initiate degradation of other acid vulnerable objects and materials which may be held in close proximity to the degrading PVC. The result of this type of degradation is the production of a conjugated polyene which is capable of absorbing UV light which results in discolouration of the polymer[19].

2.2.2 Oxidative degradation

Oxygen and / or ozone are involved in the degradation mechanisms of most plastics. Oxidation is possible not only in the latter stages of a plastics life but also during processing[3]. Oxygen permeates in to the bulk of the plastic where chemical reactions can take place. However, plastics have different oxygen permeabilities which means that some plastics may be more susceptible to oxidation and degrade at a faster rate. Those with high oxygen permeability (amorphous plastics) will be more vulnerable to oxidation than plastics with a lower oxygen permeability (crystalline plastics)[17]. The chemical bonds within a polymer chain will have different reactivities, for example unsaturated bonds within a polymer will react more readily with oxygen and ozone than more stable single bonds[3]. Equally, branched polymer chains which contain a tertiary carbon atom will also be a potential site for oxidation.

Oxidation of plastics proceeds via a free radical chain reaction with three distinct stages: initiation, chain propagation and termination. There are several reactions which take place during oxidation which differ in each plastic. The initiation reaction can proceed via a direct reaction between the polymer (R) and molecular oxygen (Figure 2.11) which is known as autoxidation[17].

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}$$

Figure 2.11. Reaction of polymer with molecular oxygen

The oxygen molecule has two unpaired electrons in the ground state which remove the most reactive hydrogen from the polymer to generate two free radicals[16, 17]. Kelen[17] explained this feature of the reaction by using polypropylene as an example. Polypropylene has low oxidative stability due to the presence of reactive tertiary H atoms (the H atom attached to a tertiary carbon) in every monomeric unit[17]. In polypropylene, the tertiary H atom is removed since the C-H bond has the lowest bond dissociation energy and is therefore the most suitable reaction site[17]. This type of direct oxidation initiation can take place under ambient conditions; however it is likely that the polymer will be exposed to light (photo-oxidation) and heat (thermo-oxidation) which will accelerate the oxidation reaction. Increasing the temperature of a polymer will subsequently increase the rate of photo-oxidation[20]. The rate of oxygen diffusion into a polymer increases with temperature resulting in products of oxidation[20]. Such products (e.g. carbonyl containing compounds) will consequently absorb UV light resulting in discolouration of the polymer.

Oxidative degradation has an induction period during which time the polymer remains visually unchanged, the rate of oxidation at this stage is so slow that it is negligible to begin with[21]. After this period, the rate of oxidation steadily accelerates to a constant rate[17, 21]. The products of the oxidative degradation then accelerate further degradation in a cycle known as autocatalysis.

2.2.3 Photo-degradation

The radiation from the sun which reaches the earth's surface extends over a wide wavelength range incorporating the infra red (> 700 nm), through the visible spectrum (400-700 nm) to the ultraviolet (<400 nm, with a cut off of approximately 300 nm)[16, 21]. The equivalent energies (170, 300 and 390 kJ mol^{-1}, respectively) of these photons of light may be sufficient to break C-C and C-H bonds (420 and 340 kJ mol^{-1} respectively), in some case the bond energies may be much lower when neighbouring groups are aromatic or unsaturated in nature[21]. The short wavelength ultraviolet (UV) light is the most damaging since it is highest in energy.

In practical terms, polymers are more susceptible to longer wavelengths of light (> 300 nm). Chromophoric groups (unsaturated bonds) which may be present within a polymer, such groups may include carbonyl groups or ethylenic groups, are capable of absorbing radiation and have absorption maxima between 200-400 nm[22]. The absorbed energy is transferred through the polymer to the bond to be broken and results in homolytic bond scission and the formation of free radicals. The free radicals may then rapidly react with oxygen and initiate oxidation. Since light is attenuated within the polymer, the most severe damage will be close to the surface of the polymer.

2.2.4 Photo-oxidation

When light is involved in initiating oxidation reactions, it is known as photo-oxidation or photo-initiated oxidation. As has been previously discussed, the plastic must contain chromophoric groups in order to absorb light. Plastics containing many chromophoric groups within the polymer chains will be vulnerable to degradation, but that does not mean that plastics such as polyethylene (which contains saturated bonds) are free from the risk of oxidative degradation[21]. In reality the majority of plastics contain structural defects within the polymer chains and contain impurities introduced during manufacture which are capable of absorbing UV radiation. The impurities and structural defects are suspected to be oxidation products which are formed during high temperature processing in the presence of atmospheric oxygen[23]. This implies that many plastics will be susceptible to photo-oxidation, though it is recognised that some will be much more vulnerable to this type of degradation than others.

Regardless of how oxidation begins (photo-initiated, by hydrogen abstraction in direct oxidation, by initiator decomposition, etc.) a chain reaction ensues which will cause complete deterioration of the polymer. In each of the three stages there is more than one possible route; therefore it is a generic scheme that is outlined below (Figure 2.12).

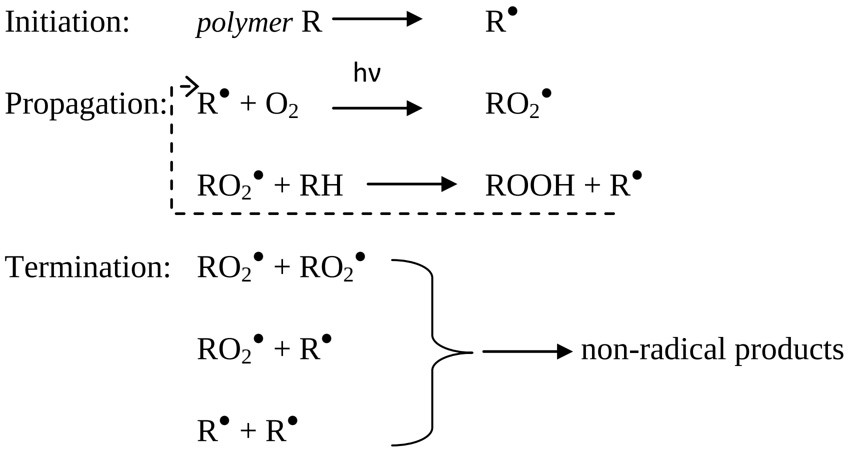

Figure 2.12. Free-radical chain reaction of oxidative degradation

Once initiation has commenced, the labile free radicals ($R^{\bullet}$) which are produced react with oxygen to form hydroperoxy radicals ($RO_2^{\bullet}$)[3, 21, 23]. These radicals then react with more polymer (RH) to produce hydroperoxides (ROOH). This part of the reaction is termed the propagation step since free radicals are continually formed in a cycle permitting continual degradation (denoted by the dashed arrow in the propagation step). In addition, the hydroperoxides (ROOH) may decompose as a result of oxygen-oxygen bond scission (induced by UV light or heat) to produce free radicals which are capable of hydrogen abstraction from the polymer to initiate further degradation of the polymer[17, 21, 23]. Furthermore, the hydroperoxides (in very small amounts) may also be present as a result of polymer processing and may decompose to produce free radicals (Figure 2.13), which may act as initiators for the free-radical chain reaction[24].

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}^{\bullet} + {}^{\bullet}\mathrm{OH}$$

Figure 2.13. Hydroperoxide decomposition to generate free radicals

Termination of the reaction occurs when radicals react with each other to form non-radical products which can include esters and ketones[3]. The generation of such carbonyl containing products during oxidative degradation results in the discolouration of the degrading plastic. The overall degradation reaction is auto-accelerating with a slow initiation stage, followed by a rapid increase in the rate of the reaction during the propagation stage and then slowing once more during termination[3].

2.2.5 Hydrolytic degradation

Hydrolysis commonly affects polyurethanes, polyesters, and polycarbonates[21]. Hydrolysable linkages tend to be within the main polymer chain which results in main chain scission. This causes a reduction in molecular weight which causes a loss of mechanical properties[25]. Polyesters can differ slightly in that the hydrolysable linkage may be in the main chain as in polyester polyurethanes or in a pendant group as in the polyacrylate series. When the hydrolysable linkage is a pendant group the effect of hydrolysis is not as severe since main chain scission does not occur.

The rate of diffusion of water in to a polymer will depend on whether the sample is crystalline or amorphous. Water will easily diffuse in to amorphous polymers but the inaccessibility of crystalline polymers to water diffusion will mean they are less likely to suffer hydrolytic degradation. A polymer may also be made vulnerable to hydrolysis due to poor manufacturing processes. An example of this problem commonly occurs in the condensation polymer polycarbonate. Immediately after production polycarbonates need to be thoroughly dried to reduce the moisture content to within set guidelines, otherwise moisture could be trapped within the bulk polymer and cause hydrolysis during the subsequent hot melt processing to final products[20]. A common indicator of insufficient pre-drying is splay marks within a polycarbonate product. Acidic or basic conditions are capable of initiating hydrolysis and polymers which have previously been subjected to oxidation will become more polar. Therefore, it possible that as a polymer ages it will become more susceptible to hydrolysis. Polymers such as polyethylene and polypropylene are hydrophobic and are unlikely to be vulnerable to hydrolysis[3].

2.2.6 Degradation caused by additives

Additives are used to improve the properties of polymers for a given application. However, care should be taken when selecting additives since, under the right circumstances, additives may be detrimental to the stability of a polymer. Wright[20] outlines a case where the selection of additives was given little thought by the manufacturers. Brominated flame retardants were used in high impact polystyrene (HIPS) since the plastic was to be used in computer hardware housings and needed to be of low fire risk in the event of an electrical failure. However, the manufacturers failed to recognise that brominated flame retardants are strong absorbers of UV light and actually absorb UV light more effectively than the polymer itself.

Flame retardants generally lower the resistance of a polymer to UV degradation, though the extent of this effect is dependent upon the chemistry of the additive[20]. Low resistance to UV light is not a problem when the polymer will be relatively protected from UV light exposure. For example, the polyurethane foam commonly used in household furniture contains flame retardants to comply with EU legislation. In such circumstances, the foam is almost always contained within a cover of some sort (e.g. cushion covers or within mattresses) and as a result will be exposed to very low levels of UV light. Therefore, the fact that brominated flame retardants are effective UV absorbers will be of little consequence in this particular application. On the contrary, computer housings may well be subjected to UV light exposure, therefore the use of such brominated flame retardants actually render the polymer less stable to UV light, but reduce the fire risk of the polymer. The ability to absorb UV light will cause discolouration of the computer housing. Plastic discolouration might be expected to begin once the computer had been purchased by a consumer and was part way through its service life. However, in addition to the inappropriate selection of flame retardants, the manufacturers selected inappropriate packaging for the computers. As a result of a new marketing strategy, the computers were displayed in shops in transparent packaging and so were subjected to photo-degradation and subsequent discolouration before being purchased by consumers[20].

2.3 Degradation of the 9 plastic types selected for this study

It is unlikely that a plastic will degrade via one single pathway. It is almost certain that a plastic will degrade by a combination of the degradation pathways briefly outlined above. In addition, the pathways above have focused on the degradation of the polymer alone. When in reality, the degradation of a plastic (which contains polymer, stabilisers, plasticisers and colourants etc) is much more complicated. The diversity of plastic formulations means that even though two plastics may contain the same polymer, the differences in additives means that the two plastics may degrade by different mechanisms and at different rates. It can be challenging to predict the ways in which a plastic will degrade; however much research has been conducted in to the degradation of plastics within a heritage context. In the sections that follow much of this research has been drawn together to discuss the most common ways in which the 9 polymers (41 individual samples) selected for use in this study degrade.

2.3.1 Degradation of rubber

Rubber degradation may be visible on the surface of an object as cracks and bloom formation and in physical terms the object may also become hard and brittle[26]. Oxygen is capable of permeating between the polymer chains due to the amorphous nature of rubber and the presence of double bonds in the polymer backbone mean that rubber is vulnerable to oxidative degradation[27]. Oxidation proceeds via a free-radical mechanism (Figure 2.12) which will result in either chain scission or cross-linking or perhaps both depending on the type or rubber[24]. Somers[24] *et al*. stated that natural rubber will soften at first as a result of chain scission- which is the breakdown of the polymer chain in to shorter fragments characterised by a reduction in molecular weight. The chain scission is then followed by cross-linking which causes a hardening of the polymer and slight increase in molecular weight[24]. Modern rubber formulations may contain antioxidants which tend to work in one of two ways. The first is by reacting with free radicals so that they do not react with the polymer chain and the second method is reacting with hydroperoxides to generate stable end groups[24].

Rubber is particularly susceptible to ozonolysis which is the reaction of ozone with organic compounds containing double bonds, such as those in natural rubber, to form products which contain a carbon to oxygen double bond[27]. Although the concentration of ozone present in the atmosphere is low, it is sufficient to cause degradation[24]. The reaction proceeds via the addition of ozone (which is highly unstable and therefore reactive) across the double bond to generate a molozonide[28], shown in Figure 2.14. The molozonide rapidly dissociates to give a zwitterions (step A), the unstable nature of the zwitterion causes it to break down to form another zwitterion and a carbonyl compound (step B)[21, 29]. The remaining zwitterion may then be stabilised by a number of different processes which can include the formation of an aldehyde or ketone[29]. Further oxidation of the aldehydes would produce acids. Such acids have the potential to be detrimental to the stability of the rubber object itself and to other materials in close proximity (c.f. Chapter 7).

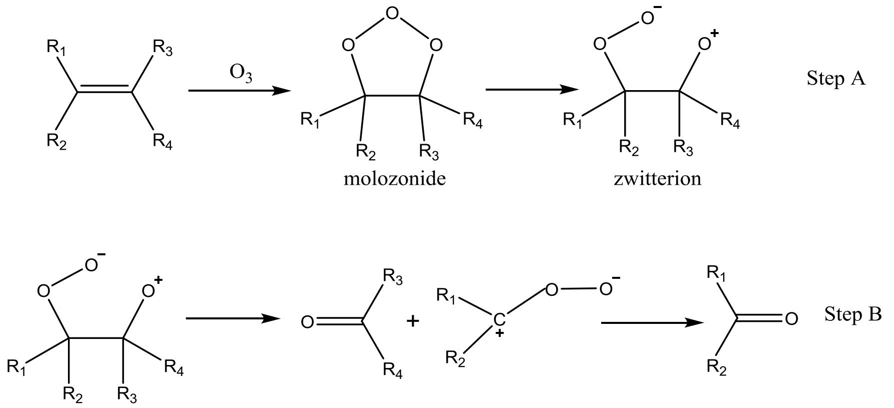

Figure 2.14. Ozonolysis of rubber

Ozonolysis causes rubber to crack, a condition known as ozone cracking. It is particularly common in rubber objects which are under stress such as tyres, rubber seals and tubing. Ozone cracking is easily identifiable on the surface of rubber objects since the cracks occur perpendicular to the direction in which the stress is applied[30]. Although the rate of this type of degradation is sluggish in modern day rubber due to the application of anti-ozonants (which preferentially react with ozone to prevent it from reacting with the unsaturated bonds in the polymer backbone), all rubbers historical or modern will still degrade by ozonolysis.

In addition to oxidation and ozonolysis, rubber is susceptible to photodegradation due the presence of chromophoric groups in the polymer backbone. UV light will be absorbed by the unsaturated bonds in the backbone resulting in bond scission and the formation of free radicals[21]. The generated radicals are perfect oxidation initiators and will then go on to react rapidly with oxygen (as seen in the propagation step of free-radical oxidation mechanism in Figure 2.12).

2.3.2 Degradation of cellulose nitrate

Degradation of cellulose nitrate can proceed via thermal, photochemical, hydrolytic and physical pathways, which will ultimately lead to the demise of the object. Since cellulose nitrate is thermally unstable, it will spontaneously decompose to release the highly toxic and oxidising gas nitrogen dioxide (NO_2), even at room temperature[3, 31, 32]. The denitration process which liberates nitrogen dioxide is due to the cleavage of the weak N-O bond bound to the cellulose ring, which occurs at positions 2 and 3 in the cellulose ring (Figure 2.15)[3, 33, 34]. Positions 2 and 3 (secondary group) in the cellulose ring are more susceptible to denitration than position 6 (primary group) since they have lower bond energy[35].

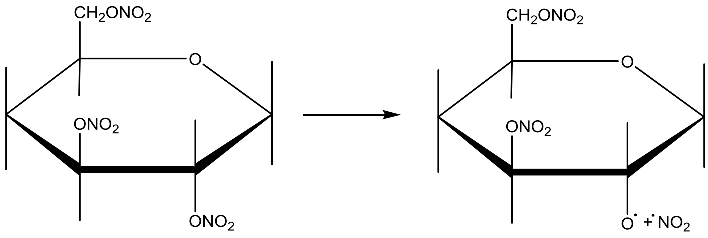

Figure 2.15. Denitration of cellulose nitrate[3]

The liberated nitrogen dioxide gas can then react with water and oxygen in the air to form nitric acid. The nitric acid can then cause further denitration and liberation of nitrogen dioxide, which will go on to react with moisture and oxygen to form more nitric acid. This process is autocatalytic and is hugely detrimental to the object itself and to other vulnerable objects in the near vicinity[31, 36]. The reaction is exothermic and in three-dimensional objects where the evolved gases may be trapped within the object and encouraging more decomposition, a point could be reached where the gas build up and generated heat cause spontaneous combustion of the object[37]. In addition, if residual acid is not removed during the stabilisation step in the manufacture of the product then sulfate esters may be formed as a secondary product[38]. The sulfate esters can then form free sulfuric acid which, when combined with nitric acid, could increase the speed of degradation[8, 32].

Not only do the acids encourage further denitration, but the acids can also break down the polymer chains by breaking the bond between the cellulose rings. This is known as chain scission and ultimately breaks the backbone of the polymer, resulting in a shortening of the polymer chains and a reduction in molecular weight[39]. Visually, this gives the plastics the appearance of a network of internal cracks, known as crazing. As chain scission continues, the networks of cracks make their way to the surface of the object. At this stage the cracking is so extensive that the object begins to completely disintegrate, which is known as crizzling.

Discolouration is common and is caused by exposure to ultraviolet (UV) light. Cellulose nitrate is particularly vulnerable to UV light of wavelengths 360-400 nm[33]. Discolouration can begin before an object joins a heritage collection and once the process has started it cannot be stopped, it will continue even if the object is stored in darkness[33, 40]. At higher energy wavelengths (< 360 nm), the cellulose ring structure is broken down and rapid disintegration of the object occurs[33, 41].

Degradation of cellulose nitrate can also result from the loss of the plasticiser which causes the plastic to crack and become brittle. Camphor, the most common plasticiser used in cellulose nitrate, has a relatively high vapour pressure, which means that it is volatile and sublimes at room temperature. The loss of camphor from cellulose nitrate plastic generates a distinctive odour of mothballs. The strong smell is often used as a marker of cellulose nitrate and can also indicate that degradation is occurring. The sublimation of camphor from the plastic creates a network of surface cracks which expose a fresh inner surface, which in turn promotes further loss of camphor and a cycle begins. In addition, water and oxygen can ingress through the newly formed cracks and react with nitrogen dioxide to generate nitric acid and once again form an autocatalytic cycle of degradation.

Quye[38, 42] *et al.* conducted studies which examined the degradation of cellulose nitrate using both laboratory prepared samples and museum artefacts. The results indicated that samples which appeared to be in a bad condition (for example, weeping, crazed or discoloured) had a higher level of residual sulfate, which suggests that sulfate initiates or accelerates degradation[38]. The residual sulfate is generally present as a result of inadequate washing during the stabilisation stage of manufacture. This implies that an object may be predisposed to degradation as a result of poor manufacturing processes. In addition, the authors examined the effect of humidity on the degradation of cellulose nitrate and established that samples exposed to humid environments degraded at a much faster rate than those in lower relative humidity conditions[42]. Therefore, despite an object's predisposition to degradation it is still important to maintain low temperature, humidity and light exposure in the storage environment of collections since this will slow deterioration and increase the lifetime of the objects.

2.3.3 Degradation of cellulose acetate

Cellulose acetate can suffer from a phenomenon frequently referred to as the "vinegar syndrome" which can be described as the formation of acetic acid as a result of degradation. The chemical process of degradation is known as deacetylation (Figure 2.16), during the process acetyl ($COCH_3$) groups on the cellulose ring are replaced with hydroxyl groups[35, 36, 43-45]. The smell of acetic acid often alerts conservators to the fact that degradation has begun, with most human noses having a threshold of 0.5 ppm (~ 3000 $\mu g\ m^{-3}$)[46].

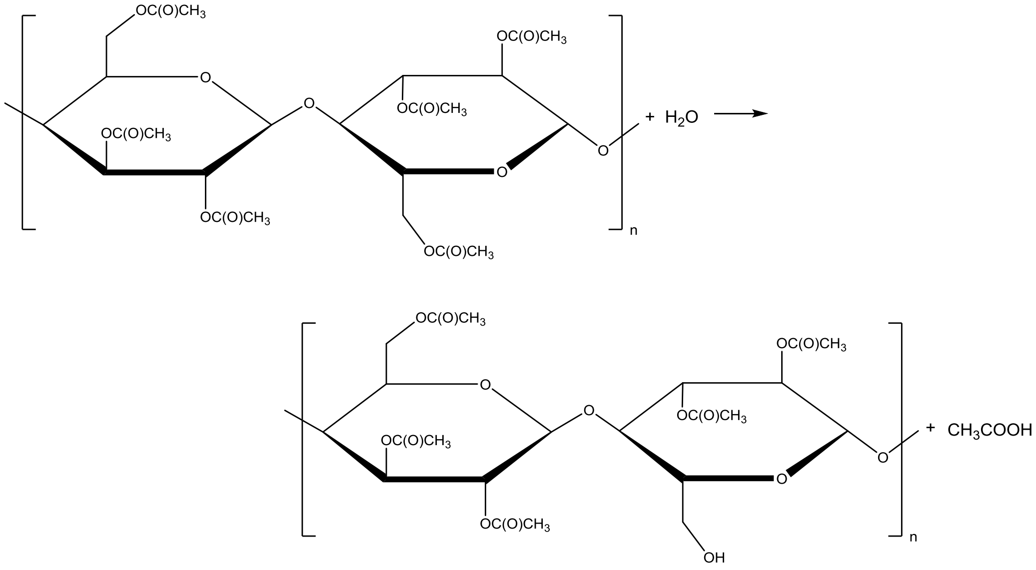

Figure 2.16. Deacetylation of cellulose triacetate[3]

Deacetylation of cellulose triacetate has been shown to proceed in a particular manner with acetyl loss occurring initially from C_2 position with a fast rate of reaction, then a slower reaction rate with acetate loss from C_6 position and subsequently C_3 position[47] (Figure 2.17).

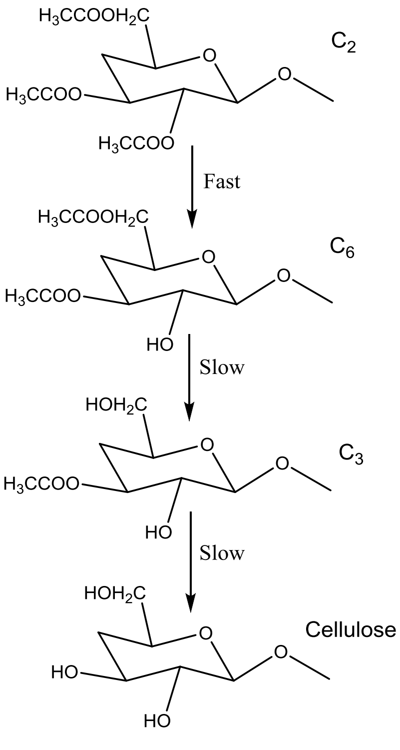

Figure 2.17.Acetyl loss succession[48]

The relative reactivities of the acetyl groups seems unusual since it would normally be presumed that C_2 and C_3 would have comparable rates of reaction since they are both secondary groups and C_6 is a primary group. However, Derham[47] *et al*. demonstrated through molecular modelling that in the helical structure adopted by cellulose acetate, C_2 and C_6 acetyls were the most exposed sites and were therefore the most reactive. The acetic acid which was generated during the reaction catalysed further deacetylation of the polymer in an autocatalytic cycle[45]. Cross contamination of the acid may induce the degradation of other cellulose acetate artefacts in the near vicinity which may have previously been relatively stable- commonly referred to as 'Dolls Disease'[49]. Furthermore, acid trapped within the bulk of the polymer can catalyse the hydrolysis of the C-O bonds in the backbone of the polymer, known as glycosidic bond cleavage[50]. Chain scission causes a shortening of the polymer chains producing a brittle polymer vulnerable to physical damage[45]. The chain scission is initiated by the effects of light, but is accelerated by the presence of acid[48].

The deacetylation process impedes the polymer's ability to retain its plasticiser, since it is believed that the plasticiser is no longer soluble in the polymer once deacetylation has begun[50]. Therefore, the plasticiser can migrate to the surface of the plastic causing a sticky residue which can collect particulate matter and give the object a grimy appearance[48]. In addition, the loss of plasticiser causes the plastic to not only become brittle and vulnerable to damage but also to warp and shrink[36, 50, 51]. Plasticisers account for 20-40 % (w/w) of cellulose acetate and examples include triphenyl phosphate and various phthalate esters[51, 52]. Furthermore, Shinagawa[53] *et al*. have shown that plasticiser breakdown may accelerate the degradation of cellulose acetate. It was proposed that triphenyl phosphate (TPP) decomposed to produce diphenyl phosphate (DPP) and phenol under humid accelerated ageing conditions. DPP is a strong acid and is therefore capable of catalysing hydrolysis, increasing the rate of degradation. Loss of plasticiser and chain scission allow water ingress which will accelerate degradation.

Allen[54] *et al*. have conducted extensive studies on cellulose acetate degradation and in one such example reported that the degradation process is dependent on the moisture uptake of the cellulose acetate object and on the build-up of acid surrounding the object. The moisture taken up by the object will accelerate hydrolysis causing the release of acetic acid, which will further accelerate the degradation process. The authors suggest a range of storage conditions suitable for the stabilisation of cellulose acetate objects. In the case of new cellulose acetate objects, storage in a dry atmosphere at 0 °C was suggested and for older cellulose acetate objects which were already emitting acetic acid, storage at temperatures below -18 °C was suggested since this would freeze any acetic acid present, which has a melt point of 17 °C.

Similarly, Ballany[50] *et al*. identified that the rate of deacetylation and subsequent plasticiser loss was markedly increased when the temperature was raised. Furthermore, they recognised that plasticiser loss was linked to an increase in the relative humidity since the plasticiser migrated from the plastic in high moisture environments. These findings enabled the authors to suggest that cellulose acetate objects should be stored and displayed at low temperature and relative humidity environments. The authors also recommend the use of ventilation or scavengers to prevent a potential acid build-up in the environment surrounding cellulose acetate objects, which may otherwise catalyse further degradation of the objects themselves or other acid sensitive objects in the near vicinity.

2.3.4 Degradation of poly(vinyl chloride)

Degradation of plasticised PVC is often initially noticed as a surface shine to the object[35]. This glossy and tacky surface is referred to as ‘weeping’ or ‘sweating’ and can give the object a grubby appearance since dust and other particles stick to the surface. It is caused by the transfer of plasticiser from inside the object to the surface. Shashoua[3] outlined an extreme example of weeping in the case of two crash test dummies that were made in the 1970s. The surfaces of the dummies had become increasingly shiny, so much so that conservators had to insert collection vessels into the showcases to collect the plasticiser which was dripping from the arms and legs of the dummies.

Plasticised PVC can contain up to 50 % by weight of plasticiser and although many different plasticisers have been used in PVC formulations, the most common is di-(2-

ethylhexyl) phthalate (DEHP)[18, 55, 56]. Since plasticisers are not chemically bound to the polymer chains but rather are held in place by weak Van der Waals forces, the plasticisers can move to the polymer surface quite readily at low temperature. The rate at which the plasticiser is lost from the plastic is dependent on its diffusion from the bulk to the surface and its evaporation from the surface into the air (which is dependent on vapour pressure)[57]. Indeed, there may be a situation where the plasticiser will migrate into a different medium. For instance, a PVC object which is in storage may be packaged up for safe keeping in a protective material. The plasticiser may move through the bulk of the object to the surface where it migrates to the absorbent packing material. This migration is dependent on pressure (originating from the internal stress of the object, or the pressure of the absorbent material on the surface of the object) and on the compatibility of the absorbent material for the plasticiser[18].

Dehydrochlorination, the sequential loss of hydrogen chloride, is the main destructive form of deterioration of PVC and results in the formation of a conjugated polyene[3, 58]. The exact mechanism is still the subject of debate. However, it is assumed that breakdown begins at weak points within the polymer chain, which can be as a result of structure irregularities and impurities since these have a lower thermal stability than the linked monomer units of the polymer chain. Dehydrochlorination begins with the cleavage of a carbon-chlorine bond which is followed by the abstraction of a hydrogen atom, which results in double bond formation in the polymer backbone[4] (Figure 2.18). The next chlorine is highly reactive and is readily lost and so another hydrogen atom is abstracted and so on. This process continues in an autocatalytic fashion in what is known as an ‘unzipping’ mechanism to form a conjugated polyene. The conjugated system is then capable of absorbing light in the UV and visible range of the spectrum, which results in discolouration of the polymer.

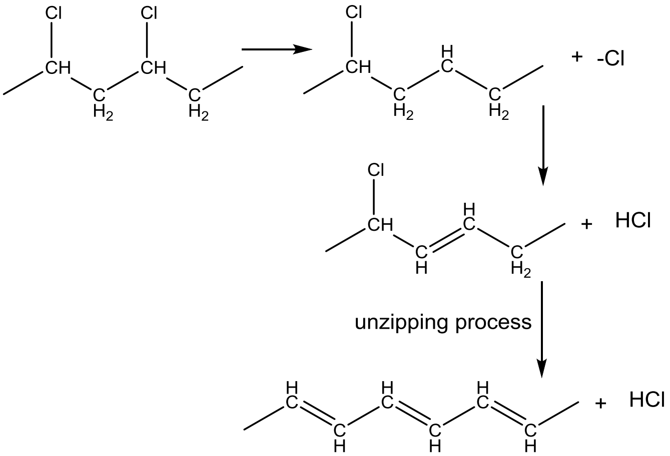

Figure 2.18. Dehydrochlorination of PVC[18]

Shashoua[35] reported that the extent of degradation could be monitored by the corresponding colour changes. During the formation of the conjugated polyene, when approximately 7-11 repeat units had been formed, the wavelength absorption was in the long range part of the spectrum (violet, blue and green)[3, 35]. The absorption maxima were linked to a particular polyene length, thereby allowing the extent of degradation to be tracked by colour changes in the polymer from white (if uncoloured) to yellow, then to orange and red and finally to brown and black[3, 4].

The loss of plasticiser has been linked to the rate and severity of PVC degradation[57]. Phthalate plasticisers, such as di-2-ethylhexyl phthalate (DEHP), are thought to retard PVC degradation[57]. Beltrán and Marcilla suggested that the ester groups of the plasticiser solvate the reactive groups of the polymer chain which were considered to be the weak initiation points[59]. As a result the dehydrochlorination and subsequent polyene formation were retarded. Therefore, when plasticiser migrates to the surface and is lost, the polymer can be vulnerable to degradation. Shashoua[35] suggested that in order to increase the lifetime of a PVC object the amount of plasticiser lost must be minimised. Ventilation or the use of adsorbents tend to be standard practice; however they should not be employed in this case since they would accelerate the action of plasticiser loss and as a result encourage dehydrochlorination[35]. Instead, PVC objects should be stored and displayed in a protective environment, such as a glass jar, which is impermeable and will prevent the loss of plasticiser. It is common for heritage institutions to store objects in polyethylene bags, but as Shashoua explained in the example to follow this was not appropriate for the storage of PVC[3,

[35]. A fishing box which comprised of low density polyethylene contained heavily plasticised lures which were stored for approximately twenty years. The plasticiser migrated from the PVC and was absorbed by the polyethylene causing it to soften and deform in such a way that an impression of the lures was embedded within the polyethylene[3, 35].

2.3.5 Degradation of polyethylene

Polyethylene within heritage collections will be in one of two forms, high density polyethylene (HDPE) or low density polyethylene (LDPE). Since HDPE contains linear polymer chains which closely pack together, the oxygen permeability is low and therefore oxidation is generally very slow to progress. In LDPE there is a small percentage of branching which permits oxygen to permeate the polymer. In addition, the presence of branching will mean that a small number of tertiary carbons (a C atom bonded to three other carbon atoms and a hydrogen atom) will be present. Tertiary carbons create weak points within polymer chains which are perfect reactive sites for oxidation.

Grassie[21] outlined the effect of polymer chain branching on oxidisability by comparing LDPE, HDPE and polypropylene and demonstrated that polypropylene was most susceptible to oxidation since it had the highest degree of branching and therefore had a greater number of reactive tertiary carbons. HDPE was the least vulnerable to oxidation since branching is very low. The oxidisability of LDPE lay between polypropylene and HDPE since it is lightly branched. The concept outlined by Grassie[21] applies to an ideal situation. In reality, the presence of additives or impurities, as a result of production and/or processing, could cause an increase in oxidisability where it may not be otherwise expected.

T. B. van Oosten[60] stated that in terms of polyethylene the most important degradation process within a heritage environment is that of photo-oxidation. The presence of chromophores (from impurities) within the plastic enables the absorption of UV light. The absorbed UV light can induce homolytic bond scission generating free radicals which can initiate oxidation. Research was conducted to examine the effects of UV light on a range of polyethylene Tupperware® samples to determine the average lifetime such an object may have in heritage collections[60]. Selected samples, which included a non-coloured semi-opaque sample, a non-coloured transparent sample, a blue opaque sample and a white opaque sample (all produced circa 1975) and a transparent film (produced in 1993), were artificially aged at approximately 30 °C using commercial instrumentation which contained a filtered xenon lamp. The irradiance measured at 340 nm was 0.3 W m^{-2} and samples were exposed for 760 h, which the authors likened to the equivalent of approximately one hundred and fifty years of museum light exposure at 100 lux. Fourier transform-infared (FTIR) spectroscopy was employed to monitor the changes within the plastic samples on exposure to UV light. It was demonstrated that as photo-oxidative degradation progressed the formation of carbonyl containing oxidative products increased, as monitored by FTIR spectroscopy since ketones absorb at 1720-1715 cm^{-1}, aldehydes absorb at 1730 cm^{-1}, carboxylic acids absorb at 1712-1705 cm^{-1} and esters absorb at 1740 cm^{-1} in the FTIR spectrum[60].

In terms of visible changes after 760 h of light exposure the non-coloured transparent sample and the white opaque sample remained unchanged. The blue opaque sample had faded in colour and the transparent film had lost some of its sheen. The non-coloured semi-opaque sample appeared more opaque after light exposure. It was therefore concluded that if such artificial degradation was equivalent to 150 y in a museum environment then the degradation was considered as minor, indicating that PE samples potentially have a relatively long life expectancy within collections.

2.3.6 Degradation of polypropylene

The free-radical chain reaction of oxidative degradation (at room temperature) would be extremely slow or almost negligible if the process were initiated by the direct reaction of molecular oxygen with the polymer[17]. The endothermic nature of the reaction means that for most polymers it would not be kinetically or thermodynamically favourable, so without any other source of radicals the process of oxidation would not be considered as harmful. However, Kelen[17] reported that the likelihood of the direct reaction between molecular oxygen and the polymer was substantially increased when the polymer contained reactive H atoms. This was the case for polypropylene which has relatively low oxidative stability due to the presence of reactive tertiary C atoms in each monomeric unit[17]. The reactive H atom on the tertiary C is abstracted by the molecular oxygen since the C-H bond has the lowest bond dissociation energy and is therefore the most suitable reaction site[17]. Free radicals are generated by the direct reaction of molecular oxygen and the polypropylene polymer in the initiation step of the free-radical mechanism of degradation which is shown in the simplified general reaction scheme of Figure 2.19.

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}$$

Figure 2.19. Initiation step of free-radical oxidative degradation

The free radicals ($R^{\bullet}$) which are produced in the initiation step react with oxygen to form hydroperoxy radicals ($RO_2^{\bullet}$)[3, 21, 23]. These radicals then react with more polymer (RH) to produce hydroperoxides (ROOH). The formation hydroperoxides occurs during the induction period and when there is sufficient build-up of them in the propagation stage the rate of oxidation increases (auto-accelerating). The oxidation reaction is also accelerated by the presence of light resulting in the discolouration, embrittlement, surface cracking and reduction in the molecular weight of the polypropylene polymer[61]. Although aliphatic hydrocarbons would not generally be considered as being vulnerable to UV light due to the lack of chromophoric groups, polypropylene is particularly susceptible to light in the region of 290-400 nm due to the presence of impurities in the polymer[62, 63].

The length of the induction period will vary from object to object but depends on the availability of oxygen. In large objects where the polymer is of considerable thickness the diffusion of oxygen in to the bulk of the polymer will affect the length of the induction period[61]. Conversely, thin specimens will have a higher diffusion rate of oxygen and, therefore, a shorter induction period. Polymers such as polypropylene which are known to be susceptible to oxidation and photodegradation may contain large amounts of anti-oxidants and light stabilisers which will increase the induction period[64]. The induction period may also be shortened when the temperature is increased.

2.3.7 Degradation of polystyrene

Polystyrene is an amorphous polymer which enables oxygen to permeate between the chains and it contains tertiary carbons (highly reactive sites for oxidation). Therefore the polymer should be readily oxidised, but in actual fact the polymer is relatively stable[21]. The reason for this is that PS at room temperature is below its glass transition temperature (T_g), which causes chain motion to be restricted because of a lack of free volume (space between the polymer chains)[21]. As a result, the ability of oxygen to permeate the polymers chains is not as great as it may be in polypropylene for instance.

Polystyrene homopolymer strongly absorbs light of wavelengths below 290 nm due to the presence of the benzene ring (chromophoric group)[21]. Despite this, the polymer is relatively stable in UV light since the benzene ring acts as an energy sink and dissipates the energy[21]. The strongly absorbed UV light, especially short wavelengths, will be attenuated as it travels through the polymer. This results in a reactions being concentrated in the surface layers of the polymer, a phenomenon often known as the ‘skin effect’.

There are many examples of modified styrene polymers in modern day use which can be less stable to degradation as a direct result of that modification. For example, high impact polystyrene (HIPS) is a graft copolymer with a structure in which polystyrene forms a backbone and polybutadiene grafts on to the backbone forming branches. The polybutadiene rubber is highly elastic and improves the impact resistance of polystyrene by making more flexible, hence the prefix ‘high impact’ polystyrene. The flexible domains of the polybutadiene grafted on to the polystyrene backbone make it easier for oxygen to diffuse in to the polymer matrix making it more susceptible to oxidation than polystyrene homopolymer[21]. The unsaturated carbon to carbon bonds within the polybutadiene portion are the points where oxidation, ozonolysis and photo-degradation can occur. Therefore, the polybutadiene portion will degrade at a much faster rate than the polystyrene portion of the polymer. So although polybutadiene improves the impact resistance of polystyrene in the short term, over time the degradation of the polybutadiene will cause the polystyrene to become hard and brittle once more and become discoloured.

2.3.8 Degradation of polyurethane

A large proportion of polyurethane plastics in heritage collections are in the form of foams. By their very nature they are susceptible to deterioration since their cell-like structure (approximately 3 % solid material and 97 % air by volume) allows the ingress of oxygen, light and moisture[65, 66]. Polyurethane foams suffer from loss of physical strength as a result of degradation which is manifested as crumbling of the foam structure. Discolouration is also common and often intensifies as the foam object deteriorates. Weeping may also occur and is observable as a sticky residue on the surface of the foam.

The nature and extent of degradation is reliant on a combination of internal and external factors. Internal factors are considered to be characteristic of the polyurethane and its specific formulation. Degradation will likely begin at weak points within the polymer chain, such as the urethane, ester and ether linkages[65]. Chain scission can occur at these weak points leading to cross-linking which reduces the flexibility of the foam causing it to become brittle and easily damaged[65]. The polyol used to make the polyurethane is another important internal factor affecting degradation. Several studies have focussed on the degradation of polyurethane foam and identified that ester based polyurethanes are most susceptible to hydrolysis, whereas ether based polyurethanes are more sensitive to oxidation[35, 66-69]. The presence of additives such as antioxidants and UV-stabilisers will also have a bearing on the process of degradation.

External factors include exposure to light, humidity and heat. Although light is an external factor, the stability of the polymer in light will be dictated by the polymers formulation. The aliphatic diisocyanates are more photo-stable than their aromatic counterparts; therefore, the latter readily discolours. The presence of impurities (which contain chromophoric groups) residual from the manufacturing process will absorb UV light. Furthermore, the products of oxidative degradation, such as carbonyl containing compounds will be capable of absorbing UV light resulting in the discolouration of the polyurethane.

As previously noted, ester-based polyurethanes are most susceptible to hydrolysis with the ester and urethane linkages most vulnerable[70]. Hydrolysis results in chain scission and the creation of a polymer with two or more shorter chains, since the ester will revert to the parent acid and alcohol[13, 35, 70]. This causes crumbling which begins on the exposed surfaces and as the top surface disintegrates from the main object a fresh inner surface is exposed supporting more degradation and so the process continues. The generated acid for each ester group hydrolysed will catalyse further hydrolysis leading to an autocatalytic reaction[71].

Ether based polyurethanes are most susceptible to oxidation which is initiated and accelerated by light and heat[13, 72]. In the thermo-oxidation of ether based polyurethanes the hydrogen on the carbon in the alpha position to the ether linkage is abstracted[70, 73]. Oxygen then reacts with the newly formed radical and results in the formation of hydroperoxy radicals. Another hydrogen is then abstracted from the remaining polymer chain by the hydroperoxy radical to form hydroperoxides (ROOH), which in turn can decompose to produce more free radicals to further feed the process of the free-radical degradation mechanism. The photo-oxidation of polyurethanes is still an area open to debate. The first potential mechanism reported that aromatic diisocyanates methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) were photo-oxidised via a quinoid route[13, 70, 74]. The resulting quinone-imide structure is an effective chromophore causing yellowing of the polymer[13]. The second potential mechanism was urethane bond scission, which could take place in one of two positions. The first was the carbon to nitrogen bond; scission in this location would result in the formation of an amino radical and a formate radical[13]. Further breakdown of the formate radical resulted in the liberation of carbon dioxide and the generation of an alkyl radical. The second was the carbon to oxygen bond; scission at this bond would result in the formation of a carbamyl radical and an alkoxy radical. The carbamyl radical can decompose to generate carbon monoxide and an amino radical. The third potential mechanism was a rearrangement, the product of which may undergo further degradation to produce azo-containing compounds[13].

A study by Lovett and Eastop[69] used accelerated ageing experiments on samples of new ester based polyurethane foam to learn more about degradation processes. The samples were maintained at 70 °C and exposed to variable humidity and oxygen environments. The samples were monitored at regular intervals over a period of 4 weeks to record the physical changes, such as discolouration and crumbling. The results demonstrated that samples had a progressive discolouration from mild to severe as the level of humidity increased. Samples ranged in colour from the original white of the control sample, to yellow in the low-medium humidity samples and brown in the samples which were exposed to 100 % humidity. Furthermore, the beakers of solution used to control the relative humidity had also discoloured. When tested, it was noted that the pH of the solutions had reduced from pH 7 to pH 3, which was assumed to be as a result of acidic volatiles being released during the hydrolytic degradation of the polyurethane samples. The samples exposed to varying oxygen levels demonstrated much less discolouration. The results of the study show that hydrolysis is the primary degradation pathway of ester based polyurethane[69]. Hydrolytic degradation breaks the weak ester bond to form an alcohol and an acid. The acid can then further catalyse ester hydrolysis and the reduction in chain length results in crumbling[70]. At high humidity the degradation is severe, creating chromophores which are the cause of the colour change of the sample[69]. The authors proposed a series of recommendations for the care of artefacts containing polyester based polyurethane foams, which include storing such objects in low relative humidity- provided it has been ascertained that the object is ester and not ether based. The emission of acidic volatiles during degradation means that other objects vulnerable to acid should not be stored in close proximity to degrading ester based polyurethane. Furthermore, the authors recommend against storing actively degrading ester polyurethanes in a sealed environment as the acidic products will accelerate the rate of degradation.

2.3.9 Degradation of polycarbonate

Although polycarbonate is considered a tough polymer and is used in many applications, such as automotive parts, digital data storage (CDs and DVDs) and as a safer alternative to glass, it does degrade as a result of exposure to sunlight, oxygen and humidity. Many studies have examined the degradation of non-stabilised polycarbonate through simulated (accelerated) ageing to mimic outdoor exposure in order to make more accurate lifetime predictions and to understand the complex degradation mechanisms[25, 75-83]. Discussions are still on-going with regards to the chemistry of the degradation mechanisms. In addition, concerns have been raised regarding the wavelengths of light used to irradiate samples in sunlight simulation experiments and whether they are realistic since wavelengths less than 290 nm from sunlight are blocked by the ozone layer.

The studies involving simulated ageing have shown that photodegradation of polycarbonate may proceed by different chemical pathways depending on the wavelength of light used to irradiate the polymer. It has been shown that polycarbonate irradiated with short wavelength UV light of 254 nm induces photo-Fries chemistry[83, 84]. Irradiation with a longer wavelength of light (>310 nm) was shown to induced photo-oxidation reactions[79, 83]. The shorter wavelength (λ=254 nm) will be absorbed by the chromophoric aromatic carbonate groups which will result in the scission of the CO-O bond to form two radicals. Then two successive photo-Fries rearrangements take place forming phenylsalicylate and dihydroxybenzophenone units[79, 83]. Pickett[83] reported that the photo-Fries rearrangement was only effective below 290 nm, which is not realistically expected in natural sunlight. There is ambiguity as to whether the products of photo-Fries will promote photo-oxidation. Speculation within literature of the role photo-Fries products in subsequent reactions is contradictory and still not fully elucidated. Photo-oxidation is possible upon irradiation with longer wavelengths (>310 nm) and although some researchers consider the initiation of the reaction to be as a result of UV light absorption by chromophoric impurities, others believe that the reaction is initiated or influenced by a photo-Fries process[79]. The photo-initiated oxidation of polycarbonate is reported to involve direct hydrogen abstraction from the gem-dimethyl side chain to form radical species[79]. A free-radical reaction of oxidative degradation proceeds terminating in the formation of alcohols and ketones[79, 85]. Regardless of the effect that photo-Fries products may have on the mechanism, the degradation will ultimately cause yellowing and a decrease in physical properties of the polymer.

Polycarbonate is also vulnerable to hydrolytic degradation, as examined in a number of studies[81, 82, 86-88]. The reaction of polycarbonate with pure water is very slow, though the reaction is catalysed by acids and bases, which may be left over from the manufacturing process at low concentrations, or from the degradation of additives, or from monomer impurities[25]. Since the carbonate linkage is part of the main chain, hydrolysis results in chain scission which causes a rapid loss of mechanical strength which will be indicated as a network of cracks within the polymer[21]. T. B. van Oosten[68] outlined an example of hydrolytic degradation of a polycarbonate which occurred in a Dutch museum. The polycarbonate was used as a protective frame construction to cover some prints that were on display in a gallery which did not possess any form of climate control. Within two years of installation curators noticed that the polycarbonate frame displayed crazing. It was later noted that the prints were hung against a cold wall and that the temperature difference between the cold wall and warm gallery may have encouraged the migration of moisture into and then out of the polycarbonate sheet each day and night. Over the course of the two years, moisture migrated in to the bulk of the polymer enabling hydrolytic degradation.

Golovoy and Zinbo[81, 82] reported that as the temperature and relative humidity increased the equilibrium water sorption of a range of polycarbonate samples also increased. The equilibrium water sorption is defined as the percentage weight gain of polycarbonate samples in a temperature controlled humidity chamber where they are exposed to water vapour[81]. They demonstrated the phenomenon of super-saturation which occurs when a polymer at high-temperature equilibrium is cooled down to room temperature[82]. The authors conducted this experiment by immersing the polycarbonate samples in a water bath at 100 °C and then transferring them to water of room temperature. Super-saturation causes the generation of aqueous microcavities within the polymer which are visually apparent. The authors highlighted that thermal cycling of polycarbonate in a high humidity environment, rather than immersion in aqueous media, may also result in the formation of microcavities. Linking back to the example of polycarbonate degradation in the Dutch museum, the constant thermal cycling of the polycarbonate frame in the microclimate of the gallery and the presence of uncontrolled humidity would result in the absorption and loss of water[82]. This repeated action most likely resulted in the formation of microcavities which were then activation sites for cracking causing a loss of mechanical strength in addition to the hydrolytic action causing chain scission[82].

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CHAPTER 3

ANALYTICAL TECHNIQUES

Contents of Chapter 3

3 Analytical techniques

3.1 Infrared spectroscopy[1-4]

Infrared (IR) spectroscopy is a technique that uses radiation in the infrared region of the electromagnetic spectrum to identify functional groups present within a sample. The IR region of the electromagnetic spectrum ranges from the red edge of the visible spectrum at 700 nm to the microwave region of the spectrum at 1 mm. The region can be subdivided in different ways, though the most commonly recognised scheme splits the IR region into three portions: near-IR, mid-IR and far-IR. The mid-IR (4000-400 cm^{-1}) region is used, as in this research, to study the fundamental vibrations within molecules since the strongest absorptions occur in this region.

Wavenumber, the reciprocal of wavelength ($1/\lambda$), is commonly expressed in cm^{-1} and is the typical convention used in IR spectroscopy. An IR spectrum is a plot of wavenumber against absorbance and denotes how much light was absorbed by a sample at a particular wavenumber. By convention, wavenumber always decreases along the length of the x-axis (4000 $cm^{-1} \rightarrow$ 400 cm^{-1}).

The amount of light absorbed by a sample can be calculated using the following equation:

$$A = \log\left(\frac{I_0}{I}\right)$$

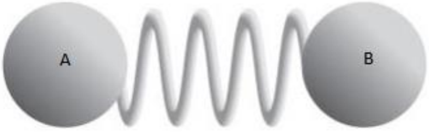
Where A= absorbance, I_0= intensity in background spectrum and I= intensity in sample spectrum.

Molecules will absorb IR radiation when the incident radiation has a frequency equal to that of the natural molecular vibration. In other words, the energy absorbed will be equal to the energy difference between one vibrational state and another. Bonds vibrate with specific frequencies, which is analogous to the behaviour of a vibrating spring. Hooke’s law can be applied to determine the frequency of a bond vibration.

A simple model to describe the law is outlined below (Figure 3.1) and consists of two masses (A & B) connected by a spring.

Hooke's Law

$$v = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$



Where v = vibrational frequency, c = velocity of light, K = force constant of bond between A & B and μ = the reduced mass of A & B

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Figure 3.1. Hooke's law

The frequency of the bond vibration for the diatomic molecule in Figure 3.1 is related to the mass of atoms A and B and the strength of the bond between atoms A and B (analogous to the stiffness of a spring). Examination of the equation of Hooke's law indicates that the smaller the mass of atoms A and B the higher the frequency of vibration. In addition, a strong bond (stiff spring) will vibrate at a higher frequency than a weak bond. In terms of bonds, triple bonds are stronger than double bonds and double bonds are stronger than single bonds, therefore, triple bonds will vibrate with the highest frequency.

The application of Hooke's law to diatomic molecules has limitations. Hooke's law assumes that the energy required to compress a spring is the same as that required to extend a spring; which is known as harmonic motion. In terms of molecular bonds, it is not possible to compress a bond beyond a particular point due to the build-up of repulsive forces from the electron clouds surrounding the two atoms and this results in a rapid increase in the potential energy. During bond extension the bond weakens and will break when the vibrational energy level reaches the dissociation energy (D_E). Once again there is a sharp increase in the potential energy during bond extension. Since molecules do not follow spring like harmonic motion exactly, they are known as anharmonic oscillators.

Figure 3.2 is a potential energy diagram that shows the high potential energy which occurs during bond compression and bond extension that ultimately leads to bond dissociation. The potential energy is lowest when equilibrium (r_e) is established between the attractive and repulsive forces of the two atoms in the bond.

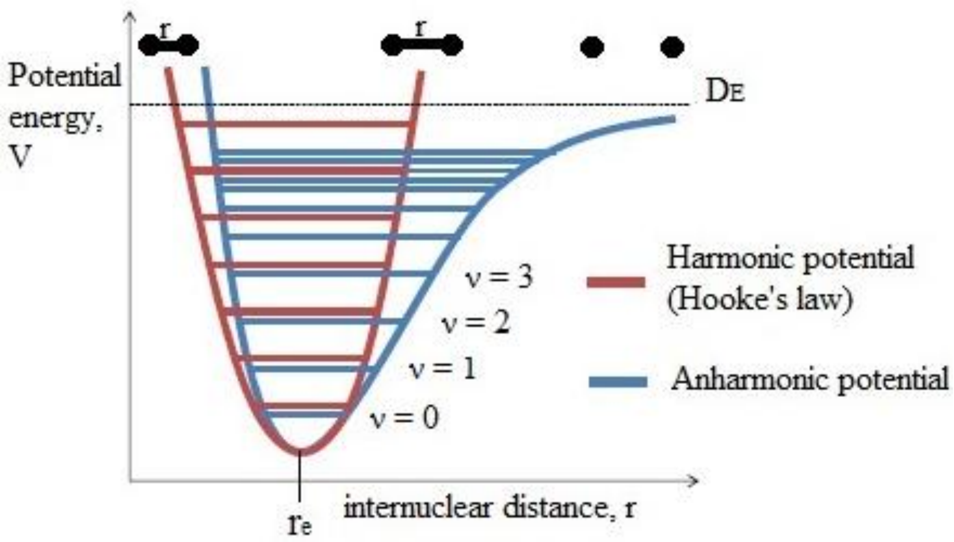


Figure 3.2. Potential energy diagram for diatomic molecule

In harmonic oscillator theory the fundamental transition (most intense) is from levels ν_0 to ν_1 in Figure 3.2. The Boltzmann distribution gives the relative population of molecules in each level and is dependent on temperature. At room temperature, for most molecules, only the lower levels will be populated, which is why the transition from levels ν_0 to ν_1 is most intense. Transitions which occur from levels ν_1 to ν_2, for instance, will be much weaker due to the lower population of molecules in those levels. Furthermore, in harmonic oscillator theory the energy levels are equally spaced and the selection rule indicates that the transition should occur only between levels which are one unit apart ($\Delta\nu = +/- 1$). However, examination of the potential energy diagram (Figure 3.2) demonstrates that in anharmonic potential the energy levels are more closely spaced as the internuclear distance increases, which means that less energy is required for transitions to occur. This creates the possibility for overtones to occur (ν_0 to ν_2 for example). Such transitions break the selection rule and are technically forbidden, however they are possible though they are very weak.

To absorb infrared radiation there must be a change in the dipole moment of the molecule. Dipole moments occur due to the uneven distribution of charge from valency electrons across a heteronuclear diatomic molecule. Molecules can vibrate in different vibrational modes. The number of expected vibrational modes for a molecule containing N atoms can be calculated. Linear molecules have 3N – 5 vibrational degrees of freedom and non-linear molecules have 3N – 6 vibrational degrees of freedom. IR spectroscopy examines a number of possible vibrations that are based on stretching and bending of bonds within a molecule (Figure 3.3). Stretching modes involve a change in bond length and can be either symmetric (in-phase) or asymmetric (out-of-phase). Bending vibrations involve a change in bond angle and include scissoring (deformation), rocking, wagging and twisting.

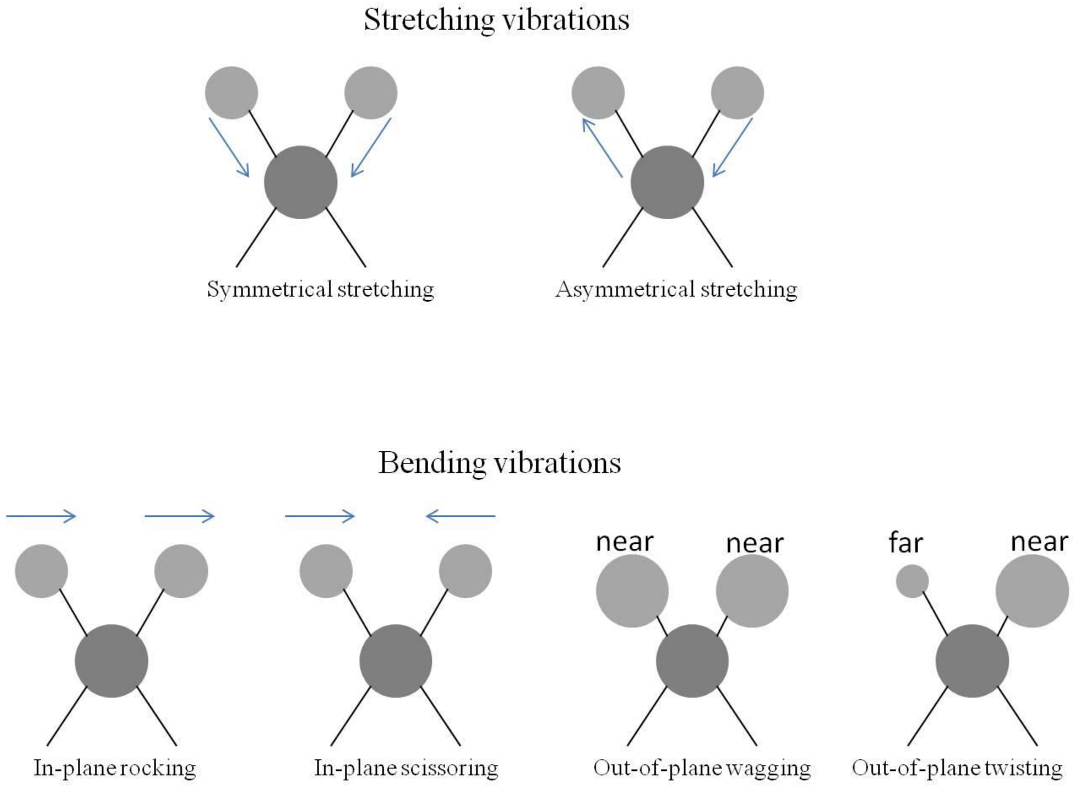


Figure 3.3. Localised vibrations of a methylene functional group

In a complex molecule a range of bending and stretching modes can occur simultaneously giving rise to a complex absorption spectrum that is unique to that particular molecule. Therefore, the interpretation of an infrared spectrum by identification of characteristic absorptions will aid identification of a sample under study.

3.1.1 Fourier transform infrared spectroscopy

In simple terms, the aim of IR spectroscopy is to measure how much IR radiation is absorbed by a sample at a given frequency. The simplest method of doing this is to use a dispersive instrument which employs a monochromator. The monochromator limits the radiation and enables the user to scan through each frequency in turn and measure the amount of radiation absorbed by the sample. Dispersive instruments are slow since the monochromator must scan incrementally through each frequency. To overcome this problem Fourier-transform infrared (FTIR) spectrometers are used and are now more commonly utilised than dispersive instruments. An FTIR spectrometer comprises of three basic components: a source, a Michelson interferometer and a detector.

The source of infrared radiation most commonly used is an ‘air-cooled’ source. It comprises of a nichrome (a non-magnetic alloy of nickel and chromium) wire coil, backed with a mirror to ensure the maximum amount of radiation is directed towards the interferometer[1]. An electrical flow is passed through the wire and due to the high resistance of the wire it becomes very hot, emitting radiation in the mid-IR region.

A Michelson interferometer can split a beam of IR radiation in two and then recombine the two beams once a path difference has been introduced, creating an interference pattern (Figure 3.4)[3]. The interferometer comprises of a beam splitter and two mirrors (one fixed and one adjustable). IR radiation exiting the source is bisected by the beam splitter (a half-silvered 45° mirror so that half the beam is transmitted and half the beam is reflected); two resultant beams are formed at right angles to each other[5]. The two beams travel away from each other on different paths and more crucially they travel different path lengths, since one of the mirrors is moveable the path length of one of the beams can lengthen or shorten compared to the fixed path length of the other beam.

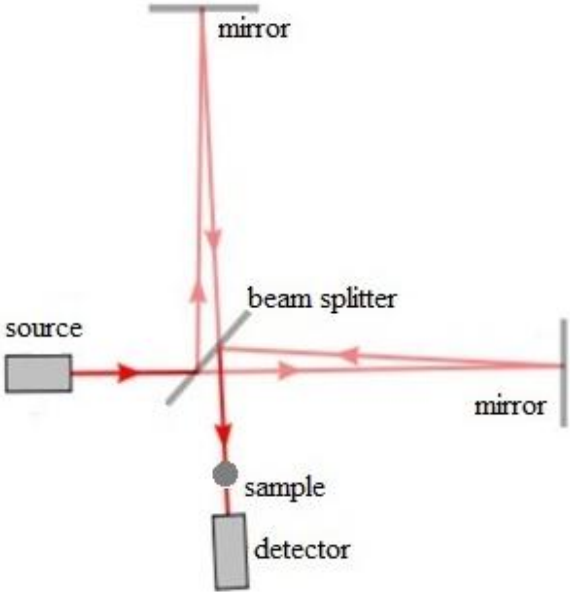


Figure 3.4. A Michelson interferometer

The separated beams reflect from the mirrors and travel back to the beam splitter where the beams recombine. When the two beams recombine the difference in path length between the two beams causes them to constructively or destructively interfere with each other, resulting in a signal called an interferogram. The recombined beam then interacts with the sample (which will absorb some radiation) before travelling to the detector.

The detector needs to convert a light signal to an electrical signal and it does this by way of a detector element. The detector element used in this research was deuterated triglycine sulfate (DTGS). The principle of operation is that the electrical polarisation (or charge distribution) of DTGS varies with temperature which causes a current to flow when the temperature changes[1]. The electrical pulse which is generated is measured by electrical contacts on the surface of the element[1].

The Fourier transform algorithm is needed to convert the interferogram into a meaningful spectrum. The interferogram is a function of the change in path length of the two beams and must be converted in to the frequency domain using the mathematical function[2]. The algorithm contains a number of steps and is conducted by a computer software package.

There are various advantages of FTIR over dispersive spectrometers. Since FTIR spectrometers have only one moving part (one adjustable mirror), the instrument is subject to less mechanical wear than dispersive counterparts. All frequencies of IR radiation are recorded simultaneously (Felgett's advantage), rather than incrementally as in dispersive instruments which means that one scan can be collected within a second. Using multiple scans increases the sensitivity since the signal-to-noise ratio is directly proportional to the square root of the number of scans taken. Since there are no diffraction gratings or prisms the resolution is not limited meaning there is greater optical throughput (Jaquinot's advantage) in FTIR spectrometers. Since the data is in a digital form, specialised software can be utilised to manipulate and examine spectra.

3.1.2 Attenuated total reflectance- Fourier transform infrared spectroscopy

In attenuated total reflectance (ATR) the IR radiation is directed through a crystal of high refractive index and encounters the boundary of a sample of lower refractive index[1]. The incident radiation approaches the boundary between the crystal and the sample at an angle, which is referred to as the angle of incidence. When the incident radiation encounters the surface boundary, some of the radiation will be refracted out of the crystal and into the sample and some will be reflected off the internal surface of the crystal (Figure 3.5).

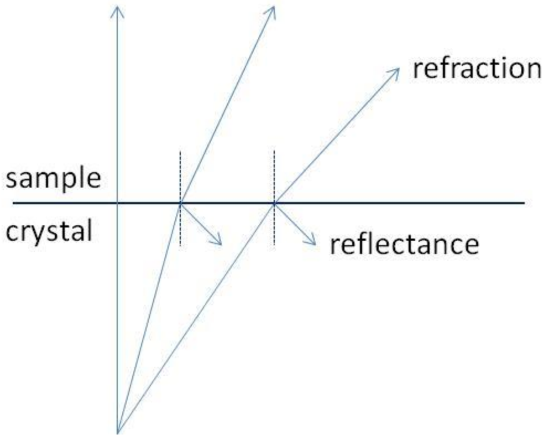


Figure 3.5. Interaction of light with a crystal

The angle of incidence (θ_i) is very important and dictates by how much the incident radiation will be refracted or reflected. At a particular angle of incidence the angle of refraction (θ_r) will reach 90°, which means that the beam will no longer be refracted out of the crystal but will be reflected from the internal surface of the crystal and stay within the crystal. When this occurs it is known as total internal reflectance. There is a minimum angle of incidence which must be reached in order for total internal reflectance to occur; it is known as the critical angle (θ_c). At all angles above this critical angle ($\theta_i \geq \theta_c$) total internal reflection will take place (Figure 3.6).

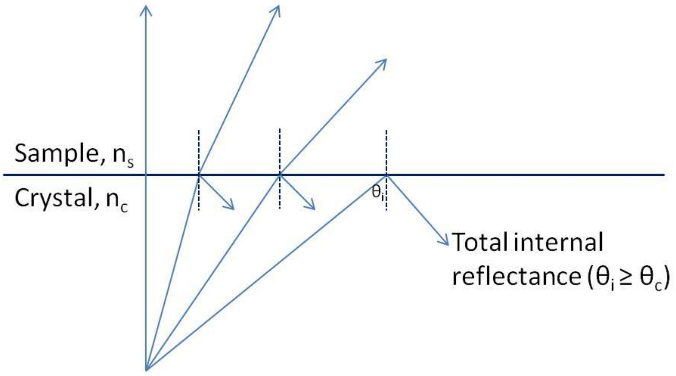


Figure 3.6. Total internal reflectance

The critical angle is dependent upon the refractive indices of the crystal (η_c) and the sample (η_s). It can be calculated by the rearrangement of the equation given by Snell's law, which states that:

$$\eta_c \sin \theta_i = \eta_s \sin \theta_r$$

Where θ_i is the angle of incidence and θ_r is the angle of refraction. Rearranging Snell's law gives:

$$\sin \theta_i = (\eta_s / \eta_c) \sin \theta_r$$

The above equation can be simplified by remembering that at the point of total internal reflection the angle of refraction (θ_r) is equal to 90°; therefore the critical angle has been reached. So the angle of incidence must be equal to the critical angle ($\theta_i = \theta_c$).

Since θ_r is equal to 90° and:

$$\text{Sin } 90 = 1$$

The equation can be rearranged and it is possible to solve for the critical angle (θ_c).

$$\theta_c = \sin^{-1} (\eta_s / \eta_c)$$

Therefore total internal reflectance occurs when the refractive index of the crystal is higher than that of the sample ($\eta_c > \eta_s$) and when the angle of incidence is greater than the critical angle ($\theta_i > \theta_c$). The sample cannot have a refractive index higher than that of the crystal since fundamentally the sine of an angle cannot be greater than 1. In such a case total internal reflectance would not occur. An example of this would be using a diamond crystal ($\eta = 2.4$) to analyse a sample of carbon black filled rubber ($\eta > 2.4$), total internal reflectance is not possible. A crystal of with a higher refractive index, such as germanium ($\eta = 4$), would need to be used.

Sample information is obtained by an evanescent wave which is formed as a result of total internal reflectance. The evanescent wave extends beyond the crystal surface and into the sample, penetrating the sample surface by a few microns (0.5-5 µm). This occurs because at the point of internal reflection, on the crystal surface, the inbound and outbound IR beams occupy the same volume and interact with each other undergoing constructive interference[1]. This increase in amplitude causes the wave to penetrate into the sample (Figure 3.7). Since the evanescent wave penetrates the sample by a very small amount, it is imperative that the sample is held in very close contact with the crystal. When the sample absorbs IR radiation the evanescent wave which penetrates the sample will be altered since some of the radiation has been absorbed, this is known as attenuation. The remainder of the evanescent wave exits the opposite end of the crystal and is passed to the detector. Single reflection (single bounce) ATR accessories are common and are suitable for polymer analysis, though multi-bounce systems are also available which provide increased sensitivity.

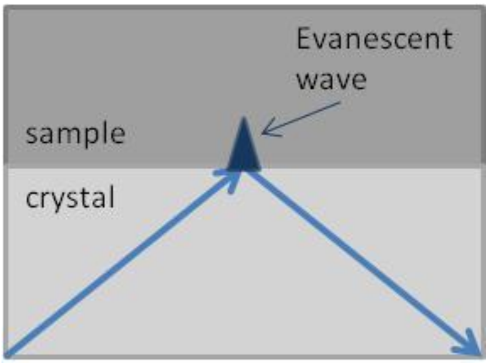


Figure 3.7. Single reflection ATR

It is important that the refractive index of the crystal be much higher than that of the sample or total internal reflectance will not occur. There are various crystal materials available, though diamond is commonly used due to its durability and chemical inertness. The computer interface which is used to control the ATR-FTIR generally contains a spectral library which can be used to identify the sample under analysis.

3.1.3 Principal component analysis (PCA)

A method of determining correlations in spectral data sets is to use PCA which describes the data, not by wavenumber, but using a smaller number of 'latent' variables, called principal components (PCs). The PCs, obtained from the original data must reflect the underlying structure of the data, both in terms of the relationships between the different measured samples (herein polymer samples) and the relationship between the different measurement variables (e.g spectral wavenumber). Comparison of the samples' PCs will permit easy detection of correlations between samples and / or their original variables.

To start with the data can be represented as a matrix (X). The matrix contains N rows which represent the different samples and K columns which represent the variables. The matrix can be considered as comprising of two components: (i) the underlying structure (systematic variation) in the data and (ii) random fluctuations, termed noise, due to the sampling procedure. The data matrix is represented as:

$$X = M + E$$

Where M represents the 'model' or underlying structure of the data, and E is the noise or random fluctuations. Both M and E have dimensions N x K, therefore, the result of PCA is that model matrix M can be reduced to two smaller matrices, T and P, such that:

$$M = T \times P$$

Therefore,

$$X = (T \times P) + E$$

Where T is known as the scores matrix which highlights any sample patterns, and P is termed the loadings matrix which describes any relationships between the individual measurement variables. Provided that E contains noise only, then T and P (the scores and loadings matrices, respectively) will fully describe the structure of the original data matrix. Overall, PCA produces a model which has fewer latent variables than original variables, but with no loss of information.

3.2 Collection of volatile organic compounds by air sampling methods

Solid sorbents are available in three forms: inorganic sorbents (e.g. silica gels), carbon based porous sorbents (e.g. activated charcoal) and porous polymer sorbents (e.g. poly(2,6-diphenylphenylene oxide)). The amount of a given compound which can be adsorbed depends on the surface area of the sorbent and the polarity of the surface determines the type of compounds which can be collected. To collect volatile organic compounds (VOCs) from an air stream, a sorbent commonly used is poly(2,6-diphenyl phenylene oxide), known as the registered trademark Tenax® (Figure 3.8). It is suitable for sampling a wide range of VOCs with a boiling point greater than 60 °C including most non-polar VOCs, aldehydes (>C_4), acids (>C_3), terpenes and slightly polar VOCs.

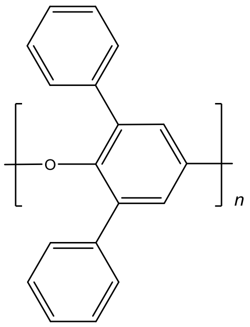


Figure 3.8. Tenax® (poly(2,6-diphenyl phenylene oxide))

The sorbent is packed in to stainless steel sampling tubes, which are commercially available (Perkin Elmer, USA). The sampling tubes are 8.9 cm in length and 0.64 cm in diameter and contain 100 mg of Tenax sorbent, held in the centre of the tube by small stainless steel separating sieves. The benefit of Tenax sorbent is that it has a low affinity for water and does not require the use of solvents to desorb the VOCs from the sorbent for analysis.

Two sampling methodologies are possible when sampling VOCs emitted by plastic objects when using Tenax sampling tubes: active and passive sampling. Active sampling involves actively drawing air through the sorbent bed in order for VOCs to be trapped. Air can be drawn by the mechanical action of a hand pump in the most basic of set-ups or by the use of a flow controlled electric pump. Active sampling is a rapid method which may take only a few minutes, or a few hours, to collect air samples. This type of sampling is useful when a large sample volume is required. There are drawbacks to this type of sampling within a heritage environment. Firstly, sampling in an enclosed space such as an object display case may cause a dilution effect since air from the gallery will be drawn to replace the air drawn through the pump. It is therefore recommended that no more than 20% of the volume of the enclosure be extracted. Pumps take up space and sampling in a confined display case can be difficult. In addition, institutions need to consider how the noise of the sampling pumps or their visibility would impact on the experience of the visiting public. Pumps may be battery operated or mains supplied, if the latter were to be used then access to mains electricity would be required and trip hazards for cables would need to be assessed.

To overcome many of these problems passive sampling may be used. In this type of sampling the VOCs are allowed to diffuse into the sampler and be trapped on the sorbent. The drawback to this technique is that long sampling times are required, often up to 28 days, which creates the possibility for highly volatile VOCs to be trapped and then lost again if they do not have a strong interaction with the sorbent causing the potential for an underestimation of very volatile compounds. Therefore passive samplers are most suited to monitor the mean concentration rather than the peak concentrations of compounds. Despite these drawbacks passive sampling is often the method of choice when sampling within heritage institutions. Using the sampling tubes in passive mode means that no pump is required. Not only does this mean that the tubes are relatively discrete, but there is no associated noise and no requirement for mains electricity. The lack of a pump and the space it would have consumed allows multiple tubes to be deployed in one area. The set up times are extremely quick and enable conservators to place the sampling tubes in display cases with minimal fuss and minimal impact to the equilibrium of the air to be sampled.

After sampling, the collected VOCs are transferred to a gas chromatograph coupled to a mass spectrometer. At elevated temperatures the sorbent becomes ineffective at retaining adsorbed compounds. Therefore heating the tubes releases the trapped VOCs which are then carried by a continuous stream of inert carrier gas into the gas chromatograph- a technique known as thermal desorption. Thermal desorption is useful since no sample preparation is necessary, there is no interference from a solvent and there is the potential for automation.

In this study a form of active sampling was used in the collection of VOCs from the reference plastic samples which was part of the method development. The field testing of catalogued heritage objects used passive sampling only.

3.2.1 Diffusion theory

In passive sampling, VOCs travel by molecular diffusion from an area of high concentration (area being sampled) to an area of low concentration (inside the sampling tube). In practice it is assumed that at the sorbent surface there is essentially a concentration of zero. Calculation of the vapour phase concentrations of VOCs is possible and may often be quoted as a ‘per toluene equivalent’ concentration. An equation derived from Fick’s law of diffusion can be used to calculate the concentration (C) of a specific VOC in the sampled environment.

$$C = \frac{ML}{D_{1,2}At}$$

Where M is the mass (per toluene equivalent) of VOC collected (µg), L is the length of the diffusion tube (m), $D_{1,2}$ is the diffusion coefficient of the VOC in air (m^2s^{-1}), A is the cross-sectional area of the diffusion tube (m^2) and t is the sampling/exposure time (s).

This calculation is commonly used to determine the concentration of a compound collected using simple Palmes diffusion type sampling tubes. Such tubes have an opening at one end and the sorbent (trap) at the other end of the tube and are often used to collect a small number of specific compounds (e.g. acetic and formic acid). This study used thermal desorption tubes, which work on the same principle, except that the sorbent is in the centre of the tube and both ends of the tube are open for diffusion, Figure 3.9, meaning that there are two diffusion lengths. In addition, thermal desorption tubes containing Tenax sorbent are capable of collecting a large number of VOCs compared to the more traditional Palmes diffusion tubes. In effect, the thermal desorption tubes can be considered as two diffusion tubes used in parallel.

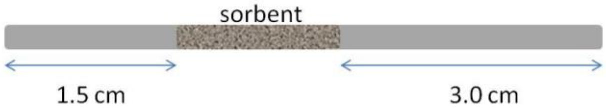


Figure 3.9. Thermal desorption tube containing Tenax sorbent

The sampling rate for each end of the sampling tube can also be calculated from Fick's first law

$$S_R = D\left(\frac{A}{L}\right)$$

Where A is the cross-sectional area, L is the diffusion length and D is the diffusion coefficient of a specific VOC. Using the diffusion coefficient of toluene as an example and combining the sampling rate for each end of the tube, the total sampling rate equals approximately 2.4 L d^{-1}.

There are some points for consideration when choosing the type of passive sampler for a sampling campaign. In the early days, the main reason for conducting indoor air sampling was to determine what vapour phase compounds company personnel may be exposed to. With this in mind, many of the early samplers were badge type samplers intended to be worn by personnel to monitor their exposure to specific compounds. Such badge type samplers had problems associated with the effects of air velocity. In areas of low air velocity there is the potential for laminar boundary layers to exist. The stagnant air surrounding the face of sampling tube will, in effect, increase the diffusion length causing an underestimation of the concentration of VOCs. Conversely, in areas of high air velocity eddy diffusion is possible. In this case VOCs are effectively pushed in to the entrance of sampling tube after which they start to diffuse along the tube. This essentially shortens the diffusion length and results in an overestimation of the concentration of VOCs. However, when the ratio of the diffusion length to the cross sectional area of the sampling tube is greater than 3 the effect of eddy diffusion or laminar boundary layers is not significant[6]. Therefore, most modern sampling tubes, such as the thermal desorption tubes used within this study, are manufactured to exceed this ratio in order to overcome the problems associated with air velocity[7].

3.2.2 Micro-chamber/thermal extractor™ [8]

The micro-chamber/thermal extractor™ (µ-CTE™) (Markes International, Llantrisant) offers a rapid means of sampling VOCs from polymers (and many other materials). Multiple samples can be tested simultaneously with no need for sample preparation and depending on the configuration of the instrument, surface or bulk emission testing can be conducted. The instrument within this study was configured for bulk emission testing and complied with ASTM D7706-11 standard method for the rapid screening of VOC emissions from products.

The µ-CTE™ (model M-CTE120) instrument (Figure 3.10) was capable of operating between 23 °C and 120 °C and contained six individual stainless steel micro-chambers (44 cm^3 interior volume) which were simultaneously flushed with clean dry air preheated to the same temperature as the chambers. Each chamber exhaust point was connected to a Tenax sampling tube to collect VOCs that had accumulated inside each emission chamber containing the sample during the equilibration period. The instrument maintained a constant flow of air through the chambers, regardless of the impedance of a sampling tube, using a unique flow controller.

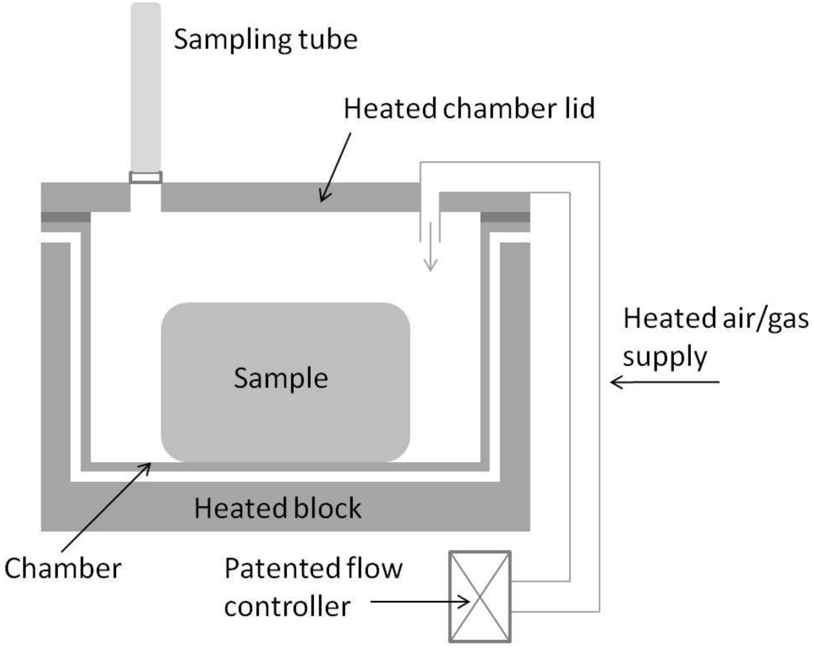


Figure 3.10. Micro-chamber/thermal extractor™

All the micro-chamber components were heated (including chamber, chamber lids and gas/air tubing) which prevented surface adsorption/condensation. The internal surfaces of the chamber and lid were inert coated steel which minimised sink effects and made the instrumentation suitable for thermally labile species. The air/gas inlet is orientated to be perpendicular to the surface of the sample in order to maximise turbulence within the chamber and surface are velocities are approximately uniform across the sample surface. VOCs collected on to thermal desorption tubes were then subsequently analysed using thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS).

3.3 Introduction to chromatography

The physical separation of chemical analytes in a complex mixture is known as chromatography. Mikhail Tswett (also Tsvet) is credited with the invention of chromatography circa. 1900 which he used for the separation of plant pigments by passing solutions of pigments through calcium carbonate packed columns[9, 10]. As the solutions separated there were well-defined coloured bands which appeared on the column. The coloured bands were the inspiration for the name chromatography since from the greek *chroma* means ‘colour’ and *graphein* means ‘to write’[10].

In chromatography the analytes in a mixture that are to be separated are distributed between two phases. The analyte mixture is carried by a flow of gas or liquid (known as the mobile phase) through or over the stationary phase during separation. The analytes are separated based on the differences in the rate of migration between the individual analytes within the mixture. Chromatography may be classified as planar or column chromatography, however this thesis will focus solely on the latter chromatographic method.

Column chromatography involves the use of a column (a narrow bore tube) which contains the stationary phase through which the mobile phase (gas or liquid) is driven under pressure or in some cases by gravity. Classification of the chromatographic method is based on the nature of the mobile phase. When a liquid mobile phase is used the chromatographic method is classed as liquid chromatography. This type of chromatography is commonly used for the separation of analytes which are of low molecular weight, low volatility, low thermal stability or which may be ionic in nature. When a gas is used as the mobile phase the method is classified as gas chromatography. This type of chromatography is well suited for the separation of analytes which are reasonably volatile, have low molecular weight and high thermal stability (so that the analytes can be vaporised without decomposition).

An analyte mixture which enters in to a column will distribute itself between the two phases (mobile and stationary phase). The analytes within the mixture will have different relative affinities for the stationary and mobile phase and will travel through the column at different rates as a result. Therefore, those analytes which have a strong affinity for the mobile phase will migrate through the column with the mobile phase and will exit the end of the column first. Analytes which have an affinity for the stationary phase will be retained longer and will move slowly through the column and exit the column later. When the separated analytes exit the column they are said to have 'eluted' from the column. As the separated analytes elute from the column they will pass by a detector which records a signal and plots the intensity of that signal as a function of time, which creates a peak for each analyte on a plot known as a chromatogram. Ideally, chromatographic peaks should have a Gaussian distribution giving symmetrical peaks.

3.3.1 Gas chromatography

There are two forms of gas chromatography (GC): gas-liquid and gas-solid chromatography. However, it is the former that is most pertinent to this thesis. In gas-liquid chromatography (often just shortened to gas chromatography), the mobile phase is a gas and the stationary phase is a liquid or gum which is coated on to an inert solid support by chemical bonding or adsorption. A schematic of a general GC system is outlined in Figure 3.11. Typically, the sample under analysis (solid, liquid or gas) is introduced in to chromatographic system by some means via the sample inlet, vaporised and directed on to the column for separation. Each of the components within the GC system will be discussed in further detail.

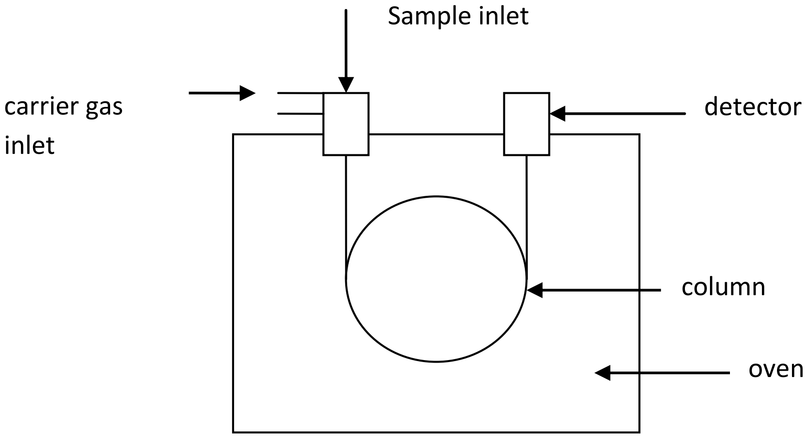


Figure 3.11. Main components in a GC

The mobile phase, more commonly referred to as the carrier gas, needs to be chemically inert. Typical carrier gases include nitrogen, argon or helium, with the latter the most commonly used.

Sample introduction may be conducted in several ways, the most common and simple method is the injection of a liquid sample via micro-syringe, which can be done manually or with the use of auto-samplers. Sample volume can vary between instruments; however a sample in the order of a few micro-litres is typical. Solid samples may also be analysed, they can be made in to solution and injected in to the sample inlet or they may be pyrolysed using additional instrumentation. The injection port is generally heated (to at least 50 °C above the boiling point of least volatile component of the sample mixture) to vaporise liquid samples before the mobile phase (carrier gas) carries the analytes on to the column for separation. Gas (head-space) samples may be collected by gas syringe and injected in to the sample inlet in much the same way as liquids. Solid phase micro extraction (SPME) is another method of sample introduction. SPME involves extracting volatile and semi-volatile analytes of interest from a sample (solid, liquid or gas) onto a chemically modified fused silica fibre, housed within a hollow needle. After sampling the fibre can be inserted in to the heated injection port of the GC instrument where extracted analytes can be desorbed from the fibre and analysed. In this technique the SPME fibre may be dipped in to a liquid or suspended in the head-space above the liquid, exposed to an environment or may be in direct contact with the sample.

The sample introduction technique most pertinent to this research is thermal desorption tubes containing a solid sorbent on to which volatile and semi-volatile analytes are collected before being thermally desorbed and directed into a GCMS instrument. Specialised instrumentation is required to introduce sample analytes in to a GC system from thermal desorption tubes. A thermal desorption unit (TDU) is coupled to the GC instrument and thermally desorbs volatiles from the solid sorbent by heating the desorption tube in a stream of inert gas carrier gas. As the sorbent heats up, the volatiles are desorbed and transferred by the gas stream on to a cold trap at –30 °C. The volatile analytes cool and condense on the trap, after which the trap heats extremely rapidly and analytes are transferred with the carrier gas as a focussed band onto the GC column for separation.

Columns are typically of the packed, or capillary, variety and differ in the way that the liquid stationary phase is supported on the column. In packed columns the liquid stationary phase is coated on to small particles which are packed in to the glass column. Capillary columns are available in two forms: wall coated open tubular (WCOT) and support coated open tubular (SCOT). WCOT columns have the stationary phase applied directly on to the inside wall of the column, whereas in SCOT columns a thin film lines the inside of the column on to which the stationary phase is coated. In addition, the outside of capillary columns are coated with polyimide to protect them from damage. In both types of column the analytes partition into the organic stationary phase.

Columns may vary in length from a few metres to 50 metres or more and can contain a range of different stationary phases. From the outset the most obvious requirements for a liquid stationary phase include low volatility (boiling point should be a minimum of 100 °C higher than the maximum column operating temperature) and thermally stable. The chemical nature of the stationary phase is important if the analytes are to be suitably partitioned in to the stationary phase. The distribution coefficient or partition ratio (k_A) should not be too small or too large. If the K_A is very small the analytes will not be retained within the column long enough to be separated and if the k_A is too large the analytes will have very long retention times making chromatography inefficient. For chromatography to be successful consideration should be given to the type of column used. Analytes need to be compatible, to a certain extent, with the polarity of the stationary phase. For instance, polar columns which contain functional groups such as –OH and –CO will be suitable for the separation of polar analytes such as alcohols and acids. When there is good compatibility between the polarity of the stationary phase and the polarity of the analytes, separation (or order of elution from the column) will be in the order of increasing boiling point of the analytes. The thermostated oven is therefore crucial for boiling point based separation of analytes. Temperature programming is typically employed to give good resolution and efficient chromatography. Many stationary phases are based on poly(dimethyl siloxane) (Figure 3.12) which is non-polar.

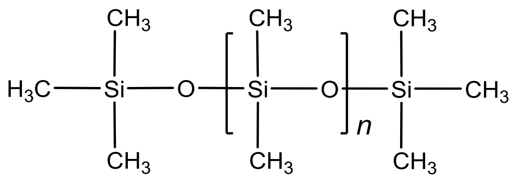


Figure 3.12. Poly(dimethyl siloxane) stationary phase

Modifying the polydimethyl siloxane structure, by removing a small proportion of the methyl groups, will alter the polarity of that stationary phase. For instance, the column used within this research contained the stationary phase 5% phenyl-poly(dimethyl siloxane). In this example, a phenyl group replaces a methyl group on 5% (by number) of the silicon atoms in the polymer and results in a less non-polar stationary phase. So by varying the amount of substitution and the substituent group the polarity can be modified to vary degrees.

3.3.2 Migration rates of analytes

The ability of a column to be able to separate analytes is dependent upon the rates at which the analytes are eluted from the column. Furthermore, the rate of elution is affected by the extent to which the analytes partition between the stationary and mobile phases. When an analyte mixture is introduced onto the column a dynamic equilibrium is established for each analyte in the mixture and remains constant throughout the chromatographic period. For instance, when analyte A is introduced on to the column it will equilibrate between the two phases and can be described as:

$$A_{MP} \rightleftharpoons A_{SP}$$

The equilibrium constant (K) may be known as the distribution coefficient, partition coefficient or partition ratio. It is the ratio of the concentration of a given analyte (A, B or C etc.) in the stationary phase to the concentration in the mobile phase and can be expressed as:

$$K = {}^{[A]_{SP}}\!\Big/\!{}_{[A]_{MP}}$$

Where $[A]_{SP}$ and $[A]_{MP}$ refer to the concentration of analyte A in the stationary and mobile phases, respectively. The larger the value of K the greater the affinity analyte A has for the stationary phase and the longer the analyte will take to pass through the chromatographic system. In order for separation to be effective the distribution coefficients of analytes A, B and C etc. within the mixture should be different.

The time between the introduction of the analyte mixture on to the column and an analyte reaching the detector is known as the retention time (t_R). Depending on interaction with the stationary phase and the flow rate of the mobile phase, each analyte will have a specific retention time. The retention time of an analyte should always be longer than the dead time, also known as void time or mobile phase holdup time, t_M. The dead time is the time taken for an unretained analyte to pass through the column. The retention (or capacity) factor, k, is used to describe the migration rates of analytes on columns and can be expressed as:

$$k = \frac{t_R - t_M}{t_M}$$

When the retention factor of a given analyte is less than one, this indicates that elution is so rapid that accurate determination of retention time is challenging. Equally, when the retention factor is larger (~20 - 30) the elution times are exceptionally long.

Therefore, the ideal retention factor should be in the region of 1- 5 for effective chromatography[10]. The separation (or selectivity) factor, α, may also be used to describe the effectiveness of chromatography. The separation factor describes the separation of two analytes, A and B:

$$\alpha = \frac{k_{\mathrm{B}}}{k_{\mathrm{A}}}$$

Where k_{B} and k_{A} are the retention factors of analytes B and A, respectively. The separation factor (α) can be described as the ratio of the retention factor of the more strongly retained analyte B to the retention factor of the less strongly retained analyte A[10]. The separation factor should be greater than 1 for efficient separation of the analytes.

3.3.3 Column efficiency

The efficiency of separation of a chromatographic column can be described in terms of the number of theoretical plates within the column[11]. This concept assumes that the column contains a large number of separate layers, which are termed theoretical plates. Although they do not physically exist, the concept of theoretical plates aids the understanding of column efficiency. The separation equilibrium of the analytes between the mobile and stationary phases occurs within the plates; therefore, a theoretical plate represents a single equilibrium step. The analytes will pass from one plate to the next down the column. The greater the number of theoretical plates, the better the resolving power (efficiency) of the column. The number of theoretical plates (N) can be expressed as:

$$\mathrm{N} = \mathrm{X}\left(\frac{\mathrm{t_R}}{\sigma}\right)$$

Where t_R is the retention time of an analyte and σ is the peak width (both of which need to have the same units, which may be minutes or millimetres, in order for N to be unitless). The value σ depends on where the width of the peak is measured, which determines the value of X. Measuring the width of the base of the peak (w_b) dictates that X is equal to 16. When the width of the peak is measured at half peak height

(w_h) X is equal to 5.545. Capillary columns such as that used in this study, can have up to 300,000 theoretical plates which makes them much more efficient than their packed column counterparts which only have up to 3000 plates. In a very simplistic fashion the number of theoretical plates can be thought of as the number of times and analyte interacts with the stationary phase. As capillary columns have a very high number of theoretical plates they are suitable for the separation of complex mixtures.

The plate height (H) is a useful way of comparing the efficiency of different columns. It can be expressed as the length of the column (L) divided by the number of theoretical plates (N):

$$\mathrm{H} = \frac{\mathrm{L}}{\mathrm{N}}$$

The plate height should be as small as possible in order to avoid a long column.

3.3.4 Factors that affect column efficiency

The theory of column efficiency in terms of theoretical plates and equilibrium models has limitations since it does not adequately describe the action of separation in a quantitative way. In reality, there are certain factors, such as mobile phase flow rate, which can have an effect on the separation efficiency. Efficient chromatography is demonstrated by the production of sharp, symmetrical chromatographic peaks but such factors can result in a broadening of chromatographic peaks. Band broadening, causing the loss of column efficiency, is the phenomenon of analyte peaks becoming broader as they travel through the column. J. van Deemter demonstrated that band broadening in packed columns is the summation of interdependent effects from various sources[11]. An equation the bears his name expresses plate height (H) as:

$$\mathrm{H} = \mathrm{A} + \frac{\mathrm{B}}{\bar{\mathrm{u}}} + \mathrm{C}\bar{\mathrm{u}}$$

The $\bar{u}$ term is the average linear velocity of the mobile phase and A, B and C are constants for a particular system and are related to three major contributions. The effect of band broadening is much more apparent in packed columns than in capillary columns. The average linear velocity (ū) can be calculated by dividing the column length with the dead time.

$$\bar{u} = \frac{L}{t_M}$$

The A term is caused as a result of the random and unequal pathways that analytes will take through the stationary phase (Eddy diffusion). This term is characteristic of the column packing and is independent of mobile phase velocity. The A term can be minimised by ensuring the particles of the packing are more uniform in size and shape and packed in to the column efficiently, ensuring no voids.

The B term represents longitudinal molecular diffusion of analytes in the mobile phase due to the concentration gradients within the column[11]. The analyte concentration is greater at the centre of the band than at the edge and so an analyte can migrate from the concentrated centre of the band to the more dilute edges. This type of band broadening is common in gas chromatography where the rate of diffusion is high, but of little significance in liquid chromatography since the rate of diffusion is lower in liquid mobile phases. Broadening caused by longitudinal molecular diffusion is inversely proportional to mobile phase velocity. By increasing the flow rate of the mobile phase the effect of diffusion can be minimised since the analytes do not have sufficient time to diffuse from the centre of the band to the outer edges before they are eluted from the column.

The C term is as a result of mass transfer due to the finite time required for analyte distribution equilibrium between the stationary and mobile phases to be established. The quicker equilibrium is established between the two phases the less that broadening occurs. The broadening caused by this term is proportional to the mobile phase velocity. The term can be minimised by reducing the average linear velocity of the mobile phase and reducing the film thickness of the stationary phase.

However, in capillary columns there is no internal column packing and so there is no A term. The Golay equation is a modification of the van Deemter equation and can be expressed as:

$$\mathrm{H} = \frac{\mathrm{B}}{\bar{\mathrm{u}}} + (\mathrm{C_s} + \mathrm{C_m})\bar{\mathrm{u}}$$

The B term still applies as it does for the van Deemter equation. However, the C term is now comprised of two contributions, C_s and C_m. The C_s term is similar to that previously described by van Deemter. The C_m term is specific to capillary columns and describes the mass transfer of analytes in the mobile phase. In a simplistic way this can be visualised as the effect of drag, caused by the capillary walls, on the analytes as they pass through the column (Figure 3.13).

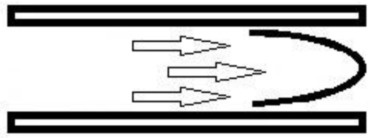


Figure 3.13. C_m term caused by drag of analytes against walls of the capillary column

The term can be minimised by decreasing the rate flow rate of the mobile phase and decreasing the radius of the column.

3.3.5 Mass spectrometry

The separated analytes then pass from the GC column into a mass spectrometer (MS) via a heated transfer line. In the MS molecular ions are created under vacuum in the ionisation process by removing an electron from the analytes. The ions are then separated according to their mass-to-charge (m/z) ratios and are detected and recorded according to their abundance.

As the analytes enter the MS they are ionised by a process known as electron impact ionisation. In this process analytes are bombarded by a stream of high energy electrons (produced by an electron impact (EI) source), which are directed with an electron acceleration of 70 eV towards an anode which is positioned perpendicular to the flow of analytes entering the MS system from the GC[12].

When the electrons collide with the analyte molecules (M), one or more electrons are ejected from the analyte molecules to produce positively charged molecular ions (M^+).

$$M + e^- \rightarrow M^+ + 2e^-$$

$$M^+ \rightarrow X^+ + Y^\bullet$$

The molecular ions can fragment to produce more ions (X^+), radicals ($Y^\bullet$) or neutral fragments, although only ions can be detected by the mass analyser. Since the system is held under vacuum the ions are able to travel to the mass analyser without further collisions. A mass analyser is used to separate the ions according to their mass-to-charge ratio. In this study a quadrupole mass analyser was used (Figure 3.14).

The trajectory of the ions through the quadrupole will vary due to their mass to charge ratio which enables their separation. A quadrupole contains four rods (electrodes), where opposite pairs of rods are electronically connected. The rods are polarised so that only ions of a specific mass-to-charge ratio can successfully pass through the rods and reach the detector on the other side. The travelling ions are focused at the centre of the four rods, the positive ions will be attracted to the negative rods. The polarisation of the rods causes the ions to be deflected as they travel, with ions of low mass deflected off course more than ions of high mass. In addition, the larger the charge on the ion (e.g. +2) the easier it will be to deflect. If ions collide with any of the four rods, their associated charge is lost and they do not make it through the quadrupole to the detector.

To control which ions make it to the detector, the rods have a fixed DC potential applied to them so that one pair of rods act as anodes and the other pair as cathodes[13]. Then two alternating potentials are applied to the two pairs of rods to induce 180° out-of-phase AC potentials across the anodes and cathodes[13]. This causes the ions to move in a helical motion towards the detector. By controlling the ratio of voltages only certain ions of a specific mass-to-charge ratio will reach the detector, all other ions will be deflected and collide with the rods and be lost. By slowly varying the applied voltages stepwise, the instrument can scan through the various mass-to-charge ratios.

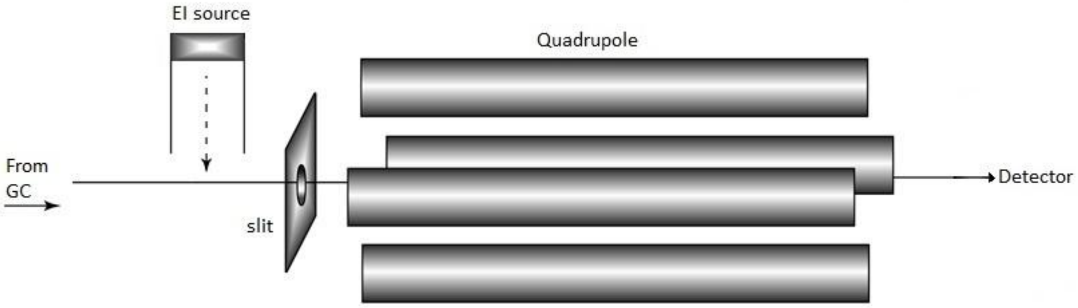


Figure 3.14. Basic schematic of a mass spectrometer with a quadrupole mass analyser

An electron multiplier detector was used in this research and is one of the most widely used detectors within mass spectrometry. When the ions pass from the quadrupole to the electron multiplier they strike a dynode which contains electrode surfaces which are coated in a copper-beryllium alloy[12]. When struck the electrode surfaces release a burst of electrons. These electrons can then go on to strike other dynodes which in turn release more electrons in a cascading fashion, creating an amplification effect. Finally the electrons strike an anode to generate a current and produce a signal.

The mass spectrum which is produced enables the identification of the analytes under study. In electron ionisation (used in this research) the resultant mass spectrum will have only a small amount (if any) of the molecular ion, which will generally appear as the highest mass in the spectrum. This is true provided no other isotopes are present. Using pentane (C_5H_{12}) as an example (Figure 3.15), the molecular ion (M^+) should appear at m/z 72. However, a small peak may also be present at m/z 73 which is as a result of the ^{13}C isotope which is approximately 1.1% abundant. This much smaller peak is known as the M+1 peak and the greater the number of carbons in an analyte the greater the chances of having a ^{13}C isotope.

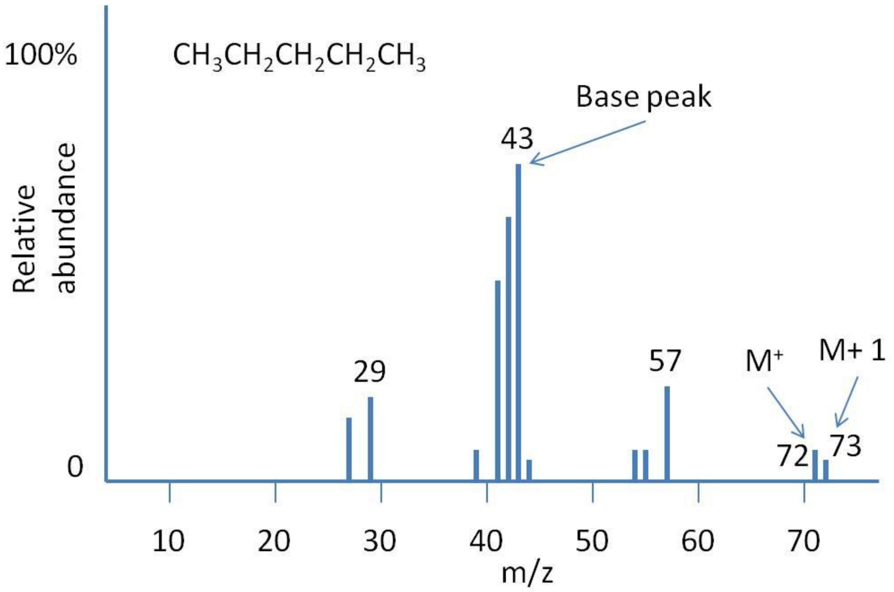


Figure 3.15. Mass spectrum of pentane

The energy used in electron ionisation (EI) is high enough to cause substantial fragmentation, so much so that only a small amount of molecular ion may remain (if at all) and for this reason EI is often referred to as a hard ionisation process. The spectrum in Figure 3.15 is an over simplification since not all mass spectra will have a molecular ion peak. There are many peaks present within a mass spectrum; some of which are produced from the further fragmentation of other fragments. Not all the peaks need to be identified, but there are some key points to note when interpreting spectra.

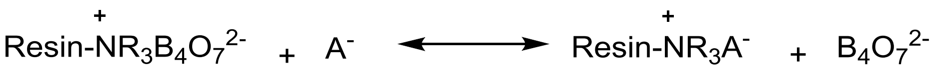
The base peak is the largest peak in the spectrum since it represents the fragment produced in the greatest abundance and is generally given an arbitrary value of 100% relative abundance and all other peaks are measured relative to the base peak. The fragment which is represented by the base peak is either a very stable ion or it can be produced in multiple ways from the fragmentation of the molecular ion. Figure 3.15 shows mass spectrum of pentane, the base peak at m/z 43 which by rough calculation cannot contain four carbons (12 x 4 = 48), therefore assuming 3 carbons (3 x 12 = 36), a mass of 7 needs to be accounted for. It can be deduced that m/z 43 corresponds to $CH_3CH_2CH_2^+$ fragment. In a similar fashion m/z 57 can be calculated as corresponding to $CH_3CH_2CH_2CH_2^+$ and m/z 29 corresponds to $CH_3CH_2^+$. These fragments are the result of simple cleavage and are relatively easy to interpret. In reality it is very time consuming to examine the mass spectrum for each peak in a chromatogram. Fortunately modern GC-MS instruments come with commercial libraries (e.g. the NIST Mass Spectral Library) which contain several hundreds of thousands of mass spectra for comparison. The software which operates the instrument searches the database and enables users to qualitatively identify samples.

3.4 Ion chromatography

Ion-exchange chromatography, often shortened to ion chromatography (IC), is an example of liquid chromatography and operates on the principle of ion exchange[10]. The stationary phase (which is known as the ion exchanger in IC) is an insoluble synthetic polymer resin material which contains fixed charge-bearing functional groups and oppositely charged mobile counter ions. Analytes (ions) are transported through the column by the eluent and are separated on account of their affinities for the stationary phase. Analytes with a weak affinity for the stationary phase will elute first.

The eluent is continuously passed through the system at a constant flow rate by the pump. Eluents containing sodium tetraborate decahydrate are commonly used for the separation of anions[14, 15]. In cation analysis, the eluent is dependent on the type of column used, but may include hydrochloric or sulfuric acid[14, 15]. Throughout this research a Dionex (Sunnyvale, USA) ion chromatograph was employed and will be the basis of the following discussion. The sample injection valve the sample into a sample loop, typical injection volumes are in the region 5-100 µL[16]. The sample then passes through a guard column which attempts to retard the flow of possible contaminants onto the separation column. The guard column is much smaller than the separation column but contains a similar polymeric matrix. After passing through the guard column, the eluent transports the sample onto the separating column.

The separation column contains a synthetic polymer resin produced by the copolymerisation of styrene and divinyl benzene to give a significantly cross-linked and mechanically stable matrix which is stable over a broad pH range (0-14)[16]. The PS/DVB matrix is sulfonated in anion exchange columns to impart an intermediate layer of 10-20 µm. Furthermore, a thin layer of latex particles, which are usually aminated, surround the PS/DVB core. Such anion exchangers are known as latex-agglomerated anion exchangers. These particles provide the groups necessary for anion exchange. For instance, when an eluent containing tetraborate anions is pumped through the anion exchange separation column, the anions will locate the positive charge of the quaternary ammonium groups on the resin matrix by electrostatic attraction so that the quaternary ammonium groups are held in their tetraborate form, thereby keeping the column electrically neutral. When sample anion A^- is injected in to the separating column the sample anion is exchanged for the tetraborate anion on the resin matrix in a reversible equilibrium process (Figure 3.16).



$$\text{Resin-}\overset{+}{N}R_3B_4O_7^{2-} + A^- \longleftrightarrow \text{Resin-}\overset{+}{N}R_3A^- + B_4O_7^{2-}$$

Figure 3.16. Anion exchange

The sample anion will be temporarily retained on the resin matrix for a period of time which is dependent on its affinity for that stationary phase. The eluent anions and sample anions will compete for the stationary phase. Therefore eluent anions will be replaced with incoming sample anions which will, in turn, be displaced by more incoming eluent anions. The anions therefore move down the column via the repeated interaction and displacement action.

Eluent anion efficiency can be estimated based on the selectivity coefficient of the anion for the stationary phase[16]. A high selectivity factor implies that the eluent anion has a strong interaction with the stationary phase and will easily displace sample anions from the surface of the stationary phase. Reduction in the ionic strength of the eluent will increase the retention of the sample anions. Generally, the selectivity coefficient of the eluent anion and the sample anion should be similar so that there is effective competition for the stationary phase sites which will produce reasonable retention times for sample anions. The eluent anions used within this study are tetraborate anions since they have a low affinity for the stationary phase, which makes them suitable for the separation of short chain aliphatic carboxylic acids, such as acetic acid[16]. The effective separation and the order of elution of sample anions are determined by their affinity for the stationary phase. For example, monovalent sample anions will have a weak interaction with the sites of the stationary phase, causing them to move quickly through the column. Divalent and polyvalent anions will be retained longer. Anion size is also important since small anions are able to move through the column more quickly. The degree of hydration of the analyte ion will alter the strength of the interaction with the stationary phase, since a large degree of hydration with shield the ion from the station phase.

A suppressor system is placed directly after the column and enables more sensitive detection by the conductivity detector. The eluent has high conductivity which will reduce the sensitivity of the detector due to low signal-to-noise ratio. This problem can be overcome by the use of a suppressor which is used to chemically suppress the conductivity of the eluent and convert the sample ions in to a more conductive form[16]. By reducing the eluent conductivity, the analyte response on the detector is enhanced. In this research an anion self-regenerating suppressor (ASRS) was used. Unlike the old type suppressors where an external regenerent flow was required to supply the suppressor with hydrogen ions, the more modern ASRS electrolyses water in the system to produce the required hydrogen ions. In a system where sodium tetraborate decahydrate is used as the eluent and the sample is potassium acetate, hydrogen ions are produced at the anode by the electrolysis of water (Figure 3.17). The H^+ ions proceed to move through the sulfonated cation exchange membrane in to the eluent channel. The H^+ ions in the eluent channel combine with the borate ions to produce boric acid (H_3BO_3) which is weakly conducting; therefore the eluent conductivity has been reduced. The potassium ions (K^+) move away from the eluent channel toward the negatively charged cathode and combine with hydroxide ions and flow to waste, therefore the K^+ counter ions of the sample are replaced with H^+ ions.

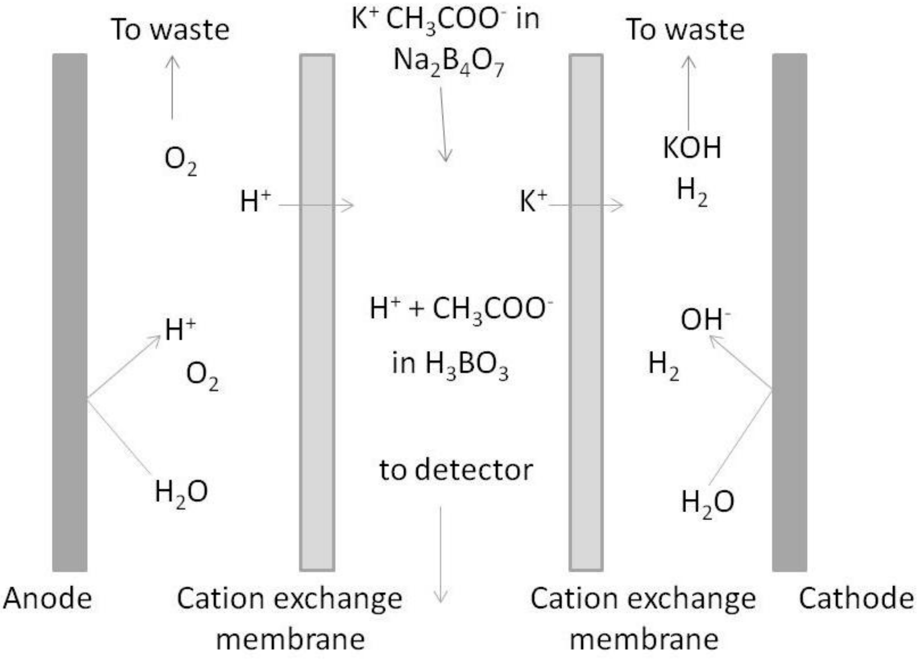


Figure 3.17. Anion self regenerating suppressor (ASRS)

The conductivity detector is the most commonly utilised detector in ion chromatography. The conductivity cell consists of two platinum electrodes which are fixed in position to which an alternating potential is applied. The potential will flow through the ionic solution between the two electrodes with a certain electrical conductance and a Wheatstone bridge is used to measure the resistance of the cell. In the conductivity cell, at any given moment, anions will migrate towards the anode (positively charged) and cations move towards the cathode (negatively charged) and the measured electrical conductivity is given in Siemens per cm (S cm^{-1}). The response of the detector is proportional to the conductivity of ionic solution.

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CHAPTER 4

Collation and assessment of a historical plastic reference collection using attenuated total reflectance-Fourier transform infra-red spectroscopy (ATR-FTIR)

Contents of Chapter 4

4 Collation and assessment of a historical plastic reference collection using attenuated ATR-FTIR

4.1 Infrared spectroscopy for the identification of plastic heritage objects

Within the field of heritage science the focus is very much on the use of non-destructive methods of analysis. Therefore, Fourier transform infrared (FTIR) spectroscopy is commonly used to determine the polymer type within plastic objects[1-7]. If the sample is small and transparent it can be inserted into the IR beam of a conventional transmission instrument. If a larger object is to be analysed sampling would be required however the sample removed from the object can be retained and reanalysed at a later date if necessary.

Thickett and Richardson[2] employed the use of vibrational spectroscopic techniques to characterise plastic objects from the Secret Wartime Tunnels in Dover and the Royal Observers Corps Bunker in York. By removing small samples from areas where a break was already present, the plastic cladding on an XB10 telephone cabinet from the site in Dover was identified. Attenuated total reflectance (ATR) FTIR was used to collect a number of spectra which were subsequently compared with the Hummel spectroscopic library to identify the historical sample as Delrin®, which is the registered trade name for acetal resin produced by DuPont[8]. Further confirmation of the identity of the historical sample was obtained by comparing the sample spectra with spectra from a commercially purchased Delrin® sample. In addition, complementary Raman spectroscopy was conducted on the both the historical sample and the commercially obtained sample and a match was obtained.

At the Royal Observers Corps Bunker in York, 50 small samples, which were representative of the collection, were collected with the aim of characterising them using 3 vibrational spectroscopic techniques. ATR-FTIR was initially employed to characterise the samples to provide curators with an idea of the range of plastics within the collection. ATR-FTIR was shown to be a beneficial technique since a small sample (with no preparation required) was sufficient for obtaining good spectra and, depending on the ATR-crystal used, the instrument coped well with highly absorbing samples such as rubber containing carbon black fillers. However, it was also noted that there are drawbacks; such as the requirement of a sample albeit small. Two portable near-infra red (NIR) reflectance spectrometers were also used to non-invasively sample objects. The first of the two NIR reflectance spectrometers was a Perkin Elmer Fourier transform Spectrum One NTS with an Axiom fibre optic probe attachment operating in the spectral range 12000 - 4000 cm^{-1} with wavenumber resolution of 8 cm^{-1}. A Manfrotto articulated arm was used to position the probe close to the surface of the object under study making the technique non-contact. The infrared beam could theoretically achieve a sampling depth of approximately a few millimetres and so the instrument was used to characterise the composition of foam padding used in a seat without removing the seat cover. However, the fabric seat cover was a heavy and tight weave which prevented penetration of the IR light to the foam underneath; although the seat cover itself was successfully characterised as a polyester/elastomer blend. The second instrument was an ASD LabSpec 2500 dispersive NIR instrument with confocal fibre optic probes operating in the combined VIS/NIR spectral region 28570 - 4000 cm^{-1}. The small dimensions of the LabSpec instrument and the use of confocal optics enabled sampling in areas which had previously been inaccessible, such as the inner workings of some teleprinters. The drawback of the instrument was the lack of compatibility of the format of the generated spectra with the format of the reference library, making sample identification difficult. In conclusion the study demonstrated that NIR techniques were useful for polymer identification but had some limitations, which included high absorbance by dark samples, high specular reflectance from polished surfaces and poor scattering by samples that were translucent.

Asensio *et al*.[5] utilised ATR-FTIR spectroscopy to characterise polymeric materials (adhesives, coatings, varnishes, fixatives) that are routinely used to store, transport, exhibit or package artwork. Prior to ATR-FTIR spectroscopic analysis morophological examination of each of the samples was conducted to determine whether the sample was a foam, non-woven fabric, multilayer or composite material. Marvelseal®, Tyvek® tape and Lampraseal® were identified as multilayer composite materials; Cell-Aire®, Ethafoam®, Plastazote® and the poly(ethylene) rod were identified as cellular plastics or foams. Further interpretation was possible since closed cells were identified in Cell-Aire®, Ethafoam®, and Plastazote®, while open cells were identified in the poly(ethylene) rod. As some of the polymeric materials under analysis appeared to be comprised of more than one layer (as determined by morphological examination by microscopy), great care was taken to analyse samples on both sides and in various orientations to ensure each layer was successfully assessed. Finally, Tyvek® tape was identified as poly(butyl acrylate) which is a pressure sensitive adhesive with a high density polyethylene support. Although the results of this study indicated that ATR-FTIR spectroscopy could be successfully deployed for this type of object assessment it was highlighted that the technique was suitable for surface analysis only and that caution should be taken when objects contain multilayered materials.

T. B. van Oosten *et al*.[6] used ATR-FTIR spectroscopy to monitor the effectiveness of UV absorbers and heat stabilisers as a potential conservation treatment for polypropylene based works of art. The hydrophobic nature of polypropylene means that it can be difficult to obtain good adhesion of a consolidant to the surface of the polymer. To obtain optimal adhesion, here the surface energy of the polypropylene was increased with corona and atmospheric air plasma treatments which caused oxidising effects creating polar carbonyl and hydroxyl groups on the surface of the polymer; making the treated polymer more reactive and enabling better adhesion of the consolidant. A range of consolidants and application methods were employed before the samples were artificially light aged in a Xenotest for up to 643 h at 105000 lux with a relative humidity of 40 % RH and temperature of 50 °C. Since ATR-FTIR spectroscopy is a surface technique, a small area on the surface of the treated samples was cleaned with alcohol to remove the consolidant layer prior to spectral measurement to monitor potential degradation with ageing time; the intensity of the absorption peak at 1711 cm^{-1} was divided by the intensity of the absorption peak at 1850 cm^{-1} and plotted against ageing time. It was shown that untreated polypropylene deteriorated with ageing time, whereas polypropylene samples treated with consolidant had no signs of degradation under the consolidant layer.

The literature outlined above demonstrates the suitability of FTIR spectroscopy for assessment of polymeric materials, particularly when combined with an ATR accessory, although it normally requires removal of a small sample for analysis. There are situations when samples are not available for analysis. One such case in California involved a range of objects created by the so-called ‘Finish Fetish’ artists Peter Alexander, Robert Irwin, John McCracken, De Wain Valentine, Larry Bell, Billy Al Bengston, Craig Kauffman and Helen Pashigan[9]. The sculptors produced a range of seamless, brightly coloured and pristine objects from a range of new resins and plastics which were rapidly being developed in post war USA for use in aeronautical and automobile industries. The artists took these new materials and produced objects that were inspired by the California landscape and culture. The objects were in excellent condition and so to characterise the materials used by the artists a hand-held ATR-FTIR instrument was used. The sculpture by De Wain Valentine was successfully identified as polyester resin based on characteristic ester absorptions at 1719, 1250 and 1116 cm^{-1} and aliphatic absorptions at 2959 – 2856 cm^{-1}, which was later confirmed by comparing the collected spectra with a reference sample.

4.2 Collection of reference samples

A selection of sacrificial samples was selected for the initial stages of this research. The samples included natural, semi-synthetic and synthetic plastics from nine different plastic types. Samples varied in age, composition, function, provenance and previous environmental exposure and were selected to mimic real heritage objects. The forty one samples selected for study had not been previously analysed and so no information was known about the prior history of the samples, which is often the case with real heritage objects within collections. The samples were taken from three different sources: 16 samples were acquired from the polymer collection held at the Centre for Sustainable Heritage at University College London (UCL) (7 out of the 16 samples were taken from a commercially available resin kit, ResinKit^{TM}, Woonsocket, USA); 10 industrial samples were supplied by the Scottish Plastic and Rubber Association (SPRA); and the remaining 15 samples were taken from the University of Strathclyde (UoS) Polymer Reference Collection. Samples were cut in to replicate sub-samples, but were otherwise unmodified. The sub-samples ranged in size from 1.3 cm^2 to 10.6 cm^2, each having an approximate mass of 100 mg. The 9 plastic types included cellulose acetate, cellulose nitrate, rubber, polystyrene, poly(vinyl chloride), polypropylene, polyethylene, polycarbonate and polyurethane. Table 4.1 lists the 41 samples examined in this study. In addition, all of the samples were examined visually and a physical description was noted for each. All of the samples were considered to be in a good condition with no obvious signs of degradation, with the exception of two of the rubber samples (HS268 and HS269) which had a cracked appearance and a distinctive rubbery odour.

Table 4.1. Reference collection of samples studied in this research

Sample	Source	Object	Description
Polystyrene			
HS 36	UCL	ResinKit™	Colourless, transparent, rigid
HS 38	UCL	ResinKit™	White, opaque, rigid
HS 405	UoS	Stereo cassette player	White, opaque, rigid
HS 409	UoS	Cassette tape	Grey, opaque, rigid
HS 446	SPRA	Moulded shape	Colourless, transparent, rigid
Cellulose acetate			
HS 91	UCL	Crumb brush	Pink, opaque, rigid
HS 474	UoS	Thin film	Colourless, transparent
HS 475	UoS	Thin film	Colourless, transparent
HS 476	UoS	Thin film	Colourless, transparent
HS 477	UoS	Thin film	Colourless, transparent
Cellulose nitrate			
HS 270	UCL	Comb	White, opaque, rigid
HS 271	UCL	Cigarette case	Mock tortoiseshell, transparent, rigid
HS 248	UCL	Ruler	Orange, transparent, rigid

Table 4.1 (*continued*). Reference collection of samples studied in this research

Sample	Source	Object	Description
PVC			
HS 62	UCL	ResinKit™	Colourless, transparent, rigid
HS 415	UoS	Swim arm bands	Yellow, opaque, textured, pliable
HS 424	UoS	Record	Black, opaque, ridged, pliable
HS 430	UoS	Money wallet	Black, opaque, pliable
HS 468	SPRA	Moulded shape	Grey, opaque, rigid
Polyurethane			
HS69	UCL	ResinKit™	Colourless, transparent, elastomer
HS 86	UCL	Packing material	White, foam
HS 458	SPRA	Packing material	Pink, antistatic foam
HS 461	SPRA	Packing material	Black, foam
HS 464	SPRA	Packing material	Grey, foam
Polypropylene			
HS 77	UCL	ResinKit™	White, opaque, rigid
HS 400	UoS	Thermos® flask	Black, opaque, rigid
HS 403	UoS	Thermos® flask cup	White, opaque, rigid
HS 416	UoS	Tupperware® box	Brown, opaque, rigid
HS 444	SPRA	Moulded object	Colourless, semi-transparent, rigid
Polyethylene			
HS 80	UCL	ResinKit™	White, opaque, pliable
HS 404	UoS	Scalextric crash barrier	White, opaque, pliable
HS 417	UoS	Tupperware® lid	Colourless, semi-transparent, pliable
HS 459	SPRA	Packing material	Black, crosslinked foam
HS 463	SPRA	Packing material	White, non-crosslinked foam

Table 4.1 (*continued*). Reference collection of samples studied in this research

Sample	Source	Object	Description
Rubber			
HS 268	UCL	Pipette bulb	Brown, opaque, cracked
HS 269	UCL	Dolls head	Brown, opaque, cracked
HS 103	UCL	Hot water bottle	Brown, opaque, pliable

4.3 Experimental

4.3.1 Characterisation of reference samples using ATR-FTIR spectroscopy

The ability of ATR-FTIR spectroscopy to identify and classify polymers from such a wide range of sources, (with differing formulations, additives and plasticisers) was assessed. A transportable diamond crystal attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (Agilent Technologies 5500a) was used to collect spectra in the 650-4000 cm^{-1} region. The sample and background spectra were collected using Microlab PC software in absorbance mode using 128 scans at 8 cm^{-1} resolution resulting in spectral acquisition time of 40 s. No sample preparation was required and polymers were directly analysed on the diamond window. Intimate contact of the sample with the crystal window was required to give good quality spectra; samples were clamped against the diamond window using a pressure clamp for solids. Samples were often irregularly shaped and ten spectra (n = 10) were recorded across the entire surface of the object under study.

4.3.2 Analyses of ATR-FTIR data using principal component analysis (PCA)

The spectral data were interrogated using principal component analysis (PCA) to assess whether it could be used to unambiguously identify a polymer type in a sample regardless of its age, formulation or the presence of additives or plasticisers. The collected spectra (n = 10) of the 41 samples were processed with MATLAB version 7.13.0.564 (R2011b) (Mathworks Inc., Natick, MA, USA) incorporating PLS_Toolbox version 6.7 (Eigenvector Research Inc., WA, USA) by Dr Alison Nordon (University of Strathclyde). Data were derivatised to remove baseline offset, normalised and then mean-centred prior to carrying out PCA to assess sample correlations. The pre-processing techniques used helped to reduce noise and emphasise any regions of spectral change. When analysing PCA data, the eigenplot was first examined to determine the number of PCs that reflected the variation in the data. Those PCs were then further interrogated using, in this instance, scores plots to examine sample correlations. Samples with similar spectral features should cluster together within one quadrant of the PC scores plot. Further the size of the score value indicates the strength of correlation. Samples which cluster around zero on a PC axis show no discernible spectral comparison. As the scores value increases the strength of correlation between the samples' spectra also increases.

4.3.3 Accelerated ageing of selected polymers

Accelerated degradation was conducted on polyurethane sample HS464 using an Atlas Ci4000 Weather-Ometer. This part of the study was undertaken in collaboration with the Preservation Research and Testing Division at the Library of Congress, Washington D.C. During a 3 month visit to the Library of Congress, the polyurethane samples were aged in the Weather-Ometer using the conditions outlined in Table 4.2. The xenon light source used had full spectrum from 200 nm to 750 nm with a CIRA inner, and a soda lime and float glass outer filter to provide a cut-off at 300 nm. The irradiance measured at a wavelength of 420 nm was 1 W m^{-2} (approximately 0.4 Wm^{-2} at 340 nm). The polyurethane samples were attached to acid free conservation grade cardboard, mounted in brackets and hung inside the Weather-Ometer. Samples PU2 and PU4 were protected from the UV wavelengths of light using an additional UV filter which fitted over the mounting brackets. After degradation, the samples were analysed using the same ATR-FTIR instrument and conditions outlined above and the spectra were compared to reference spectra collected from an unaged fragment of HS464 (PU 1).

Table 4.2: Ageing conditions for PU sample HS464

Sample name	Temp / ^{o}C	RH / %	UV light exposure	Time / h
PU 1 (ref)	-	-	-	-
PU 2	50	50	No	24
PU 3	50	50	Yes	24
PU 4	50	50	No	144
PU 5	50	50	Yes	144

4.4 Results

4.4.1 ATR-FTIR spectroscopic analyses of reference samples

The ATR-FTIR spectra were collected in replicate (n = 10) across the surface of the 41 sacrificial samples using the operating conditions outlined in Section 4.3.1. Collected spectroscopic data were examined to identify the main IR absorption bands and to classify the unknown polymer samples; the results are given in Table 4.3 and are compared with previously published results[2, 10-23]. Sample assignment was determined by ensuring that the associated spectra contained the main IR absorption bands listed in Table 4.3. A representative spectrum for each polymer type can be viewed at the end of the chapter.

Table 4.3. Main ATR-FTIR absorption bands

Polymer	Main IR absorption bands (cm^{-1})
Polystyrene Samples identified as belonging to this family : HS 36, 38, 405, 409 & 446	3025 (C-H) stretch 2921 & 2854 (CH_2) asymmetric & symmetric stretch 1602 ring stretch 1449 (C=C) ring 905 (C=CH) 745 & 696 (C-H) bend of aromatic ring
Cellulose acetate Samples identified as belonging to this family : HS 91, 474, 475, 476 & 477	2977 & 2932 (CH_3) asymmetric & symmetric stretch 2951 & 2880 (CH_2) asymmetric & symmetric stretch 1740 (C=O) 1367 (CH_3) bend 1218, 1162 & 1032 (ester C-O-C) stretch
Cellulose nitrate Samples identified as belonging to this family : HS 248, 270 & 271	3300-3500 O-H stretch (depends of degree of substitution or degradation) 2925 & 2854 (CH_2) asymmetric & symmetric stretch 1721 (C=O) 1647 & 1274 (NO_2) asymmetric & symmetric stretch 1155 asymmetric ring stretch 1065 (C-O) stretch in C_1-O-C_4 830 (N-O) stretch 749 (N-O) bend

Table 4.3 (*continued*). Main ATR-FTIR absorption bands

Polymer	Main IR absorption bands (cm^{-1})
Polycarbonate Samples identified as belonging to this family : HS 52, 143, 413, 466 & 467	2969 & 2869 (CH_3) asymmetric & symmetric stretch 2925 & 2854 (CH_2) asymmetric & symmetric stretch 1770 (C=O) 1594 & 1605 doublet, aromatic ring stretch 1081, 1015 & 830 (1,4 disubstituted aromatic ring)
Rubber Samples identified as belonging to this family : HS 103, 268 & 269	3350 $_{\text{broad}}$ (OH) *suggests degradation* 2943 & 2854 (CH_3) asymmetric stretch & symmetric stretch 2917 (CH_2) asymmetric stretch 1714 (C=O) *suggests degradation* 1620 (C=C) stretch 1442 & 1375 (CH_3) asymmetric & symmetric bend 1069 $_{\text{weak}}$ *suggests degradation*
Poly(vinyl chloride) Samples identified as belonging to this family : HS 62, 415, 424, 430 & 468	2925(CH_2) stretch 2861 $_{\text{shoulder}}$ (C-H) stretch *(phthalate plasticiser)* 1720 (C=O) *(phthalate plasticiser)* 1579 and 1602 doublet *(phthalate plasticiser)* 1427 (CH_2) bend 1255 (C-H) bend, in phase 961(C-C) stretch 693 (C-Cl) stretch

Table 4.3 (*continued*). Main ATR-FTIR absorption bands

Polymer	Main IR absorption bands (cm^{-1})
Polyurethane Samples identified as belonging to this family : HS 69, 86, 458, 461 & 464	3325 (N-H) stretch 2973 (C-H) stretch, asymmetric 2865 (C-H) stretch, symmetric 1725 (C=O) stretch (strong in HS69, weak in other samples) 1639 (OCONH) 1538 (N-H) deformation 1088 (OCONH) in plane
Polypropylene Samples identified as belonging to this family : HS 77, 400, 403, 417 & 444	2947 & 2869 (CH_3) asymmetric & symmetric stretch 2921 & 2839 (CH_2) asymmetric & symmetric stretch 1453 & 1378 (CH_3) asymmetric & symmetric bend 1438 (CH_2) bend 1166 & 996 indicative of isotactic form
Polyethylene Samples identified as belonging to this family : HS 80, 404, 417, 459 & 463	2917 & 2854 (CH_2) asymmetric & symmetric stretch 1470 (CH_2) bend 1378 (CH_3) symmetric bend (low density only) 719 (CH_2) rocking

Individual spectral examination was useful as it also provided further information that would not have been provided if, for example, the simple method of spectral database matching was used. Examples of the further interpretation obtained for 7 out of the 9 polymer groups are given below.

Cellulose acetate

The absorption band at 1162 cm^{-1}, for the C-O-C ester stretch, was masked slightly by overlapping absorption bands in each spectra. The overlapping bands could have been due to other additives present within the plastic. In particular, in sample HS91 the plasticiser was identified to be triphenyl phosphate (TPP) by the presence of absorption bands at 1598, 1486, 968, 767 and 689 cm^{-1} by comparison to published results[23]. Sample HS91 was later analysed by Henk van Keulen at the Cultural Heritage Agency, Amsterdam, where the presence of triphenyl phosphate was confirmed by pyrolysis-GC/MS. It has also been noted that as degradation of cellulose acetate proceeds the hydroxyl absorption band at approximately 3300 cm^{-1} becomes more intense indicating deacetylation[23]. A weak absorption band was observed in each of the spectra which would indicate that the samples had not been subjected to significant deacetylation.

Cellulose nitrate

In the case of cellulose nitrate each sample featured a peak at 1721 cm^{-1} that was attributed to a carbonyl stretch. The presence of a carbonyl containing phthalate plasticiser could not be confirmed as it was not possible to identify the other characteristic bands for phthalate plasticiser (2861, 1579 and 1602 cm^{-1}) though they may have been masked by other strong absorbance peaks[24, 25]. Stewart[26] reported camphor as having characteristic bands at 1721, 2963 and 2874 cm^{-1}, therefore it seems likely that camphor was used as the plasticiser in these samples. It has been reported previously that the extent of degradation can be quantified from FTIR spectra by taking the ratio of peak height absorbance of a functional group which was unaffected by degradation against a peak height absorbance from a functional group that was affected[26, 27]. Stewart[26] ratio-ed the NO_2 asymmetric peak at 1647 cm^{-1} and the carbonyl peak at 1721 cm^{-1} against the ether (C_1-O-C_4) peak since it was thought that the ether linkage would not be broken during degradation. It was recognised that some of the ether bonds would break as a result of hydrolysis of the cellulose nitrate chain, but it presumed that the breakage would not be significant. In other studies[20] the ratio of the NO_2 asymmetric peak at 1647 cm^{-1} against the carbonyl peak at 1721 cm^{-1} was calculated to monitor loss of nitrogen and the formation of carbonyl groups as a result of degradation. However, this method was thought be unsuitable for samples which contained camphor or phthalate esters.

Polycarbonate

The spectra of polycarbonate samples had aromatic stretches at 1594, 1605 cm^{-1}, 1081, 1015 and 830 cm^{-1} suggesting an aromatic rather than aliphatic based structure. It was therefore thought to be most likely that the samples were bisphenol A polycarbonates.

Rubber

The peak at 1665 cm^{-1},which is indicative of cis-double bonds, was masked slightly by overlapping peaks; however the remaining absorption bands were consistent with those considered to be typical of cis-1,4-polyisoprene[11, 28, 29]. The samples had additional peaks at 3350 and 1714 cm^{-1}, which were attributed to an OH (due to water uptake) and carbonyl stretch. Previous studies have reported the carbonyl stretch to be present in natural rubber samples which have been subjected to degradation[22, 30]. It could be proposed that these peaks could again be used to provide an inferential measure of the state of degradation of rubber samples. Although, it should be noted that it was quite possible that the carbonyl peak could be caused by some other component within the rubber.

Polyurethane

The sample spectra for polyurethanes HS 86, 458, 461 and 464 indicated that the samples had been produced using an ether polyol. This was confirmed by the absence of a strong sharp carbonyl band at approximately 1740 cm^{-1} and bands at 1187, 1128 and 1064 cm^{-1}, which are attributed to the C-O-C bend of the ester polyol[17]. Moreover, sample HS 69 was identified as a polyurethane elastomer with additional bands present at 2936, $1702_{shoulder}$, 1188, 1162, 1103, 1065, 1047 and 730 cm^{-1}. The bands at 1188 and 1065 cm^{-1} were attributed to the C-O-C bend of an ester polyol[17].

Polypropylene

Bands present at 1166 and 996 cm^{-1} in polypropylene spectra were indicative of the isotactic form of the polymer [31, 32]. Furthermore, sample HS 416 had an absorption band at 1740 cm^{-1} which was attributed to a carbonyl stretch thought to be present as a result of oxidative degradation of the sample.

Polyethylene

Polyethylene sample HS80 had an additional band present at 1378 cm^{-1}, which was attributed to a CH_3 bend and was indicative of low density polyethylene; which had a small amount of branching on the polymer chains. The band at 1378 cm^{-1} was not present in the other polyethylene samples (see Table 4.2) suggesting no branching in the polymer chains, indicating high density polyethylene. The presence of a small absorption band at 1732 cm^{-1} was most likely due to an degradation product of oxidation[33].

4.4.2 PCA data analyses of reference spectra

Although the polymer type of each sample was successfully characterised in this research by visual examination of collected spectra, users can often rely on the use of spectral libraries for matching the spectra of unknown materials with stored data. It is common for commercial libraries to use spectra from new (pristine) samples. However, as a plastic sample ages the search algorithms may become less effective and matches will become poorer to the point where an incorrect match could be generated. In-house built libraries which contain a range of degraded sample spectra could overcome this potential problem, however not all heritage users have such a facility. Therefore the spectra collected here were assessed using principal component analysis to examine the use of this tool to characterise plastic samples into polymer groups and also to determine whether differences could be observed depending on the degraded nature of the samples.

From the PCA results, the eigenvalue plot indicated that 10 principal components (PCs) should be used as they described 92 % of the data variation, however, only the first 4 PCs represented strong sample associations. For example, examination of the scores plot for PC 1 (see Figure 4.1) indicated that most of the sample spectra grouped around a scores value of 0 on the y-axis. A score of 0 indicates that the samples are not associated with each other or with the PC. On the other hand samples with high score values (negative or positive) indicate strong correlations between these samples. A number of samples grouped together between negative scores values of -2 and -5.5 (see triangles at the bottom right hand side of Figure 4.1). Interestingly the samples which all grouped together in this area of the figure all belonged to the cellulose acetate family; which were clearly removed from the other 8 different polymer types. A similar grouping was demonstrated for the polycarbonate samples when the scores plot for PC2 was examined (see Figure 4.2); all polycarbonate samples were plotted in the same experimental domain with scores values between -4.2 and -5.6.

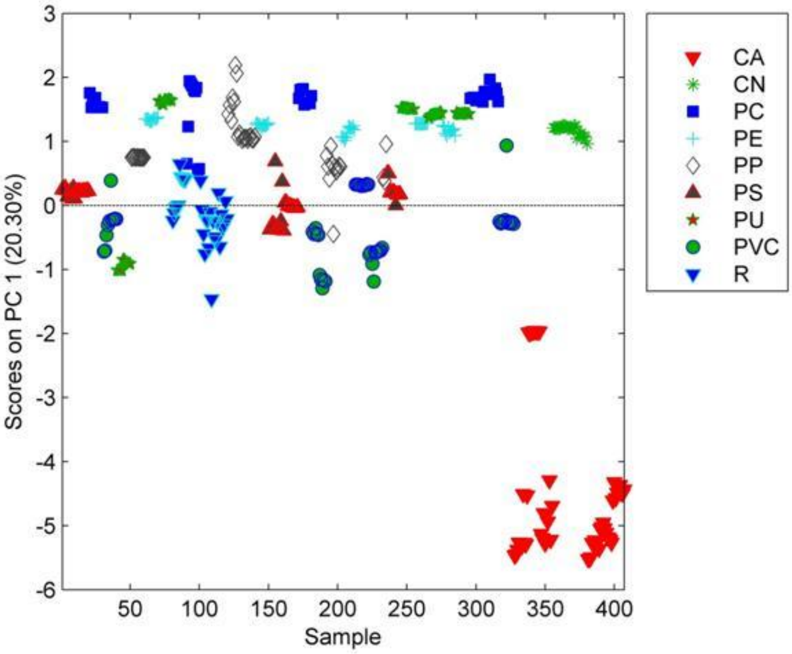


Figure 4.1. Scores plot for PC1 slowing clustering of cellulose acetate samples

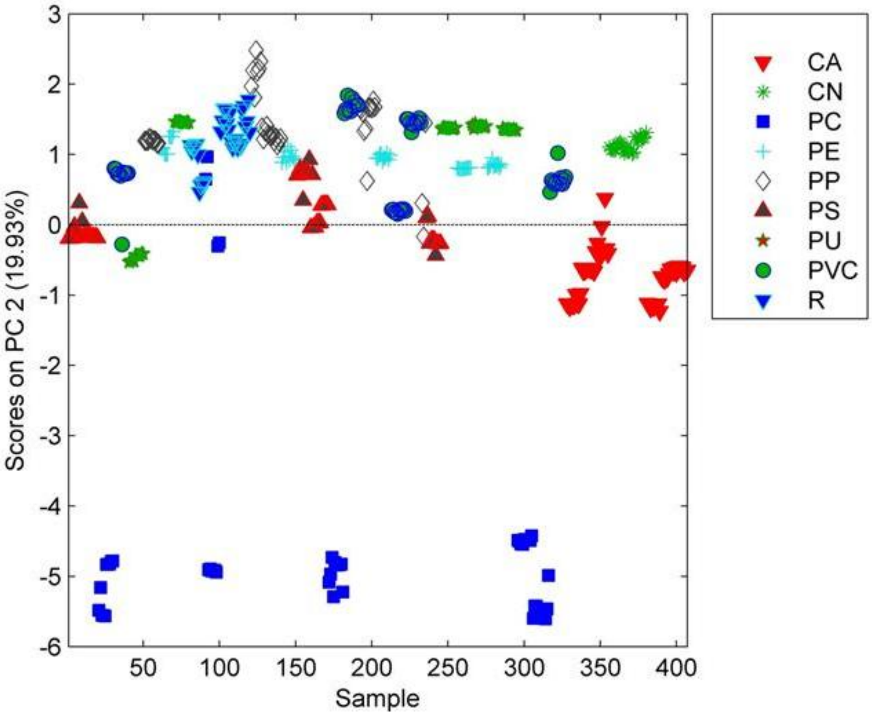


Figure 4.2. Scores plot for PC2 which shows alignment of polycarbonate samples

Examination of the scores plots for PC3 and PC4 (see Figures 4.3 and 4.4) demonstrated strong associations for polyurethane samples (scores values between -4.0 and -4.8) and cellulose nitrate samples (scores values between 4.0 and 4.5), respectively. Interestingly, the polyurethane elastomer (HS69-highlighted in Figure 4.3 with a red circle) did not fit into the grouping of polyurethane foams; this level of discrimination was not possible by examination of the original spectra. The scores plots for PC1 – PC 3 (Figures 4.1 - 4.3) show slight variation in cluster patterns. This is not unusual and was as a result of slight variation between the 10 collected spectra for a given sample that was due to the uneven sample surface. An uneven sample surface can create poorer contact between the sample and the crystal window of the ATR-FTIR, which will lead to slight differences in the spectra. However, the variation was minor and did not affect the ability to unambiguously identify samples which contained cellulose acetate, polycarbonate, polyurethane and cellulose nitrate. Where samples had a smooth and regular surface good surface contact resulted in less cluster variation (for example see Figure 4.4).

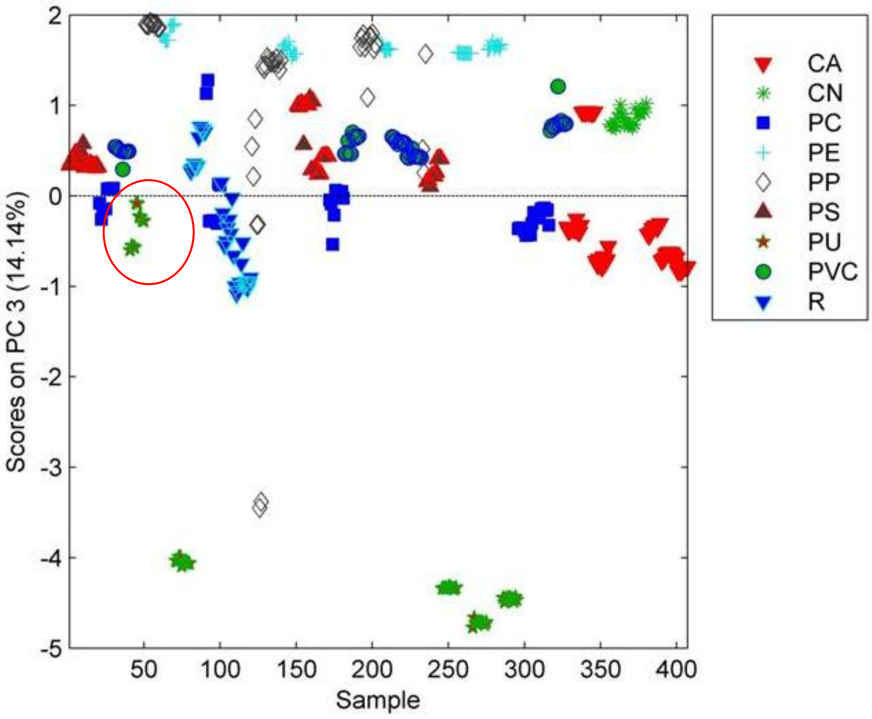


Figure 4.3. Scores plot for PC3 show associations for polyurethane foams.

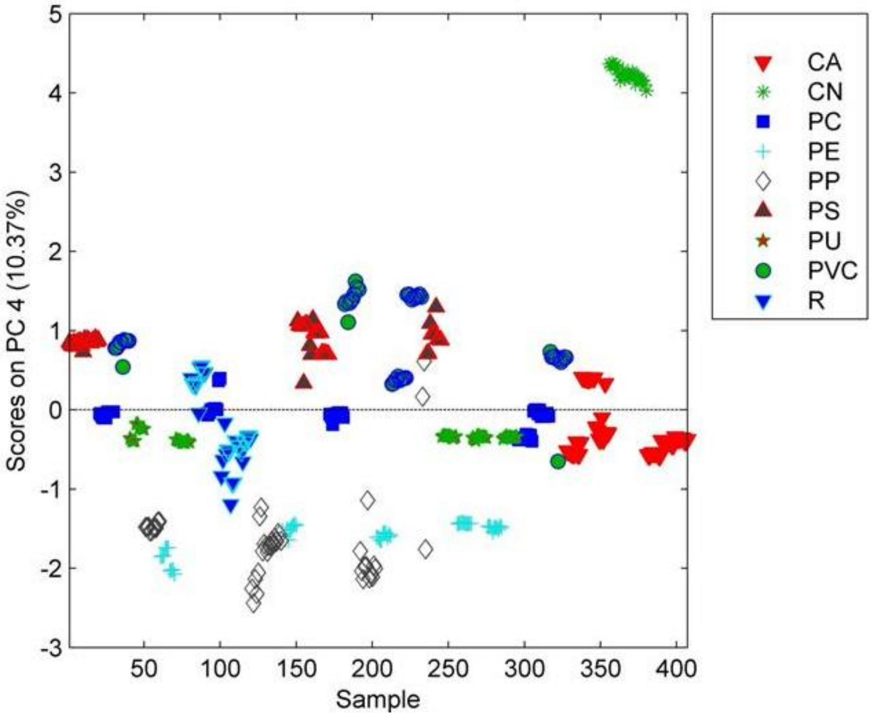


Figure 4.4. Scores plot for PC4 which demonstrates a cellulose nitrate cluster.

It was clearly demonstrated that PCA could be used to unambiguously identify polymer samples which belonged to cellulose acetate, polycarbonate, polyurethane foam or cellulose nitrate families without the use of a spectral library by examination of scores plots for PC1, PC2, PC3 or PC4, respectively. This implies that unknown samples belonging to one of these families could be classified by taking the ATR-FTIR spectrum of the unknown sample and projecting the data into the PC scores plots. Should the sample be cellulose acetate, then the sample would be plotted in the lower right hand side quadrant of the PC scores plot. If however it was composed of another polymer the same would be plotted along the zero axis. Similar comparisons can be made for samples that comprise polycarbonate, polyurethane or cellulose nitrate. However, there is no advantage of using PCA for samples which belong to the following polymer groups: polystyrene, polypropylene, polyethylene, PVC or rubber.

4.4.3 Accelerated degradation of a polyurethane sample

Knowing that the state of degradation can vary greatly between plastics of the same polymer type a small study was undertaken to investigate whether or not ATR-FTIR spectra could be used to differentiate between a plastic which was at different stages of degradation. A polyurethane foam sample (HS464) was cut in to 5 replicate sub-samples and used as a case study to assess the use of ATR-FTIR spectroscopy to discriminate between ‘unaged’ and ‘degraded’ polyurethane samples.

The 5 sub-samples of foam were placed in a Weather-Ometer and subjected to the conditions outlined in Section 4.3.3. After degradation in the Weather-Ometer, the measured replicate spectra for all 5 samples (PU 1 – PU 5) were examined visually (see Figure 4.5). Although some spectral differences were observed it was not possible to clearly distinguish between the replicate spectra (n = 5) collected for the unaged sample (PU 1) or samples degraded for 24 h protected from UV light (PU 2), 24 h exposed to UV light (PU 3), 144 h protected from UV light (PU 4) or 144 h exposed to UV light (PU 5) despite the fact that PU 5, in particular, showed significant signs of degradation, such and discolouration and crumbling. All of the other samples PU 2- PU 4 looked unchanged from the unaged sample (PU1).

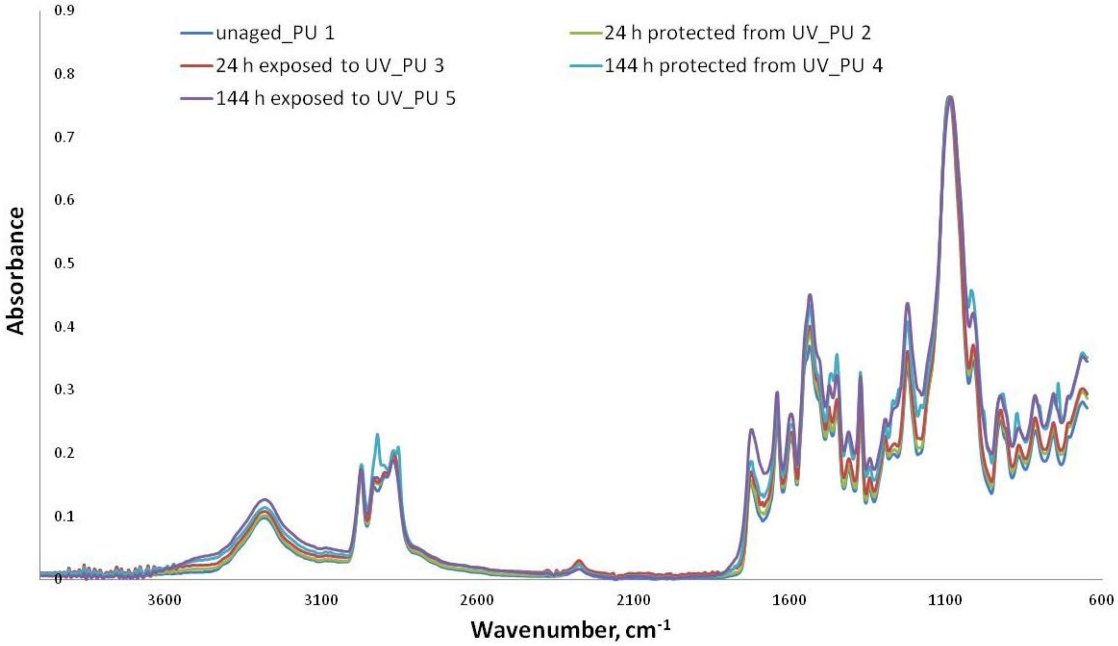


Figure 4.5: Polyurethane sample HS464 at various stages of degradation

In contrast, when the spectra were imported into MatLab, derivatised, normalised and mean-centred PCA was used to clearly differentiate the samples, as illustrated in Figure 4.6. This suggested that it would be possible to identify the early onset of degradation of polyurethane foam using PCA; not that, as reported above, this was possible by examination of spectral matching using commercial or online databases. The unaged PU 1 sample spectra were clustered together with a high PC1 score and zero PC2 score (see red triangles at far RHS of Figure 4.6). Moving down, along the PC1 axis, the next set of data that clustered together belonged to sample PU 2 (green stars). This sample had been exposed to temperature and humidity in the chamber for 24 h but protected from UV light. Moving further down along the PC1 axis, PU 3 data (blue squares) clustered together indicating that light does have an impact on the sample even after a 24 h exposure. Samples placed in the Weather-Ometer for 144 h were easily distinguished from those degraded for 24 h: Samples PU 4 (black diamonds) and PU 5 (blue crosses) had negative PC1 scores whereas samples PU 2 and PU 3 which had been degraded for only 24 h had positive PC1 scores. Examination of the PC1 score values will permit differentiation between samples which have been thermally degraded at 50 % RH for either 24 or 144 h, indicating that a chemical difference had been imparted to samples with increased exposure time. Light ageing did not appear to affect the PU sample when a degradation time of 24 h was applied (no difference in PC2 score for samples PU 2 or PU 3).

In contrast after the 144 h degradation time, spectra from the sample which was protected from light (PU 4) clustered together in the lower left hand quadrant of the scores plot (negative PC2 scores) whereas the sample which was subjected to light (PU 5) clustered together in the upper left hand quadrant of the scores plot. Using this model it would therefore be possible to determine whether unknown PU samples were ‘fresh’, thermally aged or photochemically aged by projecting its PCA result onto the PC1 versus PC2 scores plot. Therefore, despite the inability to discriminate between new and degraded polyurethane foam samples visually or by spectral comparison, PCA was used to ‘tease’ this information from derivatised spectra and samples which had been degraded (thermally or using light) were clearly distinguished from an unaged sample.

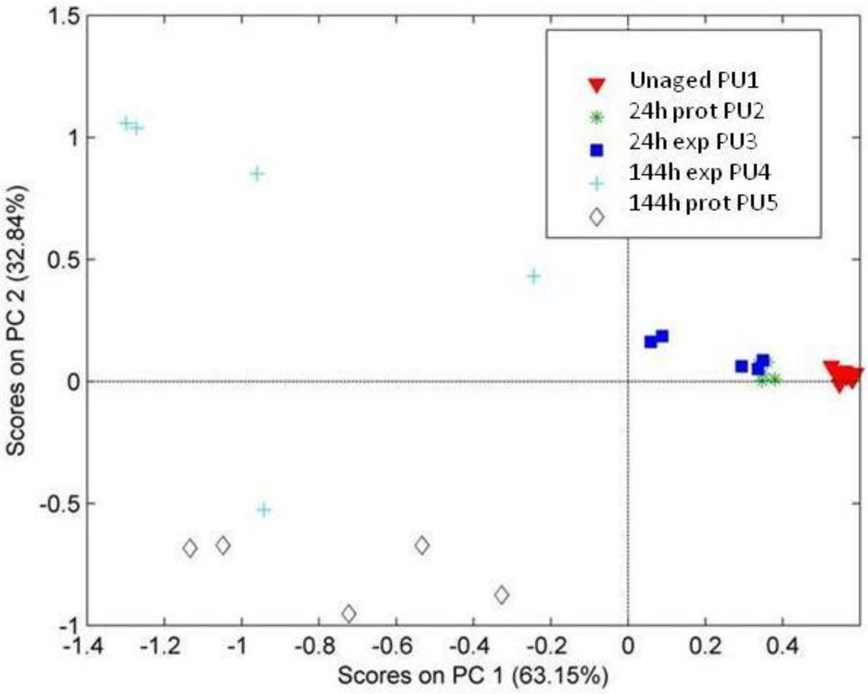


Figure 4.6: PC1 versus PC2 scores plot for unaged and aged polyurethane sample HS464.

4.5 Conclusions

4.5.1 Observed advantages and limitations of ATR-FTIR spectroscopy for polymer characterisation

The 41 sacrificial samples analysed in this study were of varying formulations, age, texture, topography, colour and shape. Nonetheless, identification of polymer type was possible without the need for sample preparation, such as solvent extraction. The use of a pressure clamp for solids was necessary to provide good contact between the sample and the diamond window used in the ATR-FTIR instrument. However, the force used to provide good contact with the crystal and the surface of the object created visible indentations on the more pliable materials such as PVC, polyethylene, polyurethane foams and rubber. It is possible to use spacers, which lessen the indentations on a measured sample by spreading the pressure over a larger area; however the use of spacers can make the analysis more cumbersome. Indentations were more pronounced on samples which were already in a degraded and vulnerable state. It is therefore suggested that analysis by ATR-FTIR using a pressure clamp for solids could be used on ‘hard’ polymer samples or, if possible, using fragments which have already fallen, or broken, from catalogued heritage objects. Otherwise small indentations will need to be tolerated during analysis and the sample area needs to be carefully selected. Difficulties were also experienced during the analysis of samples which had an unusual shape, for example, the analysis of a rounded dolls milk bottle was challenging. This polycarbonate sample had threading grooves for a screw cap and the unusual shape meant that it took some time to locate an area that gave good contact with the FTIR-ATR crystal. However it was still possible to collect spectroscopic data without further sample preparation such as using a microtome to provide a smooth surface.

It should be highlighted that the ATR technique lends itself to the analysis of smaller plastic objects due to the use of the pressure clamp. Though it is recognised that hand held devices are available which would overcome this problem. Care needs to be taken when ‘softer’ samples are analysed to ensure the imprint from the arm clamp is not visually apparent after sampling. It should also be noted that ATR-FTIR spectroscopy is a surface technique therefore caution must be used when analysing a sample which could comprise of polymer layers.

Matching unknown samples to collected data was attempted using PCA rather than spectral libraries. It was possible to unambiguously determine samples that contained cellulose acetate, polycarbonate, polyurethane foam or cellulose nitrate; regardless of the age of the sample, its formulation or the presence of additives. More importantly, although spectral features remained relatively unchanged for new and degraded samples of polyurethane, PCA was able to discriminate between samples of foam that had been treated by heat (50 °C for 24 h or 144 h) or by exposure to UV light. This provides users with a tool to identify the early stages of polyurethane deterioration, although more results are required to support this proof of concept study. In addition, only one polymer type was tested and so work would need to be continued to determine if PCA could be applied to the other plastic samples used within this study to identify various degrees of degradation.

It should also be noted that further characterisation of the reference samples was attempted using differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy. DSC was employed to determine the glass transition temperature (T_g) and the melt point of the samples. However, DSC was unsuccessful as no definitive glass transition or melt temperatures were obtained for the samples. NMR spectroscopy was used in the characterisation of the cellulose acetate and cellulose nitrate samples to determine the degree of substitution. The initial round of NMR spectroscopy involved dissolving approximately 30 mg of sample in deuterated chloroform for a period of 7 d prior to analysis. Unfortunately, the ring protons were obscured and so the degree of substitution could not be determined. A number of other rounds of NMR spectroscopic analysis were attempted after varying the dissolution time, sample surface area (ground sample versus cut sample) and the use of fresh solvent. However, each round of analysis demonstrated that the ring protons were obscured. Another round of NMR spectroscopic analysis was conducted using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent. Once again the ring protons were obscured, in this case by water. Therefore, the samples were refluxed in toluene and dried in a vacuum oven before being dissolved in fresh

$DMSO-d_6$ solvent. Analysis was then repeated, though once again the ring protons were obscured by water. Since the samples were pre-dried and that $DMSO-d_6$ is hydroscopic in nature it was assumed that the water was introduced from the solvent. Therefore, the degree of substitution was not determined from NMR spectroscopic analysis.

4.6 ATR-FTIR spectra for each reference polymer type

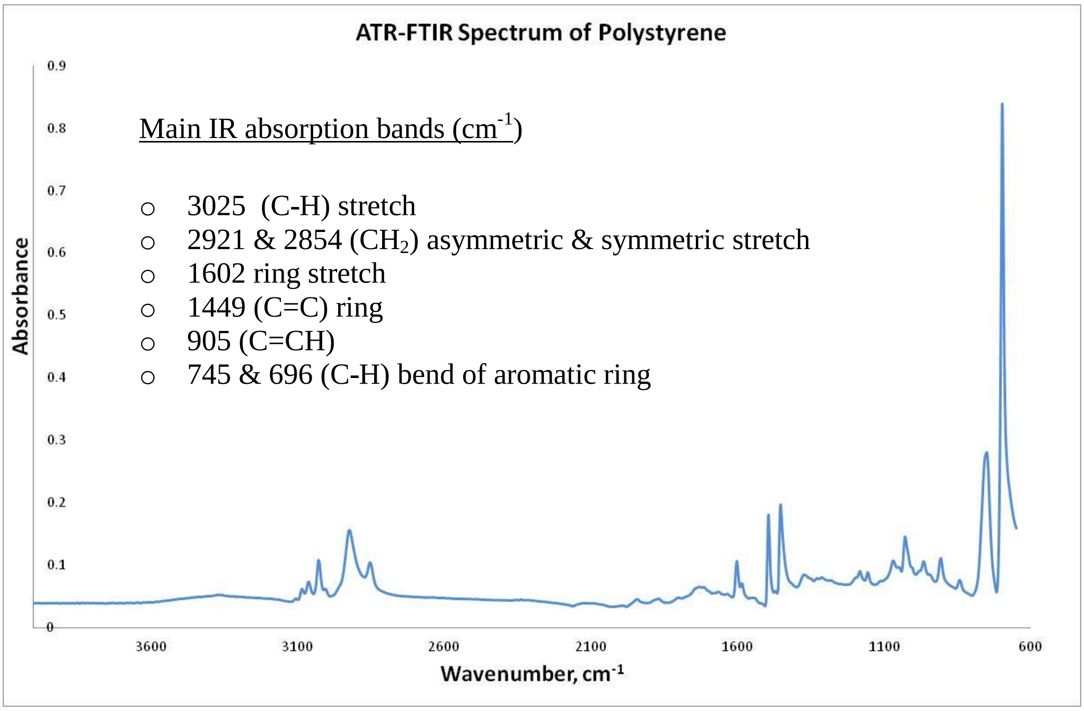
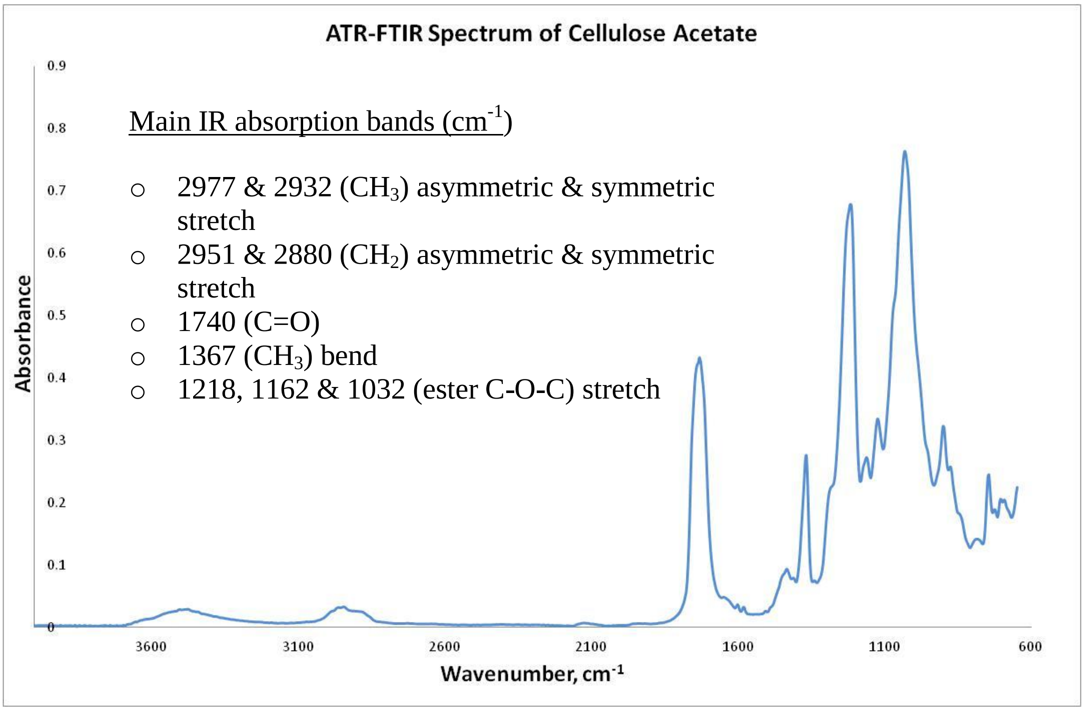


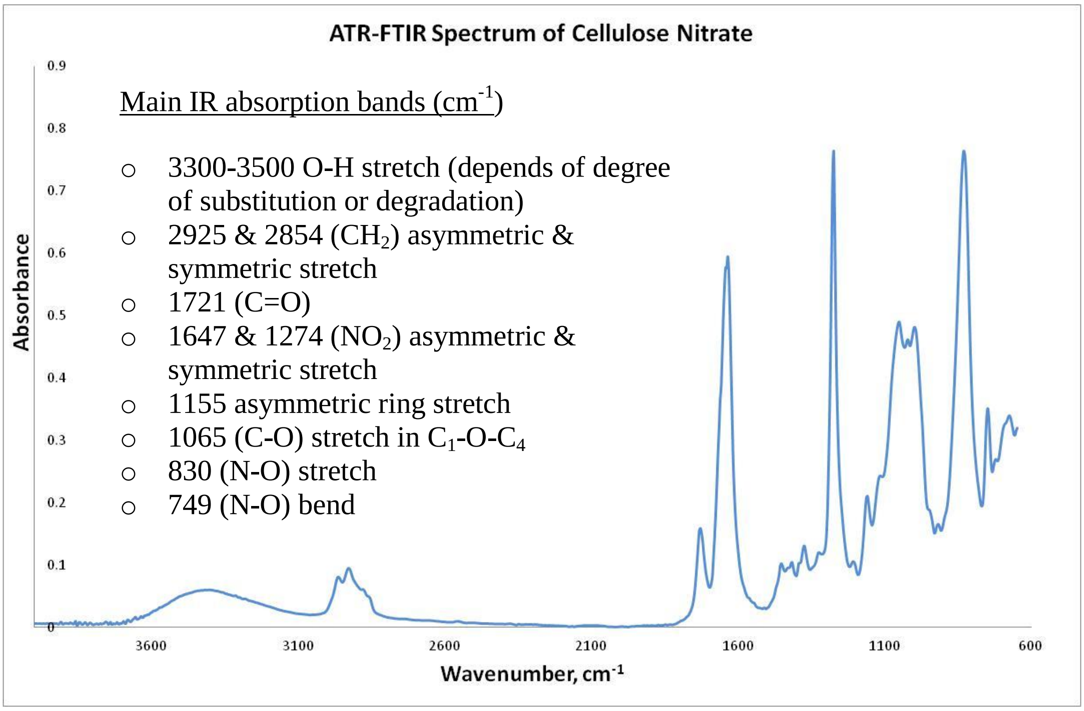
Figure 4.7. ATR-FTIR spectrum of polystyrene reference sample HS38



Main IR absorption bands (cm^{-1})

- 2977 & 2932 (CH_3) asymmetric & symmetric stretch
- 2951 & 2880 (CH_2) asymmetric & symmetric stretch
- 1740 (C=O)
- 1367 (CH_3) bend
- 1218, 1162 & 1032 (ester C-O-C) stretch

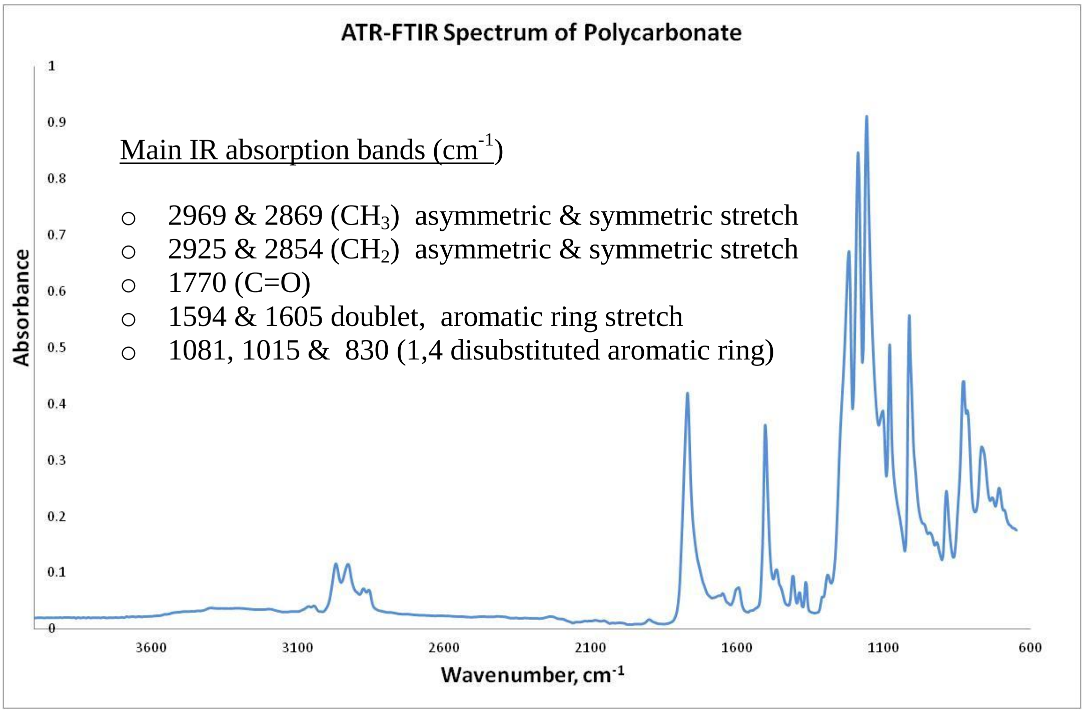
Figure 4.8. ATR-FTIR spectrum of cellulose acetate reference sample HS475



Main IR absorption bands (cm^{-1})

- 3300-3500 O-H stretch (depends of degree of substitution or degradation)
- 2925 & 2854 (CH_2) asymmetric & symmetric stretch
- 1721 (C=O)
- 1647 & 1274 (NO_2) asymmetric & symmetric stretch
- 1155 asymmetric ring stretch
- 1065 (C-O) stretch in C_1-O-C_4
- 830 (N-O) stretch
- 749 (N-O) bend

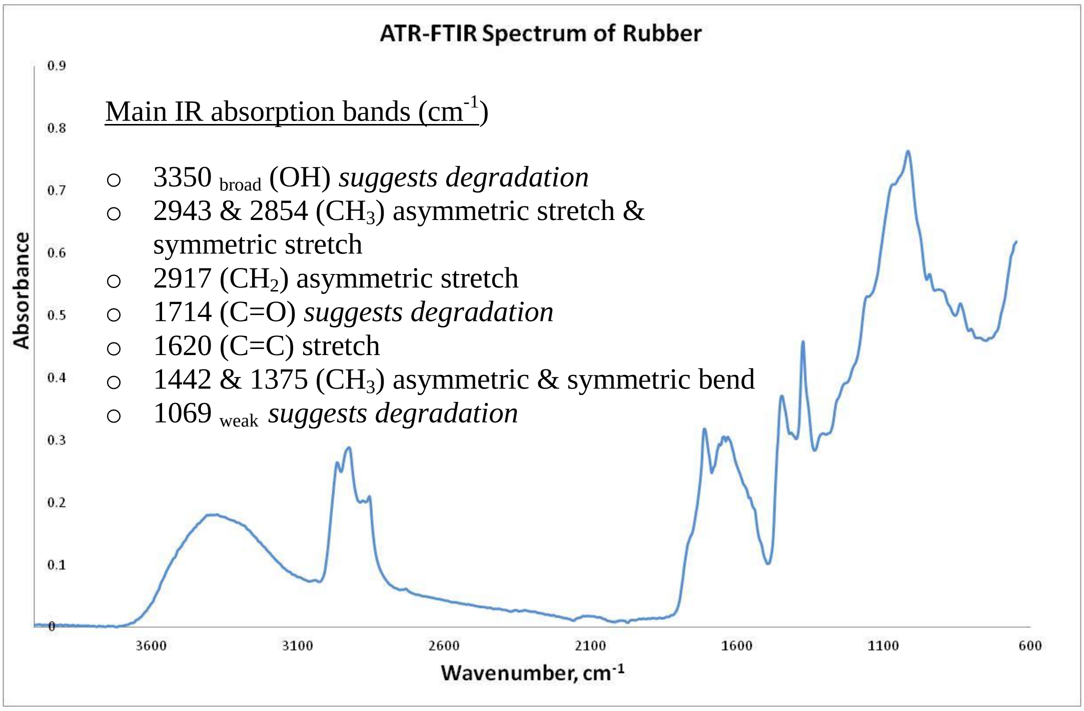
Figure 4.9. ATR-FTIR spectrum of cellulose nitrate reference sample HS248



Main IR absorption bands (cm^{-1})

- 2969 & 2869 (CH_3) asymmetric & symmetric stretch
- 2925 & 2854 (CH_2) asymmetric & symmetric stretch
- 1770 (C=O)
- 1594 & 1605 doublet, aromatic ring stretch
- 1081, 1015 & 830 (1,4 disubstituted aromatic ring)

Figure 4.10. ATR-FTIR spectrum of polycarbonate reference sample HS413



Main IR absorption bands (cm^{-1})

- 3350 $_{\text{broad}}$ (OH) *suggests degradation*
- 2943 & 2854 (CH_3) asymmetric stretch & symmetric stretch
- 2917 (CH_2) asymmetric stretch
- 1714 (C=O) *suggests degradation*
- 1620 (C=C) stretch
- 1442 & 1375 (CH_3) asymmetric & symmetric bend
- 1069 $_{\text{weak}}$ *suggests degradation*

Figure 4.11. ATR-FTIR spectrum of rubber reference sample HS268

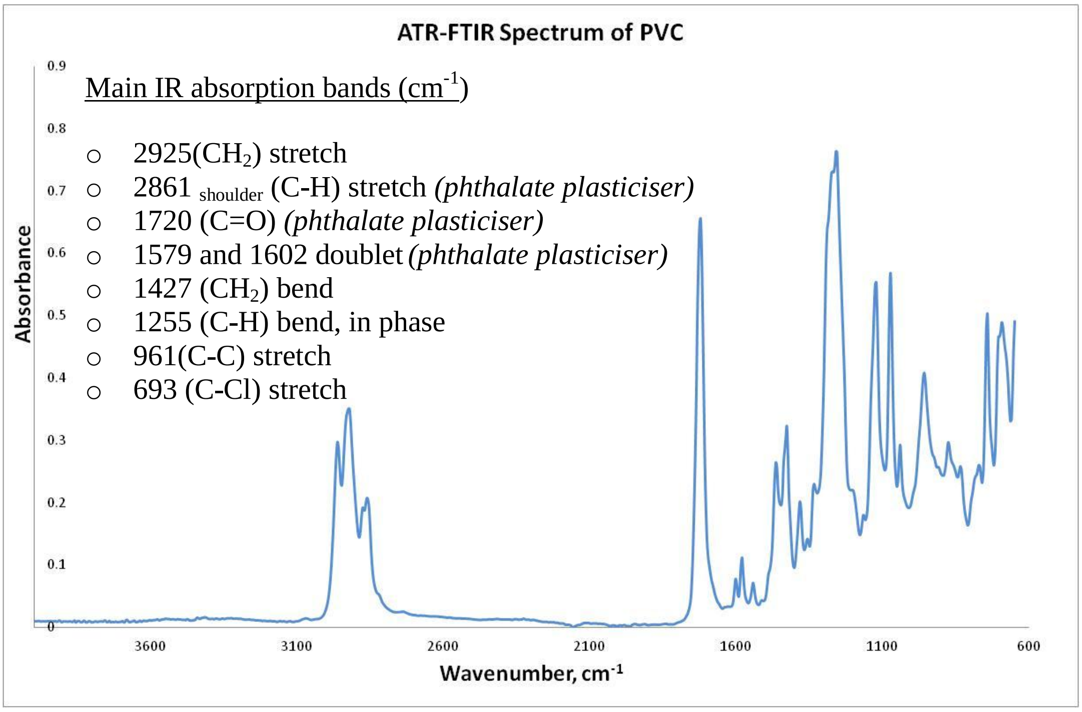


Figure 4.12. ATR-FTIR spectrum of PVC reference sample HS415

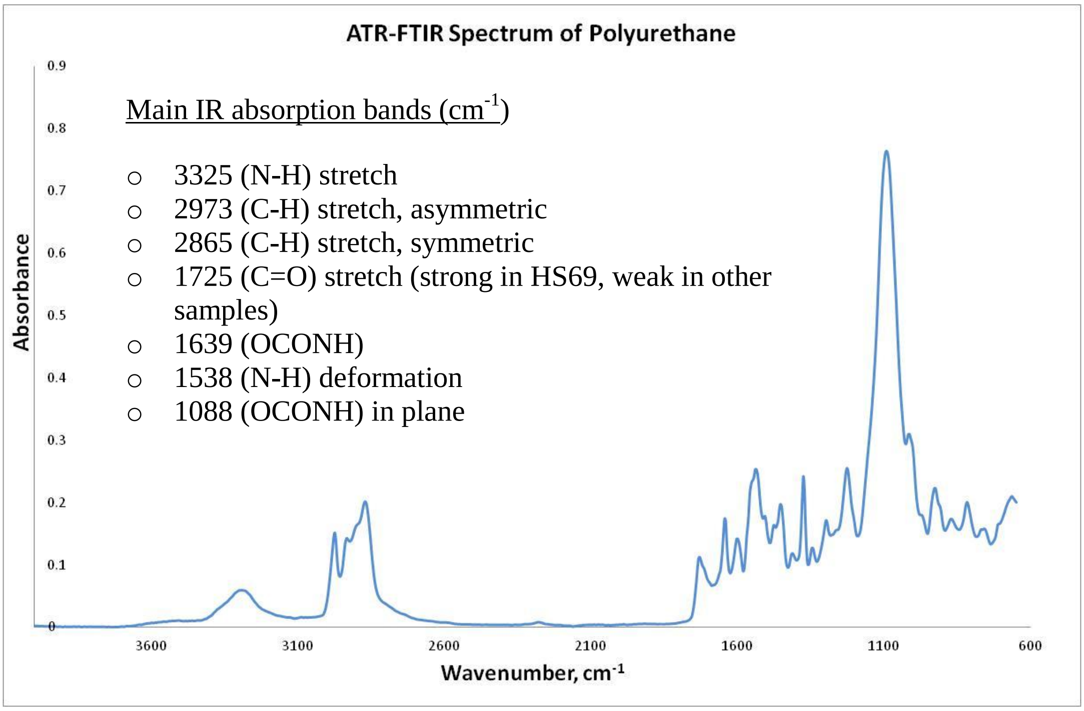


Figure 4.13. ATR-FTIR spectrum of polyurethane reference sample HS86

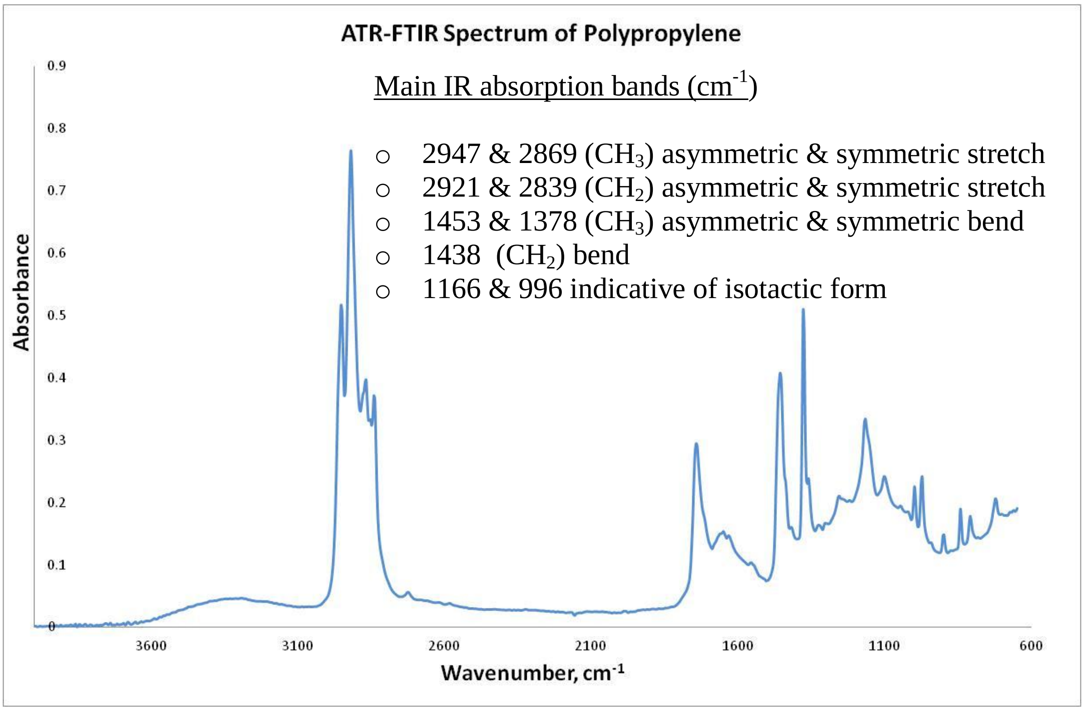


Figure 4.14. ATR-FTIR spectrum of polypropylene reference sample HS416

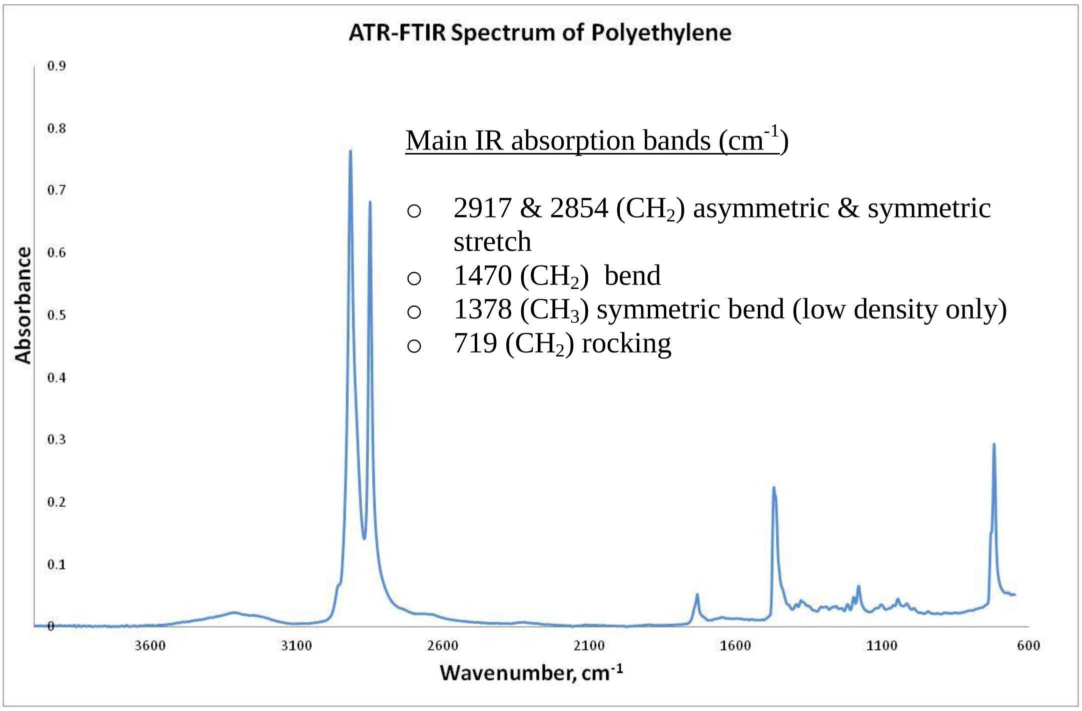


Figure 4.15. ATR-FTIR spectrum of polyethylene reference sample HS463

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CHAPTER 5

DEVELOPMENT OF A NOVEL NON-INVASIVE METHOD OF ANALYSIS FOR THE IDENTIFICATION OF POLYMERS IN HERITAGE OBJECTS

Contents of Chapter 5

5 Introduction

5.1 Measurement of VOCs emitted from polymers in heritage collections

Plastic objects can act as an emissive source and contribute to indoor air environments[1-4]. Not only are acid vapours emitted but also a wide range of volatile organic compounds (VOCs) which may impact on human health[5-8]. Moreover, emissions (both primary and secondary) from plastics may be deleterious to other objects held in close proximity to the emissive plastic object[9]. Air sampling methods have therefore been used to assess plastic emissions in heritage collections.

A commonly used approach is to collect pollutant vapours using solid phase micro-extraction (SPME) fibres which, being a solvent free method of sampling volatile analytes[10], is well suited to heritage based applications. In 2006, Albertsson *et al.*[11] investigated the use of SPME to monitor low molecular weight compounds, such as degradation products, monomer residues and additives, that had been emitted from plastics. The release of low molecular weight compounds were reported to, over time, decrease the life-expectancy of the plastic and the emitted compounds were thought to have a detrimental effect on the environment surrounding the object and on human health. Although the plastics were not monitored within a heritage context, the study demonstrated the suitability of SPME coupled with gas chromatography-mass spectrometry (GC-MS) as a technique for the collection and identification of low molecular weight compounds emitted from plastics. Approximately 200 compounds were measured including alkanes, alkenes, ketones, aldehydes, alcohols, carboxylic acids, dicarboxylic acids, ketoacids and lactones as a result of the thermo- and photo-oxidative degradation of polyethylene samples. The emission of specific compounds was also correlated with the state of degradation by measuring the polymer's molecular weight. The results indicated that the amount of lactones and dicarboxylic acids produced during thermo-oxidation, and the amount of dicarboxylic acids produced during photo-oxidation, correlated with the degree of degradation of the polymer.

Thiébaut *et al.*[12] also used SPME to examine volatile organic compounds (VOCs) emitted from plastic, specifically from magnetic tape coatings. The tapes had been stored for 12 - 25 years at room temperature without climate control and VOCs were collected using 50/30 µm divinylbenzene-carboxen-poly(dimethylsiloxane) (DVB/CAR/PDMS) SPME fibres. An assessment of eight naturally aged magnetic tapes demonstrated that emitted VOCs included a range of carboxylic acids, furanones, ketones, hydrocarbons, aldehydes, phthalates and an extensive number of esters all of which are potentially odorous. Further investigation found that the odours generated were likely to have originated as a result of the degradation of the polymeric binder rather than the film base. Though the emitted VOCs could not be correlated to magnetic tape condition, the findings demonstrated the abundance of VOCs emitted by polymeric objects.

Lattuati-Derieux *et al.*[13] examined emissions from artificially aged polyether and polyester based polyurethane foam samples by SPME. Since polyester polyurethanes (PU(ES)) are most susceptible to hydrolytic degradation pathways the modern PU(ES) foam sample was artificially thermally aged at 90 $^{\circ}$C in humid (50 % RH) conditions for up to 40 weeks. A sub-sample was removed for emissions testing from the sample in humid conditions once every week. In contrast the polyether polyurethanes (PU(ET)) being more susceptible to oxidative degradation pathways were subjected to light ageing. A Servathin light chamber was used to produce daylight 1000 W m^{-2} (without UV light) at 25 $^{\circ}$C and 50 % RH for up to 360 h and sub-samples were removed for emissions testing every day. To provide reference data, four naturally aged polyurethane objects were also tested and emissions were collected at ambient temperature over a period of 15 d. The naturally aged samples comprised of two PU(ES) and two PU(ET) samples. The ester based samples S1 and S2 were taken from a suitcase and a conditioning box, respectively. Sample S1 appeared to be in a degraded condition, while sample S2 looked to be in a good condition. The ether based samples S3 and S4 were taken from chair stuffing and the back of a chair, respectively. Sample S3 appeared to be in a poor condition and sample S4 appeared in a very good condition. It should be noted that samples S1 and S3 were yellowed and displayed a severe loss of mechanical strength, resulting in powdering. The PU(ES) samples which had been artificially aged using heat and humid conditions did not indicate any obvious changes within the pattern of emitted VOCs. The presence of diethylene glycol was noted and considered to be indicative of ester based polyurethanes. The chromatograms obtained from the two naturally aged PU(ES) samples (S1 and S2) were similar, though there was variation in the relative abundance of diethylene glycol. The variation was linked to the difference in the condition of the two foam objects. Sample S1 was in a poor condition and had a high relative abundance of diethylene glycol. Whereas samples S2 looked to be in a good condition and had a relatively small abundance of diethylene glycol. A number of phthalate esters were identified in high relative abundance within the chromatograms of the naturally aged samples, however these cannot be used as marker of polymer type. Since the chromatograms from the naturally and artificially aged PU(ES) samples clearly indicated the presence of diethylene glycol the samples were identified as poly(diethylene glycol ester) polyurethanes. The authors concluded that the presence and relative abundance of diethylene glycol could be used as an indicator of object formulation and condition, respectively. The artificially aged PU(ET) samples contained a range of glycol derivatives which were noted as increasing with ageing time. Similarly, in each of the naturally aged foams glycol derivatives were identified. The sample S3, which was previously noted as being in a very poor condition, had the highest relative abundance of glycol derivatives. The authors noted that regardless of the state of degradation it was possible to identify the presence of glycol derivatives, meaning that it is possible to use glycol derivatives as markers of ether based polyurethanes. Furthermore, the increase in relative abundance of glycol derivatives correlated with the physical state of the foams, the more degraded the foam the higher the relative abundance of glycol derivatives. Therefore, such compounds can potentially be used as degradation markers.

The most recent study, at the time of writing, which examined the volatile emissions from polymers was conducted by Lattuati-Derieux *et al*[4]. The study examined emissions from 12 new industrial plastic samples from a variety of plastic types including polystyrene, acrylonitrile-butadiene-styrene, polyethylene, polypropylene, polybutylene, homo-polymethylmethacrylate, co-polymethylmethacrylate, nylon 6, polyether and polyester based polyurethane, cellulose nitrate and poly(2,6-dimethyl-1,4-phenylene oxide). Samples (20 - 200 mg of the industrial standards) were heated in sealed vials at 60 °C for 1 h whilst VOCs emitted into the headspace were trapped onto a divinylbenzene-carboxen/poly(dimethylsiloxane) (DVB-CAR/PDMS) SPME fibre. For comparison, volatiles were measured from 3 naturally aged museum objects (cellulose nitrate, polyester and polyether based polyurethanes). The museum objects (a cellulose nitrate comb, a polyester polyurethane foam and a polyether polyurethane foam) were measured in-situ at room temperature for 15 d using a DVB-CAR/PDMS SPME fibre. The cellulose nitrate comb looked to be in an advanced state of degradation since it was broken in several places. The polyester polyurethane flexible foam (set inside a suitcase named ‘La valise des nouveaux réalistes’ created by Arman and other artists) was considered to be actively degrading since it had a yellowed appearance and a loss of structural integrity was evident by powdering of the foam. The flexible polyether foam was contained within the back of a chair from ‘Table et 6 chaises, module 400’ by Tallon and on visual inspection appeared to be in good condition. After SPME sampling, regardless of the microextraction method (with heat or at room temperature) the VOCs were thermally desorbed from the fibre in a heated injection port of a GCMS at 270 ºC for 10 min to ensure complete desorption. A Trace GC Ultra coupled with a Trace DSQ quadrupolar mass spectrometer was used. Separation was conducted using a Supelco SLB-5MS fused silica capillary column (30 m x 0.25 mm x 0.25 μm) with helium carrier gas at a flow rate of 1 cm^3 min^{-1}. The GC temperature program was 40 ºC held for 10 min then raised at 5 ºC min^{-1} to 270 ºC. Mass spectra were acquired under electron ionisation mode at 70 eV scanning in the m/z range 50-500 with chromatographic peaks identified by comparison with NIST mass spectral library.

Well resolved chromatograms were obtained from the 12 new industrial plastic samples and over 200 different VOCs were detected and identified, each of which was classified as being ‘specific’ or ‘non-specific’ to polymer type. The non-specific VOCs were further categorised as ‘additives’ or ‘other compounds’. Examples of the non-specific additive VOCs include 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) and diethyl-, diisobutyl- and dibutyl-phthalates which are used as plasticisers. ‘Other compounds’ were found to include the linear acids (n-C_1 and n-C_6 to n-C_9) since these are ubiquitous and can have a variety of sources. Specific compounds were identified that could be related to 7 of the plastic samples. These compounds could be used as unique markers of these 7 plastics which could therefore be used as a non-invasive test for polymer identification. Specific volatile monomers of methylmethacrylate and ethylacrylate, caprolactame, and isomers of dimethylbenzoquinone and phenol were identified in the chromatograms of acrylic samples, nylon 6 and poly (2,6-dimethyl-1,4-phenylene oxide) samples, respectively. These monomers may be used for unambiguous identification of polymer type. The VOCs obtained from the cellulose nitrate standard comprise of camphor isomers and other polycyclic monoterpenes such as fenchone, borneol and camphene. Camphor has been used as a plasticiser in cellulose nitrate since semi-synthetic plastic was invented and is, therefore, typically considered as a marker for the plastic. Polyester based polyurethanes were characterised by the presence of diethylene glycol, reportedly used either as a chain extender or used in the synthesis of the polyester polyol. A previous study[13] reported that hydrolytic degradation of the polyester polyol during ageing results in the emission of diethylene glycol; therefore, the compound could be used as a marker of polyester polyurethane. Polyether based polyurethanes had an abundance of glycol derivatives present in chromatograms. Such derivatives were found to include ethylene glycol, propylene glycol, dipropylene glycol and their monomethyl ether derivatives. Glycol derivatives were previously[13] identified as photo-oxidative breakdown products of the polyether polyol and, as such, were considered unique markers of polyether polyurethane.

Polystyrene and acrylonitrile-butadiene-styrene both contained styrene monomer and ethylbenzene as two of the major compounds in the chromatographic profiles. The extraction method was not suitable for compounds such as acrylonitrile, which would have enabled differentiation between the two polymers. However, styrene and ethylbenzene was used to identify the styrenic class of polymers. Similarly, the emissions could not be used to distinguish between polyethylene, polypropylene or polybutylene. Since all three polymer types are comprised of simple olefin monomers the emissions from each were dominated by linear and branched alkanes. However, a chromatogram dominated by linear and branched alkanes could be used to indicate the polyolefin polymer class.

The VOC emissions from museum objects produced well resolved chromatograms enabling unambiguous identification of polymer type. The chromatogram of the cellulose nitrate comb was dominated by camphor and related compounds enabling identification in a non-invasive manner. The polyurethane foam from the suitcase ‘La valise des nouveaux réalistes’ contained adipate derivatives (the structures of which have not been fully elucidated) and diethylene glycol. As discussed in the case of the industrial standard, diethylene glycol can be used as a unique marker of polyester polyurethane, most likely poly[di(ethylene glycol) adipate] polyurethane. The high relative abundance of diethylene glycol was indicative of the advanced state of degradation of the foam. The foam sample from the back of the chair was shown to contain glycol derivates, which have previously been shown to be markers of polyether polyurethane. The low relative abundance of these derivatives were indicative of the relatively good condition of the foam.

It has been reported that cellulose nitrate, cellulose acetate, polyurethane, poly(vinyl chloride) and rubber are the 5 least stable plastics within heritage collections[14-16]. The most recent and comprehensive study, discussed above, examined only 2 of these[4]. In addition, only 7 industrial standard samples were used in the previous study and all were in a pristine condition. With only one sample per polymer type it was not possible to determine how emissions could be altered by samples of varying age or by the addition of additives such as fillers, plasticisers and impact modifiers. There has been continued growth within the polymer industry with the production of hundreds of different plastics formulations which are now finding their way in to heritage collections. Many of these newer formulations, and their degradation pathways, have not yet been studied in detail.

The advantage of a vapour phase monitoring method for plastic object assessment are numerous but most importantly would permit deployment of a non-invasive method of analysis. There would also be no need for sample pre-treatment, nor sampling of the object and no use of lasers (e.g. in Raman spectroscopy) which leave small craters in the surface of the object. However to make this a viable technique that could be adopted by heritage institutions there was a need to examine VOC emissions from a larger range of plastics (both historic and modern plastics) of varying age and formulation. Moreover, as many institutions have no laboratory or analytical equipment there was a significant need to develop a simple, standardised method of plastic identification using VOC emissions. Despite being sensitive and reusable, solid phase micro-extraction (SPME) fibres were not used in this study. The intention, during field studies, was to post the collecting device to the site where sampling was being undertaken. In a previous study SPME fibres were removed from their holders and used to sample between the pages of a book, 3 fibres out of 7 were broken during the sampling and shipping process[17]. Therefore commercially available thermal desorption sampling tubes containing Tenax® sorbent were chosen as an appropriate collecting device for VOCs since the tubes cannot be broken during shipping or sampling and Tenax® is the benchmark sorbent used for indoor air sampling campaigns. The 41 reference samples were examined and the VOC emissions measured.

5.2. Experimental

5.2.1 Examination of VOC emissions from plastic reference samples using a micro-chamber emission instrument.

Each of the forty-one reference samples were analysed using a micro-chamber/thermal extractor™ (µ-CTE™, Markes). The plastic samples were sealed inside the micro-chambers which were held at a 23 °C for 1 h. An additional set of emission data was collected at a temperature of 70 °C which was intended to promote the emission of labile compounds from the surface of the sample but not induce thermal ageing since 70 °C was below the glass transition temperature of most of the selected samples. After the samples were contained at 23 °C or 70 °C for 1 h, dry compressed air was passed through each chamber at a flow rate of 100 cm^3 min^{-1}, for 2 min, to flush the emitted volatiles from each chamber compartment over thermal desorption sampling tubes.

5.2.2 Accelerated degradation experiments using a Weather-Ometer to light age the plastic reference samples

Reference sub-samples were subjected to accelerated degradation using light. The samples were first placed in a light box (in-house built) and exposed to ultraviolet (UV) light of 365 nm for 1 h using two UV lamps (2 x 4W BLB lamp, Uvitec-Cambridge and 4W BLB lamp, UVP Ltd, Cambridge). The samples were then transferred in to an Atlas Suntest XLS+ using Filter C (equivalent to coated quartz glass with special window glass to provide visible light only) at 36 °C and an irradiance of 750 Wm^{-2} for 168 h. The relative humidity of the light box and the Atlas Suntest XLS+ was approximately 50 % RH. Each sample was then placed back into separate chambers of the µ-CTE™ instrument for 1 h at 23 °C before the chamber was flushed with dry compressed air at 100 cm^3 min^{-1}, for 2 min and each exhaust stream passed over a thermal desorption tube containing Tenax® sorbent.

5.2.3 Analysis of thermal desorption sampling tubes by TD-GC-MS

The thermal desorption sampling tubes were analysed by thermal desorption using a Unity series 2, Markes International thermal desorption unit coupled to a gas chromatograph (7890A GC system, Agilent Technologies) mass spectrometer (5975C inert XL MSD, Agilent Technologies). Separation was performed using a capillary column (HP-5MS 30 m x 250 µm x 0.25 µm, Agilent Technologies) with a carrier gas (He) flow rate of 1 cm^3 min^{-1}. The isothermal column temperature programme was 40 °C for 10 min, then 5 °C min^{-1} to 270 °C. Mass spectra were acquired in electron ionisation mode at 70 eV in the m/z range 40-300. Analytes were identified by comparing collected data with mass spectra held in the National Institute of Standards and Technology (NIST 08) mass spectral library. A complete compilation of the obtained chromatograms can be found in Appendix B.

5.3 Results

5.3.1 VOC emissions from polystyrene samples

(HS36, HS38, HS405, HS409 and HS446)

Despite the different source, age and formulation of the samples, styrene and ethylbenzene were the main VOCs measured at 23 °C (Figure 5.1 is an illustration of the chromatogram for sample HS409) for each of the 5 polystyrene samples, which was in agreement with results of earlier publications[4, 22]. In addition emitted compounds included a range of linear and branched alkanes, aldehydes and diethyl phthalate plasticiser ; all of which were measured at a relatively low abundance. The alkanes, aldehydes and plasticisers detected are common to many plastics and cannot always be considered as being indicative of a particular plastic and were therefore considered to be non-specific VOCs in this case. Since styrene and ethylbenzene were present in all the emissions at 23 °C regardless of formulation and age, these two compounds were considered to be specific VOC markers of polystyrene.

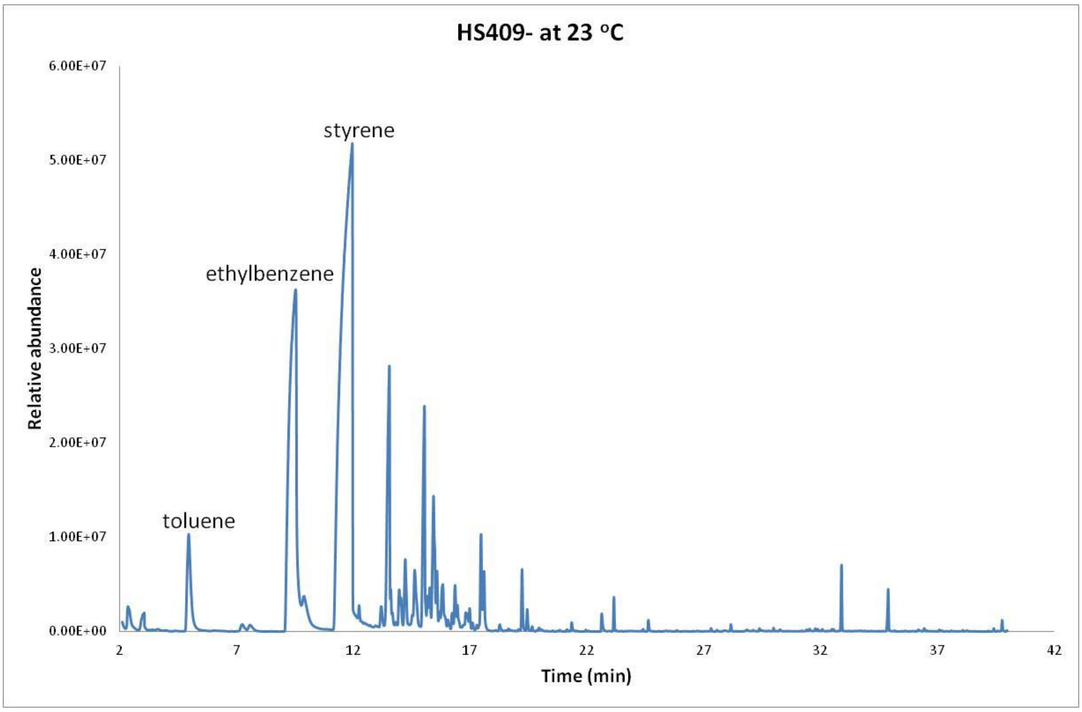

Figure 5.1. Emissions from polystyrene sample HS409 at 23 °C

After the samples were heated to 70 °C for 1 h, the emissions for each polystyrene subsample were re-measured. In general, there was an overall increase in the number of VOCs which was expected as the heat would promote volatilisation of labile compounds present in, or on, the surface of the sample. In particular, there was an increase in the number of non-specific VOCs such as the plasticiser dimethyl phthalate, which was detected at 70 °C but not at 23 °C. After heating, the dominant VOCs measured were plasticisers with HS36 and HS405 emitting diethyl phthalate and HS38, HS409 and HS446 emitting both dimethyl and diethyl phthalate. The styrene monomer and ethylbenzene were still detected in the vapour phase but their relative abundances were significantly reduced and smaller in comparison to the detected plasticisers. After heating there was no visual change to the appearance of the samples that would have indicated the release of substantial quantities of plasticiser, however it was evident that the emissions taken at 70 °C would be different to those measured at 23 °C. In this case chromatograms measured at 23 °C or 70 °C could be used as reference data for field sampling since ethylbenzene and styrene were found in chromatograms collected at either temperature, although collection at 23 ° C is recommended.

After accelerated degradation, VOCs emitted from the 5 polystyrene samples were re-measured. The appearance of samples HS38 and HS446 were visually altered as they had yellowed and the samples looked similarly degraded whereas samples HS36, HS405 and HS409 demonstrated no visual signs of degradation. Of notable interest was the omission of ethylbenzene from all 5 chromatograms and the loss of styrene emission from HS446 and HS405 (the two specific VOCs used to identify polymer type). This would imply that some polystyrene samples which may have been severely degraded may not be identified correctly using reference emission data collected from new or non-degraded samples so care would have to be taken when identifying degraded polymers using emission data alone. Conversely, if the material type was already known, the significant change in the chemical fingerprint of polystyrene chromatograms after photo degradation could prove to be very useful. Identification of the loss of ethylbenzene and the loss of styrene monomer from collected chromatograms could inform museum staff that polystyrene degradation has been initiated. In this study HS405 did not appear discoloured or degraded after accelerated degradation, whereas HS446 did appear discoloured after accelerated degradation. Consideration of their physical appearance alone could be misleading when trying to estimate the level of degradation experienced by a sample, as the emission data proves. Styrene and ethylbenzene were not measured in the emissions of either sample after accelerated degradation, demonstrating that evaluation of the emissions gives an increased level of interpretation.

In a previous study[4], Lattuati-Derieux *et al.* examined VOC emissions from polystyrene and acrylonitrile butadiene styrene (ABS) and found that it was not possible to discriminate between the two polymer types using emissions alone since they both contained residual styrene monomer and ethylbenzene. The study outlined within this thesis used a method of analysis which was not suitable for the collection and identification of nitrogen containing compounds in ABS which could have been used to differentiate between styrene and ABS. However, the reference samples used within this study had previously been characterised using ATR-FTIR spectroscopy and were identified as polystyrene. Therefore, the loss of ethylbenzene and styrene from the vapour phase after accelerated degradation was still regarded as important information. Others have used polymer thermal degradation coupled with solvent (hexane or dichloromethane) VOC trapping to detect nitrogen containing compounds[23]. Such a technique would not be practical in the type of field testing that was envisaged for use within this project.

5.3.2 VOC emissions from polyurethane samples

(HS69, HS86, HS458, HS461 and HS464).

The 5 polyurethane samples consisted of 1 elastomer (HS69) and 4 foams of varying formulation (HS86, HS458, HS461 and HS464). Previous characterisation by ATR-FTIR spectroscopy identified the elastomer as polyester polyurethane and the foams as polyether polyurethanes. At 23 °C the elastomer, HS69 emitted toluene, phenol, decane, nonanal, 2-butyl-1-octanol, 2-ethyl-1-hexanol and the antioxidant butylated hydroxytoluene (BHT). The foam samples, HS86, HS458, HS461 and HS464 emitted toluene, benzaldehyde, BHT and diethyl phthalate. In addition to these major compounds, styrene, limonene, decanal and dimethyl phthalate were detected in HS86; limonene, nonanal and dimethyl phthalate were detected in HS458 and nonanal was detected in HS464.

After heating to 70 °C for 1 h, the emission data changed and the chromatographic profiles were significantly different to those collected at 23 °C. For example, HS69 emissions were dominated by phenol, 2-ethyl-1-hexanol, 2,5-dimethyl tetradecane, 3-methyl-5-propyl nonane, 3,7-dimethyl nonane, dimethyl phthalate, diethyl phthalate and BHT. In the emissions of HS86 and HS461 acetic acid, toluene, styrene, phenol, diethyl phthalate, dimethyl phthalate and BHT were detected. In addition to these major emitted compounds 2-ethyl-1-hexanol and dodecane were also measured in HS461. Propylene glycol, styrene, phenol, nonanal, diethyl phthalate, dimethyl phthalate and BHT were detected in the headspace of HS464 and HS458. In addition, acetic acid and toluene were detected in the headspace above HS464 and 2-ethyl-1-hexanol was emitted from HS458.

Differences in the chromatograms obtained may be attributed to the stability of the samples under investigation. For example propylene glycol, which was emitted from HS464 and HS458 after heating to 70 °C, had previously been reported as a result of polyether polyol breakdown during photo-oxidation[13]. Although neither sample studied had been artificially degraded at that stage, it was proposed that they had been degrading naturally, due to prior photodegradation, resulting in the release of propylene glycol (which has very low volatility) on heating. For example, the foam sample HS458, which was originally pink in colour, had discoloured on the outer edge of the foam possibly due to previous photo-oxidation processes[14]. It should be noted the sample of foam tested was taken from an area that was not discoloured, demonstrating that even though the sample of foam looked to be in good condition, examination of the emission data suggests on-going degradation due to the presence of breakdown products such as propylene glycol. However even if data is collected at 23 °C it will be extremely difficult to use emission data to identify polyurethane samples as there were no assignable VOC combinations; thus no specific VOC markers could be identified at 23 °C .

After accelerated degradation the visual appearance of some samples had altered. Sample HS69 had yellowed, HS86 had yellowed and become friable, HS461 had become friable with no obvious discolouration, HS458 had completely disintegrated and HS464 had no visual signs of degradation. Polyether polyurethanes are reported as being susceptible to degradation via oxidation[14]. The degradation is accelerated by light, resulting in sample discolouration and significant loss of mechanical strength (manifested as crumbling). The polyether based samples examined in this study HS86, HS458 and HS461 with the exception of HS464 were found to discolour and lose mechanical strength after accelerated degradation with light, which was consistent with other reports. The probable difference in age, prior treatment and formulation (possible addition of anti-oxidants to HS464) of the samples were the likely cause of the differences in visual appearance after accelerated degradation. As had previously been noted, propylene glycol was measured in the emissions from sample HS464 after heating to 70 °C. Propylene glycol had previously been reported as a result of polyether polyol breakdown during photo-oxidation[13]. The compound was also emitted from sample HS464 after accelerated degradation; therefore, the emissions are capable of indicating that degradation is occurring before any noticeable changes in colour or mechanical strength. On examination of the emission chromatograms the large abundance of VOCs which overlapped significantly made compound identification difficult (see Figure 5.2); however some assignments were made. Sample HS69 emitted propylene glycol, dipropylene glycol, triethylene glycol and hexaethylene glycol dimethyl ether. Previously it was suggested that the presence of glycol derivatives (such as ethylene glycol, propylene glycol and their monomethyl ether derivatives) indicated breakdown products from the photo-oxidation of ether based polyurethanes[4]. However the sample HS69, analysed here, was earlier identified by ATR-FTIR spectroscopy as an ester based polyurethane. Therefore, it is recommended that care should be taken when assigning glycol derivatives to the ether or ester form of polyurethane. Acetic acid, propylene glycol and dipropylene glycol monomethyl ether were emitted by HS86. HS458 emitted acetic acid, 3-hydroxy butanone and diethyl phthalate. The emissions of HS461 included acetic acid, propylene glycol, trimethylene glycol monomethyl ether, nonanal, dipropylene glycol monomethyl ether, hexaethylene glycol dimethyl ether and diethyl phthalate. Although there were no visual signs of degradation of sample HS464, its emissions indicated the presence of propylene glycol, 1,2-ethanediol diacetate, dipropylene glycol, hexaethylene glycol dimethyl ether and diethyl phthalate. The emissions from the ether based foams (HS86, HS458, HS461 and HS464) contained compounds which were also identified by Lattuati-Derieux *et al*. [4] in their examination of VOCs from ether based polyurethane foams.

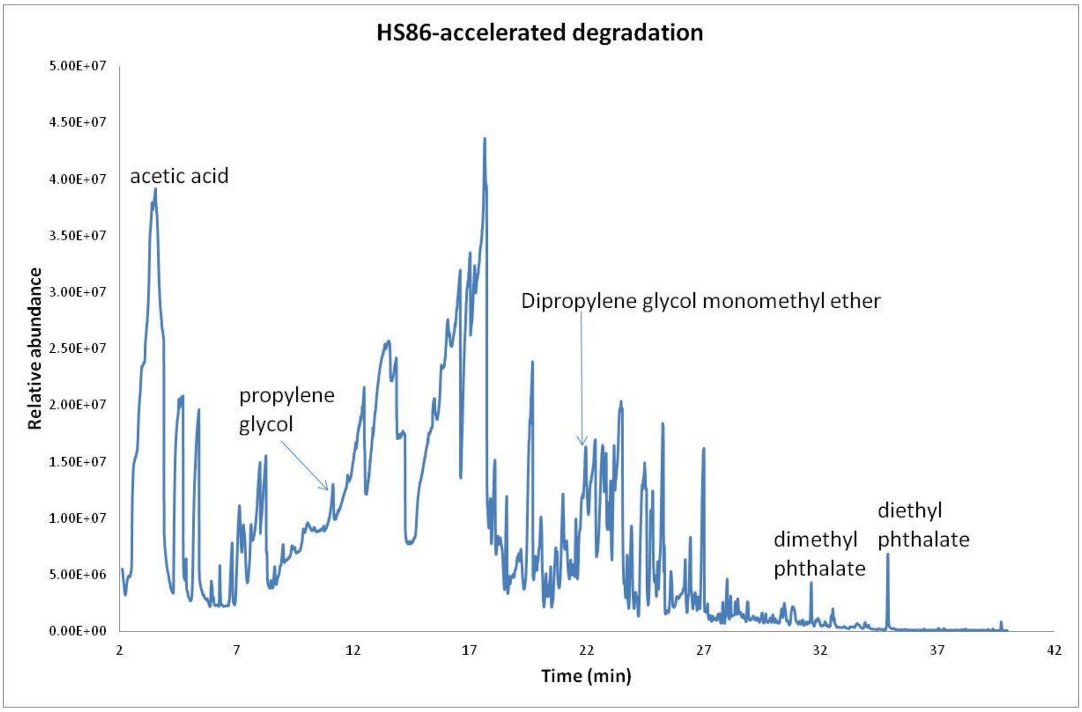

Figure 5.2. Emissions from polyurethane sample HS86 after accelerated degradation

5.3.3 VOC emissions from cellulose acetate samples

(HS91, HS474, HS475, HS476 and HS477)

A crumb brush (sample HS91), approximately 80 y old, had a very strong odour of acetic acid and had a discoloured and cracked appearance. The crumb brush was selected for use in this study because much of the previously published cellulose acetate research focused on the examination and stability of photographic films rather than moulded objects. In addition to this object, 4 thin sheets of transparent cellulose acetate (samples HS474, HS475, HS476 and HS477), which ranged between 40 and 50 y old and looked to be in good condition with no discernible odour, were also studied. Despite the observed physical differences between these samples (age and condition) acetic acid vapour was, by far, shown to be the major emission product in the headspace of HS91 (Figure 5.3) and the second major component emitted from samples HS474 - HS477 at 23 °C. In addition to acetic acid, the headspaces above the cellulose acetate thin sheets (HS474 - HS477) contained significant amounts of dimethyl and diethyl phthalate plasticisers and, to a lesser extent, the antioxidant BHT. The high relative abundance of plasticisers was expected since the sheets are highly flexible. Cellulose acetate has been the focus of many studies over the years and has been noted for the release of acetic acid vapour during degradation by the phenomenon commonly referred to as the 'vinegar syndrome'[24].

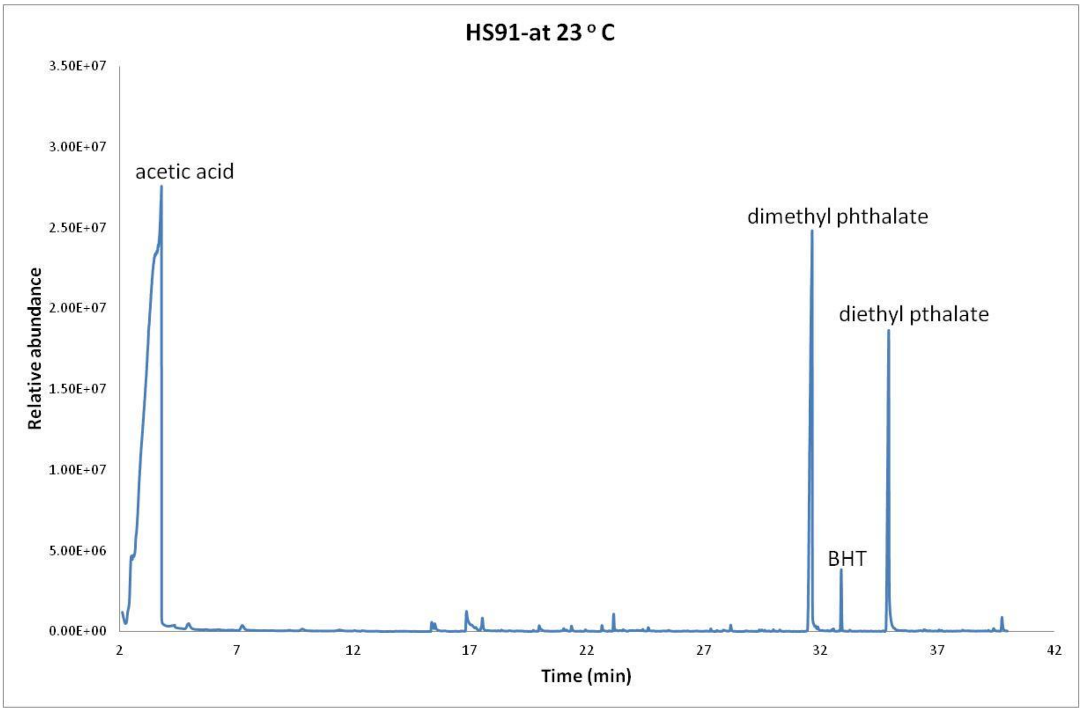

Figure 5.3. Emissions from cellulose acetate sample HS91 at 23 °C

The chromatograms collected after samples were heated to 70 °C changed considerably with very broad plasticiser peaks dominating the chromatograms. Samples HS474 and HS477 emitted dimethyl and diethyl phthalate whereas samples HS475 and HS476 emitted mainly the diethyl phthalate plasticiser. Acetic acid vapour was still detected in the vapour phase but its relative abundance was considerably reduced compared to that in the headspace at 23 °C, and in much lower relative abundance to the detected plasticisers at 70 °C. There was a marked increase in the relative abundance of acetic acid, diethyl and dimethyl phthalate from the crumb brush (sample HS91) after heating, with acetic acid being only marginally lower in relative abundance than the plasticisers. After heating there was no alteration to the appearance of any sample (observed by the naked eye) that would alert conservators to the release of such large quantities of plasticisers. The results indicated that reference data needs to be collected at 23 °C otherwise the chromatograms would be dominated by peaks from plasticisers which would be present in much lower concentration in field chromatograms collected at room temperature. At 23 °C emission data could clearly differentiate cellulose acetate in objects with chromatograms indicating the presence of specific compounds acetic acid and phthalate esters.

After accelerated degradation it was noted that sample HS91 changed colour from pale pink to cream. The emissions of this sample were dominated by a high abundance of acetic acid, dimethyl phthalate and diethyl phthalate; although the emitted vapours did not appear to be as high in relative abundance when compared to the vapours emitted after heating to 70 °C. Other notable differences included the release of toluene and phenol after accelerated degradation. Phenol has been reported as an indicator of the breakdown of triphenyl phosphate (TPP) which is commonly used as a plasticiser and flame retardant[14, 25, 26]. TPP reportedly breaks down to form phenol and diphenyl phosphate (DPP) which is acidic[27-29]. This result was validated by analysis of the sample by pyrolysis-GC/MS prior to accelerated degradation when the presence of TPP plasticiser was confirmed. Unlike the semi-volatile phthalate based plasticisers which are easily measured using thermal desorption sampling tubes, TPP is much less volatile and not so readily measured using this method. However, the more volatile degradation product of TPP, phenol, is easily detected. The other cellulose acetate thin sheet samples displayed no visual signs of deterioration after accelerated degradation although their emissions changed slightly with sample HS475 now joining HS474 and HS477 in emitting both diethyl and dimethyl phthalate. The emissions of sample HS476 remained unchanged after accelerated degradation. Cellulose acetate formulations are known to contain several plasticisers[14, 26] and from these results it was evident that Tenax® sampling tubes coupled to TD-GC-MS was a suitable method of collection for plasticiser emissions or their degradation products.

The abundance of acetic acid was highest for the crumb brush (sample HS91) but acetic acid remained extremely low in comparison to emitted plasticiser for the cellulose acetate thin films (samples HS474-HS477) regardless of whether the emissions were collected at 23 °C, 70 °C or after accelerated degradation. The differences in the emissions observed here were attributed to the stability of the cellulose acetate samples. Sample HS91 was thought to be actively degrading and thus the acid hydrolysis process (deacetylation) had already commenced releasing large quantities of acetic acid vapour. The liberation of phenol after accelerated degradation added further proof of chemical breakdown. In contrast the thin cellulose acetate sheets (samples HS474 - HS477) appeared to be in good condition and this was supported by the emissions which demonstrated a low relative abundance of acetic acid. Since cellulose acetate is known to be susceptible to hydrolysis, photo degradation (as used in the accelerated degradation within this study) was not expected to degrade these more stable cellulose acetate samples.

Since cellulose acetate objects release acid during degradation it is recommended, where possible, that they be separated from other materials in collections. Ideally, cellulose acetate objects should be stored in dry, cold conditions to slow the release of acid[30]. For financial and practical reasons this may not always be an option and so another possible storage method is to keep cellulose acetate objects in a well-ventilated area with a solid sorbent which can selectively scavenge the acidic vapours. Good ventilation and the use of scavengers will prevent a build-up of acidic vapours in the environment surrounding the object, which would increase the rate of reaction of degradation if allowed to remain.

5.3.4 VOC emissions from cellulose nitrate samples

(HS270, HS271 and HS248)

Camphor has traditionally been used as the plasticiser in cellulose nitrate formulations since the plastic was developed in 1830s[19]. Although plasticisers are not generally considered to be specific to a particular polymer here there is an exception to the rule as camphor is considered to be an indicator of cellulose nitrate containing objects. However there is also a caveat, as camphor was sometimes replaced, or used in combination, with other plasticisers such as triphenyl phosphate (TPP) or phthalates in the late 1930's[14, 19, 31]. TPP and phthalate plasticisers are used in many plastic formulations unfortunately they cannot be used alone as an indicator of cellulose nitrate. The VOC emissions of the 3 cellulose nitrate samples studied here were dominated by camphor, which was therefore considered to be a marker for cellulose nitrate. In addition to this major emitted compound, sample HS270 (Figure 5.4) emitted toluene, eucalyptol and borneol, sample HS271 emitted fenchone and sample HS248 also emitted borneol. It is therefore suggested here that the presence of camphor and the related terpenes and their derivatives could be used as key markers for the identification of cellulose nitrate as proposed previously[4].

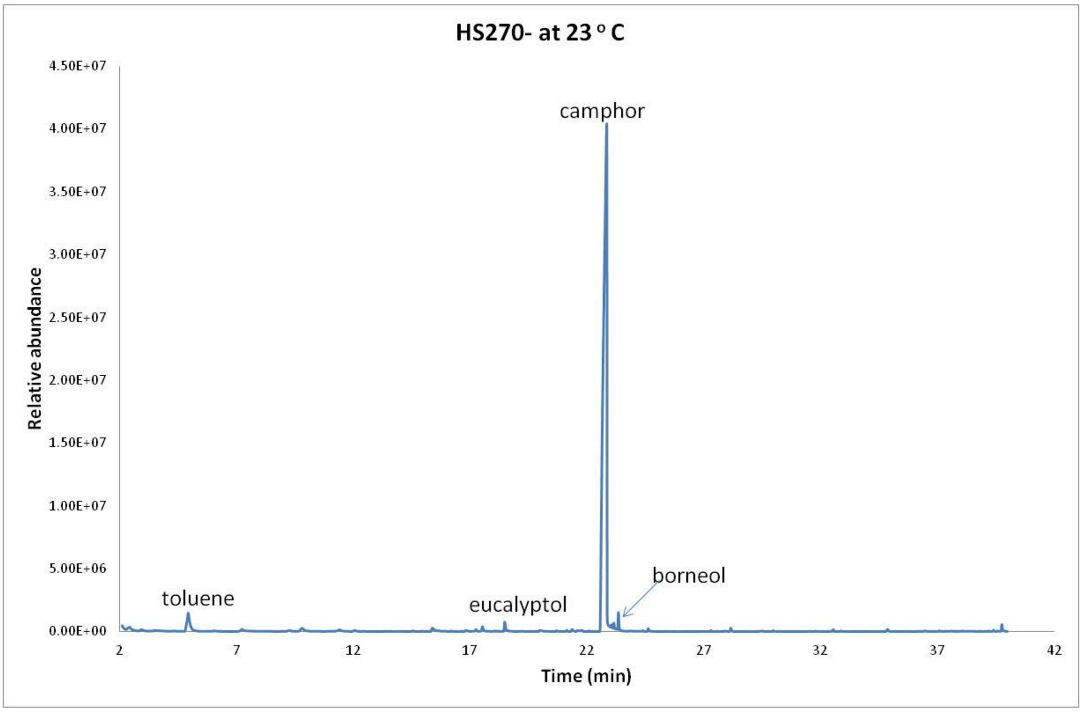

Figure 5.4. Emissions from cellulose nitrate sample HS270 at 23 °C

After heating to 70 °C the emissions remained relatively unchanged with the same major compounds being detected in the headspace above each sample. One minor change was the detection of diethyl phthalate in all 3 samples, which was large in relation to the previously monitored volatiles. There was no visual change in the appearance of the samples even though the relative abundance of emitted compounds had increased after heating. It was therefore proposed that the emissions of cellulose nitrate can be used to unambiguously identify the polymer at 23 °C with no requirement for sample heating. Indeed, as it was also possible that heating the sample to 70 °C could encourage sublimation of camphor, leading to the development of gaps between the polymer chains allowing water to ingress and initiate hydrolysis, measurement of cellulose nitrate samples at 23 °C was strongly recommended.

After accelerated degradation none of the samples showed any visual signs of deterioration. Interestingly the emissions from all samples were reduced when compared to data collected at 23 °C. Samples HS270 and HS271 displayed a significant increase in the relative abundance of diethyl phthalate plasticiser (compared to camphor) which could be problematic as the polymer becomes brittle and vulnerable to degradation when plasticiser is lost[32] [14, 33]. Although there was no observable crazing of samples after accelerated degradation, the high relative abundance of phthalate plasticisers and camphor measured confirmed that plasticiser loss was occurring[14, 19]. Should emission data be collected from degrading cellulose nitrate samples, the presence of high amounts of phthalate based plasticisers and camphor could be used as an 'early warning' indicator of cellulose nitrate breakdown prior to any observable visual change to the object. It should also be noted that NO_x vapours are emitted from degrading cellulose nitrate samples and, although not detected here using this method of determination, these vapours could also act as indicators for cellulose nitrate objects. Plasticiser loss (phthalate or camphor based) should be avoided as it creates voids between polymer chains permitting the ingress of water. The water can react with evolved NO_x vapours from the freshly exposed surfaces to form nitric acid which can attack the cellulose chain resulting in chain scission of cellulose backbone. This is eventually manifested as the formation of minute cracks or crazing within the polymer, which grow in size and number to form a large network of cracks[32]. Internal cracks are produced initially before external surface cracks and ultimately cracking will become so extensive that it is known as crizzling, which is the last stage before the object completely disintegrates.

The process of degradation is inevitable, however preventive conservation may be employed to slow the progress of degradation and increase the lifetime of the objects. In the case of cellulose nitrate, preventive conservation may involve the application of adsorbents, which may also be referred to as molecular traps or scavengers. Activated carbon (activated charcoal) has a large surface area (approximately 600-1500 m^2g^{-1}) and is effective at adsorbing nitrogen oxides produced by degrading cellulose nitrate[14, 34]. The removal of nitrogen oxides prevents the formation of nitric acid and the generation of an autocatalytic breakdown cycle. Activated carbon is an effective adsorbent for many gaseous compounds and as a result the compounds will compete with water and nitrous oxides for available sites on the adsorbent. This can reduce the overall effectiveness of the adsorbent and since the adsorbent is not self-indicating (such as inducing a colour change when exhausted) it may be difficult to know when the adsorbent requires replenishment. It is generally recommended that the activated carbon be regularly regenerated or refreshed.

5.3.5 VOC emissions from polyethylene samples

(HS80, HS404, HS417, HS459 and HS463)

The main components measured in the VOC emissions at 23 °C for the 5 polyethylene samples were linear alkanes with samples HS404, HS417 and HS463 emitting benzaldehyde, nonanal, tridecane and decanal; sample HS80 emitting BHT, tetrachloroethylene, benzaldehyde, undecane and nonanal; very low tridecane, decanal and toluene detected above sample HS459. Diethyl phthalate plasticiser was identified in all 5 samples. The VOC emissions were of very low relative abundance; however they can be used to positively identify polyethylene at 23 °C.

After heating to 70 °C there was an increase in the number and the concentration of volatiles measured in the emissions with all five samples (HS80, HS404, HS417, HS459 and HS463) emitting tetradecane, tridecane and nonanal. In addition to these three major compounds HS404 and HS463 emitted dodecane and decanal, HS80 emitted undecane and hexadecane and HS417 emitted heptadecane. Diethyl phthalate plasticiser was once again identified in all 5 samples with the addition of dimethyl phthalate in sample HS417 and 2-ethyl-1-hexanol in samples HS404 and HS459. There appeared to be no advantage to heating samples prior to the collection of emitted volatiles.

There were no visual signs of deterioration after accelerated degradation and the emissions remained relatively unchanged, with samples HS80 (see Figure 5.5), HS404, HS417 and HS463 emitting tridecane, tetradecane and diethyl phthalate. In addition to these 3 major compounds heptadecane was emitted from HS404 and

HS463, pentadecane was emitted from HS80 and HS463 and dodecane from HS80 and HS404. 2-ethyl-1-hexanol was detected in HS404 and HS459. In addition, the aldehydes nonanal and decanal were major emitted compounds in HS404, HS417, HS463 and HS459.

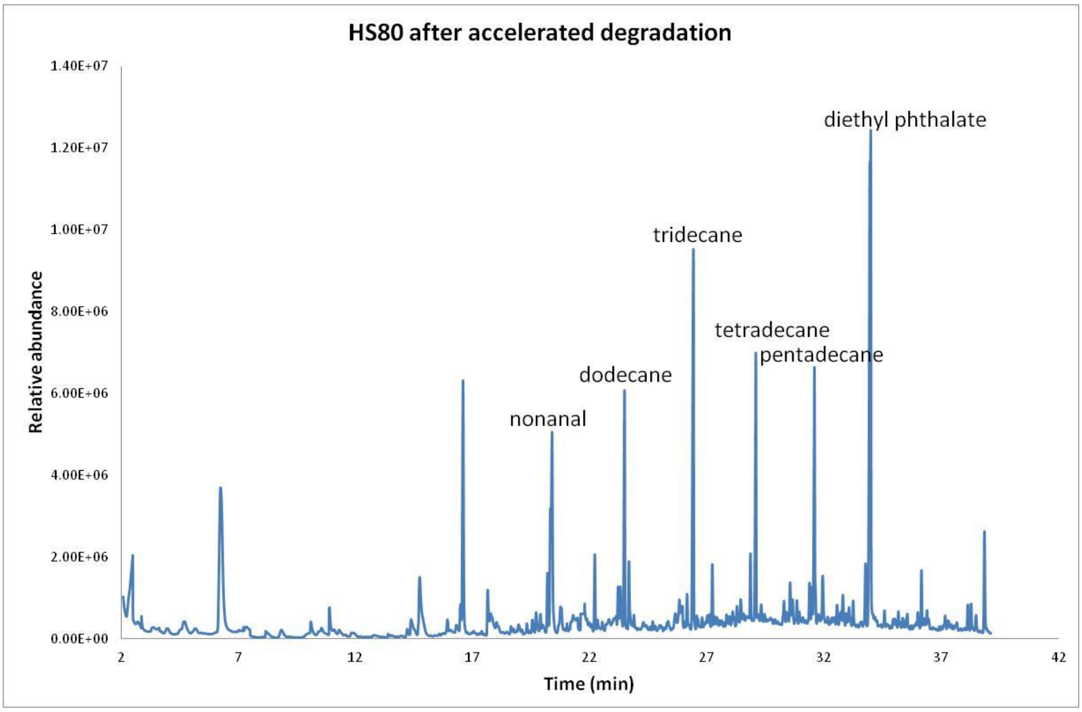

Figure 5.5. Emissions from polyethylene sample HS80 after accelerated degradation

However one key change was the presence of 2-ethyl-1-hexanol, in samples HS404 and HS459 (at 70 °C and after accelerated degradation). This compound is a breakdown product of the plasticiser di-2-ethylhexyl phthalate (DEHP)[4]. The method used in this study did not permit the detection of DEHP plasticiser by GC-MS analysis, but the presence of 2-ethyl-1-hexanol suggests that DEHP was used in these two polymer samples and that it had begun to break down. Should emission data from polyethylene samples contain this peak this would provide a warning that breakdown of the plasticiser in the object is, or has, taken place.

5.3.6 VOC emissions from polypropylene samples

(HS77, HS400, HS403, HS416 and HS444)

At 23 °C the polypropylene samples produced emissions containing vapours at relatively low abundance. The major compound emitted by HS403, HS400 and HS416 was 2,2,4,6,6-pentamethyl-heptane. In addition, 2,6-dimethyl undecane and 3,5-dimethyl octane were detected in the headspace above sample HS400, 2,5-dimethyl hexane was emitted from sample HS416 and 2,4-dimethyl heptane was emitted from sample HS444. In contrast, the emissions of sample HS77 did not contain any branched alkanes, however non-specific VOCs (benzaldehyde, toluene, benzoic acid and acetophenone) of very low concentration were identified.

After heating to 23 °C branched alkanes remained the dominant compounds in the emission data with samples HS403, HS400 and HS416 emitting 2,2,4,6,6-pentamethyl-heptane, 2,2,4,4-tetramethyl octane. In addition, sample HS403 emitted 2,6-dimethyl undecane, 2,2,4-trimethyl hexane, 2,6,11-trimethyl dodecane and BHT, sample HS400 emitted 3,5-dimethyl octane, 2,3,6-trimethyl decane and BHT, sample HS444 emitted 3,6-dimethyl decane, 2,3,6-trimethyl decane, 5-ethyl-2methyl octane, octadecane and 4-methyl octane (see Figure 5.6). The compounds detected in the vapour phase of sample HS77 were once again of low relative abundance with pentadecane, 2,4-dimethyl-1-heptene and 2,4-dimethyl heptane detected. Of the samples analysed here, 4 out of the 5 did not require heating to 70 °C as the detection of branched alkanes at 23 °C would be enough to positively identify polypropylene. However, sample HS77 did not emit any branched alkanes until it was heated to 70 °C.

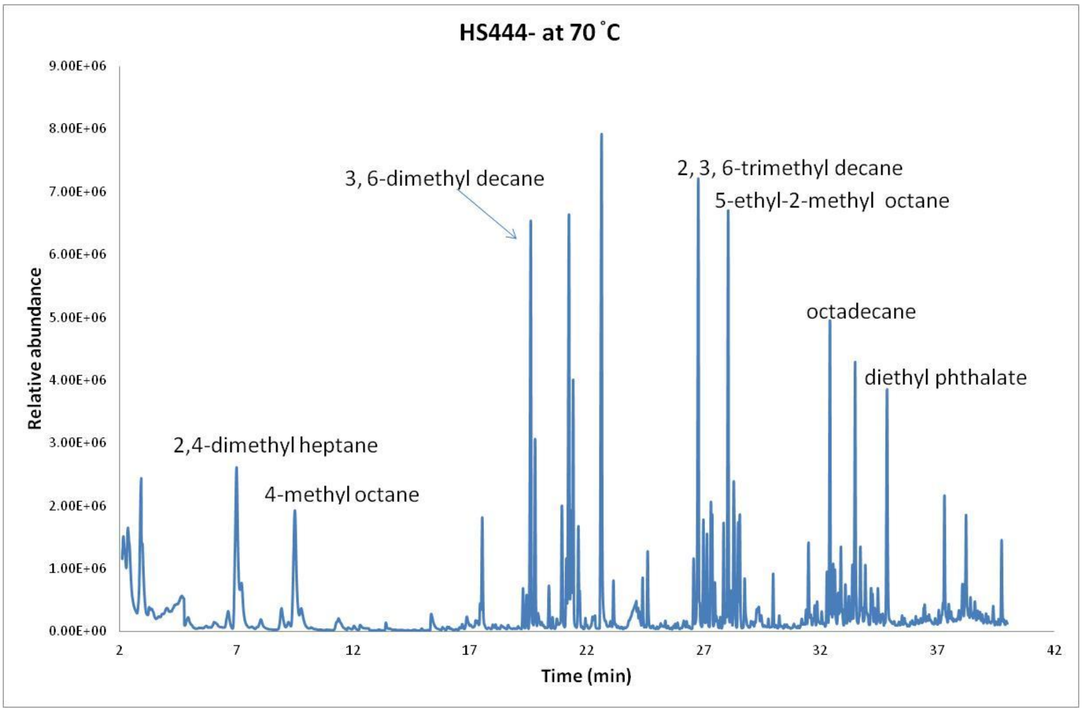

Figure 5.6. Emissions from polypropylene sample HS444 after heating to 70 ˚C

Although there were no visual signs of deterioration after accelerated degradation the emissions from each sample changed with an overall decrease in the number and abundance of branched alkanes measured. 2,2,4,6,6-pentamethyl heptane remained the dominant compound detected above samples HS400, HS403 and HS416. In addition to this dominant compound samples HS400, HS416 and HS444 emitted diethyl phthalate and dimethyl phthalate; sample HS403 also emitted 2,5,9-trimethyl decane, diethyl phthalate and dimethyl phthalate and sample HS444 emitted 4-ethyl decane. The large number of branched alkanes measured in the emissions was expected and can be used to give a tentative confirmation of polypropylene-based objects. However it should be noted that polybutylene will also produce branched alkane emissions and care would need to be taken to differentiate between polypropylene and other polyolefins, with the exception of polyethylene.

5.3.7 VOC emissions from rubber samples

(HS103, HS268 and HS269)

Of the 3 rubber samples analysed one looked to be in relatively good condition (sample HS103), whilst the cracked appearance of the samples HS268 and HS269 suggested that they were in an advanced state of degradation. At 23 °C sample HS103 produced low emissions but acetic acid and tridecane were detected in the headspace. The headspace above sample HS268 was dominated by acetic acid, 4-hydroxy-2-butanone and 5-ethyldihydro-5-methyl-2(3H)-furanone. Sample HS269 emitted acetic acid, 2-butanone and 5-ethyldihydro-5-methyl -2(3H)-furanone. The relatively high concentration of acetic acid emitted from the rubber samples were attributed to two sources. The first source was residual acid from the manufacturing process which typically used acetic acid coagulation. The other likely source was as a result of ozonolysis as outlined in Section 2.2.1. Based on the degraded appearance of some of the samples the latter was thought to be the key source of acetic acid[35-38]. Samples HS268 and HS269 were noted as having a significant odour prior to emission testing and out of the three rubber samples examined, visually they looked degraded. Therefore, the comparatively low abundance and number of compounds identified in the headspace above HS103, compared to HS268 and HS269, was understandable. The two odorous samples (HS268 and HS269) had a complex odour somewhere between a meaty ‘beef-like’ odour with a’ burnt caramel note’ which was likely attributable to the combination of furanones and ketones. Overall, the presence of acetic acid, furanones and ketones in high relative abundance could be used to identify rubber. Whereas, as shown previously, high relative abundance of acetic acid together with the presence of plasticisers could be used to identify cellulose acetate-based objects. The appearance and texture of rubber objects will differ significantly from cellulose acetate which, in combination with volatile emissions, should prevent misidentification between the two polymer types.

Hoven *et al.*[39] measured the emissions from samples of natural rubber and identified a number of compounds. Four samples were examined including cup lumps which were obtained from latex naturally coagulated; ribbed smoked sheet obtained by mixing latex with formic acid after which the coagulum was formed in to sheets and smoke dried; deproteinised rubber- which had been treated with NaOH to remove water soluble proteins; and a standard Thai rubber. Qualitative identification of the emissions was made by GC/MS using head-space sampling. The emissions were classified in to four categories based on polarity: low polarity compounds- aromatic and aliphatic hydrocarbons; moderate polarity compounds- aldehydes and ketones; high polarity compounds- carboxylic acids (C_2-C_7); and compounds containing nitrogen and sulfur[39]. Carboxylic acids were present in the emissions of all the samples and there was a correlation between the intensity of the carboxylic acid peaks in the chromatograms and the strength of the odour from the samples and the quality of the sample. Therefore, the researchers attributed carboxylic acids to be the cause of the mal-odour from rubber[39]. To further confirm this theory, water scrubber systems were used and it was found that after washing the mal-odour was significantly reduced, which was expected as the water soluble carboxylic acids would effectively be washed away. Therefore, the higher relative abundance of acetic acid in HS268 and HS269 compared with HS103 can be correlated with perceived odour strength and quality of the sample, which is similar to the results outlined by Hoven *et.al*[39].

After the samples were heated to 70 °C, the relative abundance of VOCs emitted by sample HS103 remained low; with acetic acid and toluene being the only compounds detected. Sample HS268 emitted acetic acid, toluene, 3-hydroxy-2-butanone, 4-hydroxy-2-butanone, dihydro-5-methyl-2(3H)-furanone, 3-methyl-2-heptanone, 2,5-hexandione and 2-acetyl-5-methyl furan whereas sample HS269 emitted acetic acid, toluene, 4-hydroxy-2-butanone, 3-methyl-2-heptanone, 2-acetyl-5-methylfuran, dodecane, tridecane and tetradecane. The additional compounds emitted after heating made interpretation of the chromatogram more complex and so it was suggested that, once again, 23 °C would be an appropriate temperature to measure reference VOC emission chromatograms.

After accelerated degradation, samples HS103 and HS268 had no visual signs of deterioration; however sample HS269 had reduced flexibility and had become friable. The emissions did alter for sample HS268 (see Figure 5.7) which contained acetic acid, 4-hydroxy-2-butanone, dihydro-5-methyl-2(3H)-furanone, 5-methyl-

2(3H)-furanone, 2-acetyl-5-methyl furan, nonanal and decanal. Interestingly although the appearance of sample HS269 changed dramatically the same major compounds were recorded in the emissions with one exception that the linear alkanes were no longer detected, further work is required to understand why a large change in the physical appearance of the sample did not invoke a larger change in the emissions.

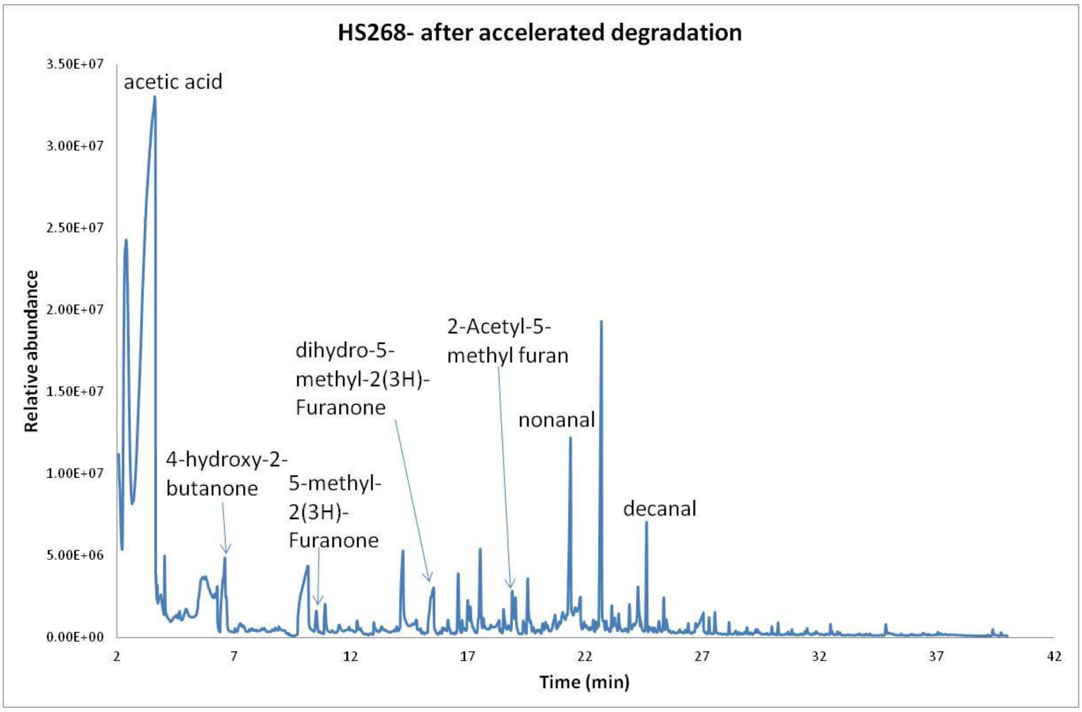

Figure 5.7. Emissions from rubber sample HS268 after accelerated degradation

5.3.8 VOC emissions from poly (vinyl chloride) samples

(HS62, HS415, HS424, HS430 and HS468)

The emissions obtained from all 5 PVC-containing samples at 23 °C contained mostly non-specific VOCs which were present in the headspace above many of the measured polymer types. It was suggested that the emissions could not be used to identify PVC- containing objects. Samples HS424 and HS430 generated emissions which contained a low abundance of VOCs, although it was possible to identify some of the emitted compounds. Sample HS424 released BHT, diethyl phthalate, decanal, nonanal, benzaldehyde, styrene, 1,3 dimethyl benzene and ethylbenzene. Sample HS430 released 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) plasticiser, acetophenone, decanal, nonanal, tridecane and BHT. 2-ethyl-1-hexanol, the breakdown product of DEHP plasticiser[40], was detected above sample HS62 and HS468 as were decanal, nonanal and diethyl phthalate. In addition phenol was detected above sample HS62 and benzaldehyde above sample HS468. Sample HS415 emitted styrene, diethyl phthalate, tridecane, dimethyl phthalate, benzaldehyde and BHT.

Significant changes in emissions were noted after the samples were heated to 70 °C. The HS424 chromatogram displayed low abundance peaks although it was possible to identify benzene, nonanal, decanal, diethyl phthalate, phenol, toluene, nonanoic acid and decanoic acid. After heating, the headspace of HS430 was dominated by TXIB plasticiser and toluene. In addition dimethyl phthalate, BHT, tridecane, decanal, nonanal and phenol were also detected. Sample HS62 was dominated by 2-ethyl-1-hexanol, phenol, 1-octanol, dodecane, diethyl phthalate and BHT. Sample HS468 remained dominated by 2-ethyl-1-hexanol and diethyl phthalate with dimethyl phthalate, decanal, nonanal, cumene and styrene also present. Sample HS415 was dominated by diethyl phthalate, toluene, dimethyl phthalate, BHT, nonanal, styrene and tridecane.

After accelerated degradation, sample HS62 demonstrated visual signs of yellowing. The emissions for this sample were dominated by 2-ethyl-1-hexanol, octane, phenol and diethyl phthalate. 1-chloro-octane was also detected, which was not detected in any of the previously collected emissions. The emissions from sample HS415 were dominated by 2-ethyl-1-hexanol, nonanal, decanal and diethyl phthalate whereas the sample HS424 contained nonanal, decanal, diethyl phthalate, dimethyl phthalate and isothiocyanato benzene. Sample HS430 contained nonanal, decanal, diethyl phthalate, dimethyl phthalate, 2-ethyl-1-hexanol and benzaldehyde (see Figure 5.8). The headspace above sample HS468 contained compounds of low abundance including nonanal, decanal, 2-ethyl-1-hexanol, diethyl phthalate and dimethyl phthalate. The emissions obtained at 23 °C, after heating to 70°C and after accelerated degradation are considered non-specific and cannot be used as key markers for the identification of PVC.

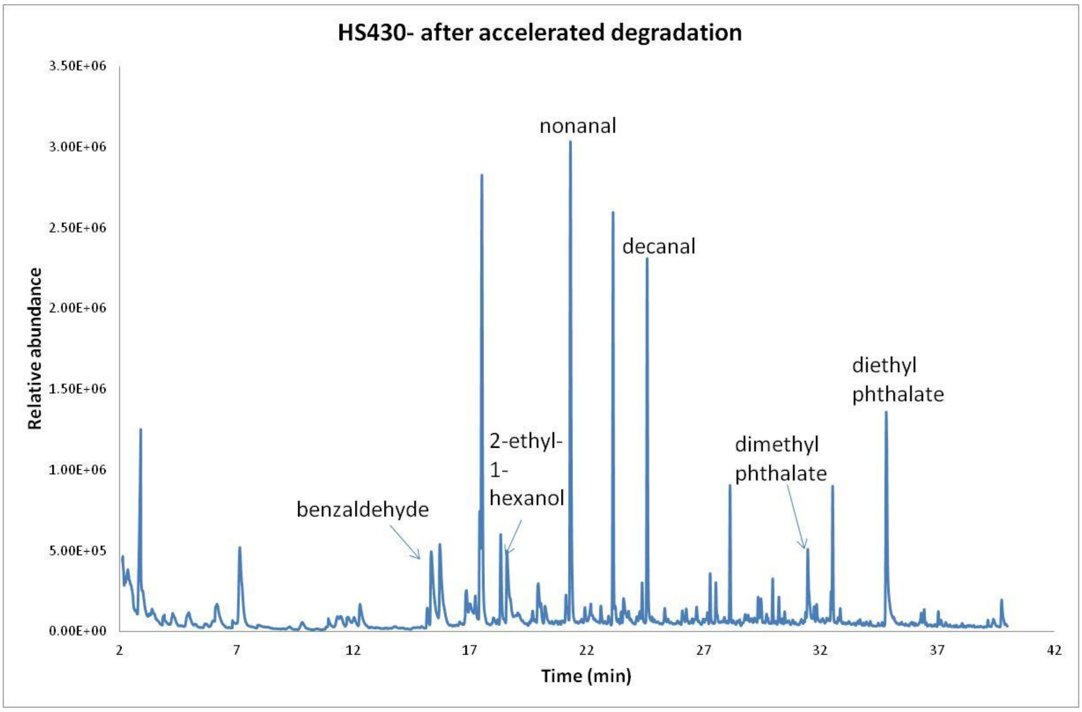

Figure 5.8. Emissions from poly (vinyl chloride) sample HS430 after accelerated degradation

5.3.9 VOC emissions from polycarbonate samples

(HS52, HS143, HS413, HS466 and HS467)

As expected, the polycarbonate samples emitted very low levels of vapours with low relative abundances of benzaldehyde, acetophenone and BHT as measured in the headspace above samples HS52, HS143, HS413 and HS 467. In addition to these three compounds sample HS143 emitted diethyl phthalate plasticiser, sample HS413 emitted nonanal and decanal and sample HS467 emitted acetic acid. As an example see Figure 5.9 which demonstrates the emissions from HS413.

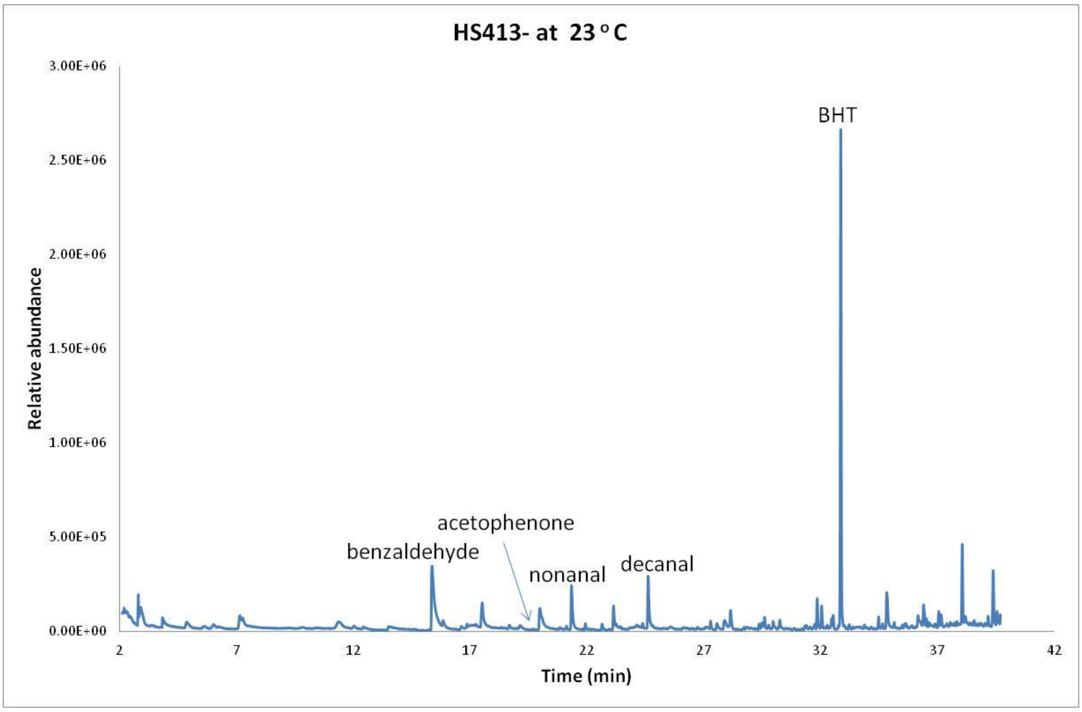

Figure 5.9. Emissions from polycarbonate sample HS413 at 23 °C

There were no significant alterations of the emissions after heating with samples HS467, HS413, HS466 and HS143 displaying low abundance peaks for acetic acid, toluene and diethyl phthalate. In addition to these compounds samples HS467 and HS413 emitted styrene and nonanal and sample HS466 emitted phenol and decanal, whereas sample HS52 emitted phenol and diethyl phthalate. After accelerated degradation there were no visual signs of deterioration on any of the samples and once again emissions were low with samples HS52, HS143, HS413, HS466 and HS467 emitting nonanal, decanal, dimethyl phthalate and diethyl phthalate. In addition to these compounds the chromatogram of the headspace above sample HS52 contained phenol and octanal and sample HS413 contained benzene. The presence of phenol in some of the samples after heating and accelerating ageing could indicate hydrolytic degradation of the samples. The weak carbonate linkage may be hydrolysed to produce phenolic end groups and carbon dioxide[41]. As the compounds detected at 23 °C, at 70 °C and after accelerated degradation are non-specific compounds found in the headspace above a variety of polymers it was noted that emission data could not be used as indicative markers of polycarbonate.

5.4 Conclusions

This study strongly supports the application of Tenax-TD-GC-MS as an in-situ, non-invasive sampling method for the analysis of emitted vapours from plastic objects. As the Tenax® adsorbent is held in a stainless steel housing unit it was easily shipped to and from sampling sites (this was the method of shipping used to collect vapours above the museum objects studied here). The ability to be able to collect phthalate ester plasticisers was also recognised as an important benefit since such compounds have been linked to detrimental effects on human health[42-44]. The emission of phthalate ester plasticisers is due to their migration through polymer objects to the surface where they may evaporate. Being able to collect and identify such plasticisers may help heritage institutions to produce guidelines on how best to handle and work with significant numbers of plastics within collections which may be emitting potentially harmful compounds.

Furthermore, the ability to identify emitted acetic acid vapours was also of great importance as it identifies objects which are a cause for concern both in terms of their own stability but also for the potential detrimental effect that acidic emissions may have on other objects. Although Tenax-TA sorbent is not the most suitable sorbent for the collection of acetic acid vapour, but was shown clearly here that it did retain acetic acid (probably not with 100 % efficiency) allowing a positive indicator of acid vapours in indoor air.

Although the vapours collected above the headspace of PVC or polycarbonate samples were labelled ‘non-specific’ and could not be used to positively identify these polymer types it was clearly demonstrated that inferential VOCs can be used to detect cellulose acetate, polyurethane, cellulose nitrate, rubber, polyethylene, polypropylene and styrenic based polymers objects at 23 °C. There appeared to be no advantage of heating samples to 70 °C prior to emission collection and VOC collection at 23 °C was recommended for assessment of polymer fragments in the micro-chamber. In this way the collected data could be compared with the emissions of objects studied in-situ in heritage environments, which will undoubtedly be collected at room temperature. The accelerated degradation studies represent the first attempt to artificially degrade samples and then assess alterations to VOC emissions using thermal desorption tubes containing Tenax-TA sorbent coupled with TD-GC-MS. Differences were observed and could be explained. This proof of concept study provided strong evidence that inferential measurement of polymer stability was possible. The use of vapour phase monitoring should not be underestimated. Should objects be assessed and characterised by 'smell' alone, this would permit assessment of museum objects without the need to sample, touch or prepare objects in any way prior to measurement. However further work would be required before emissions can be used to accurately assess the stability, or stage of deterioration of plastic objects.

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CHAPTER 6

INDOOR AIR POLLUTION WITHIN HERITAGE INSTITUTIONS

Contents of Chapter 6

6 Introduction

6.1 Air pollution within heritage institutions

The results discussed in Chapter 5 provided evidence that a newly developed proof-of-concept sampling method for the non-invasive assessment of polymer objects in heritage environments was successful for the identification of 7 commonly found polymer groups. The study used laboratory simulated experiments and sacrificial polymer fragments to better understand VOC emissions that would be measured around different plastic objects. Now that VOC patterns have been examined and it was noted that sampling at room temperature was recommended, the next step was be to sample the air around objects, in-situ, in heritage institutions. However, when the air around an object is measured, the sample will contain VOCs emitted from the object together with a wide range of VOCs which are also present in indoor air and come from numerous other sources. Thus the indoor air environment of heritage institutions must also be understood in order to make this potential new method of analysis a success.

Monitoring indoor air pollution is an important area of research. Numerous studies have highlighted the most commonly encountered pollutants within heritage institutions. Many of these pollutants originate from the off-gassing of structural and decorative materials[1-7]. More recently it was recognised that heritage objects themselves may contribute to indoor air pollution, with plastic based objects being a case in point[8]. Indoor air pollutants may catalyse the degradation of an object from which they were released, or cause cross contamination to other objects potentially inducing degradation[9]. To assess the indoor air environment there are standard methods of analyses that are typically employed. These tests range from qualitative, to pseudo-quantitative, to quantitative and provide less to more information, respectively.

Qualitative direct reading passive samplers include A-D strips[10] which change colour in the presence of acidic pollutants. Alternatively polished metal coupons are used to indicate contaminated environments as they will tarnish or corrode at ambient conditions in the presence of corrosive pollutants such as acetic acid, formic acid, hydrogen sulfide and sulfur dioxide[3]. The commercially available A-D strips are an example of a non-specific test and allow the identification of a pollutant class. The metal coupons act differently, for example lead will corrode significantly in the presence of acetic or formic acid vapours, corroding at a rate which correlates with the concentration of the acid[3, 11]. Therefore, the metal coupons can permit a better assessment of the pollutants present. The use of metal coupons is this way is a variation of the well-known Oddy test. In the Oddy test metal coupons are placed in a container with the test material and the container is heated to 60 °C at a high humidity for 28 d. Visual evidence of corrosion, or tarnishing, of the metal coupons will result in de-selection of the test material for use in museum construction. These qualitative test methods do not rely upon the diffusion of pollutant vapours, but rather rely upon the pollutant vapours reacting with an open active surface.

Pseudo-quantitative direct reading passive sampling devices include the commercially available Dräger[12] colour diffusion tubes. Here the pollutants are collected by diffusion into a tube or badge where the pollutants are chemically derivatised producing a colour change. The length of stain that develops in the tube is used to estimate the concentration of the pollutant gas being measured. Colourimetric sampling devices are available for a range of pollutants such as acetic acid[12, 13], formaldehyde[13, 14], sulfur dioxide[12, 14] and nitrogen dioxide[12, 14]. The colourimetric diffusion tubes are affected by interferences for example the acetic acid sampler is based on an acid-base indicator and so any acid present in the air will cause a colour change. The AirScan badges[15] for formaldehyde are open faced devices and do not have a diffusion barrier therefore the uptake of air is not limited, a colour change is generated upon the uptake of pollutant vapours[3].

Palmes (open path) diffusion sampling tubes can be used to monitor pollutants in indoor air. The sampling tubes do not have a physical diffusion barrier; instead the static air at the entrance of the tube is the diffusion barrier. Therefore, the rate of diffusion is controlled by the ratio of the length of the tube to the outer diameter of the tube. The sampling tubes are commercially available from Gradko International[16] and the detected pollutants include nitrogen dioxide, sulfur dioxide and ozone. For an additional cost Gradko International will analyse the sampling tubes and produce a report summarising the results. The University of Strathclyde also offer open path diffusion tubes specifically for heritage applications. The university service offers diffusion tubes suitable for monitoring acetic acid, formic acid and formaldehyde and the cost includes analysis of the tubes and the production of a report. The university supplied open-path diffusion samplers have been used to monitor organic acids and formaldehyde in heritage applications[17, 18]. The organic acid samplers contain potassium hydroxide to trap acid vapours via an acid-base reaction and the formaldehyde samplers use 2,4-dinitrophenylhydrazine to trap formaldehyde vapours as the hydrazone derivative. Collection of pollutant vapours can take up to 28 d, however the method is much more accurate than direct reading devices. In addition, diffusion samplers have lower detection limits and are pollutant specific.

All the method described above are used in heritage environments. However, the benchmark method of sampling volatile organic compounds (VOCs) indoor air is to use active sampling and collect VOCs onto Tenax sorbent tubes[19]. The porous polymeric sorbent (2,6-diphenyl-p-phenyleneoxide) which is suitable for the collection of a wide range of VOCs is packed inside stainless steel sampling tubes which may be used in active or passive mode. Both the National Institute of Occupational Safety and Health (NIOSH) and the Environmental Protection Agency (EPA) specify the use of Tenax in their standard methods. Gibson *et al*.[20] employed the use of Tenax TA sampling tubes, in active mode, to monitor the VOCs present in the indoor environments of 8 heritage institutions containing paper based collections. Three sampling locations within each institution were selected; the first two locations (referred to as locations A and B) contained paper based collections. The third location (referred to as location C) was a reference area and contained no paper based materials. The thermal desorption tubes containing Tenax were conditioned prior to deployment in a thermal desorption unit at 320 ºC for 20 min. After conditioning the tubes were sealed with brass caps and shipped to the respective heritage institutions. On site the tubes were used in active mode by employing an SKC Universal sampling pump with a flow rate of 100 cm^3 min^{-1} which was calibrated using a bubble meter. Active sampling was conducted over a period of 24 h giving an approximate sampling volume of 144 dm^3. By using a 21 analyte calibrant solution, 17 compounds were shown to be common to each heritage institution; heptane, toluene, furfural, ethylbenzene, ortho- and para-xylene, cyclohexane, nonane, 4-ethyltoluene, benzaldehyde, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, decane, limonene, acetophenone and camphor. Examination of the data indicated that furfural was the only analyte to be consistently present at significant concentrations in locations A and B (which contained paper materials) of all 8 institutions, compared with location C at each institution. The measured concentrations of furfural in locations A and B from the 8 institutions ranged from 0.2 to 110 µg m^{-3}, with a mean and standard deviation of 17.9 ± 28 µgm^{-3}. Whereas, the concentrations measured in location C were 0 to 2.4 µg m^{-3}, with a mean and standard deviation of 0.94 ± 0.81 µg m^{-3}. In the same study[20] SPME fibres (DVB/CAR/PDMS) and PDMS elastomer strips were also used to examine VOCs emitted directly from the paper materials in locations A and B from the respective heritage institutions. Combined examination of the results from all three sampling techniques indicated that acetic acid and furfural were consistently higher in concentration in the locations containing paper materials (locations A and B) compared with reference location C in each institution. As a result the authors suggested that acetic acid and furfural (and possibly trimethylbenzenes, ethyltoluene, decane and camphor) may be present in indoor air as a result of cellulose degradation and together could serve as an inferential non-invasive marker for paper deterioration.

Schieweck and Salthammer[21] used thermal desorption tubes containing Tenax to collect VOCs emitted from museum showcases. In addition, formaldehyde and organic acids were also measured due to their known corrosive impact. Two main showcase construction types consisting of old and modern-type showcases were examined. The old-type were of traditional style constructed of wood and wood based products with acid curing sealants. The more modern showcases are generally built from glass, lacquered metals and neutral curing silicone rubber. The showcases remained closed for one week prior to sampling to enable equilibrium of material emissions and air concentration to be established. During sampling the showcases remained closed and the authors also sampled the gallery to gain an understanding of the background emissions. Perkin Elmer thermal desorption tubes containing Tenax were used in active mode to collect VOCs from the museum showcases. The sampling was conducted over a period of 40 min with a pump flow rate of 150 mL min^{-1}. A range of characteristic compounds were identified from the old and modern-type showcases including alcohols, aldehydes, monoterpenes, aromatic hydrocarbons, carboxylic acids, carboxylic esters, glycol ethers and glycol esters. The results highlighted that old-type showcases which were constructed from traditional materials characteristically had a low number of different VOCs, but high levels of formaldehyde and organic acids. Results obtained from the sampling of modern-type showcases demonstrated that a broader range of VOCs were measured and that acetic acid was still relatively abundant despite the differences in construction materials.

In another study by Schieweck *et al.*[5] thermal desorption tubes containing Tenax were used to collect VOCs from the storage rooms of the Lower Saxony State Museum in Hanover, Germany. The museum recognized the importance of indoor air quality and the requirement to not only provide a healthy indoor atmosphere for visitors and staff, but to protect the cultural artefacts from deterioration caused by such air pollutants. The collection held by the museum was founded in 1852 and is comprised four departments: Natural Science (Zoology and Geology), Ethnology, Prehistory and Art gallery. Sampling of VOCs was conducted in active mode (150 mL min^{-1} for 40 min) using thermal desorption tubes containing Tenax. In this study over 40 different VOCs were identified across the various sampling areas and some of the most prominent results are discussed further. The results of VOC sampling in the art gallery store room showed high concentrations of iso-alkanes (344 μgm^{-3}), *n*-pentane (366 μgm^{-3}), 2-butanone (202 μgm^{-3}), hexanal (209 μgm^{-3}) and pentanal (200 μgm^{-3}). The curators confirmed that the gallery was recently renovated, therefore, the sealant used in the parquet flooring as well as the wall paint and coatings and their associated solvents would be responsible for the high concentration of the measured VOCs. In the geological store room the monoterpenes 3-carene (max. 76 μgm^{-3}) and α-pinene (max. 158 μgm^{-3}) were measured. These VOCs are characteristic of soft pine wood, which was present in the large number of drawers within the store room. Within the wooden drawers of the Ethnology store room significant concentrations of 1,4-dichlorobenzene (40 μgm^{-3}) and camphor (110 μgm^{-3}) were measured. The curators reported that records show that between 1956 and 1959 the drawers were disinfected with 1,4-dichlorobenzene and between 1956 and 2000 the drawers were treated with camphor to prevent against insects and fungi. The VOC sampling in this study was conducted in 2005; these results demonstrate that although treatment with these two compounds is no longer employed the compounds are still easily detected. The compound 2-ethyl-1-hexanol was also indentified in the general background of the Ethnology store room, being a breakdown product of di-2-ethyl-hexyl-phthalate (DEHP) plasticiser it is likely that the compound was emitted from a polymeric material, most likely the flooring material within the storage room. In the Zoology storage room high concentrations of benzaldehyde (58 μgm^{-3}) and benzyl alcohol (46 μgm^{-3}) were measured and attributed to the artefacts within the collection. The collection contained animal skins which may have been chemically treated. A large concentration of benzyl alcohol was also measured in the Prehistory store room, though a source was not identified. The authors conclude that the measured VOCs can be arranged in 3 groups. The first being biocides, such as camphor, 1,4-dichlorobenzene, naphthalene and benzaldehyde for example, which are probably due to the treatment of the artefacts themselves. The second group is monoterpenes such as α- and β-pinene, 3-carene and limonene for example, which are attributed to wood and derived materials. The final group is ‘other compounds’ which are most likely emitted from the building materials such as polymeric floor tiles.

6.2 Case Studies: VOC sampling of plastic objects currently held in heritage collections.

The above published literature studies highlighted an extensive range of VOCs that were collected by Tenax sampling tubes in indoor air and they would potentially confound with emissions from heritage objects. Therefore it is suggested that it is imperative that sampling blanks are taken at each location (the indoor air alone without target object) in order to rule out VOCs that are present, but not as a result of object emission. To examine the use of Tenax sampling tubes for on-site assessment of polymer objects, 7 case studies were undertaken.

6.2.1 Object descriptions and sampling locations.

A measurement ruler and a stencil, both approximately 60 y old, which are part of the collection at the Secret War Tunnels at Dover Castle, England and under the governance of English Heritage, were assessed (Figure 6.1).

Figure 6.1. Measurement ruler and stencil

The ruler appeared as though it was comprised of two polymers, a transparent plastic with an opaque insert and was noted as emitting a strong odour. The insert was yellow (though this could be discolouration rather than intentional colour) and had become cracked and warped causing the distortion of the other plastic component. The stencil was transparent and blue in colour and looked to be in a stable condition, with no obvious cracks or crazing and no odour. The ruler and stencil had been stored in boxes for a number of years in a storage room which had no climate control. The room had black-out blinds on the windows and lighting was only used when the room was populated. The measurement ruler and stencil were placed inside individual sealed glass containers to allow emitted VOCs to establish equilibrium in the headspace of the container before the Tenax sampling tubes were placed into the glass container. The sampling was conducted in passive mode for a period of 14 d at room temperature.

A collection of photographic negatives, approximately 65 y old, held in a ring binder Timecare storage box within a repository at the National Records of Scotland Edinburgh, was assessed (Figure 6.2).

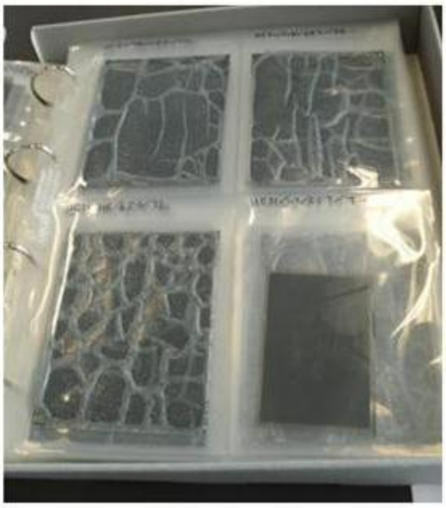

Figure 6.2. Photographic negatives in Timecare box

The photographic negatives were warped and fragile. Individual negatives were held in place inside Secol- Archival System polyester pockets. A second collection of photographic negatives, of approximately the same age, were also examined (Figure 6.3).

Figure 6.3. Loose photographic negatives in brown storage box

The negatives were stored loose with Glassine paper between each negative and were stored in a general purpose cardboard storage box. The negatives were warped and emitted a distinctive acidic odour and the Glassine paper was heavily discoloured and almost completely brown. The repository was climate controlled at 16 °C ± 2 °C with a relative humidity of 50 ± 5 % RH. The delicate nature of the photographic negatives from the National Records of Scotland meant that sampling was conducted in-situ. The negatives were not encapsulated in glass containers but were instead sampled directly from within their respective storage boxes. As a comparison, the conservation repository where the boxes of negatives were held was also sampled. Once again, sampling was conducted using thermal desorption tubes, in passive mode, over a period of 14 d in the climate controlled repository.

A storage/display box, known colloquially as a ‘crystal box’, held at The British Museum, London was assessed. The box was approximately 5 y old and was not stored in controlled environmental conditions. At the time of monitoring the object showed no visual signs of degradation. As the storage box at was too large to fit inside a glass vessel a Tenax sampling tube was placed inside the storage box and the lid was firmly closed.

In addition a small lapel pin badge was also sampled (Figure 6.4). The badge was not part of the collection at The British Museum, but was purchased by a conservator from a website since the badge closely resembled other badges which were in the collection.

Figure 6.4. Front and reverse of pin badge

The badge was a national flag pin with the national flag of Greece in coloured ink on the front, which was covered in a plastic coating. The pin badge appeared to have been produced as part of a promotion for Sweet Caporal Cigarettes according to the small advertisement on the reverse of the badge. The reverse of the badge also provided information on the badge manufacturer (The Whitehead & Hoag Co. of Newark, New Jersey) and had a patent date of 1896. The badge looked to be in good condition, except for the slight corrosion of the metal components of the badge and slight discoloration of the paper. The pin badge was placed in a sealed glass vessel with a sampling tube to passively sample the environment for 14 d.

Finally, rubber rainwear also held at The British Museum was assessed (Figure 6.5). A pair of trousers approximately 25 y old had been stacked on top of other rubber rainwear within a wooden drawer in a store room which had no environmental control system.

Figure 6.5. Rubber rainwear

The garment was in varying condition across the surface from fairly flexible in some areas, to brittle and flaking in the dark design areas and was noted as emitting a strong odour. The rubber trousers were placed in a sealed polyethylene bag for sampling in passive mode using a Tenax sampling tube for 14 d.

6.2.2 Experimental method for the analysis of objects in heritage collections

The thermal desorption sampling tubes were analysed by thermal desorption (Unity series 2, Markes International) and gas chromatograph (7890A GC system, Agilent Technologies) coupled to a mass spectrometer (5975C inert XL MSD, Agilent Technologies). Separation was performed using a capillary column (HP-5MS 30 m x 250 µm x 0.25 µm, Agilent Technologies) with a carrier gas (He) flow rate of 1 cm^3 min^{-1}. The isothermal column temperature programme was 40 $^{\circ}C$ for 10 min, then 5 $^{\circ}C$ min^{-1} to 270 $^{\circ}C$. Mass spectra were acquired in electron ionisation mode at 70 eV in the m/z range 40-300. Analytes were identified by comparing collected data with mass spectra held in the National Institute of Standards and Technology (NIST 08) mass spectral library.

6.2.3 Results of emission characterisation of objects in heritage collections

The emissions from the measurement ruler (see Figure 6.6) were dominated by a large relative abundance of camphor and 1,7,7-trimethyl-bicyclo[2.2.2]heptane-2,5-dione as well as fenchone, tetrachloroethylene and toluene. As confirmed by the examination of VOC emissions from the reference collection in Chapter 5, the presence of camphor and related terpenes allowed the unambiguous identification of this sample as cellulose nitrate. The extremely high relative abundance of these compounds demonstrated that the object was actively degrading (although this was evident by observation alone). This can be seen from the complex chromatogram (Figure 6.6) which includes VOC emissions from the ruler and also other VOCs commonly present in indoor air.

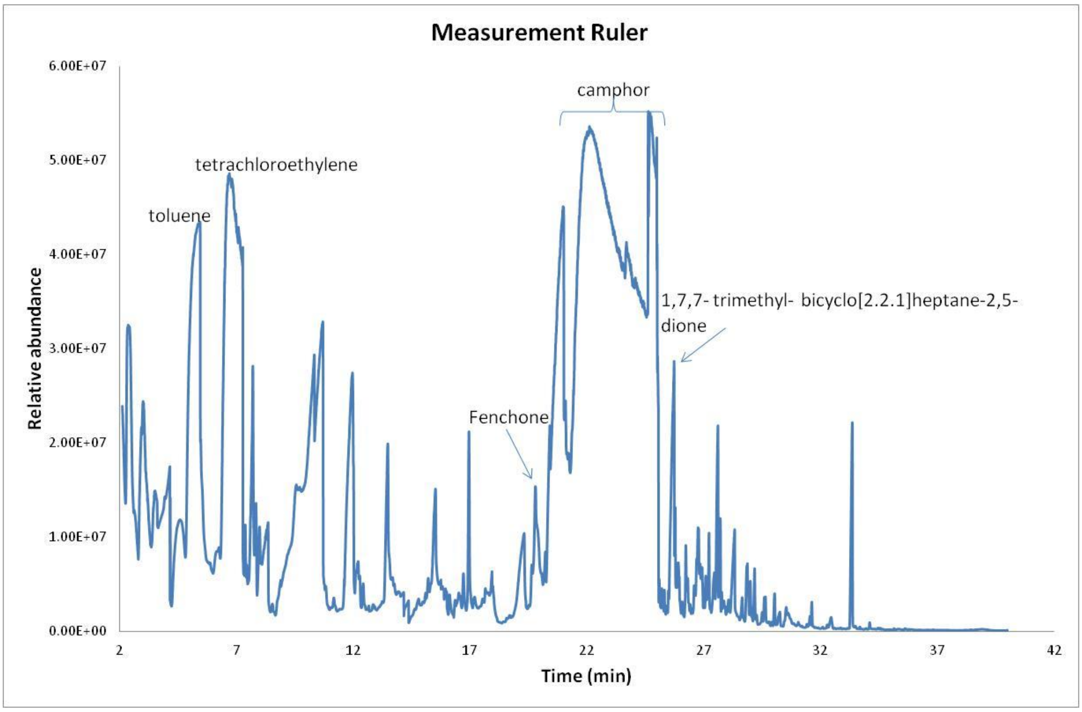

Figure 6.6. Emissions from the measurement ruler

Examination of the emissions from the blue stencil (Figure 6.7) demonstrated a significant camphor peak and a small fenchone peak which indicated that the sample was also cellulose nitrate. The broad camphor peak was not anticipated since the object appeared to be in good condition with no visible cracks and emitted no discernible odour. Although the measurement ruler and the blue stencil appeared to be quite different in terms of perceived stability (based on appearance alone), examination of the emissions have shown that both samples are emitting a high relative abundance of camphor. Not only have the emissions confirmed the extent of degradation of the ruler, but have also shown that the stencil may not as stable as was previously thought. The emissions from the blue stencil also showed the presence of tetrachloroethylene, 5,5,6-trimethylbicyclo[2.2.1]heptan-2-one and an alkylated phenol (2,4-bis(1,1-dimethylethyl)-phenol) which was most probably used as a UV stabiliser and antioxidant. Bicyclic ketones such as 1,7,7-trimethyl-bicyclo[2.2.2]heptane-2,5-dione and 5,5,6-trimethylbicyclo[2.2.1]heptan-2-one were identified in the emissions from the measurement ruler and blue stencil, respectively. Such compounds were not identified in the VOC emissions from the cellulose nitrate reference collection at room temperature, after heating or after accelerated degradation.

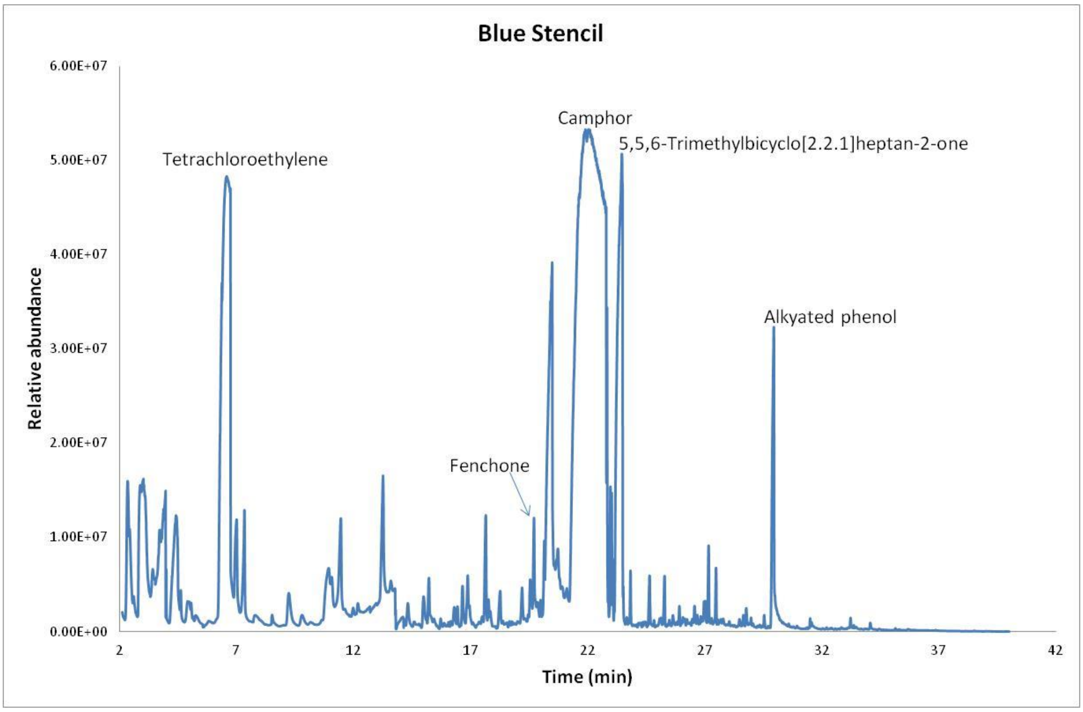

Figure 6.7. Emissions from blue stencil

The photographic negatives stored and assessed in the Timecare box demonstrated a large relative abundance of acetic acid, tetrachloroethylene and phenol in addition to 2-ethyl-1-hexanol and triethyl phosphate (see Figure 6.8). The high relative abundance of acetic acid together with the plasticiser breakdown products allowed a positive identification of this material as cellulose acetate. In addition to the non-invasive and unambiguous identification of polymer type, the presence of phenol and 2-ethyl-1-hexanol confirmed that TPP and DEHP plasticisers were used during the production of the cellulose acetate.

The photographic negatives stored in the general purpose cardboard box (Figure 6.9) were noted as having a strong acidic odour. Unsurprisingly an extremely large acetic acid peak was obtained which completely dominated the first 15 min of the chromatogram. In addition, a very large phenol peak and an alkylated phenol were also measured. The alkylated phenol (2,4-bis(1,1-dimethylethyl)-phenol) was also measured in a cellulose nitrate sample and is likely to have been added a stabiliser. Previous examination of VOCs emitted by the reference collection indicated that chromatograms containing acetic acid as the dominant peak are likely to be cellulose acetate. The high relative abundance of phenol, as previously indicated, was considered as a marker of TPP plasticiser breakdown.

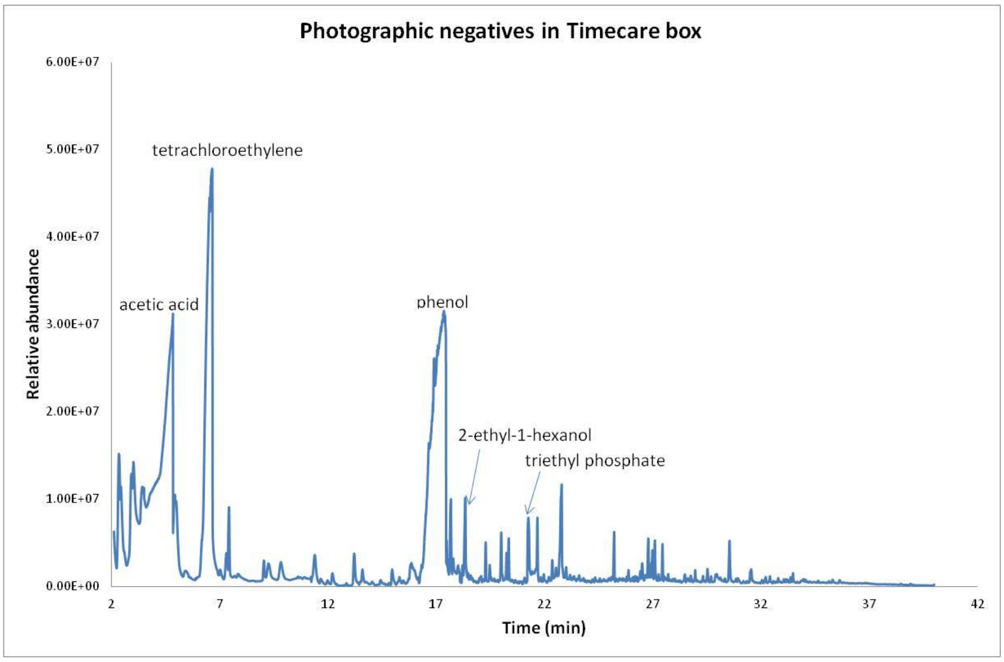

Figure 6.8. Emissions from photographic negatives stored in Timecare box

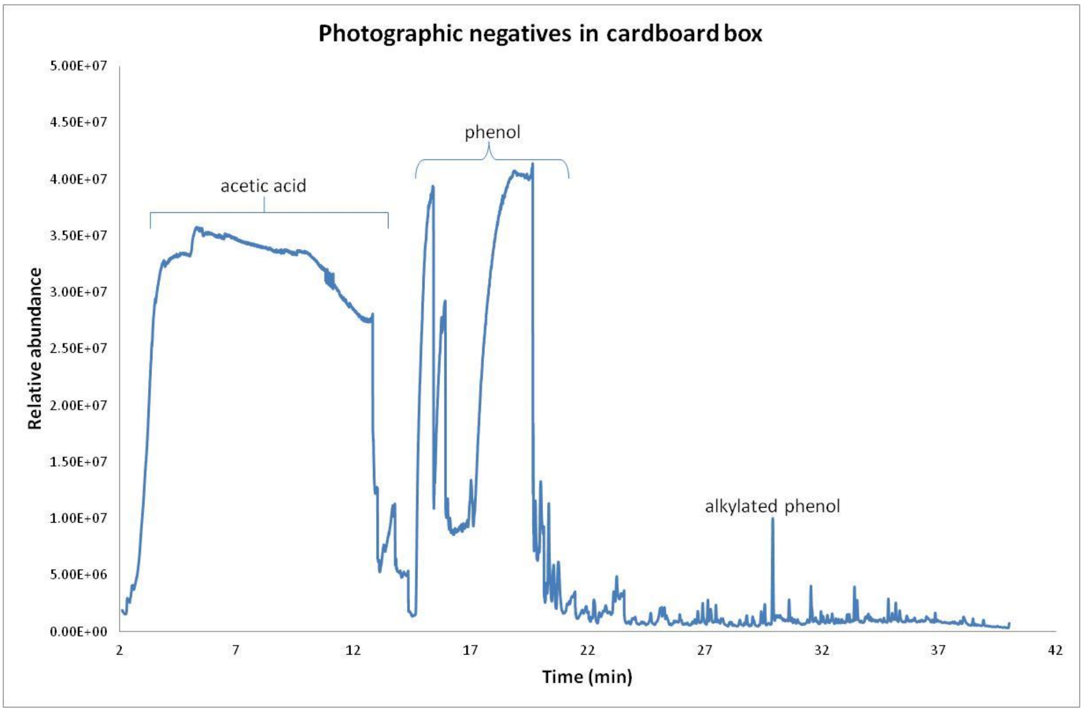

Figure 6.9. Emissions from photographic negatives stored in cardboard box

Since the photographic negatives in the Timecare box, and those in the general purpose cardboard storage box, were not placed inside sealed glass vessels for emission monitoring on account of their size, it was considered even more important to monitor the general background emissions present in the conservation repository. The relative abundance of the emissions from the conservation repository (Figure 6.10) were an order of magnitude lower than emissions obtained from either set of photographic negatives. The low relative abundance and range of volatiles, such as tetrachloroethylene, benzaldehyde, phenol, acetophenone, nonanal and tetradecane, are typical of the compounds commonly measured in indoor air[22, 23]. The VOCs will have been generated from many sources such as other objects within the repository, building materials and from cleaning products used within the building. None of the emissions measured in the repository were considered to have contributed significantly to the VOC emissions measured from either set of photographic negatives.

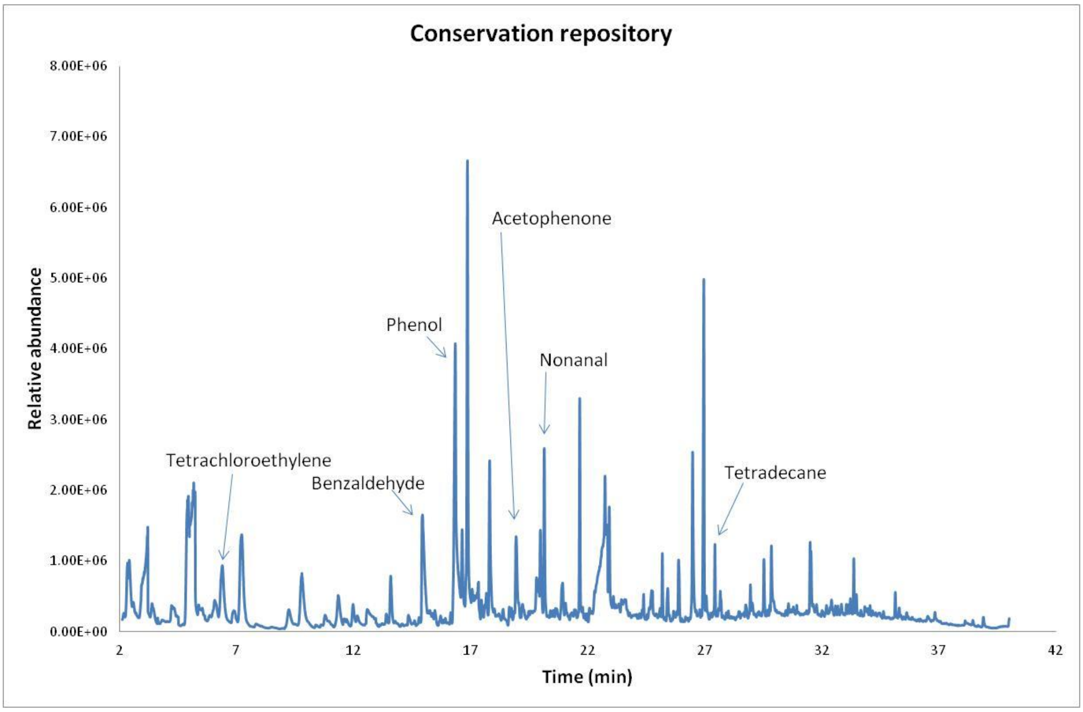

Figure 6.10. Emissions from conservation repository

The VOCs emitted by the crystal storage box (Figure 6.11) were dominated by tetrachloroethylene, styrene and 2,4-bis(1,1-dimethylethyl)-phenol, with much smaller ethylbenzene and diethyl phthalate concentrations. Although tetrachloroethylene was the largest peak observed, the presence of styrene and ethylbenzene together was indication enough that the box was a styrenic polymer (see VOC emissions from polystyrene, Section 5.3.1). In addition to the identification of the polymer, it was also possible to identify the plasticiser (diethyl phthalate) and stabiliser (2,4-bis(1,1-dimethylethyl)-phenol) used (see Figure 6.11).

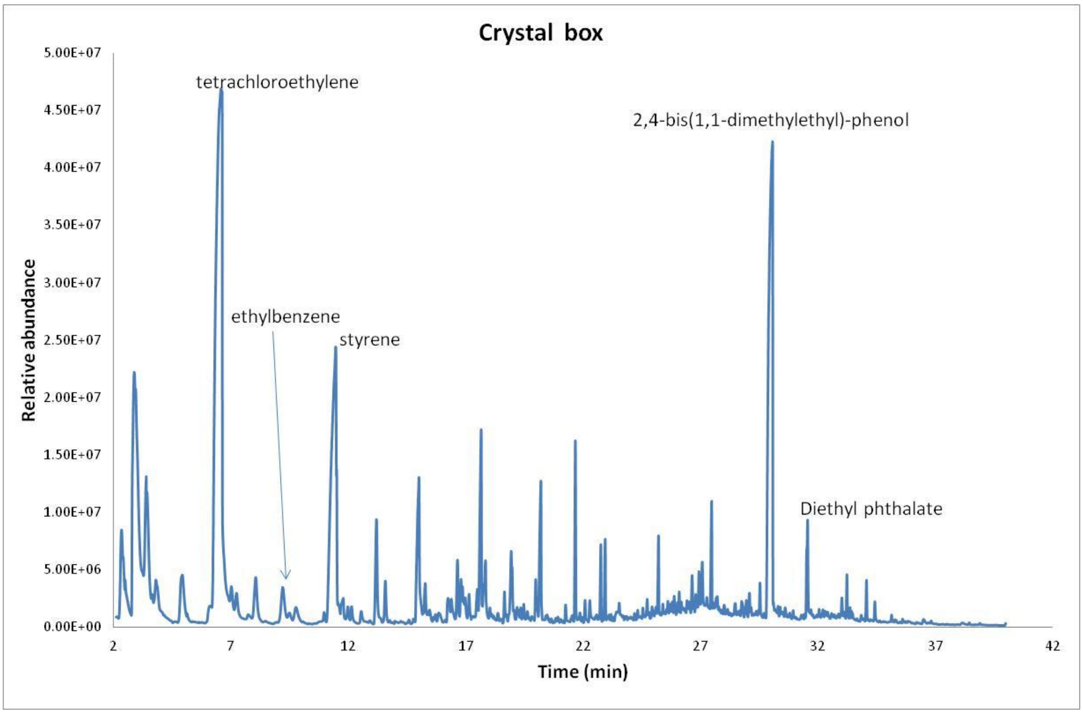

Figure 6.11. Emissions from crystal box

The VOC emissions from the pin badge (Figure 6.12) indicated the presence of camphor which was previously identified as a marker for cellulose nitrate. In addition, furfural, ethylbenzene, o-xylene, cumene and benzaldehyde were also identified. Previous research has identified furfural, in particular, as being associated with paper deterioration[20]. These results suggested that the paper inserts on the front and rear of the pin badge were deteriorating and that the plastic film covering the front of the badge was cellulose nitrate.

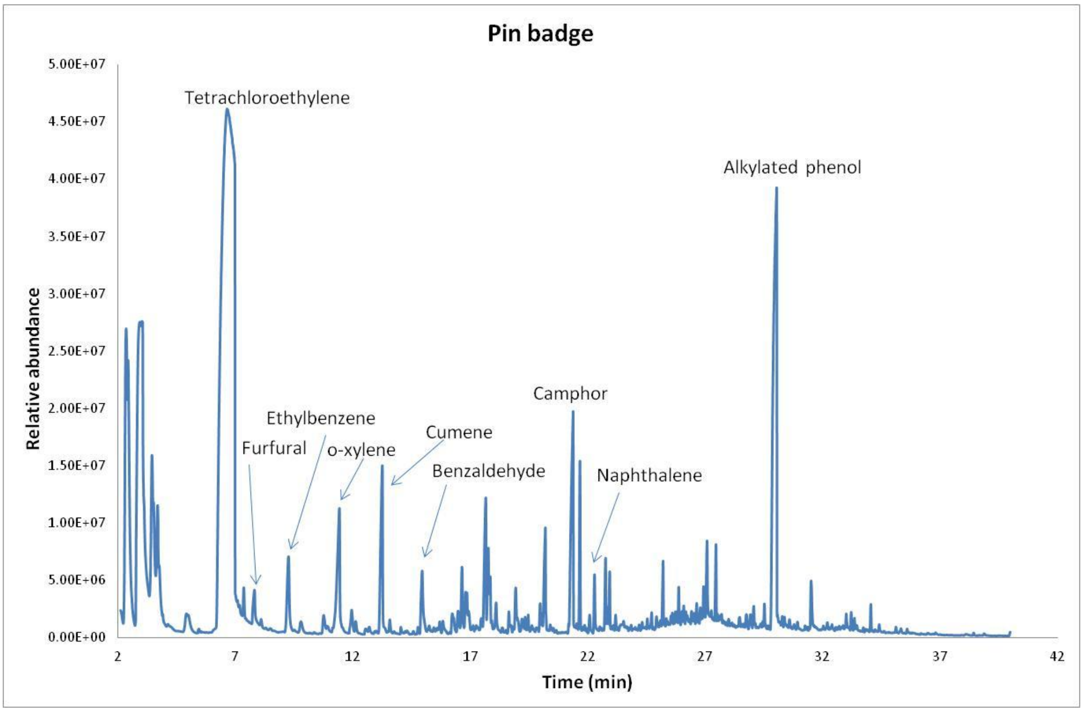

Figure 6.12. VOC emissions from the pin badge

The chromatogram obtained from the rubber trousers was complex and indicated the presence of a number of overlapping peaks, though some assignments were possible (Figure 6.13). Acetic acid, tetrachloroethylene, 3-methyl-2-heptanone, octamethyl-cyclotetrasiloxane and decamethyl-cyclopentasiloxane were identified. Here the presence of acetic acid, without triphenyl phosphate or other typical plasticisers, indicated that the material was rubber. Moreover, measurement of the different siloxane compounds suggested that the rubber garment was water-proofed using a siloxane based treatment, which appears to be failing and breaking down. The object is in a severe state (as evidenced by the VOCs emitted) and needs immediate attention to slow down the rate of degradation.

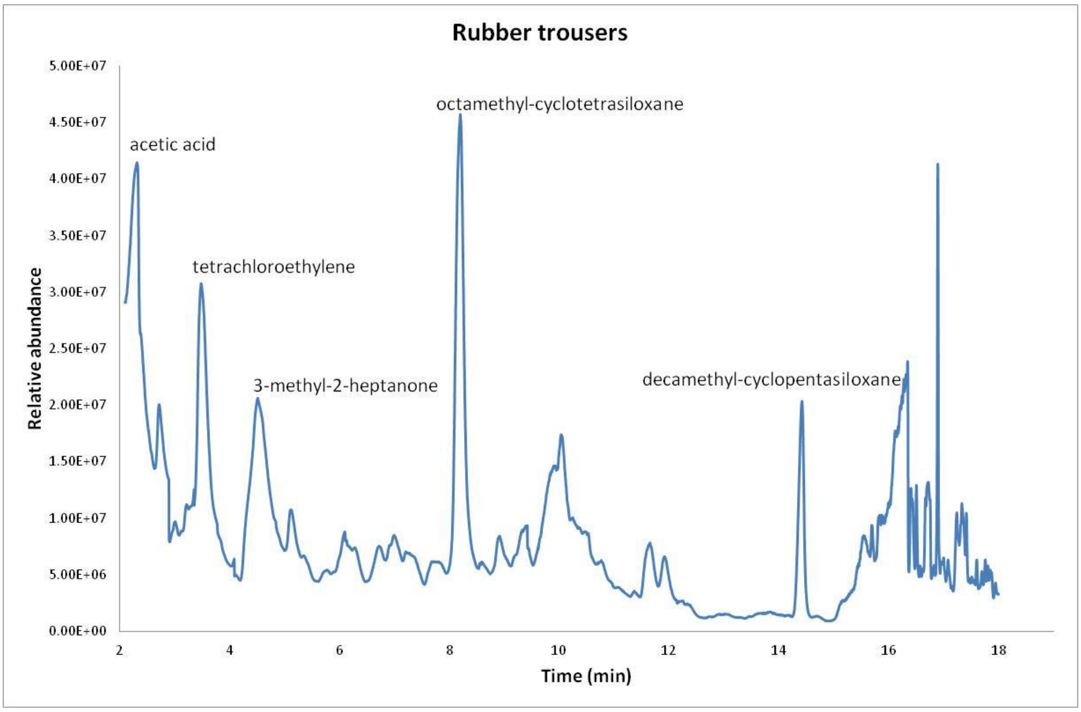

Figure 6.13. Emissions from rubber trousers

6.2.4 Conclusions and discussion of case study results

The results of the museum object case studies clearly supported the laboratory results and validated the use of Tenax-TD-GC-MS as a robust, non-invasive method of determination of objects containing cellulose nitrate, cellulose acetate or styrene. During analyses the objects were not sampled nor where they ‘touched’ by small probes, IR light or lasers. In addition to polymer identification it was also possible to obtain further information about the objects such as the types of plasticiser used during production or the addition of further treatments. Here tetrachloroethylene was measured in the headspace above all objects and at low relative abundance in the conservation repository (it was not present in blank thermal desorption sampling tubes). The exact function of tetrachloroethylene in polymer formulations was not clear, although it may have been used as a solvent during the plastic manufacturing process. The need to understand emission profiles of indoor air was also evident in the case study results where complex chromatograms were obtained. However despite the confounding of common indoor air pollutants with VOCs emitted by heritage objects, the novel non-invasive method of analysis developed was shown to be simple, easy to use, valid and provide accurate determination of various polymers in heritage objects.

This study provides evidence that VOC sampling using Tenax sampling tubes may be conducted on heritage objects regardless of their physical size. Smaller objects were encapsulated in glass, while larger objects were sampled within large polyethylene storage bags and some fragile objects were examined in-situ. A standard protocol was developed to permit sampling for 14 d when sampling was undertaken in passive mode. Subsequent examination of some of the chromatograms indicated that even 14 d may have been too long. It is therefore recommended that in situations where the object under study is noted as emitting a strong odour that 7 d in passive mode be used during the initial air sample assessment.

6.3 References

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CHAPTER 7

ACETIC ACID VAPOURS RELEASED FROM MUSEUM OBJECTS

Contents of Chapter 7

7 Introduction

Previous laboratory work (Chapter 5) and case studies (Chapter 6) identified acetic acid vapour as a primary VOC pollutant emitted from cellulose acetate and rubber objects. This is of high significance because the acetic acid vapours were almost exclusively measured in high concentration. These vapours can further promote deterioration of the source object or cause cross-contamination of susceptible objects stored or displayed in close proximity to the emission source. As stated previously, although Tenax-TA sampling tubes were used successfully to qualitatively indicate the presence of acetic acid vapours, a different method of analysis is required should quantitative assessment of emissions be required. The most effective quantitative method of sampling acetic acidic emissions in heritage environments is to use a passive sampling device that is deployed in the same way as Tenax sorbent tubes. The passive device relies on a chemical trap which uses potassium hydroxide to trap organic acids by acid-base interactions. This additional sampling study was undertaken to provide strong evidence that inferential measurement of polymer stability is possible.

7.1 Small scale investigation of the acidic emissions from selected plastic objects in heritage collections: object sampled and locations

The measurement of emissions from plastic heritage objects demonstrated that particular objects were a substantial source of acid. Acidic emissions can induce an auto-catalytic degradation cycle, or trigger the corrosion of vulnerable materials in close proximity to the deteriorating polymer[1-3]. Therefore, it was imperative to recognise and quantify the acid emissions from plastic objects to better understand how plastics within collections should be managed. By sampling the acidic emissions in addition to the VOC emissions a further level of interpretation may be possible. Within this further study a small number of samples were examined and measured for acetic acid emissions.

7.1.1 Photographic negatives at the National Records of Scotland

Two sets of photographic negatives were selected for the measurement of acidic emissions. Both sets of photographic negatives had previously been measured for VOC emissions (see Chapter 6 for object description and location).

7.1.2 Rubber garments held at the British Museum

A collection of Mexican rubberised textiles from The British Museum were being investigated for conservation treatment options and improvements to their long term storage. The handmade garments were collected from a street market in Mexico in the late 1980's. New at the time, the garments were made from cotton calico which had been coated with rubber latex on the outer side. While the curator had never seen the complete process of manufacture, at the time of purchase it was noted that other pieces of calico were stretched on a frame, and the rubber latex applied, presumably with a brush. Twenty years on, the garments were in varying condition, from fairly flexible in the light yellow areas, to brittle and flaking in the dark design areas (Figure 7.1).

Figure 7.1. Rubber rain cloak

To date, most of the garments were stacked on top of one another in a storage drawer that was kept closed because of the extreme smell of the garments inside. Concerned conservators used A-D strips to test for acid emissions by enclosing the garments in polyethylene bags. The A-D strips produced a rapid colour change, indicating the generation of acidic emissions. The potential high levels of acidic vapours emitting from the garments were of concern, especially if acid levels inside drawers were to build-up. Conservators were unsure if the acid was a product of oxidative degradation or whether it was inherent to the formulation of the rubber (residual acid from coagulation process). Therefore, a more detailed study was undertaken to identify the VOCs emitted and quantitatively measure the acid emissions[4]. In order to identify the most effective method of preventive conservation, acid measurements were conducted on each garment under three different treatment options. During acid testing the garments were each sealed in Escal® bags to ensure a standard environment and were tested in triplicate. The initial test monitored the acid emissions from each of the rubber garments which were sealed in ambient storage, the second round of testing was conducted in anoxic storage and the third was conducted in anoxic storage with a pollutant sorbent. The anoxic environment was achieved by nitrogen flushing and the addition of an oxygen absorber (Ageless®). The pollutant sorbent paper used (MicroChamber®) was wrapped around the rubber garments with a layer of acid free tissue between the surface of the garments and the pollutant sorbent paper. The aim of the different treatments was to identify the best solution for the long term storage of the garments to reduce the rate of deterioration of the rubber. The testing was conducted in the project room, which was not the usual storage environment for the rubber garments, but was the largest space available in which the garments could be laid out in sealed bags for conservation testing. Therefore, acid sampling was also conducted in the project room to determine the general background level of acid.

7.1.3 A Joseph Beuys plastic postcard, Scottish National Gallery of Modern Art

A plastic postcard entitled *Honey is Flowing* by Joseph Beuys (Figure 7.2) from the collection at The Scottish National Gallery of Modern Art exhibited signs of deterioration and was removed from display for further investigation. In Figure 7.2, the postcard is shown in its original condition on the left. The current condition of the postcard is shown on the right.

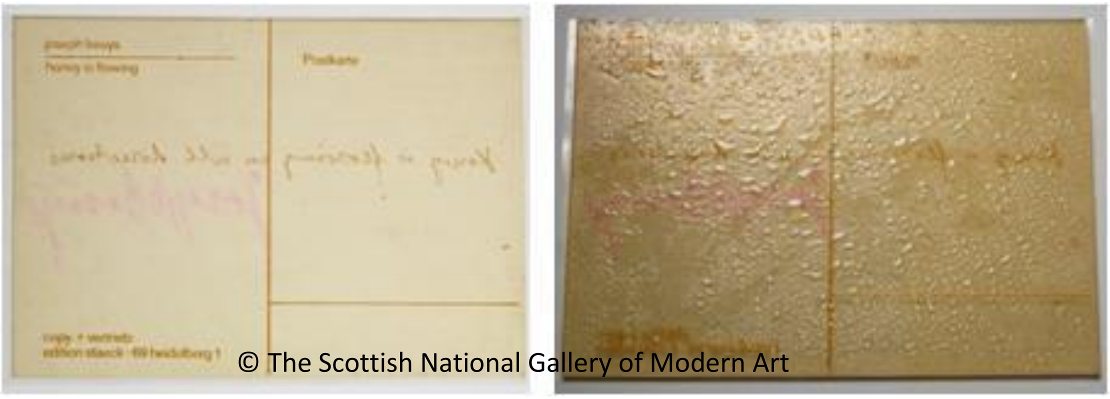

Figure 7.2 Honey is Flowing by Joseph Beuys

The postcard was not part of any previous VOC sampling campaign and was selected for acid testing only. The plastic postcard by Joseph Beuys (1921 – 1986) and was purported to be a screen print on yellow transparent polyvinyl chloride (PVC). The postcard was in a state of deterioration with large amounts of ‘sweat’ present on both sides of the postcard which was thought to be caused by plasticiser or other liquid additive migration and was noted as having a slight smell. The postcard was normally mounted in a frame made from a wood-based material when on display; however, the decision was taken to remove the postcard from the frame during sampling. Acid sampling was also conducted in the studio to determine the general background concentration of acetic acid.

7.2 Experimental

Palmes diffusion tubes (Gradko International Ltd, UK) were used to collect the acid emissions from the plastic samples. The diffusion tube used was an poly(methyl methacrylate) sampler which contained a trapping reagent on a solid support held within one of the end caps. Sampling was conducted by removing the empty end cap and allowing air to diffuse along the length of the tube to the cap containing the trapping reagent. Acetic acid sampling was conducted in duplicate and background acid concentrations were measured in suitable locations (e.g. conservation store) where the objects were being stored or displayed.

The sampling rate (S_R) of the diffusion tube was calculated using the equation;

$$S_R = D\left(\frac{A}{L}\right)$$

Where A is the cross-sectional area (9.5×10^{-5} m^2), L is the length of the tube (0.071 m) and D is the pollutant diffusion coefficient (1.1×10^{-5} m^2s^{-1}). For acetic acid the sampling rate was equal to 1.3 dm^3 per day. The volume sampled during the 14 d sampling period equated to 18.2 dm^3.

A potassium hydroxide trapping reagent was prepared by accurately weighing 0.55 g of potassium hydroxide (Sigma-Aldrich Company Ltd. Dorset, England) in to a 10 cm^3 flask with 2-3 cm^3 of deionised water added drop-wise. 1 cm^3 of ethylene glycol dimethyl ether (99.9%, Sigma Aldrich) was then added before the flask was filled to the mark with deionised water. 40 µL of the trapping reagent was measured by pipette and spread on to stainless steel mesh disks held in one of the end caps. The acetic acid emissions were trapped in the diffusion tube as the solid salt potassium acetate. At the end of the sampling period the trapped salt was then extracted from the diffusion tube with water and analysed using ion chromatography.

The trapped acetic acid was extracted from the diffusion tubes by removing the stainless steel mesh disks with tweezers and placing them into a clean Sterilin container (Sterilin Ltd, Newport). Aliquots (5 x 1 cm^3) of deionised water were used to wash out the end cap (formerly containing the mesh disks) into the Sterilin. The Sterilin was carefully agitated in order to extract the salts from the disks and in to the deionised water. The solutions were filtered using Acrodiscs (13 mm, 0.2 µm Supor membrane, PALL Life Sciences, UK) to remove any particulate matter. Acetate anion concentrations were determined with a Dionex DX 100 ion chromatograph fitted with a RFIC IonPac AS4A-SC column (250 mm with 4 mm i.d) and an AG4A guard column. A 6 mM borax (di-sodium tetraborate) eluent with a flow rate of 1 cm^3 min^{-1} was used and background conductivity was suppressed using a Dionex suppressor, model ASRS-ULTRA II (4 mm). Chromatograms were collected on a computer interface operated by the software system PeakNet. Calibration solutions, prepared in the range 0 – 4 µg mL^{-1}, were used to quantify the results and determine the concentration of acetate in each solution using linear least squares regression analysis. All sampling tubes were blank corrected.

The mass of acetic acid trapped was calculated by molar ratios. The concentration of acetate is calculated by linear least squares regression and, for example, is equal to 2 µg mL^{-1}. Since 5 mL of deionised water was used to extract the acetate from the mesh disks, the mass extracted from the disk would be equal to 10 µg. Since there is a molar ratio of one to one, the number of moles of acetate will be equal to the number of moles of acetic acid. Therefore, the mass of acetic acid trapped can be calculated by first dividing the mass of acetate extracted (10 µg) by the molecular weight of acetate (59) and then multiplication by the molecular weight of acetic acid (60) to give a mass of 10 µg. The mass of acetic acid trapped can then be used to calculate the concentration of the acid vapour in air as a time weighted average.

Since, $\mathrm{C} = \frac{\mathrm{m}}{\mathrm{V}}$

And, $\mathrm{V} = \mathrm{S_R} \times \mathrm{t}$

The calculation can be rewritten as;

$$\mathrm{C} = \frac{\mathrm{m}}{\mathrm{S_R} \times \mathrm{t}}$$

The sampling rate ($\mathrm{S_R}$) can be substituted for the full equation to give the final calculation;

$$C = \frac{m \times L}{D \times A \times t}$$

Where C is the concentration of acetic acid vapour in the air (µg m^{-3}), m is the mass of acetic acid trapped (µg), L is the length of the diffusion tube (m), D is the diffusional coefficient for acetic acid (m^{2}s^{-1}), A is the cross sectional area of the diffusion tube (m^2) and t is the sampling time in seconds.

7.3 Results

7.3.1 Acid concentrations from the photographic negatives- National Records of Scotland

The concentration of acetic acid in the conservation store room (Table 7.1) gave an indication of the general background level of acid present. The measured concentrations were slightly below the concentration typically expected (200-400 µg m^{-3}) in a heritage institution where there is no active acetic acid source. The negatives which were stored in the Timecare box looked to be in the process of degradation, indicated by the noticeable vinegar odour and slight warping. The measured concentrations of acetic acid were significantly high confirming that the process of deacetylation was occurring. The negatives which were stored in a general purpose cardboard box looked to be in a more advanced state of degradation based on the severe warping of the negatives and the overwhelming odour of acetic acid. The measured acetic acid concentrations were incredibly high, these were the highest measured within this study. The results confirmed that these particular negatives were in an advanced state of degradation and were a risk to other materials stored within close proximity. Both sets of photographic negatives were stored within a climate controlled repository, but these results demonstrated that the storage conditions alone were not enough to retard the rate of degradation. The objects would benefit from a much lower storage temperature and the use of acid scavengers. The use of scavengers would prevent much of the acetic acid cross contaminating with other objects which may be stored within the vicinity of these degrading materials.

Table 7.1. Acetic acid concentrations measured from photographic negatives

Sampling locations	Acid concentration (µg m^{-3})
Conservation store room	145
	153
Negatives in Timecare box	14690
	26616
Negatives in brown box	193793
	242073

7.3.2 Acetic acid results from rubber garments- The British Museum

The acid sampling for the rubber garments was conducted over three 14 d sampling periods (A, B and C) in the months of July and August 2013. Sampling period A was conducted in the first two weeks of July, sampling period B was the last two weeks in July and sampling period C was the first two weeks of August. It is particularly important to note that July and August 2013 were the hottest summer months experienced since 2006. In particular, from 13-19th July (which coincided with sampling period B) the average daily maximum temperatures within London were over 30 °C and on the 22nd July a peak temperature of 33.5 °C was recorded in London[5]. The increased temperatures may have skewed the results obtained from acid sampling; indeed the background acid levels measured within the project room were at their highest concentration during sampling period B, which was during the hottest part of the six week sampling block (Table 7.2).

The project room contained wooden flooring, shelving, storage crates and work benches which were the likely source of acid in the background measurements. Furthermore, the project room was used on a day to day basis with a range of possible acid sources introduced or removed from the room during the sampling period which could alter the measured background concentrations in each sampling period. Therefore, it was recognised that there was variation in the temperature, humidity and presence of potential sources during the sampling periods. Typically acetic acid concentrations measured within UK heritage institutions are somewhere in the region of 200-400 µg m^{-3} in the absence of an active source of acid, for example, degrading cellulose acetate or oak display cabinets. The concentrations measured in the project room during each of the three sampling periods were much higher than those typically found in heritage institutions and therefore confirmed that the wood flooring, shelving, work benches and storage crates were active sources of acetic acid.

In very simple and immediate terms, the conservators noticed differences between the effectiveness of the conservation treatments, by the perceived odour upon opening the sealed bags to retrieve the sampling tubes at the end of the sampling period. It was evident to the conservators that the odour of the garments wrapped in pollutant sorbent paper (sampling period C) were significantly reduced, compared with the strength of the odour from the garments when they were in the ambient storage environment (sampling period A). Conservators reported that there was still a discernible odour from the garments after anoxic storage (sampling period B), though not nearly as pungent as the odour from the garments in ambient storage.

Table 7.2 outlines the measured acid concentrations from the rubber garments at each conservation treatment stage (sampling periods A, B and C). The acetic acid concentration of the garments in the ambient and anoxic environments was extremely high. In general there was a reduction in acid moving from the ambient to the anoxic environment, but the acid concentration in anoxic storage was still very high. Conservators measured the oxygen levels inside the Escal® bags at the beginning and end of the sampling periods. In the ambient sampling environment the oxygen levels reduced during the sampling period and indicated that oxygen was being consumed by oxidative degradation reactions. The oxygen levels within the anoxic environments remained below 0.5%, but the measured acetic acid concentrations were still considerably high. This would suggest that acetic acid was not only produced as a result of oxidative degradation processes, but was inherent to the rubber material itself or due to the components used to bond the seams of the garments together or indeed due to some kind of additive. Though the exact mechanism of degradation is not known, it is postulated that the generation of acetic acid is caused by the ozonolysis of natural rubber (c.f. Chapter 2.3.1).

The measured concentration of acetic acid from the garments after anoxic storage with pollutant sorbent was greatly reduced when compared with the measured acid from the ambient or anoxic storage, which confirmed the initial conclusions drawn by the conservators based on perceived odour alone. This result indicated that that the sorbent paper was an effective method of acid trapping. The difficulty in using paper sorbent, such as MicroChamber®, is estimating when the material will be exhausted and in need of replacing. In addition, it is not known if the paper will start to re-release the acid after a certain period of time.

Table 7.2. Acetic acid concentrations measured from rubber garments

Garment	Acid conc. in ambient storage (µg m^{-3}) **A**	Acid conc. in anoxic storage (µg m^{-3}) **B**	Acid conc. in anoxic storage with sorbent (µg m^{-3}) **C**
Cloak (Am1988,08.670a)	51139	22927	1154
	44549	27083	69
	36640	30845	159
Trousers (Am1988,08.671a)	2170	14653	66
	1857	14450	813
	1704	15510	102
Trousers (Am1988,08.670b)	8912	9727	382
	25755	7608	1111
	21996	9993	2169
Background Location	Acid concentration (µg m^{-3}) **A**	Acid concentration (µg m^{-3}) **B**	Acid concentration (µg m^{-3}) **C**
Project room	1643	1464	664
	1918	3281	605
	1575	4439	709

7.3.3 Acetic acid results from Joseph Beuys plastic postcard-

The results from the acid sampling of the Beuys postcard and frame are given in Table 7.3. The concentration of acetic acid present in the studio was at a level that would typically be expected within a heritage institution where no active source of acetic acid was present, it was considered to be a low background concentration. The Beuys postcard however was emitting extremely high concentrations (9636 µg m^{-3}) of acetic acid and since the postcard was sampled in isolation it was assumed that the postcard was an active source of acid. However, such a high concentration of acetic acid was not consistent with the original description of the object on acquisition as it was stated that the postcard was made from PVC. Previous emission testing of PVC samples in Chapter 5 did not identify the presence of acetic acid at room temperature, after heating the samples or after accelerated degradation. Therefore, it may be that the postcard was not composed of PVC as was previously thought. To the conservators knowledge no analytical testing had been conducted on the postcard to confirm that it was indeed comprised of PVC. It may well be that the postcard was a PVC/polyvinyl acetate blend. The wood based frame emitted a high concentration of acid (1829 µg m^{-3}) which was expected since wood based materials are a known source of acetic acid[6]. Cross-contamination effects may also be possible with acid from the postcard adding to the acid inherently present from wood based materials.

Table 7.3. Acetic acid concentrations measured from plastic postcard

Sampling location	Acid concentration (µg m^{-3})
Studio	251
Beuys Postcard	9636
Postcard frame	1829

7.4 Conclusion of acid measurements

Previous VOC testing indicated the presence of acetic acid in the photographic negatives and the rubber garments (the postcard was not previously tested for emissions). By conducting acid sampling it was possible to quantify the levels of acetic acid emitted by the objects from each of the three heritage institutions. The study at The British Museum has enabled conservators to set out guidelines for the best storage conditions for rubber garments. Moving forward the conservators at The British Museum will need to monitor the objects and determine how often the pollutant sorbent paper will need to be replenished. A more detailed discussion of the conservation treatment trials conducted at The British Museum can be located in the Journal of the Institute of Conservation September 2014 issue, entitled ‘Investigation of Long Term Storage Solutions for Rubber Garments’ by Hacke *et al*. The acid analysis of the Beuys postcard had indicated that the original assumption of the polymers identity may be incorrect. This highlights a common problem as many institutions have not formally identified the polymers held within the collections.

This study demonstrated the dangers of misidentification or unidentified polymers in collection, since the acid generated could be detrimental to other heritage objects. The analysis of photographic negatives at the National Records of Scotland had shown the possible scale of acid emission from degrading heritage objects. Previous publications have noted that within a heritage context indoor generated pollutants, such as acetic acid, should be kept under control[7]. An 'extremely high' concentration is considered to be within the range of 600 - 1000 ppb (which is equivalent to approximately 1520 – 2530 µg m^{-3}), which is the point at which serious action should is recommended. The acid concentrations measured at the National Records of Scotland were significantly higher than the values quoted from other publications and highlight just how much acid can be generated by degrading objects.

7.5 References

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CHAPTER 8

CONCLUSIONS AND FURTHER WORK

Contents of Chapter 8

8 Conclusions and Further Work

8.1 Conclusions

The degradation of plastic heritage objects is a complicated challenge for curators and conservators to deal with since there are so many factors which influence the deterioration process. Knowledge of the prior history of each plastic object within a collection is unlikely, but knowledge of the polymer type will definitely go a long way in helping curators and conservators to make more informed decisions about how best to handle, display and store plastic objects.

Constant improvements within the field of science mean that it is no longer necessary to take a small sample in order to conduct analysis to identify the polymer type. In addition the cost of analytical equipment is reducing making analysis more affordable. Instrumentation has also reduced in physical size, meaning that much of the instrumentation is easily transportable and does not require a large amount of bench space if in a dedicated location.

Within this study an easily transportable diamond crystal attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (and laptop interface) was used to characterise the material type of forty-one reference plastic samples. The reference samples were sacrificial and were already of a manageable size meaning that ATR-FTIR spectroscopic analysis was relatively easy for the majority of samples which were of even thickness and, most, had a smooth surface. Problems were experienced when the reference samples were of uneven shape since good contact with the diamond crystal was not achieved. This problem highlighted potential difficulties in the analysis of real heritage objects which could be of any size and shape. Large or uneven heritage objects would not be suitable for analysis using this method unless a small sample could be removed or perhaps conservators could use a segment which may have broken off from a damaged area. An important point to note was the problem with surface indentations on some of the reference samples after analysis. Indentations were experienced in a number of rigid and flexible samples. For instance, indentations were found on the surface of flexible PVC, rubber and some polycarbonate samples. Careful consideration is suggested prior to the analysis of real heritage objects.

Furthermore, ATR-FTIR spectroscopy is a surface technique and caution should be used if it is suspected that the sample under study has a surface coating or is composed of layers of different polymers. For this reason, the reference samples used within this study were analysed on the front and reverse faces (n=10 on each side) to determine if there were any differences in the spectra prior to identifying the polymer type. As expected this increased the time taken to analyse each sample and for some samples caused extensive surface damage due to repeat mechanical action of arm clamp across the surface of the sample. For some samples, those of uneven size and shape, it was impossible to obtain ten spectra across both the front and rear surfaces due to the poor or lack of contact made with the crystal in particular orientations. Handheld gun type FTIR analysers are also available and may overcome the difficulty in the analysis of large or uneven heritage objects, though the analysis may still require contact with the object. Such instrumentation will be more costly than the compact type instrument used within this study.

In this study one polyurethane reference sample was selected and divided in to 5 sub-samples, each subjected to different degrees of accelerated degradation. Replicate ATR-FTIR spectra were collected from each sub-sample and interpreted visually. Although some spectral differences were noted, it was not possible to clearly distinguish between the spectra for each sub-sample. Therefore, principal component analysis (PCA) was employed to further interrogate the collected spectra. It was shown that PCA was able to clearly distinguish between the samples and was able to identify the onset of degradation. This level of interpretation was not possible by visual analysis of the spectra alone. Examination of the scores plot also indicated that as the degree of degradation increased the spread of the scores values within one sample also increased.

The difficulties associated with the use of ATR-FTIR spectroscopy to identify the polymer type of plastic heritage objects combined with the drive for non-contact and non-invasive methods of analysis justify research in to the use of volatile organic compounds (VOCs) as a method of polymer identification. Prior to sampling in the field a validation method was used to ensure that reproducible VOCs could be collected from the reference samples which were previously characterised by ATR-FTIR spectroscopy.

A micro-chamber/thermal extractor™ (μ-CTE™) was used to generate emissions from the sacrificial reference samples. The validation method identified specific VOCs for cellulose acetate, polyurethane, cellulose nitrate, rubber, polyethylene, polypropylene and styrenic based polymers. VOCs were identified from PVC and polycarbonate though they were classed as non-specific and could not be used to identify either of these two polymers. Examination of the VOCs has given a high level of interpretation. With the exception of PVC and polycarbonate, the polymer type has been identified from the emissions alone. Moreover, it has also been possible to identify the plasticisers, stabilisers and fire retardants used. This information is important not only in terms of gaining full characterisation of the plastic object, but may help curators estimate the age of the object if this information was unknown upon acquisition. The formulations of plastics have changed over the years due to the constant advent of new stabilisers, plasticisers and fire retardants. Therefore, the ability to identify a particular additive combined with knowledge on the date of introduction of that additive, curators may be able to more accurately estimate the age of an object. This may be advantageous if the authenticity of an object is in question. Furthermore, in some reference samples it was possible to identify degradation compounds even when the object displayed no visual indicators of degradation. In some samples a large relative abundance of acetic acid was identified, whilst Tenax is not a suitable sorbent for such a compound it adequately served to show the presence of acid and highlighted the requirement for further dedicated acid testing. Therefore, such information could be useful an early warning indicator that the object is unstable and should be considered a priority for conservation treatment.

The field studies involved only a small group of plastic heritage objects; however the VOCs identified were in agreement with the pattern of VOCs obtained from reference samples which enabled identification of the heritage objects. Sampling involved minimal disturbance to the objects under study and generally involved sampling in situ. The correlation between the validation method and the results of field studies are a strong indication that Tenax-TD-GC-MS is a suitable in-situ, non-invasive sampling method for the analysis of emitted vapours from plastic objects. The method is relatively cheap since the Tenax sorbent and sampling tubes are reusable and many heritage institutions may already have a GCMS instrument. In the event that an institution does not have access to a GCMS instrument, it is envisaged that the service may be provided by a university laboratory. Akin to the service already provided by the University of Strathclyde for the supply and analysis of acid and aldehyde passive sampling devices. The collection of VOCs demands very little time from heritage personnel and simply involves the deployment and collection of the tubes and ensuring a record is kept of the start and end dates and time. Analogous to the surveys that institutions conducted to determine the condition of heritage objects[1, 2], it is expected that institutions would prioritise the objects which require VOC testing. As an added benefit curators could employ the technique to identify the polymer type of a potential acquisition prior to purchase. It may well be that curators would reconsider the purchase of an object if they knew that the object was in an early state of degradation or that the polymer type was prone to rapid degradation, for example.

8.2 Further Work

This study was not exhaustive and serves as good platform on which to continue research. The study examined a select group of 9 different polymer types of varying age and formulation and has highlighted the potential of Tenax-TD-GC-MS as a suitable method of analysis. The reference samples could be increased to include a more representative group of samples to reflect the diverse nature of plastics commonly found in heritage collections. The number of different plastics manufactured worldwide has increased exponentially since the days of the first semi-synthetic plastics. The problem of polymer degradation within heritage collections is only just beginning and much more research needs to be conducted since many polymers are now produced to degrade easily for recycling and environmental reasons.

This study provides strong evidence that inferential measurement of polymer stability is possible. However further work would be required before emissions can be used to accurately assess the stability, or stage of deterioration of plastic objects. A more controlled, step-wise accelerated degradation would be required to fully investigate the changes in emission with the stage of degradation. It would also be beneficial to monitor changes in the ATR-FTIR spectra as degradation proceeds. The effect of humidity is an important aspect in the degradation processes of some polymers; however it was not possible to control humidity during the collection of VOCs or during the accelerated degradation process. The supplier of the micro-chamber/thermal extractor™ has since launched (April 2014) a new accessory which can control the humidity within the chambers. Such a device would enable a constant humidity within the chambers and a method would need to be developed to ensure a controllable humidity during accelerated degradation in the light box and the Atlas Suntest XLS+.

The work undertaken during this thesis was conducted to determine VOC associations, or patterns that could be used to identify or characterise polymer materials present in heritage objects. This was shown to be a valid method for seven out of the nine polymer groups tested with key analyte markers being determined. Now that the emissions are better understood, future work would be required to either identify or develop portable instruments that could be used to measure volatiles on-site. During the Heritage Smells project a field asymmetric ion mobility spectrometer (FAIMS) instrument was assessed for VOC collection however the indoor air matrix was too complicated to permit its use in this way. To be successful, analyte separation would be required prior to the MS measurement and this could be a further avenue of work. Perhaps a simple column, containing stationary phase, could be placed at the inlet of the portable MS instrument? It is also possible that new portable, affordable, MS will enter the market place in the next few years. Now that volatile targets have been identified then the use of emerging instruments could be tested.

8.3 References

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APPENDIX A

PREPARATION OF NATURAL, SEMI-SYNTHETIC AND SYNTHETIC POLYMERS

Preparation of natural, semi-synthetic and synthetic polymers

A.1 Chemical modification of naturally occurring polymers

Natural rubber is a naturally occurring alkene polymer, but unlike most other simple alkene polymers (e.g. polyethylene) it is produced from a diene monomer, in this case isoprene (2-methyl-1,3-butadiene), see Figure A.1.

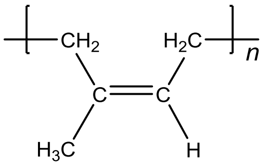


Figure A.1. polyisoprene (C_5H_8) repeat unit

Natural rubber (1,4-polyisoprene) consists of long flexible polymer chains containing a double bond at every fourth carbon. In reality, natural rubber comprises of a mixture of 1, 4 and 3, 4 addition units, equating to approximately 95% and 5% of the chain, respectively[1]. The presence of the double bond and the different substituent groups attached to each carbon within the double bond means that there is the potential for variation in the orientation of those substituents. Geometric isomerism or *cis-trans* isomerism are the terms used to differentiate between the different forms of orientation. It has been shown that natural rubber is comprised of *cis*-polyisoprene (Figure A.2), where the –H and $–CH_3$ groups are on the same side of the double bond, rather than across the double bond as is the case in the *trans* form[2, 3]. In the *cis* form the polymer chains are unable to pack together due to their irregular conformation which means that the polymer cannot crystallise and is, therefore, an amorphous polymer. *Trans*-1,4-polyisoprene is more commonly known as gutta percha[4]. It is also a naturally occurring polymer where the latex material is obtained from the 'palaquium gutta' tree, also of South America. The regular conformation of the chains means that they can pack together, which results in a rigid polymer.

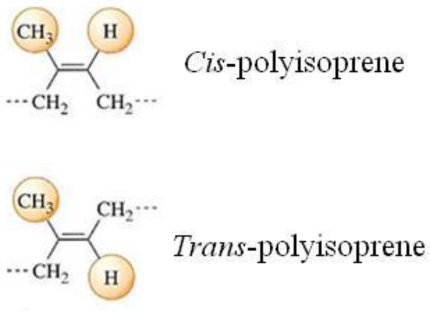


Figure A.2. Cis and trans forms of polyisoprene

Traditionally, early manufacturing processes used in South America natural rubber was extracted from the milky latex solution by coagulation using the precipitation agents acetic acid or formic acid[2, 5-7]. The coagulated rubber was then passed through rollers to produce a sheet[2, 8]. However, when natural rubber first reached Europe it was regarded as an interesting material but with little practical use due to its sticky consistency when warm and its rigidity when cool. Charles Goodyear developed the first method of altering the properties of rubber by mixing it with sulfur and white lead[9]. At first Goodyear thought that mixing rubber with sulfur had done nothing to alter the properties of natural rubber since it still had a sticky texture. However, it is alleged that Goodyear had left his natural rubber and sulfur mixture on a hot stove only to find that instead of the material becoming soft and flowing it remained intact[10]. When the material was peeled away from the surface of the stove it was noted that the material had a charred appearance which Goodyear referred to as ‘curing’. The material no longer had a sticky texture and was elastic over a wider temperature range.

The process became known as ‘vulcanisation’ and revolutionised the ways in which rubber could be utilised[2, 11]. The sulfur created links between the polymer chains, known as cross-linking, which resulted in a product which remained elastic over a wider temperature range. The mechanism by which cross-linking occurs within rubber is still unclear[12, 13]. When a polymer is heated or cooled the polymer will expand or shrink, respectively. This is the case in un-vulcanised natural rubber- when heated the polymer chains expand and move more freely, resulting in a soft and sticky material. Conversely, on cooling natural rubber, the polymer chains shrink and pack together making a rigid material. Since natural rubber was being used for products such as the soles of shoes, having a material which became brittle in cold weather or soft and sticky in warmer weather was not particularly useful. The process of vulcanisation caused a small percentage of cross-linking; therefore the movement of the polymer chains was restricted slightly. By restricting the movement of the polymer chains by a small amount, extremes of expansion and shrinkage were not so easy, therefore the vulcanised material stayed relatively flexible across a broader temperature range and is able to bear loads and recover from deformation[13].

The reaction of sulfur with rubber is very slow and so modern day production uses accelerators and activators to reduce the reaction time[6]. Only a few percent of sulfur is required to produce a rubber which is elastic over a broad temperature range. A much higher percentage (up to 30 %) of sulfur will crosslink the polymer so much that it produces a very hard rubber, more commonly referred to as ebonite[6, 14, 15]. Ebonite was used to make buttons, brooches and decorative items and so is commonly found within heritage collections, though it now finds its main application in the casing of car batteries and in bowling balls[6, 13]. In addition to accelerators and activators, other major additives in rubber include anti-ozonants, antioxidants, softeners, plasticisers, fillers, pigments and processing aids[4].

A.3 Preparation of cellulose based semi-synthetic plastics

The cellulose esters (cellulose nitrate and cellulose acetate) were the first semi-synthetic plastics to be produced. Cellulose nitrate and cellulose acetate were produced from cellulose most commonly in the form of cotton linters since they contain mostly pure cellulose[16, 17]. There are other sources of cellulose which could be used though they are generally less pure, for example wood which contains approximately 50 % cellulose[18, 19]. Cellulose is a linear polymer of β-D-glucose monomers linked by 1,4-β-glycosidic bonds with intermolecular hydrogen bonds holding the chains together[20], shown in Figure A.3.

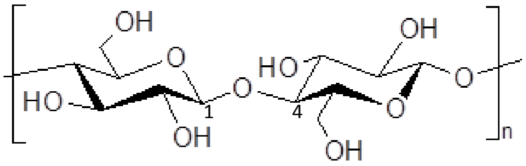


Figure A.3. Cellulose structure

Intermolecular and intramolecular hydrogen bonding interactions of cellulose molecules cause the formation of a fibrous structure. The chains wrap around each other to form a helical structure known as an elementary fibril. In turn, the elementary fibrils wrap around each other to produce a much thicker section known as a microfibril[2]. The microfibrils then interweave further to form fibrils, which further entwine to form the final fibre structure[21].

When the cellulose source is cotton linters, it must first be prepared by removing impurities such as lignin and wax with an alkali treatment, such as a solution of sodium hydroxide for instance[22, 23]. Excess alkali is removed by washing before and the cellulose may then be bleached with sodium hypochlorite before being dried in preparation for nitration or acetylation (sections A.3.1 and A.3.2, respectively).

A.3.1 Preparation of cellulose nitrate

Following tradition, the term nitration will be used to describe the esterification of cellulose with nitric acid. The cellulose source was most commonly cotton linters which were purified by an alkali wash prior to nitration. The stainless steel nitration bath generally contained a mixture of nitric acid, water and sulfuric acid[24, 25]. The cotton linters and nitrating mixture were blended with large stirrers at a controlled temperature of approximately 35 °C. The hydroxyl groups on the cellulose were esterified with sulfate ions which were then substituted with nitrate ions. The reaction is summarised in Figure A.4.

$$3HNO_3 + C_6H_{10}O_5 \rightleftharpoons C_6H_7(NO_2)_3O_5 + 3H_2O$$

Figure A.4. Nitration of cellulose to cellulose nitrate

Since the reaction is reversible, sulfuric acid was required to move the reaction to completion by absorbing the water formed during esterification[24]. Controlling the reaction delivered a cellulose nitrate (CN) product with the required degree of substitution (Figure A.5). It was achieved by altering the concentration of the acid reagent mixtures, the temperature of the reaction and the reaction time[26]. Replacement of one, two or three hydroxyl groups on each cellulose ring produced cellulose mononitrate, dinitrate or trinitrate, respectively with theoretical nitrogen contents of 6.76 %, 11.12 % or 14.15 %, respectively[4, 22]. The mononitrate and trinitrate forms were produced for specialist applications, therefore, most cellulose nitrate plastic was generally produced with an average degree of substitution between 1.9 and 2.7 hydroxyl groups (or approximately 10-12 % nitrogen)[4, 27].

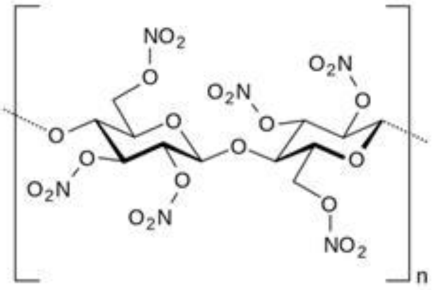


Figure A.5. Cellulose trinitrate

Following nitration the polymer would contain considerable amounts of residual acids which must be reduced or they would make the final product highly unstable. The acids would be capable of rapidly catalysing decomposition, which was the likely cause of the explosion in Faversham[4, 28]. Initially the polymer would be spun in a centrifuge to remove the majority of the residual acid and would then be steeped in excess water to further displace any remaining acid[28]. The water was then removed from the polymer by washing in alcohol in preparation for the next stage of processing.

The product would be brittle at this stage and not easy to shape, therefore plasticiser would be added to increase the flexibility of the polymer. The most common plasticiser that was used in early formulations of CN was camphor, which was obtained from the cinnamomum camphora evergreen tree [29, 30]. In addition, additives such as fillers, stabilisers and colourants would possibly be added to the CN depending on the requirements of the final product. Fillers, such as calcium carbonate, would be used to impart an opaque appearance. Stabilisers are used to slow the degradation of the plastic by inhibiting a degradation process[31]. A variety of colourants may be used for aesthetic purposes.

A.3.2 Preparation of cellulose acetate

Cellulose acetate was first developed by Schützenberger in 1865 by heating acetic acid and cotton linters in a sealed tube[16]. Cellulose was converted to cellulose acetate using a mixture of acetic acid and acetic anhydride in the presence of a small amount of sulfuric acid catalyst[21]. The overall reaction can be summarised as shown in Figure A.6.

$$C_6H_{10}O_5 + (CH_3CO)_2O \xrightarrow[CH_3COOH]{H_2SO_4} C_6H_7O_5(CH_3O)_3 + CH_3COOH$$

Figure A.6. Acetylation of cellulose to cellulose acetate

The initial stage of the reaction generated cellulose triacetate since acetylation of all hydroxyl groups took place[32]. The cellulose triacetate would then be isolated for further processing or the reaction would be continued to stage two which involved the partial hydrolysis of cellulose triacetate. Hydrolysis of selected acetyl groups and restoring some of the hydroxyl groups generated a cellulose acetate with a lower degree of substitution (Figure A.7), which was suitable for a greater range of applications[28].

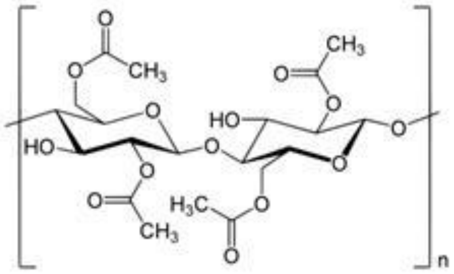


Figure A.7. Cellulose diacetate

In industrial processes the cellulose fibres were purified using alkali treatments and then pre-treated with acetic acid and a small amount of sulfuric acid prior to acetylation[21, 28]. The acetic acid caused the fibres to swell and allowed the acetylating reagents to penetrate between the fibres, making all the hydroxyl groups accessible, yielding a more uniformed final product[33-35]. The benefit of using acetic acid was that it does not need to be removed prior to the acetylation process. Acetic anhydride was converted to acetic acid during acetylation meaning that acetic acid recovery could be conducted at the completion of the reaction process[35]. The small quantity of sulfuric acid catalyst added in the pre-treatment stage also aided fibre swelling and caused a reduction in chain length since the acid catalysed the hydrolysis of the glycosidic bonds[28].

Once the fibres were swollen they were treated with a mixture of pre-cooled dilute acetic acid, sulfuric acid catalyst and acetic anhydride[33]. The mixture was pre-cooled since the acetylation reaction was exothermic and the temperature needed to be maintained at around 50 °C to minimise the possibility of molecular weight reduction of the final product[36]. Both acetic acid and acetic anhydride have been considered as acetylating reagents, however only acetic anhydride has had significant commercial applications since reactions involving only acetic acid as the acetylating reagent were sluggish and the resulting cellulose acetate had a low degree of substitution[28]. In most industrial processes the acetylation took place in a solvent which was most commonly acetic acid (solution acetate process) but may also have been conducted in methylene chloride (methylene chloride process)[28, 34]. The solution acetate process was regarded as a homogeneous system even though the start of the reaction was heterogeneous. The process began with the suspension of cellulose fibres in an acetylating reagent, solvent and catalyst mixture. As the acetylation reaction proceeded, the fibres dissolved forming a homogeneous viscous solution, which could then be uniformly hydrolysed to produce the required degree of substitution[28]. The fibre acetate process (heterogeneous system) could also be employed in which the cellulose acetate was formed in a non-solvent. Therefore the solid and liquid phases remained throughout the reaction as the product was insoluble in the non-solvent[28, 35]. The fibre acetate process was not commonly employed since uniform hydrolysis of the acetyl groups to the required degree of substitution was not possible[28]. Balser *et al.*[28] reported that the sulfuric acid bonds to the hydroxyl groups of the cellulose to form the intermediate cellulose sulfate ester acid. It has also been reported that sulfuric acid reacts with acetic anhydride to form acetyl sulfuric acid[28, 32, 37, 38]. It is, therefore, assumed that both sulfuric acid and acetyl sulfuric acid are involved in the acetylation of cellulose. Balser et al.[28] noted that it was likely that the acetic acid-acetic anhydride mixture reacted with the cellulose sulfate ester acid intermediate to remove the sulfate ester group and replace it with an acetyl group.

The solution was then transferred to a ripening vessel, where the cellulose triacetate was partially hydrolysed to the diacetate which had, on average, 2.4 acetate groups per cellulose[39]. Partial hydrolysis or ripening involved the slow addition of water and monitoring the solubility of the product. The hydrolysis of the acetyl groups was catalysed by the sulfuric acid and the quantity of water could be adjusted to control the reaction[28]. When the product became soluble in acetone, the diacetate form of cellulose acetate had been achieved and the ripening process would be halted by the addition of sodium acetate or magnesium chloride[28, 36, 40]. Differences in the degree of substitution affect the solubility of the cellulose acetate and can have an impact on the products suitability for a given application. For instance, the triacetate form which had a degree of substitution of 3 was soluble in chloroform, whereas the diacetate form was soluble in acetone[41]. Littlejohn *et al.* [36] highlighted that cellulose acetate often had a specific degree of substitution if it was intended for use in a particular application. Cellulose acetate which was used in cinematic film generally had a degree of substitution between 2.9 and 2.92, conversely general plastic grade cellulose acetate tended to have a lower degree of substitution between 2.5 and 2.7.

After ripening the cellulose acetate was precipitated from the solution which involved the addition of large amounts of water and vigorous stirring. The addition of water had the benefit of removing any remaining sulfate ester groups[28]. The cellulose acetate product was then centrifuged and washed with more water to try and remove as much free acid as possible since that can be detrimental to the stability of the final product[36]. Stabilisation generally involved the use of pressurised steam before the product was rinsed in cold water and dried. Cellulose acetate was then generally compounded with plasticisers to improve the flow properties of the final product. The unplasticised form does soften with heat, but the degree of flow is too low for the product to be sufficiently moulded or formed with heat alone, so plasticisers must be used[40].

Brydson[4] reported that the most common plasticisers used in cellulose acetate were dimethyl phthalate (DMP), triacetin and triphenyl phosphate (TPP). DMP was the most commonly used since it was relatively cheap and had good compatibility with the polymer enabling a flexible product with suitable flow properties[4, 40]. The disadvantage of DMP plasticiser was that it was highly volatile, which could reduce the longevity of the product. For this reason, diethyl phthalate (DEP) was sometimes used as a plasticiser since it was less volatile than DMP, but it was less effective at providing good flow properties and flexibility. Alternatively, DMP may have been used in combination with less volatile plasticisers such as TPP[40]. The TPP used had a dual purpose, in the first instance it reduced the volatility of DMP plasticiser, but perhaps more importantly it acted as a fire retardant since adding DMP to cellulose acetate increased the flammability of the polymer[40]. Another plasticiser used in CN was triacetin which was highly volatile and reduced the polymers resistance to water but had good compatibility for the polymer. Triacetin was readily hydrolysed meaning that the weathering and ageing properties of the product would be very poor, for that reason its use in cellulose acetate plastics was ceased many years ago[40]. Triphenyl phosphate was the least compatible of the three plasticisers, though TPP was often used in combination with DMP, as previously noted[4, 40]. The advantage of TPP was that it imparted flame and water resistance to the final product. Products containing TPP tended to be harder and slightly less flexible than products containing phthalate esters[40].

A.4 Synthetic polymers produced via chain growth polymerisation

Of the 9 polymer types selected for this study 4 were produced via chain-growth polymerisation (PVC, polyethylene, polypropylene and polystyrene) the chemistry of each will be briefly discussed.

A.4.1 Poly(vinyl chloride)

In the late 1920s commercial interest in vinyl polymers began when a number of patents were filed for the copolymer vinyl chloride- vinyl acetate[4, 42]. At the time, production of the poly(vinyl chloride) (PVC) homopolymer was not possible since processing had to be conducted at approximately 160 °C, which was close to the temperature of decomposition (170 °C). This created a very narrow temperature range over which to process the plastic without causing degradation[4].

By the 1930s it had been demonstrated that the incorporation of plasticisers would lower the processing temperature to approximately 120 °C. This made processing much easier and enabled large scale production of the PVC homopolymer. The application of a small quantity plasticiser produced a rigid but more easily processed polymer. In the rigid form it was commonly used in the manufacture of double glazed window frames and doors (known as uPVC), as well as pipes and guttering. The addition of a large percentage of plasticiser produced a highly flexible product which has been used in rainwear, electrical wire insulation and flooring, for example.

The commercial manufacture of PVC begins by chlorinating ethylene to produce 1,2-dichloroethane (Figure A.8).

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Figure A.8. Formation of 1,2-dichloroethane

A high temperature is then used to thermally decompose 1,2-dichloroethane to produce the vinyl chloride monomer (C_2H_3Cl) and hydrogen chloride (Figure A.9).

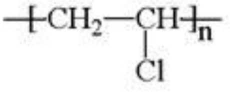
$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

Figure A.9. Thermal decomposition of 1,2-dichloroethane

The hydrogen chloride by-product is used to produce more 1,2-dichloroethane by oxychlorination- the process of chlorinating hydrocarbons (in this case ethylene) using oxygen and hydrogen chloride.

Polymerisation of the vinyl chloride monomer generally proceeds via a free-radical polymerisation in suspension. In a pressurised vessel, under nitrogen, the dispersing agent gelatine is added with an initiator (typically caproyl peroxide) and monomer to demineralised water[6]. The suspension is stirred vigorously for approximately 12 hours to obtain spherical particles which can be processed into final products[4, 6, 43].

The repeat unit for PVC, Figure A.10, shows a chlorine atom on every second carbon. The chlorine atom creates stiffness within the polymer chain resulting in a rigid polymer. This is caused by the strong carbon-chlorine dipole interactions between the polymer chains. Therefore, PVC is much more polar than polyethylene, for example.



$$-\!\!\left[CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n\!\!-$$

Figure A.10. Poly (vinyl chloride) repeat unit

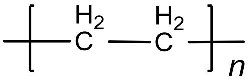
The polymer can have one of three conformations: atactic, isotactic and syndiotactic. Generally, commercial PVC is in the atactic form (amorphous), though there are small portions of crystalline structure (syndiotactic form) within the polymer. It is thought that the small crystalline portions are of the syndiotactic form rather than isotactic form, since the former minimises steric hindrance[43]. Highly crystalline PVC polymer (high syndiotactic content) may be produced by altering the conditions of polymerisation to include low temperature and specific solvents[42].

Although PVC is a linear polymer, chain branching of commercial PVC is common[44]. Titow estimated that there are up to 20 branches per 1000 carbon atoms and that 5 out of each 1000 carbons has a methyl branch while 2 out of every 1000 carbons has more than 5 carbons in the branch[42]. The presence of branch junctions can create the possibility of tertiary chlorines[42]. The formation of such tertiary chlorines is possible via radical transfer to the polymer during polymerisation[42, 44]. Wypych[44] reported that there is an increase in the concentration of tertiary chlorines as monomer conversion increases above a critical point (~60% conversion). If such sites are present, they are highly reactive sites for the initiation of thermal or photodegradation. Furthermore, double bonds may be present within the polymer backbone and may account for up to 15 bonds per 1000 carbons which creates more potential weak sites for degradation to begin[42].

A.4.2 Polyethylene

Polyethylene (PE) was first produced commercially in 1939 by chemists at Imperial Chemical Industries (ICI) and has found use in a variety of applications since it is cheap to produce and has good mechanical properties. It should be noted that within the United Kingdom the polymer polyethylene may be known colloquially as polythene. Since the majority of literature within the field of cultural heritage uses the name polyethylene, for consistency, this terminology will be adopted throughout this thesis. The monomer, ethylene, was traditionally obtained as a by-product from the sugar industry[4]. Ethyl alcohol was obtained from molasses which would be dehydrated to produce ethylene. However, modern processes now obtain ethylene from the cracking of ethane and propane from petroleum gas[4].

The structural repeat unit of the polymer is shown in Figure A.11.



$$-\!\left[CH_2-CH_2\right]_n\!-$$

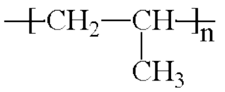
Figure A.11. Polyethylene repeat unit

PE can be prepared in various ways, though FRP and the use of Ziegler-Natta catalysts are the two methods most commonly employed. In FRP the free-radical initiator benzoyl peroxide is typically used and polymerisation is conducted in a continuous fashion. Generally the reactants are passed through stirred reactors which must be carefully controlled due to the high heat of polymerisation[4]. In addition, it is possible for side reactions to occur which are exothermic in nature, as a result it is quite easy for the reaction to become out of control. PE product prepared by high pressure FRP is termed low density PE and consists of lightly branched linear chains (density 0.915-0.94 g cm^{-3}) which make the product suitable for use in carrier bags and packaging[4].

Polymerisation may also proceed via the use of Ziegler-Natta catalysts. In this method the reactants are fed in to a reactor which contains liquid hydrocarbon as a diluent[4]. Unlike the FRP method, polymerisation using Zeigler-Natta catalysts takes place at low pressure and temperature. The catalyst complex is fed in to the main reactor which is free from oxygen and water since these can reduce the effectiveness of the catalyst[4]. As the polymer is formed in solution the catalyst precipitates from the slurry. The slurry is then transferred in to catalyst decomposition vessel which is flushed with ethanol or water to destroy the catalyst and the polymer is then purified of metallic catalyst fragments[4]. The use of Ziegler-Natta catalysts enables a controlled reaction producing polymers with a density of approximately 0.945 g cm^{-3}, such products are known as high density PE (HDPE)[4]. HDPE contains linear chains which produces a product suitable for use in food containers and bottles.

A.4.3 Polypropylene

Polypropylene (PP) was developed in the mid 1950s and has similar properties to PE since they have related structural repeat units. The repeat unit for PP (Figure A.12) has a substituted methyl group.



$$-\!\!\left[CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} \right]_n$$

Figure A.12 Structural repeat unit of polypropylene

Polymerisation is generally conducted using Ziegler-Natta catalysts since they are capable of controlling the stereoregularity of the PP products formed. The propylene monomer is prepared by the cracking of petroleum products in much the same way as the ethylene monomer is obtained for PE production. The earliest process to be developed commercially was the suspension process, in which the reactants were transferred in to a polymerisation vessel under pressure at a temperature of approximately 60 °C to produce 80-85 % conversion to polymer[4]. After conversion the polymerisation vessel would contain a mixture of polymer (of differing tacticity), solvent, monomer and catalyst[4]. Separating of these components begins in a flash drum which removes unreacted monomer for recycling. The slurry is then centrifuged which removes solvent and most of the atactic form of PP since it is soluble in the solvent. The catalyst is then destroyed and removed and the final isotactic polymer is washed and dried[4].

The presence of a methyl group on alternate carbons atoms along the length of the polymer backbone leads to PP products with different tacticity. Atactic PP, a by-product of the isotactic form, is amorphous in nature with poor mechanical properties since the random arrangement of the methyl group on either side of the polymer backbone prevents the chains packing together efficiently. The isotactic polymer is highly crystalline and more rigid since the polymer chains are able to pack together. Syndiotactic polymer is not commercially produced except for very specific purposes on a small scale, but it does have good heat resistance and clarity. The methyl group restricts the rotation of the polymer chains which creates a stiffer polymer which makes PP ideal for use in bottles, casings and sturdy packaging[45].

Further processing typically involves the addition of anti-oxidants and other additives. The presence of tertiary carbon atoms within the polymer backbone creates weak sites for oxidation to occur and so PP is vulnerable to oxidation. The most commonly used antioxidants in PP tend to be of the phenol-alkane type such as 1, 1, 3-tris-(4-hydroxy-2-methyl-5-t-butylphenyl)butane[4]. Antioxidants inhibit oxidation by reacting with the free radicals that are produced by the action of heat and light on the plastic product.

A.4.4 Polystyrene

Commercial interest in polystyrene (PS) began in earnest in the 1930s in Germany at the company IG Farben. However, it is widely recognised that E. Simon synthesised PS 100 years earlier[4]. In the 1830s Simon believed that he had produced an oxidation product of a compound he called styrol, but in actual fact had produced polystyrene[4]. The styrene monomer is a colourless liquid and is synthesised in three stages. The process first involves the reaction between ethene and benzene in the presence of aluminium chloride catalyst at a temperature of 95 °C to produce ethylbenzene (Figure A.13)[4]. The second step involves the dehydrogenation of ethylbenzene at high temperature (> 600 °C) to produce styrene monomer (Figure A.13). Since dehydrogenation produces a mixture of components (approximately 37 % styrene, 61 % ethylbenzene and 2 % aromatic hydrocarbon, e.g. benzene and toluene), purification is required to obtain suitable monomer[4]. The purification process involves distillation of the mixture with the addition of polymerisation inhibitors since there is a risk of styrene polymerising at the temperatures used in distillation.

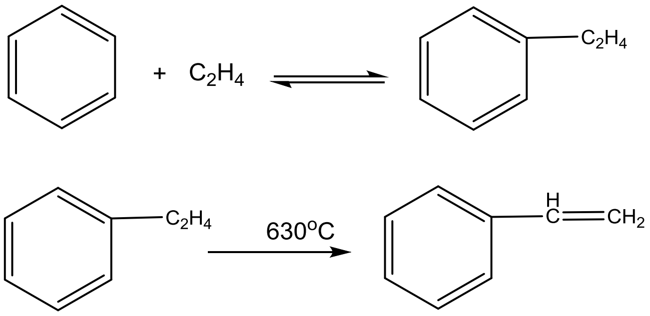


Figure A.13. Production of styrene monomer

Polymerisation of polystyrene is most commonly conducted in bulk and since the reaction needs to be rigorously controlled, a very specific procedure is used. The styrene monomer is prepolymerised using heat instead of initiators. This involves heating the prepolymerisation vessels to 80 °C for two days or until ~35 % conversion to polymer has been obtained[6]. The mixture of unreacted monomer and polymer is then passed in to a tower of 7.5 m high which is fitted with heating and cooling jackets. There is a temperature gradient down the length of the tower with the top of the tower the coolest portion at 100 °C, the centre of the tower at 150 °C and the base of the tower at 180 °C. The high temperature at the base of the tower ensures that a good conversion is obtained and that the excess styrene monomer boils off (b.p of styrene 145 °C)[4]. The polymer is collected at the base of the tower and further processed.

The repeat structure is given in Figure A.14 and shows that an aromatic ring is attached to alternate carbons along the backbone of the polymer. The aromatic group is bulky which restricts the rotation of the polymer chains resulting in a rigid polymer which makes it suitable for use in the casings of electronic appliances.

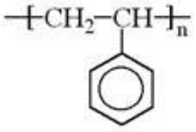


Figure A.14. Structural repeat unit of polystyrene

Since PS is produced from an asymmetric vinyl monomer the final polymer can have one of three forms: atactic, isotactic and syndiotactic, although isotactic PS tends not to be produced commercially. Typically PS is produced in atactic form (known as general-purpose polystyrene) where the substituent groups are randomly situated on either side of the polymer chain. This form of polystyrene is the cheapest to produce and is used in many disposable items such as coffee cups and cutlery.

The syndiotactic form of PS, made by Ziegler-Natta polymerisation, where the substituent groups alternate from side to side along the length of the chain is produced only for specific applications. The regular arrangement allows a highly ordered (semi-crystalline) structure making a strong polymer which has a high melting point and has a good resistance to moisture and chemicals[12].

A.5 Synthetic polymers produced via step growth polymerisation

Of the 9 polymer types selected for this study two were produced via step-growth polymerisation (polyurethane and polycarbonate) the chemistry of both will be briefly discussed.

A.5.1 Polyurethane

Polyurethanes were first developed in 1937 by Otto Bayer and are now one of the most widely used classes of polymer. Polyurethanes are used to produce foams, elastomers, fibres and adhesives with a range of different properties making them suitable for a variety of applications. Despite the differences in physical properties, they each contain urethane linkages which are formed by the exothermic reaction between an isocyanate and an alcohol (Figure A.15)[4, 46, 47].

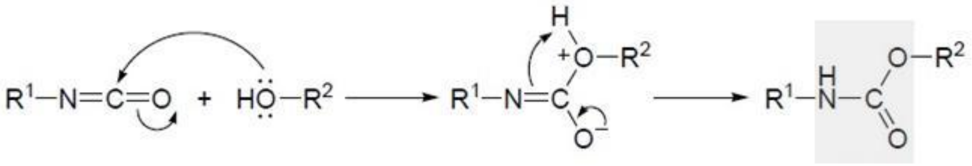


Figure A.15. Formation of urethane linkages

Diisocyanates (with two reactive isocyanate groups per molecule) and polyols (compounds with at least 2 hydroxyl groups) will react by the same reaction to form polyurethane polymers[4], with the general structure shown in Figure A.16.

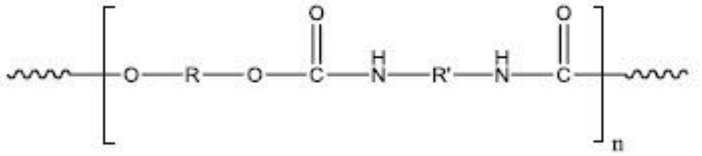


Figure A.16. General structural repeat unit for polyurethane[48]

Polyols (also known as long-chain diols or macrodiols) may be one of two types, polyester or polyether polyols, which can alter the properties of the final polyurethane product. The former was originally used in the production of polyurethanes, especially in foams, until it was recognised that polyether polyols were better suited to the manufacture of flexible foams since they were cheaper, less viscous and less susceptible to hydrolytic degradation[49]. Therefore, modern formulations predominantly make use of polyether polyols, unless good tensile properties and oil and abrasion resistance are required, in which case polyester polyols may still be used[49]. Polyester polyols were produced by the condensation reaction of a diol (e.g. ethylene or propylene glycol) with a dicarboxylic acid (such as adipic acid)[4] [50-52]. Later, polyether polyols were introduced by DuPont in the mid 1950s. They are typically formed by the base-catalysed addition of ethylene or propylene oxide on to a hydroxyl or amine containing initiator[50-52]. Poly(tetramethylene ether) glycol was the first commercially available polyether polyol and was produced by the polymerisation of tetrahydrofuran[52]. The nature of the polyol may also affect the flexibility of the final product. Polyols with long chain length will produce polymers which are very flexible (e.g. elastomers), conversely polyols with short chain length will produce a more rigid polymer[46].

The diisocyanates used to produce polyurethanes may be aliphatic or aromatic in nature which can impart different properties to the final product. Aliphatic diisocyanates, such as hexamethylene diisocyanate (HDI), are more photostable than aromatic diisocyanates such as methylene diphenyl diisocyanate (MDI), which is one of the most commonly used aromatic diisocyanates (Figure A.17)[46, 52, 53].

Hexamethylene diisocyanate (HDI) Methylene diphenyl diisocyanate (MDI)

Figure A.17. Examples of aromatic and aliphatic diisocyanates

This can cause aromatic diisocyanate based polyurethanes to be susceptible to discolouration (yellowing) as a result of exposure to UV light. Highly crystalline diisocyanates, such as hexamethylene diisocyanate (HDI), are more resistant to hydrolytic degradation than aromatic diisocyanates. Despite the benefits of aliphatic diisocyanates in improving the stability of the final product, aliphatic diisocyanates tend to be more expensive than their aromatic counterparts due to their lower polymerisation reactivity[46].

The synthesis reaction is termed a polyaddition since the reaction proceeds without the elimination of a small molecule (such as water), following the step-growth mechanism[12]. The carbon of the isocyanate group is highly electrophilic as a result of the electronegative nitrogen and oxygen on either side. The electrophilic nature of the carbon makes it vulnerable to nucleophilic attack from reagents such as alcohols, water, acids and amines[12]. When the diisocyanate contains an aromatic ring conjugation is created with the isocyanate group, which further increases the electrophilic nature of the carbon making it more reactive, which is why aromatic diisocyanates are more reactive than their aliphatic counterparts. The polyaddition reaction follows a step-growth mechanism whereby dimers, trimers and oligomers take part in the formation of the polymer chain. Since the starting reagents contain at least two isocyanate and two hydroxyl groups they react to form a dimer. Therefore the hydroxyl group at one end and the isocyanate group at the other end of the dimer can react with more starting reagents to form a trimer, or indeed the dimer may react with other dimers, trimers or oligomers. Either way the chain length grows to produce a high molecular weight polymer.

To produce polyurethane foam, water was traditionally added to the diisocyanate and polyol during synthesis (Figure A.18) to react with diisocyanates to produce carbamic acid, which is unstable and decomposes to generate an amine and carbon dioxide[12]. The generated amine reacts rapidly with other isocyanate molecules to form a substituted urea[47].

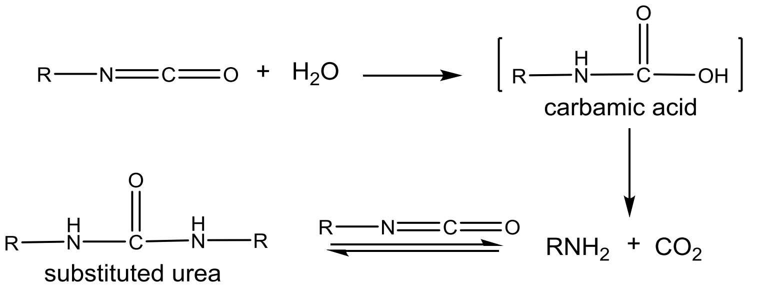


Figure A.18. Reaction of water with an isocyanate to form a substituted urea[48]

The evolved carbon dioxide gas creates bubbles and expands within the polymer matrix to produce a honeycomb cell structure. The foam product is therefore likely to contain polyurea and polyurethane segments. Alternatively, blowing agents such as trichlorofluoromethane (CCl_3F) may be used. Chlorofluorocarbons (CFCs) are volatile liquids and since the polymerisation process is exothermic, the heat generated is sufficient to vaporise the liquid creating gas bubbles and subsequently a foam structure. However, the use of CFCs has since been banned due to their suspected destructive effects on the ozone layer, but historically they were used until the 1970s.

Polyurethane elastomers are produced by the reaction of three important components: a diisocyanate, a long polyol and a chain extender[52]. Prisacariu[52] describes the resulting elastomer as a copolymer of sorts, Figure A.19, in which the polyol sections are termed soft segments and the diisocyanate-chain extender sections are termed hard segments. Chain extenders tend to be low molecular weight (<400) materials which react with the isocyanate groups to form the hard segment.

The reaction of a diisocyanate and a polyol without the use of chain extenders results in an elastomer which has poor mechanical properties.

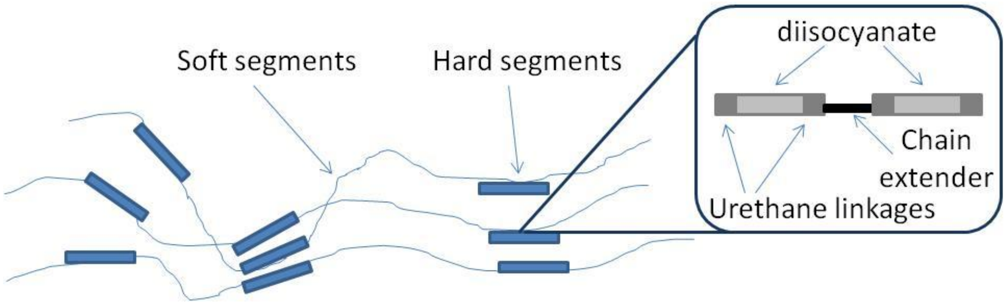


Figure A.19. Simplified structure of a polyurethane elastomer

The hard and soft segments are linked by the urethane groups (-NHCO-O-), depicted in the enlarged area of Figure A.19. The urethane groups are also capable of forming hydrogen bonds between the ether bond (C-O) or ester bond (CO-O) of the polyol soft segments of adjacent polymer chains[52]. This hydrogen bonding interaction prevents the chains from moving too much keeping the polymer elastic over a wide temperature range[52].

A.5.2 Polycarbonate

Polycarbonate is a so-called high performance polymer (HPP) or engineering plastic, which is strong and durable and unlike most other thermoplastics is thermally stable at high temperature. Characteristically HPPs are thermally stable, rigid and tough[45] due to the presence of stable aromatic groups and resonance stabilised systems[45, 54]. Since their invention in the 1930s, a variety of PC formulations have been developed including those containing aliphatic groups, but such polymers had low melting points and were easily hydrolysed making them commercially unsuccessful[4]. The polycarbonates discussed here are based on bisphenol A which contains aromatic groups and the structural repeat unit of polycarbonate is shown in Figure A.20.

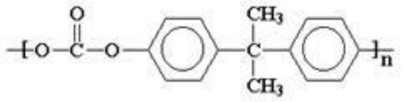


Figure A.20. Structural repeat unit of polycarbonate

The steric hindrance caused by the aromatic and methyl groups restricts movement of the polymer chains creating a rigid structure[45]. However, the rigidity is offset slightly by the carbon-oxygen bonds which impart a limited amount of flexibility to the polymer chains[45].

Bisphenol A based PCs are commonly synthesised from bisphenol A and phosgene (carbonyl chloride), in what may be referred to as the phosgenation process (Figure A.21). Typically, bisphenol A is dissolved in excess pyridine in a reaction vessel and stirred at 25-30 °C while phosgene is bubbled through the solution[4]. The organic solvent pyridine (C_5H_5N) is a hydrohalide acceptor which can remove the hydrochloric acid formed in the phosgenation process. On reaction with hydrochloric acid, pyridine forms the salt pyridine hydrochloride ($C_5H_5N{\cdot}HCl$) which precipitates out of solution[55]. As the polymer forms the viscosity increases to the point where stirring is no longer possible. Methanol (CH_3OH) is then added to the reaction vessel to dissolve pyridine hydrochloride to enable recovery of the polymer.

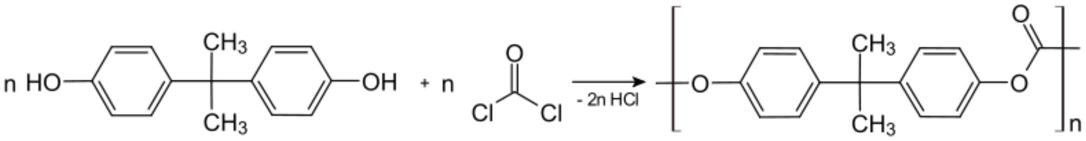


Figure A.21. Phosgenation process

The polymer is then recovered and made in to various products by extrusion or moulding. In the extrusion process the melt is forced through a die to give the products its final shape and is rapidly cooled- polycarbonate sheets are commonly made this way. In the moulding process the melt is pressed in to a mould, it is cooled within the mould before being released. This method is used for highly specific products such as car parts. Polycarbonate is more expensive to produce than commodity polymers such as polyethylene, polypropylene and polystyrene, but it is tough and has excellent optical qualities with glass-like transparency and is therefore used as an alternative to glass in glazing or in safety goggles which need to be much tougher than glass. The thermoplastic nature of the polymer means that it can easily be recycled. Polycarbonate is also commonly used in CDs, DVDs and engineering applications.

A.6 References

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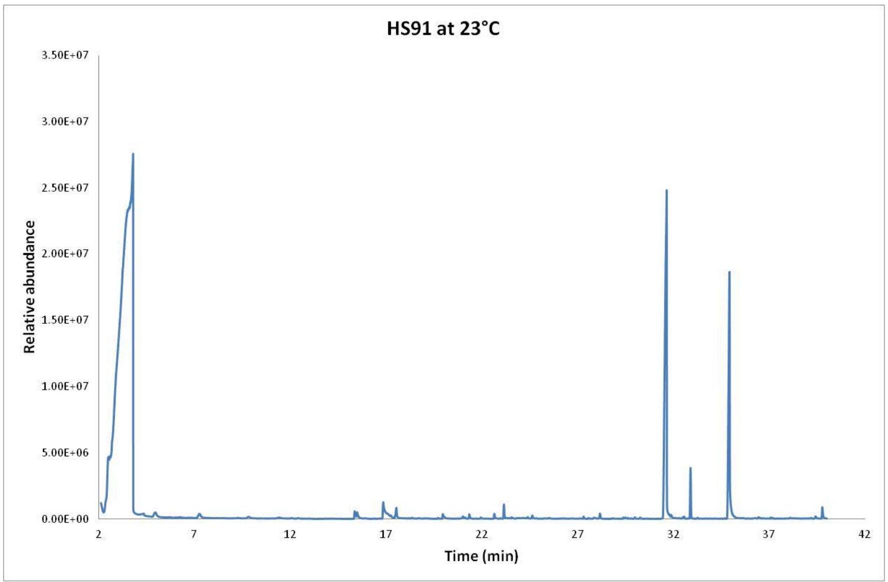
APPENDIX B

CHROMATOGRAMS OF VOC EMISSIONS FROM REFERENCE SAMPLES

CELLULOSE ACETATE


HS91 at 23°C
Relative abundance
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
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5.00E+06
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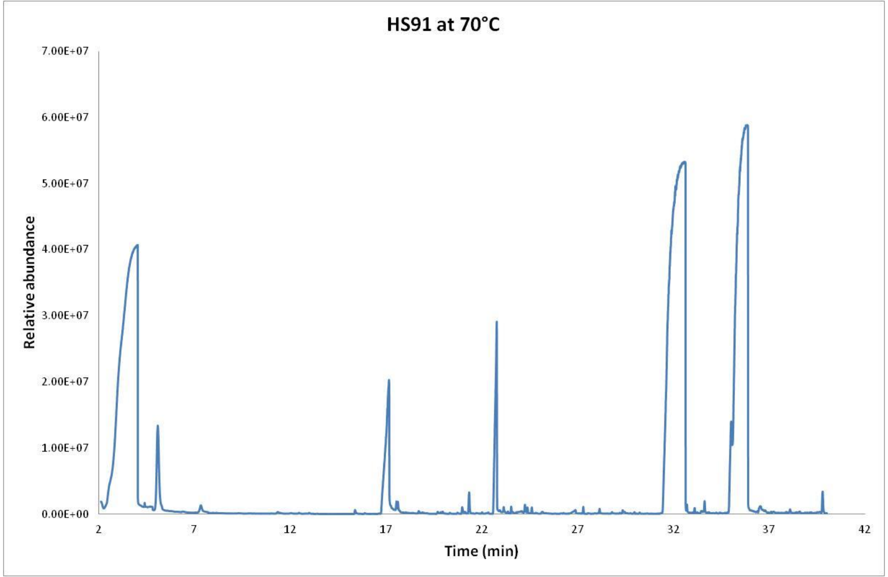
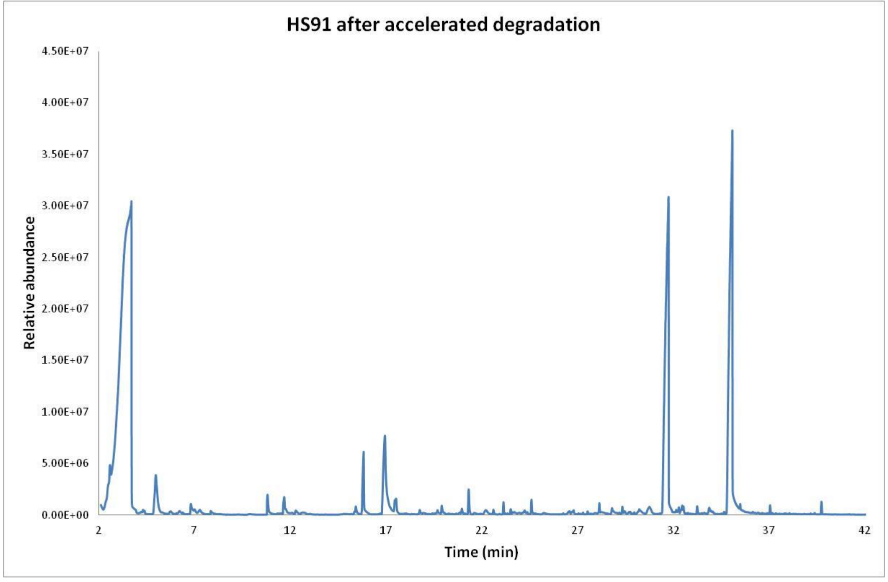
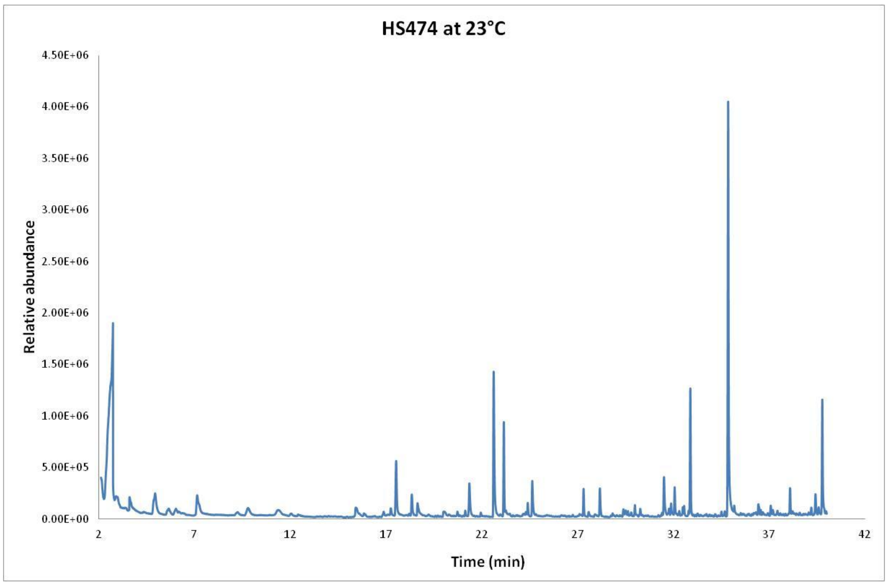
2
7
12
17
22
27
32
37
42
Time (min)


HS91 at 70°C
Relative abundance
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS91 after accelerated degradation
Relative abundance
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS474 at 23°C
Relative abundance
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4.00E+06
3.50E+06
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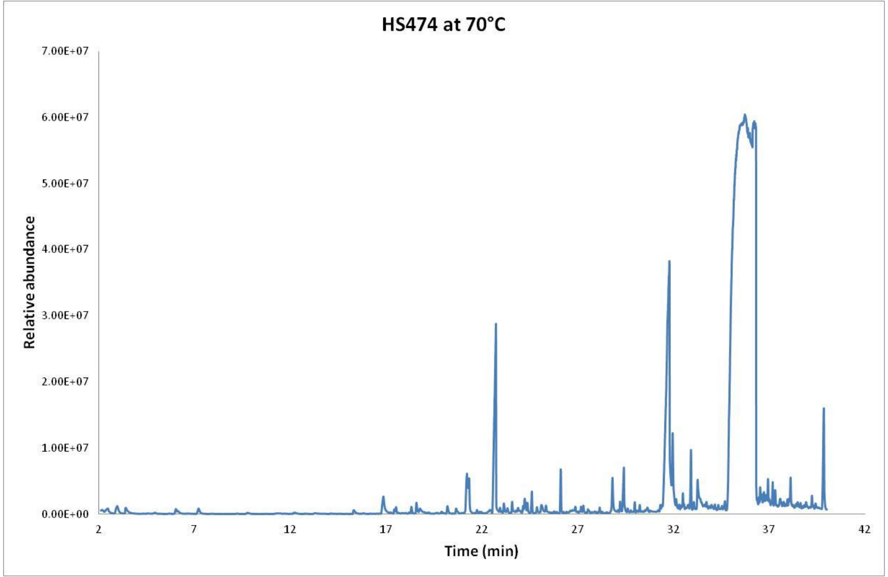
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS474 at 70°C
Relative abundance
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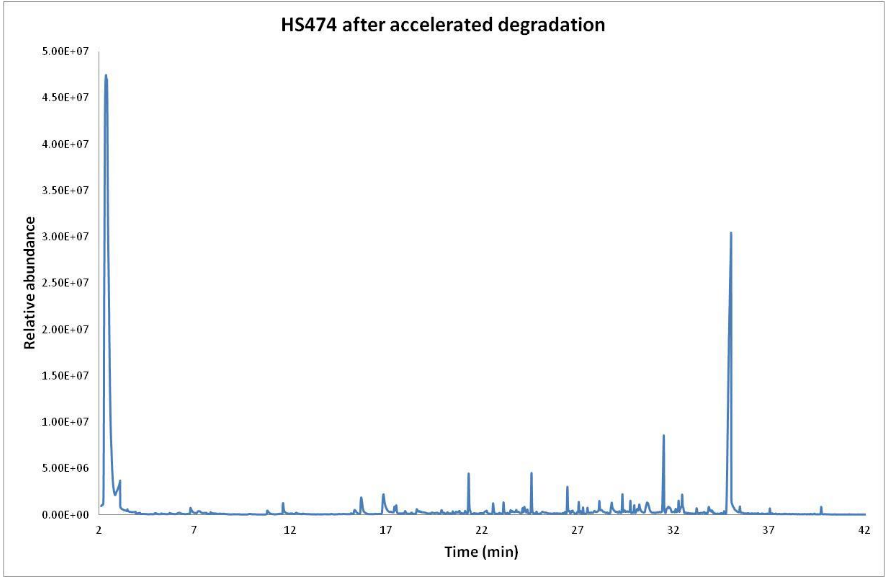
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS474 after accelerated degradation
Relative abundance
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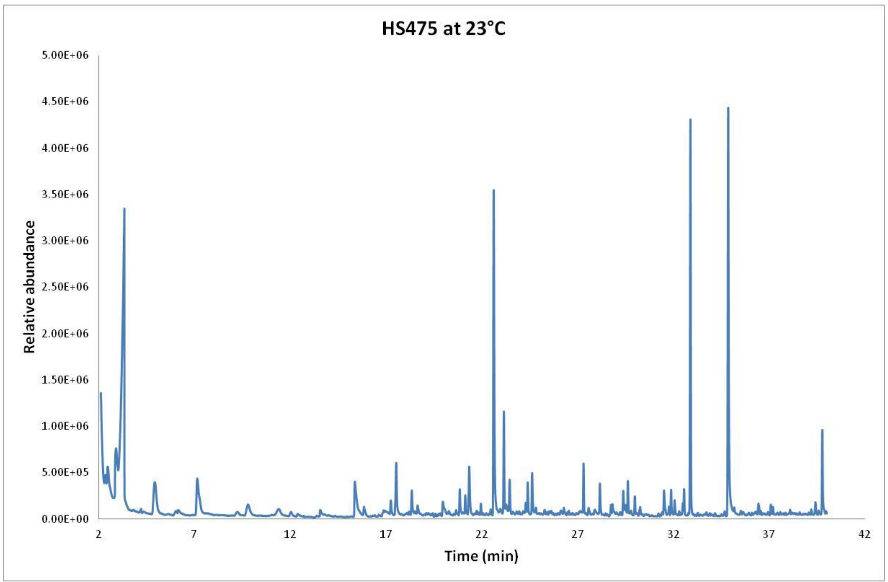
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS475 at 23°C
Relative abundance
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4.50E+06
4.00E+06
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
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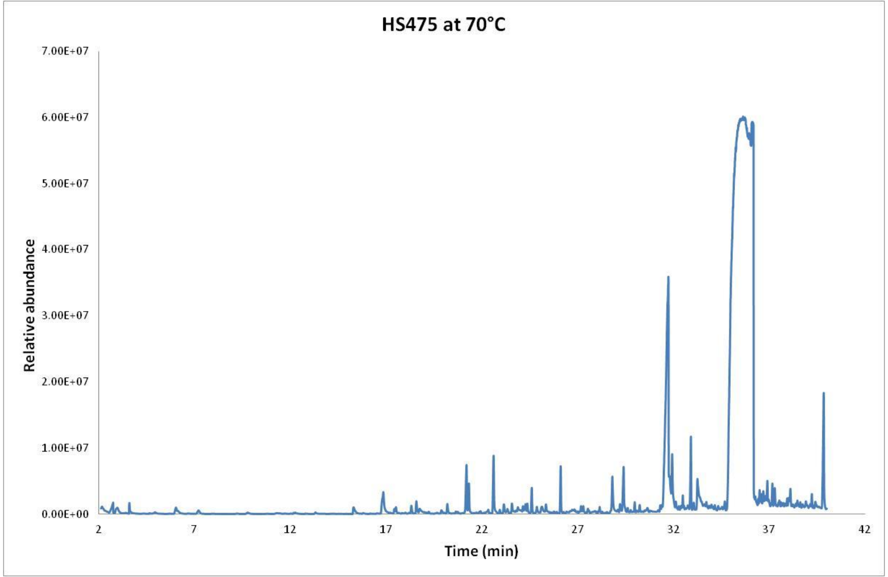
2
7
12
17
22
27
32
37
42
Time (min)


HS475 at 70°C
Relative abundance
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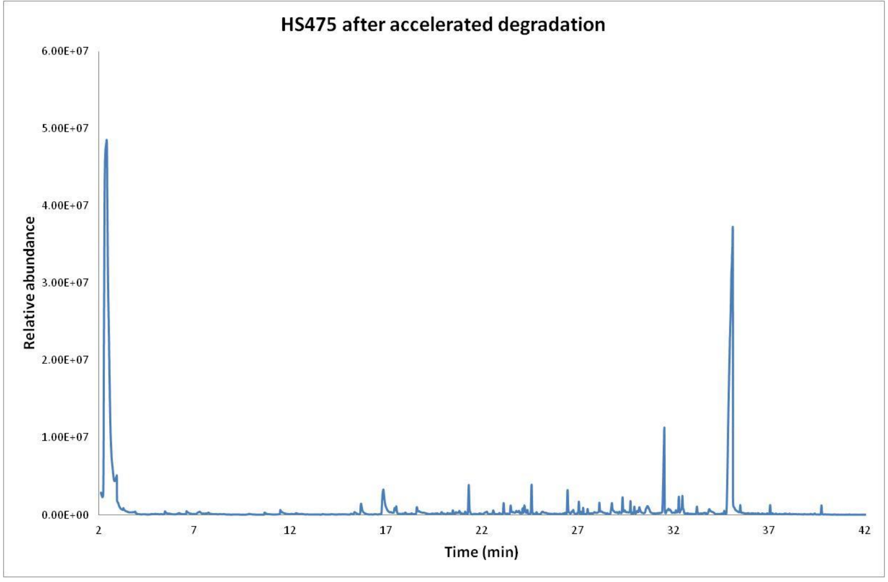
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS475 after accelerated degradation
Relative abundance
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5.00E+07
4.00E+07
3.00E+07
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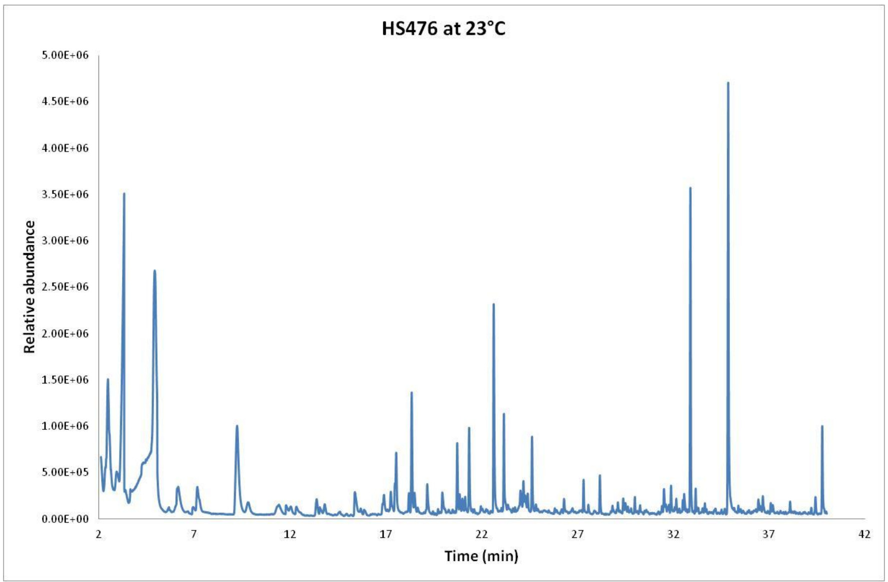
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS476 at 23°C
Relative abundance
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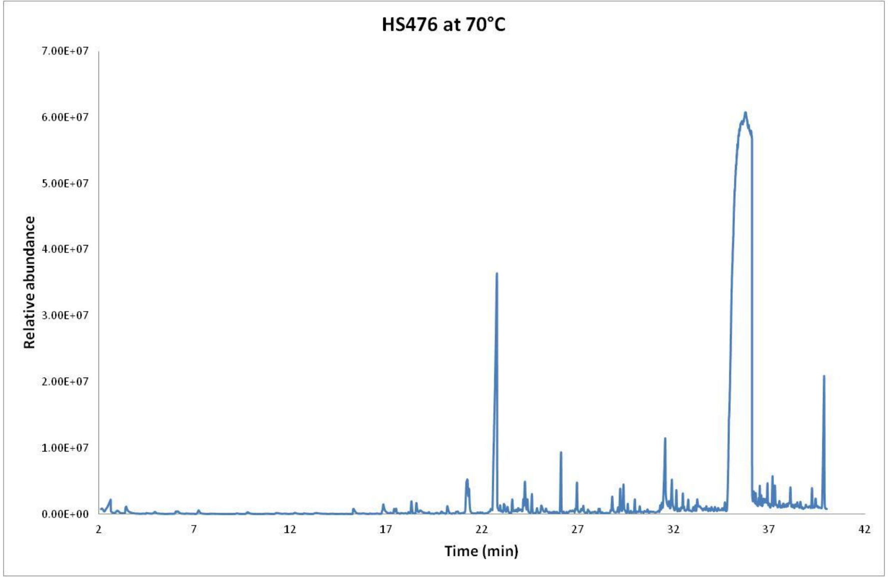
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS476 at 70°C
Relative abundance
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
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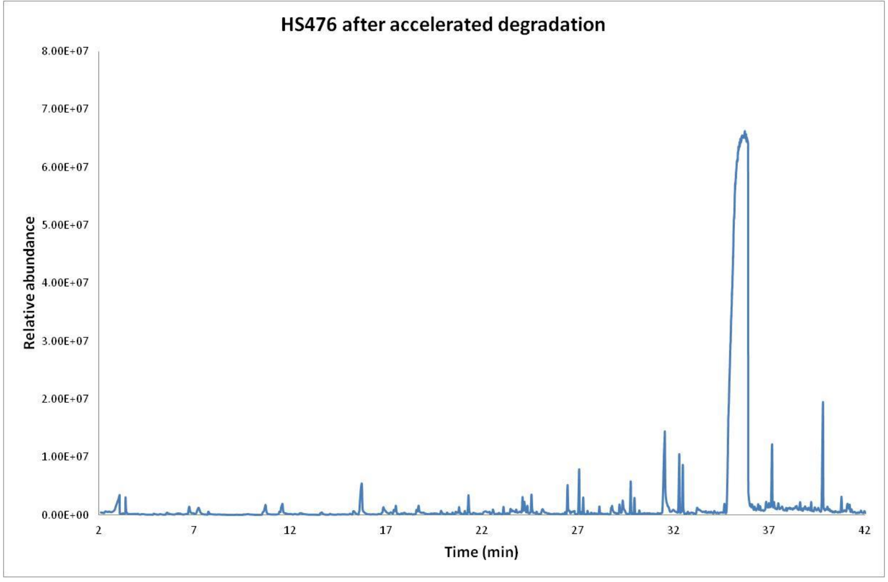
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS476 after accelerated degradation
Relative abundance
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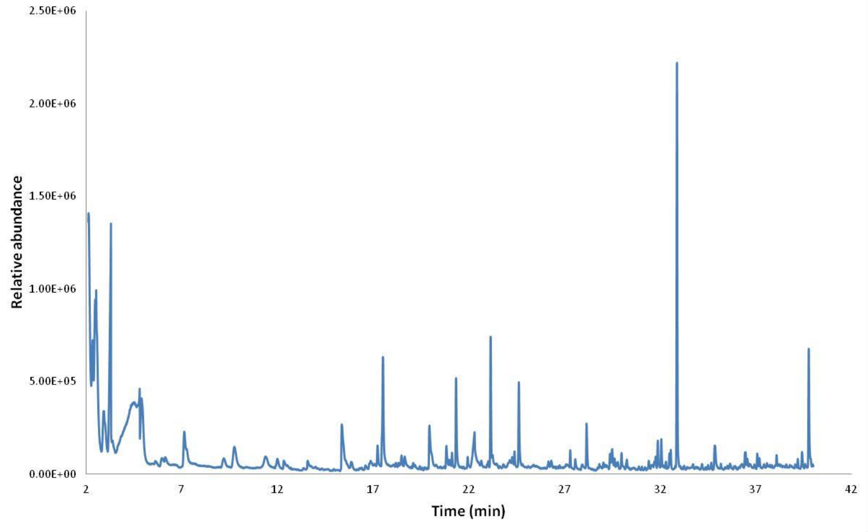
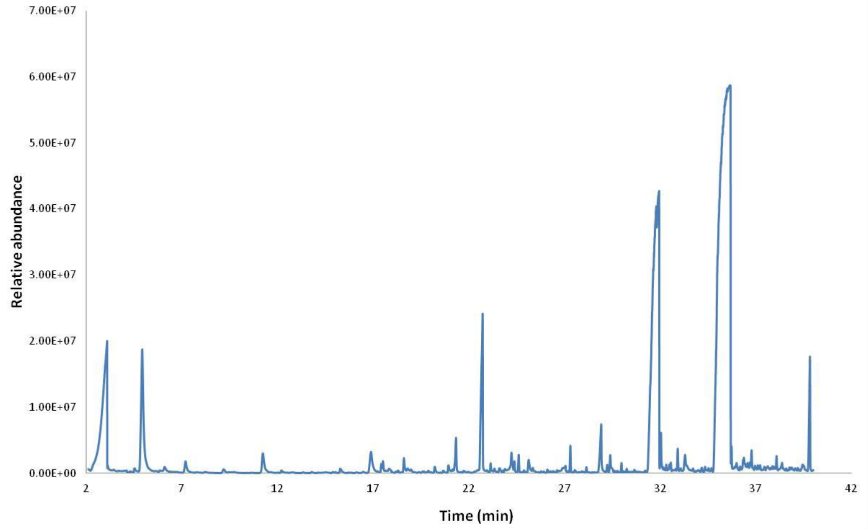
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

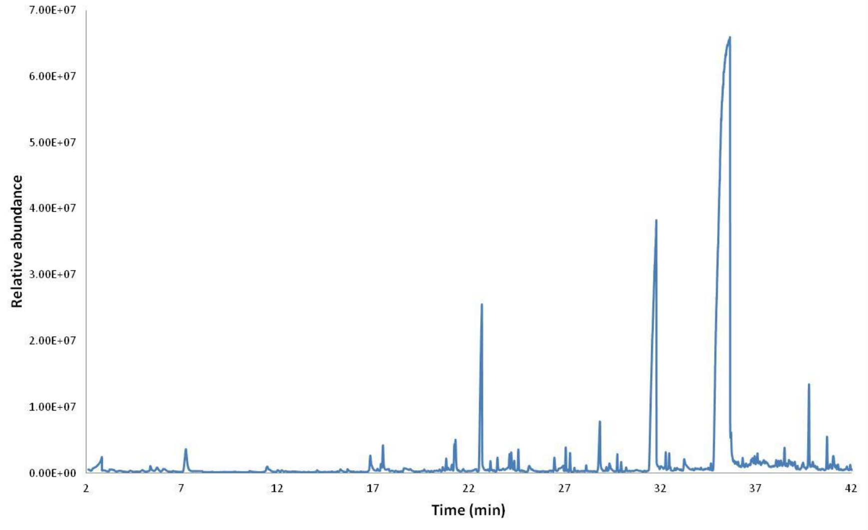
HS477 at 23°C



HS477 at 70°C



HS477 after accelerated degradation



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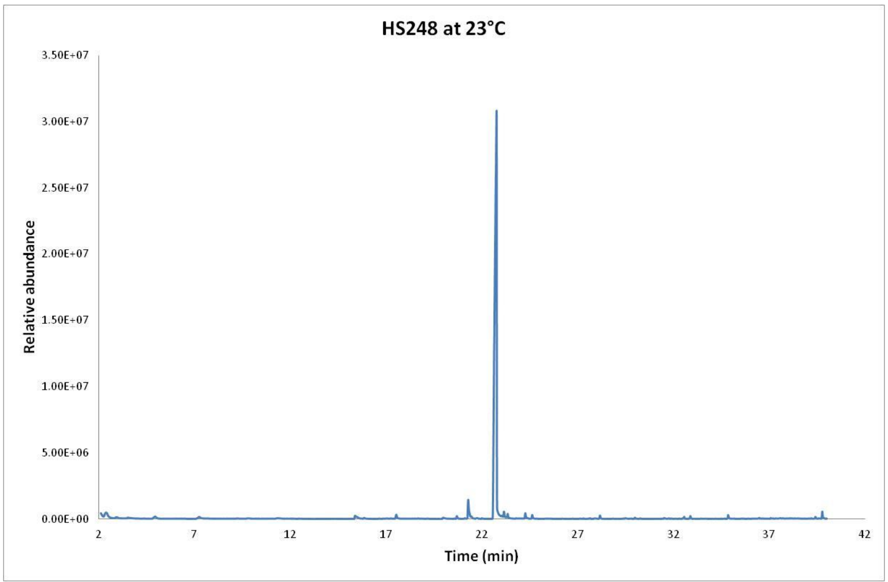
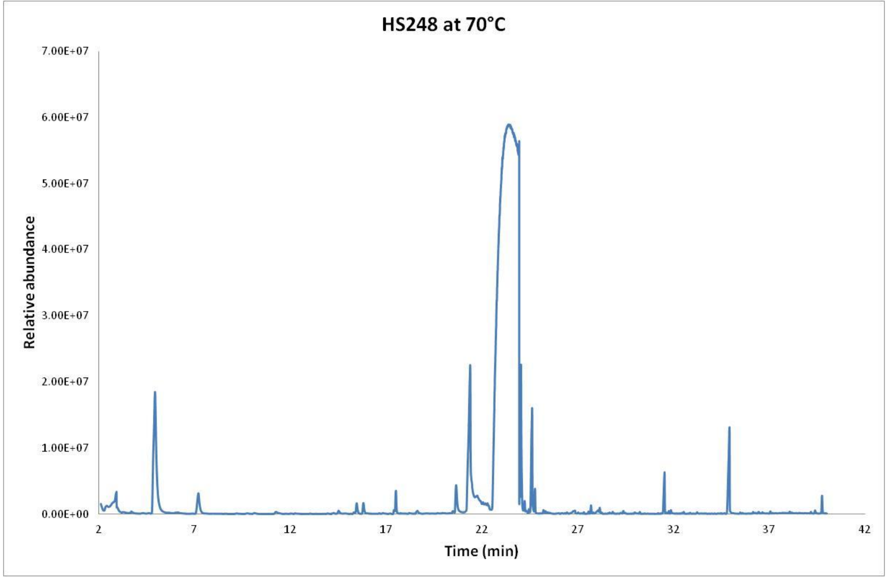
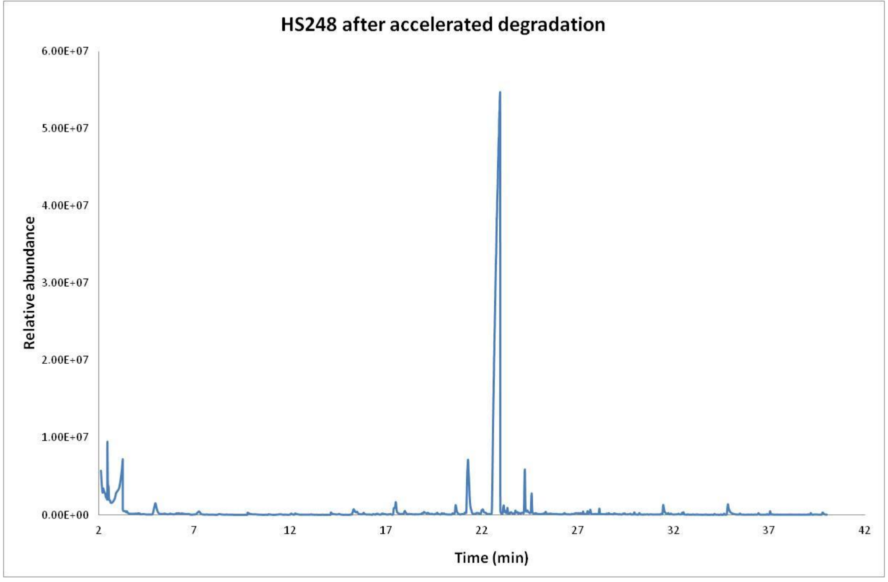
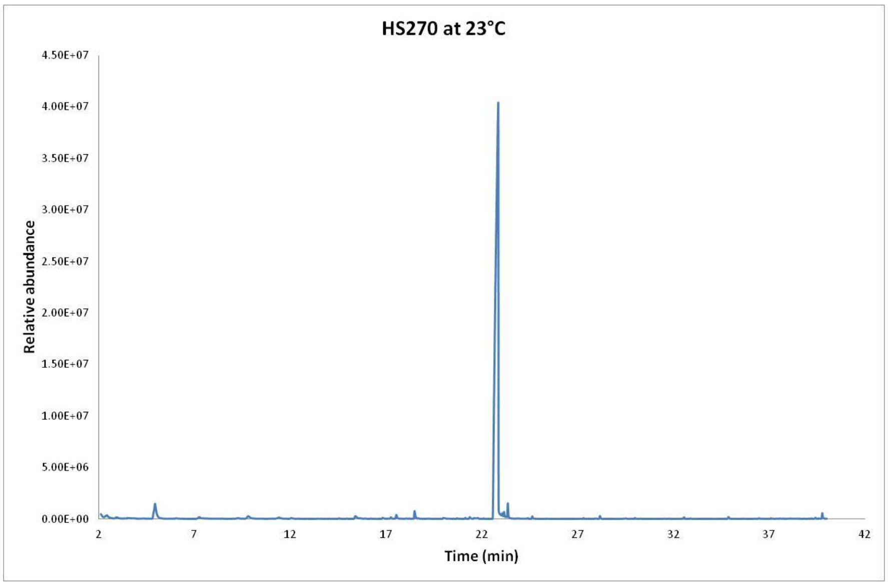
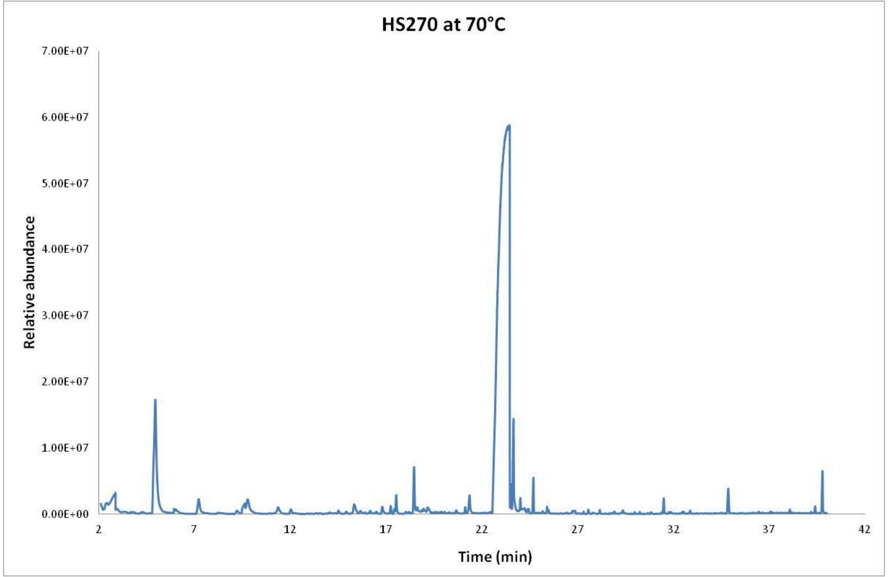

HS248 at 23°C


HS248 at 70°C


HS248 after accelerated degradation


HS270 at 23°C
Relative abundance
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS270 at 70°C
Relative abundance
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6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
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2
7
12
17
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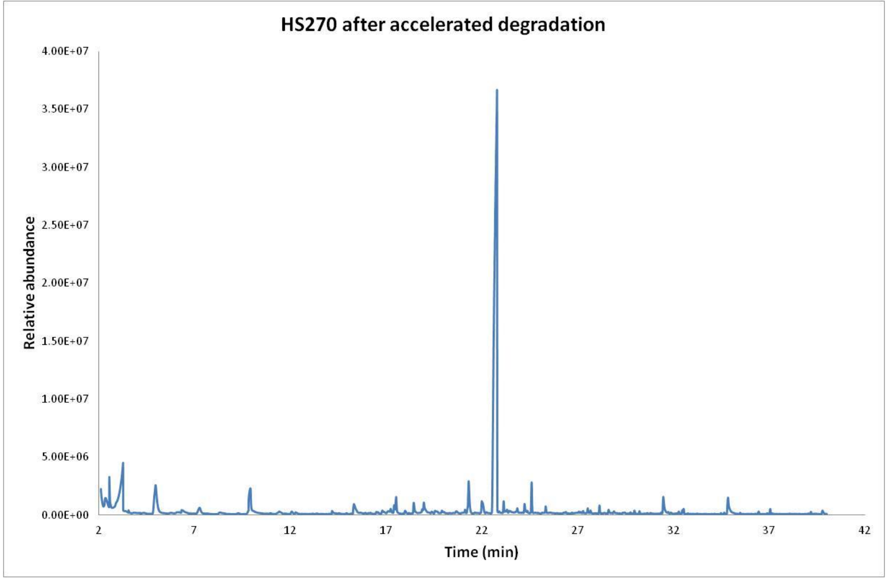
37
42
Time (min)


HS270 after accelerated degradation
Relative abundance
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2.50E+07
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1.50E+07
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2
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12
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22
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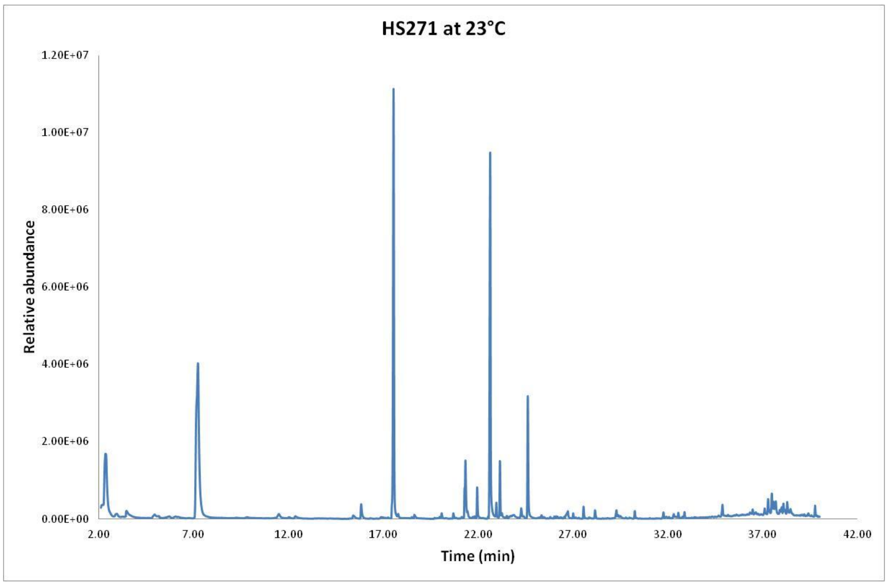
42
Time (min)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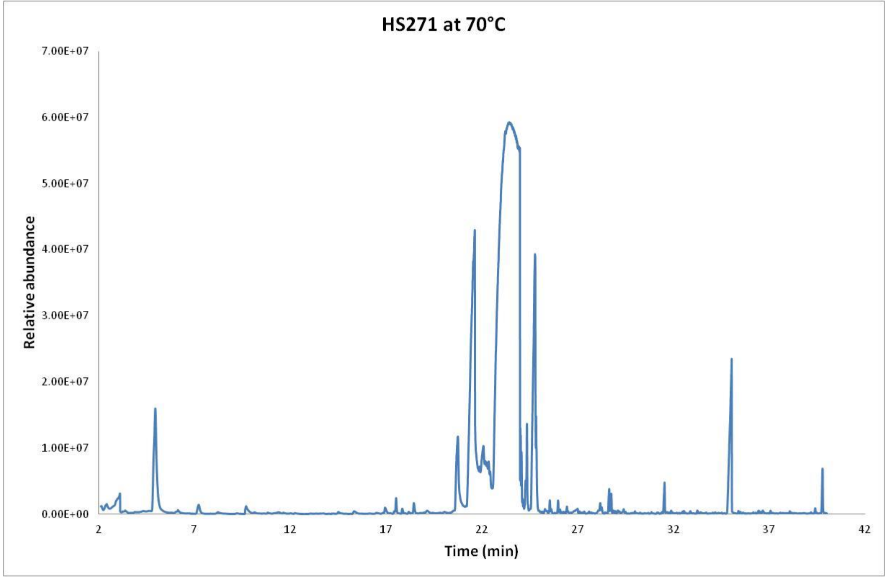
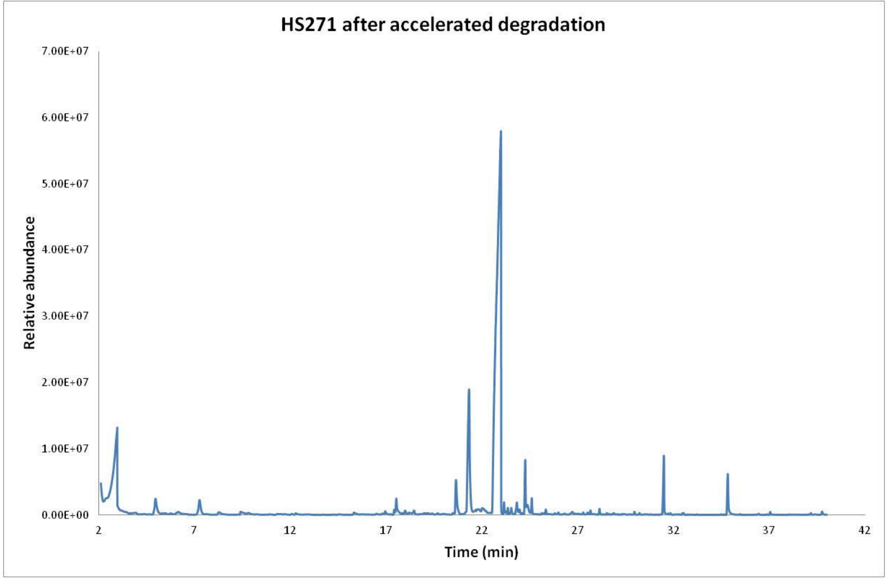
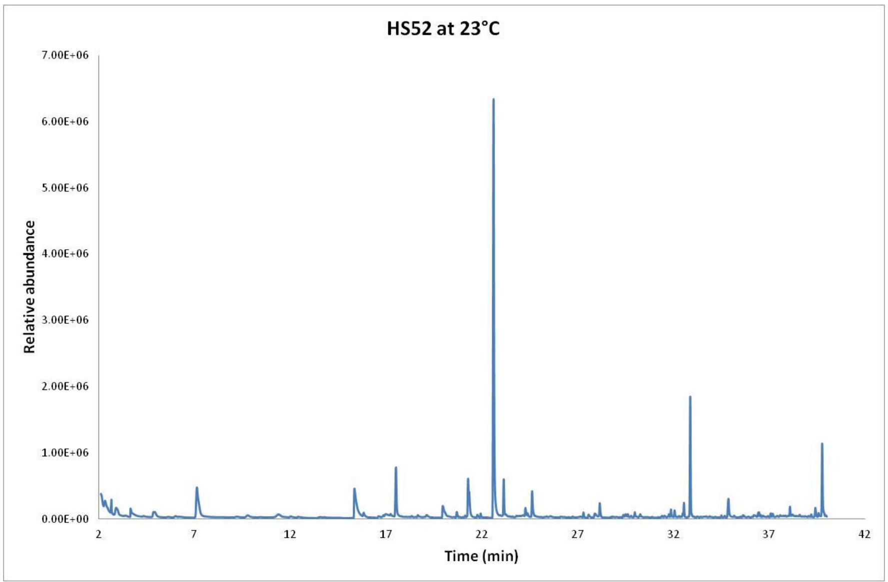
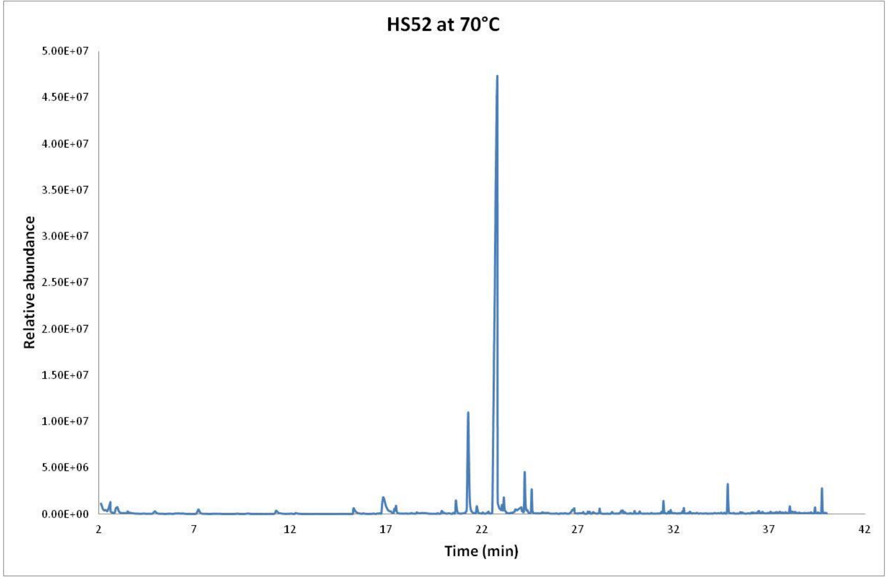
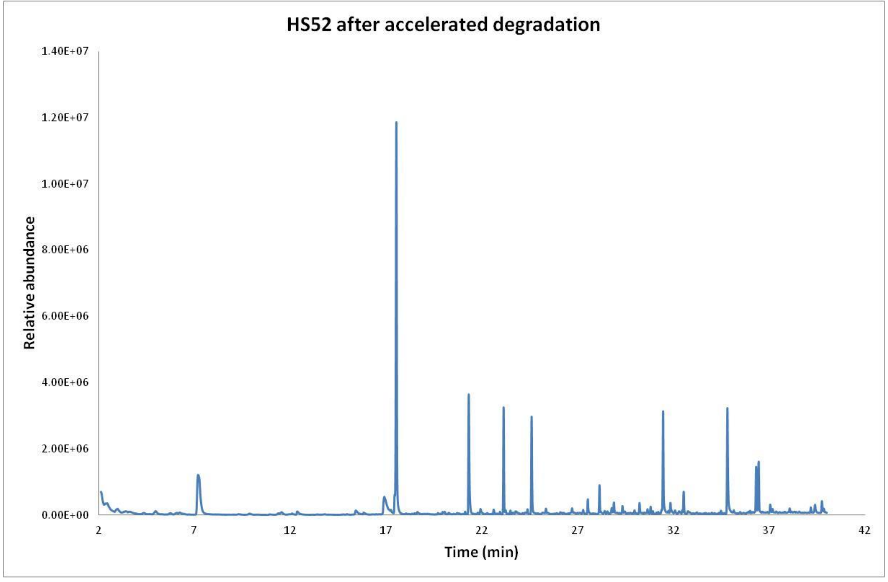

HS271 at 70°C

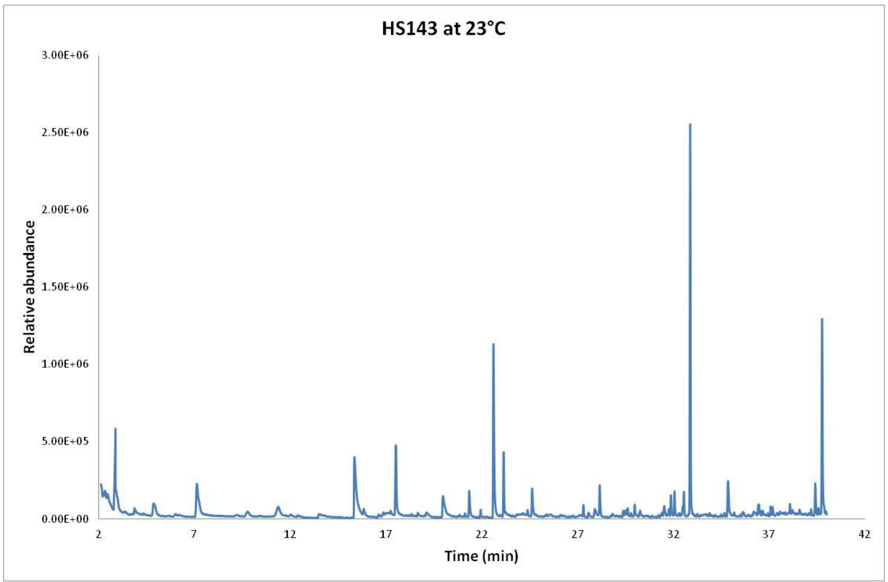

HS271 after accelerated degradation

POLYCARBONATE


HS52 at 23°C


HS52 at 70°C


HS52 after accelerated degradation


HS143 at 23°C
Relative abundance
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
2
7
12
17
22
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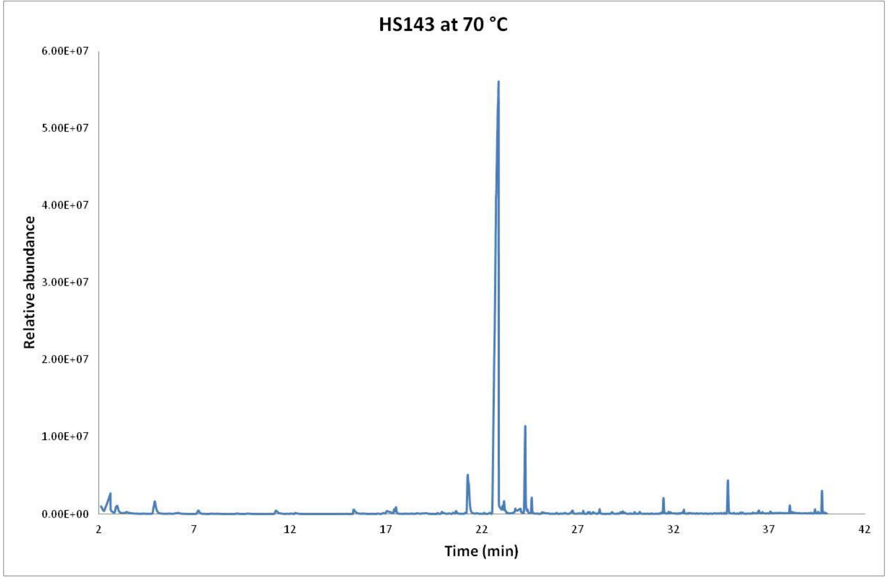
32
37
42
Time (min)


HS143 at 70 °C
Relative abundance
6.00E+07
5.00E+07
4.00E+07
3.00E+07
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1.00E+07
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2
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12
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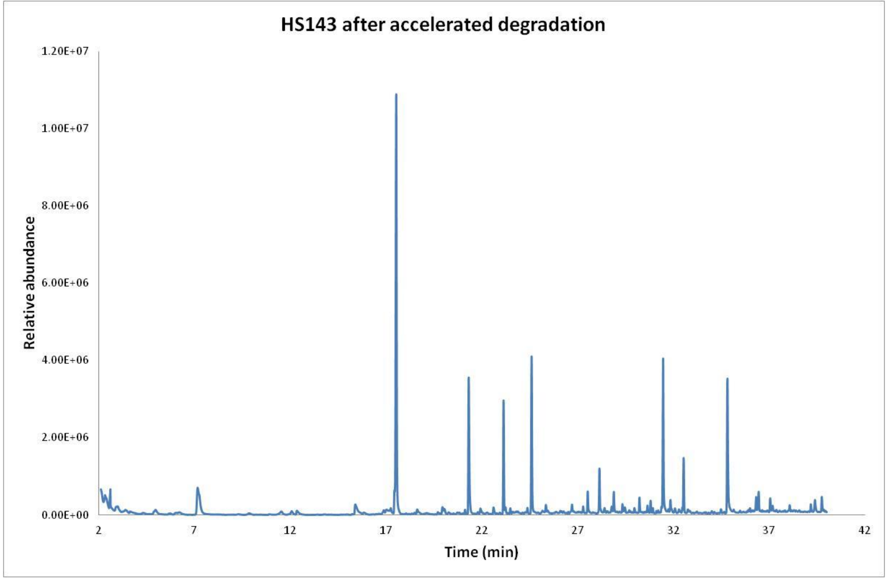
22
27
32
37
42
Time (min)


HS143 after accelerated degradation
Relative abundance
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1.00E+07
8.00E+06
6.00E+06
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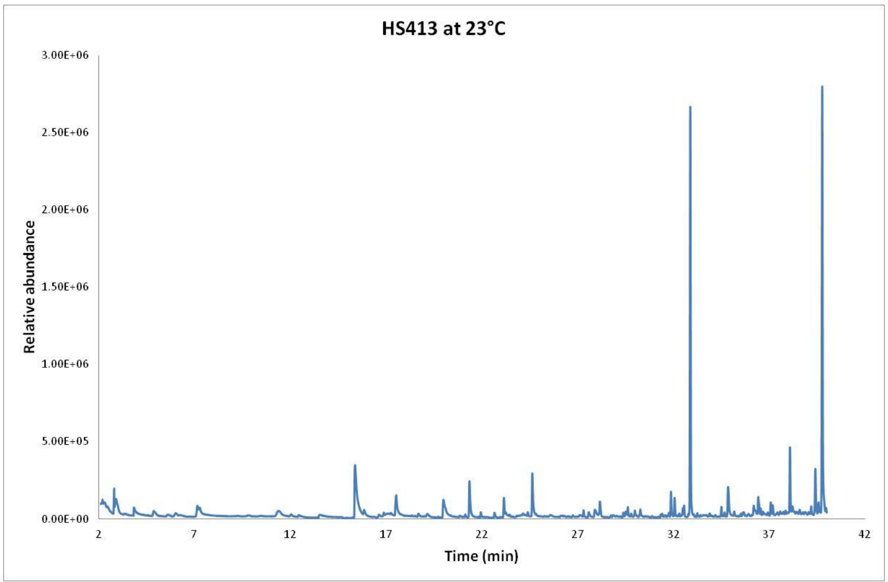
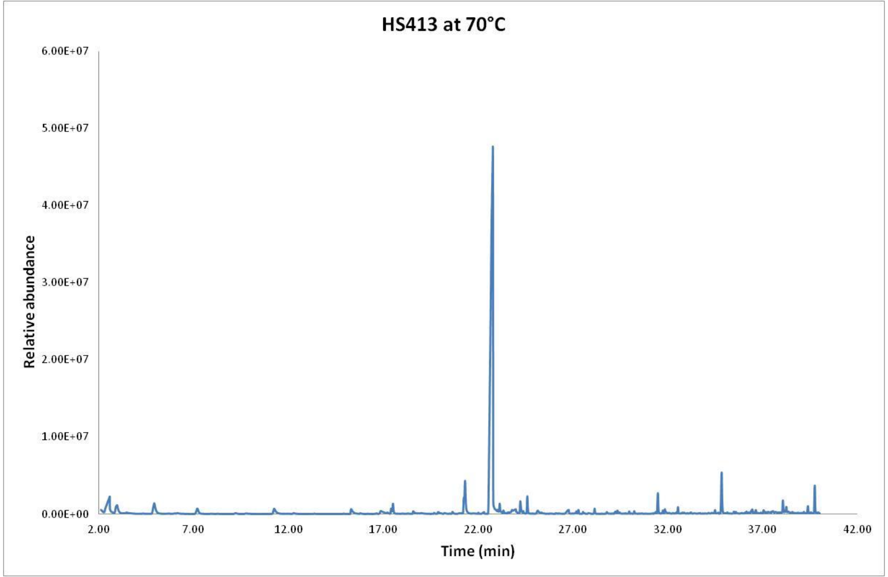
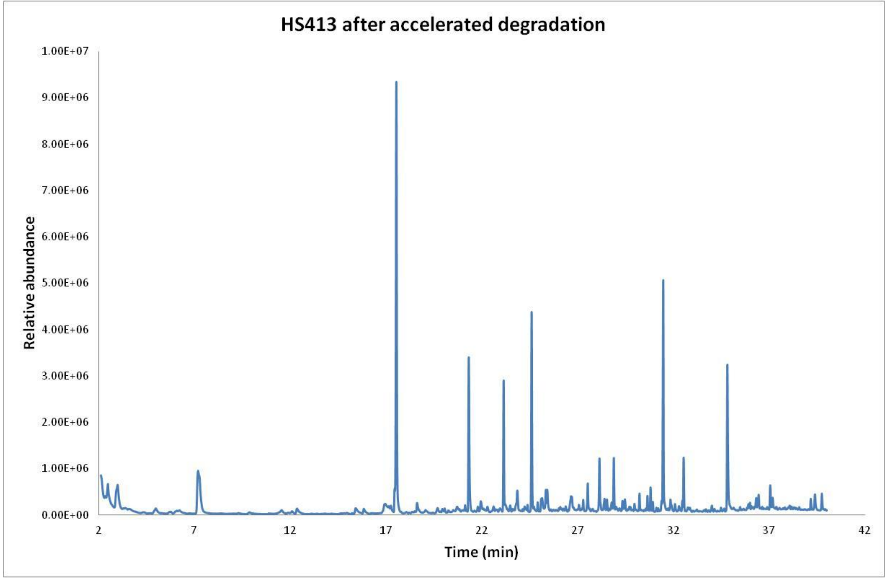
2.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)



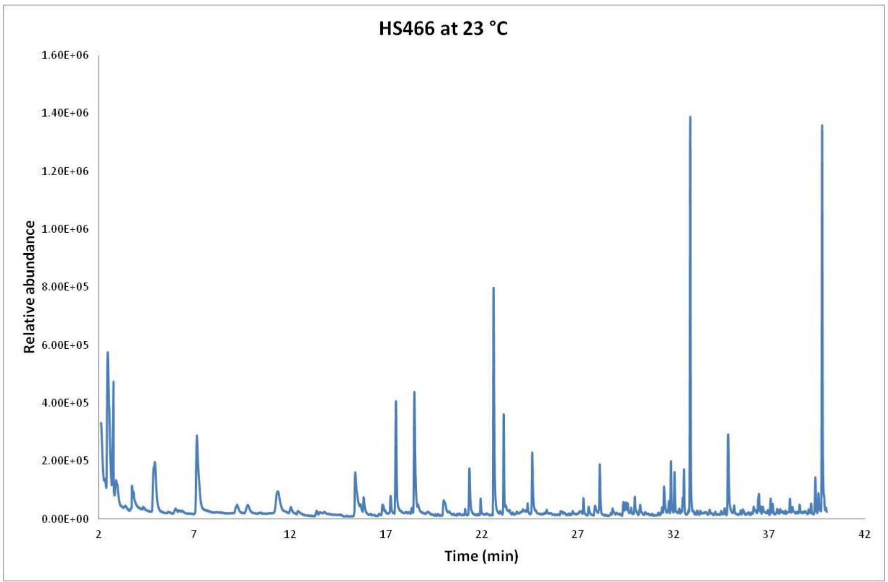
HS413 at 23°C

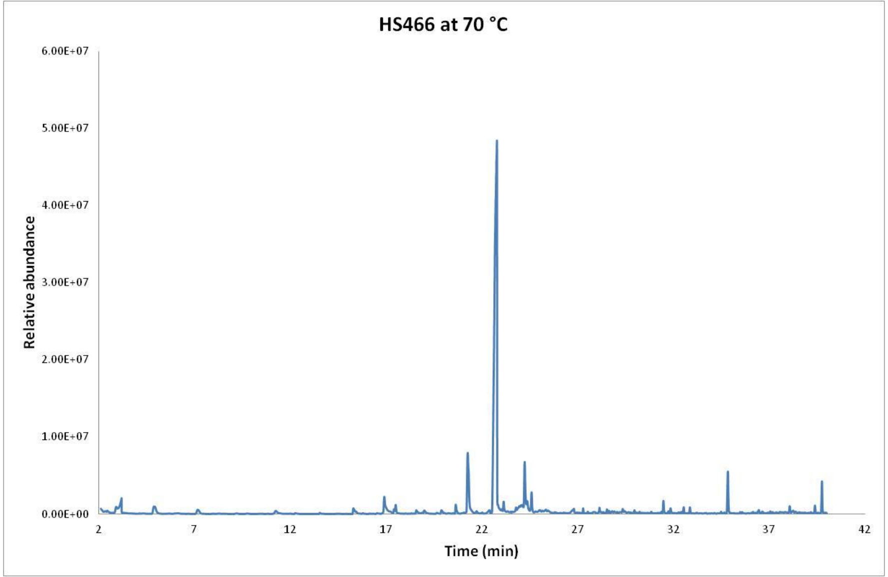


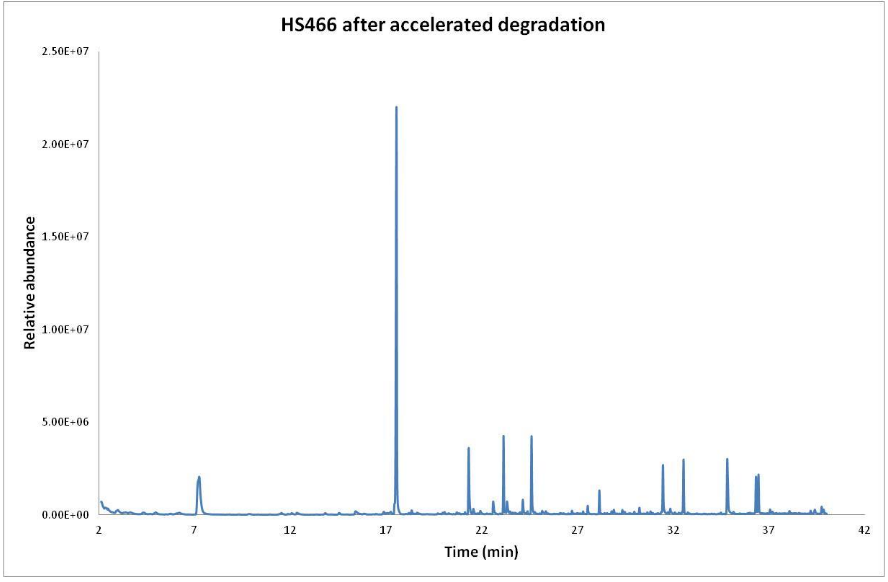
HS413 at 70°C

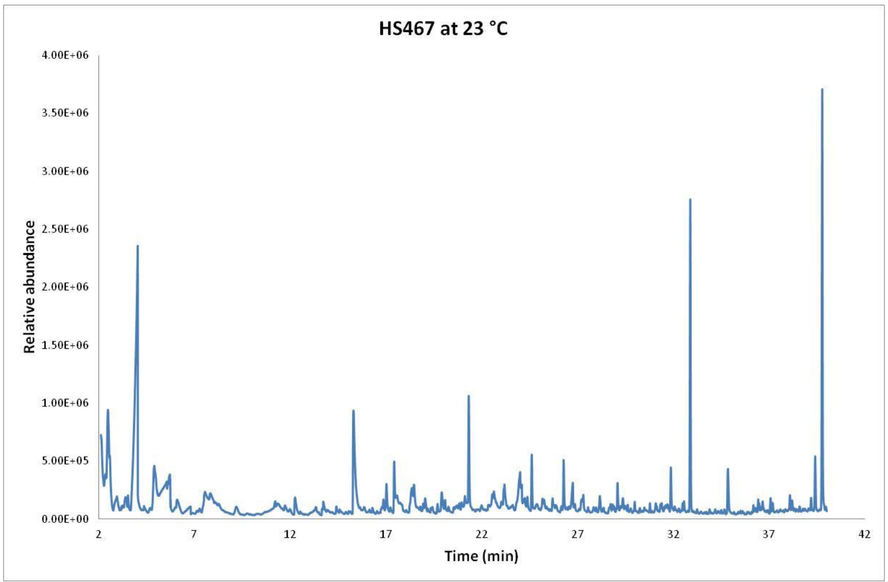


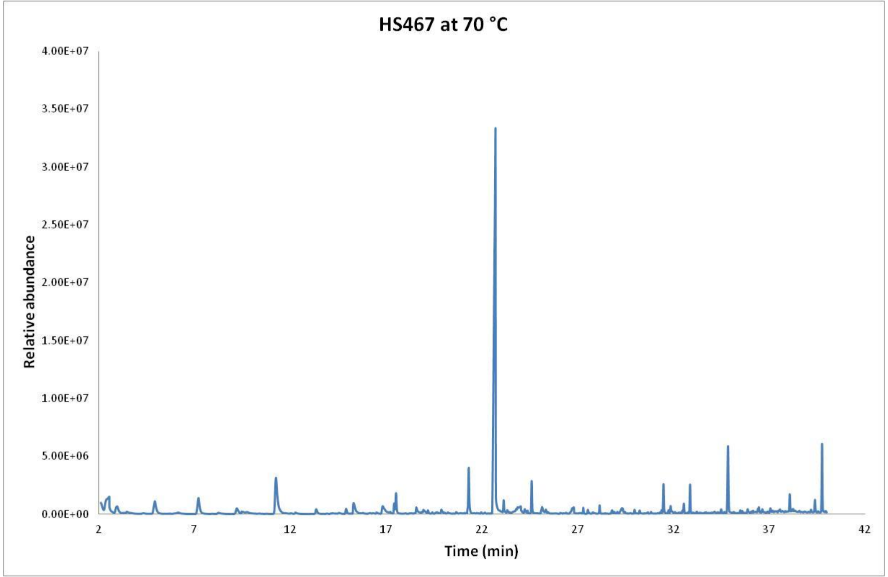
HS413 after accelerated degradation

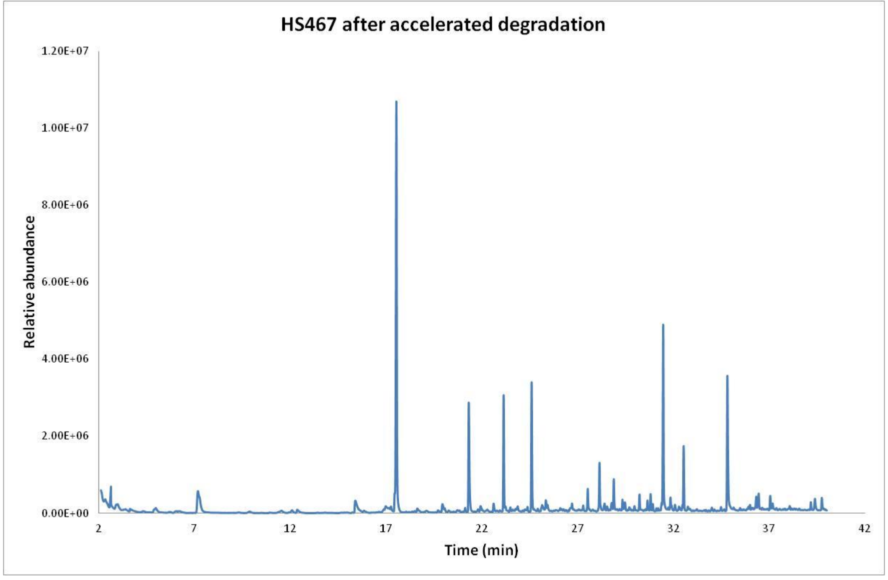

HS466 at 23 °C


HS466 at 70 °C

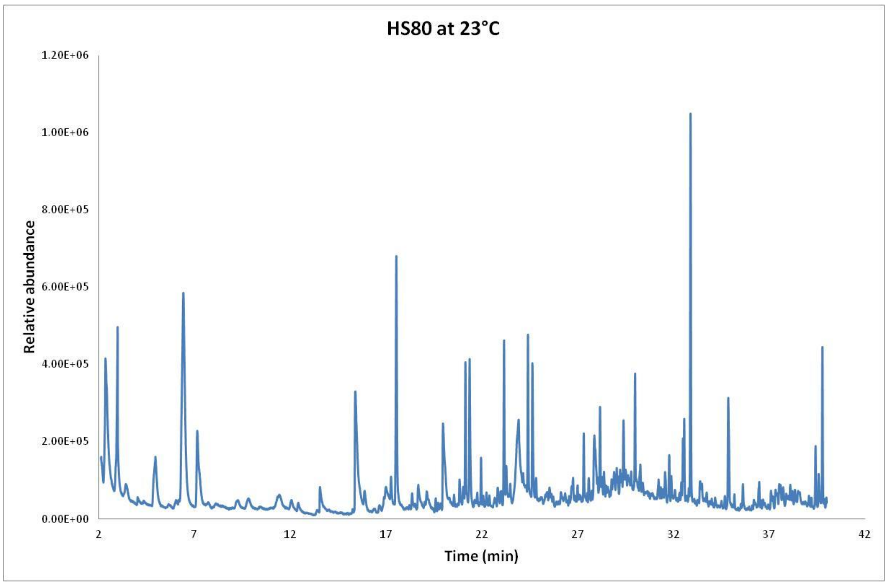

HS466 after accelerated degradation

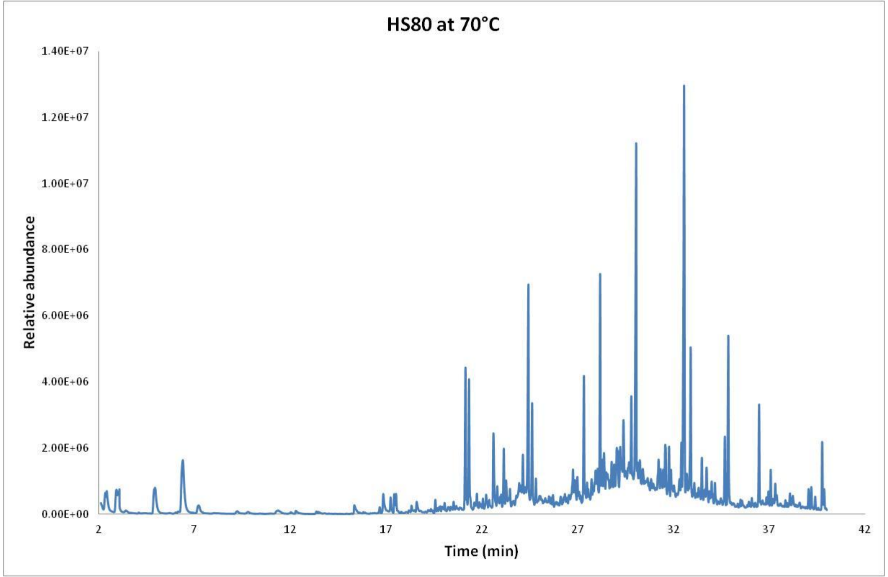

HS467 at 23 °C
Relative abundance
4.00E+06
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

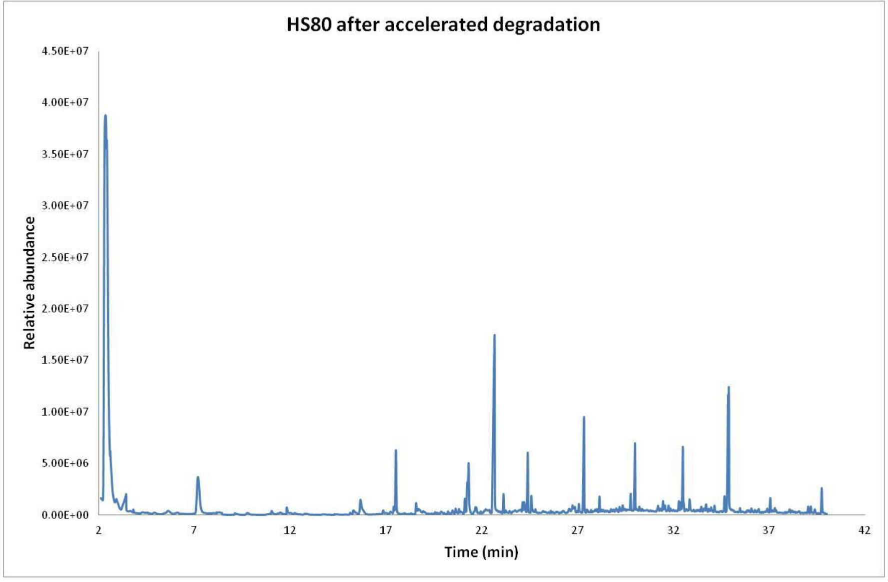

HS467 at 70 °C
Relative abundance
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

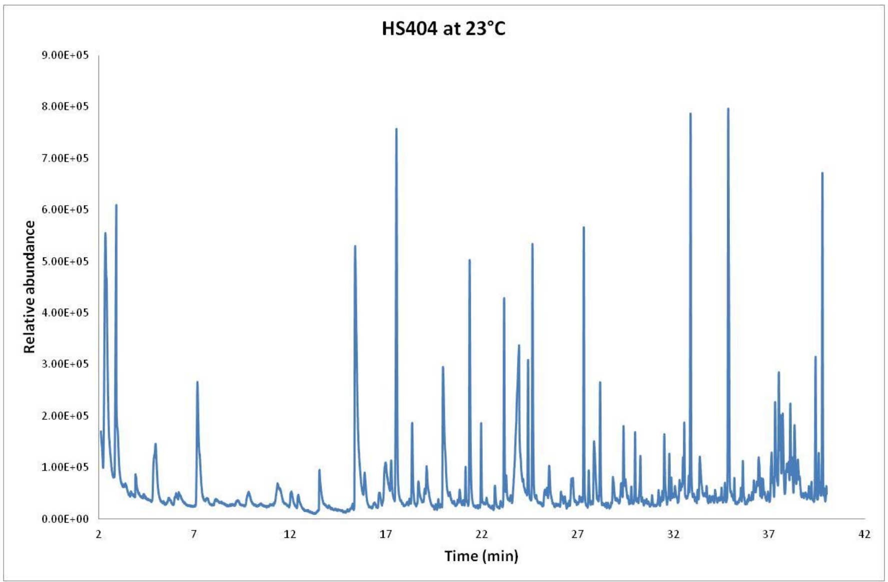

HS467 after accelerated degradation
Relative abundance
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

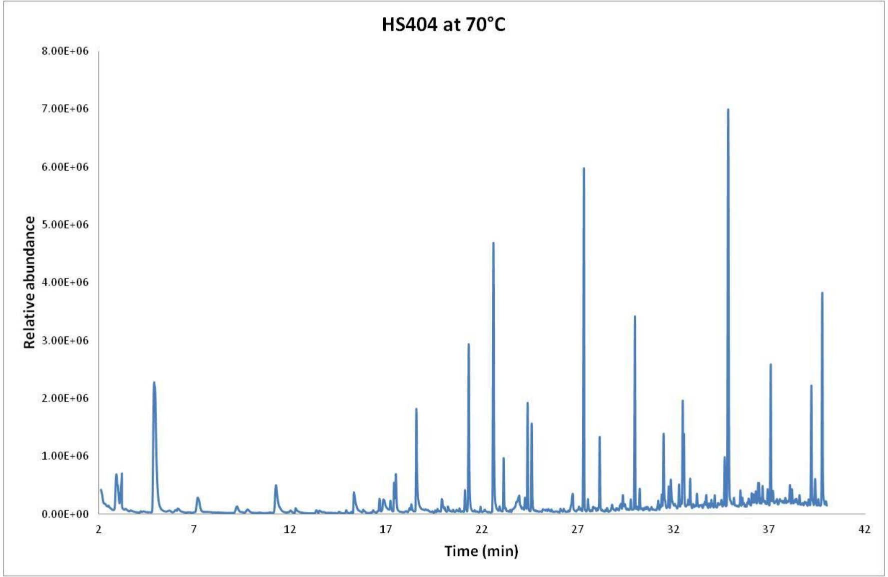
POLYETHYLENE

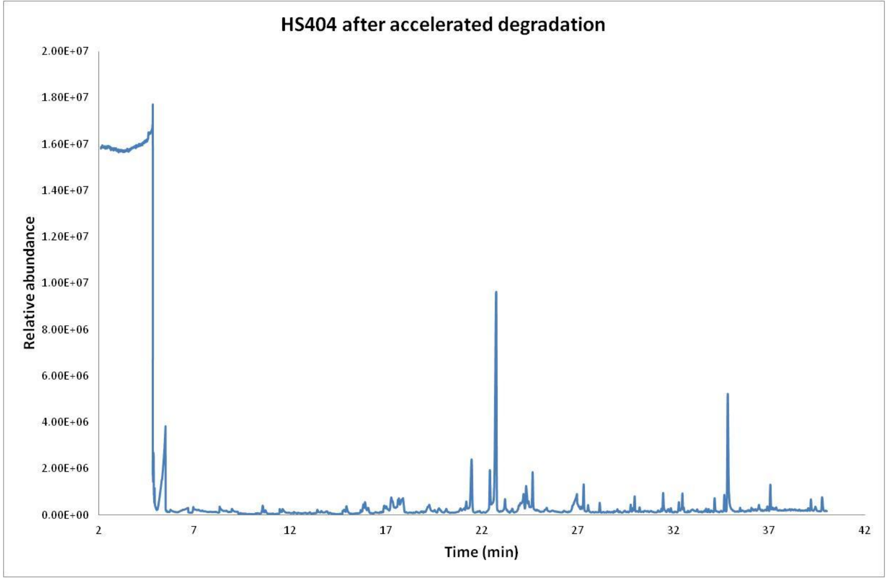

HS80 at 23°C

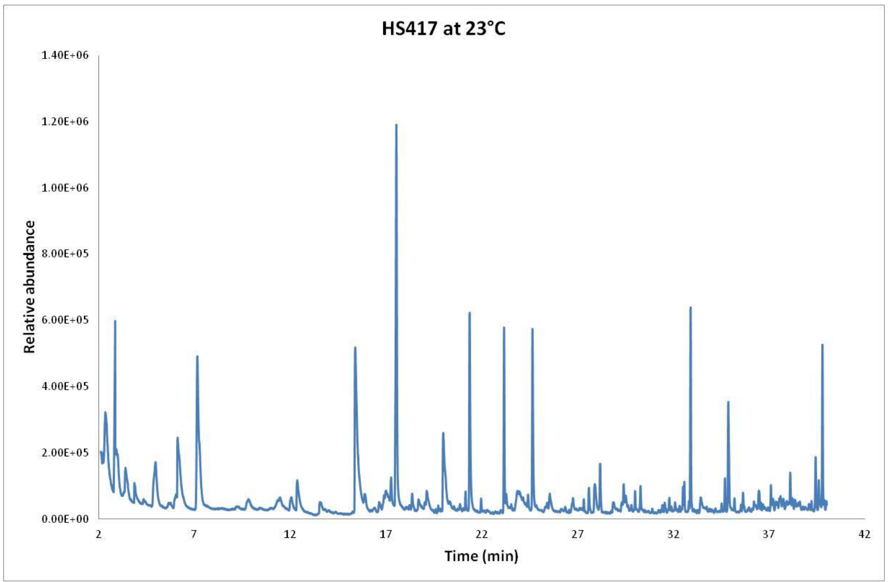

HS80 at 70°C

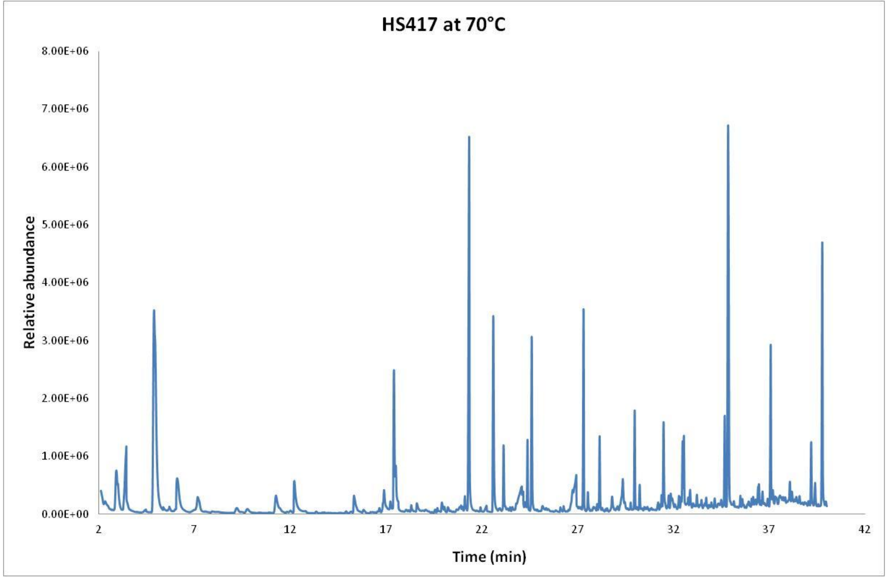

HS80 after accelerated degradation

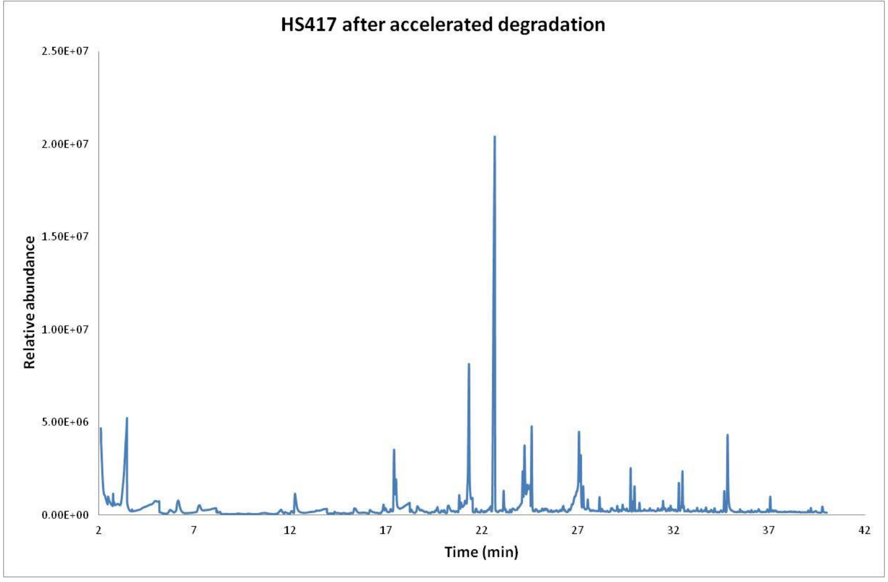

HS404 at 23°C

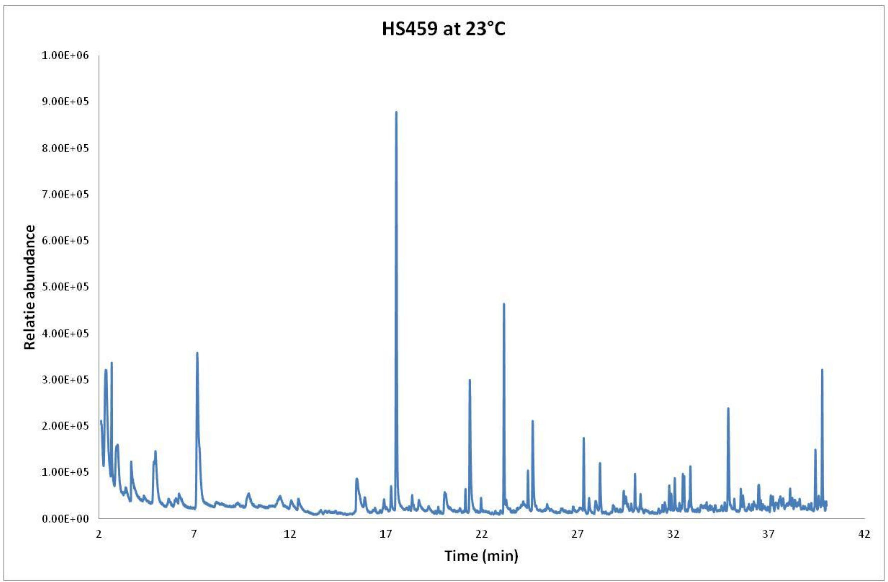

HS404 at 70°C

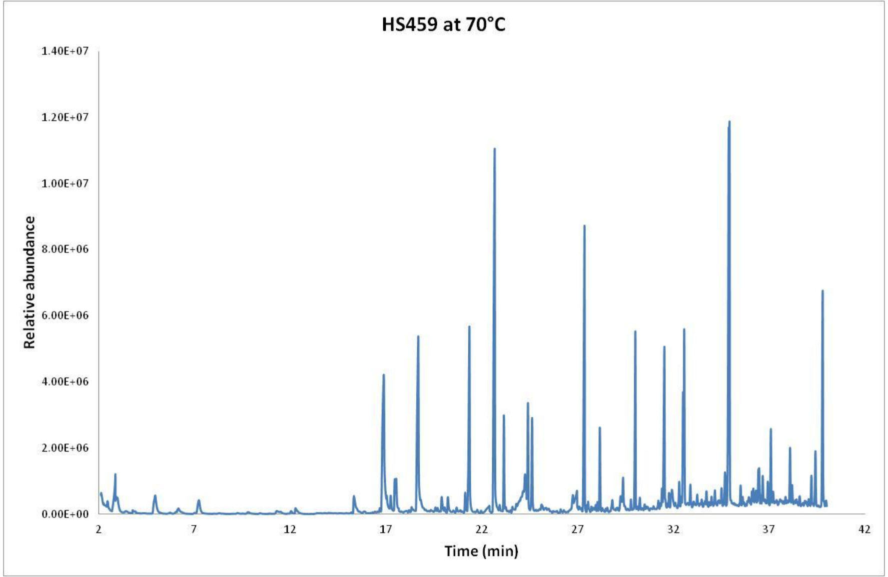

HS404 after accelerated degradation

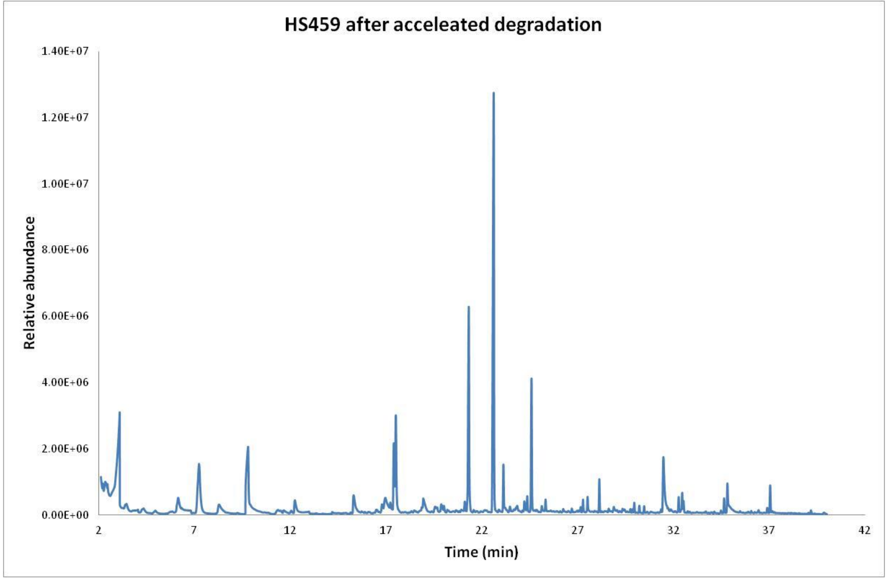

HS417 at 23°C
Relative abundance
1.40E+06
1.20E+06
1.00E+06
8.00E+05
6.00E+05
4.00E+05
2.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

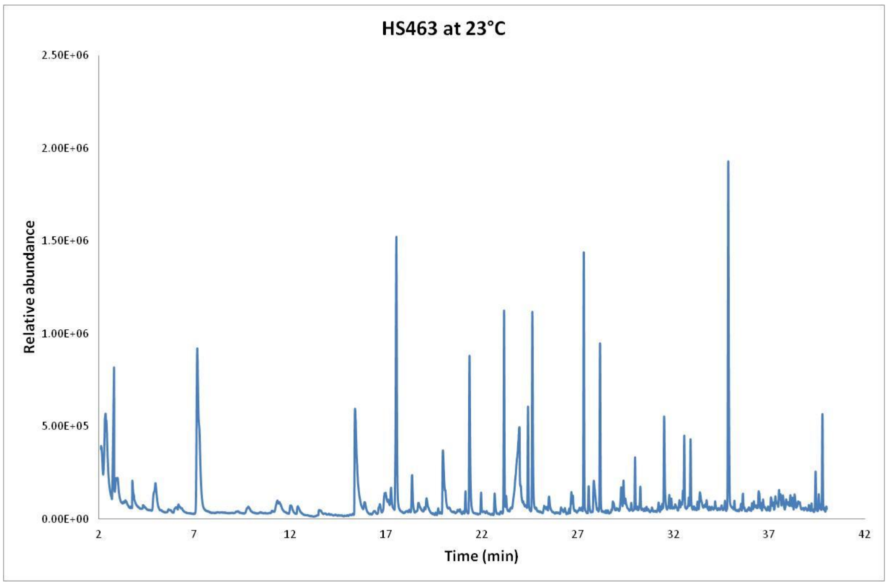

HS417 at 70°C
Relative abundance
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

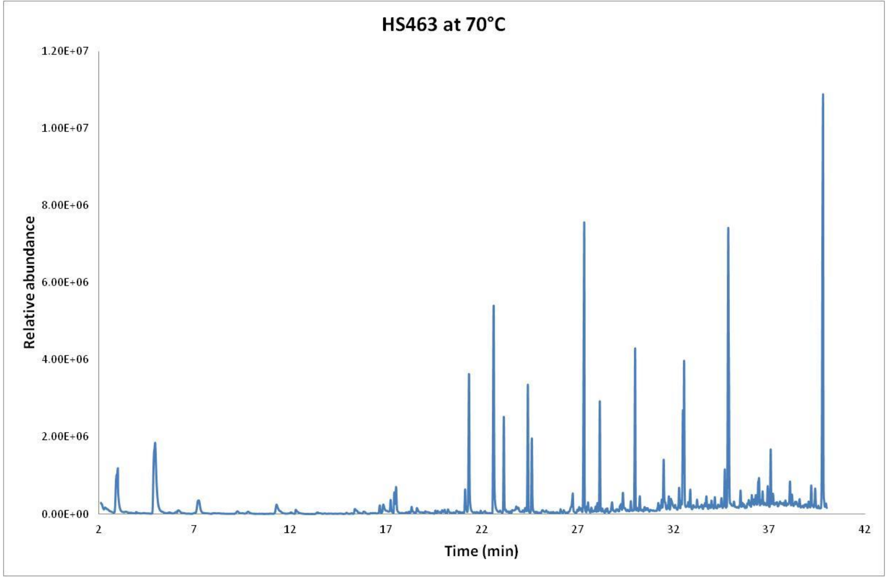

HS417 after accelerated degradation
Relative abundance
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

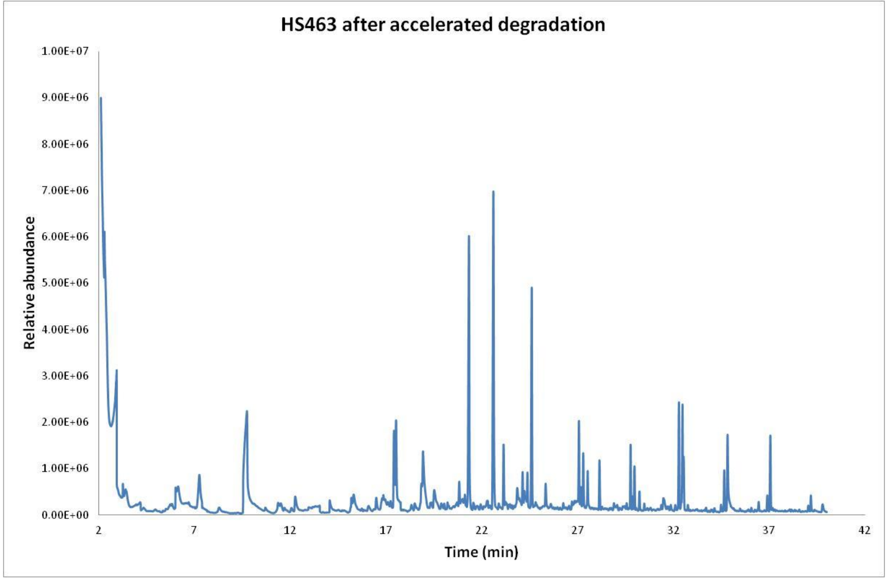

HS459 at 23°C
Relatie abundance
1.00E+06
9.00E+05
8.00E+05
7.00E+05
6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS459 at 70°C
Relative abundance
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

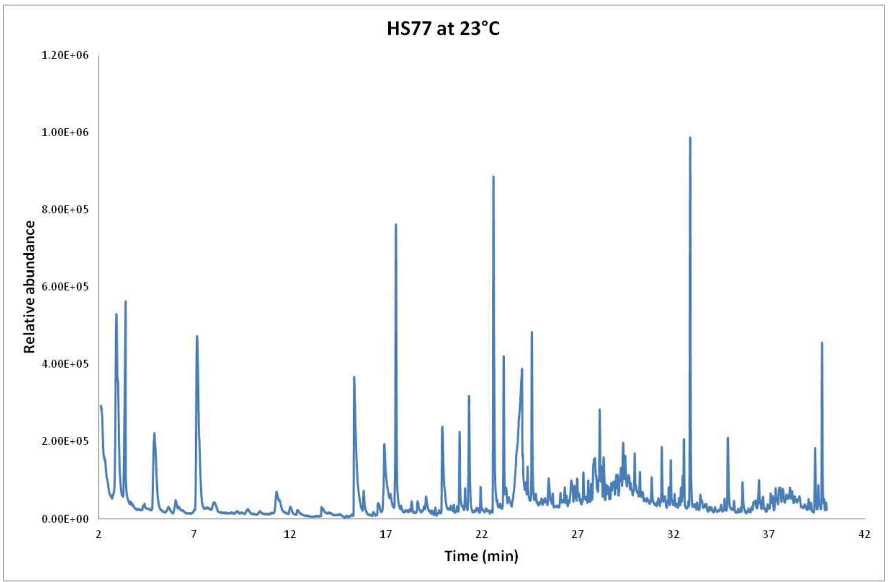

HS459 after acceleated degradation
Relative abundance
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

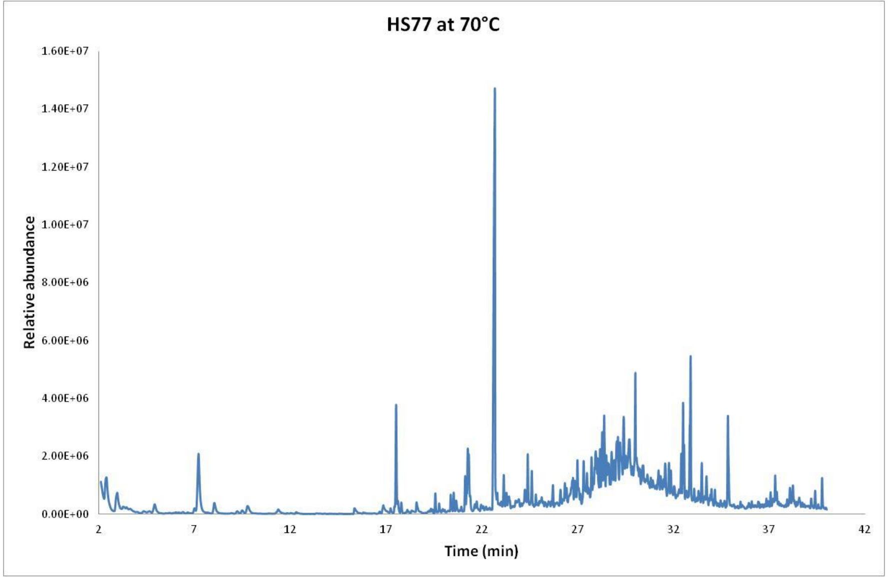

HS463 at 23°C

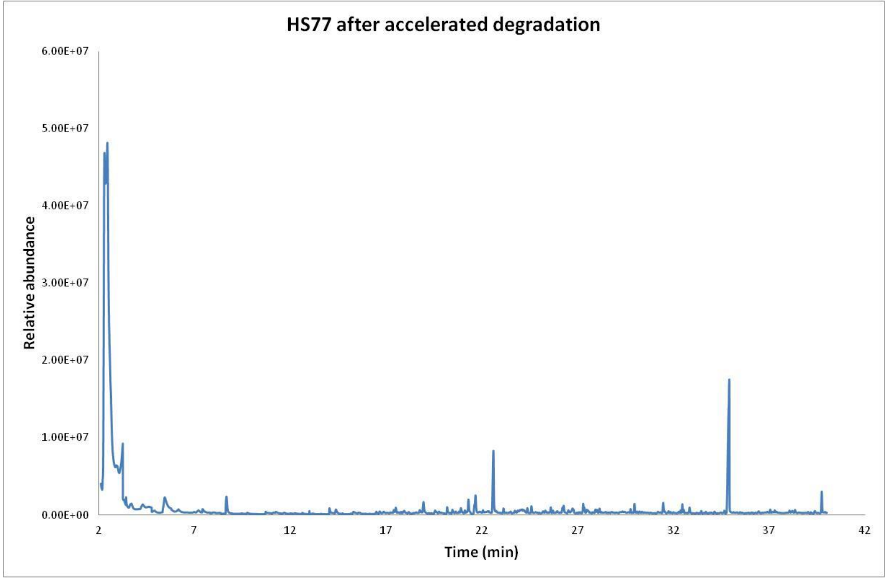

HS463 at 70°C

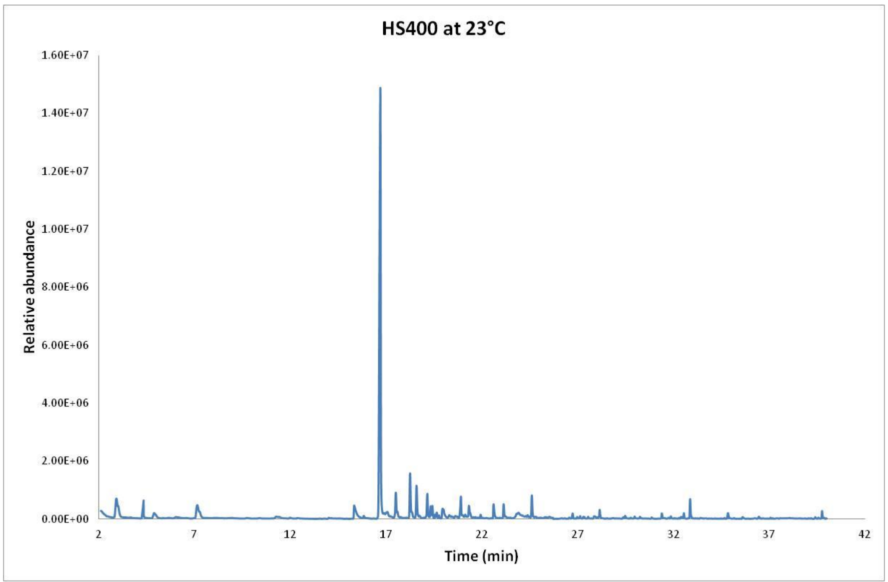

HS463 after accelerated degradation

POLYPROPYLENE

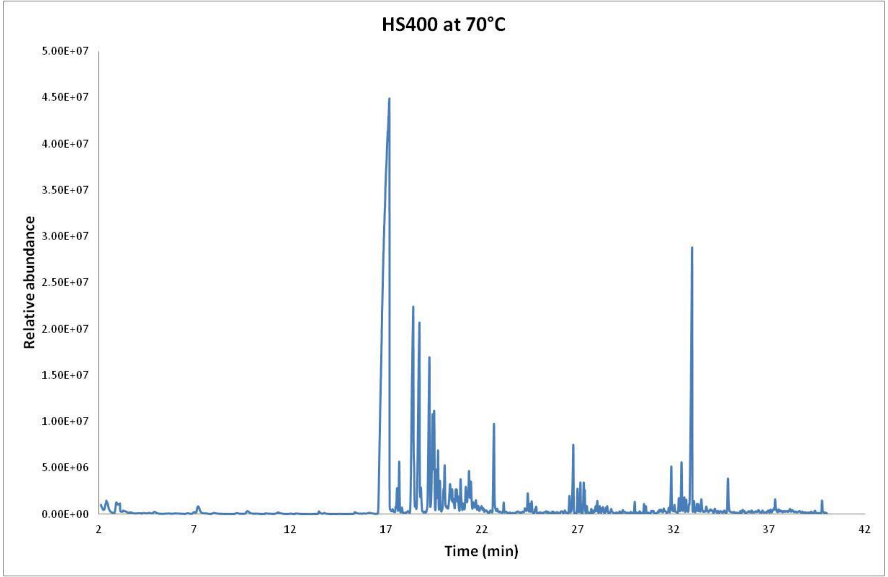

HS77 at 23°C
Relative abundance
0.00E+00
2.00E+05
4.00E+05
6.00E+05
8.00E+05
1.00E+06
1.20E+06
2
7
12
17
22
27
32
37
42
Time (min)


HS77 at 70°C
Relative abundance
0.00E+00
2.00E+06
4.00E+06
6.00E+06
8.00E+06
1.00E+07
1.20E+07
1.40E+07
1.60E+07
2
7
12
17
22
27
32
37
42
Time (min)

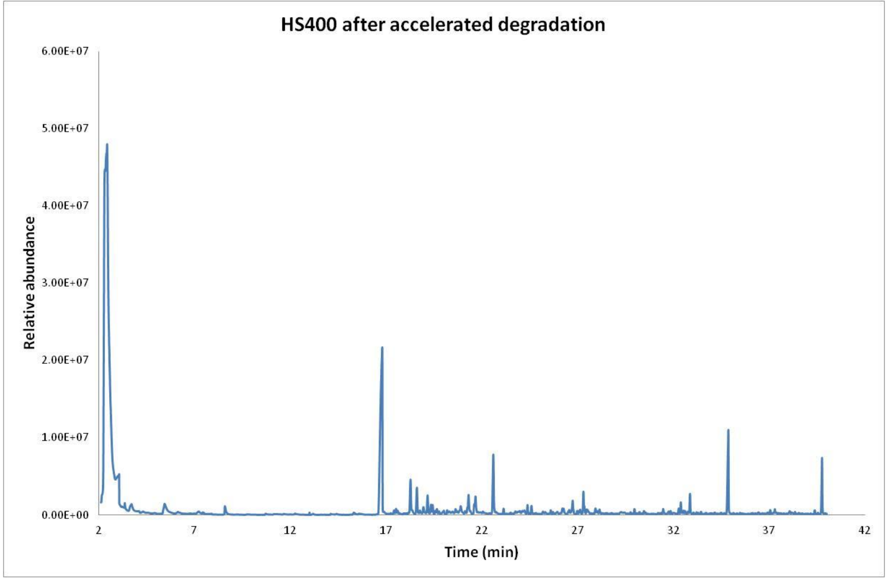

HS77 after accelerated degradation
Relative abundance
0.00E+00
1.00E+07
2.00E+07
3.00E+07
4.00E+07
5.00E+07
6.00E+07
2
7
12
17
22
27
32
37
42
Time (min)



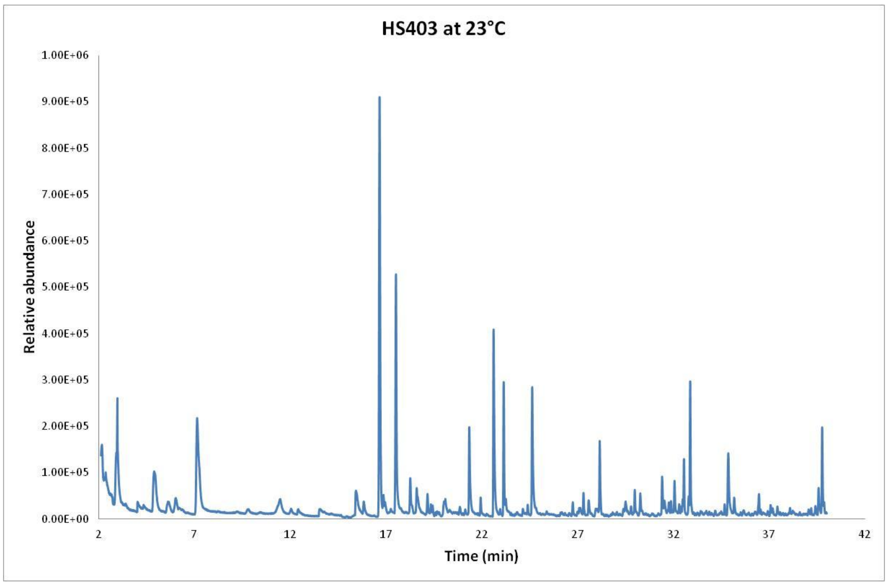
HS400 at 23°C

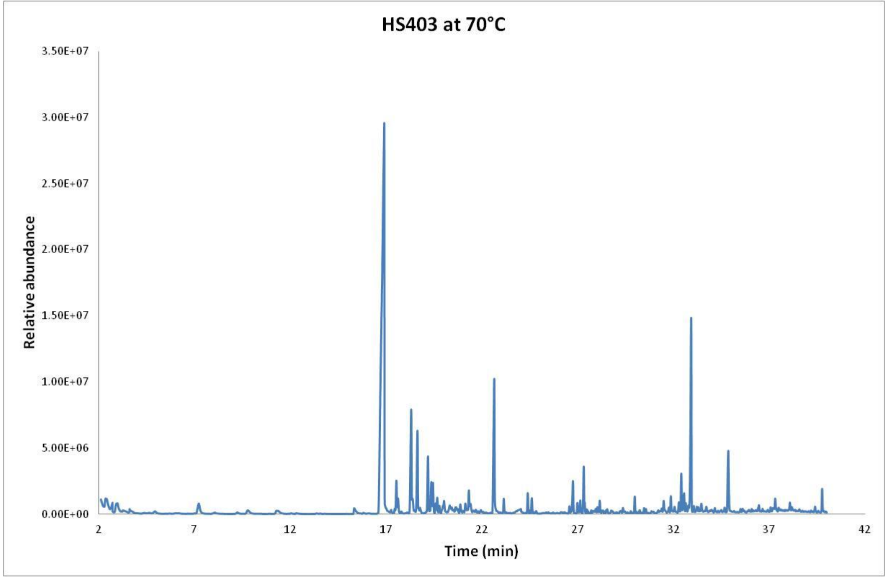


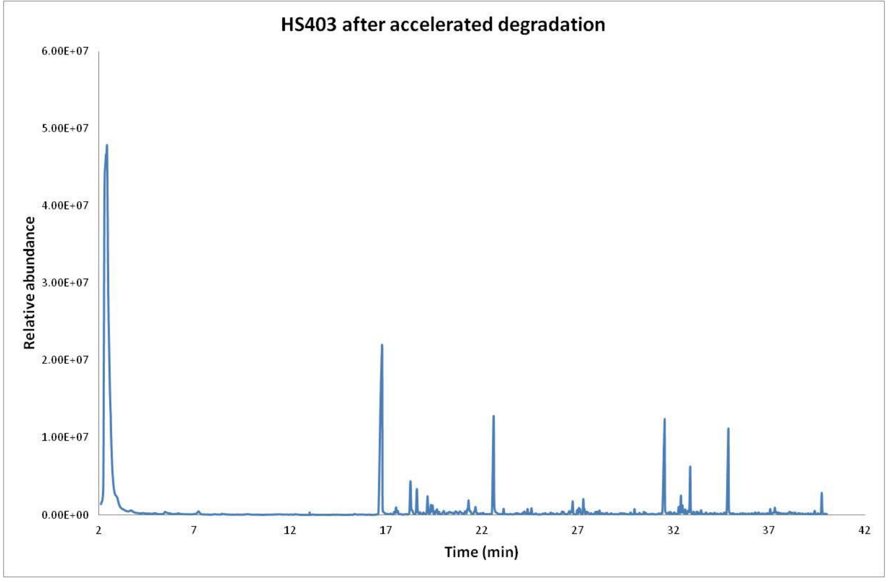
HS400 at 70°C

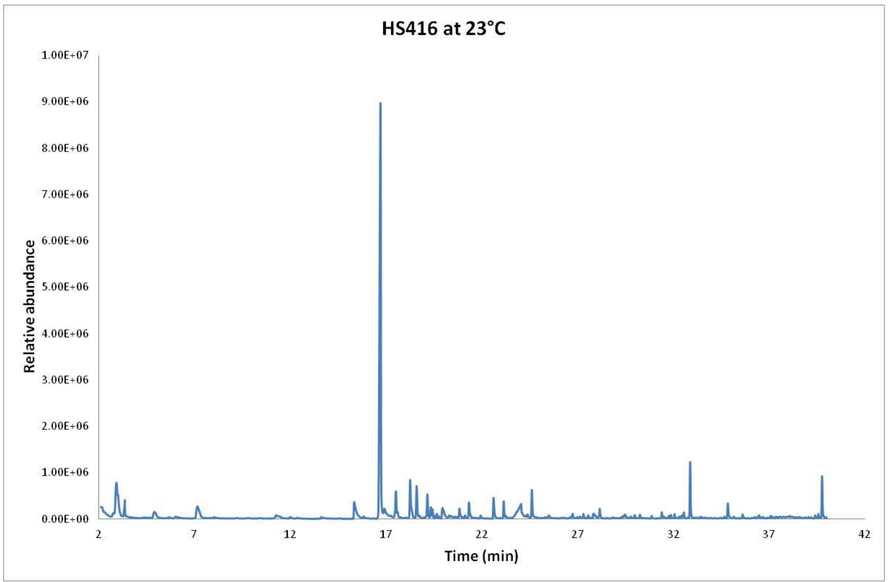


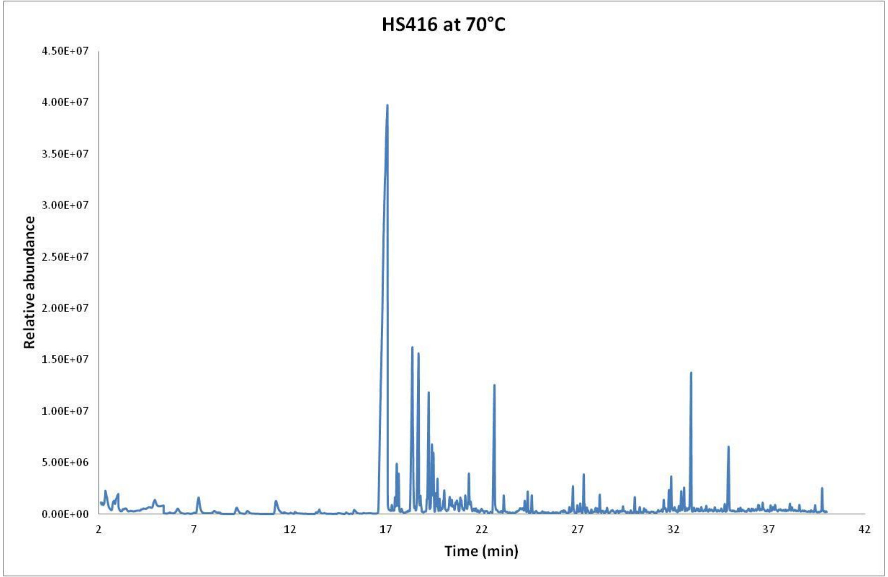
HS400 after accelerated degradation

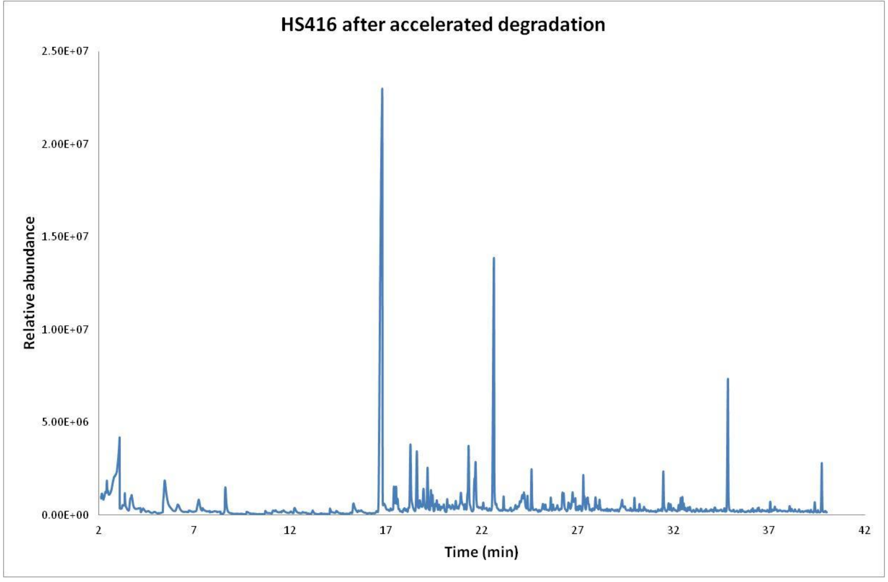

HS403 at 23°C

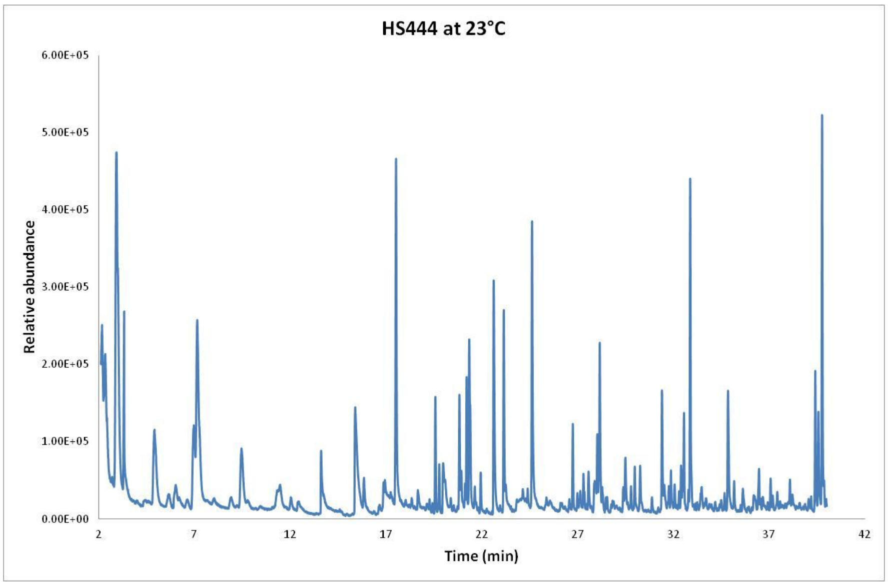

HS403 at 70°C

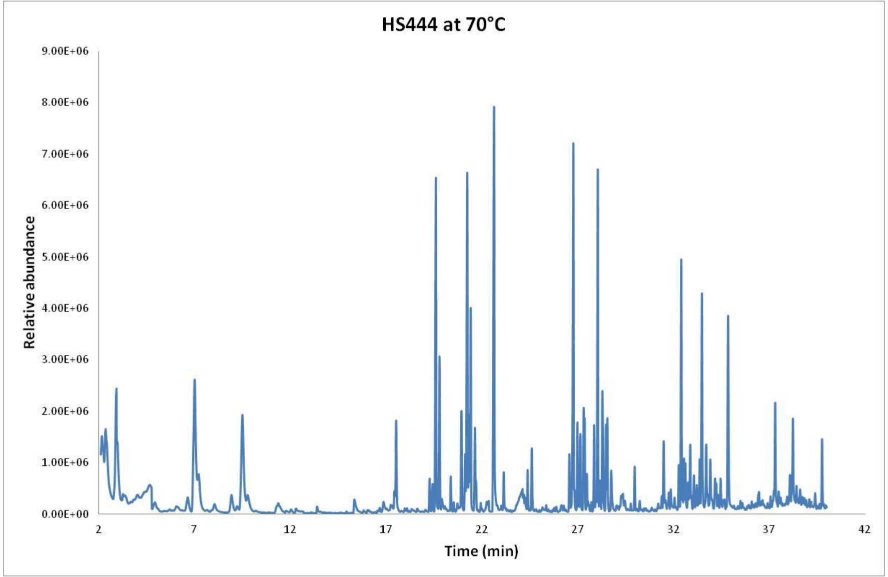

HS403 after accelerated degradation

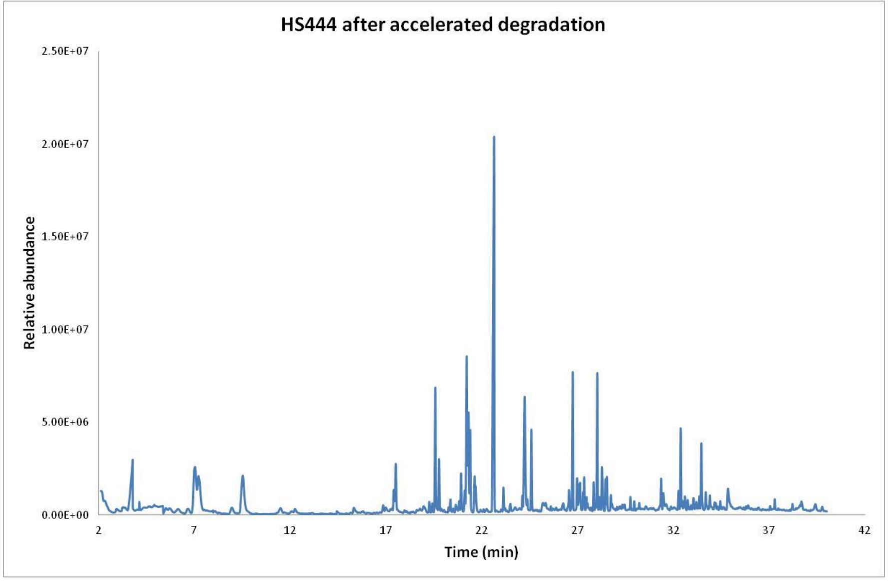

HS416 at 23°C
Relative abundance
1.00E+07
9.00E+06
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS416 at 70°C
Relative abundance
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

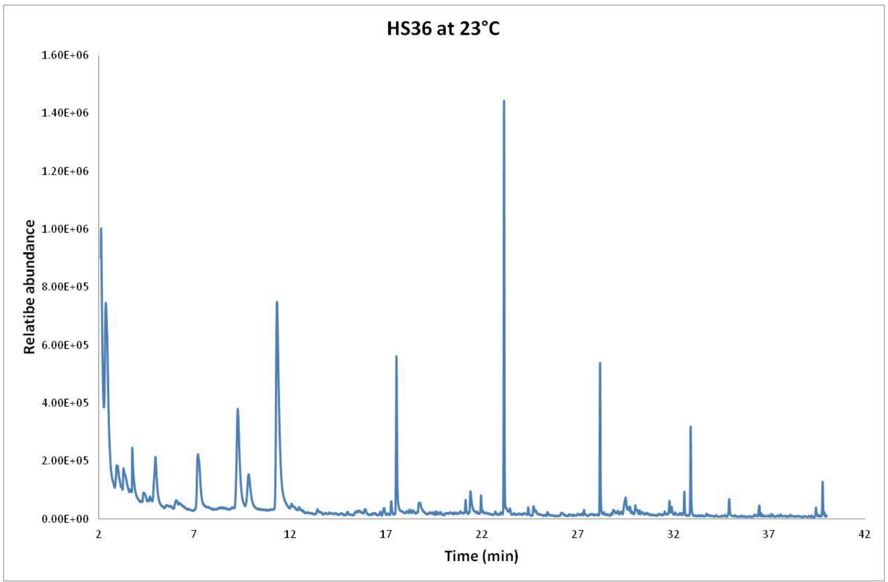

HS416 after accelerated degradation
Relative abundance
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

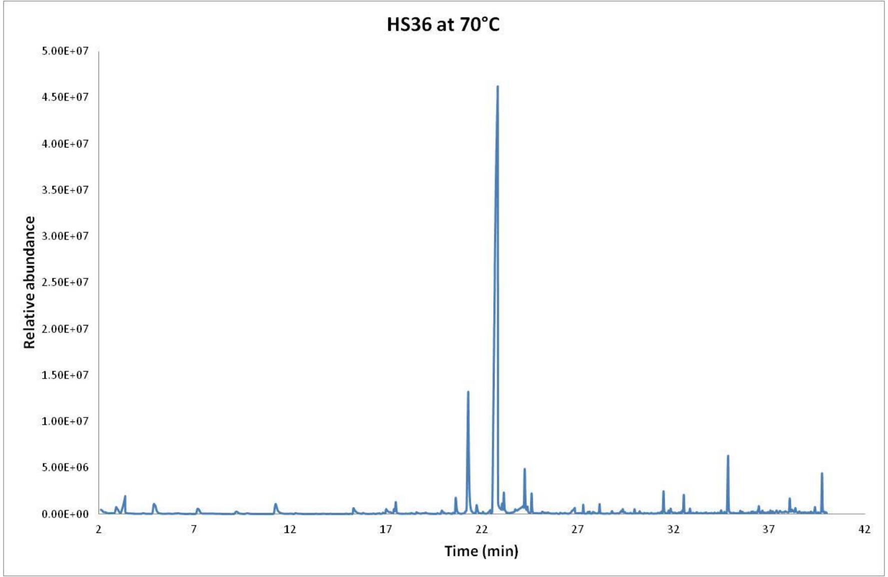

HS444 at 23°C
Relative abundance
6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

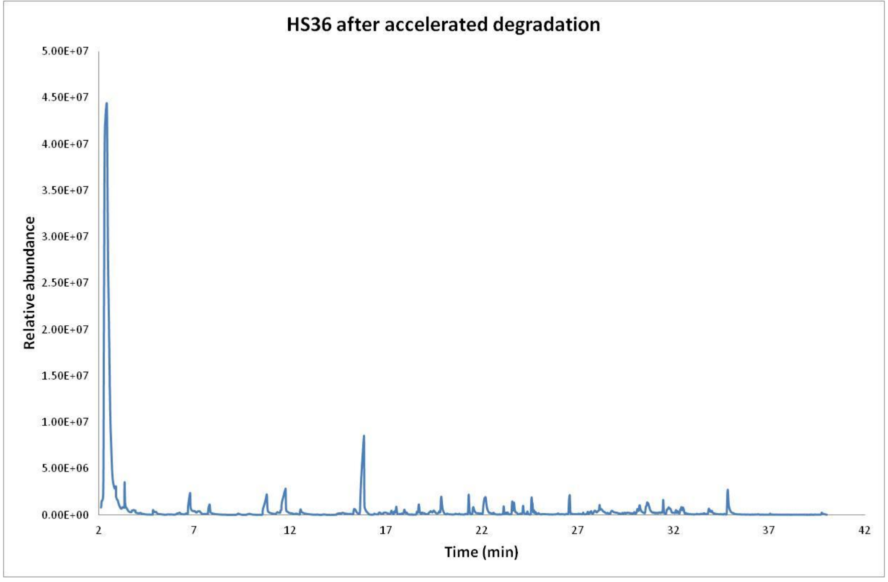

HS444 at 70°C
Relative abundance
9.00E+06
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

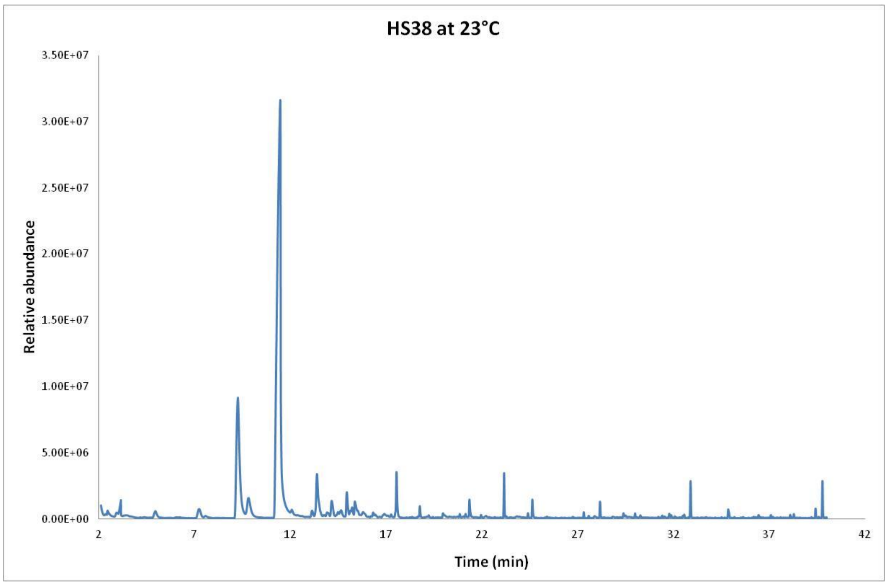

HS444 after accelerated degradation
Relative abundance
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

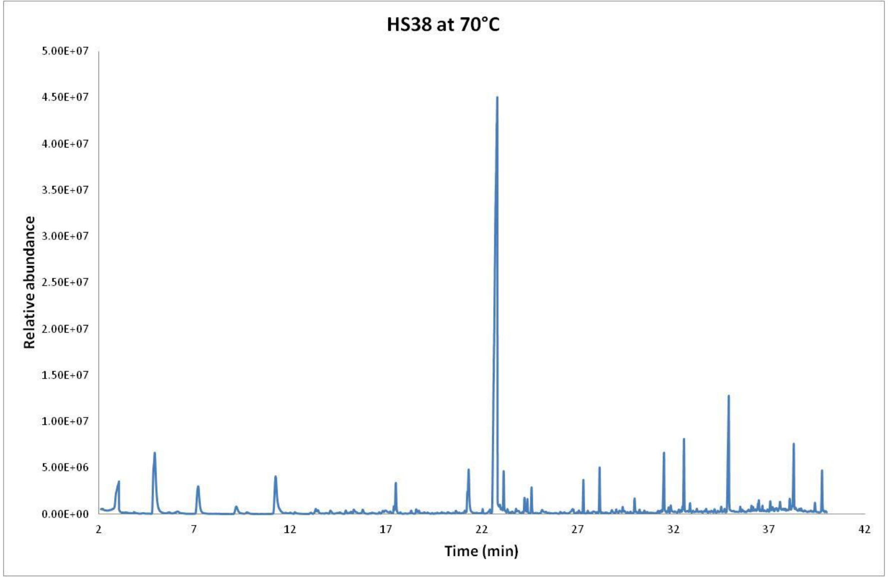
POLYSTYRENE

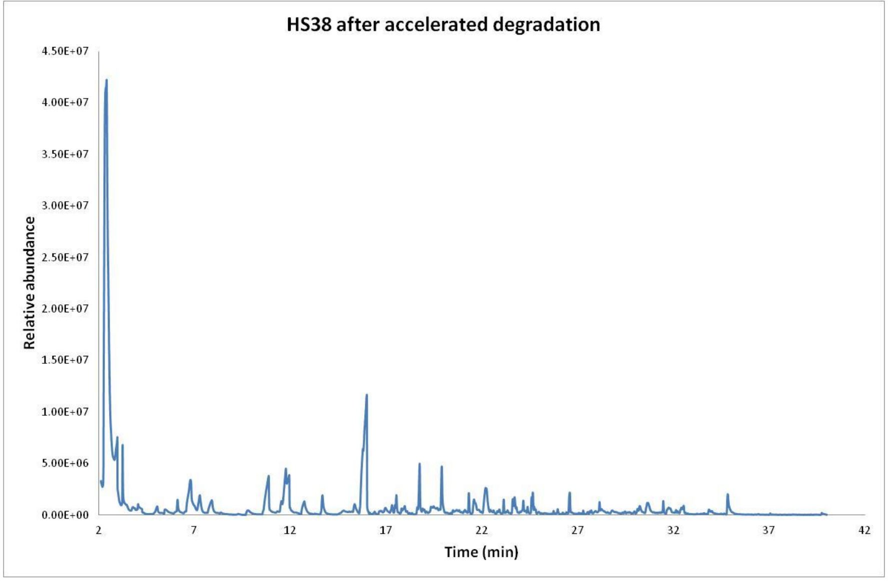

HS36 at 23°C
Relatibe abundance
1.60E+06
1.40E+06
1.20E+06
1.00E+06
8.00E+05
6.00E+05
4.00E+05
2.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

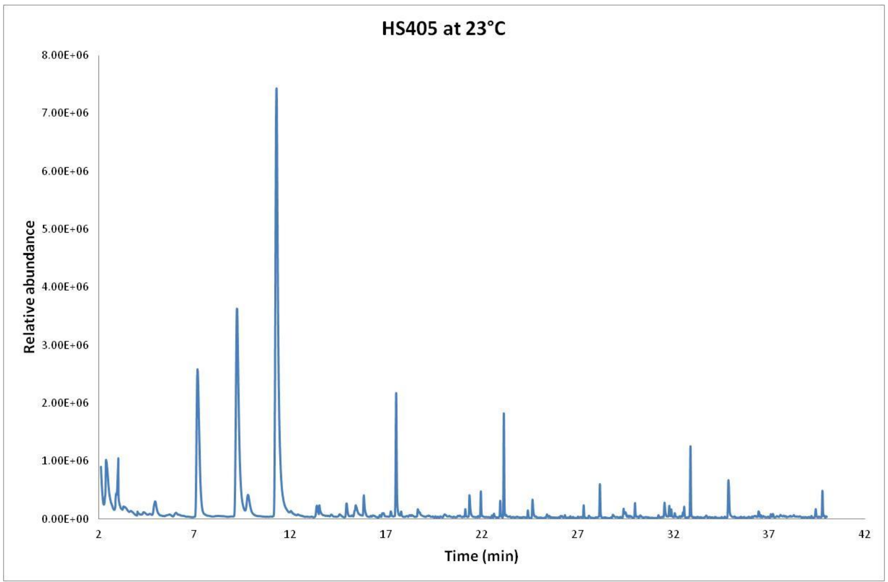

HS36 at 70°C
Relative abundance
5.00E+07
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

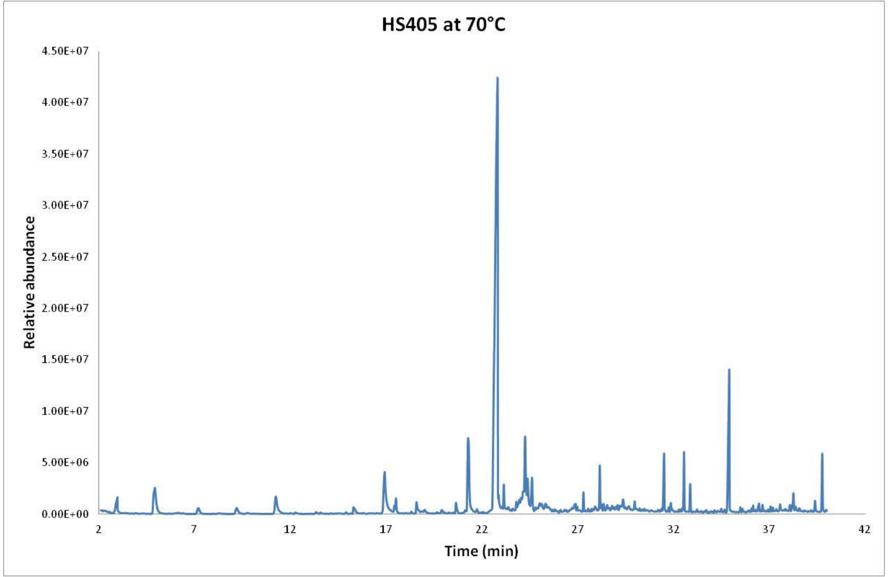

HS36 after accelerated degradation
Relative abundance
5.00E+07
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

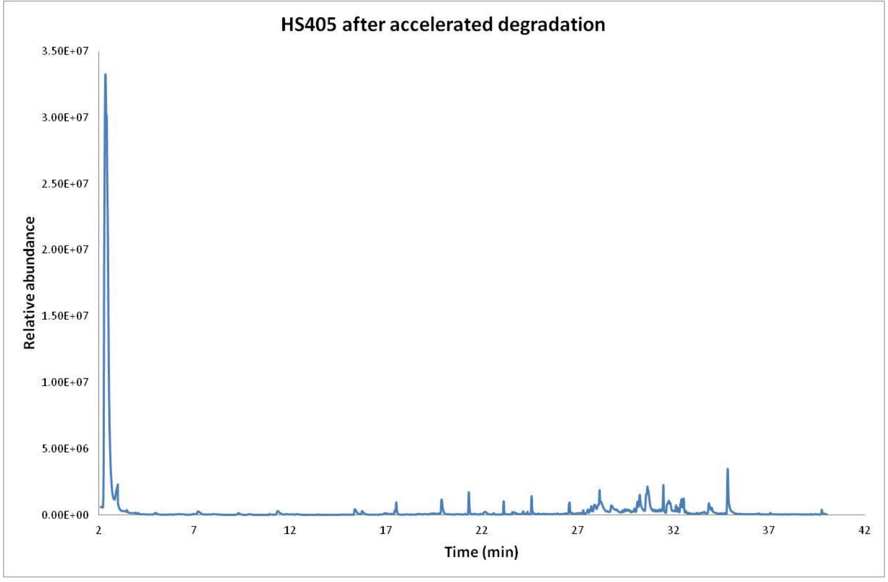

HS38 at 23°C
Relative abundance
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

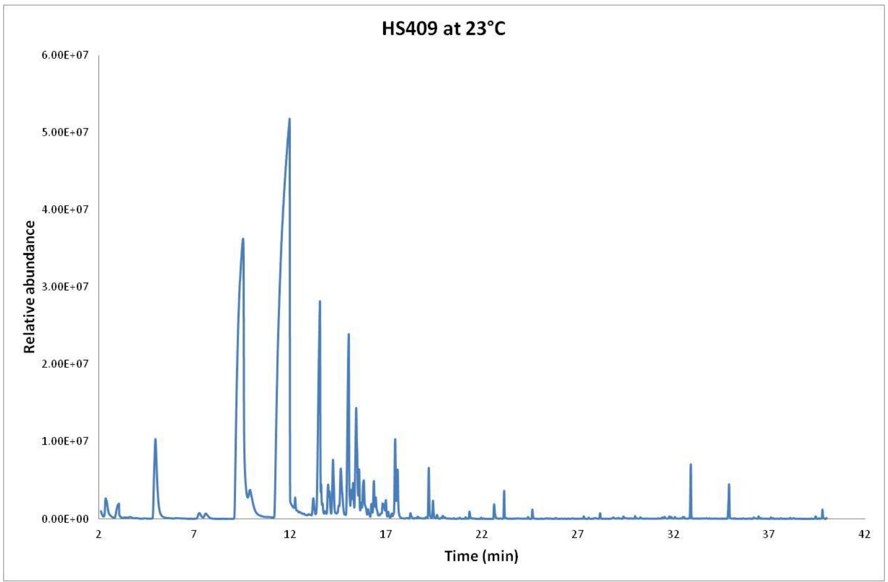

HS38 at 70°C
Relative abundance
5.00E+07
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

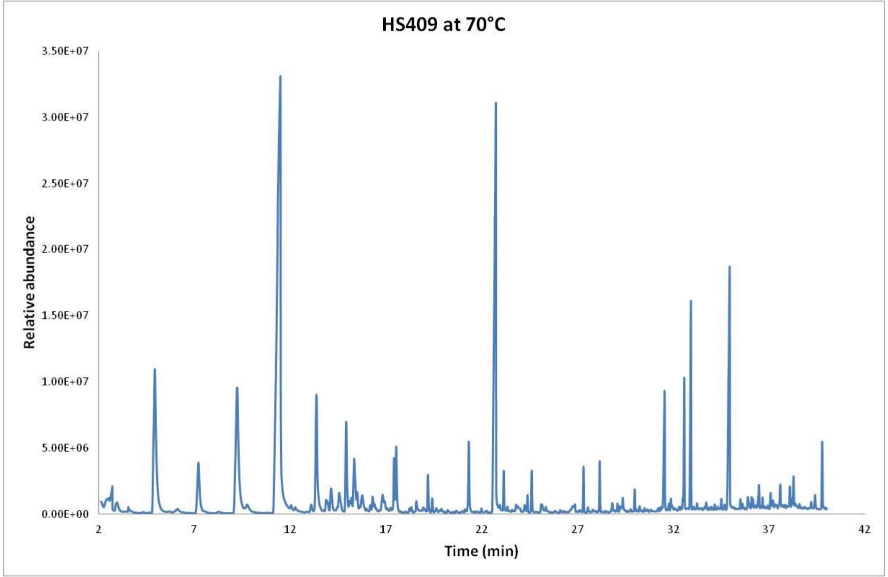

HS38 after accelerated degradation
Relative abundance
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

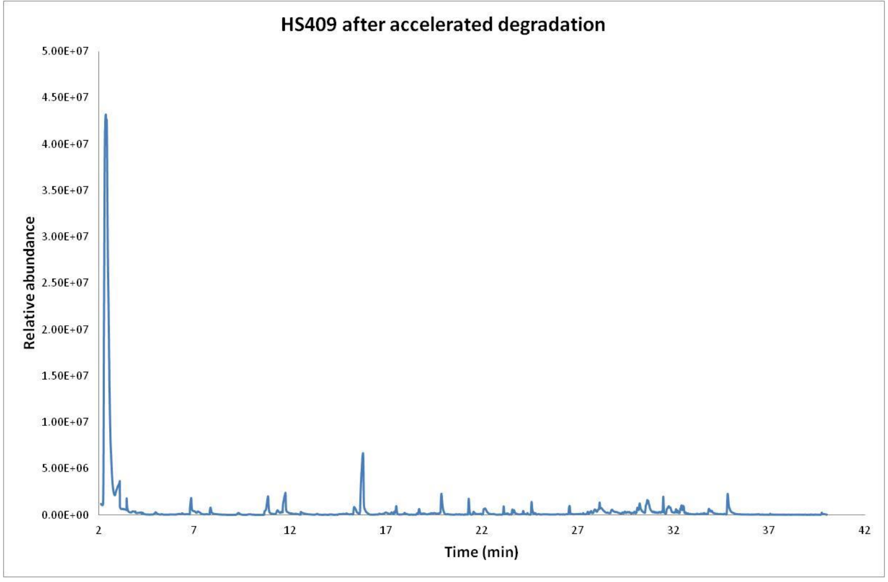

HS405 at 23°C
Relative abundance
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

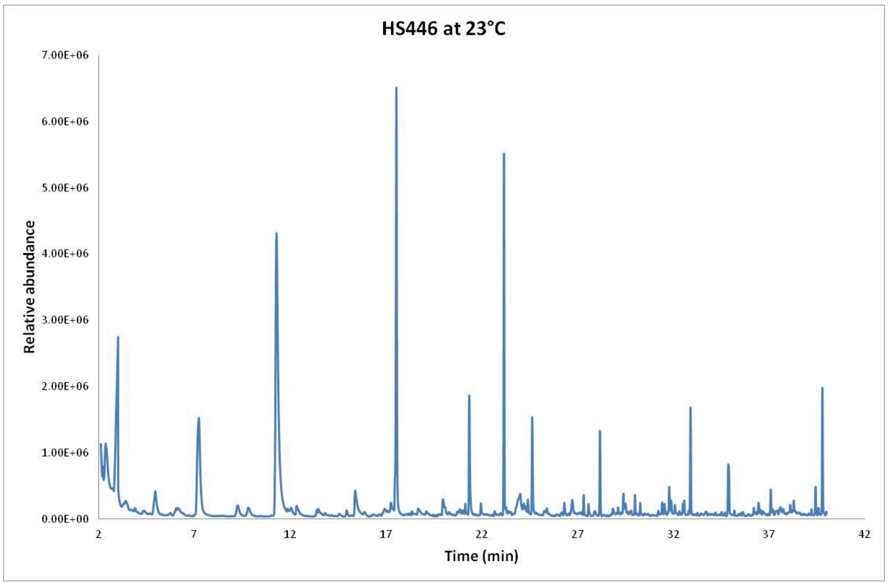

HS405 at 70°C
Relative abundance
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS405 after accelerated degradation
Relative abundance
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

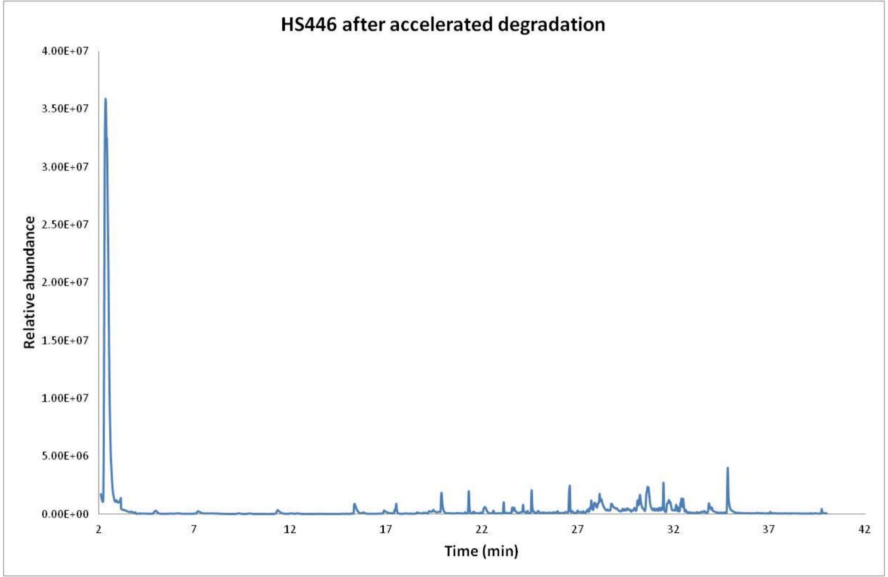

HS409 at 23°C


HS409 at 70°C

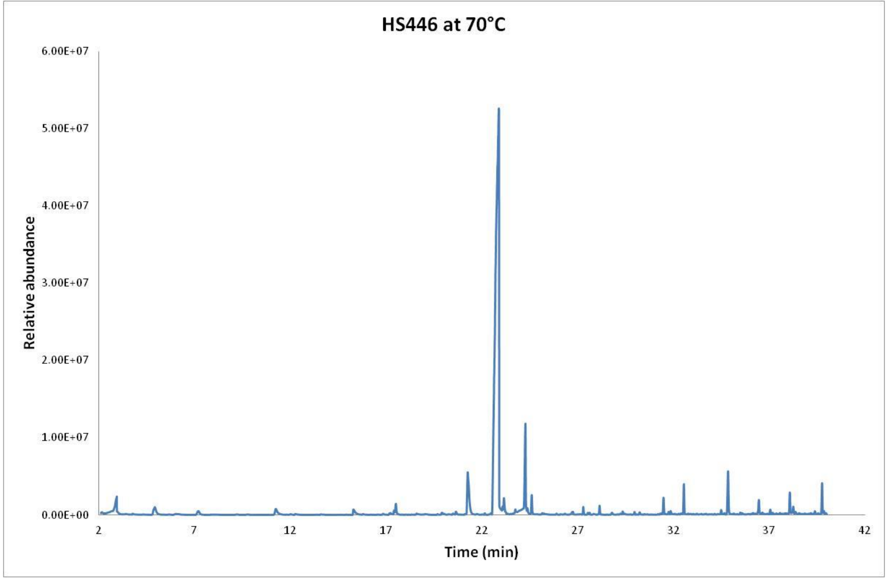

HS409 after accelerated degradation



HS446 at 23°C

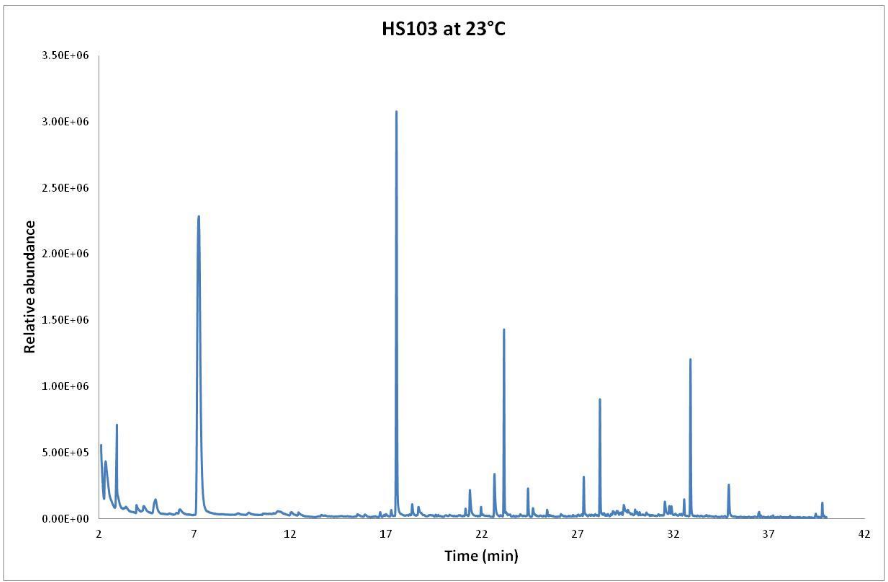


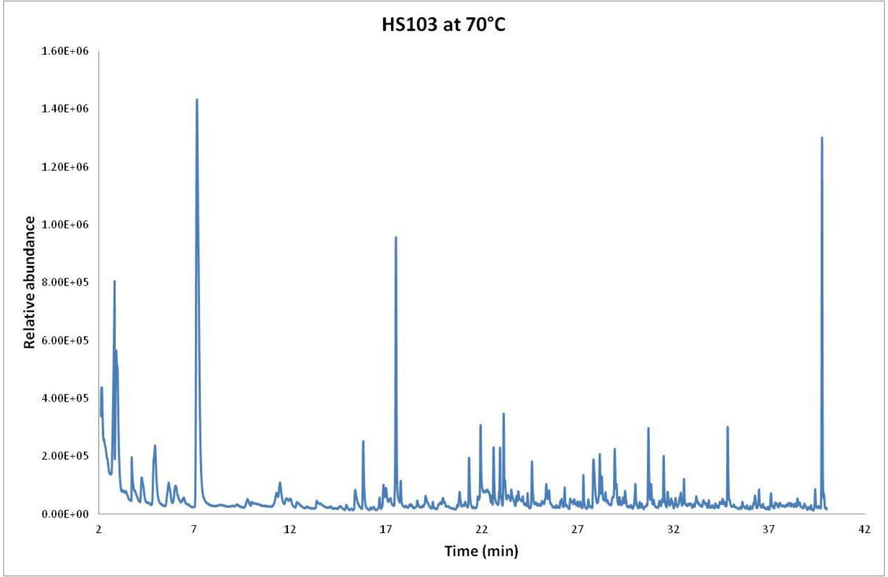
HS446 after accelerated degradation

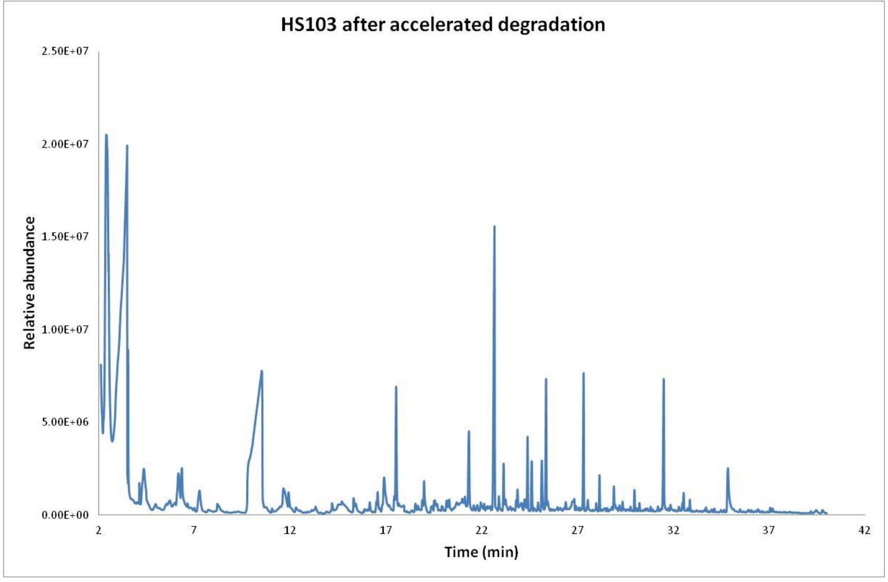


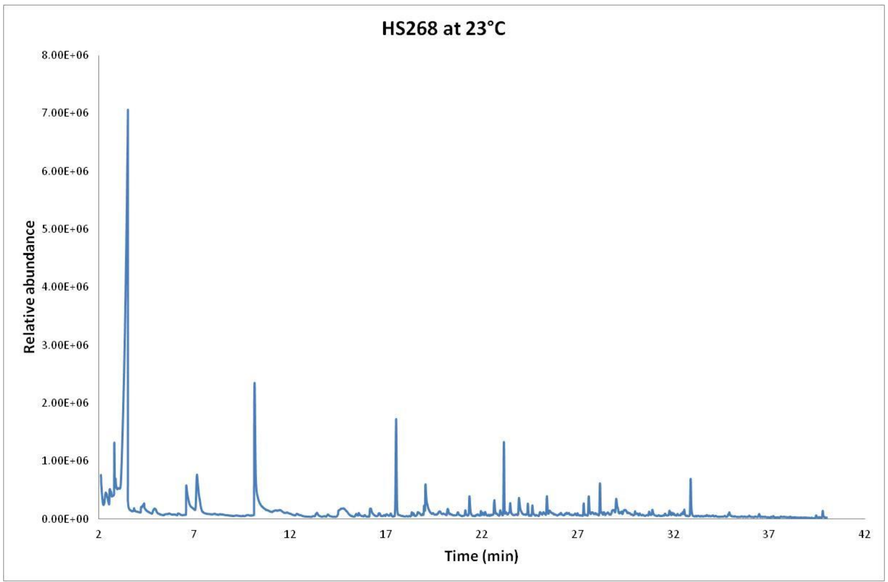
HS446 at 70°C

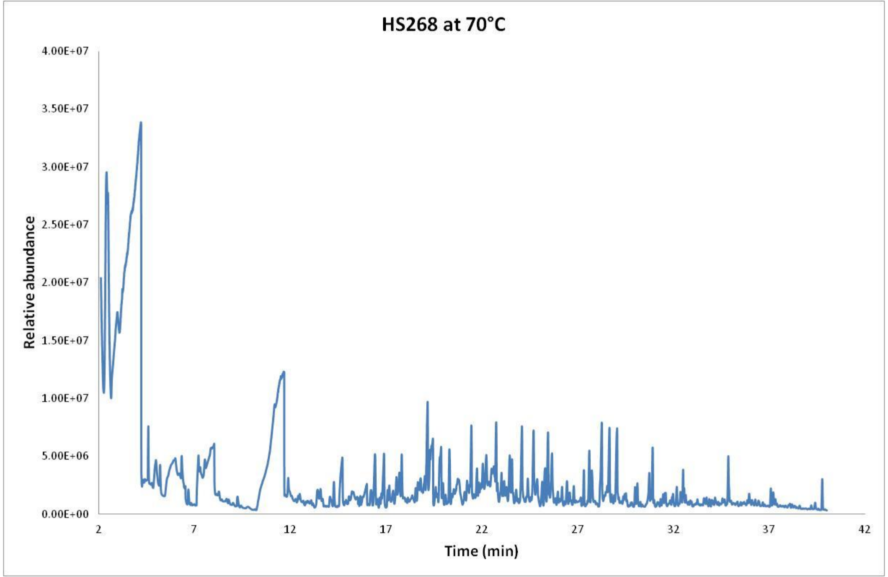
RUBBER

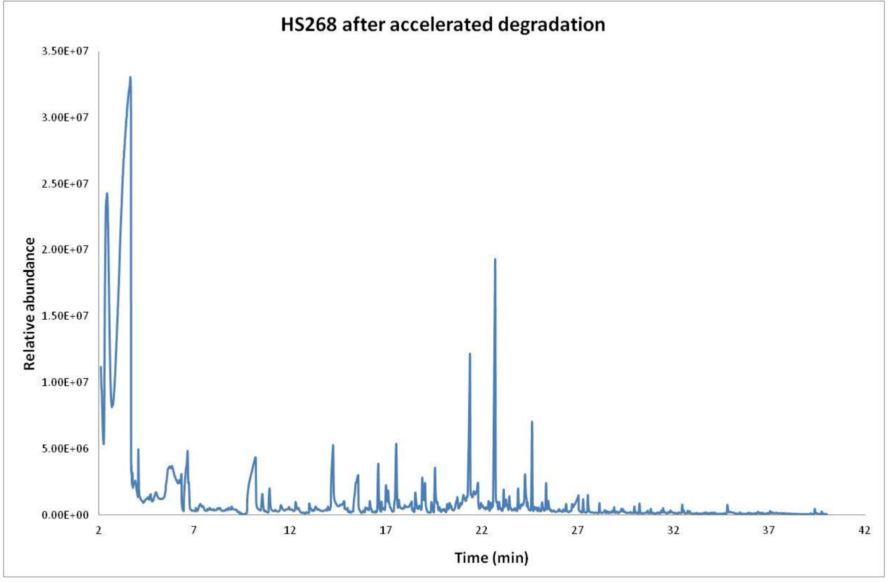

HS103 at 23°C

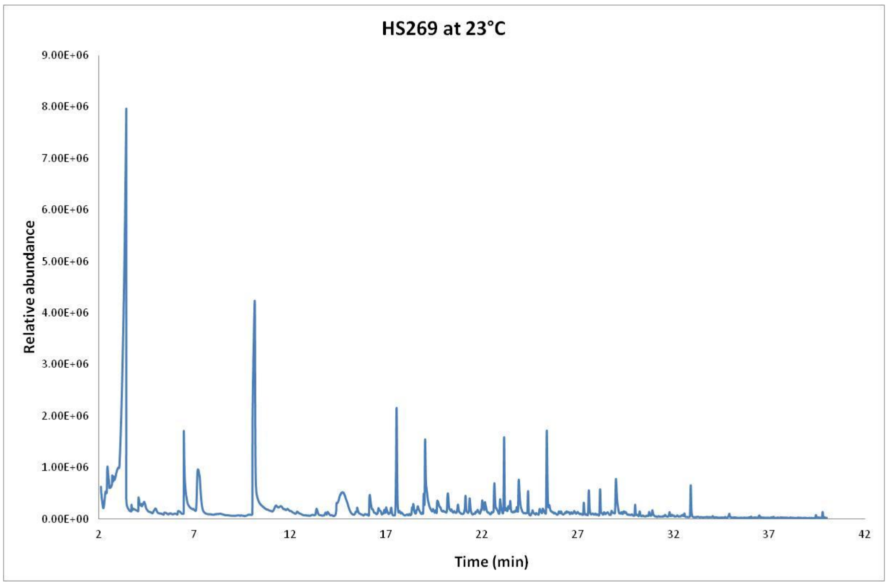

HS103 at 70°C


HS103 after accelerated degradation

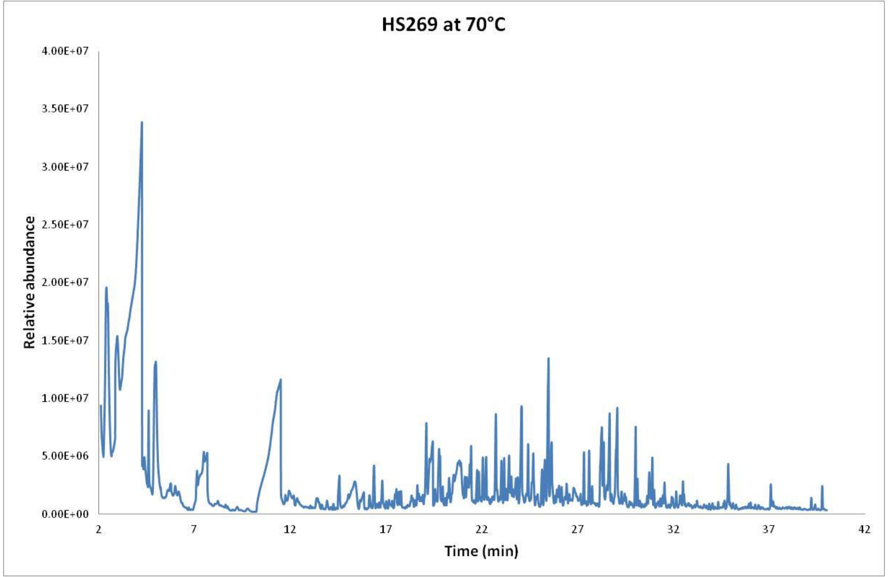

HS268 at 23°C
Relative abundance
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS268 at 70°C
Relative abundance
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

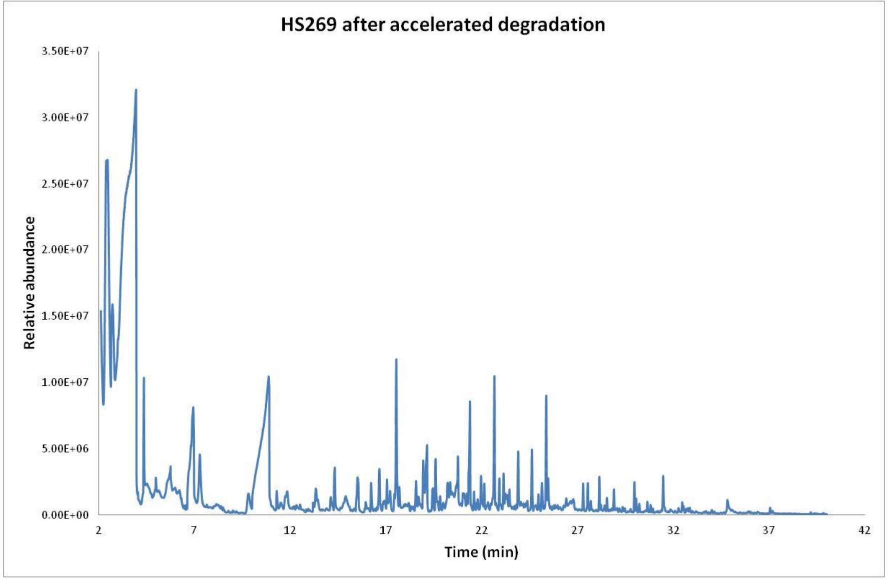

HS268 after accelerated degradation
Relative abundance
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)



HS269 at 23°C

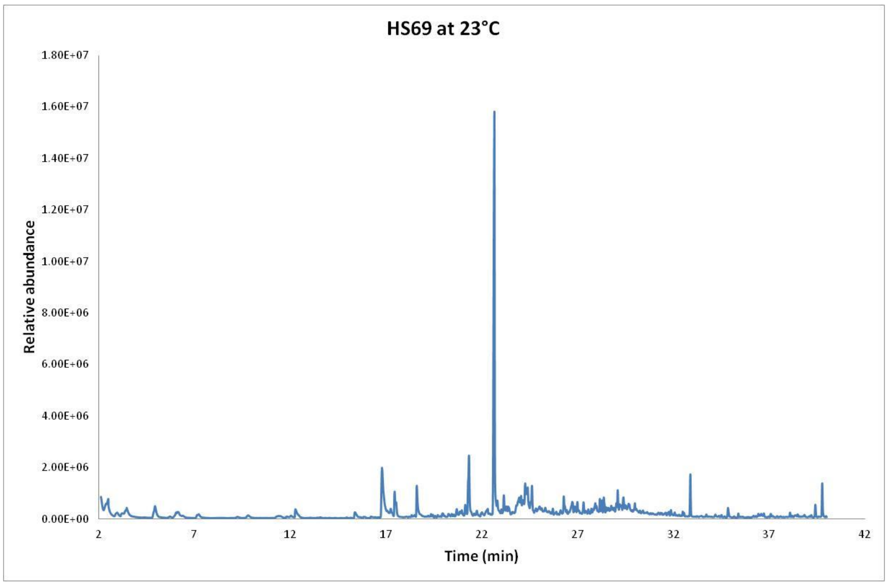


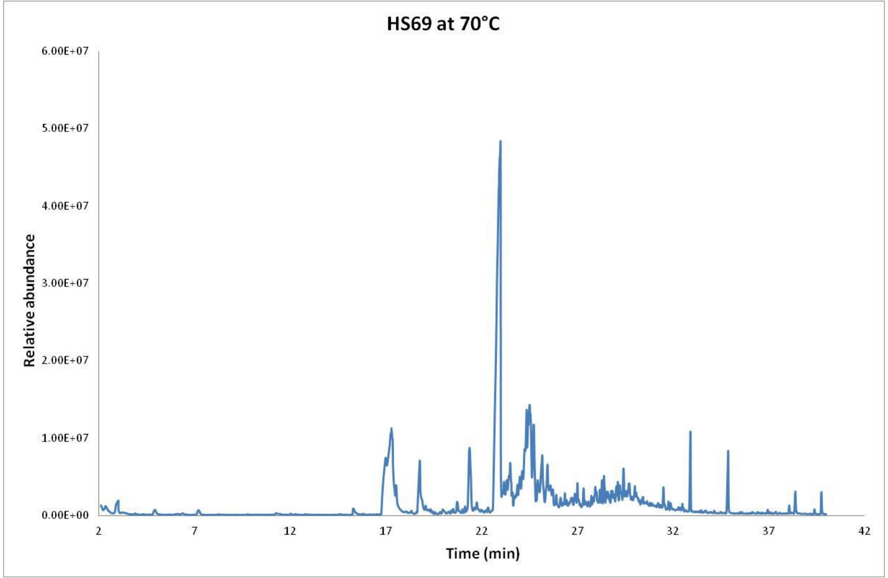
HS269 at 70°C

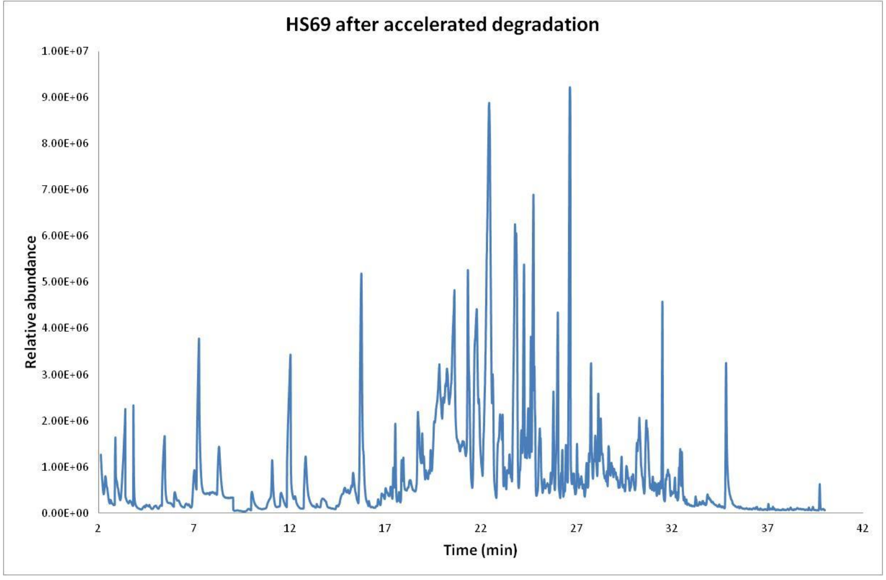


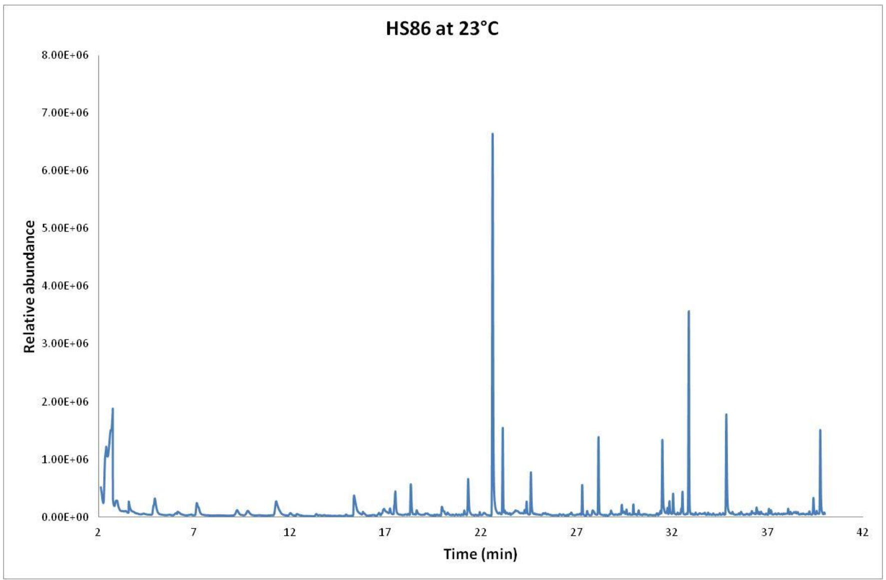
HS269 after accelerated degradation

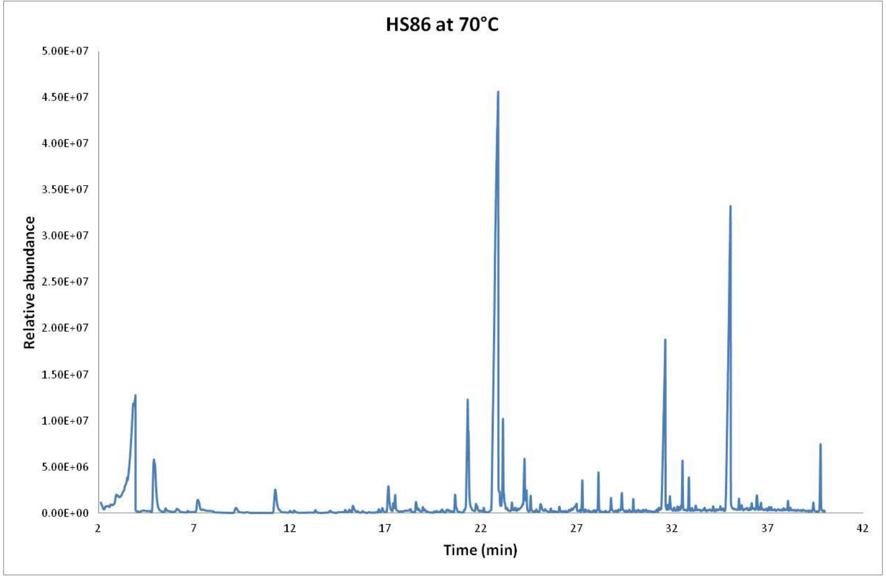
POLYURETHANE

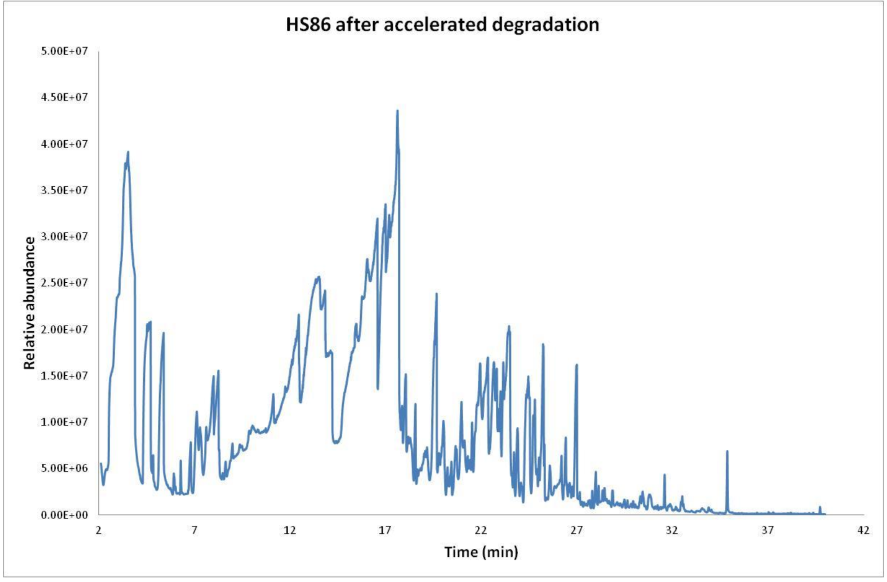

HS69 at 23°C
Relative abundance
1.80E+07
1.60E+07
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

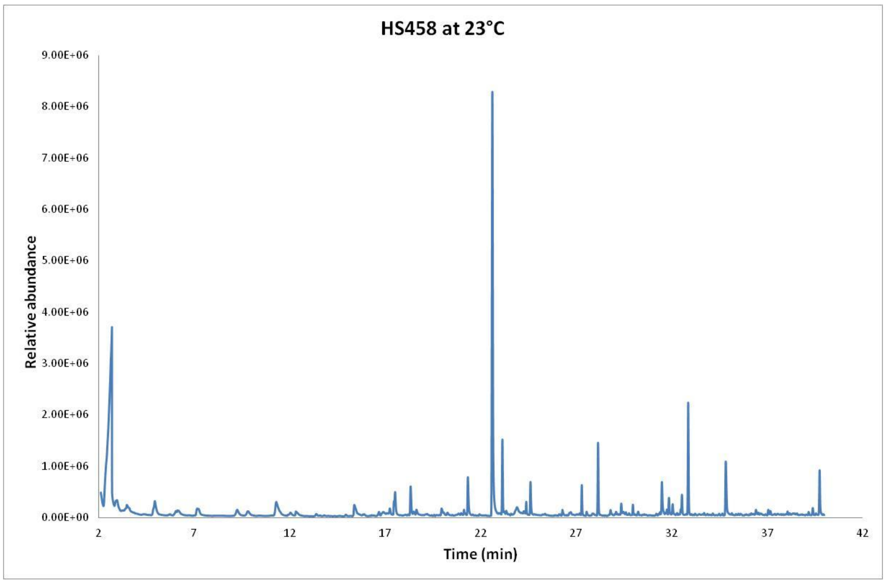

HS69 at 70°C
Relative abundance
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

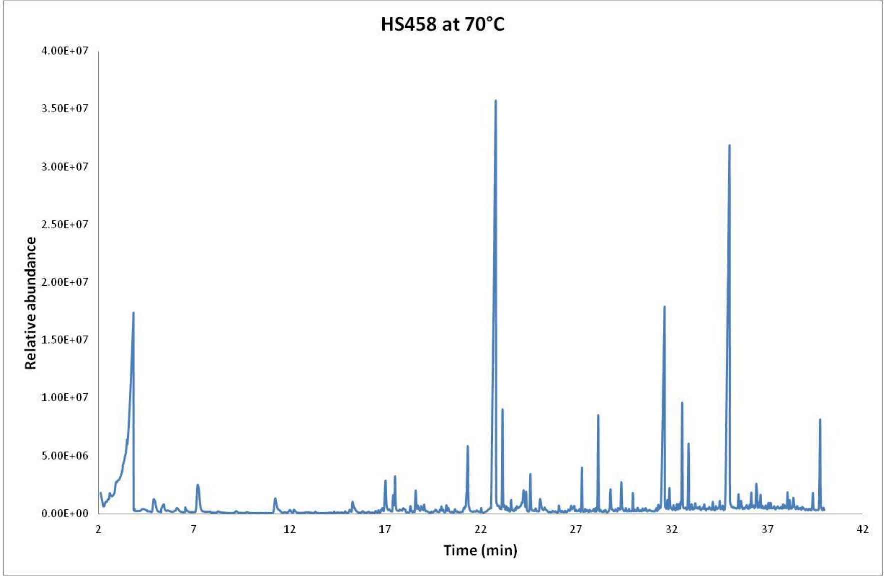

HS69 after accelerated degradation
Relative abundance
1.00E+07
9.00E+06
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

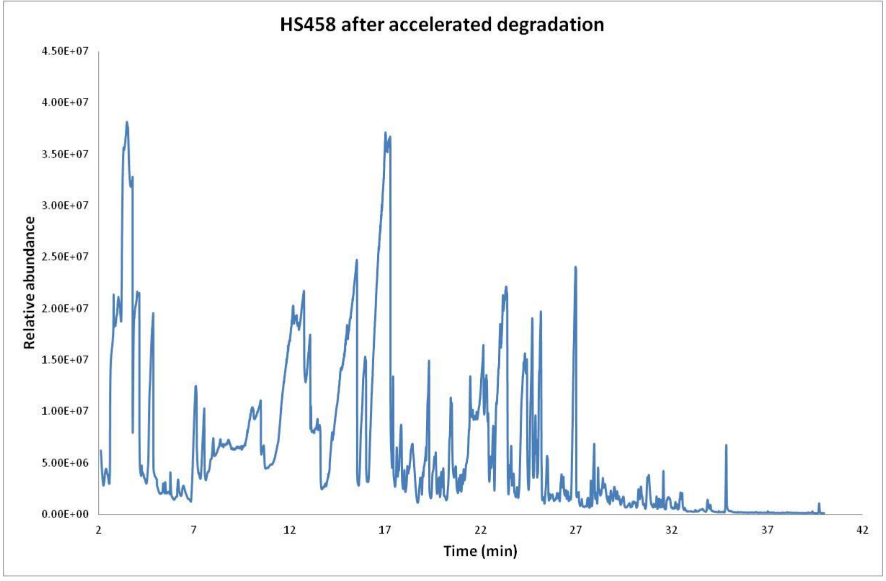

HS86 at 23°C
Relative abundance
8.00E+06
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

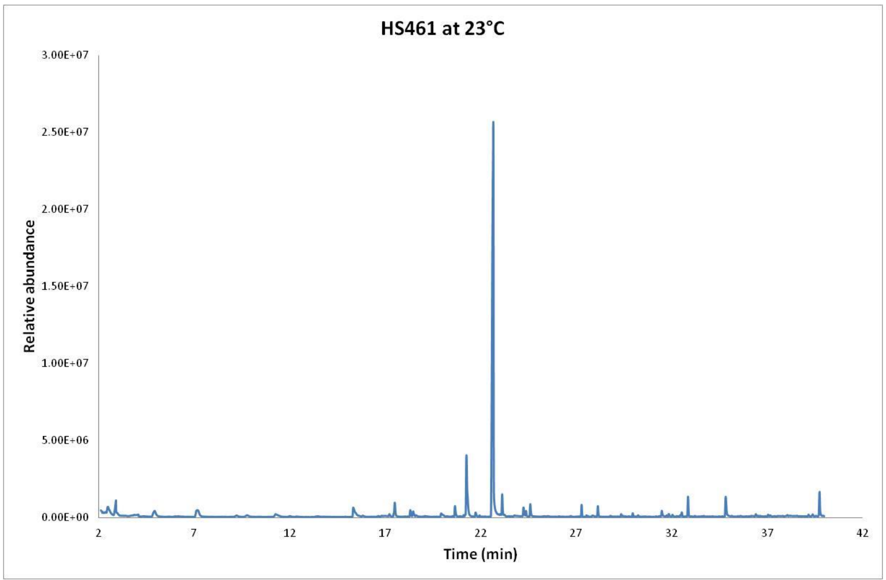

HS86 at 70°C
Relative abundance
5.00E+07
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

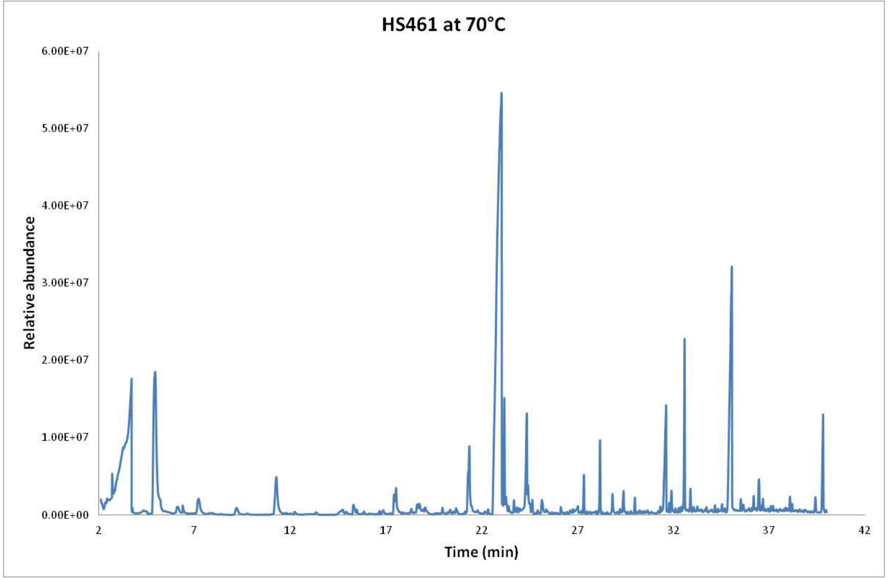

HS86 after accelerated degradation
Relative abundance
5.00E+07
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

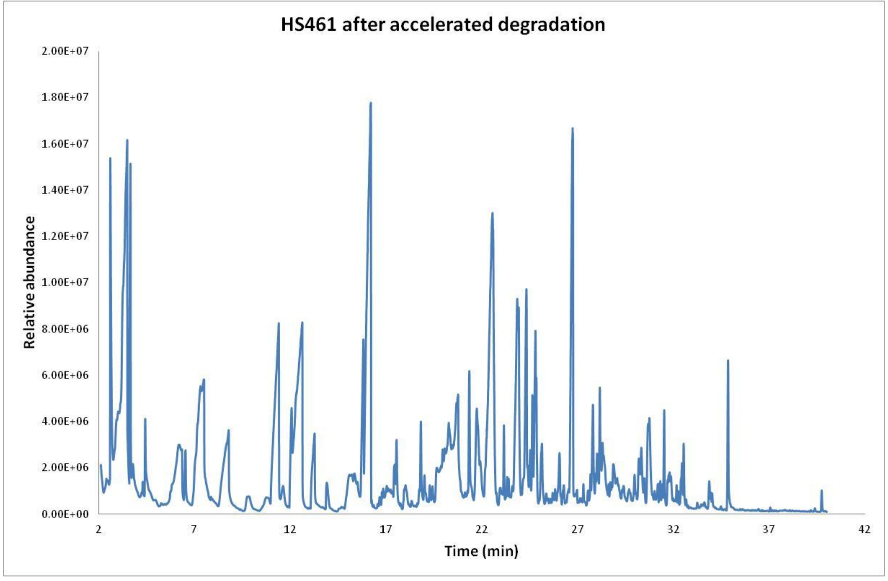

HS458 at 23°C

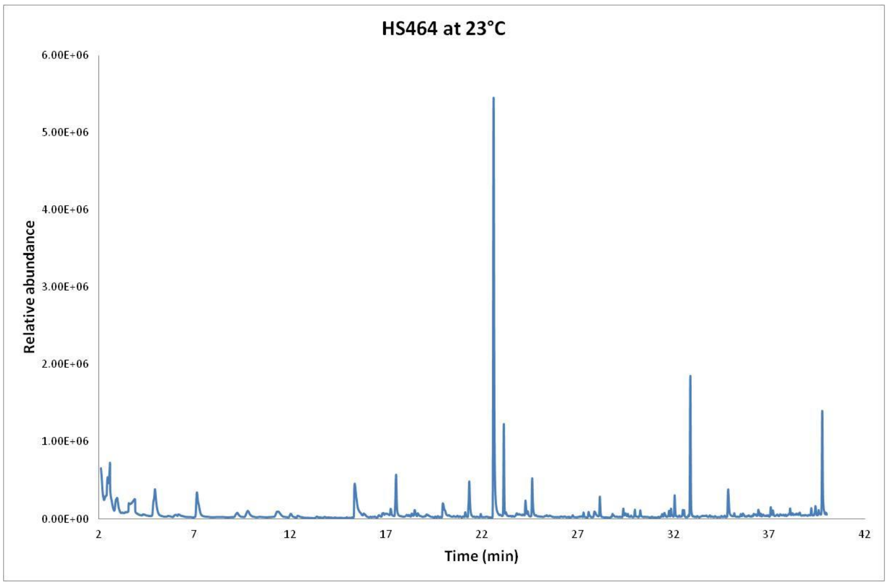

HS458 at 70°C

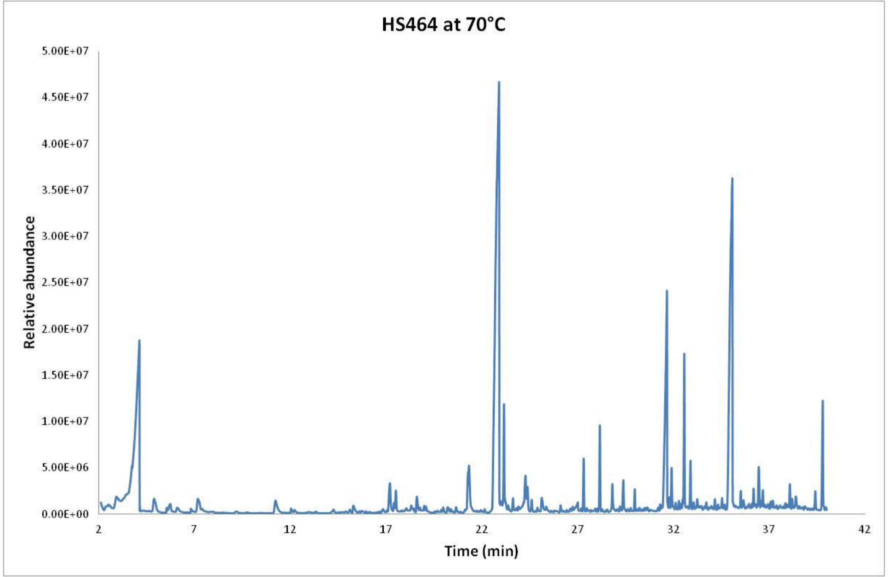

HS458 after accelerated degradation

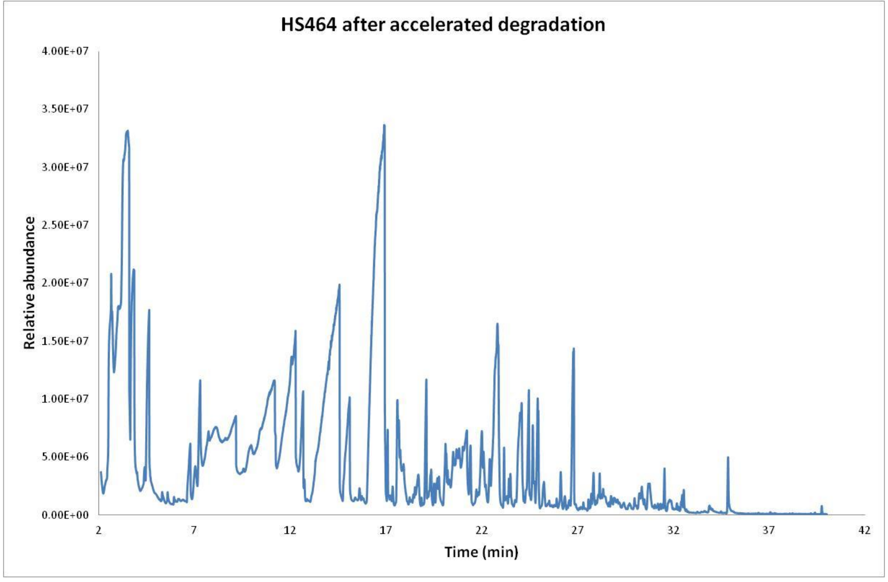

HS461 at 23°C
Relative abundance
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS461 at 70°C
Relative abundance
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

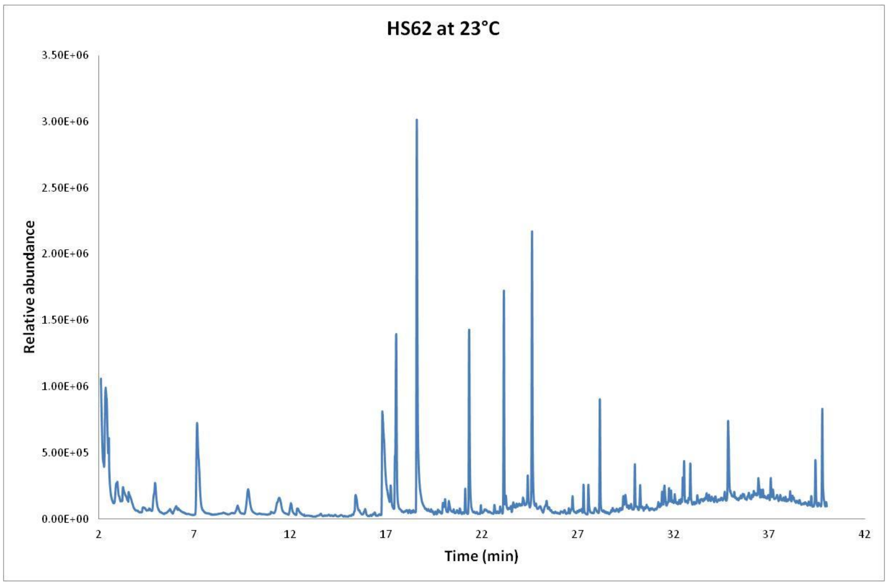

HS461 after accelerated degradation
Relative abundance
2.00E+07
1.80E+07
1.60E+07
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

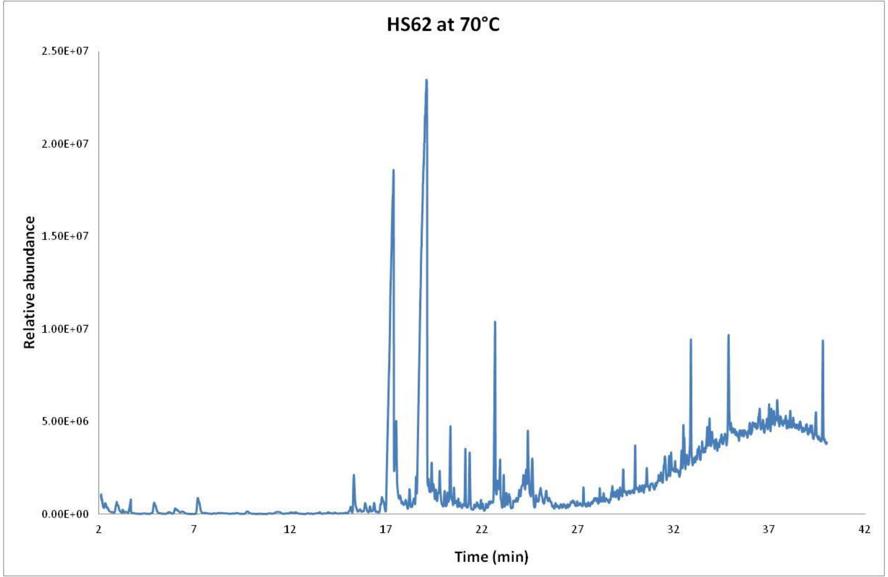

HS464 at 23°C
Relative abundance
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

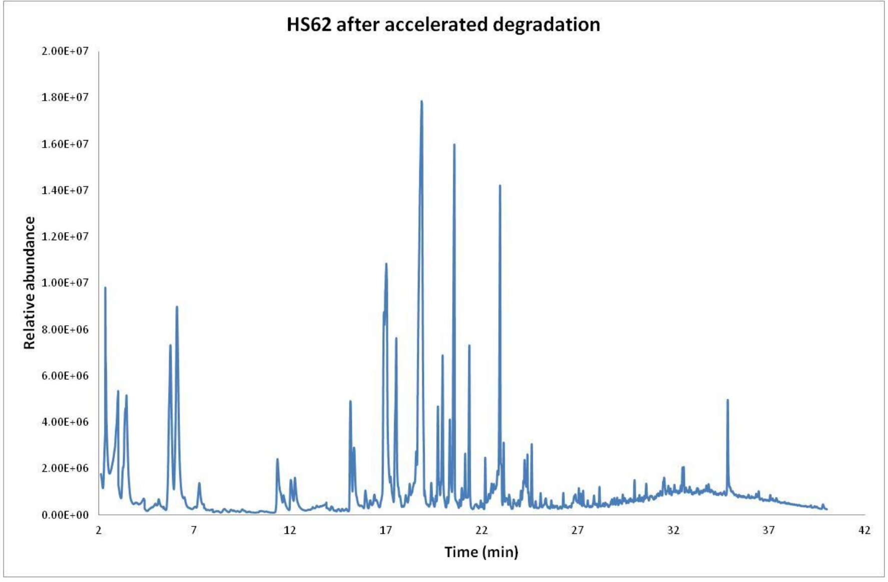

HS464 at 70°C
Relative abundance
5.00E+07
4.50E+07
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS464 after accelerated degradation
Relative abundance
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)

PVC


HS62 at 23°C
Relative abundance
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS62 at 70°C
Relative abundance
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
2
7
12
17
22
27
32
37
42
Time (min)


HS62 after accelerated degradation
Relative abundance
2.00E+07
1.80E+07
1.60E+07
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
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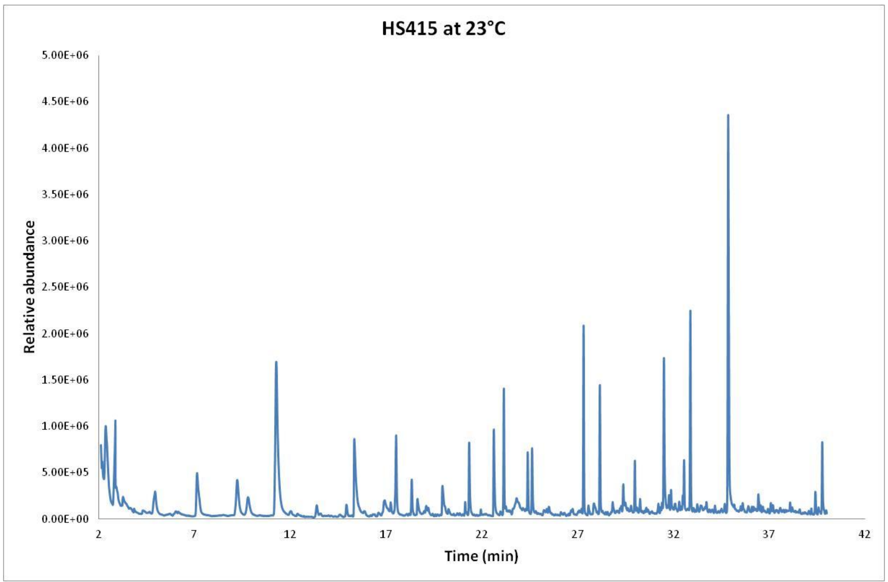
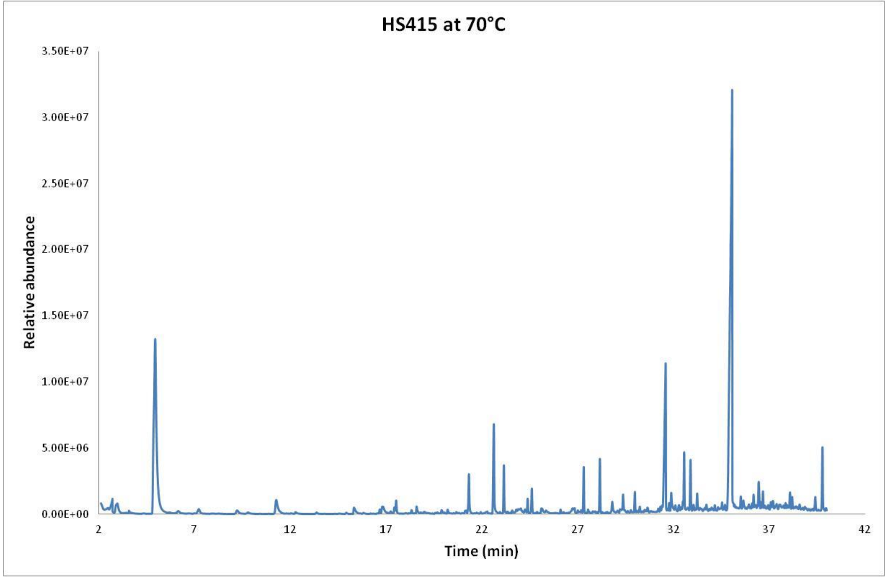
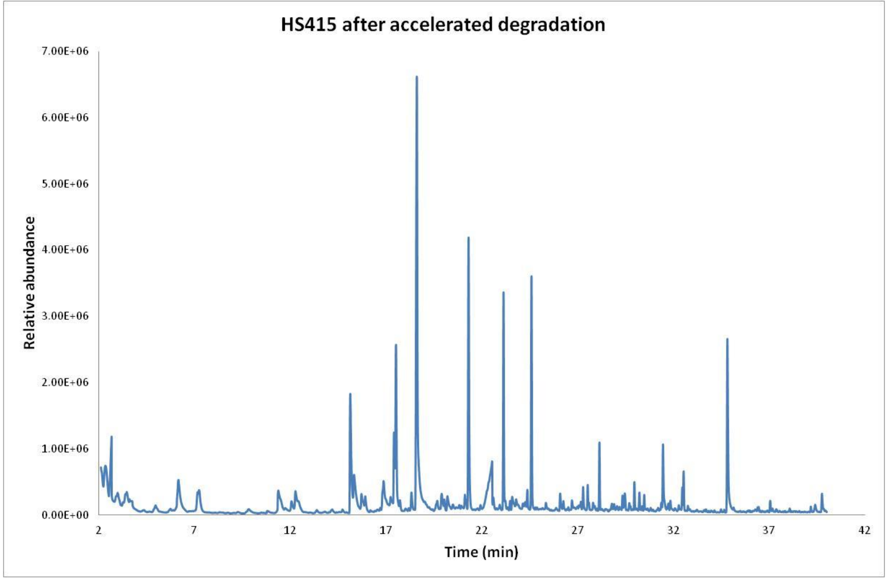
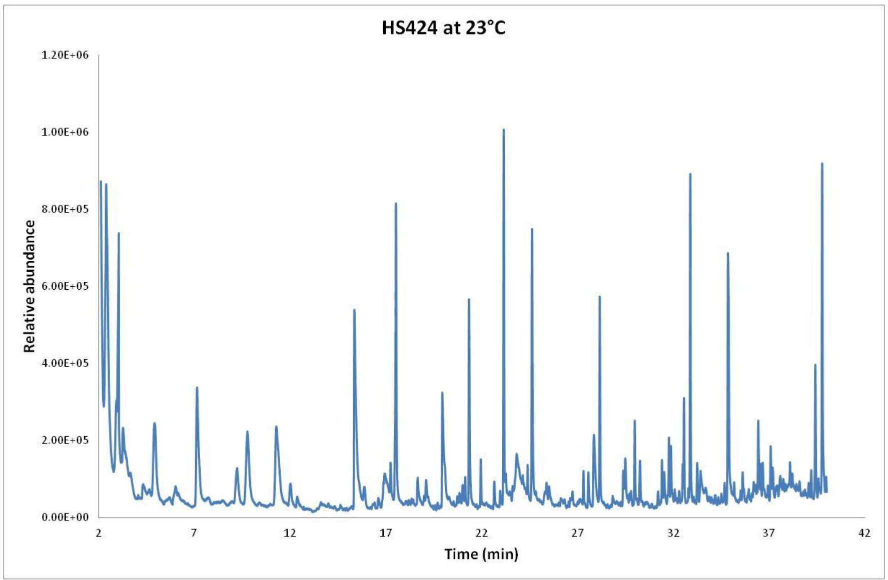
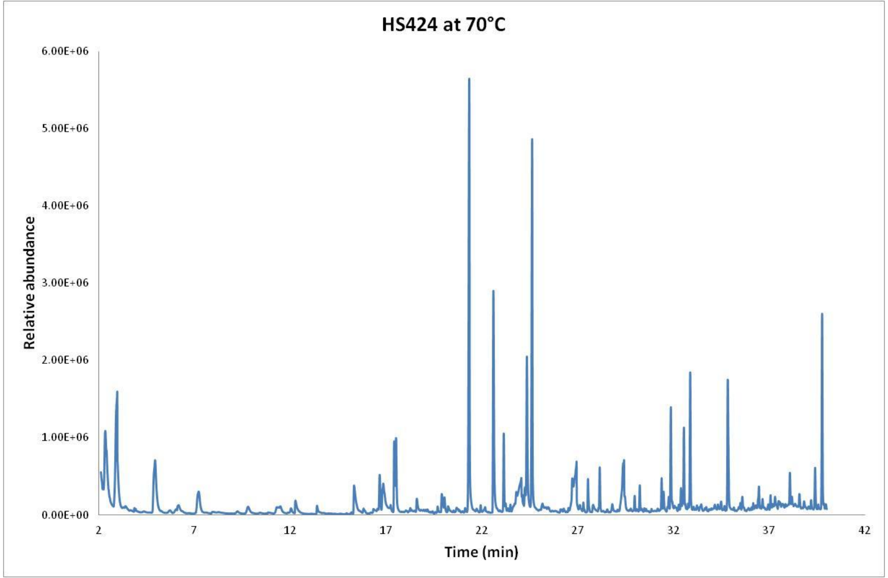
2
7
12
17
22
27
32
37
42
Time (min)

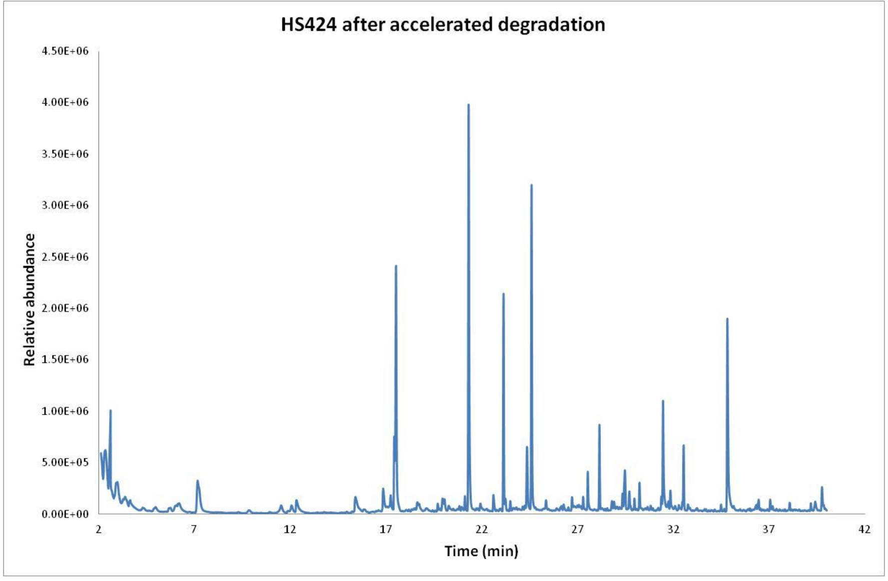

HS415 at 23°C

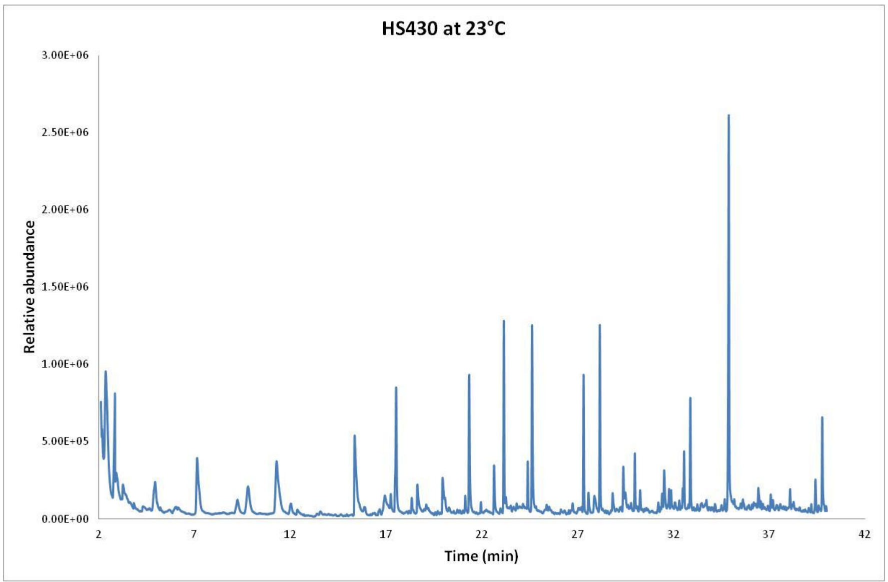

HS415 at 70°C

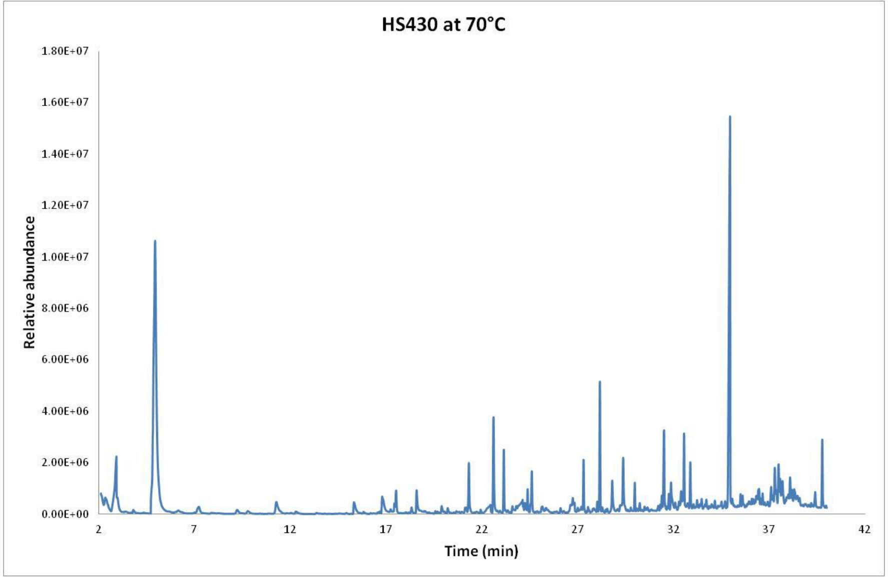

HS415 after accelerated degradation

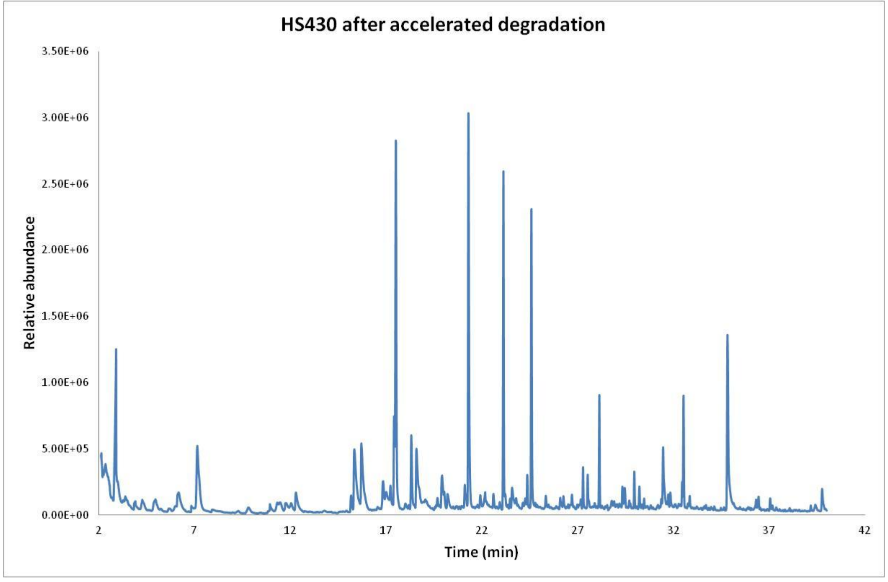

HS424 at 23°C

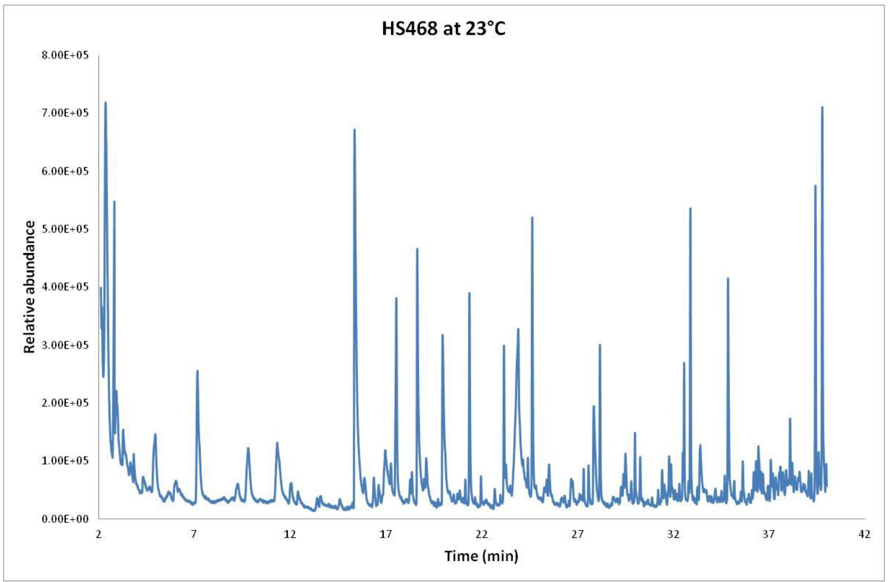

HS424 at 70°C

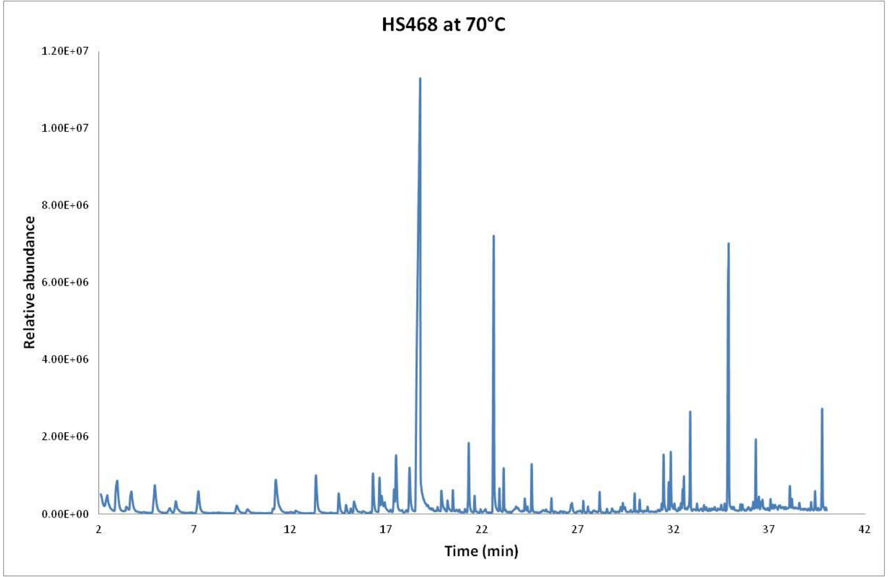

HS424 after accelerated degradation

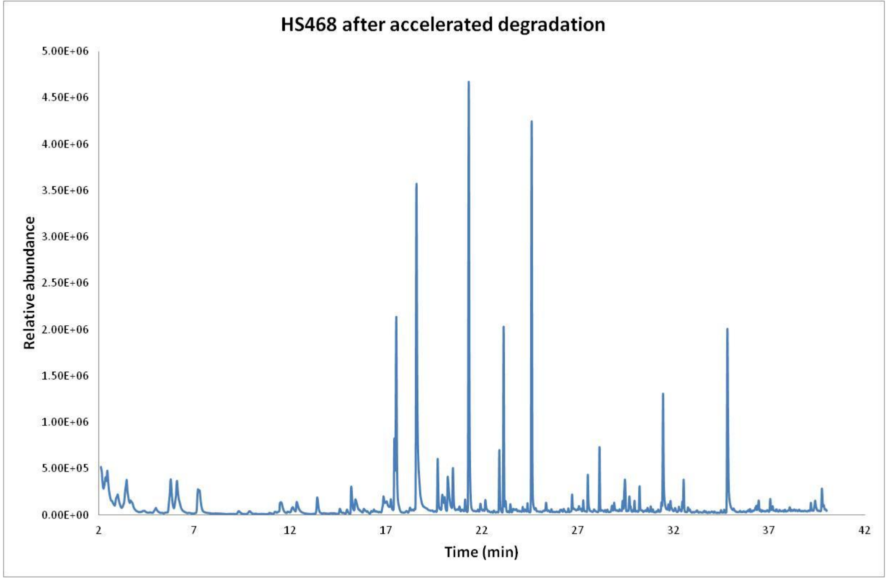

HS430 at 23°C


HS430 at 70°C


HS430 after accelerated degradation


HS468 at 23°C

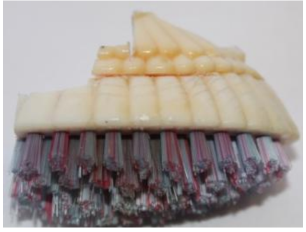

HS468 at 70°C


HS468 after accelerated degradation

APPENDIX C

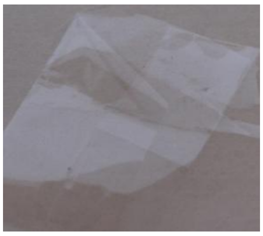
PHOTOGRAPHS OF REFERENCE SAMPLES

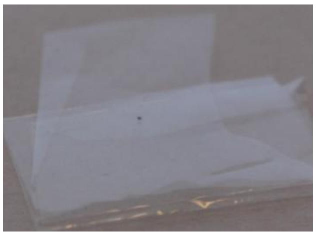
Cellulose acetate


HS91

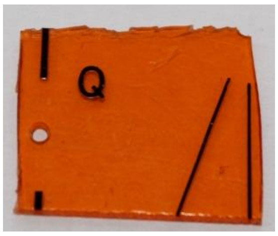

HS474


HS475


HS476


HS477

Cellulose nitrate



HS248


HS270


HS271

Polycarbonate


HS52


HS143

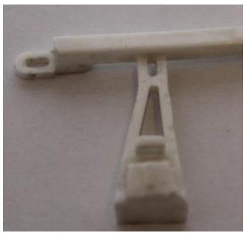

HS413


HS466


HS467

Polyethylene


HS80


HS404


HS417


HS459


HS463

Polypropylene


HS77


HS400


HS403


HS416


HS444

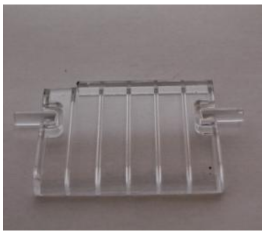
Polystyrene


HS36

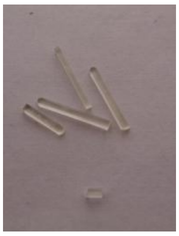

HS37


HS405


HS409


HS446

Polyurethane


HS69


HS86


HS458


HS461


HS464

PVC

HS62

HS415

HS424

HS430

HS468

Rubber

HS103

HS268

HS269

PUBLICATIONS

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HERITAGE SCIENCE

RESEARCH ARTICLE Open Access

Assessment of historical polymers using attenuated total reflectance-Fourier transform infra-red spectroscopy with principal component analysis

Gemma Mitchell[1], Fenella France[2], Alison Nordon[1], Pik Leung Tang[3] and Lorraine T Gibson[1*]

Abstract

Introduction: Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy with a diamond ATR crystal was used to examine 41 historical polymer fragments and a selection of polyurethane fragments subjected to accelerated ageing. The advantages and limitations of FTIR data for polymer assessment is discussed. Moreover the efficacy of the data interpretation tool principal component analysis (PCA) is debated for potential applications in polymer characterisation and polymer degradation.

Results: Analysis of polymer fragments by ATR-FTIR spectra was shown, as expected, to be an ideal method for polymer classification. Curved surfaces could be tolerated when spectral data were carefully collected, similarly opaque samples could be analysed due to the reflective nature of the FTIR technique used. More importantly perhaps, these results reaffirm the necessity to examine individual spectra as further information can be obtained which allow a better understanding of the material's stability. It was possible to identify potential degradation of cellulose nitrate and rubber, discriminate between the ether and ester-form of polyurethane, and discriminate between high and low density polyethylene. It was also shown that PCA could be used to unambiguously identify samples which contained cellulose acetate, cellulose nitrate, polycarbonate or polyurethane with a selection of known samples, but without the use of a spectral library.

Conclusions: This study supports previous publication results indicating that ATR-FTIR is a useful tool for the examination of objects containing polymers. Here it was shown that polymers could be characterised in object fragments that were not specially prepared and without the use of a spectral library. PCA was shown to be a useful tool for the unambiguous identification of cellulose acetate, cellulose nitrate, polycarbonate or polyurethane polymers in historical plastics with different additives, plasticisers or age. More excitingly, even though spectral features were similar for new and aged samples of polyurethane, PCA was able to discriminate between samples of foam that had been treated by heat (50°C for 24 h or 144 h) or by exposure to light, although more results for other polymeric materials are required to support this proof of concept study.

Keywords: ATR-FTIR, Plastics, Heritage collections, Degradation, Principal component analysis

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Introduction

Objects that contain synthetic, complex and inherently unstable modern materials, particularly polymer-based materials, are becoming integral parts of heritage collections at ever increasing rates; reflecting both the growing use of these materials in modern society and an interest in their own artistic qualities and interpretation. Many synthetic polymers were sought after as they were made to imitate more expensive materials such as tortoiseshell [1,2] and ivory [1,3]. Now polymers feature in museum collections in a wide variety of forms from packing materials and storage containers to sculpture, jewellery, toys and cinematic film. There are also many examples of natural plastic materials within heritage collections such as shellac, gutta percha and horn. Such materials were moulded and used for a variety of applications including buttons, brooches and liquid receptacles [4]. Unsurprisingly polymeric materials are present in almost all heritage collections across the world and represent a tribute to industrial, social or cultural progress.

As relatively recent additions to heritage collections these contemporary materials are less well studied and their chemical decomposition pathways have not yet been fully elucidated. Moreover, it is often difficult to determine the nature of the polymer used within an object making it difficult to determine appropriate storage conditions or assess an object's potential to degrade under the imposed environmental storage or display conditions. Deterioration of many thousands of polymer, or polymer-containing objects, is now becoming apparent and research questions regarding the durability of contemporary art objects need to be addressed. The concept of degradation and useful lifetime can often be indistinct. The polymer industry regard a polymer as being degraded when it loses a particular percentage of the object's original weight, at which stage the plastic is considered to have reached the end of its useful lifetime. In a heritage context the definition is not as well defined and objects often have to be considered on a case by case basis. With regards to heritage objects the term 'useful lifetime' can often be misunderstood. Objects are not necessarily 'in-use' in a traditional sense, but rather are on display or in storage. In general, most heritage institutions would regard an object as being at the end of its useful lifetime when it shows significant loss of quality or when the original meaning of the object is no longer perceivable. In addition, an object may be considered at the end of its lifetime when its degradation is causing an adverse impact on other collection items, at which point it will be removed from exhibition.

Previous museum surveys in the 1990´s [5,6], provided a snapshot of polymer object condition at the time of monitoring. In a survey based at the British Museum, the number of polymer objects was so large (> 3000 objects) that only a representative part of the collection was examined and visual signs of degradation and requirement for conservation work were noted together with the surrounding environmental conditions [6]. The types of polymers identified in the collection included cellulose acetate, Bakelite (phenol formaldehyde), cellulose nitrate, polyurethane, polypropylene, polyethylene, nylon, polystyrene, rubber and poly (vinyl chloride) (PVC). The results of the study highlighted that 27.5% of the collection required no treatment, 60% was deemed a low conservation priority and 12% required essential work. In addition, approximately 0.6% of the objects surveyed were in need of immediate conservation treatment; all of these contained PVC and were actively degrading and producing surface tackiness as a result of plasticiser migration. More recently, a survey was conducted in the furniture collection at the Victoria and Albert Museum as part of the Popart project [7]. The objects ranged in date from the 1930's to modern day and included historic plastics to modern recycled materials. Of the 200 objects surveyed 57% were found to be in good condition, 28% were recorded to be in a fair state (interpreted as having minor damage such as discolouration), 12% were in a poor condition (physical damage was present with brittleness and sweating of objects being a possibility). Only 3% of the objects studied were classed as unacceptable and therefore chemically unstable; this time the most unstable objects contained polyurethane.

Deterioration of polymeric objects can manifest itself in many ways. Materials can change colour, become physically deformed and fragile or may break apart into hundreds of smaller pieces. An additional problem that should not be underestimated is that during the deterioration process volatile organic compounds (VOCs) are often emitted from the surface of the object as it degrades. These VOCs, if acidic, can further exacerbate the object's chemical decay pathway (e.g. inducing an autocatalytic degradation cycle) or it could induce the corrosion of metal or calcareous objects held in close proximity to the degrading polymer [8]. Cellulose acetate, cellulose nitrate and PVC are materials which are known to emit acetic acid, nitric acid or hydrochloric acids, respectively, during degradation [9-12]. For example, conservators at the British Museum were alerted to nitric acid emission from a cellulose nitrate shadow puppet when the tissue paper used to pack the puppet became increasingly yellow and brittle to the touch [13]. In addition, the metal rivets which held the puppet together were corroded and the legs of the puppet had become severely crazed. Tests identified the plastic as cellulose nitrate and found a pH gradient across the object with the legs being highly acidic (pH 3.2 ± 0.2) and the body less so (pH 5 ± 0.2).

In this research study, 41 unknown polymer fragments were collected from standard reference materials (ResinKit™, Woonsocket, USA), industrial standards (supplied by the Scottish Plastic and Rubber Association, SPRA) and objects from private collections (see Table 1). The ability of ATR-FTIR spectroscopy to identify and classify polymers from such a wide range of sources, (with differing formulations, additives and plasticisers) was assessed. Samples were not modified prior to analysis and ranged in size from 1.3 cm^2 to 10.6 cm^2, each having an approximate mass of 100 mg. Classification was attempted based on a visual assessment of spectroscopic data after which the data was analysed by PCA. Knowing that the age of plastic materials ranges dramatically in heritage collections, 5 polyurethane fragments were also subjected to accelerated ageing and the collected spectral data were reassessed visually and using PCA to assess the utility of the spectroscopic method for the analysis of polymers in historical collections.

Results and discussion

Polymer characterisation of 41 sample fragments

The 41 sample fragments analysed in this study were of varying formulations, age, texture, topography, colour and shape. Nonetheless, identification of polymer type was possible without the need for sample preparation, such as solvent extraction. The use of a pressure clamp for solids was necessary to provide good contact between the sample and the diamond window used in the ATR-FTIR instrument. However, the force used to provide good contact with the crystal and the surface of the object created visual indentations on the more pliable materials such as PVC, polyethylene, polyurethane foams and rubber. It is possible to use spacers, which lessen the indentations on a measured sample by spreading the pressure over a larger area, however the use of spacers can make the analysis more cumbersome. Indentations were more pronounced on samples which were already in a degraded and vulnerable state. It is therefore suggested that analysis by ATR-FTIR using a pressure clamp for solids could be used on ‘hard’ polymer samples or, if possible, using fragments which have already fallen, or broken, from catalogued heritage objects. Otherwise small indentations will need to be tolerated during analysis and the sample area needs to be carefully selected. Difficulties were also experienced during the analysis of samples which had an unusual shape, for example, the analysis of a rounded dolls milk bottle was challenging. This polycarbonate sample had threading indentations for a screw cap and the unusual shape meant that it took some time to locate an area that gave good contact with the FTIR-ATR crystal. However it was still possible to collect spectroscopic data without further sample preparation such as using a microtome to provide a smooth surface.

The ATR-FTIR spectra were collected in replicate (n = 10) across the surface of the 41 polymer fragments. Collected spectroscopic data were examined to identify the main IR absorption bands and to classify the unknown polymer fragments; the results are given in Table 2 and compared with previously published results [14-26]. Not all users of ATR-FTIR possess a polymer sample library therefore representative spectra for each polymer type can be viewed within the additional information section in the online version of this paper (see Additional file 1, Additional file 2, Additional file 3, Additional file 4, Additional file 5, Additional file 6, Additional file 7, Additional file 8, Additional file 9). In addition, examination of individual spectra can provide the user with further interpretation that is not otherwise possible if, for example, spectral database matching was used rather than spectra interpretation. Examples are given below.

In the case of cellulose nitrate each sample analysed featured a peak at 1721 cm^{-1} that was attributed to a carbonyl stretch. The presence of a carbonyl containing plasticiser, such as camphor or phthalate ester, was ruled out as it was not possible to identify the other characteristic bands for camphor (2963 and 2874 cm^{-1}) [27], or phthalate plasticiser (2861, 1579 and 1602 cm^{-1}) [28,29]. It was therefore proposed that the carbonyl stretch indicated sample degradation and the intensity of this peak could potentially be used to indicate the state of degradation [25]. The spectra of polycarbonate samples had aromatic stretches at 1594, 1605, 1081, 1015 and 830 cm^{-1} suggesting an aromatic, rather than aliphatic, base structure, most likely bisphenol A. The spectra from rubber samples had additional peaks at 3350 and 1714 cm^{-1}, which were attributed to an OH and carbonyl stretch. Nor and Ebdon [30] reported these peaks to be present in natural rubber samples which had been degraded by ozonolysis. It is therefore proposed that these peaks could again be used to provide an inferential measure of the state of degradation of rubber samples. The spectra of polyurethane samples HS 86, 458, 461 and 464 indicated these samples were produced using an ether polyol. This was confirmed by the absence of bands at 1187, 1128 and 1064 cm^{-1} which are attributed to the C-O-C bend of the ester polyol [22]. Moreover, sample HS 69 could be identified as a polyurethane elastomer with additional bands present at 2936, 1702_{shoulder}, 1188, 1162, 1103, 1065, 1047 and 730 cm^{-1}. The bands at 1188 and 1065 cm^{-1} were attributed to the C-O-C bend of an ester polyol. Bands present at 1166 and 996 cm^{-1} in polypropylene spectra were indicative of the isotactic form of this material [31,32]. Furthermore, sample HS 416 had an absorption band at 1740 cm^{-1}

Table 1 Polymers selected for analysis in this study

Sample	Source	Object	Description
Polystyrene			
HS 36	ResinKit™		Colourless, transparent, rigid
HS 38	ResinKit™		White, opaque, rigid
HS 405	Private collection	Stereo cassette player	White, opaque, rigid
HS 409	Private collection	Cassette tape	Grey, opaque, rigid
HS 446	SPRA	Moulded shape	Colourless, transparent, rigid
Cellulose acetate			
HS 91	Private collection	Crumb brush	Pink, opaque, rigid
HS 474	Private collection	Thin film	Colourless, transparent
HS 475	Private collection	Thin film	Colourless, transparent
HS 476	Private collection	Thin film	Colourless, transparent
HS 477	Private collection	Thin film	Colourless, transparent
Cellulose nitrate			
HS 270	Private collection	Comb	White, opaque, rigid
HS 271	Private collection	Cigarette case	Mock tortoiseshell, transparent, rigid
HS 248	Private collection	Ruler	Orange, transparent, rigid
Polycarbonate			
HS 52	ResinKit™		Colourless, transparent, rigid
HS 143	Private collection	Dolls milk bottle	Green, transparent, curved, rigid
HS 413	Private collection	Drinking glass	Colourless, transparent, curved, rigid
HS 466	SPRA	Moulded shape	Colourless, transparent, rigid
HS 467	SPRA	Raw polymer beads	Colourless, transparent, rigid
Rubber			
HS 268	Private collection	Pipette bulb	Brown, opaque, cracked
HS 269	Private collection	Dolls head	Brown, opaque, cracked
HS 103	Private collection	Hot water bottle	Brown, opaque, pliable
PVC			
HS 62	ResinKit™		Colourless, transparent, rigid
HS 415	Private collection	Swim arm bands	Yellow, opaque, textured, pliable
HS 424	Private collection	Record	Black, opaque, ridged, pliable
HS 430	Private collection	Money wallet	Black, opaque, pliable
HS 468	SPRA	Moulded shape	Grey, opaque, rigid
Polyurethane			
HS69	ResinKit™		Colourless, transparent, elastomer
HS 86	Private collection	Packing material	White, foam
HS 458	SPRA	Packing material	Pink, antistatic foam
HS 461	SPRA	Packing material	Black, foam
HS 464	SPRA	Packing material	Grey, foam
Polypropylene			
HS 77	ResinKit™		White, opaque, rigid
HS 400	Private collection	Thermos® flask	Black, opaque, rigid
HS 403	Private collection	Thermos® flask cup	White, opaque, rigid
HS 416	Private collection	Tupperware® box	Brown, opaque, rigid
HS 444	SPRA	Moulded object	Colourless, semi-transparent, rigid

Table 1 Polymers selected for analysis in this study *(Continued)*

Polyethylene			
HS 80	ResinKit™		White, opaque, pliable
HS 404	Private collection	Scalextric crash barrier	White, opaque, pliable
HS 417	Private collection	Tupperware® lid	Colourless, semi-transparent, pliable
HS 459	SPRA	Packing material	Black, crosslinked foam
HS 463	SPRA	Packing material	White, non-crosslinked foam

which was attributed to a carbonyl stretch present due to oxidative degradation of the sample. Polyethylene sample HS80 had an additional band present at 1378 cm^{-1}, which was attributed to a CH_3 bend and is indicative of low density polyethylene; which has a small amount of branching on the polymer chains. The band at 1378 cm^{-1} was not present in the other polyethylene samples (see Table 2) suggesting no branching in the polymer chains, indicating high density polyethylene.

Principal component analysis of measurement data for 41 fragments

Although the polymers present in all samples were successfully characterised here by visual examination of collected spectra, users can often rely on the use of spectral libraries for matching the spectra of unknown materials with stored data. It is common for commercial libraries to use spectra from new (pristine) samples. However, as a plastic sample ages the search algorithms may become less effective and matches will become poorer to the point where an incorrect match could be generated. In-house built libraries which contain a range of degraded sample spectra could overcome this potential problem, however not all users have such a facility. Therefore, spectral data was interrogated using principal component analysis to assess whether it could be used to unambiguously identify a polymer type in a sample regardless of its age, formulation or the presence of additives and plasticisers. The collected spectra (n = 10) of the 41 samples were exported into MatLab, derivatised, normalised and mean centred before principal component analysis (PCA) was used to assess sample correlations.

From the PCA results, the eigenvalue plot indicated that 10 principal components (PCs) could be used to describe 92% of the data variation, however the first 4 PCs showed specific sample types which tended to be distinct from the other samples. Examination of the scores plot for PC 1 (see Figure 1) indicated that most of the samples have scores values between −1.5 and 2, with samples of the same type having similar scores, e.g. all the polycarbonate samples have a PC1 score value of 1.5 to 1.75. However, the PC1 scores values observed for cellulose acetate (−5.5 to −2) are clearly distinct (see triangles at the bottom right hand side of Figure 1) from those observed for the other 8 different polymer types, suggesting that PC1 can be used to discriminate cellulose acetate. The scores plots for PC2, PC3 and PC4 (see Figures 2, 3 and 4), demonstrated distinct scores values for polycarbonate samples (PC2 scores values between −4.2 and −5.6), polyurethane samples (PC3 scores values between −4.0 and −4.8) and cellulose nitrate samples (PC4 scores values between 4.0 and 4.5), respectively. Interestingly, the polyurethane elastomer (HS69-highlighted in Figure 3 with a red circle) did not fit into the grouping of polyurethane foams; this level of discrimination was not possible by examination of the original spectra. A range of scores values are observed for the 10 repeat measurements of individual samples owing to slight variations in the sample surface. An uneven sample surface can create poorer contact between the sample and the crystal window of the ATR-FTIR, which will lead to slight differences in the spectra. However, the variation was minor and did not affect the ability to unambiguously identify samples which contained cellulose acetate, polycarbonate, polyurethane and cellulose nitrate on the basis of their PC1, PC2, PC3 and PC4 scores, respectively. Where samples had a smooth and regular surface good surface contact resulted in less cluster variation (for example see Figure 4). Here it was necessary to have samples of known type to undertake the PCA analyses, however it is proposed that sample classification of unknowns would be possible with the use of clustering and discrimination tools.

Examination of aged polyurethane samples

A polyurethane foam sample was cut (n = 5) and used as a case study to assess the use of ATR-FTIR to discriminate between ‘fresh’ and ‘aged’ polyurethane samples. The 5 sections of foam were placed in a Weather-Ometer and subjected to the conditions given in Table 3. After ageing the measured original replicate spectra for all 5 samples (PU1 – PU5) were examined visually and although some spectral differences were observed it was not possible to clearly distinguish between the replicate spectra (n = 10) collected for the unaged sample (PU1) or samples aged for 24 h in the dark (PU2), 24 h in the light (PU3), 144 h in the dark (PU4) or 144 h in the light

Table 2 Main ATR-FTIR absorption bands

Polymer	Main IR absorption bands (cm^{-1})
Polystyrene (HS 36, 38, 405, 409 & 446)	3025 (C-H) stretch
	2921 & 2854 (CH_2) asymmetric & symmetric stretch
	1602 ring stretch
	1449 (C = C) ring
	905 (C = CH)
	745 & 696 (C-H) bend of aromatic ring
Cellulose acetate (HS 91, 474, 475, 476 & 477)	2977 & 2932 (CH_3) asymmetric & symmetric stretch
	2951 & 2880 (CH_2) asymmetric & symmetric stretch
	1740 (C = O)
	1367 (CH_3) bend
	1032 (C-O) stretch
Cellulose nitrate (HS 248, 270 & 271)	2925 & 2854 (CH_2) asymmetric & symmetric stretch
	1721 (C = O)
	1647 & 1274 (NO_2) asymmetric & symmetric stretch
	1155 asymmetric ring stretch
	1065 (C-O) stretch
	830 (N-O) stretch
	749 (N-O) bend
Polycarbonate (HS 52, 143, 413, 466 & 467)	2969 & 2869 (CH_3) asymmetric & symmetric stretch
	2925 & 2854 (CH_2) asymmetric & symmetric stretch
	1770 (C = O)
	1594 & 1605 doublet, aromatic ring stretch
	1081, 1015 & 830 (1,4 disubstituted aromatic ring)
Rubber (HS 103, 268 & 269)	3350_{broad} (OH) *suggests degradation*
	2943 & 2854 (CH_3) asymmetric stretch & symmetric stretch
	2917 (CH_2) asymmetric stretch
	1714 (C = O) *suggests degradation*
	1620 (C = C) stretch
	1442 & 1375 (CH_3) asymmetric & symmetric bend
	1069_{weak} *suggests degradation*
Poly(vinyl chloride) (HS 62, 415, 424, 430 & 468)	2925 (CH_2) stretch
	$2861_{shoulder}$ (C-H) stretch *(phthalate plasticiser)*
	1720 (C = O) *(phthalate plasticiser)*
	1579 and 1602 doublet *(phthalate plasticiser)*
	1427 (CH_2) bend
	1255 (C-H) bend, in phase
	961(C-C) stretch
	693 (C-Cl) stretch
Polyurethane (HS 69, 86, 458, 461 & 464)	3325 (N-H) stretch
	2973 (C-H) stretch, asymmetric
	2865 (C-H) stretch, symmetric
	1725 (C = O) stretch
	1639 (OCONH)

Table 2 Main ATR-FTIR absorption bands *(Continued)*

	1538 (N-H) deformation
	1088 (OCONH) in plane
Polypropylene (HS 77, 400, 403, 416 & 444)	2947 & 2869 (CH$_3$) asymmetric & symmetric stretch
	2921 & 2839 (CH$_2$) asymmetric & symmetric stretch
	1453 & 1378 (CH$_3$) asymmetric & symmetric bend
	1438 (CH$_2$) bend
	1166 & 996 indicative of isotactic form
Polyethylene (HS 80, 404, 417, 459 & 463)	2917 & 2854 (CH$_2$) asymmetric & symmetric stretch
	1470 (CH$_2$) bend
	1378 (CH$_3$) symmetric bend (low density only)
	719 (CH$_2$) rocking

(PU5) despite the fact that PU5, in particular, showed significant signs of degradation, such as discolouration and crumbling. All of the other samples PU2-4 looked unchanged from the unaged sample (PU1). When the replicate spectra were imported into Matlab, derivatised, normalised and mean-centred PCA was able to clearly differentiate the samples, as illustrated in Figure 5. This would suggest that it is possible to identify the early onset of degradation of polyurethane foam using PCA; this would not be possible by spectral matching using commercial or online databases. The unaged PU1 sample spectra were clustered together with a high PC1 score and zero PC2 score (see triangles at far RHS of the figure). Moving down along the PC1 axis, the next set of data that clustered together belonged to PU2 (stars), this sample was exposed in the chamber for 24 h but protected from light. Moving further down along the PC1 axis, PU3 data (squares) clustered together indicating that light does have an impact on the sample even after a 24 h exposure. Samples placed in the Weather-Ometer for 144 h were easily distinguished from those aged for 24 h: Samples PU4 (diamonds) and PU5 (crosses) had negative PC1 scores whereas samples PU2 and PU3 had positive PC1 scores. Examination of the PC1 score values will permit differentiation between samples which have been thermally aged at 50% RH for either 24 or 144 h, indicating that a chemical difference had been imparted to samples with increased exposure time. Light ageing did not appear to affect the PU sample when an ageing time of 24 h was applied (no difference in PC2 score for PU2 or PU3). In contrast after the 144 h ageing time, spectra from the sample which was protected from light (PU4) clustered together in the lower left hand quadrant of the scores plot (negative PC2 scores) whereas the sample which was subjected to light (PU5) clustered together in the upper left hand quadrant of the scores plot. Using this model it would therefore be possible to determine whether unknown PU samples were 'fresh', thermally aged or photochemically aged by projecting its PCA result onto the PC1 versus PC2 scores plot.

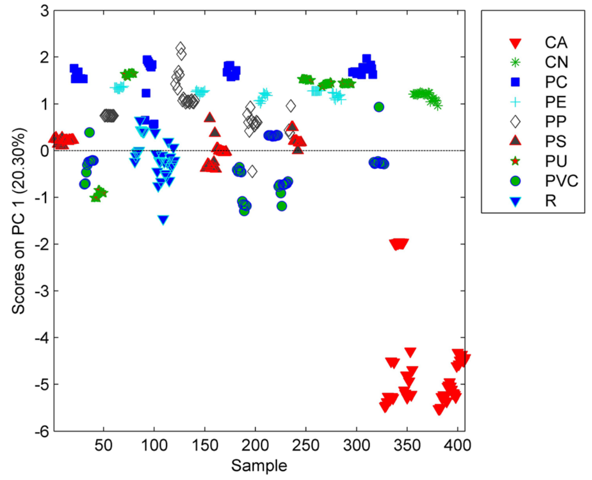

Figure 1 Scores plot for PC1.

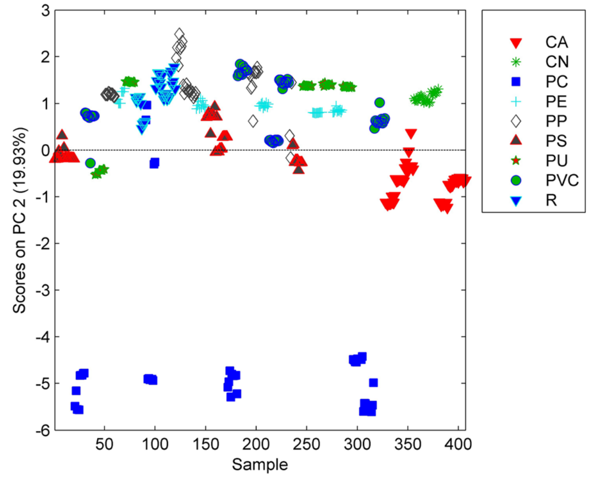

Figure 2 Scores plot for PC2.

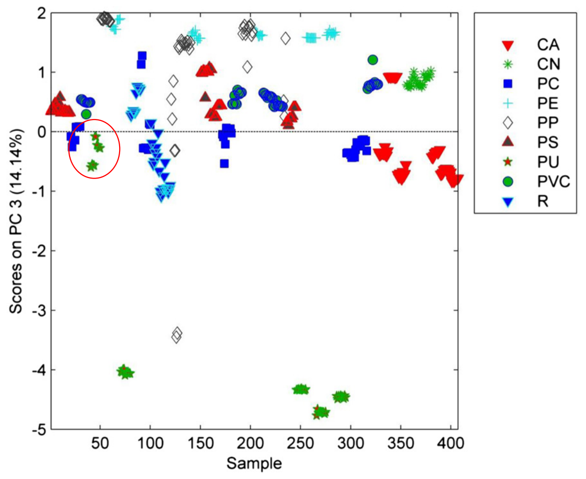

Figure 3 Scores plot for PC3.

Experimental

Details of instrumentation

A transportable diamond crystal attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (Agilent Technologies 5500a) was used to collect spectra in the 650–4000 cm^{-1} region. The spectra were collected using Microlab PC software in absorbance mode using 128 scans at 8 cm^{-1} resolution. No sample preparation was required and polymers were directly analysed on the diamond window. Intimate contact of the sample with the crystal window was required to give good quality spectra; samples were clamped against the diamond window using a pressure clamp for solids. Samples were often irregularly shaped and ten spectra (n = 10) were recorded across the entire surface of the object under study. Spectra were processed with MATLAB version 7.13.0.564 (R2011b) (Mathworks Inc., Natick, MA, USA) incorporating PLS_Toolbox version 6.7 (Eigenvector Research Inc., WA, USA). Data were derivatised (Savitzky Golay 1st derivative filter with 13 points and a 2nd order polynomial) to remove baseline offset, normalised to the largest peak and then mean centred prior to carrying out PCA. The pre-processing techniques used helped to reduce noise and emphasise any regions of spectral change.

Table 3 Ageing conditions for PU sample HS464

Sample name	Temp / °C	RH / %	Light exposure	Time / h
PU 1 (ref)	-	-	-	-
PU 2	50	50	No	24
PU 3	50	50	Yes	24
PU 4	50	50	No	144
PU5	50	50	Yes	144

Principal component analysis (PCA)

A method of determining correlations in spectral data sets is to use PCA which describes the data, not by wavenumber, but using a smaller number of 'latent' variables, called principal components (PCs). The PC's, obtained from the original data must reflect the underlying structure of the data, both in terms of the relationships between the different samples (objects) and the relationship between the different measurement variables (e.g. spectral wavenumber). Comparison of the samples' principal components will permit easy detection of correlations between samples and/or their original variables. When analysing PCA data, the eigenplot is first examined to determine the number of PCs that reflect the variation in the data. Those PCs are then further interrogated using, in this instance, scores plots to examine sample correlations. Samples with similar

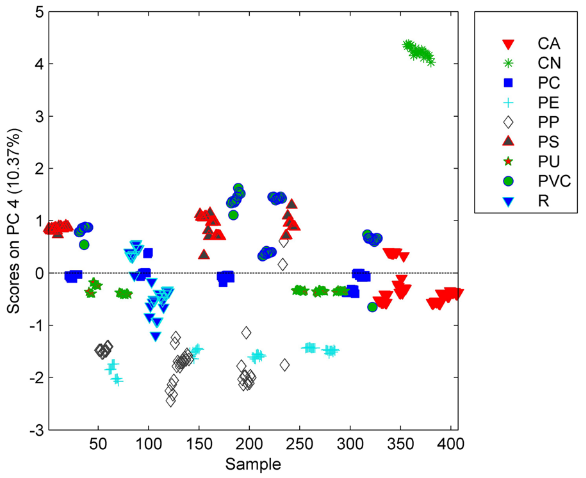

Figure 4 Scores plot for PC4.

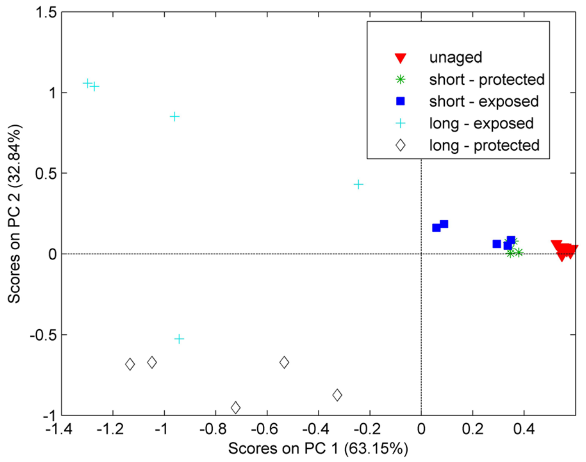

Figure 5 PC1 versus PC2 scores plot for unaged and aged polyurethane sample HS464.

spectral features should cluster together in the scores plot where the PCs contain information on these spectral features.

Accelerated ageing conditions

Accelerated ageing was conducted on polyurethane sample HS464. Artificial ageing was conducted using an Atlas Ci4000 Weather-Ometer and the conditions used are given in Table 3. The xenon light source used had full spectrum from 200 nm to 750 nm with a CIRA inner, and a soda lime and float glass outer filter to provide a cut-off at 300 nm. The irradiance measured at a wavelength of 420 nm was 1 Wm^{-2} (approximately 0.4 Wm^{-2} at 340 nm); samples PU2 and PU4 were protected from the light using an additional UV filter. The polyurethane fragments were attached to acid free conservation grade cardboard, mounted in brackets and hung inside the Weather-Ometer. After ageing, the samples were analysed using the same ATR-FTIR instrument and conditions outlined above and the spectra were compared to reference spectra collected from an unaged fragment of HS464.

Conclusions

ATR-FTIR spectroscopy was, once again, shown to be a suitable method of characterisation of unknown polymers commonly found in heritage collections. Here the spectra were interpreted by band assignment rather than using spectral matching via libraries. Polymer fragments were analysed without sample pre-treatment and were easily identified by visual examination of the collected spectra. The technique lends itself to the analysis of smaller polymer samples (due to the use of the pressure clamp) or polymer fragments. Care needs to be taken when 'softer' samples are analysed to ensure the imprint from the arm clamp is not visually apparent after sampling. It should also be noted that ATR-FTIR spectroscopy is a surface technique therefore caution must be used when analysing a sample which could comprise of polymer layers. Matching unknown samples to collected data was attempted using PCA rather than spectral libraries. It was possible to unambiguously determine samples that contained cellulose acetate, polycarbonate, polyurethane foam or cellulose nitrate; regardless of the age of the sample, its formulation or the presence of additives. More importantly, PCA was used to differentiate polyurethane samples that had been aged using thermal- or photo-ageing treatment despite the inability to see visual changes in either the material or the collected spectra. This provides users with a tool to identify the early stages of polyurethane deterioration. Similar work is now being conducted on the other polymer family groups identified in this study.

Additional files

Additional file 1: **ATR-FTIR spectrum of polystyrene.**
Additional file 2: **ATR-FTIR spectrum of cellulose acetate.**
Additional file 3: **ATR-FTIR spectrum of cellulose nitrate.**
Additional file 4: **ATR-FTIR spectrum of polycarbonate.**
Additional file 5: **ATR-FTIR spectrum of rubber.**
Additional file 6: **ATR-FTIR spectrum of poly (vinyl chloride).**
Additional file 7: **ATR-FTIR spectrum of polyurethane.**
Additional file 8: **ATR-FTIR spectrum of polyethylene.**
Additional file 9: **ATR-FTIR spectrum of polypropylene.**

Abbreviations

ATR-FTIR: Attenuated total reflectance-Fourier transform infrared; VOC: Volatile organic compound; PCA: Principal component analysis; SPRA: Scottish Plastic and Rubber Association; CA: Cellulose acetate; CN: Cellulose nitrate; PC: Polycarbonate; PE: Polyethylene; PP: Polypropylene; PS: Polystyrene; PU: Polyurethane; PVC: Polyvinylchloride; R: Rubber.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

GM: Analysis and ageing of plastic samples, data interpretation and write article. LTG: design of experiments, data interpretation and article review. FF: design of experiments and article review. AN: Principal component analysis and article review. PTL: ATR-FTIR instrumentation and article review. All authors have read and approved the final manuscript.

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Emissions from polymeric materials: Characterised by thermal desorption-gas chromatography

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ABSTRACT

Since being recognised as a potential emissive source, plastics in heritage collections are being investigated to understand the chemical compounds they release and how they might affect the stability of other heritage objects. There is a requirement for non-invasive methods of analyses to identify unknown plastics and the emitted volatiles they generate. Therefore, Tenax-TA sampling tubes were used to collect the emitted volatiles from 41 samples of 9 polymer types of varying formulation, provenance and age. Thermal desorption-gas chromatography coupled with mass spectrometry (TD-GC/MS) has been successfully used to separate and identify the emissions of the 41 samples at 23 °C, after heating to 70 °C and after accelerated degradation.

1. Introduction

Monitoring indoor air pollution within cultural institutions is an important area of research and many studies have highlighted the pollutants which are commonly encountered [1–5]. Elucidating the source of a particular pollutant can be difficult, but it is now understood that heritage objects can act as an emissive source. Heritage objects containing plastics is a case in point [6,7]. Plastic objects, which are now commonplace in everyday life, feature heavily in heritage collections and provide information on industrial, social and cultural progress. The effect of harmful emissions from such plastic materials is not a new problem. Indeed the prevalence of plastics in our day-to-day lives has raised safety concerns previously in relation to the emission of volatile organic compounds (VOCs) and their effect on human health [8]. Being recognised as a potential emission source, heritage institutions have investigated the chemical compounds released from a wide range of plastic objects and how they might affect the stability of other heritage objects held in close proximity to the emitting object [9–12].

There is an obvious need for methods of analyses which can identify unknown plastics in heritage collections and determine which are emitting potentially harmful vapours (which can be harmful to other objects or to human health). One previous study [11], examined a number of industrial plastic samples from a variety of polymer families including styrenic (*polystyrene and acrylonitrile–butadiene–styrene*), polyolefin (*polyethylene, polypropylene and polybutylene*), acrylic (*homo-polymethylmethacrylate and co-polymethylmethacrylate*), polyamide (*nylon 6*), polyurethane (*polyether and polyester base polyurethane*), cellulose ester (*cellulose nitrate*) and poly (phenylene oxide) (*poly(2,6-dimethyl-1,4-phenylene oxide)*). The samples were heated to 60 °C for 1 h whilst VOCs were trapped using a divinylbenzene-carboxen/poly(dimethylsiloxane) (DVB-CAR/PDMS) fibre. In addition, volatiles emitted from 3 naturally aged museum objects (cellulose nitrate, polyester and polyether based polyurethanes) were measured by placing the DVB-CAR/PDMS fibre in close proximity to the objects at room temperature for 15 days. Compounds were identified that may be related to 7 of the new standard plastics (nylon 6, cellulose nitrate, polyester and polyether based polyurethane, poly (2,6-dimethyl-1,4-phenylene oxide), homo-polymethylmethacrylate and co-polymethylmethacrylate) and used as unique markers as a non-invasive test for polymer identification.

Cellulose nitrate, cellulose acetate, polyurethane, poly(vinyl chloride) and rubber are the least stable plastics within heritage collections [13–15]. The previous study examined only two of the five plastics which are of major concern within heritage institutions [11]. In addition, only 7 standard samples were used in the previous

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study and all were new. With only one sample per polymer type it is not known how the emissions could be affected by samples of varying age or by the addition of additives such as fillers, plasticisers and impact modifiers. Therefore, there is a need to examine a large range of plastics of varying age and formulation. By studying the emissions of multiple samples per plastic type, within sample variation can be examined to gain a better understanding of the emissions from plastics and whether they can be reliably used as a method of non-invasive identification regardless of age, formulation or additives.

In this paper a more extensive investigation was undertaken, specifically focussing on VOC emissions from a wide range of plastics commonly found within heritage collections; cellulose acetate, cellulose nitrate, polyurethane, polycarbonate, rubber, poly(vinyl chloride), polyethylene, polypropylene and polystyrene. In total 41 samples (at least three per polymer type) were assessed and emissions were collected at 23 °C and at 70 °C. Despite being sensitive and reusable, SPME fibres were not used in this study as the intention was to post the collecting device to the site where sampling was being undertaken. In a previous study undertaken by the authors where SPME fibres were removed from their holders and used to sample between the pages of a book, 3 fibres out of 7 were broken during the sampling and shipping process [16]. Therefore commercially available Tenax-TA sampling tubes were chosen as an appropriate collecting device for VOCs since the tubes can't be broken during shipping or sampling and Tenax-TA is the benchmark adsorbent used for indoor air sampling campaigns. Moreover to examine the potential variation in emissions when plastic objects age fragments from each polymer object were subjected to accelerated degradation before re-examination of emissions. To determine the utility of the developed method for plastic identification, or stability classification, a number of objects currently held in heritage collections were encapsulated in a sealed container to allow emitted VOCs to establish an equilibrium in the headspace of the container before being sampled using Tenax-TA as the adsorbent.

2. Experimental

2.1. Pre-sampling phase to ensure accurate characterisation of polymer samples

The aim of this study was the assessment of a non-invasive characterisation method of analysis for polymeric materials using VOC emission data. Prior to collection of VOCs from the 41 reference samples each was first analysed by attenuated total reflectance-Fourier transform infrared analysis (ATR-FTIR) to ensure accurate determination of polymer type [17]. After this analysis was conducted the VOC emission data could be collected and correlated to polymer type. In the field, emissions only will be collected and used to determine the polymer type contained in an object, allowing a non-invasive assessment of the object (e.g. without the need for contact sampling by ATR-FTIR). The reference samples used in this study were obtained from a variety of sources, see Table 1.

ResinKit™ (Woonsocket, USA) standard samples were part of the UCL Centre for Sustainable Heritage Historical Polymer Reference Collection. The Scottish Plastic and Rubber Association (SPRA) provided industrial standards in a variety of forms. The remaining samples were from the University of Strathclyde Polymer Reference Collection. Samples varied in age, shape, size, colour, texture and formulation and were cut in to replicate sub-samples each having an approximate mass of 100 mg. The polymer reference collections at the University of Strathclyde (UoS) and UCL Centre for Sustainable Heritage are available to research groups for further studies if requested.

Table 1
The 41 samples selected for this study.

Sample	Source	Object	Description
Polystyrene			
HS36	UCL	ResinKit™	Colourless, transparent, rigid
HS38	UCL	ResinKit™	White, opaque, rigid
HS405	UoS	Stereo cassette player	White, opaque, rigid
HS409	UoS	Cassette tape	Grey, opaque, rigid
HS446	SPRA	Moulded shape	Colourless, transparent, rigid
Cellulose acetate			
HS91	UCL	Crumb brush	Pink, opaque, rigid
HS474	UoS	Thin film	Colourless, transparent
HS475	UoS	Thin film	Colourless, transparent
HS476	UoS	Thin film	Colourless, transparent
HS477	UoS	Thin film	Colourless, transparent
Cellulose nitrate			
HS270	UCL	Comb	White, opaque, rigid
HS271	UCL	Cigarette case	Mock tortoiseshell, transparent, rigid
HS248	UCL	Ruler	Orange, transparent, rigid
Polycarbonate			
HS52	UCL	ResinKit™	Colourless, transparent, rigid
HS143	UCL	Dolls milk bottle	Green, transparent, curved, rigid
HS413	UoS	Drinking glass	Colourless, transparent, curved, rigid
HS466	SPRA	Moulded shape	Colourless, transparent, rigid
HS467	SPRA	Raw polymer beads	Colourless, transparent, rigid
Rubber			
HS268	UCL	Pipette bulb	Brown, opaque, cracked
HS269	UCL	Dolls head	Brown, opaque, cracked
HS103	UCL	Hot water bottle	Brown, opaque, pliable
PVC			
HS62	UCL	ResinKit™	Colourless, transparent, rigid
HS415	UoS	Swim arm bands	Yellow, opaque, textured, pliable
HS424	UoS	Record	Black, opaque, ridged, pliable
HS430	UoS	Money wallet	Black, opaque, pliable
HS468	SPRA	Moulded shape	Grey, opaque, rigid
Polyurethane			
HS69	UCL	ResinKit™	Colourless, transparent, elastomer
HS86	UCL	Packing material	White, foam
HS458	SPRA	Packing material	Pink, antistatic foam
HS461	SPRA	Packing material	Black, foam
HS464	SPRA	Packing material	Grey, foam
Polypropylene			
HS77	UCL	ResinKit™	White, opaque, rigid
HS400	UoS	Thermos® flask	Black, opaque, rigid
HS403	UoS	Thermos® flask cup	White, opaque, rigid
HS416	UoS	Tupperware® box	Brown, opaque, rigid
HS444	SPRA	Moulded object	Colourless, semi-transparent, rigid
Polyethylene			
HS80	UCL	ResinKit™	White, opaque, pliable
HS404	UoS	Scalextric crash barrier	White, opaque, pliable
HS417	UoS	Tupperware® lid	Colourless, semi-transparent, pliable
HS459	SPRA	Packing material	Black, crosslinked foam
HS463	SPRA	Packing material	White, non-crosslinked foam

2.2. Determination of emissions from reference plastic samples

Before plastic objects were sampled in the field a validation method was used to ensure reproducible VOCs could be collected from the characterised reference samples. Sub-samples of each were analysed using a micro-chamber/thermal extractor™ (μ-CTE™) chamber. The μ-CTE™ (Markes International, Llantrisant) instrument was capable of operating between 23 °C and 120 °C and contained six individual stainless steel micro-chambers (44 cm^3 interior volume) which were simultaneously flushed with dry air preheated to the same temperature as the chambers. Each chamber outlet was connected to a Tenax-TA sampling tube to collect VOCs

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and semi-volatile organic compounds (SVOCs) that had accumulated inside each emission chamber containing the reference material. As there was a maximum of 5 sub-samples for each polymer type (see Table 1), each was placed in its own emission chamber with the 6th chamber being left empty to act as a sampling blank. The plastic samples were sealed inside the micro-chambers which were held at a 23 °C for 1 h. An additional set of emission data was collected at a temperature of 70 °C which was intended to promote the emission of labile compounds from the surface of the sample but not induce thermal ageing. After the samples were contained at 23 or 70 °C for 1 h, dry compressed air was passed through each chamber at a flow rate of 100 cm^3 min^{-1}, for 2 min, to flush the emitted volatiles from each chamber compartment through Tenax-TA sampling tubes.

2.3. Accelerated degradation experiments

Samples were also subjected to accelerated degradation using light. The samples were first placed in a light box (in-house built) and exposed to ultraviolet (UV) light of 365 nm for 1 h using two UV lamps (2 × 4W BLB lamp, Uvitec-Cambridge and 4W BLB lamp, UVP Ltd- Cambridge). The samples were then transferred in to an Atlas Suntest XLS+ using Filter C (equivalent to coated quartz glass with special window glass to provide visible light only) at 36 °C and an irradiance of 750 Wm^{-2} for 168 h. The relative humidity of the light box and the Atlas Suntest XLS+ was approximately 50% RH. Each sample was then placed back into separate chambers of the μ-CTE™ instrument for 1 h at 23 °C before the chamber was flushed with dry compressed air at 100 cm^3 min^{-1}, for 2 min and each exhaust stream passed over a Tenax-TA sampling tube.

2.4. Analysis of Tenax-TA sampling tubes by thermal desorption gas chromatography mass spectrometry (TD-GC-MS)

The thermal desorption sampling tubes were analysed by thermal desorption (Unity series 2, Markes International) and gas chromatograph (7890A GC system, Agilent Technologies) coupled to a mass spectrometer (5975C inert XL MSD, Agilent Technologies). Separation was performed using a capillary column (HP-5MS 30 m × 250 μm × 0.25 μm, Agilent Technologies) with a carrier gas (He) flow rate of 1 cm^3 min^{-1}. The isothermal column temperature programme was 40 °C for 10 min, then 5 °C min^{-1}–270 °C. Mass spectra were acquired in electron ionisation mode at 70 eV in the m/z range 40–300. Analytes were identified by comparing collected data with mass spectra held in the National Institute of Standards and Technology (NIST 08) mass spectral library.

2.5. Case studies: the measurement of emissions from objects currently held in heritage institutions

A measurement ruler, approximately 60 y old, which is part of the collection at the Secret War Tunnels at Dover Castle England and under the governance of English Heritage, was assessed. The ruler had been stored in a box for a number of years. The storage room had no climate control, black-out blinds and lighting was only used when the room was populated. The ruler was thought to be in an advanced state of degradation as it was severely cracked, warped and was reported to emit a strong odour. To sample the VOCs emitting from the object it was sealed inside a glass vessel with a Tenax-TA sampling tube for 14 days.

A collection of photographic negatives, approximately 65 y old, held in a Timecare storage box within a repository at the National Records of Scotland Edinburgh, was assessed as the photographs had become warped and there were reports of a strong odour inside the storage box. The repository was climate controlled at 16 °C ± 2 °C with a relative humidity of 50 ± 5% RH. Tenax-TA sampling tubes were placed inside the box to sample the environment for 14 days.

A ‘crystal storage/display box’ held at The British Museum, London was assessed. The box was approximately 5 y old and was not stored in controlled environmental conditions. At the time of monitoring the object showed no visual signs of degradation and the Tenax-TA sampling tubes were placed inside the box to sample the air for 14 days.

3. Results and discussion

3.1. Emission results from the reference materials placed in the μ-CTE™ instrument

The VOCs emitted from all reference materials were collected at room temperature (23 °C) to reflect sampling temperatures during field monitoring. Previous studies [11,18–20] focussing on emissions from polymeric objects have typically heated samples to 70 °C before the collection of VOCs. To determine whether the emission chromatograms collected at higher temperature, which crucially would be used as reference chromatograms to identify polymer type in the field, have different emission profiles to those collected at room temperature, all reference samples were heated to 70° C for 1 h in the μ-CTE™ instrument prior to collection of VOCs. The results of each polymer type will be discussed in turn.

3.1.1. Polystyrene emissions

Despite the different source, age and formulation of the samples, styrene and ethylbenzene were the main VOCs measured at 23 °C (Fig. 1 is an illustration of the chromatogram for sample HS409) for each of the 5 polystyrene samples, which was in agreement with results of earlier publications [11,21]. In addition to these 2 major emitted compounds a range of linear and branched alkanes, aldehydes and diethyl phthalate plasticiser were measured, but at a relatively low abundance. The alkanes, aldehydes and plasticisers detected are common to many plastics and cannot always be considered as being indicative of a particular plastic and are therefore considered to be ‘non-specific’ VOCs in this case. Since styrene and ethylbenzene were present in all the emissions at 23 °C regardless of formulation and age, these two compounds were considered to be ‘specific VOC’ markers of polystyrene.

After the samples were heated to 70 °C for 1 h, the emissions for each polystyrene subsample were re-measured. In general, there was an overall increase in the number of VOCs which was expected as the heat would promote volatilisation of labile compounds present in, or on, the surface of the sample. In particular, there was an increase in the number of non-specific VOCs such as the plasticiser dimethyl phthalate, which was detected at 70 °C but not at 23 °C. After heating, the dominant VOCs measured were plasticisers with HS36 and HS405 emitting diethyl phthalate and HS38, HS409 and HS446 emitting both dimethyl and diethyl phthalate. The styrene monomer and ethylbenzene were still detected in the vapour phase but their relative abundances were significantly reduced and smaller in comparison to the detected plasticisers. After heating there was no visual change to the samples that would have indicated the release of substantial quantities of plasticiser, however it was evident that the emissions taken at 70 °C would be different to those measured at 23 °C. In this case chromatograms measured at 23 °C or 70 °C could be used as reference data for field sampling.

After accelerated degradation, VOCs emitted from the 5 polystyrene samples were re-measured. Samples HS38 and HS446 were visually altered as they had yellowed and the samples looked similarly degraded whereas samples HS36, HS405 and HS409

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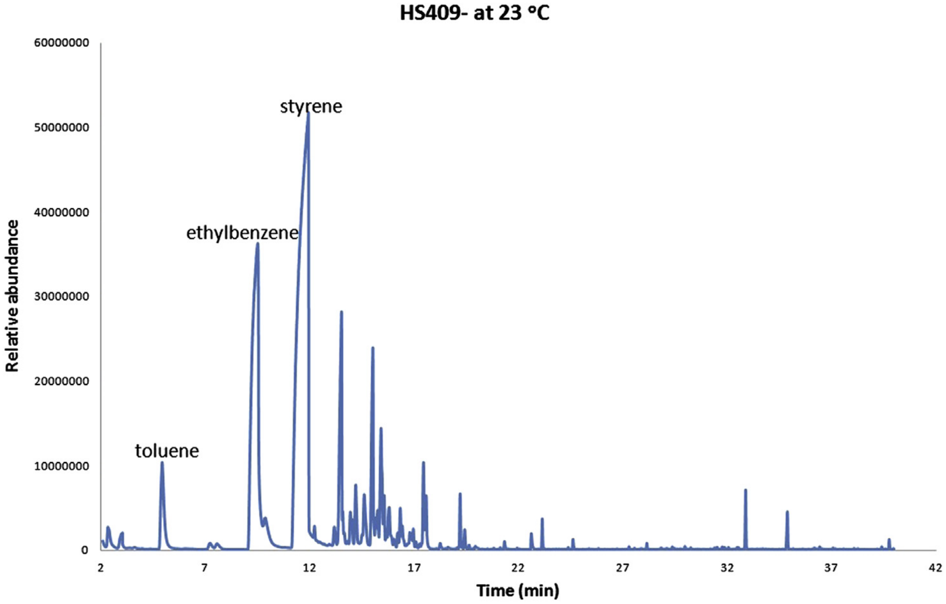

Fig. 1. Emissions from polystyrene sample HS409 at 23 °C.

demonstrated no visual signs of degradation. Of notable interest was the omission of ethylbenzene from all 5 chromatograms and the loss of styrene emission from HS446 and HS405 (the two specific VOCs used to identify polymer type). This would imply that some polystyrene samples which have been severely degraded may not be identified correctly using reference emission data collected from new or non-degraded samples so care would have to be taken when identifying degraded polymers using emission data alone. Conversely, if the material type was already known, the significant change in the chemical fingerprint of polystyrene chromatograms after photo degradation could prove to be very useful. Identification of the loss of ethylbenzene and the loss of styrene monomer from collected chromatograms could inform museum staff that polystyrene degradation has been initiated. In this study HS405 did not look degraded but the emission data confirmed that chemical transformations within the polymer had taken place.

In a previous study, Lattuati-Derieux et al. [11] examined VOC emissions from polystyrene and acrylonitrile butadiene styrene (ABS) and found that it was not possible to discriminate between the two polymer types using emissions alone since they both contained residual styrene monomer and ethylbenzene. The authors noted that their method of analysis was not suitable for the collection and identification of nitrogen containing compounds in ABS which could have been used to differentiate between styrene and ABS.

3.1.2. *Polyurethane emissions*

The 5 polyurethane samples consisted of 1 elastomer (HS69) and 4 foams of varying formulation (HS86, HS458, HS461 and HS464). Previous characterisation by ATR-FTIR spectroscopy identified the elastomer as polyester polyurethane and the foams as polyether polyurethanes. At 23 °C the elastomer, HS69 emitted toluene, phenol, decane, nonanal, 2-butyl-1-octanol, 2-ethyl-1-hexanol and the antioxidant butylated hydroxytoluene (BHT). Whereas the foam samples, HS86, HS464, HS458 and HS461 emitted toluene, benzaldehyde, BHT and diethyl phthalate. In addition to these major compounds, styrene, limonene, decanal and dimethyl phthalate were detected in HS86; limonene, nonanal and dimethyl phthalate were detected in HS458 and nonanal was detected in HS464. After heating to 70 °C for 1 h, the emission data changed and the chromatographic profiles were significantly different to those collected at 23 °C. For example, HS69 emissions were dominated by phenol, 2-ethyl-1-hexanol, 2,5-dimethyl tetradecane, 3-methyl-5-propyl nonane, 3,7-dimethyl nonane, dimethyl phthalate, diethyl phthalate and BHT. In the emissions of HS86 and HS461 acetic acid, toluene, styrene, phenol, diethyl phthalate, dimethyl phthalate and BHT were detected. In addition to these major emitted compounds 2-ethyl-1-hexanol and dodecane were also measured in HS461. Propylene glycol, styrene, phenol, nonanal, diethyl phthalate, dimethyl phthalate and BHT were detected in the headspace of HS464 and HS458. In addition, acetic acid and toluene were detected in the headspace above HS464 and 2-ethyl-1-hexanol was emitted from HS458.

Differences in the chromatograms obtained may be attributed to the stability of the samples under investigation. For example propylene glycol, which was emitted from HS464 and HS458 after heating to 70 °C, had previously been reported as a result of polyether polyol breakdown during photo degradation [22]. Although neither sample studied here had been artificially degraded, it is proposed that they had been degrading naturally resulting in the release of propylene glycol (which has very low volatility) on heating. For example, the foam sample HS458, which was originally pink in colour had discoloured on the outer edge of the foam possibly due to previous photo-oxidation processes. It should be noted the sample of foam tested was not discoloured, demonstrating that even though the sample of foam looked to be in good condition, examination of the emission data suggests on-going degradation due to the presence of breakdown products such as propylene glycol. In combination, these results suggest that to identify polyurethane samples in field studies reference chromatographic data must be obtained from samples held at 23 °C as heating to 70 °C results in alteration of the samples' emission profile. However even if data is collected at 23 °C it will be extremely difficult to use emission data to identify polyurethane samples as there were no assignable VOC combinations; thus no specific VOC markers could be identified.

After accelerated photo degradation sample HS69 had yellowed, HS86 had yellowed and become friable, HS461 had become friable, HS458 had completely disintegrated and HS464 had no visual signs of degradation. On examination of the emission chromatograms

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the large abundance of VOCs which overlapped significantly made compound identification difficult (see Fig. 2); however some assignments were made. Sample HS69 emitted propylene glycol, dipropylene glycol, triethylene glycol and hexaethylene glycol dimethyl ether were detected. Previously [11] it was suggested that the presence of glycol derivatives indicated an ether based polyurethane, however the sample analysed here was identified by ATR-FTIR spectroscopy as an ester based polyurethane. Care should be taken when assigning glycol derivatives to the ether or ester form of polyurethane. Acetic acid, propylene glycol, 1,2-dimethyl hydrazine, propyl hydrazine and dipropylene glycol monomethyl ether were emitted by HS86. To the authors' knowledge, hydrazine compounds have not been detected in the emissions of historic polyurethanes before, however such compounds are known to have been used in the production of polyurethane [23,24]. HS458 emitted acetic acid, 3-hydroxy butanone, 1-methylpropyl hydrazine and diethyl phthalate. The emissions of HS461 included acetic acid, propylene glycol, trimethylene glycol monomethyl ether, nonanal, dipropylene glycol monomethyl ether, hexaethylene glycol dimethyl ether and diethyl phthalate. Significantly, although there were no visual signs of degradation of sample HS464, its emissions indicated the presence of propylene glycol, 1,2-ethanediol diacetate, dipropylene glycol, hexaethylene glycol dimethyl ether and diethyl phthalate. Interestingly, emission data can be used to identify degraded polyurethanes as the glycol derivatives can be used as VOC markers.

3.1.3. *Cellulose acetate (CA) emissions*

A crumb brush (sample HS91), of approximate age 80 y old, had a very strong odour of acetic acid, had visual signs of discolouration and cracking. The moulded object was selected for use in this study because much of the previous CA research focused on the examination and stability of photographic films rather than moulded objects. In addition to this object, 4 thin sheets of transparent CA (samples HS474, HS475, HS476 and HS477), which ranged between 40 and 50 y old and looked to be in good condition with no discernible odour, were also studied. Despite the observed physical differences between these samples (age and condition) acetic acid vapour was, by far, shown to be the major emission product in the headspace of HS91 (see Fig. 3) and the second major component emitted from samples HS474 – HS477 at 23 °C. In addition to acetic acid, the headspaces above the CA thin sheets (HS474 – HS477) contained significant amounts of dimethyl and diethyl phthalate plasticisers and, to a lesser extent, the antioxidant BHT. The high relative abundance of plasticisers was expected since the sheets are highly flexible. CA has been the focus of many studies over the years and has been noted for the release of acetic acid vapour during degradation by the phenomenon commonly referred to as the 'vinegar syndrome' [25].

The chromatograms collected after samples were heated to 70 °C changed considerably with very broad plasticiser peaks dominating the chromatograms. Samples HS474 and HS477 emitted dimethyl and diethyl phthalate whereas samples HS475 and HS476 emitted mainly the diethyl phthalate plasticiser. Acetic acid vapour was still detected in the vapour phase but its relative abundance was considerably reduced compared to that in the headspace at 23 °C, and in much lower relative abundance to the detected plasticisers at 70 °C. There was a marked increase in the relative abundance of acetic acid, diethyl and dimethyl phthalate from the crumb brush, (sample HS91) after heating, with acetic acid being only marginally lower in relative abundance than the plasticisers. After heating no visual changes of any sample were observed by the naked eye that would alert conservators to the release of such large quantities of plasticisers. The results indicated that reference data needs to be collected at 23 °C otherwise the chromatograms would be dominated by peaks from plasticisers which would be present in much lower concentration in field chromatograms collected at room temperature. At 23 °C emission data could clearly differentiate cellulose acetate in objects with chromatograms indicating the presence of specific compounds acetic acid and phthalate esters.

After accelerated degradation it was noted that sample HS91 changed colour from pale pink to cream. The emissions of this sample were dominated by a high relative abundance of acetic acid, dimethyl phthalate and diethyl phthalate; though the emitted vapours did not appear to be as high in relative abundance when compared to the vapours emitted after heating to 70 °C. Other notable differences included the release of toluene and phenol after

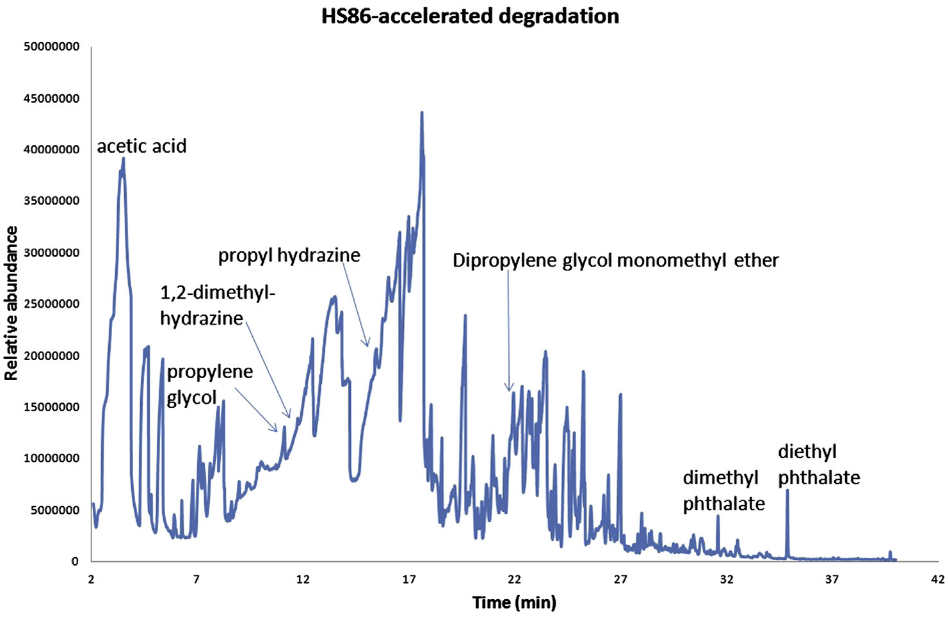

Fig. 2. Emissions from polyurethane sample HS86 after accelerated degradation.

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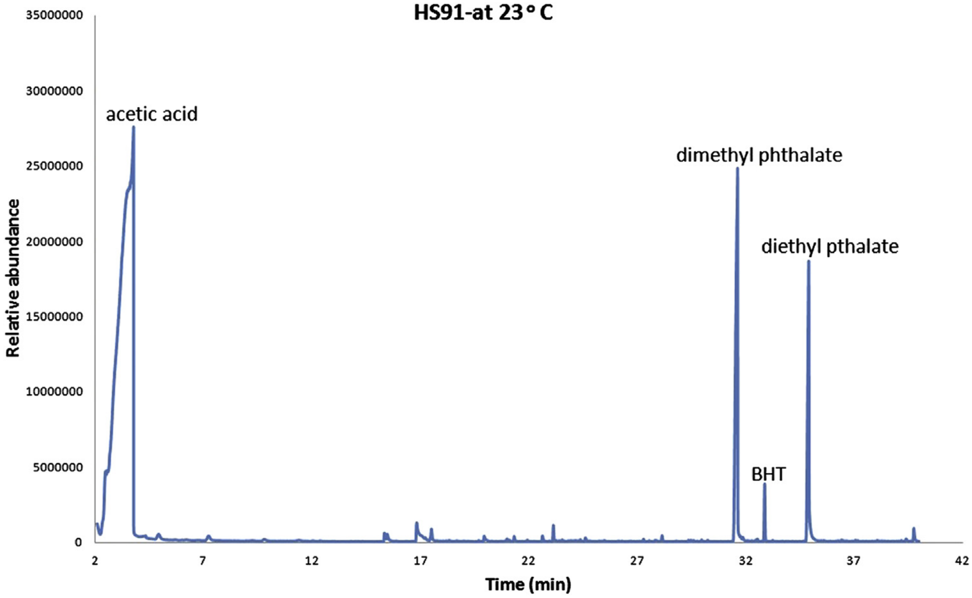

Fig. 3. Emissions from CA sample HS91 at 23 °C.

accelerated degradation. Phenol has reported to be an indicator of triphenyl phosphate (TPP) plasticiser breakdown [13] and this result was validated by analysis of the sample by nuclear magnetic resonance spectroscopy prior to accelerated degradation when the presence of TPP plasticiser was confirmed. The other CA thin sheet samples displayed no visual signs of deterioration after accelerated degradation although their emissions changed slightly with sample HS475 now joining HS474 and HS477 in emitting both diethyl and dimethyl phthalate. The emissions of sample HS476 remained unchanged after accelerated degradation. This sample was 10 y younger than the other thin sheet samples and could be more stable. CA formulations are known to contain several plasticisers [13,26] and from these results it was evident that Tenax-TA sampling tubes coupled to TD-GC-MS was a suitable method of collection for plasticiser emissions or their degradation products.

The relative abundance of acetic acid was most significant for the crumb brush (sample HS91) but it remained extremely low in comparison to emitted plasticiser for the CA thin films (samples HS474-HS477) regardless of whether the emissions were collected at 23 °C, 70 °C or after accelerated degradation. CA is known to degrade primarily via hydrolysis during which the acetate groups on the cellulose ring are replaced by hydroxyl groups generating the emission of acetic acid [25,27]. The differences in the emissions observed here were attributed to the stability of the CA samples. Sample HS91 was thought to be actively degrading and thus the hydrolytic reaction had already commenced releasing large quantities of acetic acid vapour. The liberation of phenol after accelerated degradation added further proof of chemical breakdown. In contrast the thin CA sheets (samples HS474 – HS477) appeared to be in good condition and this was supported by the emissions which demonstrated a low relative abundance of acetic acid. Since CA is known to be susceptible to hydrolysis photo degradation, as used in this study, was not expected to degrade these more stable CA samples.

3.1.4. *Cellulose nitrate emissions*

Camphor has traditionally been used as the plasticiser in cellulose nitrate formulations since it was developed in 1830s [18]. Although plasticisers are not generally considered to be specific to a particular polymer here there is an exception to the rule as camphor is considered to be an indicator of cellulose nitrate containing objects. However there is a caveat, as camphor was sometimes replaced with other plasticisers such as triphenyl phosphate or phthalates in the late 1930's [13,18,28]. As these plasticisers are used in many plastic formulations unfortunately they cannot be used as an indicator of cellulose nitrate. That said, the VOC emissions of the 3 cellulose nitrate samples studied here were dominated by camphor. In addition to this major emitted compound, sample HS270 emitted toluene, eucalyptol and borneol (see Fig. 4), sample HS271 emitted fenchone and sample HS248 also emitted borneol. It is therefore suggested here that the presence of camphor and the related terpenes could be used as key markers for the identification of cellulose nitrate as proposed previously [11].

After heating to 70 °C for 1 h the emissions remained relatively unchanged with the same major compounds being detected in the headspace above each sample. One minor change was the detection of diethyl phthalate in all 3 samples, which was large in relation to the previously monitored volatiles. There was no visual change in the samples even though the relative abundance of emitted compounds had increased after heating. It is therefore proposed that the emissions of cellulose nitrate can be used to unambiguously identify the polymer at 23 °C with no requirement for sample heating. Indeed, as it is also possible that heating the sample to 70 °C could encourage sublimation of camphor, leading to the development of gaps between the polymer chains allowing water to ingress and initiate hydrolysis, measurement of cellulose nitrate samples at 23 °C is strongly recommended.

After accelerated degradation, none of the samples showed any visual signs of deterioration. Interestingly the emissions from all samples were reduced when compared to data collected at 23 °C. Samples HS270 and HS271 displayed a significant increase in the relative abundance of diethyl phthalate plasticiser (compared to camphor) which could be problematic as the polymer becomes brittle and vulnerable to degradation when plasticiser is lost [29] [13,30]. Although there was no observable crazing of samples after accelerated degradation, the high relative abundance of phthalate plasticisers measured confirmed that degradation processes had been initiated (potentially due to nitrate ester cleavage) [13,18]. Should emission data be collected from degrading cellulose nitrate samples the presence of high amounts of diethyl phthalate could be used as an 'early warning' indicator of cellulose nitrate

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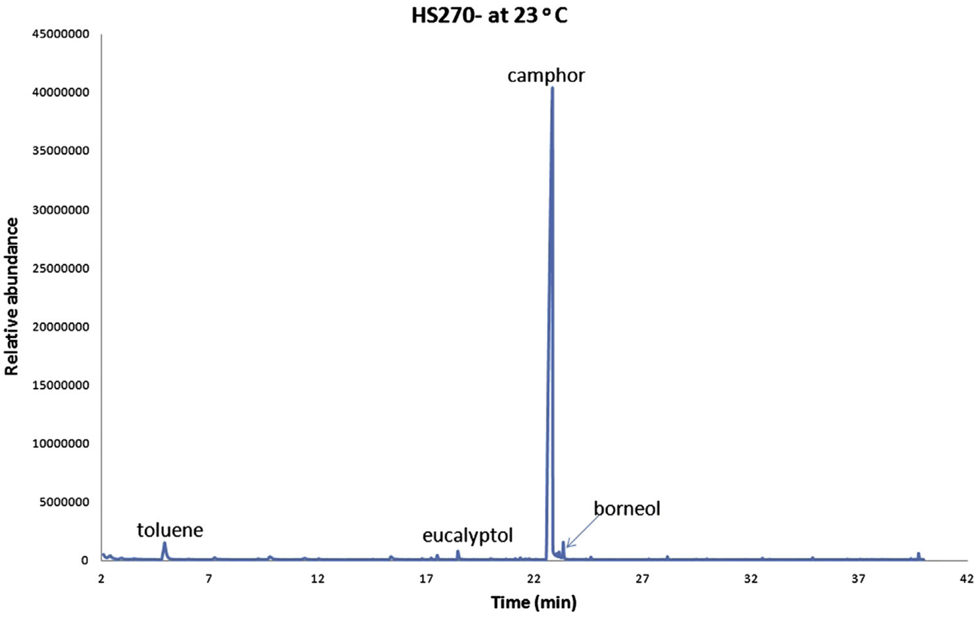

Fig. 4. Emissions from cellulose nitrate sample HS270 at 23 °C.

breakdown prior to any observable visual change to the object. It should also be noted that NO_x vapours are emitted from cellulose nitrate samples and although not detected here using this method of determination, these vapours could also act as indicators for cellulose nitrate objects.

3.1.5. *Polyethylene emissions*

The main components measured in the VOC emissions at 23 °C for the 5 polyethylene samples were linear alkanes with samples HS404, HS417 and HS463 emitting benzaldehyde, nonanal, tridecane and decanal; sample HS80 emitting BHT, tetrachloroethylene, benzaldehyde, undecane and nonanal; and lower concentrations of tridecane, decanal and toluene detected above sample HS459. Diethyl phthalate plasticiser was identified in all 5 samples. The VOC emissions were of very low relative abundance; however they can be used to positively identify polyethylene at 23 °C.

After heating to 70 °C there was an increase in the number and the relative abundance of volatiles measured in the emissions with samples HS80, HS404, HS417, HS459 and HS463 emitting tetradecane, tridecane and nonanal. In addition to these three major compounds HS404 and HS463 emitted dodecane and decanal, HS80 emitted undecane and hexadecane and HS417 emitted heptadecane. Diethyl phthalate plasticiser was once again identified in all 5 samples with the addition of dimethyl phthalate in sample HS417 and 2-ethyl-1-hexanol in samples HS404 and HS459. There appears to be no advantage to heating samples prior to the collection of emitted volatiles.

There were no visual signs of deterioration after accelerated degradation and the emissions remained relatively unchanged, with samples HS80 (see Fig. 5), HS404, HS417 and HS463 emitting tridecane, tetradecane and diethyl phthalate. In addition to these 3 major compounds heptadecane was emitted from HS404 and HS463, pentadecane was emitted from HS80 and HS463 and dodecane from HS80 and HS404. 2-ethyl-1-hexanol was detected in HS404 and HS459. In addition, the aldehydes nonanal and decanal were major emitted compounds in HS404, HS417, HS463 and HS459.

However one key change was the presence of 2-ethyl-1-hexanol, in samples HS404 and HS459 (at 70 °C and after accelerated degradation). This compound is a breakdown product of the plasticiser di-2-ethylhexyl phthalate (DEHP) [11]. The method used in this study did not permit the detection of DEHP plasticiser by GC–MS analysis, but the presence of 2-ethyl-1-hexanol suggests that DEHP was used in these two polymer samples and that it had begun to breakdown. Should emission data from polyethylene samples contain this peak this would provide a warning that breakdown of the plasticiser in the object is, or has, taken place.

3.1.6. *Polypropylene emissions*

At 23 °C the polypropylene samples produced emissions containing vapours at relatively low abundance. The major compound emitted by HS403, HS400 and HS416 was 2,2,4,6,6-pentamethylheptane. In addition, 2,6-dimethyl undecane and 3,5-dimethyl octane were detected in the headspace above sample HS400, 2,5-dimethyl hexane was emitted from sample HS416 and 2,4-dimethyl heptane was emitted from sample HS444. In contrast, the emissions of sample HS77 did not contain any branched alkanes, however non-specific VOCs (benzaldehyde, toluene, benzoic acid and acetophenone) of very low relative abundance were identified.

After heating branched alkanes remained the dominant compounds in the emission data with samples HS403, HS400 and HS416 emitting 2,2,4,6,6-pentamethyl-heptane, 2,2,4,4-tetramethyl octane. In addition, sample HS403 emitted 2,6-dimethyl undecane, 2,2,4-trimethyl hexane, 2,6,11-trimethyl dodecane and BHT, sample HS400 emitted 3,5-dimethyl octane, 2,3,6-trimethyl decane and BHT, sample HS444 emitted 3,6-dimethyl decane, 2,3,6-trimethyl decane, 5-ethyl-2methyl octane, octadecane and 4-methyl octane (see Fig. 6). The compounds detected in the vapour phase of sample HS77 were once again of low relative abundance with pentadecane, 2,4-dimethyl-1-heptene and 2,4-dimethyl heptane detected. Of the samples analysed here, 4 out of the 5 did not require heating to 70 °C as the detection of branched alkanes at 23 °C would be enough to positively identify polypropylene. However, sample HS77 did not emit any branched alkanes until it was heated to 70 °C.

Although there were no visual signs of deterioration after accelerated degradation the emissions from each sample changed with an overall decrease in the number and relative abundance of branched

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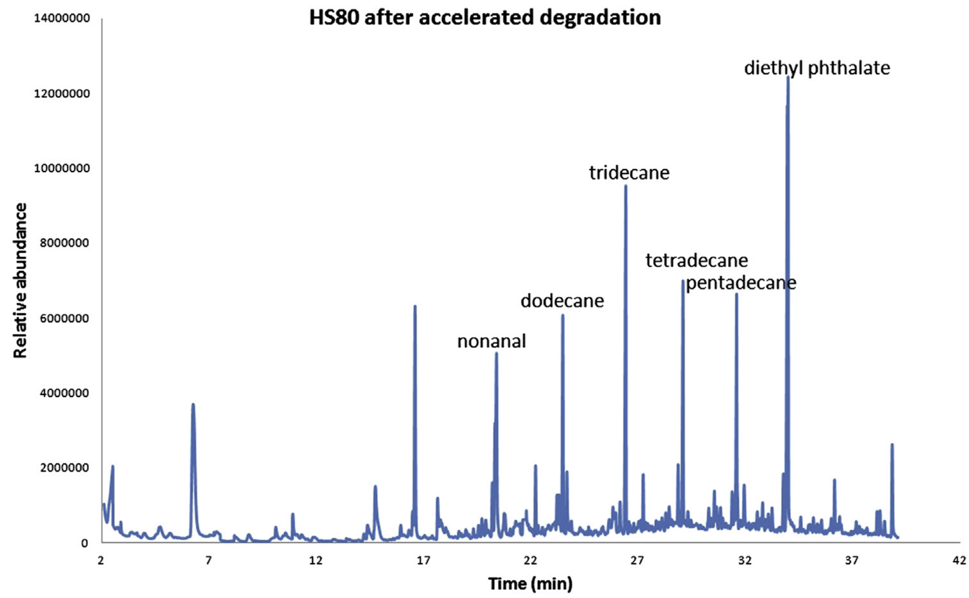

Fig. 5. Emissions from polyethylene sample HS80 after accelerated degradation.

alkanes measured. 2,2,4,6,6-pentamethyl heptane remained the dominant compound detected above samples HS400, HS403 and HS416. In addition to this dominant compound samples HS400, HS416 and HS444 emitted diethyl phthalate and dimethyl phthalate; sample HS403 also emitted 2,5,9-trimethyl decane, diethyl phthalate and dimethyl phthalate and sample HS444 emitted 4-ethyl decane. The large number of branched alkanes measured in the emissions was expected and can be used to give a tentative confirmation of polypropylene-based objects. However it should be noted that polybutylene will also produce branched alkane emissions and care would need to be taken to differentiate between polypropylene and other polyolefins, with the exception of polyethylene.

3.1.7. Rubber emissions

Of the 3 rubber samples analysed one looked to be in relatively good condition (sample HS103), whilst the cracked appearance of samples HS268 and HS269 suggested that they were in an advanced state of degradation. At 23 °C sample HS103 produced low emissions but acetic acid and tridecane were detected in the headspace. The headspace above sample HS268 was dominated by acetic acid, 4-hydroxy-2-butanone and 5-ethyldihydro-5-methyl-2(3H)-furanone. Sample HS269 emitted acetic acid, 2-butanone and 5-ethyldihydro-5-methyl-2(3H)-furanone. It has previously been reported that furan derivatives are used to control the stereo specificity of synthetic rubber [31]. Large amounts of acetic acid were detected from the rubber samples which could have been present as residual acid used during the manufacturing process [32–34]. Overall, the presence of both acetic acid and furan derivatives in high concentration can be used to identify rubber (whereas, as shown previously, high relative abundance of acetic acid together with the presence of plasticisers could be used to identify CA-based objects).

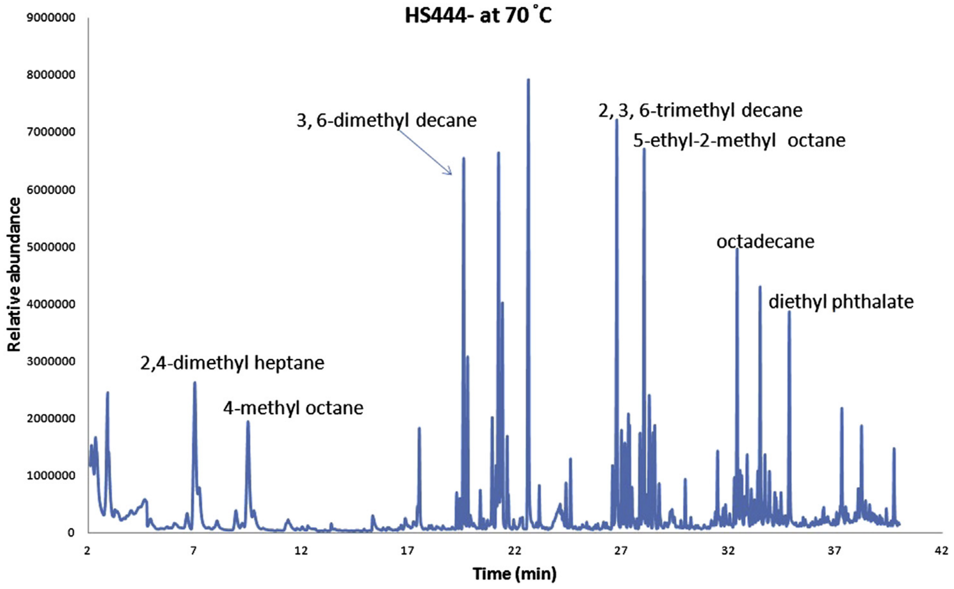

Fig. 6. Emissions from polypropylene sample HS444 after heating to 70 °C.

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After the samples were heated to 70 °C, the relative abundance of VOCs emitted by sample HS103 remained low; with acetic acid and toluene being the only compounds detected. Sample HS268 emitted acetic acid, toluene, 3-hydroxy-2-butanone, 4-hydroxy-2-butanone, dihydro-5-methyl-2(3H)-furanone, 3-methyl-2-heptanone, 2,5-hexandione and 2-acetyl-5-methyl furan whereas sample HS269 emitted acetic acid, toluene, 4-hydroxy-2-butanone, 3-methyl-2-heptanone, 2-acetyl-5-methyl furan, dodecane, tridecane and tetradecane. The data suggested that, once again, 23 °C would be the most appropriate temperature to measure reference chromatograms.

After accelerated degradation, samples HS103 and HS268 had no visual signs of deterioration; however sample HS269 had reduced flexibility and had become friable. The emissions did alter for sample HS268 (see Fig. 7) which contained acetic acid, 4-hydroxy-2-butanone, dihydro-5-methyl-2(3H)-furanone, 5-methyl-2(3H)-furanone, 2-acetyl-5-methyl furan, nonanal and decanal. Interestingly although the appearance of sample HS269 changed dramatically the same major compounds were recorded in the emissions with one exception that the linear alkanes were no longer detected, further work is required to understand why a large change in the physical appearance of the sample did not invoke a larger change in the emissions.

3.1.8. *Poly (vinyl chloride) emissions*

The emissions obtained from all 5 PVC-containing samples at 23 °C contained mostly non-specific VOCs which were present in the headspace above many of the measured polymer types. It was suggested that the emissions could not be used to identify PVC-containing objects. Samples HS424 and HS430 generated emissions which contained a low abundance of VOCs, although it was possible to identify some of the emitted compounds. Sample HS424 released BHT, diethyl phthalate, decanal, nonanal, benzaldehyde, styrene, 1,3 dimethyl benzene and ethylbenzene. Sample HS430 released 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) plasticiser, acetophenone, decanal, nonanal, tridecane and BHT. 2-ethyl-1-hexanol, the breakdown product of DEHP plasticiser, was detected above sample HS62 and HS468 as were decanal, nonanal and diethyl phthalate. In addition phenol was detected above sample HS62 and benzaldehyde above sample HS468. Sample HS415 emitted styrene, diethyl phthalate, tridecane, dimethyl phthalate, benzaldehyde and BHT.

Significant changes in emissions were noted after the samples were heated to 70 °C. HS424 continued to be dominated with low abundance peaks although it was possible to identify benzene, nonanal, decanal, diethyl phthalate, phenol, toluene, nonanoic acid, decanoic acid and isothiocyanato benzene. After heating, the headspace of HS430 was dominated by TXIB plasticiser and toluene. In addition dimethyl phthalate, BHT, tridecane, decanal, nonanal and phenol were also detected. Sample HS62 was dominated by 2-ethyl-1-hexanol, phenol, 1-octanol, dodecane, diethyl phthalate and BHT. Sample HS468 remained dominated by 2-ethyl-1-hexanol and diethyl phthalate with dimethyl phthalate, decanal, nonanal, cumene and styrene also present. Sample HS415 was dominated by diethyl phthalate, toluene, dimethyl phthalate, BHT, nonanal, styrene and tridecane.

After accelerated degradation, sample HS62 demonstrated visual signs of yellowing. The emissions for this sample were dominated by 2-ethyl-1-hexanol, octane, phenol and diethyl phthalate. 1-chloro-octane was also detected, which was not detected in any of the previously collected emissions. The emissions from sample HS415 were dominated by 2-ethyl-1-hexanol, nonanal, decanal and diethyl phthalate whereas the sample HS424 contained nonanal, decanal, diethyl phthalate, dimethyl phthalate and isothiocyanato benzene. Sample HS430 contained nonanal, decanal, diethyl phthalate, dimethyl phthalate, 2-ethyl-1-hexanol and benzaldehyde (see Fig. 8). The headspace above sample HS468 contained compounds of low abundance including nonanal, decanal, 2-ethyl-1-hexanol, diethyl phthalate and dimethyl phthalate.

3.1.9. *Polycarbonate emissions*

As expected, the polycarbonate samples emitted very low levels of vapours with low relative abundances of benzaldehyde, acetophenone and BHT measured in the headspace above samples HS52, HS143, HS413 and HS467. In addition to these 3 compounds sample HS143 emitted diethyl phthalate plasticiser, sample HS413 emitted nonanal and decanal and sample HS467 emitted acetic acid. As an example see Fig. 9 which illustrates the emissions from HS413.

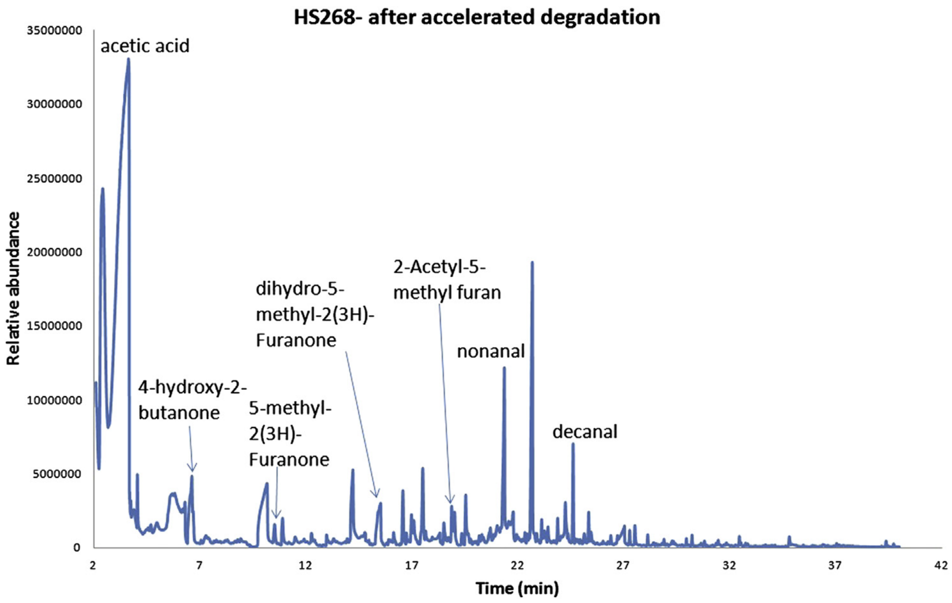

Fig. 7. Emissions from rubber sample HS268 after accelerated degradation.

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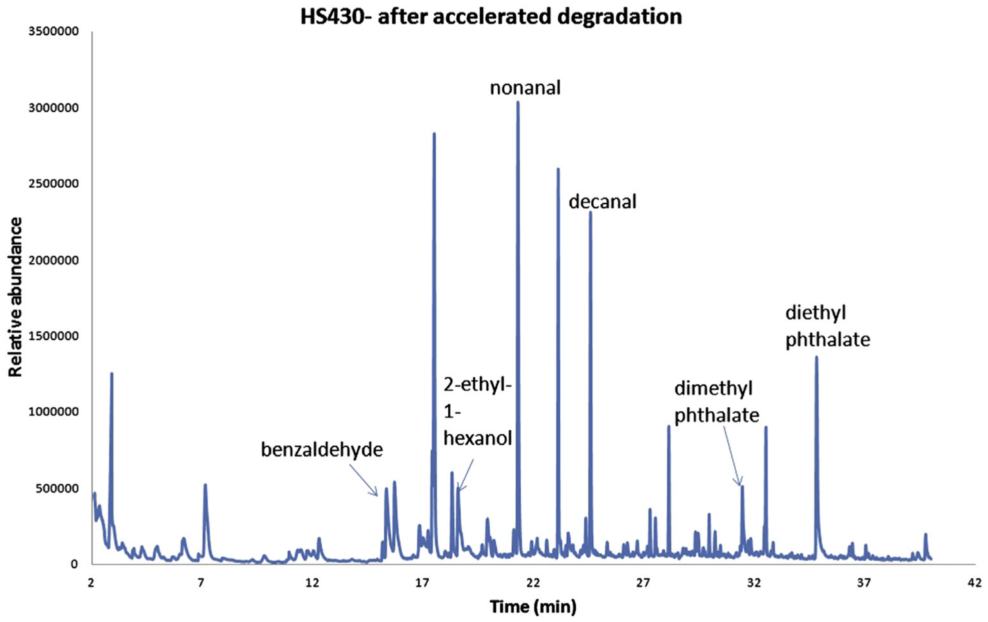

Fig. 8. Emissions from poly (vinyl chloride) sample HS430 after accelerated degradation.

There were no significant alterations of the emissions after heating with samples HS467, HS413, HS466 and HS143 displaying low abundance peaks for acetic acid, toluene and diethyl phthalate. In addition to these compounds samples HS467 and HS413 emitted styrene and nonanal and sample HS466 emitted phenol and decanal, whereas sample HS52 emitted phenol and diethyl phthalate. After accelerated degradation there were no visual signs of deterioration on any of the samples and once again emissions were low with samples HS52, HS143, HS413, HS466 and HS467 emitting nonanal, decanal, dimethyl phthalate and diethyl phthalate. In addition to these compounds the chromatograph of the headspace above sample HS52 contained phenol and octanal and sample HS413 contained benzene.

As the compounds detected at 23 °C, at 70 °C and after accelerated degradation are non-specific compounds found in the headspace above a variety of polymers it was noted that emission data could not be used as indicative markers of polycarbonate.

3.2. *Case study of museum objects*

The emissions from the measurement ruler (see Fig. 10) were dominated by a large relative abundance of camphor and 1,7,7-trimethyl-bicyclo[2.2.2]heptane-2,5-dione, fenchone, borneol, tetrachloroethylene and toluene. As confirmed by the micro-chamber emission experiments, the presence of camphor and other related terpenoids allowed the unambiguous identification of this sample as cellulose nitrate. The extremely high relative abundance of these compounds demonstrated that the object was actively degrading (although this was evident by observation alone).

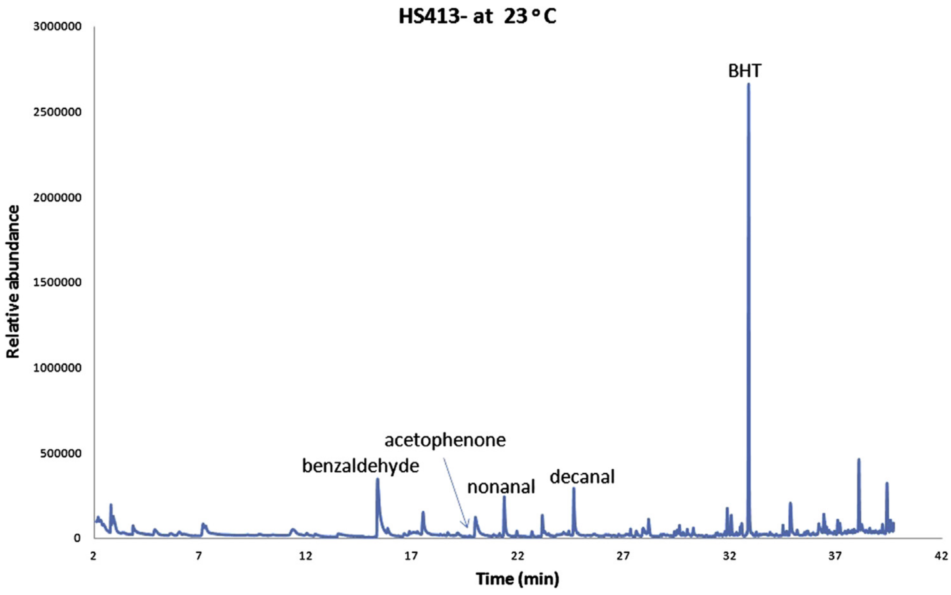

Fig. 9. Emissions from polycarbonate sample HS413 at 23 °C.

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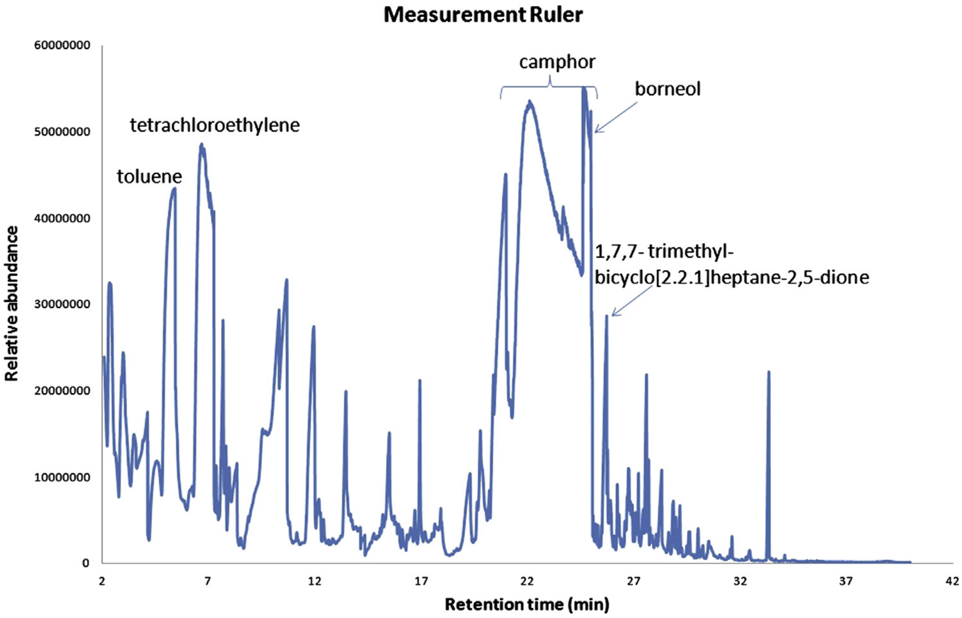

Fig. 10. Emissions from the measurement ruler.

The photographic negatives demonstrated a large relative abundance of acetic acid, tetrachloroethylene and phenol in addition to 2-ethyl-1-hexanol and triethyl phosphate (see Fig. 11). The high relative abundance of acetic acid together with the plasticiser breakdown products allowed a positive identification of this material as cellulose acetate. In addition to the non-invasive and unambiguous identification of polymer type, the presence of phenol and 2-ethyl-1-hexanol confirmed that TPP and DEHP plasticisers were used during the production of these negatives.

Emissions from a crystal box which appeared to be in good condition were also sampled. The vapour phase was dominated by tetrachloroethylene, styrene and 3,3-bis(1,1-dimethylethyl)-phenol. Although tetrachloroethylene was the largest peak observed, being a dominant peak the presence of styrene was indication enough that the box was a styrenic polymer. The emissions from the crystal box are given in Fig. 12.

The results of the museum object case studies clearly support the laboratory results and validate the use of Tenax-TA-TD-GC-MS as a robust, non-invasive method of determination of objects containing cellulose nitrate, cellulose acetate or styrene. During analyses the objects were not sampled nor where they 'touched' by small probes, IR light or lasers. In addition to polymer identification it was also possible to obtain further information about the objects such as the types of plasticiser used during production or the addition of further treatments. Here tetrachloroethylene was measured in the headspace above all 3 heritage objects (note it was not present in blank Tenax-TA sampling tubes). The exact function of tetrachloroethylene in polymer formulations was not clear to the

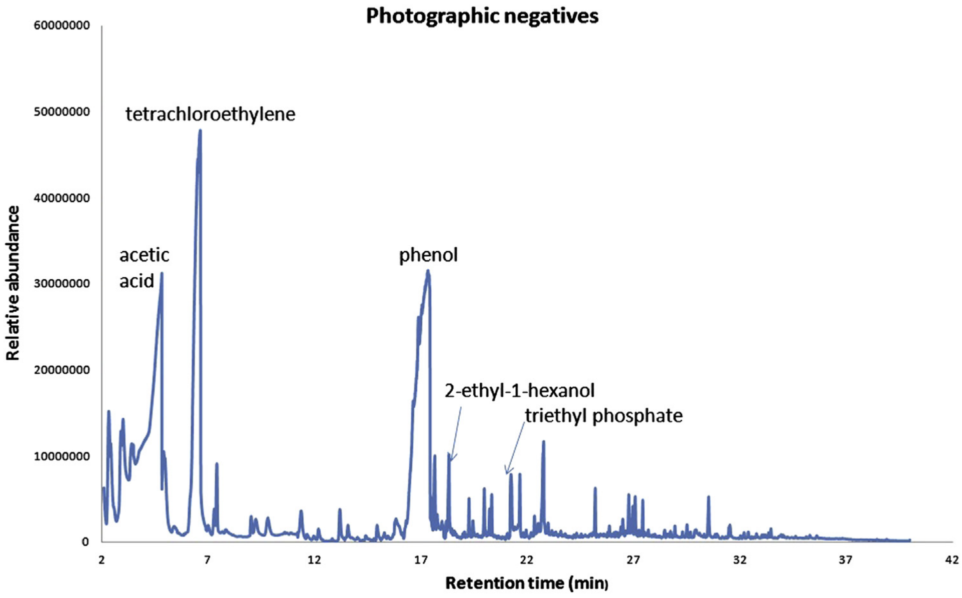

Fig. 11. Emissions of photographic negatives.

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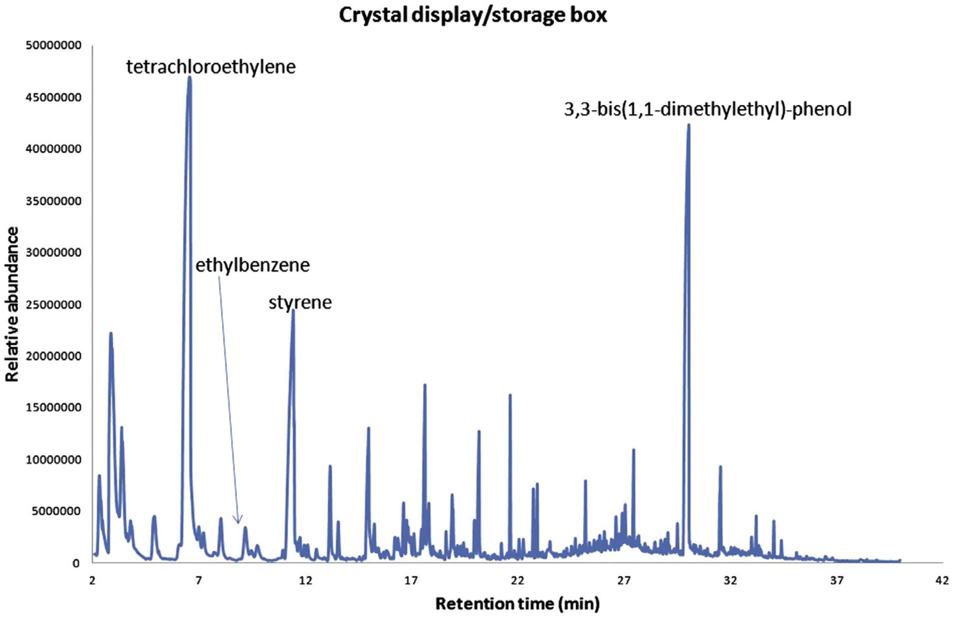

Fig. 12. Emissions from crystal box.

authors, although it was suspected that it could have been used as a solvent during the plastic manufacturing process.

4. Conclusions

This study strongly supports the application of Tenax-TA-TD-GC-MS as an in-situ, non-invasive sampling method for the analysis of emitted vapours from plastic objects. As the Tenax-TA adsorbent is held in a stainless steel housing unit it can be posted by mail to and from sampling sites (this was the method of shipping used to collect vapours above the museum objects studied here).

Although the vapours collected above the headspace of PVC or polycarbonate samples were labelled ‘non-specific’ and could not be used to positively identify these polymer types it was clearly demonstrated that inferential VOCs can be used to detect cellulose acetate, polyurethane, cellulose nitrate, rubber, polyethylene, polypropylene and styrenic based polymers objects at 23 °C. There appeared to be no advantage of heating samples to 70 °C prior to emission collection and VOC collection at 23 °C is recommended based on the assessment of polymer fragments in the micro-chamber. In this way the collected data can be compared with the emissions of objects studied in-situ in heritage environments, which will undoubtedly be collected at room temperature. The accelerated degradation studies represent the first attempt to artificially degrade samples and then assess alterations to emissions using Tenax-TA-TD-GC-MS. Differences were observed and could be explained. This proof of concept study provides strong evidence that inferential measurement of polymer stability is possible. However further work would be required before emissions can be used to accurately assess the stability, or stage of deterioration, of plastic objects.

Acknowledgements

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Investigation of long term storage solutions for rubber garments

Keywords
rubber; cotton; acetic acid; anoxia; volatile organic compounds (VOCs); MicroChamber®

Introduction

A collection of eight Mexican rubberised garments intended as rain-proof horse-riding gear and acquired new from markets in Mexico in the late 1980s was investigated in order to assess conservation treatment options, to improve their long term storage and to investigate the origin of the strong odour associated with the garments. The garments were made from cotton calico which had been coated with rubber latex on the outer side. The rubber coating was yellow or red in colour and decorated with darker brown geometric designs and outlines of horses (Fig. 1).

The garments were emitting a powerful, unpleasant odour which was the motivation for this investigation. It was feared that the off-gassing could be harmful to the objects themselves as well as to other objects in the vicinity and the staff working in the British Museum Textile Centre, where the eight garments were housed in a single storage drawer.

Natural rubber and the production of rubberised textiles[1]

Nearly 500 different species of plants produce an exudate of latex from which natural rubber can be obtained, but the main commercial source is the rubber tree (*Hevea brasiliensis*). Fresh latex is an aqueous dispersion that will coagulate and dry into a soft rubber if exposed to air. Rubber was processed and utilised in Mesoamerica millennia before the Europeans arrived.[2] It became a curiosity import product in Europe from the sixteenth century onwards and during the nineteenth century evolved into a vast global industry with a multitude of sophisticated processing routes.

The early European and North American commercial ventures in rubber technology centred around the production of rubberised textiles, in particular by Charles Macintosh and Thomas Hancock in Manchester (1820s), Luke Baldwin and Edward Chafee in Roxbury, Massachusetts (1830s) and Nathaniel Hayward and Charles Goodyear, also based in Massachusetts, who are both credited with the invention of vulcanisation in the late 1830s. Charles Macintosh pioneered the waterproofing of textiles with a solution of liquid rubber solubilised in coal tar naphtha. However, the resulting fabrics were fraught with problems such as stickiness, degradation at high summer temperatures and embrittlement at low winter temperatures. Edward Chaffee in Roxbury tried to improve the production of rubber coated textiles by masticating (mechanically working or kneading) the rubber and calendering it onto textiles under high pressure. It was not until the invention of vulcanisation, however, that the severe problems could really be solved.

In more recent commercial use, for ease of handling and transportation fresh latex is usually coagulated and precipitated with the addition of

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[1] F.W. Billmeyer Jr, 'Natural Rubber and Other Polyisoprenes', in *Textbook of Polymer Science* (New York: John Wiley & Sons, Inc., 1962), 378–83; W.J. Roff and J.R. Scott, 'Section 29. Natural Rubber', in *Fibres, Films, Plastics and Rubbers. Handbook of Common Polymers* (London: Butterworths, 1971), 313–41; J.L. White, 'Chapter 3.4 Overview of the Development of Rubber Fabrication Industry and Processing Technology', in *Rubber Processing, Technology—Materials—Principles* (München: Carl Hanser Verlag, 1995), 48–54.

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Fig. 1 Examples of Mexican rubber garments. From top left to bottom right: trousers Am1988,08.670.b; trousers Am1986,07.234.b (inside out detail); trousers Am1988,08.671.a; rain cape Am1986,07.234.a (detail of design); jacket Am1988,08.671.b; rain cape Am1988,08.670.a. © Trustees of the British Museum.

acetic acid (or more recently formic acid[3]) and formed into sheets. Such rubber sheets can then be masticated mechanically and compounded (mixed) with additives such as surfactants, fillers, vulcanising agents, protective agents, colourants, softeners and lubricants to produce rubbers of any desired consistency. Such reprocessed coagulated rubbers are then ready for further processing and formation by spreading, dipping or calendering (for example for rubber sheeting or coated textiles) and foaming or moulding for shaped rubber goods. The final step is usually curing, sometimes at elevated temperatures or under steam, to allow the vulcanisation agents to react with the rubber polymer (*cis*-1,4-polyisoprene) and form cross-links between polymer chains. Vulcanisation dramatically improves the properties of natural rubber by decreasing its flow and increasing its tensile strength. Vulcanisation can also alter properties such as elasticity, stickiness and resistance to solvents, heat and low temperatures. The most common vulcanising agent is sulfur.

The rubberised garments investigated in this study were not made industrially. Whilst the British Museum curator who acquired the garments did not see the process, she was told at the time of purchase that the calico was stretched on a frame and latex or rubber applied, presumably with a brush. This implies the use of rubber in liquid form which can be commercially obtained either as a fresh latex dispersion stabilised with ammonia or as a reprocessed coagulated rubber. Following the coating of the calico, the rubber will have been cured and possibly vulcanised but there are no details of this final step occurring with these particular garments.

Condition of the rubberised garments and conservation treatment tests

The majority of the garments were stored folded, some with sharp creases and one pair of trousers was stored inside out so that the design area was

[3] BASF The Chemical Company, 'Latex Coagulation with Formic Acid from BASF', 2013, http://www.intermediates.basf.com/chemicals/formic-acid/latex-coagulation (accessed 31 October 2013).

hidden (Fig. 1). The joins in the garments were predominantly adhered rather than stitched. Some exudate was noted coming from the adhesive. Most surfaces were covered in a white deposit that was identified by Fourier transform infrared (FTIR) spectroscopy as talc, which may have been applied to avoid the rubber surfaces from sticking during and after application of the liquid latex rubber coatings onto the cotton calico.[4]

There was a slight stickiness on the calico side of some garments, but otherwise the cotton calico appeared to be in good condition, showing no apparent discolouration. The rubber was in varying condition, from relatively good and flexible in the yellow areas to brittle and cracked in the dark areas, with fragments delaminating from some creased edges. It was unclear how the dark design areas were created; some areas appeared to be painted while in other areas the colouration was more integral to the rubber. The application of an iron-containing earth pigment could have been a possible explanation for the marked deterioration in the dark design areas since iron is known to increase the rate of oxidation of rubber. However, elemental analysis of samples from the dark design areas using scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis showed no difference in composition of samples from the yellow or red areas, indicating that the colouration was not created using inorganic pigments.[5] Another possibility might be localised heat application to create the designs by scorching the rubber; this would also result in highly oxidised dark areas. The elemental analysis did show the presence of sulfur in all samples, indicating that the rubber was vulcanised.

Preliminary conservation tests were undertaken as part of an examination and assessment of three of the Mexican rubberised garments following concerns over the strong smell they were emitting as well as their folded storage conditions. This included determining whether reshaping of the folded garments was possible using the gentle application of heat. A Leister Hot Air Blower with adjustable heat and air pressure was used to first test the effects of gentle heat on a rubber shoe from the Organic Artefacts Conservation Studio material handling collection, with the lowest possible settings. A gentle flow of warm air (measured at 30–40°C) was applied with continuous motion for one or two minutes at a time but not for more than five minutes in total. The tests indicated that the trial rubber object softened slightly and sufficiently to allow reshaping. The same low settings were then tested on a small area (of approximately 10 cm) along the inner surfaces of a crease in an area of yellow rubber on the upper part of one pair of trousers (Am1988,08.670b). After each application of gentle heat, the crease in the trousers was carefully manipulated and opened out by gradually padding along the line of the crease with a roll of acid-free tissue covered with silicone release Melinex. Using gentle heat application it therefore appeared possible to reduce some of the severe creases and reshape the rubber garments, in particular where the rubber was still relatively flexible and could be handled as shown in Fig. 2.

Fig. 2 Reshaping tests with gentle heat application using a Leister Hot Air Blower.

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[4] Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 6700 spectrometer with a Continuum IR microscope equipped with MCT/A detectors. The sample was analysed in transmission mode, flattened in a diamond micro-compression cell. The cell was opened and the flattened sample supported on one diamond window, a clean area of which was used for a background spectrum. The field of view was controlled by the sliding aperture which, when fully open, gives a maximum area of analysis of $150 \times 150 \mu m$. The spectrum was acquired over a range of 4000–650 cm^{-1} using 32 scans at a resolution of 4 cm^{-1} and automatic gain.

[5] Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis was carried out using a Hitachi S3700N Variable Pressure SEM equipped with an Oxford Instrument INCA EDX microanalysis system with an INCAx-act Silicon Drift Detector (SDD). The samples were analysed at 40 Pa pressure at a working distance of approximately 10 mm. The accelerating voltage was 20 kV. EDX spectra were collected for 100s live time.

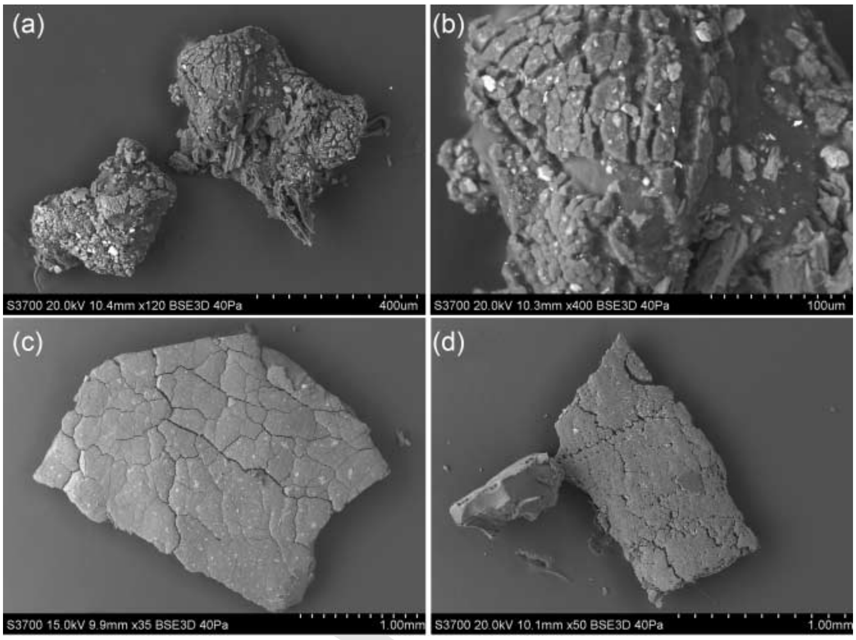

Fig. 3 SEM back-scattered electron images of samples from trousers Am1988,08.670.b: (a) and (b) yellow rubber samples; (c) black rubber sample; (d) dark brown rubber sample.

Rubber deterioration and emission of volatile organic compounds (VOCs)

Rubber in an indoor environment deteriorates primarily by oxidation leading to embrittlement and the formation of cracks on exposed surfaces.[6] Scanning electron microscopy (SEM) can be used to examine the topography of the material revealing the extent of deterioration. In the micrographs shown in Fig. 3 (a and b), a sample of yellow rubber deemed to be in good visual condition clearly revealed a degraded cracked surface layer that had been pulled apart by the still elastic rubber matrix below. In addition, in Fig. 3 (c and d), the micrographs of embrittled samples of black and brown rubber were shown to have deep surface cracks, pitting and sharp break edges indicating a severe loss of elasticity.

Oxidation of rubber is marked by an increase in carbonyl, hydroxyl and hydroperoxide groups, and a loss of unsaturation in the *cis*-1,4-polyisoprene polymer chains. This molecular change was confirmed by examination of the FTIR spectra of rubber samples from areas in varying condition, including the still flexible yellow and red rubber areas versus the brittle brown and black areas (Fig. 4). The results were in keeping with published FTIR data on degrading *cis*-1,4-polyisoprene.[7]

The mal-odour of rubbers of different qualities is mainly attributed to low molecular weight volatile fatty acids such as acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid and valeric acid.[8] A study investigating the VOCs from rubber artefacts in the British Museum collection also found acetic acid as a major emission product.[9] In addition, both studies identified a variety of nitrogen and sulfur-containing aromatic and aliphatic VOCs.[10]

The odour of the Mexican rubber garments studied here was typical of rubber and acetic acid but also included unidentifiable pungent notes. Initial acid detection tests were carried out using A-D strips® sealed in polyethylene enclosures with the garments. Their rapid discolouration from blue to green and yellow confirmed the off-gassing of volatile acids. The VOCs and other volatile chemicals emitted by the garments were

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[6] Robert W. Keller, ‘Oxidation and Ozonation of Rubber’, *Rubber Chemistry and Technology* 58, no. 3 (1985): 637–52.

[7] Gemma Mitchell, Fenella France, Alison Nordon, Pik Leung Tang and Lorraine T. Gibson, ‘Assessment of Historical Polymers Using Attenuated Total Reflectance-Fourier Transform Infra-Red Spectroscopy with Principal Component Analysis’, *Heritage Science* 1, no. 28 (2013), http://www.heritagesciencejournal.com/content/1/1/28 (accessed 3 December 2013); Francisco Helder A. Rodrigues, Judith P.A. Feitosa, Nágila M.P.S. Ricardo, Francisco Célio F. de França and José Oswaldo B. Carioca, ‘Antioxidant Activity of Cashew Nut Shell Liquid (CNSL) Derivatives in the Thermal Oxidation

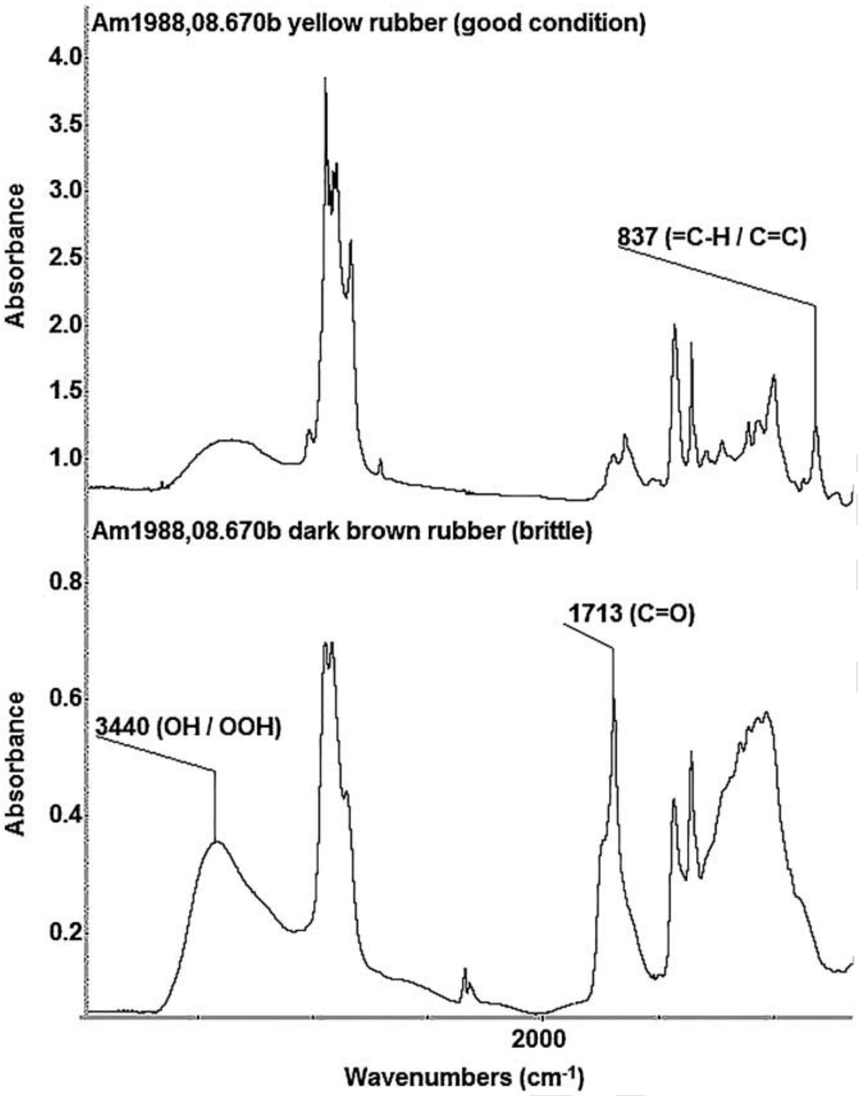

Fig. 4 FTIR spectra of rubber samples in varying condition from trousers Am1988,08.670.b.

further investigated with the aid of passive sampling diffusion tubes and subsequent chromatographic analysis.[11] Aldehydes were trapped in 2,4-dinitrophenylhydrazine (DNPH) diffusion tubes and the resulting hydrazone measured using high performance liquid chromatography (HPLC).[12] Acetic and formic acids were trapped in potassium hydroxide diffusion tubes and the resulting formates and acetates quantified using ion chromatography (IC).[13] The trapping agent in the VOC diffusion tubes was poly(2,6-diphenylphenylene oxide), commercially known as Tenax. The use of Tenax in the trapping and analysis of VOCs is well documented, as its high surface area, low affinity for water and high thermal stability make it ideal for this purpose.[14] The trapped VOCs were measured using thermal desorption gas chromatography mass spectrometry (TD-GC-MS).[15]

1 Off-gassing test set-up: measurements of aldehydes, acids and VOCs around rubber garments in ambient conditions

In order to determine the VOCs and other volatiles emitted from the garments under ambient conditions, in May and June 2012 two of the rubber garments (trousers Am1988,08.670.b and rain cape Am1988,08.672) were

of Synthetic *cis*-1,4-Polyisoprene', *Journal of the Brazilian Chemical Society* 17, no. 2 (2006): 265–71.

[8] Vipavee P. Hoven, Kesinee Rattanakaran and Yasuyuki Tanaka, 'Determination of Chemical Components that Cause Mal-odour from Natural Rubber', *Rubber Chemistry and Technology* 76, no. 5 (2003): 1128–44.

[9] Joanne Dyer, Clare Ward, Nicole Rode, Marei Hacke and Yvonne Shashoua, 'Reassessment of Anoxic Storage of Ethnographic Rubber Objects', in *Preprints ICOM-CC 16th Triennial Conference*, Lisbon, 19–23 September 2011, paper 0401: 1–10.

[10] Hoven, Rattanakaran and Tanaka, 'Determination of Chemical Components'; Dyer et al., 'Reassessment of Anoxic Storage'.

placed in two separate enclosures along with diffusion tubes suitable for the trapping of aldehydes, acids and separate sampling tubes for the sampling of VOCs.

The enclosures were created using heat-sealed polyethylene film and the sampling duration was 25 days at 18–22°C and 34–64% relative humidity (RH).[16] To provide comparative background measurements, the environment in the Special Projects Room in the Organic Artefact Conservation Studio, where the garments were stored during the conservation tests, and in the corridor outside that room were also studied. For this initial screening of the VOCs emitted, it was of interest to determine the range of VOCs emitted rather than attempt a quantitative analysis and the decision was made to use cheap and readily available polyethylene for the enclosures despite its known gas permeability.

The aldehyde tubes, targeting formaldehyde in particular, indicated very low emission of formaldehyde from the sampled rubber garments (Table 1). Acid emissions, in particular of acetic acid, were extremely high for both garments, with concentrations around 6000 μgm^{-3} (Table 2).

The results from the VOCs' sampling tubes indicated that tetrachloroethylene, alkanes, methyl- and dimethylalkanes, cyclosiloxanes and benzoic acid were present at varying levels in both the background samples as well as the object enclosures. Table 3 summarises the VOCs detected in each of the sampling locations, giving their concentration in μgm^{-3}. Typical gas chromatograms obtained from the background samples and from the enclosures containing the rubber garments are shown in Fig. 5.

In the corridor areas, the most significant VOCs were found to be alkanes, isoalkanes and tetrachloroethylene. Alkanes and isoalkanes are typically generated by building materials such as synthetic resins, paints and residual solvents. The source of the tetrachloroethylene could not be identified, but the concentration detected was significantly below the European Union time-weighted average workplace exposure limit (EU TWA WEL) of 138mgm^{-3}.[17] Acetophenone, ethylbenzene and toluene were also detected. These substances are common VOCs emitted by cellulosic materials, and were likely to have been generated by natural ageing of materials in the sampling location.

No VOCs were detected in the enclosures that were not also present in the background samples and the majority of the compounds detected

Table 1 Concentration of formaldehyde in the sampled environments.

Sampling tube	Concentration of formaldehyde (μgm^{-3})
Corridor background	<LoD
Room background	<LoD
Rubber rain cape Am1988,08.672	52
Rubber trousers Am1988,08.670.b	8

Note: <LoD: below limit of detection.

Table 2 Concentrations of acetic acid and formic acid in the sampled environments.

Sampling tube	Concentration of acetic acid (μgm^{-3})	Concentration of formic acid (μgm^{-3})
Corridor background	<LoD	<LoD
Room background	214	337
Rubber rain cape Am1988,08.672	6543	1479
Rubber trousers Am1988,08.670.b	5815	2696

Note: <LoD: below limit of detection.

11 Iain D. Rushworth, Catherine Higgitt, Margaret Smith and Lorraine T. Gibson, 'Non-Invasive Multiresidue Screening Methods for the Determination of Pesticides in Heritage Collections', *Heritage Science* 2, no. 3 (2014), http://www.heritagesciencejournal.com/content/2/1/3 (accessed 18 February 2014); Gemma Mitchell, 'Title to be Confirmed By Author' (PhD thesis, Department of Pure and Applied Chemistry, University of Strathclyde, 2014 expected). AQ2

12 Aldehydes, such as formaldehyde, were trapped in diffusion tubes by reacting with a trapping solution. In this study 2,4-dinitrophenylhydrazine (2,4-DNPH) was used as the trapping reagent, converting trapped formaldehyde to the hydrazone derivative (F-DNPH). To extract the trapped analytes from the sampling tube, the filter paper (trap) was removed from the cap with tweezers and placed into a beaker (which had been pre-washed and cleaned with acetonitrile). To the beaker, 3 mL of acetonitrile (99.99%, Fisher Scientific, Loughborough) was added to extract the analytes. Next, an Acrodisc (13 mm, 0.2 μm Supor membrane, PALL Life Sciences, UK) was cleaned by flushing through with 3 mL of acetonitrile and consequently dried by pumping air through the Acrodisc for 1 minute. The syringe was then used to collect approximately 2 mL of the extracted solution of which the first 0.5 mL was disposed of to waste. The remaining portion of the extracted solution was passed through the Acrodisc into a small vial and the filtered solutions were analysed by a (Spectra Series P100) HPLC. An acetonitrile:-water eluent (30:70) was used at a flow rate of 1.5 mL.min^{-1}. A 100 mm column (4.6 mm i.d.) containing Microsorb MV 100-3 C8 stationary phase was used with a 50 μL sample loop and ultraviolet detection at 350 nm. The detector output signals were collected on a Spectra Physics SP4290 integrator. Prior to sample analyses, calibration curves were created using F-DNPH standard solutions at concentrations of 2, 8, 12, 16 or 20μg.mL^{-1}. The standards were prepared from a stock solution (1 mg.mL^{-1}) prepared by weighing accurately 10 mg of F-DNPH (99.9%, Supelco, Pennsylvania, USA) and dissolving in 50 mL acetonitrile using a volumetric flask. The calibration curves were used to quantify the results and determine the concentration of F-DNPH in each solution using linear least squares regression analysis. The concentration of aldehydes in the sampled environment around each object was then calculated using Fick's

Table 3 Summary of VOCs detected in each sampling location. Calibrations were performed as toluene equivalents unless otherwise stated; substances marked with * were calculated against pure standards, as opposed to toluene equivalents.

	Corridor background	**Room background**	**Rain cape Am1988,08.672**	**Trousers Am1988,08.670.b**
Substance	**Concentration μgm^{-3}**			
Acetophenone*	1.59	8.16		
Alkanes	35.50	12.30	7.20	11.20
Benzoic acid	13.30	33.20	17.20	24.60
Butanoic acid, butyl ester		3.23		2.28
Ethylbenzene*	2.03	0.90		
Isoalkanes	37.90	15.65	89.00	9.36
Nonanoic acid	2.04	3.11		
Pentafluoropropionic acid, octadecyl ester	3.18		0.40	3.03
Siloxanes	1.47	0.67	37.30	32.70
Tetrachloroethylene	36.30	18.80		16.80
Toluene*	5.16	1.82		

(with the exception of tetrachloroethylene) are commonly found in indoor air, and have been reported in several museum environments.[18] The most significant difference noted between the enclosures and the background samples was in the concentration of cyclosiloxanes detected. Cyclosiloxanes are typically emitted by silicone sealants but can also be emitted by personal care products. The total concentration of the detected cyclic volatile methyl-siloxanes was 32.8 μgm^{-3} for the trousers and 37.3 μgm^{-3} for the rain cape. Background analysis of the corridors showed siloxane concentrations of 1.47 and 0.67 μgm^{-3}. This might suggest that siloxanes had been involved in the manufacture of the garments and could, for example, be attributable to an aerosol-based waterproofing treatment, as these typically contain mixtures of cyclic siloxanes.[19]

The results from the VOCs' analysis did not clarify the source of the strong odour associated with the garments. This may be attributed to the particular analytical method used, which did not specifically target the low molecular weight organic acids, and reduced sulfur gases such as hydrogen sulfide and carbonyl sulfide compounds often responsible for such odours,[20] but was rather aimed towards VOCs of potential health and safety concerns such as pesticides.[21] None of the VOCs detected around the rubber garments nor in the background samples were detected at concentrations that would give rise to health and safety concerns.

Preventive conservation: investigating anoxic storage for rubber garments

It is well understood that low oxygen (anoxic) storage is of great benefit in the preventive conservation of rubber artefacts.[22] Enclosure of the garments in an anoxic environment was therefore considered as a solution for the long term storage of the Mexican rubber garments. However, the detection of high levels of volatile acids gave rise to concerns for the long term stability of the cotton calico, which could be subjected to increased acid hydrolysis if the acid levels inside the anoxic enclosures were to increase.

If the acids off-gassed by the rubber garments developed as a result of oxidation processes, then enclosing the garments in a low oxygen enclosure would be expected to help to reduce the evolution of further acids. However, if the acids were inherently present in the rubber, for example as residues from a coagulation process, then anoxic enclosures would do little to reduce the emission of acids and could lead to damaging

first law of diffusion which states that concentration, $C = ML/DAt$, where M is the mass of aldehyde collected (μg), L is the length of the diffusion tube (0.071 m), D is the diffusion coefficient of the aldehyde in air ($1.7 \times 10^{-5} m^2.s^{-1}$ for formaldehyde), A is the cross-sectional area of the diffusion tube ($9.5 \times 10^{-5} m^2$) and t is the sampling/exposure time (s). Exposure of the sampling tube is measured in seconds, and the mass (μg) of aldehyde trapped is determined experimentally, giving an overall aldehyde concentration in μgm^{-3}.

13 Organic acids, such as acetic and formic acid, were trapped in diffusion tubes by reacting with a potassium hydroxide trapping solution, trapping acetic and formic acids as potassium acetate and potassium formate, respectively. The trapped analytes were extracted from the diffusion tubes by removing the stainless steel mesh disks (traps) and placing them into a clean Sterilin container. Aliquots (5×1 mL) of distilled water were used to wash out the cap (formerly containing the mesh disks) into the Sterilin container. With the lid placed on the Sterilin container, the disks were carefully shaken in order to extract the salts from the disks into the distilled water. The solutions were analysed by ion chromatography (IC) after they were filtered using Acrodiscs (13 mm, 0.2 μm Supor membrane, PALL Life Sciences, UK) to determine the concentration of acetic and formic ions. The instrument used was a Dionex DX 100 ion chromatograph fitted with a RFIC IonPac AS4A-SC column (250 mm with 4 mm i.d) and a borax eluent flow rate of 1 $mL.min^{-1}$. Background conductivity was suppressed using a Dionex suppressor [model ASRS-ULTRA II (4 mm)]. Chromatograms were collected on a computer interface operated by the software system PeakNet. Calibrant solutions, prepared in the range 0–4$\mu g.mL^{-1}$, were used to quantify the results and determine the concentration of acetate and formate in each solution using linear least squares regression analysis. A calculation was then used to convert from the acetate and formate concentration in solution to the mass of acetic and formic acid that was washed from the sampling disks. An average mass was then taken from the diffusion tube fridge blanks and subtracted from each of the sampling tubes to produce a blank corrected mass of acid. The concentration of acetic and formic acid in the sampled environment around each object was then calculated using Fick's

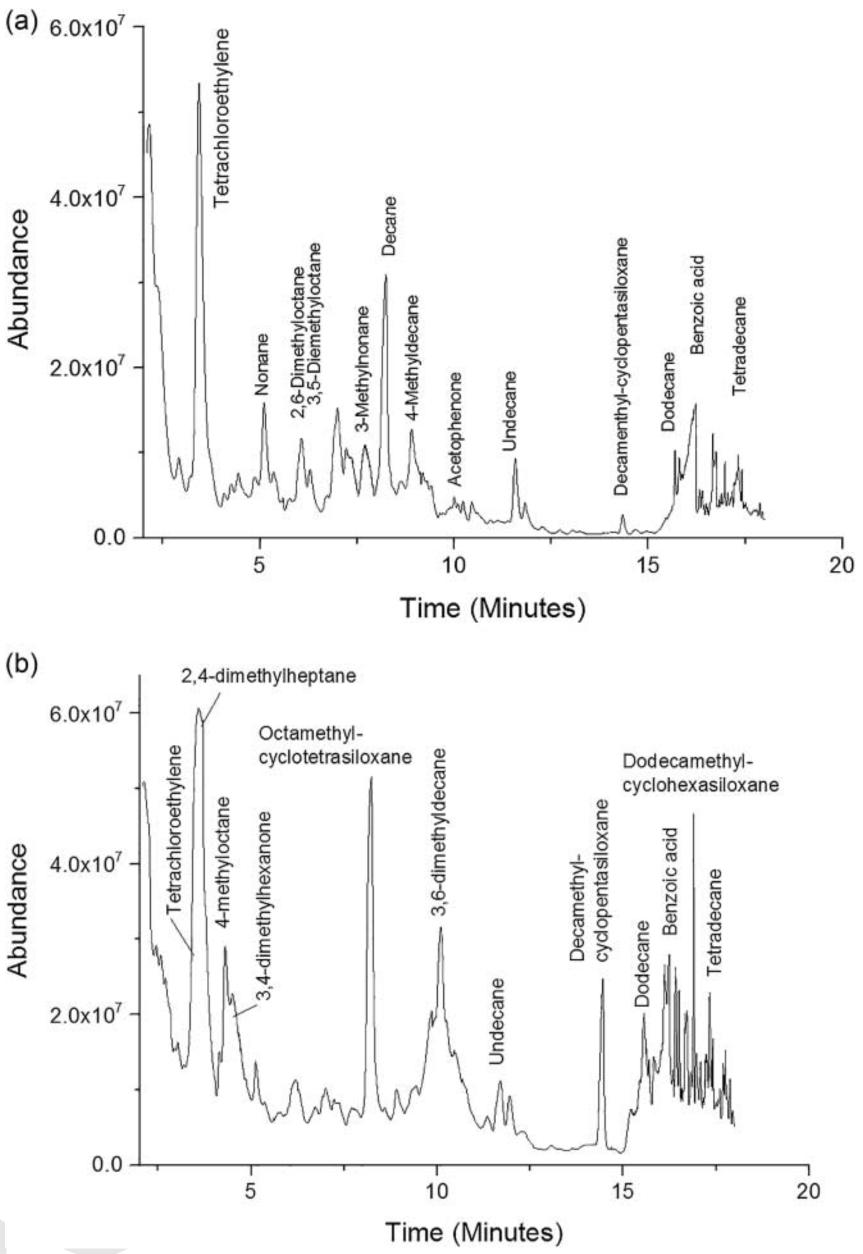

Fig. 5 (a) Total ion chromatogram for the sample from the corridor location. (b) Total ion chromatogram obtained from rain cape Am1988,08.672.

first law of diffusion which states that concentration, $C = ML/DAt$, where M is the mass of acid collected (μg), L is the length of the diffusion tube (0.071 m), D is the diffusion coefficient of the acid in air (1.1×10^{-5}m^2.s^{-1} for acetic acid and 1.27×10^{-5}m^2.s^{-1} for formic acid), A is the cross-sectional area of the diffusion tube (9.5×10^{-5}m^2) and t is the sampling/exposure time (s). Exposure of the sampling tube is measured in seconds, and the mass (μg) of pollutant trapped is determined experimentally, giving an overall acid concentration in μgm^{-3}.

build-up inside the enclosure. It was therefore of interest to determine whether the use of pollutant sorbents (activated carbon, zeolites and alkaline buffers) would have a mitigating impact on the acid levels in the enclosed environment.

Other VOCs determined in the study under ambient conditions were not considered to be at concentrations that could present health and safety risks and were not deemed to impact on the rate of deterioration of either rubber or cotton and were therefore not considered further. However, some VOCs associated with the deterioration of rubber, for example reduced sulfide gases, would not have been trapped by the experimental method employed but their presence can be assumed.[23] Such compounds may lead to the evolution of further detrimental pollutants such as sulfuric acid or related sulfur oxides. It was therefore deemed prudent to test a sorbent that was known to be able to not only take up large amounts of acetic acid but would also offer protection from a wide range of other VOCs.

MicroChamber® products containing activated carbon, zeolite and alkaline buffer appeared to possess the required qualities and are claimed to offer protection from ozone, sulfur dioxide, nitrogen oxides, hydrogen peroxide, aldehydes and acids.[24] The inclusion of the three different types of sorbent may improve their individual sorption capacity through synergistic effects. MicroChamber® General Purpose Black/White Paper was chosen for this investigation because of its reported properties. It consists of acid- and lignin-free laminated paper with an alkaline buffer and activated carbon in the black layer and alkaline buffer and zeolite in the white layer. The supplier provides no information on the type of alkaline buffer or activated carbon used. In general, activated carbon is derived from a variety of carbonaceous sources modified to produce a graphite-like material with a very large surface area that is capable of adsorbing a very wide variety of molecules. The SPZ zeolite in the MicroChamber® products is a proprietary material and no information regarding its composition is provided other than to note that it is a synthetic zeolite with acid resistance and hydrophobic properties.[25] In general, zeolites are porous frameworks of aluminosilicates that are capable of trapping many different molecules depending on the pore sizes, shapes and polarities. There are few independent research studies on the efficacy of the MicroChamber® products and some are tentative in their recommendation[26] or even suggest that activated charcoal and zeolites may release adsorbed acids once their sorption capacity is saturated, thereby becoming emission sources themselves.[27] However MicroChamber® General Purpose Black/White Paper offered a practical material to use within enclosures as it comes in a convenient form as a roll of 180gm^{-2} weight paper of around 85 cm width and 30 m length. This means that the required shapes could be cut to fully wrap the garments rather than relying on the use of sachets (or similar) of sorbent materials that would require some gas circulation within the enclosures for the VOCs to effectively reach the sorbents.

1 Off-gassing test set-up: acid level measurements around rubber garments in ambient, anoxic and anoxic plus MicroChamber® enclosures

In order to investigate whether a low oxygen environment would reduce the production of acid degradation products and whether MicroChamber® sorbents were effective at reducing the concentration of acids and VOCs in enclosures containing the rubber garments, a series of experiments were undertaken. Since the mid-1990s there have been numerous developments in the products used for the creation of anoxic packaging for the long term storage of museum artefacts.[28] For the experiments undertaken in this study, the enclosures were created using oxygen-impermeable Escal® film that was heat-sealed with a cross-weld sealer. The three environments investigated were a sealed ambient environment; a sealed anoxic environment; and sealing the garment under anoxic conditions in the presence of MicroChamber® paper. The anoxic environments were created by first flushing the Escal® enclosures with a stream of nitrogen until the oxygen level inside measured less than 0.5% and then adding RP system® (RP-K) and Ageless® (Ageless-Z) oxygen absorbers (Table 4).[29] Ageless Eye® oxygen indicators were also added to each anoxic enclosure to ensure easy monitoring of the oxygen levels as these indicators turn from pink to purple if oxygen levels rise to 0.5% or higher, for example in the case of a leak.

In July and August 2013, three garments (trousers Am1988,08.670.b and Am1988,08.671.a, and rain cape Am1988,08.670.a) were each placed in the three different enclosed environments with each containing three acid

[14] A. Kumar and I. Víden, 'Volatile Organic Compounds: Sampling Methods and Their Worldwide Profile in Ambient Air', *Environmental Monitoring and Assessment* 131 (2007): 301–21; D.A. Sarigiannis, S.P. Karakitsios, A. Gotti, I.L. Liakos and A. Katsoyiannis, 'Exposure to Major Volatile Organic Compounds and Carbonyls in European Indoor Environments and Associated Health Risk', *Environment International* 37 (2011): 743–65; Alexandra Schieweck and Tunga Salthammer, 'Indoor Air Quality in Passive-type Museum Showcases', *Journal of Cultural Heritage* 12 (2011): 205–13; S.A. Idris, C. Robertson, M.A. Morris and L.T. Gibson, 'A Comparative Study of Selected Sorbents for Sampling of Aromatic VOCs from Indoor Air', *Analytical Methods* (2010): 1803–9.

[15] Tenax sampling tubes (Markes International Ltd, Llantrisant) were conditioned using a Markes Unity^2 thermal desorption unit for 30 min at 320°C using He as the carrier gas. Immediately after conditioning, the sampling tubes were sealed using brass caps and PTFE ferrules. Once received at the sampling site, to deploy the sampling tubes the two brass caps were removed and the sampling tube was placed at the sampling location and exposed in passive mode before being resealed prior to analysis. Trapped analytes were recovered by thermal desorption using a Markes International Unity^2 thermal desorption unit connected to an Agilent 5890 GC-MS according to the method described in Rushworth et al., 'Non-Invasive Multiresidue Screening Methods'. Each sampling tube was heated for 10 min at 320°C using He as the carrier gas at 1 mL.min^{-1} and desorbed analytes passed onto a cold trap held at −30°C. In the second stage of the desorption process the cold trap was rapidly heated at approximately 99°C.s^{-1} to 300°C, permitting a sharp band of vapour to pass into the GC-MS. Helium, at a flow rate of 1 mL.min^{-1}, was used as the GC-MS carrier gas with a DB-5MS (30 m × 250μm × 0.25μm film thickness) capillary column (Agilent Technologies UK Ltd, Stockport). The GC column was heated using the following conditions: hold at 65°C for 5 min, ramp at 5°C.min^{-1} to 90°C with a 5 min hold, ramp at 30°C.min^{-1} to 180°C and a 5 min hold before increasing at 20°C.min^{-1} to 220°C and holding for 5 min to give a final analysis time of 30 min. Mass spectrometric detection was used in scan mode over 30–450amu, with an electron energy of 70eV and a solvent delay of 2 min.

Table 4 Test set-up for rubber garments in ambient, anoxic and anoxic plus MicroChamber® enclosures.

Enclosure code*	Sampled rubber garment	Approximate volume of enclosure (L)	Number of packets of enclosed oxygen absorbers			Theoretical air volume amount which enclosed oxygen absorbers can scavenge (L)
			RP20 K	RP3 K	Ageless-Z200	
a X+	Trouser Am1988,08.670.b	37	1	2	9	11.6
a X	Trouser Am1988,08.671.a	51	1	3	11	13.6
a A	Rain cape Am1988,08.670.a	150	–	–	–	–
b A	Trouser Am1988,08.670.b	37	–	–	–	–
b X+	Trouser Am1988,08.671.a	51	1	3	11	13.6
b X	Rain cape Am1988,08.670.a	150	8	7	30	48.1
c X	Trouser Am1988,08.670.b	37	1	2	9	11.6
c A	Trouser Am1988,08.671.a	51	–	–	–	–
c X+	Rain cape Am1988,08.670.a	150	8	7	30	48.1

Note: * Enclosure code: test period a, b or c; test type A: ambient; X: anoxic; X+: anoxic + MicroChamber®.

diffusion tubes. The MicroChamber® paper was wrapped around the garments to fully surround them, with the white (zeolite) side facing inwards and interleaving acid-free tissue paper separating the rubber garment from direct contact with the MicroChamber® paper. The diffusion tubes were placed directly onto the garment, inside the tissue paper and MicroChamber® wrapping. The environment within the storage room (S21a, Blythe House) housing the enclosures was also sampled in triplicate to provide a background indoor air concentration. Although ideally the VOCs inside an equivalent set of enclosures without rubber garments would also have been monitored, the limited analytical resources available precluded this, but previous work by one of the authors suggests the Escal® enclosures would not be the source of the VOCs of interest. Each garment was placed within each of the three environments in turn, with a sampling period of 14 days for each set of conditions (Fig. 6). There was a degree of variation in the ambient temperature and relative humidity conditions between each of the three test periods a, b and c (Fig. 7).[30]

Upon opening the enclosures after each test period, a, b and c, it was obvious that the MicroChamber® paper had greatly reduced the emitted odours from the rubber garments to a hardly noticeable level. In contrast, the enclosures with ambient oxygen levels released pungent odours while the smell released from the anoxic enclosures appeared to be somewhat less powerful.

Oxygen levels inside the enclosures were measured upon sealing and again immediately before opening them at the end of each test period (Table 5). The enclosures for the two trousers (Am1988,08.670.b and Am1988,08.671.a) showed low levels of air leakage while the enclosure for the rain cape (Am1988,08.670.a) was well-sealed, with oxygen levels dropping below 0.05%, as would be expected based on the quantity of oxygen absorbers used. After each test period, the Escal® film enclosures were inspected for any creases or scratches which were then sealed either with Septa foam stickers or by heat-sealing if close to the edges of the

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Linear regression analysis was performed to determine the mass of analyte trapped by the tube. Calibration was performed by injecting increasing volumes of a mixed-VOC standard over the range of 0–200 ng. Analytes were identified using a probability-based match with a reference standard taken from the NIST library. Linear regression analysis was performed to determine the mass of analyte trapped by the tube. The mass (ng) was divided by the sampling volume (L) to give a concentration in $\mu g L^{-1}$. Masses were reported as per toluene equivalent, with the exception of naphthalene, ethylbenzene and acetophenone.

16 A digital hygrometer was used to monitor the environmental conditions during the tests.

17 *SCOEL/SUM/133 Recommendation of the Scientific Committee on Occupational Exposure Limits for Tetrachloroethylene (Perchloroethylene)*, 2009, http://ec.europa.eu (accessed 2 June 2014).

18 A. Schieweck, B. Lohrengel, N. Siwinski, C. Genning and T. Salthammer, 'Organic and Inorganic Pollutants in Storage Rooms of the Lower Saxony State Museum Hanover, Germany', *Atmospheric Environment* 39 (2005): 6098–108; Schieweck and Salthammer, 'Indoor Air Quality'.

19 Beverly K. Kemerer, 'Cleaning and Waterproofing Composition', United States, patent no. US4708807 A, Applied for on behalf of Dow Corning (1987), http://patft.uspto.gov/netacgi/nph-Parser?Sect2=PTO1&Sect2=HITOFF&p=1&u=/netahtml/PTO/search-bool.html&r=1&f=G&l=50&d=PALL&RefSrch=yes&Query=PN/4708807 (accessed 3 December 2013).

20 Hoven, Rattanakaran and Tanaka, 'Determination of Chemical Components'; Dyer et al., 'Reassessment of Anoxic Storage'.

21 Rushworth et al., 'Non-Invasive Multiresidue Screening Methods'.

22 Miriam Clavir, 'An Initial Approach to the Stabilization of Rubber from Archaeological Sites and in Museum Collections', *Journal of the International Institute for Conservation—Canadian Group* 7 (1982): 3–10; Yvonne Shashoua and Scott Thomsen, 'A Field Trial for the Use of Ageless in the Preservation of Rubber in Museum Collections', in *Saving the Twentieth Century: The Conservation of Modern Materials. Proceedings of a Conference*, Ottawa, Canada, 15–20 September 1991, ed. David W. Grattan (Canadian Conservation Institute, 1993), 363–72; Yvonne Shashoua,

Colour online, B/W in print

Fig. 6 Enclosures with acid diffusion tubes during test period a. From bottom to top: Am1988,08.670.a in a sealed ambient enclosure; tubes for background comparative measurements of the store room environment; Am1988,08.671.a in an anoxic enclosure; and Am1988,08.670.b in an anoxic enclosure with MicroChamber® paper. © Trustees of the British Museum.

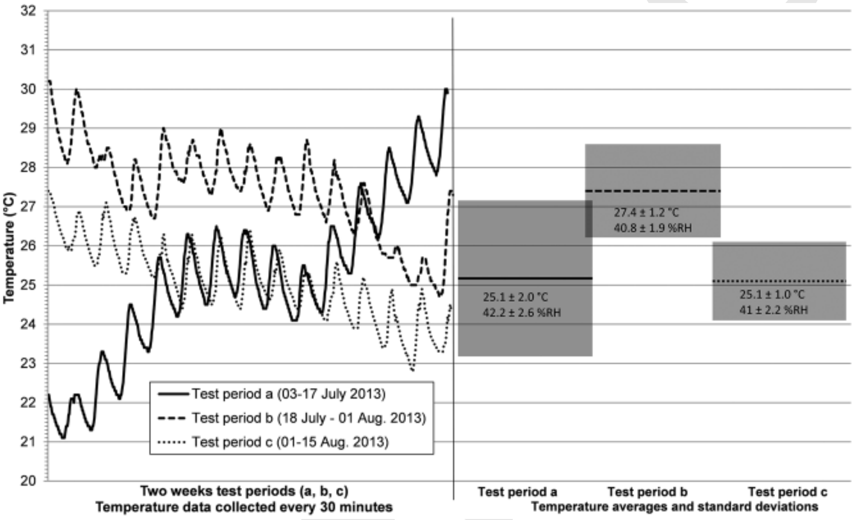

Fig. 7 Logged temperature and relative humidity data for test periods a, b and c (standard deviations shown as grey boxes).

enclosures. The oxygen levels in the ambient enclosures were significantly reduced after the 14-day test periods, indicating that up to 7% of oxygen was consumed in oxidation reactions, probably primarily by deterioration of the rubber and with some contribution of oxidation of other materials in the enclosures (VOCs, cotton calico, polyethylene foam used for support and padding and the polyethylene inner layer of the Escal® film).

The diffusion tube measurements revealed extremely high concentrations of both acetic and formic acids in the ambient and the anoxic enclosures. In these enclosures, the acetic acid concentrations were often many times higher than the formic acid concentrations and both followed approximately the same trends (Table 6, Fig. 8).

'Ageless® Oxygen Absorber: From Theory to Practice', in *ICOM-CC 12th Triennial Meeting Preprints*, Lyon, 29 August–3 September 1999, ed. J. Bridgland (London: James & James, 1999), 881–7; Dyer et al., 'Reassessment of Anoxic Storage'.

23 Hoven, Rattanakaran and Tanaka, 'Determination of Chemical Components'; Dyer et al., 'Reassessment of Anoxic Storage'.

24 Siegfried Rempel, 'Zeolite Molecular Traps and Their Use in Preventative Conservation', *WAAC Newsletter* 18, no. 1 (1996): 12–8; Pamela B. Hatchfield, *Pollutants in the Museum Environment: Practical Strategies for Problem Solving in Design, Exhibition and Storage* (London: Archetype Publications, 2002), 122.

25 Rempel, 'Zeolite Molecular Traps'.

26 Terry T. Schaeffer, J.R. Druzik and Chail Norton, 'The Efficacy of Micro-Chamber Boards in Passepartout for Paper-based Art', *The Book and Paper Group Annual* 23 (2004): 87–8.

27 Agnes W. Brokerhof, 'Application of Sorbents to Protect Calcareous Materials against Acetic Acid Vapours', in *Contributions to Conservation: Research in Conservation at the Netherlands Institute for Cultural Heritage (ICN Instituut Collectie Nederlands)*, ed. Jaap A. Mosk and Norman H. Tennent (London: James & James, Science Publishers Ltd, 2002), 16–24.

Table 5 Oxygen (O$_2$%) levels measured in the various enclosures.

Sampled rubber garment or background	Enclosure code*	O$_2$% when sealing enclosure	O$_2$% after 14-day test period
Trouser Am1988,08.670.b	a X+	0.46	2.25
	c X	0.20	1.40
	b A	20.00	15.60
Trouser Am1988,08.671.a	b X+	0.45	0.01
	a X	0.45	1.54
	c A	20.30	13.30
Rain cape Am1988,08.670.a	c X+	0.45	0.02
	b X	0.45	0.01
	a A	20.00	18.10

Note: * Enclosure code: test period a, b or c; test type A: ambient; X: anoxic; X+: anoxic + MicroChamber®.

Table 6 Concentrations of acetic and formic acids in the sampled enclosures

Sampled rubber garment or background	Enclosure code*	Concentration of acetic acid (μgm^{-3})	Concentration of formic acid (μgm^{-3})
Trouser Am1988,08.670.b	a X+	383	249
		1112	370
		2169	715
	c X	9727	4786
		7609	2822
		9994	4139
	b A	8912	2613
		25,756	3648
		21,996	2839
Trouser Am1988,08.671.a	b X+	66	130
		813	179
		102	130
	a X	14,653	2295
		14,450	2965
		15,510	2863
	c A	2171	986
		1858	886
		1704	768
Rain cape Am1988,08.670.a	c X+	1155	131
		69	115
		160	231
	b X	22,928	6034
		27,089	6768
		30,845	7766
	a A	51,139	11,492
		44,550	10,123
		36,640	7407
Background store room (S21a Blythe House)	a	1643	252
		1919	315
		1576	246
	b	1464	247
		3282	248
		4939	248
	c	665	220
		606	229
		709	232

Note: * Enclosure code: test period a, b or c; test type A: ambient; X: anoxic; X+: anoxic + MicroChamber®).

The concentration of acetic acid in the enclosures with the rubber garments was up to 50 times higher than the background concentration measured in the store room. Monitoring campaigns of acetic acid concentrations in various UK heritage institutions have shown that a background concentration in the region of 200–400 μgm^{-3} is generally expected in areas where there is no active source of acetic acid (such as wood, wood-based

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[28] Yvonne Shashoua, 'Recent Investigation into Barrier Films for Use in Preventive Conservation at the British Museum', *Scottish Society for Conservation and Restoration SSCR Journal* 3, no. 2 (1992): 12–3; Shashoua, 'Ageless® Oxygen Absorber'; David W. Grattan and Mark Gilberg, 'Ageless Oxygen Absorber: Chemical and Physical Properties', *Studies in Conservation* 39 (1994): 210–4; John Burke, 'Anoxic Microenvironments: A Simple Guide', *SPNHC Leaflets A Technical Publication Series of the Society for the Preservation of Natural History Collections* 1, no. 1 (1996): 1–4; Vicen Carrió and Suzie Stevenson, 'Assessment of Materials used for Anoxic Microenvironments', in *Conservation Science 2002*, ed. Joyce H. Townsend, Katherine Eremin and Annemie Adriaens (London: Archetype Publication, 2002), 32–8; David McPhail, Eric Lam and Adrian Doyle, 'The Heat Sealing of Escal® Barrier Films', *The Conservator*, no. 27 (2003): 107–16.

[29] Oxygen measurements were carried out using a Systech Mapcheck oxygen monitor. The measurements were taken during the nitrogen flushing of enclosures before they were fully sealed by placing the probe into the enclosures but not directly into the nitrogen stream. For measurements of sealed enclosures a hypodermic needle was attached to the probe and the enclosures were punctured with the needle through a rubber foam sticker and the instrument drew a predetermined volume of gas out of the enclosures. The punctured area was then heat-sealed again.

[30] The environmental conditions in the room were recorded using a Hanwell HumBug temperature and relative humidity logger.

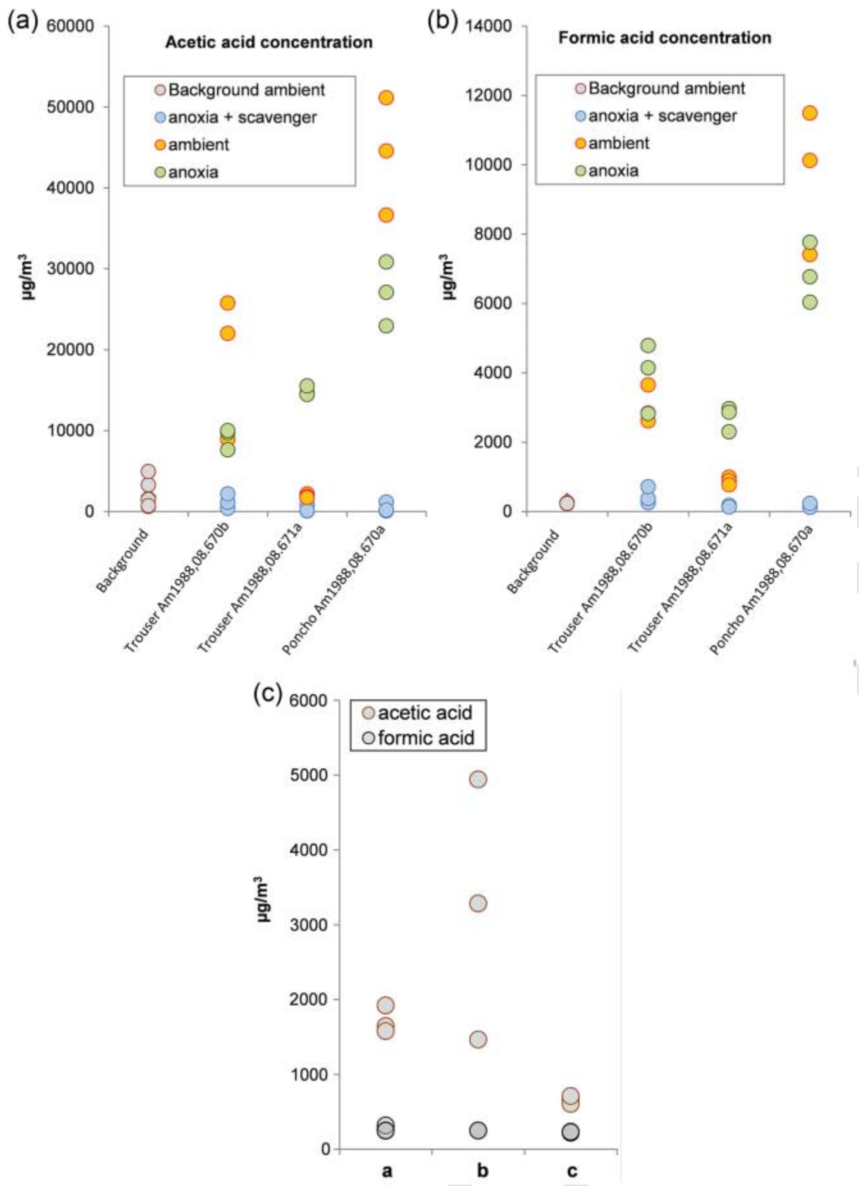

Fig. 8 (a) Acetic acid and (b) formic acid concentrations measured in the ambient, anoxic and anoxic plus MicroChamber® enclosures containing rubber garments. (c) Background acid concentrations measured in the store room (Blythe House, S21A) during test periods a, b and c.

products or cellulose acetate).[31] The average concentration of acetic acid in the store room was measured at 1867 µgm^{-3} indicating an active source of acid. The source could be attributed to the high wood and plywood content in the flooring, furniture and packaging materials in the store room. Grzywacz has reported 'action limits' for a range of important gaseous pollutants in heritage environments and considers acetic acid in the range 600–1000ppb (equivalent to approximately 1500–2500 µgm^{-3}) to be an 'extremely high' acid concentration.[32] The store room is not used for museum objects that are vulnerable to acidic environments and contains predominantly large plaster cast copies and is sometimes used as a temporary packing area for large scale crates for objects due to go out on loan. The enclosed rubber garments were in this area during the tests carried out in this study only.

The fact that there was no apparent reduction in acid levels in the anoxic enclosures compared to the ambient enclosures suggested that the emitted

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[31] Mitchell, 'Title to be confirmed'. AQ3

[32] Cecily M. Grzywacz, *Monitoring for Gaseous Pollutants in Museum Environments: Tools for Conservation* (Los Angeles: Getty Publicaions, 2006), 109–10.

acids are inherently present in the rubber garments rather than being produced solely by oxidation. This suggested that during the original production of the garments a reprocessed coagulated rubber latex was used. By contrast, the acid levels measured in the anoxic enclosures with MicroChamber® paper were greatly reduced. In fact, in most cases the acetic acid measurements for the anoxic plus MicroChamber® enclosures were lower than those for the store room background. These were very encouraging results, especially since the diffusion tubes were placed between the rubber garments and the MicroChamber® paper so that emission from the rubber passed the diffusion tubes first before being adsorbed by the MicroChamber® paper.

The acetic acid levels measured in the two-week exposure periods were many times higher than those measured in the preliminary investigation of the off-gassing from the rubber garments under ambient conditions (as reported above and in Table 2). This may be partially attributable to the fully sealed Escal® barrier film enclosures used in the anoxic enclosures compared to the permeable polyethylene enclosures used in the preliminary investigation. However, this is unlikely to fully account for the difference found for the same garment (trousers Am1988,08.670.b) with 5815 μgm^{-3} acetic acid measured in the preliminary test compared to an average of 18,888 μgm^{-3} acetic acid in the ambient enclosure during test period b. The more likely reason for the great rise in acetic acid emissions from the rubber garments is the difference in temperature from 18–22°C during the preliminary test to 26.2–28.6°C during test period b. This temperature dependency is also illustrated in Fig. 8c, showing the store room background measurements during the three test periods a, b and c. Acetic acid levels were highest during test period b which coincided with the hottest summer weeks. By contrast, the formic acid levels appeared unaffected by temperature.

The triplicate repeat measurements were a useful way of assessing the reliability of the results and, as can be seen from Fig. 8, there were few real outliers. In general the data spread became wider as the acid concentrations increased. Additional sources of error were the varying enclosure volumes provided by the flexible barrier film, variations in temperature, variations of ventilation in the store room and changes of furniture and boxes near the diffusion tubes in the store room. Error calculations were therefore not attempted.

Current storage of the rubber garments and further work

At the end of the enclosure tests it was decided to reseal the three garments, wrapped in MicroChamber® paper, in their Escal® enclosures under anoxic conditions with the inclusion of oxygen absorbers and Ageless Eye® indicators for easy monitoring (Fig. 9). The remaining unpackaged garments in the storage drawer were covered with a layer of MicroChamber® paper to help reduce the powerful smell that was emitted from that drawer. Since these investigations did not address the concerns around the saturation levels of MicroChamber® paper and its potential for releasing acids once sorption capacity is saturated, it is planned to measure the acid levels inside the enclosures again after a period of one or two years. A better idea about the long term behaviour of MicroChamber® paper under high acid emission conditions may then be determined. Investigation of the MicroChamber® paper may also provide greater insight into the VOCs off-gassed by the garments and the origin of the pronounced odour.

Should this small collection of rubber garments become a priority in the future, then an assessment of the feasibility of carrying out remedial conservation treatments to directly reduce the acid levels could be undertaken. This could involve swabbing, poultices and/or immersion tests using

Fig. 9 Rubber garments in anoxic enclosures with MicroChamber® paper. © Trustees of the British Museum.

deionised water on a representative garment. If the garments can be safely rinsed or washed, acidic residues left over from the original production could be reduced, as well as acids and other soluble deterioration products that have formed since. Following such a treatment, the testing described above using the sequence of different enclosures could be repeated and the acids off-gassed analysed in order to determine the impact of the washing on acid emission levels. Additionally, it might be possible to safely reduce creases and folds in the garments by the gentle application of heat. Following reshaping, and for long term storage, the garments should be laid flat and fully supported on archival boards (possibly with MicroChamber® paper wrapped around each garment) and packed individually with spacers so that they do not compress each other.

Conclusions

A collection of 1980s Mexican rubber garments emitting a powerful odour and showing signs of deterioration was investigated in order to assess conservation treatment options, to improve their long term storage conditions and to investigate the source of the associated odour. Initial tests undertaken using A-D strips® suggested significant levels of volatile acids were being off-gassed from the garments. FTIR analysis confirmed the chemical alteration of rubber in deteriorated areas with an increase in carbonyl, hydroxyl and hydroperoxide groups and a decrease of unsaturation in the *cis*-1,4-polyisoprene polymer chains. The progressive nature of the embrittlement of rubber was visually demonstrated in SEM micrographs. Remedial conservation tests demonstrated the potential for the reshaping of the garments using the application of gentle heat and recommendations were made for the potential future treatment of the collection.

Passive diffusion tubes for aldehydes, acids and VOCs were used for sampling the environment around rubber garments. The results showed very low emissions of aldehydes and no VOCs at concentrations that would present any health and safety concerns. The VOCs detected included tetrachloroethylene, alkanes, methyl- and dimethylalkanes, cyclosiloxanes and benzoic acid. Only the siloxanes were present at levels significantly above the room background and were attributed to the garment manufacturing process, possibly from the application of an additional waterproofing treatment. The measured acetic acid concentrations on the other hand were classed as 'extremely high' and were shown to be temperature dependent. While the preservation of rubber can be greatly enhanced by long term storage in anoxic environments, the risk of acid levels building up inside the anoxic enclosures was a cause of concern in terms of the long term preservation of the garments' cotton fabric backings. The source of the pronounced odour could not be definitively identified but may be attributed to low molecular weight organic acids and reduced sulfur gases.

Test set-ups in sealed ambient and anoxic conditions, with and without the inclusion of MicroChamber® paper, showed the effectiveness of this pollutant sorbent in reducing acetic acid levels as well as other VOCs responsible for the pungent odour emitted by the garments. The concentrations of acetic acid inside the enclosures without MicroChamber® paper were up to 50 times higher than the store room background levels while the inclusion of MicroChamber® paper reduced the acetic acid levels significantly below the background levels. Anoxic enclosure alone did not appear to reduce the emission of acetic acid indicating that the acid source is predominantly due to residual acid from the manufacturing process, possibly from the rubber latex coagulation stage, rather than being entirely a product of deterioration by oxidation. Nevertheless, anoxic enclosures did appear to reduce the emission of other VOCs as indicated by the reduction in the odour released from the enclosures upon opening after each test period, even without the addition of MicroChamber® paper. For the anoxic enclosures with MicroChamber® paper, the odour released upon opening the enclosure was almost imperceptible. Thus for this particular set of rubber garments, anoxic enclosures with MicroChamber® paper appear to offers a practical storage solution to reduce the odour associated with the garments while also minimising further oxidative damage. The three garments stored in this way will continued to be monitored to assess the long term effectiveness of the storage.

Acknowledgements

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Abstract

A collection of 1980s Mexican rubberised cotton garments was investigated in order to assess conservation treatment options, to improve their long term storage conditions and to investigate the origin of the strong odour associated with the garments. Chemical and mechanical deterioration of the rubber was confirmed by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Recommendations for remedial conservation were made after re-shaping tests using the application of gentle heat. Passive diffusion tube sampling was carried out to assess the levels of acids, aldehydes and VOCs emitted from the garments. Very high concentrations of acetic acid off-gassing were confirmed and deemed a risk to the cotton fabric. Test set-ups in sealed ambient and anoxic conditions, with and without the inclusion of MicroChamber® paper, showed the effectiveness of this pollutant sorbent in reducing acetic acid levels as well as general odour emitted by the garments.

Résumé

«Enquête sur les méthodes de stockage à long terme pour les vêtements en caoutchouc»
Une collection de vêtements mexicains en coton vulcanisé de 1980 a été étudiée afin d'évaluer les options de traitement de conservation, améliorer leurs conditions de stockage à long terme et comprendre l'origine de la forte odeur associée à ces vêtements. La détérioration chimique et mécanique du caoutchouc a été confirmée par la spectroscopie infrarouge à transformée de Fourier (FTIR) et le microscope électronique à balayage (MEB). Des recommandations pour la conservation curative ont été faites suite à des essais de remise en forme à l'aide de chaleur douce. Un prélèvement sur tube à diffusion passive a été effectué pour mesurer les différents niveaux d'acides, d'aldéhydes et de composés organiques volatils émis par les vêtements. Des concentrations très élevées d'acide acétique par dégagement gazeux ont été confirmées et ont été jugées dommageables pour le tissu de coton. Des tests effectués sous anoxie dans une chambre scellée, avec et sans ajout de papier MicroChamber®, ont montré l'efficacité de ce matériau d'adsorption des polluants dans la réduction des concentrations d'acide acétique ainsi que dans la diminution de l'odeur générale émise par les vêtements.

Zusammenfassung

„Lösungen zur Langzeitlagerung von Gummibekleidung“

Eine Sammlung mexikanischer gummierter Baumwollbekleidung der 1980er Jahre wurde untersucht, um Optionen zu Konservierungsmaßnahmen zu evaluieren, ihre Langzeitlagerungsbedingungen zu verbessern, und um die Quelle des starken Geruchs, der mit den Kleidungsstücken verbunden ist, zu erforschen. Chemischer und mechanischer Abbau des Gummis wurde mittels Fourier Transforminfrarotspektroskopie (FTIR) und dem Elektronenrastermikroskop bestätigt. Vorschläge zur Konservierung wurden formuliert, nachdem Tests zum Rückformen der Kleidungsstücke mit sanfter Hitze ausgeführt worden waren. Um Messwerte der Säuren, Aldehyden und VOC’s die von den Kleidungsstücken freigesetzt werden zu erstellen, wurden passive Diffusionssammler eingesetzt. Es wurden sehr hohe Werte für Essigsäure bestätigt, welche ein Risiko für die Baumwolle darstellen. Weitere Tests, die sowohl unter Umgebungsbedingungen als auch unter Sauerstoffausschluß mit und ohne MicroChamber® Papier ausgeführt wurden, beweisen die Effektivität dieses Schadstoffsorptionsmittels, sowohl beim Reduzieren der Essigsäurewerte als auch beim Reduzieren der Geruchswerte im allgemeinen.

Resumen

“Investigación de soluciones de almacenaje a largo plazo para ropas de goma”

Con el fin de evaluar las opciones de tratamiento de conservación, la mejora de las condiciones de almacenaje a largo plazo así como el origen del fuerte olor relacionado con las prendas, se inició una investigación de una colección de ropas de algodón engomadas de los años 80. Usando espectroscopía infrarroja transformada de Fourier (FTIR) y microscopía electrónica de barrido (SEM), se confirmó que la goma estaba sufriendo un deterioro químico y mecánico. Después de hacer pruebas para remodelar aplicando calor suave se hicieron recomendaciones correctivas de conservación. Para evaluar los niveles de ácidos, aldehídos y de compuestos orgánicos volátiles (COV) emitidos por las prendas se llevó a cabo un muestreo de tubo de difusión pasiva. Se confirmó la presencia de altas concentraciones de descarga gaseosa de acido acético lo que supone un riesgo para la tela de algodón. Pruebas en configuraciones de ambientes cerrados y condiciones de anoxia con y sin la inclusión de papel de MicroChamber® demostraron la eficacia de este absorbente de contaminante en la reducción de ácido acético y de los niveles del olor emitido por la ropa en general.

Biographies

Marei Hacke studied Textile Science and Technology in Berlin and Manchester. She received her PhD in 2006 for research conducted within the European project on the Monitoring of Damage in Historic Tapestries. Before joining the science group at the British Museum in March 2007 she spent six months as a fellow at the Smithsonian Museum Conservation Institute. Her areas of expertise cover the study of polymeric materials, in particular textiles, paper, plastics and conservation materials testing.

Jo Willey is currently working as a Preventive Conservator for the World Conservation and Exhibition Centre collections move at the British Museum. She completed a BA with Honours in Archaeology at the University of Sydney in Australia before studying the conservation of cultural materials at the University of Canberra in Australia, specialising in Objects Conservation. After graduating she was awarded a Getty Post-Graduate Objects Conservation Fellowship at the University of Arizona in the US, followed by an A.W. Mellon Post-Graduate Research Fellowship in the Sherman Fairchild Centre for Objects Conservation at the Metropolitan Museum of Art in New York. Since then she has worked as an Objects Conservator in museums in Australia and Europe.

Gemma Mitchell is completing her PhD studies within the Analytical Chemistry Department at the University of Strathclyde, Glasgow. She is part of a team led by Dr L.T. Gibson working on the Heritage Smells! project funded by the Science and Heritage programme. Specifically her research relates to the analysis of VOCs from modern and contemporary materials used in museum objects.

Iain D. Rushworth is a researcher at the University of Strathclyde, Glasgow. He completed his MSci degree in forensic and analytical chemistry at Strathclyde in 2008. He is due to complete a PhD in analytical chemistry at Strathclyde under Dr Lorraine T. Gibson in the summer of 2014. His current research interests are vapour phase analysis of VOCs, and non-invasive screening methods for the determination of pesticides and chemical hazards in heritage collections.

Catherine Higgitt completed a PhD in chemistry at York in 1998. After seven years as an organic analyst at the National Gallery, in 2007 she moved to the British Museum as Head of Science. Her particular interests are in the analysis of amorphous organic materials associated with, or used in the vicinity of, art and cultural heritage artefacts including natural product materials, colourants, modern conservation materials, polymers and VOCs, using a combination of spectroscopic and chromatographic techniques. Research interests also include the ageing and deterioration of such materials and their interaction with pigments and object surfaces.

Lorraine T. Gibson is a Senior Lecturer in Analytical Chemistry at the University of Strathclyde, Glasgow. Research interests include heritage science, silica nanoparticles, environmental monitoring and remediation. Specifically her heritage-related research includes studies on object deterioration, pollution monitoring, sorbent synthesis and design, the development of sensors for VOCs and pesticides. She has served two terms as Vice-President of the Analytical Division of the Royal Society of Chemistry (AD-RSC), is a committee member of the Science and Heritage subgroup of the Analytical Methods Committee and is a founding member of the international Indoor Air Quality (IAQ) conference series.

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