From Samples to Complex Objects

Detecting Material Degradation in Plastic Artworks

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I, Mark Kearney confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

[redacted]—

Mark Kearney

Everyone gets everything he wants. I wanted a mission, and for my sins, they gave me one. Brought it up to me like room service.

Captain Benjamin L. Willard, Apocalypse Now

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Abstract

The prevalence of polymers in our daily lives has slowly begun to be reflected within the collections of various museums. The realisation that not all plastic objects are as stable as more traditional materials – such as metal or stone – has ushered in a host of new challenges. Central to understanding the broader issues relating to 'modern polymeric materials' is the ability to identify their base polymer and monitor their degradation.

By exploiting the natural phenomena by which plastic objects emit volatile organic compounds (VOCs), this thesis aimed to investigate the use of VOCs, via solid phase microextraction (SPME) gas chromatography mass spectrometry (GC/MS), to monitor the degradation of art and design objects made in part or exclusively from plastics.

This project highlighted the binary nature of SPME analysis – one the one hand the methodology is able to detect identification and degradation markers emitted from an object with ease. On the other, tracking those markers over long time periods is extremely difficult. The project noted a number of influencing factors to the resulting VOC profile with fluctuations in temperature seen to cause the greatest difficulty.

Experiments investigating temperature's role showed that VOC emissions were depressed when analysed at lower temperatures, however, no consistency was found between either the different samples or the different VOCs examined. Therefore, no conversion factor can be applied to either sample or VOC in order to account for a change in temperature.

Principal component analysis (PCA) highlighted the importance of examining a VOC profile emitted from an object rather than relying on

a single VOC. Through the use of PCA it was possible to distinguish many of the different temperature and aging combinations.

Impact Report

This project concerned itself with improving the disciplines understanding of how to monitor the degradation of modern polymeric materials. Its foundation was the *Heritage Smells!* project which developed and proposed a methodology for the examination of emitted VOCs from this material type. This project moved the discipline forward by examining whole objects, examining the external influences and limitations on the methodology, and building a clearer understanding of how degradation progresses as a material ages.

From an academic standpoint this project developed a new framework under which Solid Phase Microextraction GC/MS can be deployed. Furthermore, this project identified weaknesses in the methodology and undertook research to quantify these limitations to reinforce the working parameters of the framework. Finally, through this project a research pathway has been laid out in which the impact of VOC analysis can be fully maximised in future research projects.

There are a number of tangible benefits which this project has been able to provide to the wider heritage community. A by-product of the research into temperature effects was a clearer understanding of how materials behave in cooler storage conditions. As the heritage industry strives for greater efficiencies and sustainability this research provides both the evidence and the framework needed to justify certain policy shifts within the industry. The project also has the potential to shift professional practice by virtue of its insights into how exactly VOCs should be measured as well as how, using the developed methodology, individual institutions could build evidence for their own policy initiatives. There are also benefits to the objects themselves; objects of historic or artistic significance that are comprised in part or wholly of modern polymeric materials are entering into institutions in greater numbers as their cultural importance rises. This project has not only shown how to monitor their decay but also how to preserve them for a greater period of time.

This research project has the scope to impact institutions at all levels. Locally the project has reinforced UCL's reputation as modern materials research centre and expanded its research capacity in the area. The project's heritage partner, Tate, also gained valuable insight into their collection and storage environment which will aid its policy direction moving forward. The project has also helped the wider national heritage field though the publications and workshops which were held during its duration. These events facilitated those institutions who were not direction involved with the project to gain access to its findings before publication of the full thesis. The project gained international impact via its role as part of a wider Horizon 2020 European Union funded project NANORESTART. Collaborations with partners in France (ARKEMA) and Slovenia (Kemijski Inštitut) fostered new working relationships with the UK and aided in the successful development of the research framework.

This project had a number of tangible impacts during its lifetime. Two peer reviewed papers were published based on its findings –

1. Kearney, M. *et al.* (2018) 'Characterisation of VOCs Surrounding Naum Gabo's Construction in Space "Two Cones", (Tate) by in situ SPME GC-MS Monitoring', *Studies in Conservation*. 63(sup1), pp. 369–371. doi: 10.1080/00393630.2018.1486530.
2. Kearney, M. *et al.* (2020) 'Factors affecting the practicality of solid-phase microextraction VOC analysis of artworks featuring polymeric materials in open environments', *Microchemical Journal*, 155, p. 104711. doi: 10.1016/j.microc.2020.104711.

Four presentations were given two at international conferences and two UK based workshops –

1. Future Talks 017 , Munich, Germany, 2017
2. Technart, Bruges, Belgium, 2019
3. Tate Research Seminar, London, UK, 2018
4. UCL Plastics Workshop, London, UK, 2019

These talks exposed a larger number of participants to the research findings. Included in attendance at the UCL workshop were representatives from The British Museum, The British Library, The Victoria and Albert Museum, The Science Museum, and The Welcome Trust. The international conferences engaged with members from the Getty Conservation Institute and the Canadian Conservation Institute.

Four posters were delivered, again at major international conferences for both heritage and polymer science audiences –

1. 8th Mass Spectrometry and Chromatography (MaSC), Évora, Portugal 2017
2. NANORESTART, Copenhagen, Denmark, 2018
3. 10th International Conference of Modification, Degradation and Stabilization of Polymers (MoDeSt2018), Tokyo, Japan, 2018
4. IIC 2018 Turin Congress, Turin, Italy, 2018

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Chapter 1 Examining Historic Polymer Objects within the Context of a Museum –

1.1 Plastics – Where have they come from?

It would be fair to assert that the general public think of 'plastics', or what will be known as modern polymeric materials in this thesis, as being a relatively contemporary invention. However, given that the earliest examples of what we now commonly refer to as 'plastic' originated in the middle of the 19th century, within a heritage reference frame there is little contemporary about them. However, what is contemporary about these materials is the framework under which they have been conceived and manufactured. Unlike 'traditional' materials such as stone or wood, whose tools and workflows have been unchanged for centuries, from their very conception modern polymeric materials have utilized the latest understanding of material science to formulate, rather than craft, material to the required needs.

By the 1850s the properties of raw natural materials were being altered, in a process which has been likened to alchemy (Barthes, 1957) that renders the final material greater than the sum of its parts. This is clearly seen in the development of the semi-synthetic polymer cellulose nitrate (CN), first manufactured and exhibited at the Great International Exhibition in 1862 by Alexander Parkes and marketed as Parkesine (Shashoua, 2008, p.3), which is a combination of cellulose, a naturally forming compound commonly found in cotton, and nitric acid – hence the term semi-synthetic. Through further innovation the commercial product Celluloid (CN mixed with camphor) would be developed (Gilbert, 2017). CN had the ability to be manufactured in such a way as to mimic natural materials that were often far more costly to acquire. Ivory has been used for billiard balls, boning for corsets, the handles of hairbrushes while tortoiseshell had been utilized for combs, spectacle frames, and jewellery. It is certainly true that in the case of the tortoise the intensive farming of the animal had brought it to the verge of extinction, however, CN's ability to mimic the characteristics of these rare and luxurious materials helped to ease the pressure on their farming (Hainschwang *et al.*, 2011). The lower cost also allowed more people to acquire these mass-market objects which in turn helped to develop a more consumeristic society and in turn devalued the allure of the materials it was counterfeiting (Boyd, 2011). CN was also highly flammable; its manufacturing method is dangerously similar to the explosive 'Gun Cotton'. This led to a number of accidental fires, most notably the Cleveland Clinic Fire of 1929 with the loss of 123 lives[1] due the ignition of CN film negatives (National Board of Fire Underwriters and the Ohio Inspection Bureau, 1929; Clifton, 2013). Due in part to safety concerns, and to the need for slightly different properties a new material was developed – cellulose acetate (CA). Within the context of the film industry this new material was marketed as 'safety film' (Hainschwang *et al.*, 2011).

It was not until the turn of the 20th century until the first truly synthetic 'plastic', Bakelite, was developed by Leo Baekeland (Baekeland, 1909). The insulating properties of Bakelite were instantly sought by the newly emerging electricity industry. In a stepwise synergetic collaboration with the radio industry, which itself was dependent on electricity, Bakelite became the vanguard material in radios in the new zeitgeist of design – modernism (Hand *et al.*, 2004; Schwartz, 2006; Crespy *et al.*, 2008; Osdene, 2018). By this point CA had also flourished in its use in the film industry where it was used for still and motion picture film base; these alliances also marked a change in the use of plastics, moving away from mimicking a natural material towards objects whose inherent

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[1] CN is now recommended to be stored in cool conditions and in a fireproof housing. Its manufacture is so dangerous that a risk assessment to manufacture a sample as part of another project at ISH was rejected on safety grounds by UCL.

value was imparted by the material properties they were made from (Boyd, 2011; Fisher, 2013).

The interwar years saw a number of fully synthetic polymers developed. However, the second world war limited their commercial potential. The war did not limit their production though with one estimate of production increasing four-fold between 1939 and 1945 (Freinkel, 2011).

The newly acquired manufacturing capacity was shifted from the war effort to consumers after the end of the war. Again this is seen in production terms which again dramatically increased between 1950 and 1970 by *"twentyfold to more than 25 metric tons [per year]"*(Chalmin, 2019). In essence, modern polymeric materials had become ubiquitous within post-war society with many countries including Britain, the USA, the Netherlands and Germany having developed a robust consumer plastics industry (British Plastics Federation (BPF), no date); (Strasser, 2019); (Lintsen *et al.*, 2015); (Rubin, 2008)).

Yet it was this very ubiquity which would lead to the third and current phase of modern polymeric materials' interactions with society. As early as the 1970s consumers began to question both the functionality of the materials (an example being with tales of cracking PVC coats in winter) and their toxicity (Fisher, 2013). Today we see an intense backlash against 'plastics' with more and more initiatives for 'sustainable' and 'reusable' products free from plastics. Much of the issue stems from the waste generated in modern lifestyles and the impact which modern polymeric materials have on the wider environment after the end of their useful lives (Buranyi, 2018; Pooler, 2020; Smith, 2020). For their part the plastics industry has identified that the *"Elimination of problematic or unnecessary plastic packaging through redesign, innovation, and new delivery models is a priority"* (British Plastics Federation (BPF), 2018). However, it remains to be seen if modern polymeric materials will rekindle the allure they had in the inter-war years. As Freinkel noted in her address to the Long Now Foundation - "*the relationship [between plastics & society] must be repaired because plastics are only going to be more important, not less important, to us in the future*"(Freinkel, 2012).

The status of modern polymeric materials has been intertwined with the social and moral behaviours of our society since their inception. As such, they form a vital part of our social, design, and artistic history. As the retelling of this history gains ever greater importance within our museums, their inclusion will only increase, even if their perceived social importance wanes. Over the coming sections, I will examine how museum professionals have identified the modern polymeric materials within widely varying collection types, how they have dealt with the fragility of many of the early material types, and how new analytical technology can aid in prolonging their lifespan for future generations.

1.2 Plastics within Museum Collections

As was previously discussed modern polymeric materials, as we commonly know them today, are not necessarily a contemporary material with many formulations having been in circulation for over 150 years. In their early incarnation, they mimicked a range of high-value natural materials and were utilised in the trickle-down democratization of design. The consequence of this is that historic polymer objects are found in a range of different collection types.

Some of the earliest collection survey work was carried out in the early 1990s by the larger London museums – The Victoria and Albert (V&A), The British Museum (BM), and The Science Museum. These early forays ranged from a simple count of the objects (circa 1,500 items at the Science Museum (Mossman, in Grattan, 1991)) to a more detailed examination of the state of the collection at the Museum of Childhood, which is under the direction of the V&A (Then *et al.*, 1993).

The V&A survey is an interesting case as it was followed shortly by additional work with other departments within the museum (Keneghan, 1996). This second survey not only expanded beyond what would be a polymer-rich collection at the Museum of Childhood, but into collections which one would not necessarily associate with modern polymeric materials.

This revelation coined a term which is still active within the community almost 25 years later *"Plastics denial syndrome"*. Many of those in charge of collections are only now coming to the realisation that polymers have infiltrated their collections – be it the cellulose nitrate masquerading as amber in departments of Egyptology, casein buttons in early 20th century couture dresses, or 3-D printed gap fills in 18th century furniture.

Yet despite the initial flurry of surveys in the subject in the early 1990's there seems to have been comparatively little published in the following years. The European Union funded project POPART did carry a mandate for the surveying of collections, and it was published (Lavédrine, 2012). However, there is anecdotal evidence which shows that institutions are simply not publishing the data they collect (Lambert, 2012). This reality hinders a researcher's ability to compile lists of polymer types prevalent within collections, accurately judge the current state of historic polymer objects within collections, and assess the future capacity needed for conservation.

These early surveys also introduced the term '*malignant plastics*' into the conservation vocabulary (Williams, 2002). This term relates to the five most common modern materials which prove problematic for museums – cellulose nitrate (CN), cellulose acetate (CA), polyvinyl chloride (PVC), polyurethane (PU), and vulcanized natural rubber (NR). It's understandable that those materials which cause the greatest concern have attracted the initial interest in research. However, this is at the expense of those materials which appear to be stable. However, as Williams (2002) rightly points out, other *benign plastics* carry their own risks. Work carried out in *POPART* in the early 2010s focused on materials such as poly(methyl methacrylate) (PMMA) which had been identified as being problematic in their own way (i.e. with respect to scratching during cleaning). There are signs that modern materials outside of those classified as malignant are attracting research interest; *NANORESTART NANOmaterials for the REStoration of works of ART,* the E.U funded project from which this project received funding, had provisions for the care & conservation of 3-D printed materials (Coon *et al.*, 2016)

Both the term 'malignant plastics' combined with the concept, introduced by Keneghan, of denial regarding the presence of modern polymeric materials within collections gives some indication as to the reputation of these objects held by museum professionals. This is likely a result of their behaviour as they age. Many of the early semi-synthetic materials undergo what can only be described as catastrophic degradation patterns as they age, wherein they effectively turn to dust. Fully synthetic materials such as flexible PVC can leach plasticisers. This leads to physical stability issues for the material itself while also causing a secondary issue of dust and contaminants adhering to the sticky plasticiser coated surface. PMMA, which is often utilized for its transparent properties is easy scratched thereby ruining its intended function. Shashoua (2008, pp.162) sets out a comprehensive list of degradation patterns. Other issues which influence the materials perception is the speed at which they degrade, and the irreversibility of this degradation. For example, it is very difficult to regain the cushioning effect polyurethane foams are often used for when they have been reduced to a fine dust. Both CN & CA can rapidly degrade over the course of a few months,[2] and combined with their degradation profile this can lead to the total disintegration of the material as well as potential cross-infection of neighbouring objects: it is clear why professionals are very concerned with the stability of modern polymeric objects within their collections.

1.2.1 Current pathways for identification of historic polymer objects

One of the concerns highlighted by the Practitioners Survey (King, work in preparation), which was undertaken by the COMPLEX working group at UCL, was that there was a lack of clear identification of the modern materials used in historic polymer objects within collections. There was also a clear hierarchy to the methods which have been employed when identification was attempted.

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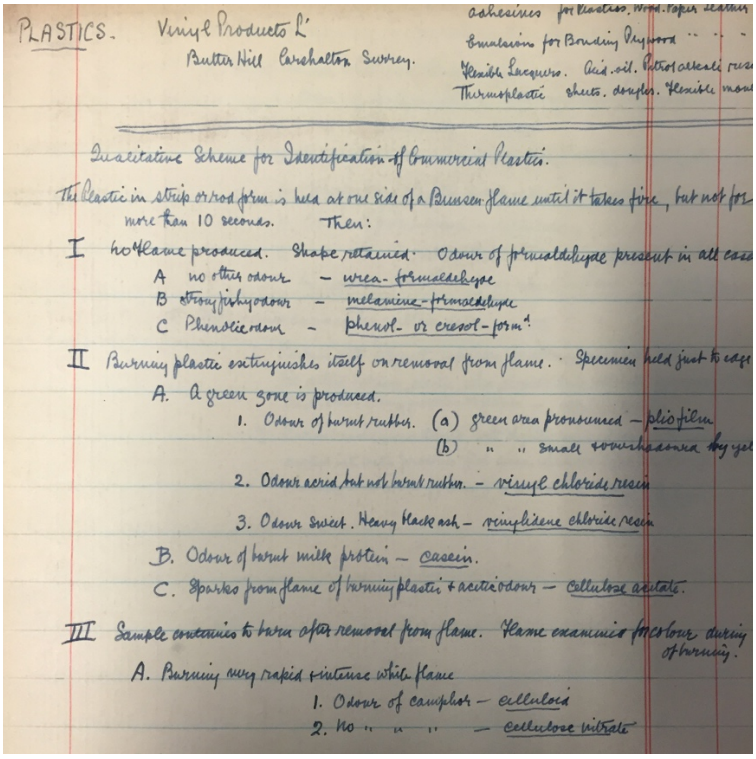
[2] As was personally observed by the author of the objects from the V&A used as samples later in this thesis.

There are a number of common methods which are utilized in the identification of base polymer within collections. They can be broken down into three main categories –

- Historic – those involving *burn tests* for example or previous working knowledge of polymers, or known history of use of named and well-defined products
- Sensory – Based on tactile qualities or smell under the framework of a flow chart.
- Analytical – Through the use of analytical equipment such as Fourier transform infrared (FTIR) spectroscopy

1.2.1.1 Historic

Within conservation ethics there are key tenets to do no harm and for any alteration to be reversible – in essence interactions with objects should be non-invasive and non-destructive (Ashley-Smith, 1982; AIC, 1994; ICOMOS, 1999; Roemer, 2016). However, before these charters were in place there was a tendency for polymers to be identified by way of a *burn test* or *pin test.* These tests required the destruction of a small quantity of the object by lighting them on fire and noting the smell of the fumes released when the flame had been extinguished. Figure 1-1 shows an entry in a notebook by a conservator at Tate Britain from what is believed to be the 1960s.



PLASTICS. Vinyl Products L

Butter Hill Carshalton Surrey.

adhesives for Plastics, Wood, Paper, leather

Emulsions for Bonding Plywood " " "

Flexible Lacquers. Acid. oil. Petrol alkali res

Thermoplastic sheets. couples. Flexible mou

Qualitative Scheme for Identification of Commercial Plastics.

The Plastic in strip or rod form is held at one side of a Bunsen flame until it takes fire, but not for more than 10 seconds. Then:

I no flame produced. Shape retained. Odour of formaldehyde present in all case

A no other odour – urea-formaldehyde

B strong fishy odour – melamine-formaldehyde

C Phenolic odour – phenol- or cresol-form^d

II Burning plastic extinguishes itself on removal from flame. Specimen held just to edge

A. A green zone is produced.

1. Odour of burnt rubber. (a) green area pronounced – pliofilm

(b) " " small [illegible] dry yel

2. Odour acrid but not burnt rubber. – vinyl chloride resin

3. Odour sweet. Heavy black ash – vinylidene chloride resin

B. Odour of burnt milk protein – casein.

C. Sparks from flame of burning plastic + acetic odour – cellulose acetate.

III Sample continues to burn after removal from flame. Flame examined for colour during of burning.

A. Burning very rapid + intense white flame

1. Odour of camphor – celluloid

2. No " " " – cellulose nitrate

Figure 1-1 – An image taken from the notebook of a conservator at Tate Britain from the 1960s. It describes some of the burn tests carried out in the museum and notes the smell emitted from common early modern polymeric materials such as casein and cellulose nitrate.

There are a number of reasons why this test is no longer considered appropriate for use within a museum context such as discriminating among the vast range of newer materials which had yet to be developed when the burn tests were first introduced and not least the fact that the fumes emitted are themselves toxic to the practitioner (Health and Safety Executive (HSE), 2002).

Another method which can be classified as *Historic* is a practitioner's previous experience working with modern materials. This is classified as such because it requires significant time devoted to understanding how to accurately assess an object. There are issues with this process though – firstly it can be difficult to begin learning the different types of base polymer without confirmation from a more advanced methodology. Secondly, it requires numerous interactions with modern materials, something that can only be acquired with time and as such emerging professionals or those who only casually interact with modern materials lack this experience. Therefore, while it can be a quick and easy way to identify the base polymer of a historic polymer object, it cannot be recommended for widespread practice.

1.2.1.2 Sensory

Identification by way of sensory observation is one of the most widely used (Practitioners Survey). This encompasses the use of hands (e.g. - to feel for ridge lines from moulding) or smelling the object (e.g. the smell of vinegar from the degradation of cellulose acetate). While this category has many overlapping features of the previous, it differs by its utilization of a standard framework.

A number of different institutions have produced a framework in which sensory observations lead to the identification of the modern material used in an object. One of the earliest was a flowchart produced by the Museum of Design in Plastic, Brighton (Museum of Design in Plastics, 2017). While this work was a significant step forward, incorporating institutional knowledge from members of the Plastics Historical Society, there were known limitations. Subsequent research at the V&A museum aimed to update the MoDiP framework and adapt it to suit the needs found when examining museum collections (van Aubel, 2017). These documents form an important resource within conservation as they distil the historic knowledge of experts into a workflow which those unfamiliar with modern materials can follow. They have their limitations and are not a replacement for the analytical examination of the object, but they offer a cost-free and reasonably accurate entry into identification.

Another widely used aspect of sensory identification is the use of smell. It is pertinent to separate this method from its use in flowcharts as its use is widespread as a stand-alone method. Most commonly it is used in the identification of cellulose acetate due to the strong vinegar smell emitted caused by the production of acetic acid during degradation. This phenomenon has been utilized in a commercial product which replaces the olfactory sensor (the nose) with a strip of paper impregnated with a chemical indicator (A-D Strips). These strips, which are manufactured by the Image Permanence Institute for the detection of degrading cellulose acetate-based film stock, aim to associate a specific colour change to a four-point severity index. Some issues should be noted with these strips – they are sensitive to other acidic compounds than acetic acid, and the subjective nature of the colour change coupled with inconsistencies in the printing on the pencil used for scale comparison. Recently their use has been improved through the use of a colorimeter (Hackney, 2016). However, their use with specialized equipment is limited to well-resourced institutions.

1.2.1.3 Analytical

With respect to modern polymeric materials, which can be manufactured entirely from synthetic compounds derived from petrochemicals, a number of analytical techniques have been employed in their study which exploits these natural physical and chemical properties. These techniques have been best outlined in the identification chapter of the POPART publication (Lavédrine, 2012).

The book outlines three main spectroscopic techniques which examine modern material using different electromagnetic frequencies. Of those techniques listed by POPART, the method with widespread use within the heritage community is Fourier transform infrared (FTIR) spectroscopy. Within the context of this thesis, FTIR features as both a method to compare the performance of our proposed methodology against and to cross-validate the data collected from the new methodology.

FTIR works via two basic physical theories – the first is that the energy of radiation is a function of its frequency, which itself is a function of its wavelength –

$$E = hv = \frac{hc}{\lambda} \qquad \text{Equation 1-1}$$

The energy E is a function of h (Planck's constant) and the frequency v which is inversely proportional to its wavelength λ.

The second is that the different bonds which make up an organic molecule vibrate at different specific energies. In certain cases, and for the sake of simplification, these bonds can be thought to act as springs and to be governed by Hooke's Law. The frequency at which they vibrate is given by (Burke, 1997) :

$$\overline{v} = \frac{1}{2\pi c}\left(\frac{k(m_1 + m_2)}{m_1 m_2}\right)^{\frac{1}{2}} \qquad \text{Equation 1-2}$$

The frequency of vibration $\overline{v}$ is a function of the two masses m_1 & m_2 of the atoms and k, the force constant of the bond. c is the speed of light

During analysis, the infrared (IR) radiation emitted by the FTIR device interacts with the molecules of the sample. If the frequency of the radiation corresponds to the frequency of the vibration of one of the chemical bonds in the sample, the radiation will be absorbed. This absorption results in the vibration of that molecule and the type of vibration is dependent on the type of bond between the different molecule components. As the instrument measures across its IR range, which is typically between wavenumbers of 400-4000 cm^{-1} at a resolution of 4 cm^{-1}, what is recorded are the frequencies where absorption has taken place. FTIR spectroscopy, therefore, is a measurement of these absorptions and consequently the bonds within the sample. This is helpful for the identification of modern materials because each of the different functional groups has its own specific resonance frequency and as such one can build up a picture of the bonds found within the sample to determine its potential identification. It is also useful to detect the emergence of degradation products. For example, the formation of carboxylic acids, associated with oxidative degradation can be seen via the emergence of a peak at circa 1700-1725 cm^{-1}.

It is also worth noting some of the characteristics of specific FTIR methodologies. One of the more commonly used methods in cultural heritage is Attenuated Total Reflection (ATR) FTIR, sometimes on a micro scale. This allows for FTIR analysis of a sample with little sample preparation, and often, if the sample is small, it is possible to measure an object without taking a sample. This method exploits Snell's law and in doing so allows the incidence IR beam to penetrate the sample to a small degree. The depth to which the IR beam penetrates into the sample is a function of the respective refractive indexes, the wavelength, and the angle of incidence. It can be calculated via the formula below (Schneider *et al.*, 2013) –

$$d_s = \frac{\lambda}{2\pi n_1\sqrt{\sin^2\theta - (n_2/n_1)^2}} \qquad \text{Equation 1-3}$$

This equation gives the depth to which a wavelength λ will penetrate into the sample. n_1 is the refractive index of the ATR crystal used, while n_2 is the refractive index of the sample. θ is the angle of incidence of the IR beam onto the sample.

For example, in this research, a Bruker Alpha II was used for ATR-FTIR analysis. This has wavenumber range of 400-4000 cm^{-1}, uses a diamond crystal with a refractive index of 2.4 and an angle of incidence of 45 °. For our cellulose acetate samples, a refractive index of 1.5 equates to a penetration depth between 25 and 0.5 μm. Therefore, the ATR-FTIR analysis quoted in this thesis is, in essence, a measurement of the surface of the sample rather than its bulk. This has implications, as will be seen in Chapter 6, for our understanding of the degradation process and the effectiveness of using FTIR data on historic polymer objects.

Another analytical technique often used for the analysis of polymers is gas chromatography combined with mass spectrometry (GC/MS). As this is the main technique utilized in this research it will be discussed to a greater degree at a later stage. However, it is worth noting that it is traditionally utilized to a lesser degree than FTIR within cultural heritage for the analysis of historic polymer objects. One issue with GC/MS is that it is often coupled with pyrolysis which is a destructive sampling technique. Furthermore, it is also a costly method to use. Therefore, FTIR, which offers many of the same results but at a lower cost point and often without the need for samples (or destructive sampling) has been favoured.

1.3 Pathways to degradation

As most modern materials are manufactured for an industrial application the main stakeholder dictating their construction and consequently their lifespan is industry. Therefore, the expectations which museums place on lifespans do not align with those of industry. This concept is noted by Shashoua (2008) who uses the example of PVC windows and contrasts their normal industrial lifespan of circa 20 years to the 50-100 years museums wish to preserve collections for (Dillon *et al.*, 2013). This can place undue stress on museum professionals as they are battling against an object whose intended lifespan is significantly shorter than the mandate in which it now finds itself placed under.

Despite these realities, the mechanisms by which modern materials deteriorate are similar despite the difference contexts in which the occur. We can, therefore, speak of general pathways which most modern materials experience during degradation and can initially lean on the work provided by industrial research.

Within the degradation cycle there are two categories which can cause damage to modern materials – chemical and physical. While many of the physical degradation manifestations are related to chemical changes (which will be discussed in due course) some physical changes are user-generated and can therefore be controlled or prevented. For example, the polymer hinge on a polypropylene box does not have to be used in a museum setting and issues surrounding the loss of context, through the loss of constituent parts in a multipart object, can be limited by way of correct collections management. While physical damage to modern materials is a pressing concern, especially in terms of practical conservation treatments (Lavédrine, 2012; Kearney *et al.*, 2015; Fricker, 2016), it is not within the remit of this research. Additionally, there are numerous different mechanisms by which the different polymer base materials may degrade. The remit of this thesis is not the investigation of chemical degradation pathways and for brevity the following sections will deal with two general types which affect the stability of the materials tested in this research.

1.3.1 Degradation via interactions with oxygen

Many modern materials follow a degradation pathway that involves oxygen. In this reaction parts of the main polymer molecule are broken apart through the reaction with oxygen. As oxygen is so prevalent in the atmosphere (at 21%) there is no method, bar anoxic storage, which does not place modern materials in its direct contact.

There are two main pathways under which these reactions can be initiated or enhanced: photo-oxidation, the interaction with oxygen and light and thermo-oxidation, the interaction with oxygen and heat. Both of these lead to a situation where the mechanical properties of the material are altered, with the end-stage being the destruction of the material. As Williams notes in (Grattan, 1991, p. 140) the degradation of modern materials can lead to physical changes *"In such properties as colour, brittleness, tack, surface gloss or crazing or chalking, release of volatile substances, and many other chemical, mechanical, and physical properties*."

Oxidation follows a defined trajectory, as set out by Shashoua (2008, p. 172) – The first initiation is followed by propagation of the reaction and ends in termination. The beginning starts with the production of free radicals from the removal of the most reactive hydrogen atom in the polymer ***(R)*** in the presence of either heat or light.

$$polymer\ R \xrightarrow{light\ or\ heat} 2R^{*}$$ Equation 1-4

These free radicals ***(R*)*** then react with oxygen to form alkoxyl radicals, this in combination with the polymer in turn forms hydroperoxides.

$$R^{*} + O_2 = RO_2^{*}$$ Equation 1-5

$$RO_2^{*} + RH \longrightarrow ROOH + R^{*}$$ Equation 1-6

It is this propagation stage which causes the most damage as it provides further free radicals to continue the reaction for a longer period. The reaction is only stopped when the radical species produced react with each other and terminate the production of further radicals.

Photo-oxidation is typically associated with the exposure of the material to UV-radiation. Equation 1 works against certain polymers as at certain wavelengths the energy of the irradiance is sufficient to break the chemical bonds. UV radiation in the range of 290-400 nm has enough energy to surpass the dissociation energy (the energy required to break a bond) with the production of a free radical which, as can be seen above, leads to the degradation cycle.

1.3.2 Degradation via interactions with water

The reaction of a polymer with water, hydrolysis, can lead to the chain scission of the main polymer backbone (as seen in polyurethanes) or in a reaction which is less malicious chain scission of the side groups can occur.

Hydrolysis is the process which leads to the most widely recognised degradation syndrome within a museum context – vinegar syndrome, which is the emission of acetic acid in the degradation of cellulose acetate and is commonly identified by its smell (Allen *et al.*, 1987, 1988). In this context the reaction happens when the acetyl group bound to the cellulose is removed leaving a hydroxyl substitution *(ROH)* and acetic acid *(HOAc)* where *Ac* is the acetyl group. (Ahmad *et al.*, 2020).

$$ROAc + H_2O \longrightarrow HOAc + ROH \qquad \text{Equation 1-7}$$

There is some debate within the literature regarding the progression of this reaction with one theory being that there is a certain point at which the level of acidity is great enough to allow an autocatalytic reaction to propagate significantly faster than when the sample was below this point (Image Permanence Institute, 2001). However, several recent studies have indicated that this viewpoint is misleading and that the degradation of the base polymer can progress at a faster rate than initially thought (Knight, 2014; Ahmad *et al.*, 2020).

The hydrolysis reaction of cellulose acetate first attacks the side chain acetate groups. While this lowers the degree of substitution which in turn does lower the overall molecular weight, its effect in the initial stages of deacetylation is minor; it is the production of acetic acid which causes the main issue. Therefore, the production of acetic acid further increases the degradation of the polymer molecule and leads to an associated loss in mechanical properties by way of chain-scission.

In general terms polymers that are susceptible to a reaction with water will see a lowering of their mechanical strength. As they age and are affected by oxidation to a greater degree they will also tend to grow more polar, which in turn increases their sensitivity to hydrolysis (Shashoua, 2008; Fricker, 2016)

1.4 How does the profession deal with plastics?

1.4.1 General perception by the profession

For a profession which deals with the mitigation of change, its attitude towards the degradation of modern polymeric materials has been marked by dismay and fear. As was mentioned previously this was first noted by Keneghan who coined the term "*Plastics denial syndrome*" concerning the attitudes of some staff members to the concept of plastics within their collections (Keneghan, 1996).

The Practitioners Survey has identified that modern polymeric materials are a cause for concern for all but four of the seventy-two participants. There are analogies to be made between the negative attitudes of the heritage profession to modern polymeric materials and *Math Anxiety (MA),* a term derived from psychology describing *"a negative emotional response to current or prospective situation involving mathematics*" which can often lead a person to "*decreased maths self-confidence, enjoy maths less and may even avoid maths altogether*" (Hill *et al.*, 2016). Yet as Maloney and Beilock, (2012) note "*people's anxiety about doing math – over and above their actual math ability – is an impediment to math achievement*" – in other terms, it is not that they can't do something, but rather they *think* they can't. Heritage professionals are capable people with the profession having high levels of training - 78% of whom have at least one degree while 46% hold a post-graduate degree (Aitchison, 2013). It is clear that the perception of modern polymeric materials has been skewed in such a way so as to provoke negative responses. In the framework provided by Ashcraft, Krause and Hopko, (2007) *negative math attitudes* can lead to MA. We in the heritage profession have certainly contributed to negative attitudes surrounding modern polymeric materials – this is clearly seen in the terminology given to describe them; *Plastics denial syndrome, malignant plastics, & vinegar disease* are phrases which do not convey positive emotional responses. Ashcraft, Krause and Hopko, (2007) also note that *Inadequate skill* is a further contributing factor to MA. Again, it has been noted the heritage profession is lacking in terms of the development of strategic capacity – Madden and Learner have noted, as recently as 2014 that "*Even with knowledge transfer and recent advances in material characterization, our understanding of plastics stability remains rudimentary*" (J.Paul Getty Trust, 2014).

1.4.2 Recognition & development of the issues

Despite the recency of Madden and Learner's comments the main themes pertaining to modern polymeric research, within a heritage context, have been identified for almost thirty years. The *Saving the 20th Century* conference, held at the Canadian Conservation Institute in 1991, and its subsequent publication as post-prints in 1993, are considered as the formal start of research into modern polymer materials. The publication presents research on the topics of:

- Condition surveys & Institutional policy
- History of objects/polymers
- Degradation pathways & example case studies
- Scientific techniques & analysis results

However, after this initial gold rush of data there seems to have been a waning in the perceived enthusiasms for content. This is particularly true of the past ten years – analysis was conducted on five publication types – three conservation journals and the post-prints from two conservation conferences between the years 2009 and 2020. The journals were *Studies in Conservation, Institute for Conservation (ICON) Journal,* and the *Journal of the American Institute for Conservation (JAIC)*, while the conferences were IIC's Biennial Congress and ICOM-CC's triennial conference. Table 1-1 details the number of publications in four different categories – these categories divide the research into Treatments – papers pertaining to work which has been competed on objects or the development of treatment methodologies; Science – The methodologic development and analysis into any aspect of modern polymeric materials; Ethics & Policy – Research into the ethics of the care of modern polymeric materials & the development of institutional policies; Other – Those papers which do not satisfy the other three conditions, in this case these are generally book reviews.

	Treatment	Science	Ethics or Policy	Other	Total
Journal/Conference					
Studies In Conservation	1	7	0	1	9
JAIC	5	2	0	0	7
ICON	1*	1	2	0	4
ICOM-CC Conferences					
Lisbon 2011	5	5	0	1	11
Melbourne 2014**	9	3	1	0	13
Copenhagen 2017	3	5	0	0	8
IIC Conferences					
Los Angeles 2016	7	1	3	0	11
Turin 2018	0	2	0	0	2
Totals	31	26	6	2	65

Table 1-1 - *Use of modern materials in treatment; **Majority were posters and only abstract provided

The clear take away from this analysis is that there has not been enough work published over the past ten years given the level of anxiety felt by heritage professionals around modern polymeric materials. Nowhere is this better observed than at the IIC congress which in the five events held between 2010 and 2018 only two had publications regarding modern polymeric materials. While this is in part due to how IIC organises its conferences into themes, sometimes materials-based – with the L.A conferences being on modern and contemporary art – it does not excuse the deficit of research in the other conferences, especially with regards to treatment.

Furthermore, there is the issue surrounding posters at conferences and how they are reproduced in post-prints. For ICOM-CC conferences' posters have a short abstract accompanying them – while a very broad outline of the poster can be conveyed via 200 words, it is not a replacement for viewing the actual poster, or the depth to which the author can expand on in person, and later in a full publication. Additionally, IIC makes a distinction between posters submitted under the 'student' system and those submitted as 'normal' posters, with the abstract to the 'student' posters being unpublished in the post-prints. The consequence of this is that for the IIC Turin congress at least two posters (produced by the group based at UCL) were subsequently not published alongside the other works from that conference on the journal publisher's webpage. These policies deny professionals access to what is already a limited data pool and further compounds the issues raised by Madden and Learner. Additionally, there is a clear indication that there is significant interest in publications on the topic of modern polymeric materials – as of June 2020 the top two most read papers from *Studies in Conservation* were on the topic and the view count between first and third was over five thousand views.

Within the body of work which deals with treatment, there are two main themes which have been developing – those treatments which aim to conserve the originality of the object and return it to working order, and that which simply document and/or replace parts. The latter of these themes is best exemplified by Rivenc, Richardson and Learner (2011) & Rocha *et al.* (2011); both of these publications acknowledge the artist's intent that the object is ephemeral. This is a legitimate ethical viewpoint to hold, however, it again does not further the profession's understanding of practical treatments on historic polymer objects, nor does it account for objects whose artist is unable to comment on their conservation (through either death or disinterest). The former's theme has been best exemplified by the work of Anna Laganá whose series of publications has both provided vital information regarding the practical treatment of unsaturated polyester & PMMA and the level of research needed to develop these treatments.

In the initial study, the research questions regarding the successful conservation of the materials are outlined. The most important of these is the degree to which the refractive index of the adhesive and base polymer must be correlated (Laganá *et al.*, 2011). A number of common adhesives found in conservation are tested in this first study and recommendations are made on the best performing. Having successfully completed the exploratory stage the second publication further expands the range of adhesives tests while also tackling more intricate conservation procedures such as the repair of surface scratches (Laganà *et al.*, 2014). The second study also advanced the understand of the role of refractive index in successful treatments – "*For the filling of losses, an RI as close as possible to the RI of the object is mandatory. However, for more superficial damage… the visual performance of the resin might be weighed against its stability upon ageing*". This is vital information for professionals to have as it allows a nuanced & bespoke approach to treatments backed by research. The final study again expands the number of adhesive materials tested while introducing a new element of case-studies on 'real' objects (Laganà *et al.*, 2017). The net result of this comprehensive research, undertaken over the course of the three publications, is a methodology which is a reliable alternative to more invasive methods such as surface polishing.

1.4.3 Current research pathways

Since the *Saving the 20th Century* conference the direction of the profession has followed certain distinct '*mesocycles*' which have been outlined by Shashoua (2016). The focal points of these have been –

- Understanding degradation mechanisms and material characteristics
- Preventive conservation treatments to mitigate as much degradation as possible
- Interventive conservation treatments which aim to preserve and prolong an object's lifespan.

These mesocycles have been broadly outlined in the above text and show how the modern materials cohort of the profession has projected itself to the wider community. However, the biennial FUTURE TALKS conference series, based in Munich, Germany, gives a better understanding of the conversations which the cohort has internally. Examination of the lecture titles was conducted for all six conferences, which started in 2009 – a limitation of this is that some titles will not clearly state the intent of the lecture, however, as the post-prints are only printed in specially produced books, available at the succeeding conference, there is significant limitation to the long-term impact FUTURE TALKS can have. In the six conferences since its inception there has been an upward trend in interventive conservation treatment lectures. Furthermore, those interventive treatment reports have generally been polymer based rather than object based – for example in 2009 there were talks on *The Price of Pristine PMMA, Work In Progress – Practical Experience In The Conservation Of High-Gloss Polyester Resin and Flexible Polyvinyl Chloride Based On Exemplary Cases,* and *Stiletto. Double-Sided Problems with A Self-Adhering, Flexible PVC-Film.* This is in contrast to those delivered in 2019 where many lectures have now moved forward and begun to focus their attention on historic polymer objects and conservation specific to their individualistic needs - *Now You See It, Now You Don't. Conservation Of Lary Bell's Glass Sculpture 'Shadows', Dripping Surfaces. Exploring Degradation Mechanism Of Bio-Based Plastic Polylactide With Focus On Jerszy Seymour's 'Living*

Systems' (2007), and *Surface Deposits On Faux Leather. The Kem Weber 'Airline Chair'*.

We have therefore clearly moved to a point where the profession has the confidence to work on historic polymeric objects yet still lacks critical information in certain key areas.

1.4.4 Developing strategic capacity for future working practices

The issues highlighted above should indicate that while significant progress has been made in the understanding of how to care for historic polymer objects yet there remains a number of areas which have been slow to develop, have plateaued in their progress, or have not been fully explored yet. The publication of collection surveys has been lacking[3] which undermines efforts to plan for future needs; the conservation professional bodies have not disseminated vital information – which there is clear need and interest for; and those already working on historic polymer objects have developed their skill level to a point of working on specific objects rather than specific modern polymeric materials.

In Chapter 8.4 of this thesis, I will deliver the results of a workshop, held for heritage professionals, that outlined SPME and its use within heritage for the analysis of modern polymeric materials. However, very briefly that workshop identified that even still current professionals align with the issues discussed above.

These professionals, as will be detailed later, represented some of the most well-funded institutions in the United Kingdom – however, even these institutions faced issues with funding. Yet, despite this, the majority still acknowledged that VOC analysis was a useful tool available to

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[3] This is as likely to be due to funding constraints as anything else. However, if the priority given to undertaking these is low then any additional funding is unlikely to be spent on such endeavours

heritage. Crucially, some respondents echoed Madden and Learner's statement (J.Paul Getty Trust, 2014, pp. 8). While those who work with modern polymeric materials felt they had a good understanding of the basics, they felt that a deeper understanding was not present. The workshop also highlighted how professionals wanted to be helped by analysis – notably in aiding the identification of base polymer and diagnosing degradation mechanisms on specific objects.

Moving forward there is a clear need for a tool which addresses these gaps – a tool which allows for the identification of a wide range of modern polymeric materials so as to stay relevant as priorities shift from one type to another and aid in future collection surveys; a tool which can also monitor the degradation of different material types so as to provide detailed information to end-users; and a tool which has the specificity needed to meet the requirements of those professionals working on individual historic polymer objects. At the same time as filling these research gaps the tool must adhere to traditional conservation ethics – ideally, the tool would be non-invasive, non-destructive and easy to use.

Such a tool has been proposed in the form of a method to monitor the emission of volatile organic compounds (VOC) from individual historic polymer objects (Curran *et al.*, 2015)[4]. The remained of this thesis will focus on issues surrounding VOC analysis & the development of a methodology for its implementation within heritage settings.

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[4] Dr Curran, who co-wrote this paper, acted as lead supervisor on this PhD project.

1.5 Volatile organic compounds – An overview of use in heritage

Before moving further, it is also worth defining explicitly what the term volatile organic compound (VOC) means within the context of this thesis. This is due to the various different definitions found throughout the literature from different disciplines. For example, the Environmental Protection Agency in the United States defines VOCs *"as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions."* Within the European Union, VOCs are defined as *"any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101,3 kPa"*, which provides slightly more defined parameters than the United States (40 CFR § 51.100, no date; The European Parliament and the Council of the European Union, 2004).

There is clearly some discretion regarding the precise definition and as such for the remainder of this thesis the definition provided by Curran and Strlič (2015) that amends the European Union directive *"to incorporate any organic compounds that can be detected either by the human olfactory system, or by gas chromatographic-mass spectrometric (GC-MS based techniques, including those with boiling points above 250°C."* This takes into account the higher boiling points of some plasticisers found in historic polymer objects.

1.5.1 Environmental monitoring in heritage

The heritage field has both known of and taken an interest in the effect the environmental conditions surrounding objects, of all types, since before the 20th century (Faraday, 1859; Byne, 1899; Brommelle, 1964). Traditionally the concerns have surrounded the interactions of external pollutants, such as particles (classified as $PM_{2.5}$, PM_{10}), ozone, sulphur dioxide and nitrogen dioxide, which have for the most part been generated through the burning of fossil fuels (Grzywacz, 2006). These concerns have led to a position where institutions, both large and small, now at the bare minimum monitor temperature and relative humidity with many also monitoring dust (particulate) contamination (Prosek *et al.*, 2010; Shah *et al.*, 2011).

Recent studies surrounding indoor air quality (IAQ) from outside of the heritage field have shown that indoor/outdoor (I/O) ratios for certain VOC compounds and particulate matter are now biased towards indoor pollutants rather than the traditionally held view of external sources (Geiss *et al.*, 2011; Zhang *et al.*, 2015).

Taken as a whole, traditional environmental monitoring, while providing key information about external influences on collections have failed to take into account the role the objects themselves play in the IAQ of their surroundings. It also fails to capitalize on the information to be gained by examining their emissions. Policy documents also marginalise the effect of VOCs by suggesting the use of low-cost monitoring methods which do not indicate specific pollutants (British Standards Institution, 2012). This may in part be due to the prevailing theory that their impact will be lessened as lower emissions of the traditional VOCs are emitted into the atmosphere (Tétreault, 2003; Grzywacz, 2006), though as was pointed out above, research has shown that pollutants whose source is indoors, can be found in greater concentrations to those sourced externally.

1.5.2 How does heritage science utilize VOC analysis?

One area where VOC analysis is widely utilized within a heritage context is in the investigation of a materials potential effect on the collection it is stored or displayed with (Gibson *et al.*, 1997; Grøntoft *et al.*, 2010, 2014). This can be further divided into two trends, the first being high-level scientific analysis of display cases and their construction material and more basic pass/fail Oddy tests on a material which interacts adversely with collections (e.g. packing material, mounts etc).

The work by Dr Alexandra Schieweck at the Fraunhofer Institute has been particularly insightful with respect to the development of methodologies for the analysis of case materials (Schieweck, 2009; Schieweck *et al.*, 2009). There is a level of self-awareness with regards to the limitations of the experimental design, such as the use of non-porous, non-absorbing aluminium sheets as a substrate for their testing chamber which is balanced against the need to investigate industrial materials which are used in case construction due to the lack of conservation specific materials. This type of analysis has proven its worth in the findings that acetic acid can be formed in secondary reactions, even from materials which claim to be acid-free. The authors justify the rationale for more in-depth analysis over the easier tests because –

> *"While these simple tests may offer a kind of exposure–effect relationship, neither exact identification nor quantification of single pollutants is possible. As there are no building products available commercially which have been designed for museum purposes, it has to be considered that substances with proven low emissions regarding indoor scenarios under normal use are not necessarily qualified for application in the museum environment."* - (Schieweck *et al.*, 2009)

The justification provided here can also be applied for the need to monitor the objects themselves. As many historic polymer objects change as they age, they have the potential to emit compounds which had not been seen during their prior lifespan. These compounds can either be detrimental themselves or as Schieweck and Salthammer point out can form constituents of secondary reactions which can cause harm.

Any of the ‘simple tests’ which Schienweck and Salthammer may refer to are likely to include the Oddy test which has been in use within the heritage community since the 1970s and was originally designed for archaeological metals (Oddy, 1973). The advantage of the Oddy test is that it can be performed by those institutions whose resources are limited, combined with (in theory) an easily distinguishable pass/fail results system. Despite its prevalence, the limitations of the test have been broadly outlined since at least 1995 when Green and Thickett (1995) noted that “*It was evident that the assessment of the coupons was open to differences of opinion*”. Furthermore, the overall repeatability of the method was called into question by Pretzel and Shibayama, (2003) who noted in their tests that “*small discrepancies in methodology have a significant effect on the results of the test, leading to poor reproducibility*”.

There has been a number of research projects which aimed to build upon the work by Oddy and to minimise the experimental limitations (Strlič *et al.*, 2010; Wang *et al.*, 2011; Heine *et al.*, 2018; Korenberg *et al.*, 2018). Some projects such as that by Strlič, Cigić and Thickett (2010) aimed to amend the methodology to work for materials other than metals. Other projects aimed to improve on the repeatability of the test by improving on the methodological workflow (Korenberg *et al.*, 2018).

More recent studies have tried to bridge the divide between the high-level analysis and the Oddy test by taking the spirit of the Oddy test and combining it with evolved gas analysis–gas chromatography–mass spectrometry (Samide *et al.*, 2015, 2018). The benefits of such analysis are the specificity of the compounds found, removing the subjective nature of the Oddy test results and the rapid analysis time. Yet the fundamental issue which was described by Schieweck and Salthammer (2009) still stands – these tests evaluate materials such as packaging and not collection objects.

Returning to the concepts described in Chapter 1.4.4 the heritage industry is in need of a tool which can analyse objects in order to preserve them and limit their own degradation and their cross-contamination of other objects.

1.5.3 Testing the water for object analysis

There are however examples from the literature where VOC analysis has been conducted on objects, or whose research goal has been objects focused. However, the number of materials which this has been conducted on is limited.

Analysis of the VOCs from paper is a growing research area and shows how in an already well-established field VOC analysis can greatly inform heritage professionals about the identity of common VOCs which have been emitted, link these to degradation mechanisms and make recommendations regarding paper storage conditions to increase the lifespan of the object (Dupont *et al.*, 2000; Ramalho *et al.*, 2009; Fenech *et al.*, 2010; Strlič *et al.*, 2011; Gibson *et al.*, 2012; Tétreault *et al.*, 2013; Becker *et al.*, 2016; Battistel *et al.*, 2018).

The work by Fenech *et al.* (2010) is notable for a number of reasons – first is that through their research they further confirmed that the concentration of VOCs in museums was higher than the concentration of outdoor-generated pollutants, something which has been noted by researchers in other fields and again shows the need for VOC monitoring programs to be implemented within heritage. Secondly, their methodology using Tenax tubes had been adapted from work which had previously been designed to work with museum cabinets. This highlights that the base level technologies for VOC analysis can easily be adapted from measuring construction material to heritage objects. Finally, their results showing that archival boxes can have high levels of VOCs, specifically acetic acid, which in turn further damages the paper enclosed, shows how this type of analysis can have significant impact on standard working practices within heritage.

Research by Tétreault *et al.* (2013) is notable for correlating the effect of commonly found VOCs to the change in specific chemical properties of the material, such as the change in the degree of polymerization of the cellulose in the paper. This research is positive in two ways, the first is that it shows the relationship between degradation and VOCs (both the type and concentration). Secondly, by relating the degradation to a measurable parameter (the degree of polymerization) it facilitates scientifically backed decisions regarding collections care to be made.

Gibson *et al.* (2012) is noteworthy for the range of locations in which they monitored during their research. This demonstrates the versatility of VOC analysis insofar as its ability to be translatable between different institutions. Their research of a similar item housed at different institutions also highlights the subtitle differences seen for historical objects; unlike industry where quality control standards ensure uniformity, historic collections often greatly differ from each other and compound the need for a methodology which is adaptable to their individualistic nature.

The analysis by Gibson *et al.* (2012) is also noteworthy for a more nuanced reason. Their analysis of different institutions highlighted the difference of the library at Trinity College, Dublin. Having obtained an undergraduate degree at this university, this author can attest to the library's unique smell. Somewhat unwittingly the research team was able to capture the intangible heritage of a location and shows that VOC analysis is uniquely placed to capitalize on what is an especially difficult area of research for heritage in general. The work by Bembibre and Strlič (2017) develops the framework of VOC analysis to capture intangible heritage smells. This application of VOC research not only develops an entirely new field within heritage but the impact the research had on the general public greatly elevates the awareness of heritage science within that cohort (Greenwood, 2017; Wapner, 2017). Furthermore, this research also creates a potential revenue stream for heritage institutions who may be able to capitalize on their intangible heritage in a similar way to their physical collection.

1.6 VOC analysis of plastics

The analysis of VOCs emitted from plastic samples has been widely used in industry. This was demonstrated by Curran and Strlič (2015) in their review. It is worth acknowledging that their review clearly lays out the argument for the use of VOC analysis of polymeric material within a heritage context and as such this work will not rehash their argument. However, it is also worth noting that their publication reads less like a traditional review and more like a call to arms. It points to research gains which other fields have achieved through investment in techniques and methodology. With this in mind, this section will outline the current state of VOC analysis within a heritage context – how has the profession set about its research and how do the results align with the research gaps that were detailed in Chapter 1.4.4.

1.6.1 A snail's pace – progress in VOC analysis of historic polymer objects

The VOC analysis of historic polymer objects is extremely limited with few published papers on the topic over the past twenty years. A contributing factor to the low output is likely due to the few research groups which work in the area; there are three main groups – UCL under the direction of Dr Curran, The Getty Conservation Institute whose large remit facilitates VOC analysis as a complementary analysis tool, and a group based at Centre de Recherche sur la Conservation under the direction of Dr Lattuati-Derieux, however, this last group has not published on the topic in some time.

One of the earliest papers dealing with VOC analysis was not based on a modern polymeric material but rather a wax – however, it is included here as wax is still an organic substance and the paper gives pertinent information for polymer analysis within a heritage context (Lattuati-Derieux *et al.*, 2008). The paper sets the format for how VOC analysis is communicated. The results of the analysis are simply reported with no attempt at placing specific VOCs within relevant contexts. Identification of materials was based on direct comparison of reference samples which has been previously tested exclusively for this work. While there is significant merit to the information gained from such a study, its lack of standardization or quantification means that it is hard to translate these results to the work of others.

The second paper by the same author moves the discussion forward significantly (Lattuati-Derieux *et al.*, 2011). This paper highlights how VOC analysis can aid policy decisions by directly monitoring the effects that ageing can have on a polymer. However, while the research reports on VOCs found to be contained in the base polymer, the extraction methodology is limited in its real-world applicability. This is due to the elevated temperature at which the extraction method, head-space solid phase microextraction in this case, was conducted. Heritage institutions would never allow their collections to reach 60 °C and the authors do not offer a justification or clarification as to how the temperature difference would alter the VOC profile if measured at a more realistic museum temperature of 20 °C.

Lattuati-Derieux *et al.* (2013) is one of the first papers to offer VOC data on a broad spectrum of modern polymeric materials found within a heritage context combined with information gathered from real museum objects. This study examined both elevated and room temperature emissions yet does not offer a comparison of the two – this is vital information to exclude. Despite this omission, this paper is also important due to the classification systems which it introduces; by sorting VOC's into 'specific' vs 'non-specific' VOCs with respect to the base polymer. While this classification concept is a step forward, it is hamstrung by the choice of what to place into each category. By placing VOCs pertaining to additives in the non-specific category the reader loses critical information on the identification of certain modern polymeric materials – such as camphor which is often used for CN identification. A similar situation is seen in the poster, and accompanying journal publication by Mitchell et al.(Mitchell and Gibson, 2014; Mitchell, Higgitt, *et al.*, 2014). These researchers also aim to classify the kinds of VOCs emitted by common polymeric materials, but yet again do so at elevated temperatures which would not be seen in a heritage context. However, this paper does move the topic forward by attempting to link certain VOC emissions to the types of degradation seen by heritage professionals – such as the increased DEP emissions being linked to the embrittlement of the sample as well as oxidation products being emitted from PVC which had yellowed upon ageing.

The papers by Thiébaut are excellent examples of comprehensive VOC analysis research which examines real museum objects (Thiébaut *et al.*, 2007, 2009). Its use of a 'Sensory odour ranking' by a panel of ten people allow heritage professionals to compare their expectations of a smell/degradation relationship with the results of objective analytical tests. Furthermore, despite tests at elevated temperature we also see a comparison with room temperature sampling. This research showed that additives are harder to detect at lower temperatures. However, from the object's perspective, fewer additives emitted would likely mean the object is at a more stable state. We also see comparisons between objects based on relative abundances of different VOCs. This is vital information as it is the beginning of the development of 'VOC profiles' for both stable and degraded objects.

As with the work by Thiébaut, the research by Curran *et al.* (2014) offers a clear methodological pathway – A definitive degradation marker, in this case, a change in the degree of polymerization, is correlated to the VOC emissions and we have both elevated and room temperature measurements. This research also examined a phenomenon which many in the profession would have instinctively concluded – the damage to secondary (often healthy) objects via cross-contamination by an initial degraded object. Through this research there is now empirical data, via VOC analysis, to show that this is true. The direct impact of this VOC analysis is that it allows for a scientifically backed justification for certain collections care policies to be implemented. We are also shown that real objects, of a similar base material, do not behave exactly the same due to formulation differences. This again highlights the individualistic nature of heritage objects and the need for a tool to account for this during any monitoring programme.

In another paper, the same author as above highlights how VOC analysis can be used to examine packing material; while these are not historic objects it does progress both the methodology of the analysis and contributes to the knowledge of the suitability of industrial materials within heritage collections (Curran *et al.*, 2017). Furthermore, we learn that often materials which are thought of as safe to use in heritage context can emit acetic acid, which is harmful to objects.

Yet it is with their publication in 2018 where the author offers the greatest potential to impact the direction of VOC analysis of historic polymer objects (Curran *et al.*, 2018). Their use of a 'VOC profile' specific to that modern polymeric material combined with the use of both a calibration standard and multivariate analysis leads to a position where a heritage professional can objectively classify the health of their collection. However, its use of ground 50 mg samples is a limitation as ideally the methodology would be non-invasive, non-destructive, and scaled to real objects. Yet as a proof of concept the publication excels.

A number of other studies have reported on common VOCs which have been collected not through direct emission but via Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) (Schilling *et al.*, 2010; Giachet *et al.*, 2014; Pellizzi *et al.*, 2014). These papers use VOC analysis less for its own intrinsic value but rather as a complementary technique to the others used. This does not mean that meaningful determinations cannot be made - Giachet *et al.* (2014) give an excellent example of how matching plasticiser ratios can correlate to production year. However, the use of Py-GC/MS, which is a destructive technique, coupled with the fact that the compounds themselves were not detected via an explicit VOC analysis technique does detract somewhat from the overall relevance of the research. Yet, the information gained from these studies, in a field with already limited information, can only aid with future work which may use other techniques that directly measure VOCs.

With this is in mind, another technique, Evolved Gas Analysis (EGA), which utilizes the mechanics of Py-GC/MS but without the physical act of pyrolyzing has given deep insights into the types of VOCs contained in samples (Schilling *et al.*, 2011; La Nasa, Biale, *et al.*, 2019). EGA was mentioned previously when discussing modifications to the Oddy Test, and its main limitation for use with historic polymer objects is its destructive sampling procedure - 100 µg in the case of Schilling and Learner (2011) and 500 µg for La Nasa *et al.* (2019). The benefits are the same as with regular Py-GC/MS, an increase in the available information for future, less destructive, object analysis.

In summary – there has clearly been an evolution in the direction of the research, an initial state of simple reportage of VOCs emitted from commonly found modern polymeric materials followed by work on historic polymer objects at room temperature. There are also the beginnings of a further shift where VOCs are grouped into a profile which is then being used to judge the health of an object against its peers. However, only a few papers are developing these methodologies which limits the overall impact of the technique and fails to develop a monitoring solution for heritage professionals.

There is a clear need for an adoption of a standardized analytical method. This method needs to be adaptable to a wide range of polymer types and has the ability to examine both small and large scale objects. Curran *et al.* (2016) has proposed using solid phase microextraction (SPME) GC/MS as it has the adaptability to meet the above needs and overcome the limitations discussed so far.

1.7 Pathway to success - VOC analysis in other disciples

There are two main external factors which determine the rate of development of VOC analysis within the heritage field – time and money. The heritage industry is small and as such the available person-hours which can be spent in the development of any one technique is limited. The industry is also poorly funded so even if the capacity was present, funding it would in itself be extremely challenging.

It is therefore shrewd to examine complementary research fields for guidance on best practices and also to frame the potential impact of VOC analysis can have within heritage by comparison with what has been achieved elsewhere. In doing so it may be possible to identify common issues and explore if the solutions found by others can be adapted within a heritage framework.

1.7.1 The medical industry

The issues faced by the medical industry, with respect to VOC analysis are very close in comparison to those in the heritage industry. Instead of researching complex historic polymer objects, we have the examination of complex humans, each of whom makes up a unique system. In the past decade, a new research field has opened within medicine – breath analysis. This is the study of exhaled breath, through non-invasive means, for the purpose of diagnosing medical conditions.

One of the major issues which the medical field has had to deal with is the sheer number of VOCs which can be exhaled from human test subjects – by one account there have been 1800 different VOCs found to be emitted by various means from the human body (De Lacy Costello *et al.*, 2014). To combat this large volume the field has developed VOC profiles to diagnose specific diseases. A VOC profile is a collection of distinct VOCs which when combined together in certain ratios allows for a diagnosis to be made. For example as Di Francesco *et al.* (2005) note a collection of mostly "*alkanes, alkane derivatives, o-toluidine, aniline, and benzene derivatives … was shown to be able to discriminate patients with lung cancer at a probability level of about 70%*". Furthermore, VOC analysis offers a more bespoke and rapid identification of issues which the patient may be experiencing (Rattray *et al.*, 2014). However, as has been noted by many in the field there is currently no standard methodology for gathering analysis samples or for processing the data for the development of VOC profiles (Saalberg *et al.*, 2016; Turner, 2016; Iqbal *et al.*, 2017). For example, it is known that food alters the VOCs in breath analysis yet there is no standard method to account for this contamination (Cavaleiro Rufo *et al.*, 2015). Yet it should be noted that this limitation is acknowledged and as Dragonieri *et al.*(2017) notes there is a "*European Respiratory Society task force is ongoing for establishing guidelines to standardize methodology*".

The amount of work which has gone into developing the various profiles far exceeds the work which could be undertaken by the heritage industry. There is now an entire peer-reviewed journal dedicated to it –

The Journal of Breath Research, published by the Institute of Physics. At this point, it is more beneficial to examine the constant stream of review papers to understand industry trends. There are now reviews into lung cancer (Van Der Schee *et al.*, 2015; Behera *et al.*, 2019), illicit drug detection (Trefz *et al.*, 2017), and pneumonia (Van Oort *et al.*, 2018).

The combination of the development of VOC profiles and the volume of research into them has allowed researchers to free themselves of large analytical equipment and concentrate on the development of sensor arrays which are targeted towards those specific VOCs of most importance. These sensor arrays have been coined 'Electronic Noses' and have been widely used within medicine; as Dragonieri *et al.* (2017) notes there has been fifty-six studies which utilize some form of electronic noses in eleven different areas of medical research. These studies have been so successful that there are now commercial products which implement the technology at a cost point affordable to the general public. For example, *FoodMarble* (€169; https://foodmarble.com/) monitors VOCs to track digestive issues, *Sniffphone* (https://www.sniffphone.eu/) is concerned with diagnosing cancer, while *Mint* looks at general oral health ($99; https://www.breathometer.com/mint/).

If heritage was able to develop these VOC profiles for the five *malignant plastics* it could potentially lead to electronic noses which are specifically developed for use in heritage. This would not only lower the entry cost for smaller institutions who do not have specialized analytical equipment, but their adoption would also generate a deeper understanding of a wide range collections, something that has been shown (in Chapter 1.2) to be much needed. Additionally, the heritage science sector can learn from the mistakes of the medical field and implement a standard model at this early stage so as to limit the conflicts in different datasets in the future. There is precedent for this such an endeavour already in the form of the Infrared and Raman Users Group (IRUG) database whose data must meet certain requirements to be included.

1.7.2 The food industry

The food industry has also taken advantage of the concept of VOC profiles; they have also been at the forefront of data science methods to process the complex patterns arising for VOC analysis.

Since the creation of the European Union's Regulation No. 1151/2012 there has been an increased awareness about the quality and diversity of different foodstuffs from specific geographical areas within the Union. In order to protect local producers, the Union introduced three different classification categories - protected designation of origin (PDO), protected geographical indication (PGI) and traditional specialty guaranteed (TSG). For example, sparkling wine manufactured outside of the Champagne region of France may not be sold under the term 'Champagne'.

In order to enforce these regulations, there have been efforts made to both authenticate foods from certain regions and to monitor for contaminates (from lesser quality products) via VOC analysis. This industry can be considered complementary to heritage as the use of natural products will have natural variations within their VOC profile, much like how historic polymer objects will have variations due to composition, age, and storage conditions. The framework needed to classify foodstuffs from one specific region to the next is similar to the framework needed to determine a healthy object from one which is actively degrading.

One of the main tools utilized by researchers within this field is multivariate analysis (MVA), and one of the most commonly used is principal component analysis (PCA)(Oliveri *et al.*, 2012). It has been used to correlate cocoa beans to chocolate bars from different production countries (Acierno *et al.*, 2020), to determine the pre-processing method and to test for adulterants of oils (Rusinek *et al.*, 2020; Sun *et al.*, 2020), and to detect adulterants in coffee (Oliveira *et al.*, 2009). PCA has the ability to summarise the information contained in a very large dataset into a smaller number of '*principal components*' that maximise the variability in the original dataset. Doing this allows the data to be graphed in a way which groups similar objects together – for example allowing researchers to see the effect on volatile emissions of bread when different combinations of flour and yeast are used (Makhoul *et al.*, 2015). There are clear similarities between these combinations and the combinations of plasticiser and degradation products emitted from historic polymers objects, and it's possible that the use of PCA or other MVA would allow heritage professionals to similarly classify their samples. Curran *et al.* (2018) has already shown the possibility of this using Linear discriminant analysis (LDA) in a heritage context, however, the use of statistical methods is not yet widespread.

However, much of the food science literature is lacking in detail regarding how it pre-processes its data – in essence, to the reader the MVA is a black box which spits out a satisfactory result. Heritage can learn from this omission; by accurately reporting which VOCs were used, if any pre-processing occurred, and most importantly justifying their choice in both situations the limited number of researchers in the area can maximise their collective output through a synergistic workflow.

1.8 Solid-Phase Microextraction – A path forward.

Solid phase microextraction has been widely used within industry due to its high sensitivity. Hakkarainen (2007) noted the technique's low detection limits (around 1 ppb) and its ability to detect changes to a polymer earlier than tensile testing could. Furthermore, the method has the ability to aid in manufacturing quality control by tracking VOC emissions during the different manufacturing stages (Salazar *et al.*, 2017).

Both of these traits can be extremely useful within a heritage setting and when combined with the fact that headspace SPME is both non-invasive and non-destructive.

However, it should be noted that even within industry SPME has been known to not be the ideal choice for quantitative analysis; while this can be done and will be explored later in this thesis, the results can be difficult to achieve unless the method is carried out correctly (Hakkarainen, 2007).

Based on the advantages which industry gained from adopting SPME into their workflow it was inevitable that the technique would enter into the heritage profession.

One of the first to adapt the method for use in a heritage setting was Ormsby (2003, 2005); the introductory nature of the methodology is evident in the manner in which these publications were written, with a detailed outline of the technique and the considerations needed to implement it. Furthermore, the material examined is a hybrid – a polymer-coated paper, with the focus of the investigation into the effect the lamination would have to the paper.

Yet the slow pace of heritage research is demonstrated by the fact that it was 2016 before a methodology was fully presented for the examination of historic polymer objects (Curran *et al.*, 2016).

However, the major limitation of the work by Curran (and others) was the use of small samples which had been modified in some way (such as being ground in the case of (Curran *et al.*, 2016)) which is an unrealistic representation of the conditions which a museum professional would examine an object. The major goal of this thesis is to expand on the work by Curran explore the viability of the SPME method when examining three dimensional objects which have been unmodified.

The remainder of this chapter will focus on discussing the considerations that precipitated the development of the technique in moving from Ormsby to Curran.

1.8.1 Basic principles and key benefits

SPME is a solvent-free preparation technique where a fused silica fibre is coated with either a single compound or a mixture of different compounds, this fibre is introduced to the sample matrix either through immersion or via its headspace (HS)[5]. The method was first described by Pawliszyn in the early 1990s (Arthur *et al.*, 1990). The analytes are then either adsorbed or absorbed onto the fibre matrix; this is dependent on the type of coating used. After extraction, the analytes are desorbed via high temperatures, into a GC/MS at which point they are treated in a similar manner to traditional analytes from other GC/MS techniques such as pyrolysis. In order to maximise the efficiency of SPME certain parameters can be changed such as fibre coating, exposure time,

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[5] There is also a third exposure option – Time-weighted average. However, the mechanics of this method differ greatly compared to the other two. Because of this, and the fact it is not used in this research it will not be discussed.

exposure temperature, exposure type (HS or immersion), and the addition of an internal standard for calibration.

From a practical point of view, SPME lowers the cost (per analysis), removes the need for cumbersome sampling processes in part due to the small size of fibres, eliminates pre-concentration steps (as this happens during exposure), eliminates the need for harsh solvents, has the ability to work with complex sample matrixes, has good sensitivity with quantitative transfer to the GC, and is a non-exhaustive extraction method meaning that the majority of the sample remains after exposure. A list of key benefits has been outlined by Bojko *et al.* (2012).

1.8.2 Sampling theory & methodology

SPME theory is based on the concept that when an equilibrium between the sample matrix and the fibre is reached then the amount of analyte extracted from the sample will be in direct proportion to its original concentration within the sample (Reyes-Garcés *et al.*, 2018)

The mathematical theory behind HS-SPME, which is the methodology practised in this thesis was first set out by Zhang and Pawliszyn (1993).

In a three-phase system, such as the one utilized in this thesis, as the total concentration should stay constant it is given by –

$$C_0 V_s = C_f^{\infty} V_f + C_h^{\infty} V_h + C_s^{\infty} V_s$$ **Equation 1-8**

Where C_0 is the initial concentration and where *C* and *V* represent the concentration and volume of the fibre *(f),* the headspace *(h)* and the sample *(s) respectively.*

The partition coefficients for the different phase interactions are given by –

$$K_{fh} = \frac{C_f}{C_h}$$ **Equation 1-9**

$$K_{hs} = \frac{C_h}{C_s}$$ **Equation 1-10**

Furthermore, the mass of the analyte, n, absorbed by the coating is –

$$n = C_f V_f = \frac{K_{fh} K_{hs} V_f V_s C_0}{K_{fh} K_{hs} V_f + K_{hs} V_h + V_s}$$ **Equation 1-11**

Furthermore, as –

$$K_{fs} = K_{fh}K_{hs} = K_{fg}K_{gs}$$ Equation 1-12

We can rewrite Equation 1-11 as –

$$n = \frac{K_{fs}V_f V_s C_0}{K_{fs}V_f + K_{hs}V_h + V_s}$$ Equation 1-13

Equation 1-13 tells us two things:

- That the amount extracted is independent of the location within the system
- If the partition coefficient is known, then the original concentration can be calculated from the amount extracted

In more practical terms, so long as the fibre has been given enough time to come to equilibrium then the resulting ratios form the fibre will reflect the ratios found in the sample.

1.8.3 Fibre coating choice

There are four ways in which a fibre coating can change the real-world performance of SPME so as to be more tailored to a specific analytical need; these are the type of coating, its thickness, its polarity, and whether it is an absorbent or adsorbent type of coating.

For the work presented in this thesis a fibre with a mixture of three coatings was exclusively used. A 50/30 µm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fibre was used due to the initial research by Curran *et al.* (2016) who noted that it was –

> *"the most suitable choice for the analysis of VOC emissions from a broad range of materials as it allowed us to sample higher amounts of the wide range of VOCs including hydrocarbons,*

> *aromatic compounds, and additives found commonly in plastics such as phthalate plasticisers.”*

This type of fibre has also been widely used within a heritage context where the detection of various different types of VOCs is important (Strlič *et al.*, 2007; Thiébaut *et al.*, 2009; Bembibre *et al.*, 2017; La Nasa, Mattonai, *et al.*, 2019).

However, as will be shown, this choice of coating does significantly impact the behaviour of the fibre and alters the resulting VOC profile in a way which must be understood in order to grasp the true meaning of the results.

1.8.3.1 Adsorbing versus absorbing coatings and their implications on VOC profiles

There are two ways in which the analyte can interact with the fibre coating. With an absorption-type coating, the analyte can enter the entire volume of the coating. The fibre used during this research was an adsorbent type where analytes are trapped on the surface of small pores within the coating. A graphical representation of the two types of fibres can be seen in Figure 1-2 which has been taken from Górecki, Yu and Pawliszyn (1999)

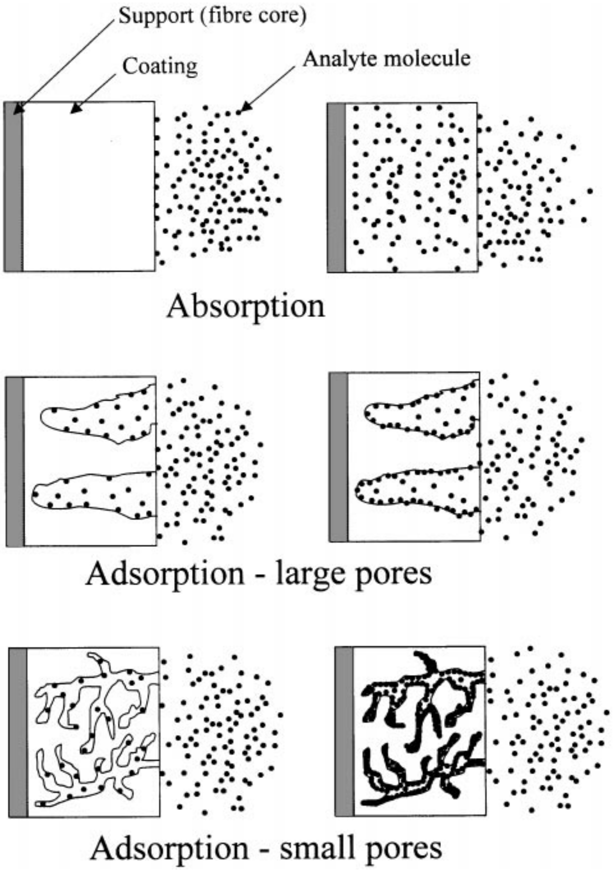


Figure 1-2 – A graphical representation of how an analyte may bind to the different types of fibre materials.

As a consequence of this, the surface area is limited. Furthermore, this can lead to competition on the fibre substrate for places. In this situation analytes which have a higher affinity, or which may be present in higher concentrations can displace those lower affinity compounds (Pawliszyn, 2012, pp 51). This leads to a change in the response of the fibre to the surrounding matrix; the amount of the replacing analyte will increase at the expense of the displaced, which will decrease.

One main way to counter this effect is to have short extraction times, however, when working within a heritage environment with low analyte concentrations the extracting times can be in the order of days rather than minutes so it is, therefore, prudent to accept that competition will take place on the fibre.

Another factor in which the coating choice affects the resulting VOC profile is the interaction between the coating and the physical characteristics of the analyte. If this compound is a flat planar structure with no substitutions it can have more of interaction via pi-pi bonds with the coating. This is in contrast to a compound which is highly branched. Additionally, the overall size of the analyte molecule is important; with smaller molecules moving faster they are not as well retained as larger analytes that move slower through the coating and are therefore retained to a greater degree.

There are also implications for the overall experimental methodology because of these interactions. If an analyte is able to strongly interact with the fibre coating, then there is the possibility that it will not be fully desorbed into the GC/MS and will be seen in further analysis runs. With limited space on the fibre for compounds, the space taken up by these carryover analytes will alter the overall VOC profile of the sample. To limit this the fibre can be reconditioned each day and can also be held for a longer and/or higher temperature during the desorbing process (Vas *et al.*, 2004; Risticevic *et al.*, 2010; Eckert *et al.*, 2018). However, these steps do lower the overall lifespan of the fibre and in our work, it was found to work only partially – two compounds, in particular, were very difficult to remove from the fibre, camphor and limonene.

1.8.4 Use of a calibration standard

In order to have the ability to either compare analysis data from two (or more) different analysis periods or for the purposes of quantification, a standard must be used. In the case of quantification, a standard is preferred because, as was noted previously, while the mathematical theory of SPME allows for a concentration value to be calculated when the different variables are known, often this is difficult to achieve in a real-world application.

The two main methods of calibration are an external standard where a substance is examined separately to the sample or an internal standard, where an additional compound of a known amount is added to the sample matrix.

The use of an internal standard has a number of drawbacks when paired with open analysis in a heritage context. An internal standard works best when it is sufficiently different to the sample so it is clearly resolved in the chromatogram but yet able to closely mimic the analytes being examined (Ouyang, 2012, pp171) – this can be very challenging in a heritage setting because the exact compounds emitted from the sample are unknown.

Another method to obtain quantification is SPME is to use an external standard. This is where a series of known quantities of a reference standard of the analyte of interest are examined separately to the test sample. For this method to be accurate the standard must be in conditions which closely match the sample matrix. The response from the real sample can be compared to the standard and can be quantified via a calibration curve.

The difficulty with this stems from the matrix conditions in which the standard is placed. As was discussed regarding the choice of fibre, the sample matrix can alter the ratio of the analytes. Therefore, for an accurate reading one must match the sample matrix in which the standard will be tested. As with the internal standard, the exact make-up of the matrix will likely be unknown in a heritage context.

However, it is still possible to achieve a calibration curve with either a single compound or mixtures which form part of the target matrix. These standards will give an approximate value of concentration which may still be helpful within a heritage context. Care should be taken with reporting these values as they will not be the true level which the sample is exposed to and therefore this limitation should always accompany such reportage.

A further modification to the external standard concept is the use of a standard mixture of compounds to track the intra-day performance of the GC/MS and as a by-product allows for the comparison of samples based on their relative normalised peak areas. In this situation, a standard mixture is examined using a methodology which may differ to that of the sample. The fundamental limitation of this method is that it does not allow for any concentration value to be given to the target sample.

The use of this method has the benefit to allow a researcher to track the performance of the GC/MS instrument and its sensitivity (which will slowly decrease after servicing and increase again upon its next service or source clean). By tracking the efficiency of the GC/MS this allows for the peak areas of the target sample to be normalised to the peak area of a compound within the standard mixture. This allows for comparisons between the normalised peak areas of compounds in the samples taken on different analysis days. This is especially helpful when the matrix of the sample is unknown, and/or likely to vary from one sample to another, and the addition of an internal standard would contravene the non-invasive nature of the analysis, which, in a heritage context is one of the greatest benefits of the technique.

1.8.5 Temperature for analysis

Equation 1-13 shows how for a three-phase system the amount of analyte extracted by the fibre is based on the original concentration, the different volumes involved and on the partition coefficient K_{fs}. To simplify the system for this discussion, one can examine a two-phase system in which the amount extracted is given by –

$$n = K_{fs} V_f V_0$$ **Equation 1-14**

Equation 1-14 is arrived at when the sample volume is very large compared to the volume of the fibre (V_f). When this occurs, the amount extracted will correspond directly with the initial concentration regardless of the initial volume of the sample.

Of these variables the partition coefficient is dependent on temperature, this was shown by Pankow (1994). When moving from one temperature to another the partition coefficient is given by Wei *et al.(*2016) –

$$\mathrm{K_T} = \mathrm{K_0}\ \frac{\mathrm{T}}{\mathrm{T_0}}\ \mathrm{e}^{\frac{\Delta \mathrm{H}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T_0}}\right)}$$ **Equation 1-15**

$$\log_{10} \mathrm{K_T} = \frac{\Delta \mathrm{H}}{2.303\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T_0}}\right) + \log_{10}\frac{\mathrm{T}}{\mathrm{T_0}} + \log_{10} \mathrm{K_0}$$ **Equation 1-16**

K_T is the distribution constant between fibre and sample at the new temperature, T, K_0 is the distribution constant at the initial T_0. ΔH is the molar change in enthalpy of the analyte when it moves from sample to fibre and R is the gas constant.

Equation 1-16 shows that by increasing the temperature the partition coefficient will be decreased. When the new K_T value is incorporated into equation 1-14 the amount of analyte extracted is shown to decrease when the analysis temperature is increased. When moving to a three-phase system one must account for the two different partition coefficients present, but the method of calculating their respective changes is the same as in equation 1-16. Therefore, the condition of decreasing analyte recovery with increasing temperature still holds.

Temperature also affects the release of volatiles from the surface of the sample matrix. In a real-world system, there are therefore two competing phenomena at play as the temperature is increased –

- An increase in the release of volatiles
- A decrease in the methods ability to collect and recover volatiles.

As with the issues surrounding matrix identification and competition, many of the concerns regarding temperature effects can be successfully mitigated in a laboratory setting; however, this is not true in an uncontrolled open heritage environment. The direct consequence of fluctuating temperature, often seen in a heritage setting, is that any value of concentration given is very unlikely to be an absolute value. Between the matrix effects seen by the fibre and the temperature-induced changes to both adsorption on the fibre and emission from the sample, a concentration value derived from a calibration curve formed in laboratory conditions, needs to be cautiously used in a heritage setting where it might form the basis of an institution policy whose scientific foundations may not be fully known. The full implications of variations to temperature are set out in chapter 6 of this thesis.

1.9 Conclusion

Over the course of this chapter the current state of the heritage sector has been described. In essence, since the beginning of the 1990's the sector has identified a clear issue in relation to the care and storage of modern polymeric materials, it has identified the major vulnerable materials which are housed within a wide range of collection types, it has identified the main pathways to degradation for specific material types, and it has done this through the development of a select number of scientific analysis tools. However, it has yet to develop the tools to systematically evaluate, monitor, and aid the conservation of specific objects. At present the field is in a transitional period between knowing what issues an object of a certain material may have but lacking the tools with which to address that individual object.

This thesis concerns itself with the development of an analysis tool which aims to aid the field in its transition from examining modern polymeric materials on a macro (collection) field of view to an object centric vantage point. It would allow those working on a range of modern polymeric materials to gain a significant insight into its base polymer, its reaction to its storage environment over long time periods, and how it behaves as it ages. More importantly, this tool will have the specificity to tackle individual objects while doing so by non-invasive and non-destructive means.

The next chapter will layout the full scope of this thesis and the decisions which informed the overall direction of work carried out over the course of this project.

Chapter 2 Scope of Work

2.1 Introduction

Chapter 1 of this thesis shows clear evidence for three important reference points which impact the path of the remaining thesis. The first is that objects found in museums, which are either in part or entirely made from a modern polymeric material are at great risk from rapid and often catastrophic degradation. The second is that SPME has the potential to offer heritage professionals a method to analyse these objects without the need to sample, or even touch the object in question. Finally, chapter 1 has shown that in other fields SPME has been successfully used for nuanced and complex applications such as medical sensing and food analysis and resulted in significant insight into the issues at hand.

The learnings from Chapter 1 show that SPME is one of the best candidates for providing the knowledge needed by the profession. While this thesis has a series of research questions to answer over the duration of the project the overall end-goal is the production of a working methodology which can be implemented by heritage professionals. The direction of the project was guided, in part, by this goal as well as providing the strengths and weaknesses of any such methodology. This enables heritage professionals to make informed decisions on when to implement it and what factors must be addressed in order to carry out successful analysis campaigns.

This current chapter outlines how the synergy between these will directly impact on the overarching research questions, the aims and objectives, and the fundamental direction of this thesis.

2.2 Research questions

Chapter 1 showed the destructive impact that some types of degradation mechanisms can have on different polymer types. Currently, there is no method which can track the overall health of the object and how it changes within a museum environment. While FTIR spectroscopy and destructive chromatography techniques have the capabilities to gain insights into degradation mechanisms present, the fundamental *'Primum non nocere' (first, do no harm)* principle involved in the care of museum collections often prohibits their use on objects of historic importance, polymer-based or not. In Chapter 1.7.1 I showed how the medical industry has utilized VOC analysis to circumvent the limitations of invasive analysis and obtain insights which would previously only have been diagnosed via highly invasive procedures. VOC analysis has also enabled earlier diagnosis.

SPME-GC/MS therefore appears as a promising method for in situ analysis of modern polymeric museum objects with the possibility of providing significant chemical insight into their composition and degradation in a completely non-invasive manner. The goal of this thesis was therefore to formulate a method for the monitoring of historic polymer objects in-situ in heritage environments. More formally, our overarching research questions are -

> *R.Q.1 – When using SPME, what is the most efficient and effective methodology to monitor the condition, via emitted VOCs, of historic polymer objects in a heritage environment?*
>
> *R.Q 2 - Can a correlation be made between VOC emissions and visible forms of deterioration in plastic artworks?*

R.Q 3 - How can we translate previous work carried out using plastic samples in a laboratory context to complex plastic objects within collections?

R.Q 4 - Can the detection of VOC emissions from plastic objects of specific polymer types, stored in heritage collections, be used as a non-destructive method for understanding ongoing degradation processes and changes in material properties?

This set of four overarching research questions immediately introduce a secondary set of sub-questions (that act somewhat as a set of objectives) which need to be answered during the progression of the project. While these questions need not be a direct waypoint in the direction of the project their consideration is nonetheless important in the successful implementation of the project & the development of practical methodologies for the study of historic polymer objects within collections -

Sub-Q 1 - What base polymer types should one focus resources on at the earliest stage of the research?

Sub-Q 2 – Where is it better to conduct research – in an open heritage environment or a more controllable laboratory?

Sub-Q 3 – What results are needed in order to form a constructive progression of the research towards the analysis of historic polymer objects within heritage environments?

2.3 Aims and objectives

The research questions outlined above give a generalized viewpoint of the topic and their broadness highlights both the initial basic state of our starting position and a large number of potential avenues for this research.

To focus resources into the most pressing issues, the aims and objectives would inherently limit the scope of the project. These limitations will be discussed later in the chapter; however, it is worth noting at this point that many of these limitations were based on conscious choices made at the very beginning of the project. A graphical representation of the decisions and focus points can be seen in Figure 2-1 at the end of this chapter.

The first project sub-question was to understand VOC analysis of three-dimensional historic polymer objects. In order to achieve this, the aim was to focus on just a single base polymer choice. By focusing on a single base polymer formulation, it allows for the efficiency of the SPME experiment to be better understood as it removes any variable which may be polymer dependent – such as particular VOC combinations behaving differently polymer to polymer, or carry-over affects unduly effecting analysis of different polymer types.

This decision, which answers *Sub-Q 1*, was directly influenced by the experience of exploratory analysis of multiple polymers during an MRes research project I conducted prior to commencing this PhD. While the results of this analysis will not feature in this thesis, three aspects had explicit influence on the decision to focus on only one polymer type –

- Significant carry-over was observed after analysis of cellulose nitrate (CN). Camphor, a very common plasticiser for CN, was difficult to remove from the fibre/column and this resulted in its appearance during the following analysis.

- Accelerated ageing, which will be described later, was shown to impact the analysis of some polymers, specifically PVC which emitted less VOCs after accelerated ageing than before (likely due to being driven off due to the effect of the elevated temperature.)

- Several polymers tested showed little or low VOC emission, such as casein or ABS. Therefore, when examining the performance of a VOC analysis methodology a polymer which is more active was preferred.

Due, in part, to these three observations, the base polymer chosen to be studied was cellulose acetate (CA) as its VOC profile did not pose a major carry-over risk and it also produced significant VOCs upon ageing which gave a wide range of compounds to study.

The results from the initial work also highlight the potential that SPME analysis may not work for all base polymer types. This is an important consideration; however, the remit of this project is to provide a proof-of-concept on a methodology. Future work can extend the scope of the methodology to include a greater number of base polymer types.

The second objective of the project was to produce a working methodology for VOC analysis to be used by conservation or heritage professionals.

This objective introduces the concept of where to monitor objects and the project aimed to investigate both open environments and controlled laboratory ones.

In utilizing a laboratory methodology, it was necessary to investigate methods of preconcentrating VOCs emitted from historic polymer objects or samples, while open analysis was needed to understand how fibre exposure times influenced resulting VOC profiles. Furthermore, it required an understanding of how external stressors, such as changes to environmental conditions and background affected the final profiles seen.

Our final objective was understanding how the resulting VOC profiles could be translated into an actionable response by heritage professionals. The results, therefore, could be placed into three subcategories – Identification (of base polymer) and degradation markers, information on chemical mechanisms and information regarding VOC concentrations. Issues regarding concentrations will be discussed further in a following section. One aim was to show that SPME analysis was capable of, at the very least, informing on the identity of the polymer and the type of degradation objects were undergoing. A secondary aim was to highlight SPME's ability to differentiate degradation mechanisms from each other. With these two aims achieved it was felt that the project could then move forward with more complex data analysis, such as tracking degradation over long periods (months to years) and also begin to perform statistical analysis of VOC profiles for deeper insights into their behaviour over time.

2.4 Contextualization of research

It is worth taking a moment to place this research into context relative to its multi-disciplinary nature straddling both analytical chemistry and conservation science. As was stated earlier, the main aim of this thesis is to directly impact the day-to-day workings of conservation scientists & practitioners who interact with historic polymer object by providing them with a working methodology to implement SPME in a heritage environment. The analytical work is aimed to act as a novel piece of applied research rather than the development of novel chemical analysis. As such it utilizes a pre-existing technique, in the form of SPME, and adapts this to form a methodology for use within the heritage industry. Therefore, certain considerations in experimental design have been made to facilitate its implementation within a heritage context, such as exposure times or samples examined.

2.5 Justification of limits for the scope of the project

2.5.1 Limiting to one base polymer type

As was mentioned previously, at the beginning of the project only one base polymer was chosen to be studied. Aside from the three points mentioned, there were some additional factors which led to CA being the material of choice.

CA is known to be one of the most problematic materials that heritage professionals must deal with as evidenced by Williams's inclusion of the material as one of the five most at risk to be found in museum collections (Williams, 2002) . As such, it was felt that, strategically, the overall impact of the project would be maximised by studying this material first and providing the field with a method for its analysis.

Secondly, as Tate was a partner on this project, this facilitated access to their collection of Naum Gabo artworks for study. While being an important artist in his own right, the materials used by the artist have been previously studied by researchers at Tate, which provides a starting point for this project. Additionally, the artist worked extensively with CA which allows for numerous different objects to be studied. As these works were produced at different times using different methods, their study also facilitates the analysis of a range of CA samples in varying states of degradation.

Finally, CA offered the ability to easily manufacture bespoke samples to meet our needs. This would prove highly beneficial during the project when samples with different plasticiser were needed.

2.5.2 Issues regarding explicit statements of concentrations

Parts of the research presented in this thesis have been previously presented at workshops & conferences. One recurring question that seems pertinent to those who have seen the presentations has been regarding the specific concentration levels of key VOCs found within the chromatogram.

During the research a discovery has been made that providing specific concentration levels is both extremely difficult and potentially less useful that other forms of data treatment.

While it is possible to produce calibration curves and to then match values found from samples to the curve this information would be limited in its usefulness. Chapter 1 outlined how the composition of the matrix and the degree to which equilibrium has been reached affects the resulting VOC profile seen by the SPME fibre. As will be laid out in Chapter 4, when measuring VOCs within an open and uncontrolled environment there are additional considerations to be taken into account which affect the resulting VOC profile. The combination of these two factors leads to the situation whereby any calculated concentration, via a calibration curve calculated within a laboratory setting, would not be a true reflection of the concentration detected in a museum environment.

Further to this is the information laid out in Chapter 1 regarding the use of SPME in other fields, specifically the medical industry. In the medical field it is common to forgo stressing the importance of single VOCs and their concentrations, but rather to focus on the collective interaction of key VOCs. Building a diagnosis on a VOC profile of relative abundances limits the error which might be introduced by a skewed value of a single VOC.

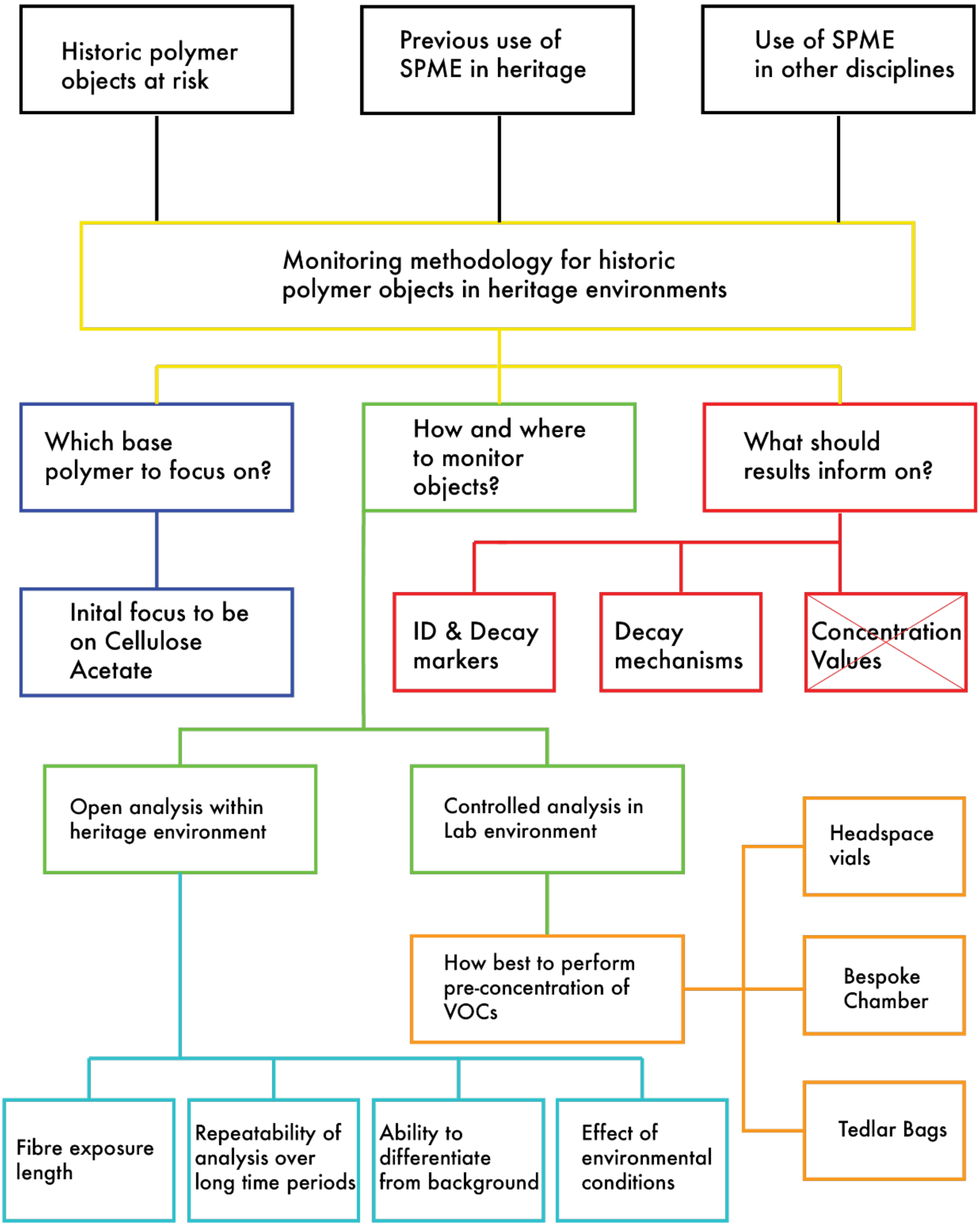


Figure 2-1 – A flowchart which illustrates the foundational choices made at the beginning of the project. Note that issues regarding concentration values were not explored – see Chapter 9 for a discussion regarding their importance.

Chapter 3 Methods

3.1 Introduction

During the literature review, which formed Chapter 1 of this thesis, I introduced the SPME technique and described the governing principles that allow it to function as effectively as it does. I also briefly outlined some of the potential limitations of SPME, in Chapter 1 which may affect the efficiency, repeatability or detection limits of the technique. The objective of this research was to investigate the relevance of SPME to the application of monitoring the degradation of plastic objects in museum collections. As such SPME is not simply a method to be utilized, it is a method to be investigated.

To facilitate this investigation several additional techniques needed to be employed to validate the information gained through SPME analysis. The working parameters for these techniques will be outlined in this chapter along with a discussion of the rationale behind the choice of samples used.

Two techniques in particular, were immediately chosen as they offered not only a scientifically quantifiable comparison but also act as a visually quantifiable cross-reference between the different techniques.

The first of these primary validation techniques is Fourier transform infrared (FTIR) spectroscopy, a type of absorption spectroscopy that has been widely utilized within both the polymer and heritage industries. FTIR spectroscopy offers insight into chemical changes which occur in the polymer during its lifespan and also offers a way to quantify some of these changes, such as loss of plasticisers (Richardson *et al.*, 2014) .

The second is colourimetry which can be used as more quantified alternative to reliance on visual indications of degradation. An important point to note is that within the heritage industry colour and its perception play a vital role in judging the degradation level and value of the object, meaning that change in colour is one of the main indicators used to determine that an object has degraded (Pastorelli *et al.*, 2014).

Later in this chapter, I will discuss in more detail the choice of samples used during the project. While this project was focused on monitoring 3-dimensional artworks within heritage environments, it was clear from an early stage that smaller, non-accessioned objects and samples would be needed for more invasive testing. Further to this, it was also necessary to choose the artworks used in case studies carefully as I needed an example which could be considered *typical* of the condition of most museum objects.

3.2 Gas Chromatography/Mass Spectrometry

At the heart of the SPME technique is its ability to interface with GC/MS and avail of those benefits it provides.

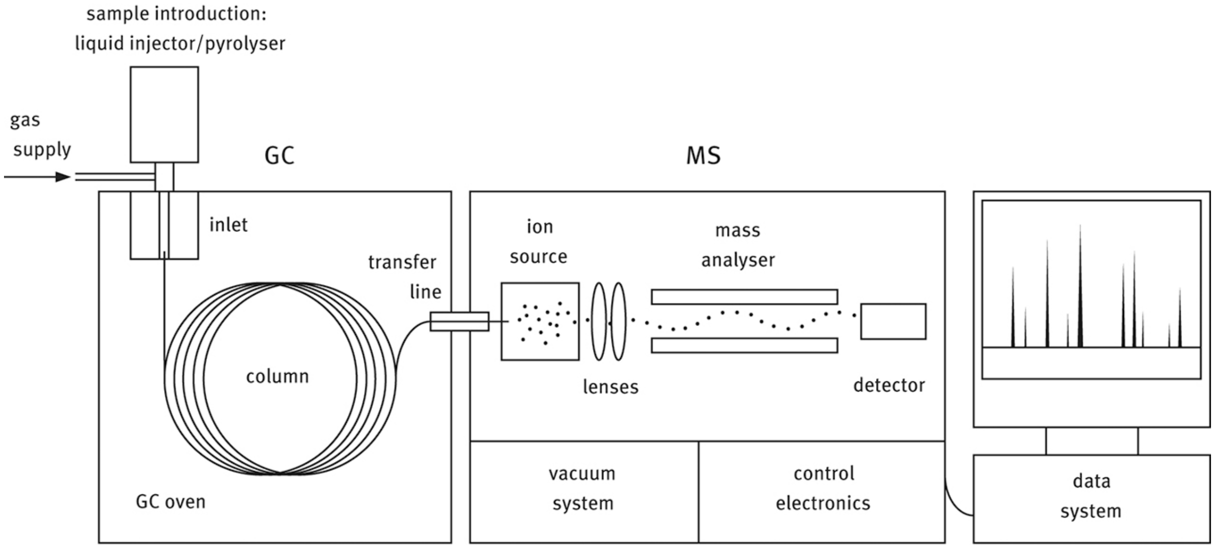


Figure 3-1 – A graphical representation of the main components of a SPME GC/MS setup. Graphic taken from Sutherland (2018).

The gas chromatograph used was a Perkin Elmer Clarus 500 which was connected to a Perkin Elmer Clarus 560D mass spectrometer. A VOCOL column (Supelco, 20% phenyl–80% methylpolysiloxane), 60 m in length and 0.25 mm in diameter was used. The instrument was controlled via the PerkinElmer® TurboMass (Version 6.1.0.1963) software.

Several different experimental campaigns were run during the project however, the basic run order of these campaigns did not differ. Details of each stage are given below. Each analysis run began with a column clean, a SPME fibre was not injected into the port of the GC/MS at this time. This clean was performed to limit any contaminations from the previous day's analysis. This was then followed by a blank fibre analysis. This was an analysis of a newly conditioned fibre which had not been exposed to any sample. Directly after this, the samples were analysed. Due to time constraints, when performing manual injection, the number of samples permitted for one day was limited to five plus a standard. The GC/MS analysis conditions between a *blank* and a *sample* were identical. The final analysis was that of an external standard which was used to both track the intra-day performance of the GC/MS and also to perform a normalization calculation on the sample results.

Before any analysis, either lab-based or within a heritage environment took place it was necessary to condition the SPME fibre. This was carried out to limit the carry-over of VOCs from previous analysis or VOCs picked up by the fibre during storage. Fibres were placed into the injector, whose temperature was held at 270 °C, for 45 minutes. The carrier gas was set to a constant flow of 1 ml/min. The split flow was set to 50 ml/min.

Below are the analysis conditions for each of the three stages:

- **Clean** – An initial temperature of 35 °C was held for 30 min. The carrier gas was helium with a constant flow of 1 ml/min. Mass spectra were collected under electron ionization (EI) mode at 70 eV and recorded from m/z = 33–300 over the same time period.

- **Blank/Sample -** A heating ramp program was performed in which an initial temperature of 50 °C was held for 5 min, this was increased 10 °C/min to 100 °C followed by increments of 5 °C/min to 200 °C and 2 °C/min to 220 °C. The system was held at 220 °C for 20 min giving a total heating time of 60 minutes. The carrier gas was helium with a constant flow of 1 ml/min. The injector temperature was 250 °C. The interface and source temperatures were 200 °C and 180 °C respectively. Mass spectra were collected under electron ionization (EI) mode at 70 eV and recorded from m/z = 45–300 over the same time period.
- **Standard -** The SPME fibre was exposed to a MISA Group 17 Non-Halogen Organic Mix (Sigma Aldrich 48133 Supelco), that contained 2000 µg/ml each of benzene, ethylbenzene, styrene, toluene and ortho-, meta- and para-xylene in methanol for 20 seconds before being analysed in the GC/MS. A ramped temperature program was followed where the initial temperature of 35 °C was held for 5 minutes then increased by 10 °C/min to 200 °C with a total time of 31.5 minutes. A solvent delay of 2 minutes was used. Mass spectra were collected under electron ionization (EI) mode at 70 eV and recorded from m/z = 45–300.

An external standard is utilized in both tracking the performance of the GC/MS instrument over a long period of time and in normalizing the collected sample data to the peak area of a specific peak found within the standard. In measuring a standard compound, in exactly the same manner each time, it is possible to track the efficiency of the GC/MS over the course of many months and years. This is due to the standard being the constant over this period. Therefore, any changes to the resulting peak areas for the chosen reference peak is due to a change in the GC/MS rather than the methodology. Peak areas from samples, once normalized to the standard peak area, are therefore not affected by any changes the GC/MS may have undergone due to e.g. deterioration of the column or the fibre and can be directly compared with each other.

Lab based analysis was conducted under normal lab temperatures. This, unless explicitly stated, was set to hold the room at approx. 22° C +/- 1° C. These normal conditions were controlled via an air conditioning unit. Any deviations from this norm were achieved through changing the settings on the air condition unit.

As discussed in Chapter 1 there are many different choices of SPME fibre, each of which will affect the resulting VOC profile (Garcia-Esteban *et al.*, 2004; Lorenzo, 2014). Previous work by Curran *et al.* (2016) has shown that the DVB/CAR/PDMS fibre had the greatest efficiency at collecting a representative profile from historic polymer objects. Specifically, Curran *et al.* (2016) showed that a DVB/CAR/PDMS fibre could to detect a wide range of relevant VOCs (such as acetic acid, phenol and both diethyl and dimethyl phthalates. In light of this information and from consulting the literature this project exclusively used a 50/30 μm DVB/CAR/PDMS fibre.

A discussion on the post-analysis data treatment can be found in Chapter 3.8.

3.3 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy has now been widely adopted by the plastics conservation community as an accurate way of polymer identification (Gómez-Sánchez *et al.*, 2011; Saviello *et al.*, 2016) and as a sensitive indicator of deterioration (Quye *et al.*, 2011; Littlejohn *et al.*, 2013). Advantages include its ease of use, clear results, comprehensive databases (such as the one provided online by the Infrared & Raman Users Group (IRUG)), and its relatively low cost.

It was important to be able to judge SPME against its industry peers and in order to do so, attenuated total reflectance (ATR - FTIR) was chosen as the preferred FTIR spectroscopy method to examine the different analysis samples. ATR also offers the main advantage of not requiring an invasive sample to be taken for analysis while still offering the majority of the benefits achieved with micro-FTIR transmission analysis.

There were four main aspects on which our analysis was focused:

- Base polymer identification combined with information on any additives
- The ability to identify and track any changes to the sample's spectrum
- Specific attention was paid to any indication of oxidation occurring in the sample, while not a major issue for CA it can act as a clear sign of active degradation
- The ability to track any loss of plasticiser between analysis runs

In order to achieve these goals, the following settings were applied using the Bruker Alpha Platinum ATR instrument via the OPUS 7.5 software (Build 7.5.18).

- Unless stated otherwise, five repeat measurements at different locations along the length of the sample (as indicated in Figure 3-2) were taken with the average of these used
- 32 scans were made for each measurement in the range of 4000 – 400 cm^{-1}

- A background was taken before the beginning of analysis which consisted of 32 scans in the range of 4000 – 400 cm^{-1}
- All scans were taken in absorbance mode
- All scans were with a resolution of 4 cm^{-1}
- Where stated, spectra were subjected to a baseline correction which involved finding the average value of the intensity between 2200 cm^{-1} and 2000 cm^{-1} and setting this to zero by subtracting this value from the intensity across the whole spectrum

Furthermore, the FTIR spectroscopy images presented in this thesis have been normalized to the largest peak in order to aid their interpretation. Normalized values have not been used in any calculations.

3.3.1 Calculations of degree of substitution and plasticiser percentage

FTIR offers a clear methodology for the identification of samples via peak allocation. However, through deeper manipulations of specific data points it is possible to also answer questions regarding the degree of substitution and the level to which plasticisers have been lost between datasets.

Carraher notes that the definition of the degree of substitution (DS) as the "*Number that designates the average number of reacted hydroxyl groups in each anhydroglucose unit in cellulose or starch.*" (Carraher, 2018, pp. 363). With respect to this thesis the degree of substitution (unless otherwise stated) refers to that of cellulose acetate and is the average number of acetyl functional groups which have been substituted for the hydroxyl group found in cellulose. As the DS is an average it can range from 0 (cellulose) and 3 (cellulose triacetate).

Within the scope of this research there are two main distinctions of cellulose acetate which are applicable – cellulose diacetate which typically has a DS of between 2.0 and 2.5 and cellulose triacetate which has a DS >2.8 (F. B. da Silva *et al.*, 2017; Mazurek *et al.*, 2019). While the difference in DS is small it does however change some of the properties of the two material types. For example, cellulose triacetate will be more hydrophobic and can have a greater crystallinity than diacetate (Carraher, 2018, pp. 330) Additionally, the DS can impact the types of solvents each compound is soluble in with those materials with a higher DS being more soluble in acetone than those with a lower DS (Samios *et al.*, 1997). Within the heritage field CA has been widely used in film stock and in animation cells. Giachet *et al.* (2014) showed that animation cells could be approximately dated by categorizing them as either diacetate or triacetate.

As FTIR has the ability to detect both a peak relating to the acetyl group (at circa 1215 cm^{-1}) and a peak relating to main cellulose unit (at circa 1030 cm^{-1}) it is possible to quantify the DS via FTIR. The resulting calculations were based on the equations provided by El Nemr *et al.*, (2015) and Cao *et al.* (2018). Samples were analysed via FTIR as described above. The five repeat measurements were then processed via MATLAB (MathWorks, Version - 2019b) where they were first baseline corrected to the mean value of the region between 2000 and 2200 cm^{-1}. Following this, the five repeats analyses for each sample were then passed through Equation 3-1 and 3-2 to arrive at the DS value. The values in equation 3-2 were obtained from Da Ros *et al.* (2020) and are based on fitting a line to the calibration curve of known DS samples of CA vs their respective DS_{Ratio} results.

The values presented in this thesis are the average values calculated from these five repeat measurements. Figure 3-2 shows the approximate location where FTIR and colour analysis was performed.

$$DS_{Ratio} = \frac{DS_{PeakValue}}{DS_{NormValue}}$$ Equation 3-1

$$DS_{Value} = 0.949 + (2.574 * DS_{Ratio}) - (0.997 * {DS_{Ratio}}^{2})$$ Equation 3-2

Equation 3-1 & 3-2 are used to calculate the degree of substitution for each sample. The DSRatio is calculated directly from FTIR data – The DSPeakValue is the intensity of the peak associated with the acetyl functional group while DSNormValue is associated with the C-O stretching and the vibration of the cellulose back bone. The DSValue is calculated using the DSRatio and a constant.

Similarly, the amount of plasticiser was also quantified via FTIR. As the characteristic peak for each plasticiser is different – in the case of triphenyl phosphate (TPP) the intensity of the peak at circa 782 cm^{-1} was used, this peak is associated with the nonplanar deformation vibrations of CH groups of the benzene ring (Skornyakov *et al.*, 1998). For diethyl phthalate (DEP) the peak intensity of the CH benzene absorption band at 748 cm^{-1} was taken. In both cases, the peak intensity at 602 cm^{-1} was used as the reference peak as it remains unchanged during aging (Richardson *et al.*, 2014). The ratio of plasticiser peak to reference peak was calculated using MATLAB with the value reported in the thesis being the average of the samples' five repeat measurements.

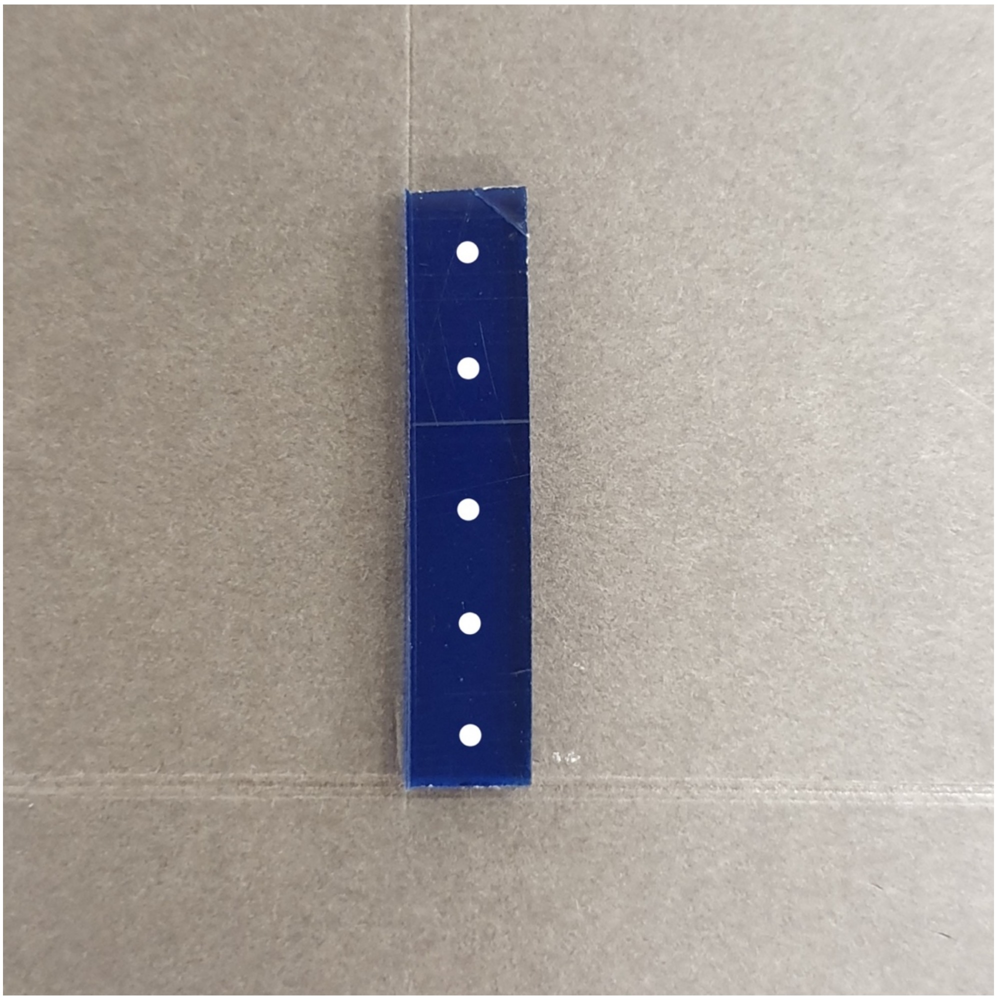


Figure 3-2 - A typical industrial sample (CA-NewCW-3A is shown here). The overlaid white dots show the approx. location where FTIR spectroscopy and colour measurements were taken. This image also shows the grey card which all colour measurements were taken on top of.

3.4 Colourimetry

Colour measurements, in the form of L*a*b* values, were taken using a LabSpec 500 connected to Indico Pro software (Version 5.6). Reflectance values were obtained between 350 and 2500 nm (at 1 nm intervals) using an attached fibre optic cable. Before starting a new sample, a baseline was taken using the Fluorilon-99W white reflectance standard (Avian Technologies). Following this, five spectra were collected from a different location on each sample, at a similar location to those taken during FTIR spectroscopy and can be seen in Figure 3-2, with the final L*a*b values being an average of these five spectra. All samples were acquired with the sample placed on top of the sample of a surface which had a consistent grey colour. As the LabSpec is not capable of automatically producing L*a*b values via its software, a MatLab program was written to facilitate this. Details of this code can be found below in Chapter 3.8.

3.5 Sample preparation

This project utilized three basic sample types during the analysis phase. Those samples were chosen to fit within the parameters of each stage's objectives. These objectives will be outlined to a greater extent in the following chapters, however, a summary of the samples and the objectives they were used for are as follows:

- 3-Dimensional art objects in the Tate collection – to investigate SPME analysis in open heritage environments
- Bespoke polymer samples manufactured specifically for this project – to investigate SPME performance under certain conditions in a lab environment
- Industrially manufactured polymer samples, sourced from various contexts, which facilitated detailed and often destructive sampling - to investigate SPME performance under certain conditions in a lab environment

Over the course of the project, three 3-Dimensional art objects were systematically studied, to varying degrees, via SPME. The artwork *Construction in Space, 'Two Cones'*, 1927 /1968 (known from here on as *T02143, Two Cones* so as to identify it as the object housed by Tate rather than other versions of the same artwork) by the Russian artist Naum Gabo, was initially chosen due to its poor condition. The artwork, seen in Figure 3-3 is extensively damaged and its current state prohibits any form of remedial conservation treatment or museum display (a recently made authorised replica is displayed instead.) It did, however, provide the best opportunity at detecting VOCs during the initial open-environment trials.

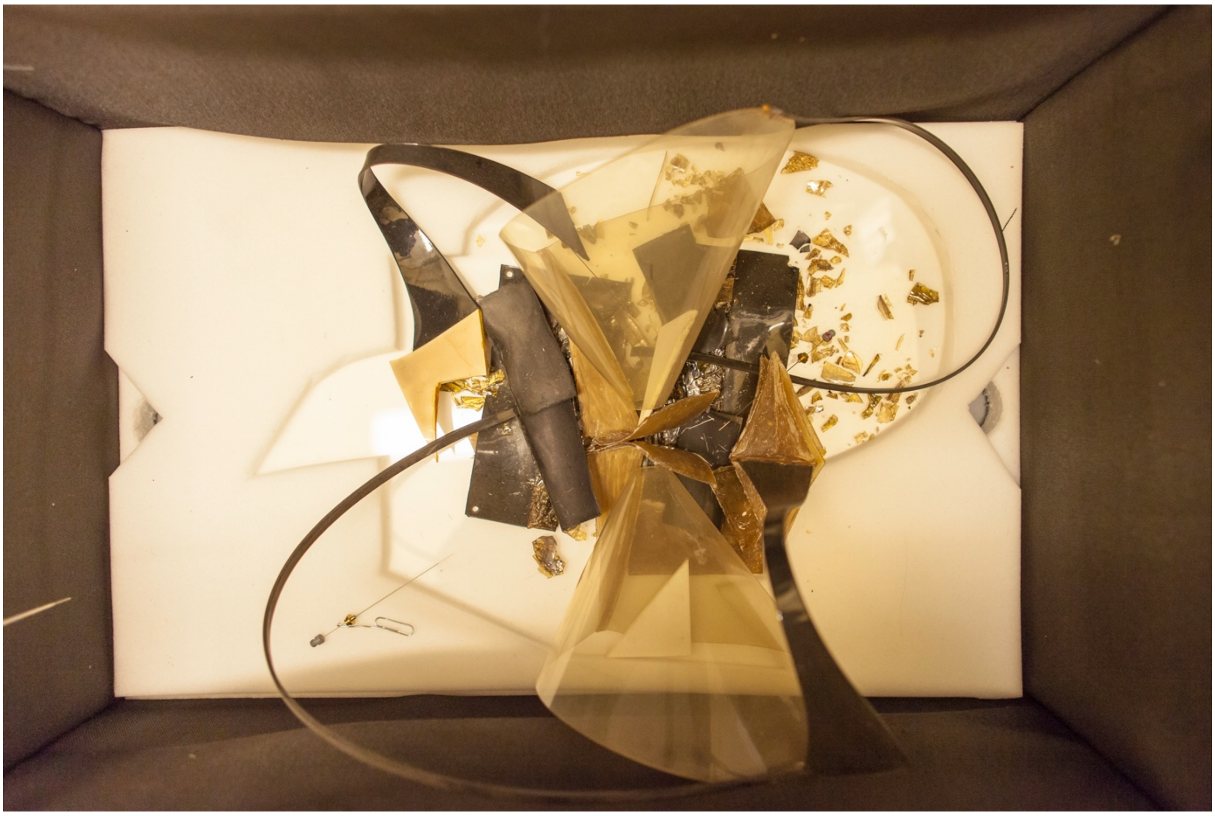


Figure 3-3 – A top view of *Construction in Space, 'Two Cones'* 1927, replica 1968 by the artist, Tate T02143, in poor condition in June 2017. The Work of Naum Gabo, © Nina & Graham Williams. The image also shows some of the SPME fibres and the black activated charcoal cloth which surrounds the objects in its polythene enclosure.

Following this, two further 3-Dimensional sculptures by Naum Gabo, *Circular Relief* c.1925 (Tate T02142) and *Model for 'Spheric Theme'* c.1937 (Tate T02173), were analysed towards the end of the project. These two objects were chosen as their condition complemented the information gained from SPME relative to that gained via *T02143, Two Cones* and offered insights into the performance of SPME with less degraded objects in an open environment setting. T02173 is in relatively good condition and is periodically on display or on loan to other museums. T02143, *Two Cones* is significantly deteriorated and is currently housed within the Sculpture Conservation studio. It no longer goes on public display but is represented by an authorised replica.

As previously mentioned, this project was focused on determining SPME's efficiency at monitoring 3-Dimensional art objects. As will be discussed in greater detail in Chapter 6, it was necessary to investigate certain aspects of the performance of SPME using smaller non-accessioned polymer samples. The specifications and objectives of these experiments required both the production of bespoke polymer samples as well as the use of those industrially manufactured.

While the author made every effort to manufacture suitable samples using the method outlined below, unfortunately, these samples contained too many air bubbles to be utilized for experiments. Therefore, the samples used during the experiments were manufactured by Dr Simoni Da Ros of UCL using the same methodology as described.

Two types of bespoke CA were manufactured at UCL specifically for this project. The first was CA with 20 % diethyl phthalate (DEP), while the second was CA with 16 % triphenyl phosphate (TPP). An outline of their manufacturing process, which was adapted from a methodology provided by Dr Emma Richardson via personal communication is detailed below:

- CA (average Mn ~30,000), TPP, and DEP (99.5 %) were purchased from Sigma Aldrich (London, United Kingdom) and used as received

- In a typical batch, 120 g of CA was placed into a round bottomed flask with 450 ml of acetone (99 %, Alfa Aesar) then placed inside

- The resultant mixture was kept in reflux for 4.5 h under continuous stirring
- After this time period, the mixture was decanted into a beaker and a pre-dissolved (in acetone) quantity of the desired plasticiser was mixed in. The quantity of the plasticiser was dependant on the final weight percentage desired
- The entire mixture was allowed to cool for 1 h under stirring then poured into a glass tray and its lid placed on
- Solvent evaporation was allowed for 1 week at room temperature. The final drying procedure was performed in a vacuum oven (150 mbar) for 96 h at 20 °C
- Once dry, samples were cut into approx. 30 mm X 5 mm samples via a small bandsaw

Two examples of industrially made CA were sourced from Colin Williamson, a private collector and expert on modern polymeric materials. They were likely produced towards the end of the 1960s by the Italian manufacturer Mazzucchelli 1849. They were chosen in part due to this provenance as well as their overall excellent condition despite their age.

3.6 Accelerated ageing

In order to produce changes to the chemical composition of both the bespoke and industrial samples, they were subjected to two periods of accelerated ageing. Furthermore, by using this method of ageing we gain an added level of consistency to the environmental conditions to which the samples have been exposed to. Accelerated ageing, commonly referred to as artificial ageing, is a common practice within heritage research (Lovett *et al.*, 2004; Feller, 2006; Maguregui *et al.*, 2009; Luxford *et al.*, 2011; Toja *et al.*, 2013)

The accelerated ageing conditions which were used during this project were a temperature of 70° C and a relative humidity of 50%. Samples were placed into a small Pyrex® glass bowl which sat on top of a shelf in a desiccator with a saturated salt solution underneath the shelf. The samples were separated from each other by way of aluminium foil. The salt used to regulate the RH was sodium bromide (purchased from Fisher Scientific, Anhydrous, 99+ % purity, Product Code.10368100) this was chosen from the table provided in Greenspan (1977). The saturated salt solution comprised of 100 ml of deionized water and 100 g of sodium bromide. Figure 3-4 shows the ageing setup before being placed into an oven. Two accelerated ageing campaigns were undertaken, the first lasted for four weeks while the second lasted for eight weeks.

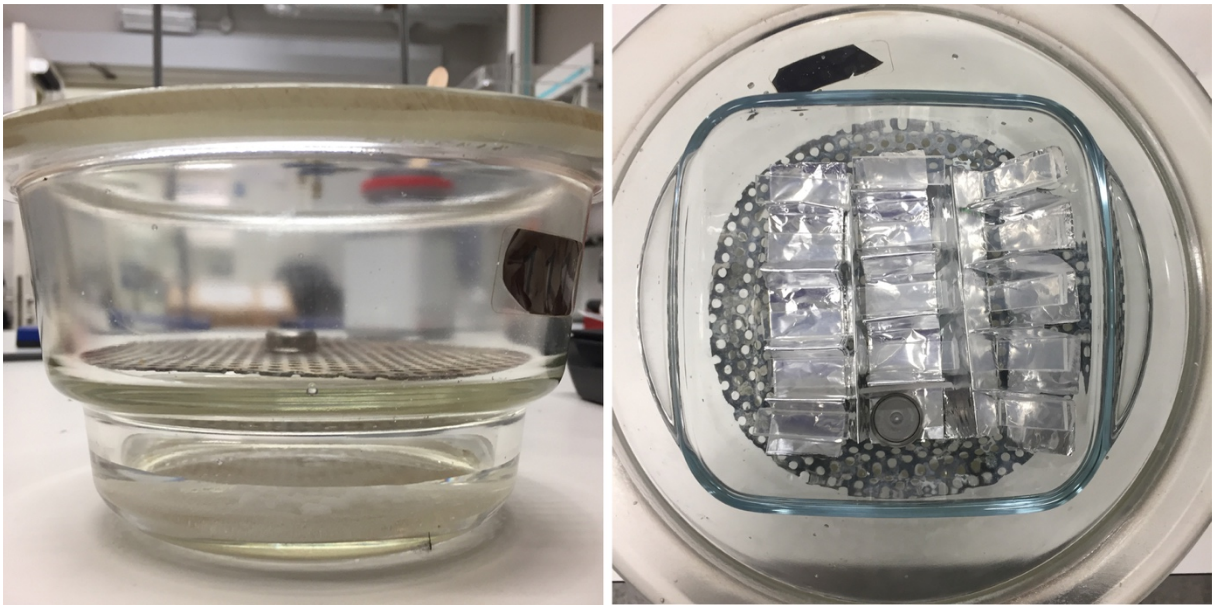


Figure 3-4 – Left: A side view of an open desiccator showing the level of the saturated salt solution and the placement of the metal shelf. Right: A top view of samples placed inside a glass bowl. Samples are separated via aluminium foil and a small iButton data logger is placed to one side to record the internal temperature and relative humidity conditions.

3.7 Importance of bespoke computer coding

The various software packages, as outlined above, generally use proprietary file formats, require a software licence and/or are not available for use via an Apple Mac operating system (which was the main computer type of the author). This caused an issue with access to the data during post-processing or when comparing between similar datasets acquired using different apparatus.

In an effort to rectify this issue it was decided that a number of MatLab programs were to be written to eliminate many of these access issues. These were supplemented with a select group of open-source software programs which aided the post-production of the raw data.

By producing MatLab programs the efficiency of the post-processing workflow was greatly increased as many files could be processed at the same time. Furthermore, it also allowed for a precise understanding of the data-processing which some 'black-box' types of software do not provide.

For data produced via SPME GC/MS the workflow typically consisted of the following:

- Raw data is copied from its original computer and imported into *OpenChrom®*
- Within *OpenChrom®*, a batch script was employed which automatically picked each peak, via the 1st derivative method, and then calculated the peak area via the trapezoidal method. Two files were produced, the first was a simple conversion of the chromatogram from the PerkinElmer proprietary file format to a CSV file format. The second file reported the peak positions and peak areas

- The CSV file was subsequently used to produce graphs of resulting chromatograms using MatLab
- The peak report file was utilized in calculating the normalized peak areas using MatLab

Peaks were identified using the 2011 version of the National Institute of Standards and Technology (NIST) Mass Spectral library which was linked to *OpenChrom®*. Two additional resources were also used when identifying VOC peaks – AMDIS, distributed by NIST, is a software program that allows for chromatogram deconvolution. This was paired with the ESCAPE library of compounds which was compiled by Michael Schilling from the Getty Conservation Institute and Henk van Keulen from RCE in the Netherlands. This library is mostly formed of compounds relevant to the analysis of Asian lacquers, however, there is some crossover with modern polymeric materials. A graphical representation of the GC/MS workflow can be seen in Figure 3-5.

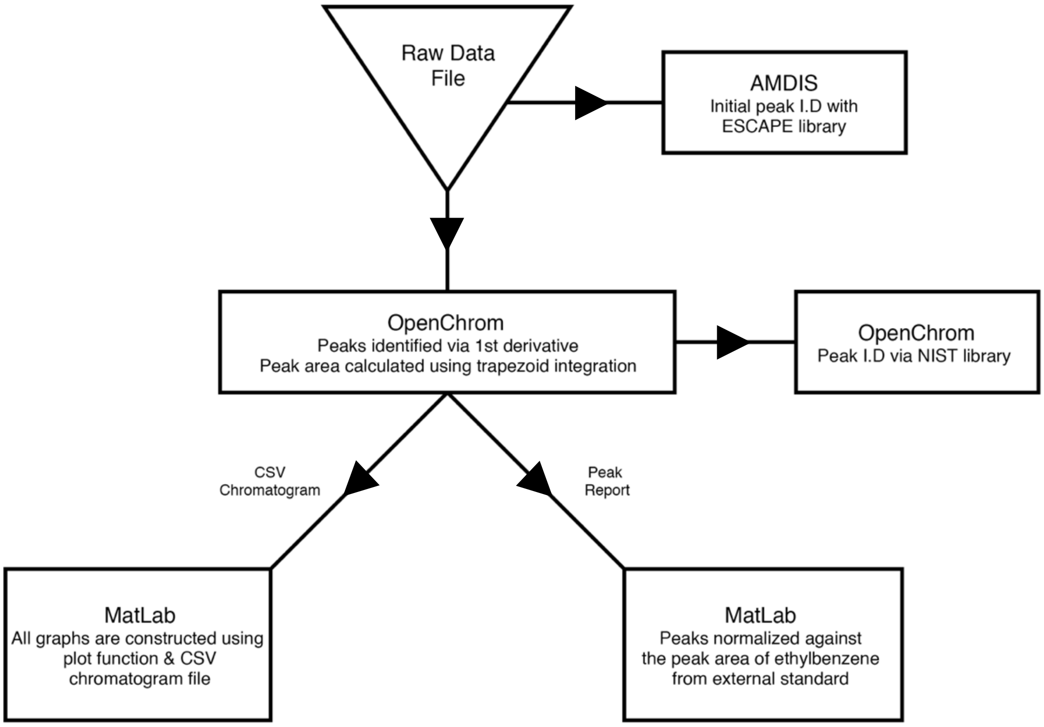


Figure 3-5 – A schematic diagram of the workflow for SPME GC/MS analysis. Note the use of MatLab Code for the production of both graphics and peak lists. The NIST Library is used throughout for the identification of compounds.

A MatLab program was also used to calculate the average FTIR spectrum for the different areas on the sample from the raw .dpt file created by OPUS. A second script also allowed the ratio of two peaks to be taken.

As previously mentioned, the LabSpec produces a spectrum in 1 nm increments between 350 and 2500. In order to calculate the L*a*b values, a MatLab program was written which followed the equations provided at the website of Bruce Lindbloom (Lindbloom, 2019). In calculating L*a*b values the program only used the reflectance values between 390 and 700 nm. This program allowed for multiple raw files to be converted to L*a*b values in a matter of seconds. It also allowed for both the viewing angle, of 10 degrees, and standard observer, D65, to be specified.

3.8 Monitoring temperature and relative humidity

Throughout the project accurate measurements of temperature and relative humidity were needed to aid different elements of the analysis. However, commercial units such as HOBO® loggers or iButtons® were not suitable or too costly to deploy. In order to meet our requirements, bespoke monitors were manufactured using commercially available temperature and relative humidity sensors on small printed circuit boards (PCBs). These PCBs were wired to a Raspberry Pi computer. The Pi was then programmed, using the Python® language, to log data at our desired resolution (normally 1 min intervals). Two types of sensors were used, a general-purpose sensor which was used to monitor the relevant ambient conditions and a second, smaller, sensor which had the ability to be sealed inside a 20 ml glass vial.

Two different versions of the Raspberry Pi were used during the project. The first type was a single Raspberry Pi 3 which had two Sensiron SHT31-D sensors (purchased from pimoroni.com and manufactured into a PCB chip by Adafruit). The accuracy of the SHT31-D was +/- 2% RH and 0.2° C. The second type was a Raspberry Pi Zero W (also purchased from pimoroni.com). Four of these Pi Zeros were used, three of which had the same Sensiron SHT31-D sensors as the Pi 3. The fourth Pi Zero had a HYT 271 sensor (purchased from farnell.com, manufactured by IST Innovative Sensor Technology) which was sealed inside a vial using a combination of PTFE septum and melted hot glue on the top cap. The accuracy of the HYT 271 sensor was +/- 1.8 % RH and 0.2° C.

Chapter 4 Initial Investigation of SPME within Museum Environments

4.1 Introduction

The preceding three chapters of this thesis have been concerned with detailing the background theory, the relevant gaps in our current knowledge, and detailing my initial thoughts on the scope the project should take. This chapter details our first foray into the practicalities of VOC analysis. It outlines our starting position and our efforts to chart the best course of action to achieve our overall project objectives. The data contained in this chapter has been previously published in *Studies in Conservation* (Kearney *et al.*, 2018, 2020)

As previously discussed, this project can trace its lineage to the *Heritage Smells!* project and as such its starting point is directly linked to its predecessor's endpoint. While Dr Curran, a researcher on *Heritage Smells!* (and my PhD supervisor), acknowledges that it showed that SPME-GC/MS is an extremely useful method for detecting compounds emitted from polymers, they also recognise *that "Heritage Smells! did not address the question of how this could be practically applied in a real museum context."* (personal communication, 2019) and to make the research *"more practically applicable in the real heritage context therefore, there was a need for a project that moved the research from the analysis of samples in the lab to the analysis of real objects in-situ"*. This viewpoint was reflected in the original project advert whose research questions included *"How can we translate the work carried out using plastic samples to complex plastic objects within collections?"* (UCL PhD Advert, 2015).

While *Heritage Smells!* was partly concerned with modern materials within collections, we have also shown, in Chapter 1, that SPME has been utilized within museums for other types of materials. However, the limiting factor with many of these previous studies was they were mostly concerned with single measurements of the overall room environment, rather than a single object (Thiébaut *et al.*, 2007; Bembibre *et al.*, 2017). As such little can be garnered about the performance of repeated SPME analysis targeted at a single object.

With these studies as our starting conditions, we judged that our initial experiment should focus on determining the behaviour of SPME when it is utilized to engage in repeated non-destructive and non-invasive analysis of several points-of-interest (POI) around a single object housed in a museum environment.

In consultation with the conservation scientist Dr Joyce Townsend (also a PhD supervisor for this project) at Tate the object chosen to study was Naum Gabo's constructivist sculpture *Construction in space 'Two Cones'* (Tate T02143, *c*.1927, this replica 1968) Figure 4-1. This object was chosen for a number of reasons:

- The object is highly degraded, and it is no longer suitable for display. It was thought that this level of degradation would offer the most viable condition for initial testing of SPME performance in an open environment
- The object has been extensively scientifically studied in the past due to its importance within its artistic movement and its maker, in addition to the fact that it was the first CA-based sculpture at Tate to show visible deterioration. This allows for cross-validation with past research carried out by Tate staff
- The object is constructed wholly with cellulose acetate (its clear plastic base is not original and is not made from CA), which, as previously mentioned, is one of the modern polymeric materials which causes the greatest concern to museums professionals

- The object is complex in its geometry, as such it offers a number of suitable points of interest to study
- It is housed within an open-toped storage crate to enable ventilation of generated acetic acid which allows for easy access during the analysis
- It is permanently housed in a secure and hence enclosed storage area within the sculpture conservation department, located at Tate Britain. This facilitates easy access to the object for the duration of the experiment, while at the same time offering few disturbances to the object or the room environment while analysis is taking place. The fact that it is no longer displayed means that it was unlikely to move location during the study

The main objective of this experiment was to act as a fact-finding study on SPME performance which would, in turn, further influence the overall direction of the PhD project. As such there were specific questions which needed to be answered:

- Is it possible to distinguish key composition and degradation VOC markers using SPME GC/MS from a single object in a heritage environment?
- Is it possible to differentiate any resulting VOC profile from the different POIs?
- Is it possible to gain any insights into the condition of the object via this methodology?
- What, if any, practical recommendations can be offered to the conservation staff following this analysis?

This starting set of research questions acted as the main focus of interest. These were questions which must be definitively answered for successful completion of the experiment. However, there was a second set of questions which, if having had a positive outcome from the first, we aimed to answer:

- What effect do long fibre exposure durations have on the resulting VOC profile?
- Does the background VOC profile unduly influence the VOC profile from an object and can the two be reliably distinguished?
- How do uncontrolled parameters such as temperature, relative humidity and air-movement affect the performance of SPME GC/MS analysis?
- Do we see any signs of competition for sites on the SPME fibre during our analysis and to what extent can this be classified?
- To what extent do the above constraints limit our ability to monitor a historic polymer object within a heritage environment?

4.2 Experimental Methodology

Chapter 3 outlined the basic experimental methodology of SPME analysis. However, there are a number of practical issues, specific to this experiment, which will be detailed below.

As mentioned previously, the object (henceforth referred to as *T02143 Two Cones)* is housed inside a plastic storage crate. This crate has an open top which is covered with fabric dust cover. The interior walls of the crate are lined with a charcoal cloth on top of a Plastazote® backing. Its base is uncovered Plastazote®. A total of four SPME fibres were placed around the object at different locations. The same fibre (which were numbered for reference) was used for each repeated analysis at each location, Table 4-1details the location of the POIs, while Figure 4-1 shows an image of the fibres placed around the object.

Location No.	Fibre No.	Fibre Placement
1	1	Background - Placed approx. five meters away from the object in one corner of the room.
2	2	Area of high degradation in centre of object. Fibre housing was placed between the delaminated object fragment with the fibre coating extending into the centre of the object.
3	3	Area of low degradation slightly away from the object. This location was favoured due to its minimal interaction with the object while still being in close proximity to it.
4	4	Area of high degradation inside one of the cones. This area was chosen due to its proximity to an area of high degradation and also due to the geometry of the cones shape.
5	5	Area of low degradation. This POI was chosen as it was the furthest point away from the object while still being inside its storage crate.

Table 4-1 - Details the fibre number at each location along with a short description of their locations about the object

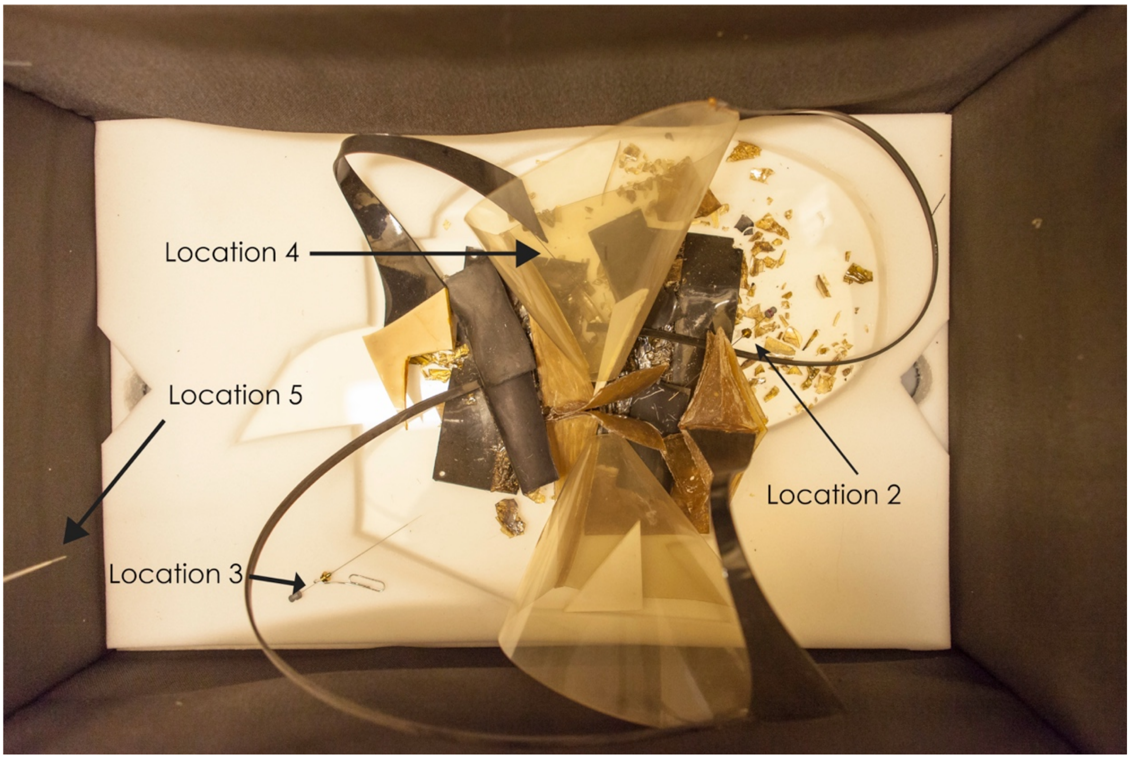


Figure 4-1 - *Construction in Space, Two Cones* ′ 1927, replica 1968 by the artist, Tate T02143. The Work of Naum Gabo, © Nina & Graham Williams. Shown in its storage crate with the location of fibre placements . Note that the fibre at location 5 is left suspended, via a thread, at the side of the storage crate.

To examine the effects of pre-concentration exposure time two periods were chosen. The first was for 1 day; this was the minimum duration that was felt would still provide reliable results from an object displaying the advanced degradation profile of T02143, *Two Cones* . The second was for 7 days; this was thought to be the longest 'convenient' time length (in terms of wait time for results and access issues) for this object. For each duration three replicate measurements were taken; due to limited resources and time constraints of the GC/MS these replicates were undertaken on separate dates. Table 4-2 outlines the dates and analysis run order for the experiments. The method for analysing the fibres is described in Chapter 3-2.

Analysis Set	**Fibres placed in**	**Fibres Taken out**	**Analysis Dates**
1 Day Set 1	13th Feb	14th Feb	Fibres 1, 2, 3 - 15th; Fibres 4 & 5 16th Feb
1 Day Set 2	13th March	14th March	Fibres 1 & 2 - 15th; Fibres 3,4,5 - 16th March
1 Day Set 3	20th March	21st March	Fibres 1, 2, 3 - 22nd; Fibres 4 & 5 - 23rd March
7 Day Set 1	20th April	27th April	Fibres 2 & 4 - 27th; Fibres 1,3,5 - 28th April
7 Day Set 2	2nd May	9th May	Fibres 2,3,4 - 10th; Fibres 1 & 5 - 11th May
7 Day Set 3	23rd May	30th May	Fibres 1 & 5 - 31st May; Fibres 2,3,4 - 1st June

Table 4-2 - Relevant dates of the analysis. Note that the overall experiment lasted for over three (calendar) months

4.3 Initial observations

The initial examination of the data indicated that both time durations made it possible to identify numerous different types of VOCs from each of the points of interest. Figure 4-2 shows a typical chromatogram from

POIs during analysis. In general, the top 13 VOCs from each POI were identifiable, with significant comparability in compound and relative abundance between each POI (Table 4-4). Figure 4-2 & Figure 4-3 also highlight the complex nature of the VOC profiles found from open museum environmental analysis.

In order to answer the research questions four compounds, found in each dataset, were chosen for in-depth analysis. These four compounds were chosen on the grounds that they corresponded, for the most part, to the four largest peaks found in each data set, as well as providing detailed information regarding the identification and degradation of the object. These compounds are:

- Acetic acid – both an identification marker and a marker for the degradation of cellulose acetate (Allen *et al.*, 1988; Knight, 2014)
- Diethyl & dimethyl phthalate – Both compounds were common plasticisers used with cellulose acetate (Wypych, 2004) and a trace of both have been detected in the flaked-off and discoloured material in the crate (Mazurek *et al.*, 2019), which indicates that a substantial proportion of the plasticiser once present is now being lost
- Phenol – Believed to be itself a degradation product of the plasticiser triphenyl phosphate, which was another common plasticiser used with cellulose acetate (Shinagawa *et al.*, 1992; J. Tsang *et al.*, 2009), and which has also been found to be present (Mazurek *et al.*, 2019, Townsend et al., 2016, Internal Tate Report). The role of phenol in the detection of triphenyl phosphate will be discussed further in Chapter 7.

Compound	Retention Time (mins)	Observed m/z values	NIST R Match value
Acetic Acid	10.82	60, 61, 46	988
Phenol	25.60	94, 66, 65	975
Dimethyl Phthalate	46.33	163, 77, 76	967
Diethyl Phthalate	54.83	149, 177, 150	958

Table 4-3 - Retention time, observed m/z values and an example value of the NIST R Match (taken from the 1-Day Set 3 Fib 2 sample) used in the identification of VOCs during the analysis.

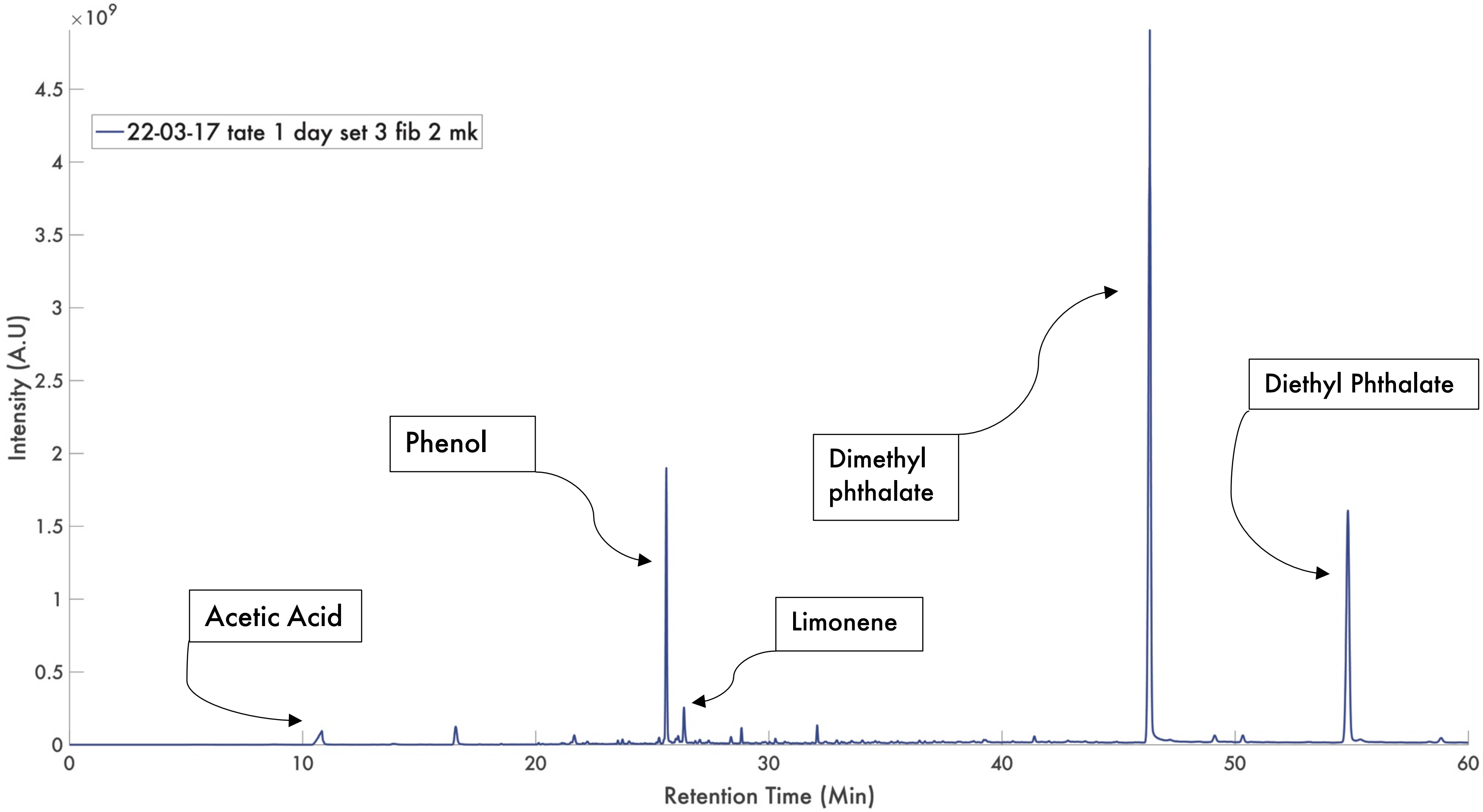


Figure 4-2 - An example of a typical TIC found during analysis of the object. Please see Table 4-4 for a list of the top 13 VOC identified from this TIC.

RTMin	Normalised Peak Area	Most intense m/z Value	NIST I.D	R.Match Value
46.34	20.01	163	Dimethyl phthalate	967
54.84	9.48	149	Diethyl Phthalate	954
25.60	4.61	94	Phenol	957
10.82	0.83	60	Acetic acid	975
26.35	0.73	68	Limonene	938
16.56	0.61	207	Hexamethyl-Cyclotrisiloxane	958
32.07	0.29	57	Decanal	919
21.65	0.25	282	Octamethyl-Cyclotetrasiloxane	663
49.11	0.24	71	Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	925
28.83	0.23	57	Nonanal	912
58.84	0.20	133	4-cyclohexyl-Phenol	847
41.39	0.16	104	1,2-Benzenedicarboxylic acid	934
28.37	0.13	79	Benzyl alcohol	917

Table 4-4 - A list of 13 of the top 15 VOCs, with relation to normalized peak area from 1-Day Set 3 Fibre 3. Note that two of the top 15 VOCs could not be identified confidently and are therefore not included here.

Table 4-4 is also clear evidence that SPME GC/MS is capable of distinguishing between identification and degradation markers for CA. Going further, our analysis indicated that for objects displaying visible degradation as pronounced as that of *T02143, Two Cones* an exposure time of 1-day to the object before GC/MS desorption was sufficient to allow for reliable determination of degradation and identification markers from all POI, including providing the ability to differentiate the background from the object (See section 4.8). This result has a direct impact on the usability of the methodology as it not only lessens the disruptive impact of the analysis on the wider storage area but also its speed falls within a reasonable timeframe for integration within current conservation workflows.

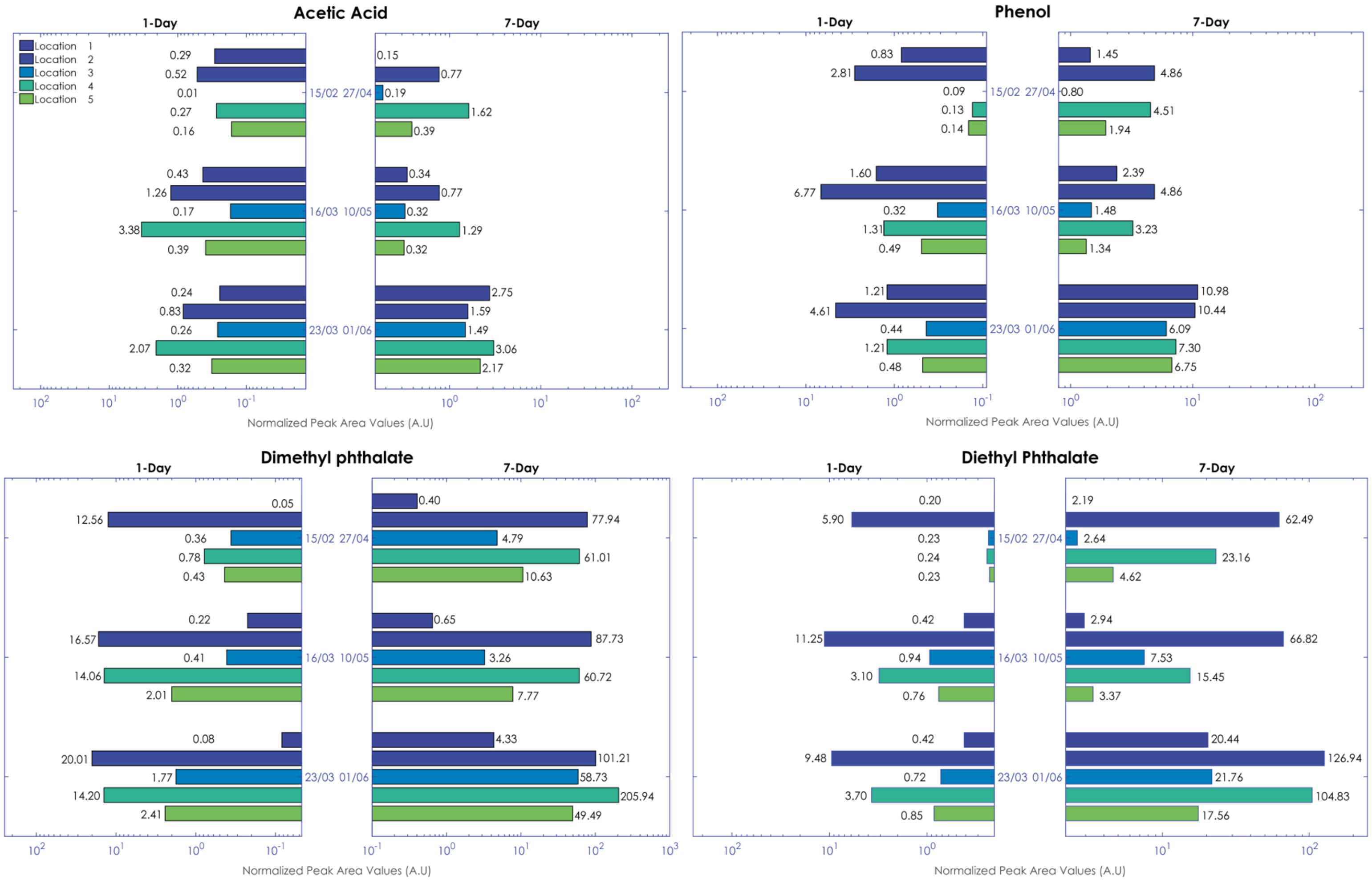


Figure 4-3 - Normalized peak areas for our four target VOCs for both 1-Day and 7-Day analysis. Dates in middle refer to the day of analysis for each set of five analysis locations. Please note the log scale.

Further to this insight, by examining the intensities of our four key VOCs between the different POI, clear differences appeared between them. Figure 4-3 highlighted how at both 1-day and 7-day durations, two distinct VOC profiles emerged – closer to the area of visibly higher degradation (locations 2 and 4) our four key VOCs were significantly higher than at the locations positioned slightly further away from the object or from the overall room conditions (locations 1,3 and 5). In general, the overall levels of the VOCs were lower for Location 1, which was the room profile. However, as will be shown in section 4-8 despite the lower trend in relative amount at Location 1, the room's condition complemented the findings for the object itself. Section 4-8 will discuss the implication to the monitoring of modern polymeric materials this finding has.

The discovery of VOC hotspots on an object of this (physical) size highlights the importance of fibre placement with relation to the object. It provides concrete evidence that monitoring historic polymer objects, with this methodology requires that fibre placement either be targeted at specific POIs, as close to the object as possible, or as a different approach, placed in the general vicinity of the object or in the room to gain an overall idea of the VOC emissions from the object as a whole, with the knowledge that VOC 'hotspots' will likely be overlooked or under-represented.

More significant than the identification of VOC 'hotspots' were the insights garnered from analysis of the two POI closest to the object. This suggested the potential for two distinct degradation mechanisms present on the same object. As can be seen in Figure 4-5, analysis from location 2, an area of visually high degradation, showed a higher ratio of phenol to acetic acid than at location 4 where the visual indication of degradation was less. Both locations were a similar distance from the centre of the object. This feature was present for both 1-day and 7-day analysis; however, the ratio was less during 7-days. The cause of this deviation will be discussed later in this chapter.

Location 2 showed significant crystal growth, much more so than at location 4, which had almost none. Micro-FTIR analysis, from a crystal from location 2 shows a good match with a laboratory sample of the plasticiser triphenyl phosphate (see Figure 4-4), although the presence of diphenyl phosphate could not be ruled out. An internal (and unpublished) Tate document on the scientific analysis of *T02143, Two Cones* also showed that triphenyl phosphate (TPP) was present on the object - (Townsend et al., 2016). When the crystal sample is viewed against a spectrum from TPP used during the production of the bespoke samples there is again a close match between the two.

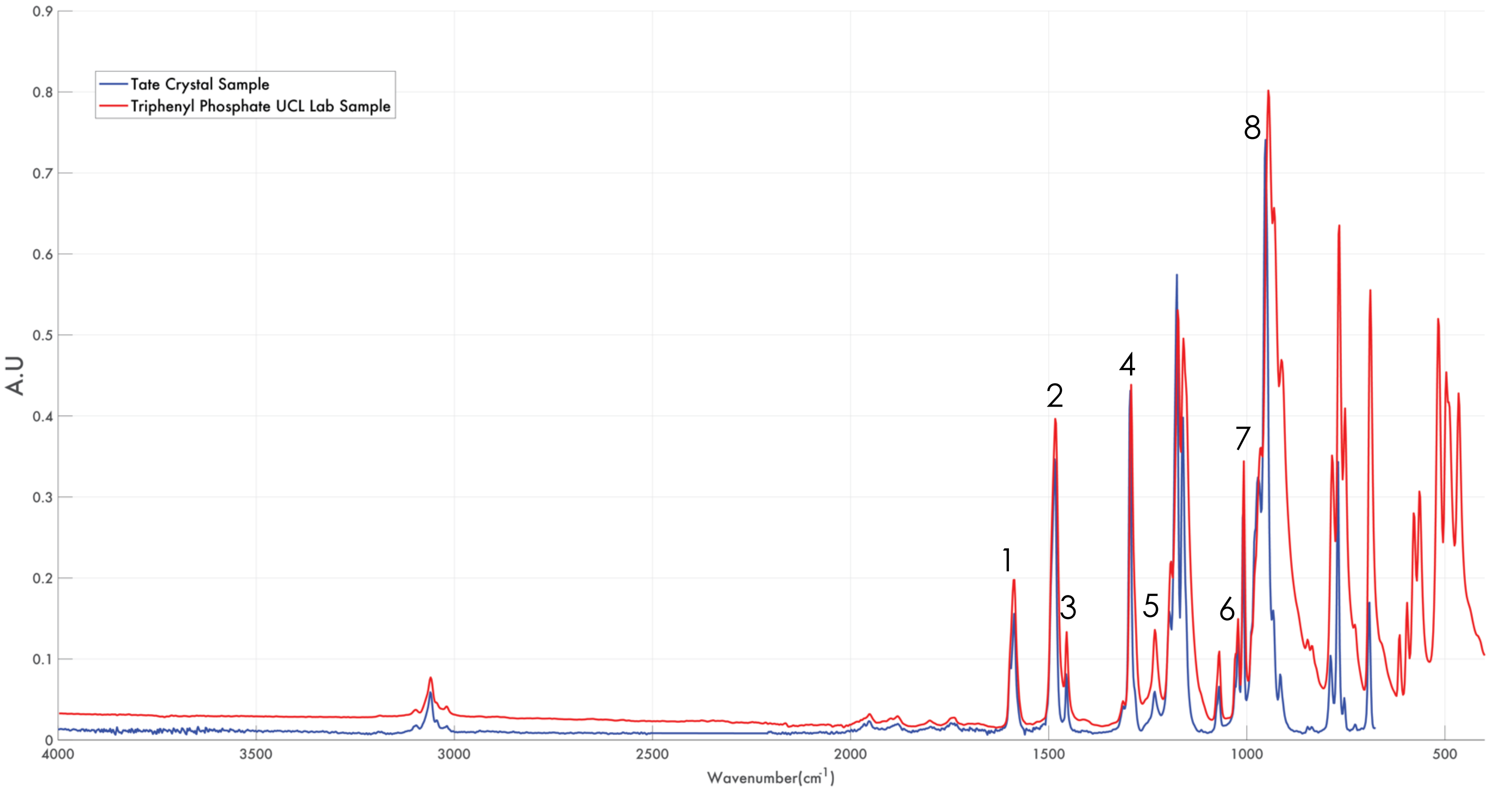


Figure 4-4 - FTIR spectra showing the crystal sample from *T02143, Two Cones*, which was obtained via micro-FTIR, and a sample of pure TPP obtained via ATR-FTIR at the laboratory in UCL. Note the similarities between the two spectra with bands at 1590 (1), 1490 (2), 1455 (3) cm^{-1} (C=C stretching), 1295 (4) cm^{-1} (P=O stretching), 1194 (5) cm^{-1} (P–O stretching), 1026 (6), 1010 (7) cm^{-1} (aromatic C–H in plane bending), with the band at 955 (8) cm^{-1} likely being the shifted 964 cm^{-1} band (O–Ph stretching) (Cucci *et al.*, 2015)

The high levels of phenol, detected via SPME, being emitted from T02143, *Two Cones* can be explained by examining the work of Shinagawa et al (1992) who outlined that the degradation of TPP, via hydrolysis, led to the formation of both phenol and diphenyl phosphate. As further corroborating evidence, Tsang et al (2009) also emphasised the phenomenon where CA plasticized with TPP appeared to degradation at faster rates than CA whose plasticiser was something else. This is due to the formation of acidic diphenyl phosphate, which (similar to the acetic acid formed through deacetylation) will catalyse the degradation of the plasticisers and polymer. Combined, these results strongly reinforce the idea that we are detecting, via SPME, two different degradation mechanisms at two different locations causing the rapid degradation of a single CA object. At location 4, we see high levels of acetic acid, due to the deacetylation of CA, while at location 2, we detect phenol due to the hydrolysis of TPP. A further discussion on the role of phenol in the degradation of CA will be presented in Chapter 7. Given the presence of acetic acid at location 2 also, it is likely that the deacetylation process is also occurring here. However, our analysis shows that location 4 represents a more high-risk area of the artwork, at which two autocatalytic processes are occurring compared with location 2.

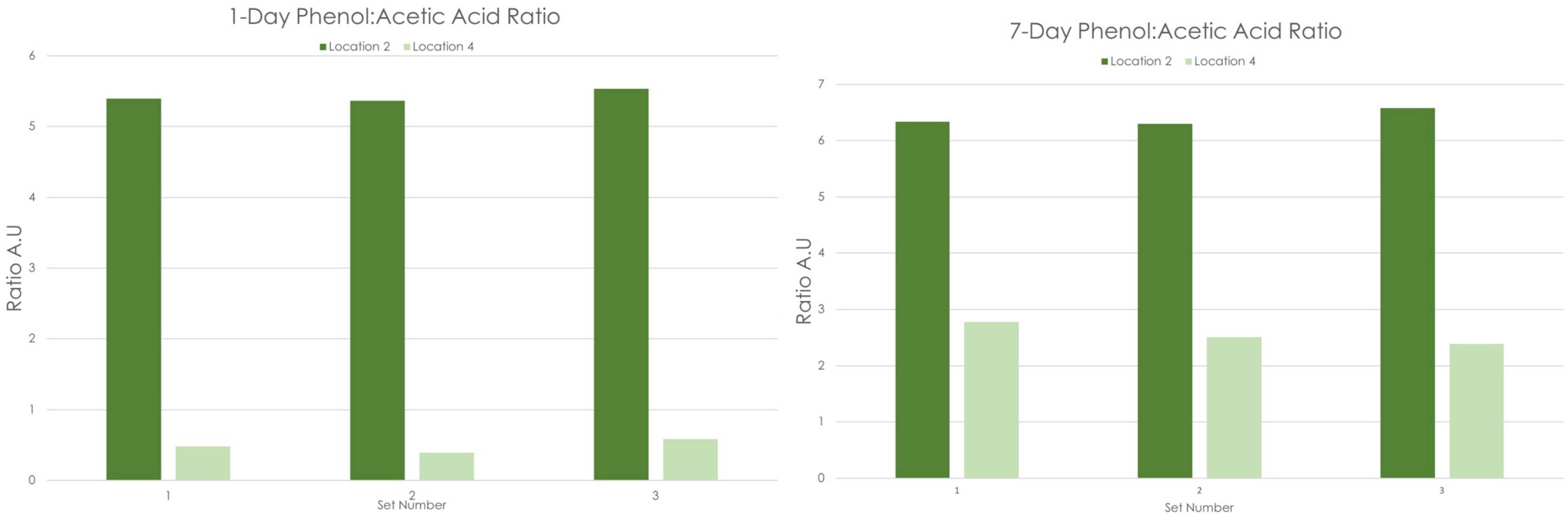


Figure 4-5 - Shows the ratio of phenol to acetic acid for locations 2 & 4 on the object at both 1-Day and 7-Day experiments. Note the consistency of each ratio and the high levels of phenol seen at location 2 and not at location 4 indicating two possible reactions occurring at the different locations.

A result of the above findings is clear evidence that current storage conditions - the open crate & charcoal cloth fitted at least 5 and possibly 10 years earlier – are not effective in mitigating the dangers posed by VOC build-up or the cross-contamination issues (Curran *et al.*, 2014) that such a work would pose if stored with other CA-based museum in a museum store. This research clearly demonstrates that new risk management strategies need to be implemented to counteract these build-ups; such strategies would likely be some form of interventive preventive conservation such as continuous air flows over the object or periodic flushing of the surrounding environment.

Of the four initial research questions posed above it is clear that even the most basic of data analysis provides positive answers with definable recommendations for museum professionals. Overall, the conclusion is that even when used in a basic form SPME GC/MS is capable of providing high-level insights into the degradation and composition of historic polymer objects through non-invasive analysis.

4.4 Deeper insights – repeatability

The above analysis, through its qualitative nature, allowed for conclusions regarding both the object and the proposed methodology to be drawn relatively easily. However, deeper insights are needed to answer the remaining research questions.

Clear differences between the datasets from the two durations of absorbance, and between laboratory analysis versus open museum environments becomes apparent when one examines their respective relative standard deviations (% RSD).

Analysis from this experiment has shown that across all locations, %RSD was very high, although a lower % RSD was found for an exposure length of 7-days than for 1-day exposure.

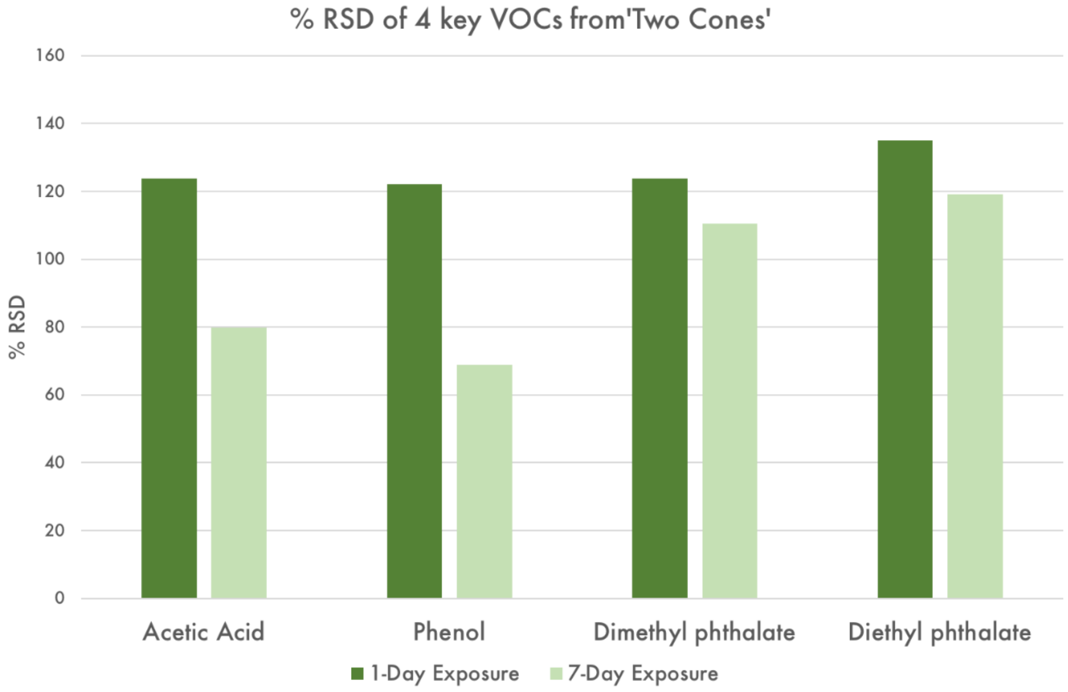


Figure 4-6 - Shows the % RSD calculated from all data for each of the four key VOCs. Dark green are results from1-Day, while light green shows 7-Day results

As can be seen from Figure 4-6, which details the resulting total % RSD for all locations for each of the four key VOCs, the % RSD is lower for 7-Day than for 1-Day suggesting that the SPME fibres have, during the 7-Day time-length, reached equilibrium or are closer to achieving this than those exposed for 1-Day.

At the shorter time length, the absorption of VOCs is governed by those VOCs who have preferential uptake by the SPME fibre at that location and for that time period. This preferential treatment is, in part, governed by the material, or combination of materials with which the SPME fibre is constructed and by the concentration. As outlined in Chapter 1.3 each fibre coating type will react differently when exposed to either polar or non-polar compounds, this results in preferential uptake of the coatings preferred compound type leading to high % RSD (Tuduri *et al.*, 2001; Bojko *et al.*, 2012).

However, at the longer timeframe, one that allows for equilibrium to be reached (or to be almost reached), the effects of this affinity phenomenon are reduced and the SPME fibre "*sees*" a more proportional and consistent viewpoint of the relative VOC concentrations present. In turn, this leads to a lower % RSD.

One drawback of the longer timeframe is that it somewhat hinders the detection of VOC hotspots, such as the ones shown in Figure 4-3. For the longer timeframes, differences between different POIs will be less significant.

If we change our point of reference and examine the data from a point-of-interest perspective, as opposed to the individual VOC one discussed above, we see an almost complete reversal in the % RSD trends (Figure 4-7). Spot analysis at each location for the 1-Day exposure time length, led (for the most part) to lower % RSD than for the same location when measured at the 7-Day exposure time. There was the exception of location 4 which recorded a higher % RSD of acetic acid and phenol.

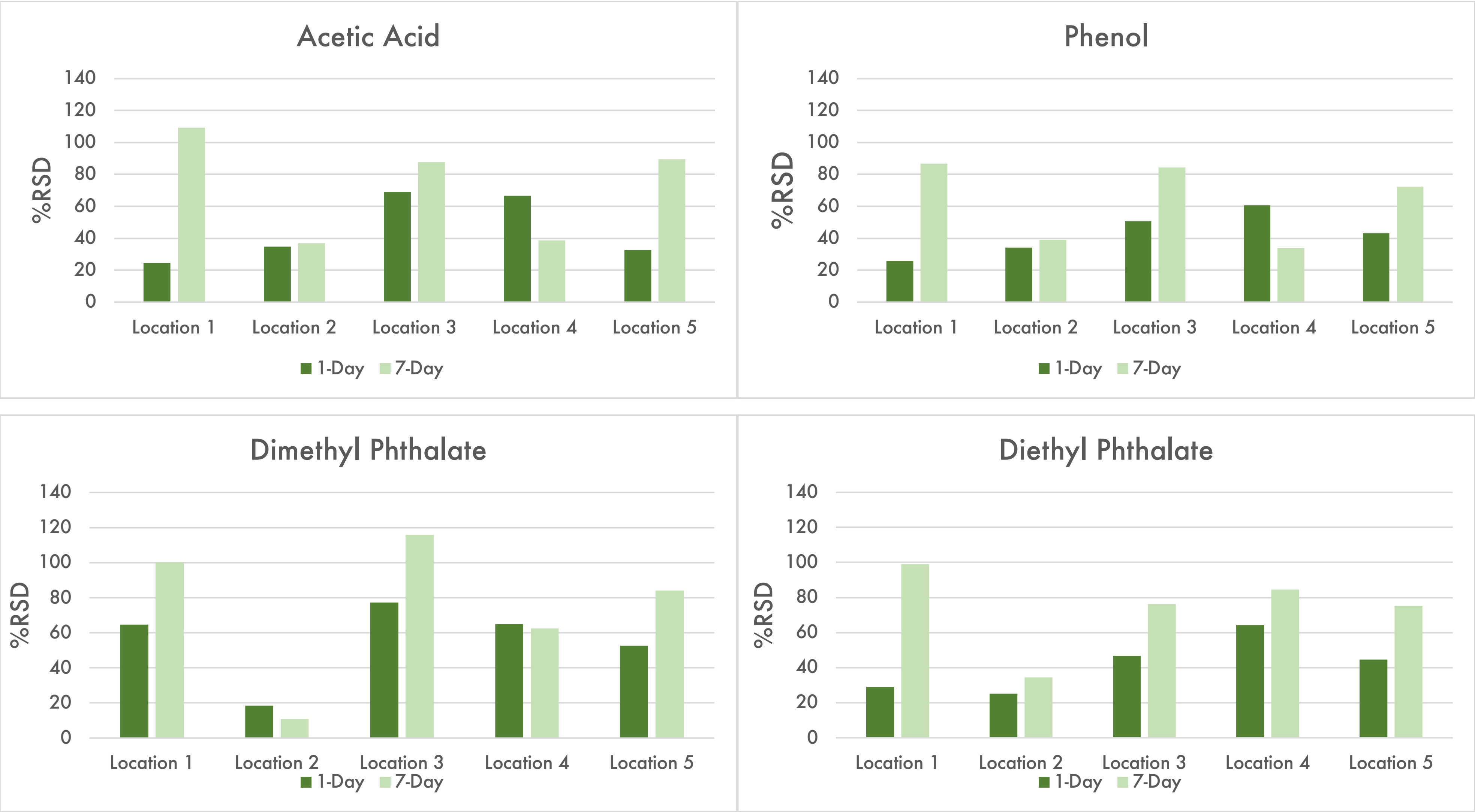


Figure 4-7 - %RSD at each location for our four key VOCs for 1-day and 7-day analysis. The results from 1-day analysis are generally lower (except for acetic acid and phenol at location 2) showing better repeatability during the 1-day analysis.

Location 4 saw the highest values for both acetic acid and phenol and as the exposure time is quite short these locations can also be governed by external considerations. Air movement is likely to be one of these, both from the disturbance caused while performing the analysis itself and from natural air movements within the storage room - the open top design of the storage crate would leave the object inside susceptible to this and is in fact a desired outcome of its design. These deviations in the air surrounding the object would in turn lead to deviations in the resulting VOC profile leading to higher % RSDs. Complementary to this are the effects of temperature (which will be discussed in greater detail later), relative humidity, air movement, air pressure and the combined effects of competition and matrix effects – all of which effect the resulting VOC profile.

Furthermore, one factor in the larger % RSD seen for the 7-Day analysis is the final Set 3 which was considerably different to the preceding two. A more detailed discussion will follow in its relevant sub-section; however, this result is highly likely due to the large increase in temperature seen during this analysis set.

There are major implications on the perceived usability of the SPME methodology from this analysis. While it is correct to say that the analysis sets performed at the 7-Day duration produced more consistent datasets of the VOC profiles at the different locations, under real-world conditions it is also more prone to external stressors and does not provided the explicit clarity needed to identify VOC hotspots around the object.

4.5 Deeper insights – laboratory versus real-world analysis

In order to comment on the differences between SPME analysis conducted in a laboratory vs in a heritage environment, it is worth commenting on the high values of RSD. As can be seen from both Figure

4-6 & 4-7, long-term SPME analysis within open environments leads to very high %RSD results. The lowest %RSD for a specific VOC, found around the object, was 68.7 % (phenol, 7 Day analysis) while the highest was 134.9 % (diethyl phthalate, 1 Day analysis). The POI with the lowest RSD, of 10.7 %, was found for dimethyl phthalate at location 2 during the 7-day analysis, while the highest, at 115.9 %, was found at location 3 for the same VOC.

The resulting %RSD do not match those previously reported in the literature where the analysis is carried out in a closed lab-based system (Buchholz *et al.*, 1994; Kusch *et al.*, 2004; Clark *et al.*, 2011; Souza-Silva, Reyes-Garcés, *et al.*, 2015; Curran *et al.*, 2018) Typically, with these studies, the resulting %RSD was less than 10 %. In the development of this project the resulting tests of polymer samples, utilising a closed system via a 20 ml glass vial, yielded %RSDs of between 5 % and 15 %. This is comparable to those found in the above literature. It is clear that the high %RSD is a feature of open museum-based analysis and not an issue with our SPME fibres or GC/MS.

The insights into the high % RSD have wide implications for both qualitative and quantitative analysis of the resulting data, and more importantly on the deployment of this methodology in a museum environment. On the one hand, the above analysis clearly demonstrates the methodology's ability to capture relevant VOC information about the object. However, on the other hand, extreme care should be taken when trying to convert this information into concentrations surrounding the object. This dichotomy has been noted in the literature before - Gómez-Ríos and Mirabelli, (2019) have explicitly stated that *"lack of understanding regarding quantitation by SPME remains a chink in its armor."*, while Pörschmann, Kopinke and Pawliszyn, (1998) have stated that "*the commonly used term 'concentration' in SPME analysis should be replaced by the more appropriate term* *'activity'*". With relation to the experiments presented here - it is likely that equilibrium was not achieved after a period of 1-Day, while 7-Day analysis sets were unduly affected by external influencers. Therefore, it is not advisable to translate the result to a concentration, via a calibration curve, achieved under laboratory conditions, at equilibrium.

4.6 Deeper insights – role of temperature

In order to examine the role of temperature during the experiments a data logger was placed next to the storage crate. However, this logger failed, and all data was lost. In light of this we must rely on temperature data from an external logger at Tate Britain. It is possible to do this as the storage room where T02143, *Two Cones* was housed during the experiment was not environmentally controlled, has one external wall, an airbrick, no heating or air conditioning, and has a large window. These factors dictate that the internal temperature is only slightly buffered from the external conditions. Therefore, it is reasonable to suggest that external trends in temperature are followed inside, even if exact temperatures are not matched.

1-Day	**Average Temp**	**Min Temp**	**Max Temp**
Set 1	8.4	4.6	13.6
Set 2	13.4	8.4	20.1
Set 3	10.1	5.6	14.3
7-Day	**Average Temp**	**Min Temp**	**Max Temp**
Set 1	11.5	3.1	21.6
Set 2	13.0	8.3	25.0
Set 3	22.2	14.2	31.3

Table 4-5 - Values of temperature during the dates in when the fibre was exposed to the museum environment. All temperatures are in degrees celsius

If we collate the information from Table 4-5 and Figure 4-3 a pattern emerges whereby the relative abundance of VOC/locations follows the external trend of temperature rise and fall. Examples include the peak area of phenol at location 2 being higher during 1-day set 2 than 1-day set 3, as is the average outdoor temperature during each analysis period. As previously mentioned, set 3 of the 7-Day analyses had a significant influence on the overall % RSD. The peak area is unchanged between *set 1* and *set 2* while a temperature difference between these two sets was only approx. 1.5° C. Conversely, during the analysis period of set 3 there is an almost 10 °C increase in the average outdoor temperature. Set 3 recorded almost double the peak area at certain locations when compared to its preceding sets.

Through examining the literature, few research papers have explored the effect of temperature on SPME performance; those that have tend to focus on a methodology that sees the fibres immersed into the sample rather that examining the headspaces such as we have (Jiang, Lin, *et al.*, 2015; Jiang, Xu, *et al.*, 2015; Lin *et al.*, 2016). When dealing with the temperature effects with relation to headspace analysis (Brunton *et al.*, 2001), the researchers have used a CAR/PDMS fibre which would behave in a different way to our fibre choice due to the difference in compound types. However, a generalized outcome is clear from the literature – an increase in temperature would lead to an increase in emission of VOCs from the object and as such result in an uptake of lower molecular weight compounds. This is observed in our research with the larger relative amounts of both acetic acid and phenol (compounds with lower molecular weights) seen at higher temperatures.

In addition to the above, there are the physical principles that govern SPME which were outlined in Chapter 1. This noted that the partition coefficient is temperature dependant and that raising the temperature will decrease this constant. The consequence of this is a lowering of the amount of sample extracted at equilibrium.

When viewed as a complete picture, the extent of the impact of temperature on the resulting VOC prolife when using SPME goes to highlight the difficultly in experiments of this type – repeated, long-term, environmentally uncontrolled monitoring. It also highlights the difficulty of explicitly stating concentrations of VOCs surrounding historic polymer objects (or any object within a museum environment).

4.7 Deeper insights – matrix effects

The SPME fibre, as discussed in Chapter 1, allows for compounds to be adsorbed into it. However, this in turns leads to competition for places on the fibre. Despite what was considered to be a *short* exposure time of 1-Day, this phenomenon would be present at both our durations. As discussed by Shirey in Pawliszyn, (2009) p.112, *"Because of limited capacity, analytes tend to compete more for the available sites [on the fibre]"*. If this occurs, then the *"response for the displaced analyte will decrease and the analyte doing the displacement will increase"*. However, as this research was exploratory in nature, it would be very difficult to measure the degree of this phenomenon as we did not know the exact make-up of the environmental matrix to develop a standard. This again reinforces the perils of defining values of concentrations surrounding historic polymer objects when monitored in this way.

4.8 Deeper insights – background

The compounds found in the background environment of the storage area, which are based on both the data specifically from location 5 and from compounds found at other locations, will have no doubt interfered with the overall interpretation of the data set at large. For example, limonene was periodically found at location 5 and in VOC profiles from the object. This compound has been found previously in heritage environments and is likely due to cleaning products (Gibson *et al.*, 2012). As was just discussed, when a compound is adsorbed onto a fibre it will dislodge those with less affinity thereby lowering their perceived amount. Therefore, in this case, limonene may not only dislodge some pertinent VOCs but also cause confusion in interpreting the information from the historic polymer object.

Section 4-3 showed a clear distinction in the VOC profile between the analysis in the room or slightly away from the object and those profiles from the different location surrounding the object was highlighted. One aspect which was not discussed was the level of confidence which one could attribute to the respective VOC profiles to the specific object of examination. One could be excused for assuming that by placing a SPME fibre inside its storage crate one would be monitoring its VOC profile. However, statistical analysis of our data shows this not to be true, and that the exact location of the fibre, with relation to the object of study, is crucial to its effective monitoring.

ANOVA analysis, using the statistical package Minitab 17, of the peak areas of our four key VOCs from locations 1 (Room background), 2 (high degradation area), and 5 (as far from object while still within its storage crate) resulted in a p-value of less than 0.05, placing it above the 95 % confidence value and indicating that at least one member of the group is statistically different from the remaining three. A post-hoc Tukey analysis revealed that locations 1 and 5 were similar with location 2 being statistically different. Through examination of each individual compound we found that acetic acid was the only VOC which was not statistically different between locations. Figure 4-8 shows the resulting boxplots from Minitab highlighting the differences in means, or in the case of acetic acid, the lack thereof, between the different groups.

These results have profound implications for future analysis using methodologies such as this. The data tells us that we are able to place the same level of confidence that a VOC profile is related to the object of study by placing a fibre approx. three meters away as we do when the fibre is placed .25 meters away.

Two acknowledgements must be made regarding these findings – the first is that reliable information about the general type (I.D markers, degradation compounds, and additives) of VOCs *surrounding* a historic polymer object are easily obtainable using this methodology, this is clearly seen in the results shown in Figure 4-3. Furthermore, they are obtainable via non-invasive and non-destructive means. Crucially though, the level of confidence one has that any VOC profile is specifically from a particular historic polymer object is directly related to how close the SPME fibre is to that object. As such, the most pressing question, at the beginning of any monitoring program, must be what level of confidence the researcher wishes to attribute any VOC profile to any one object.

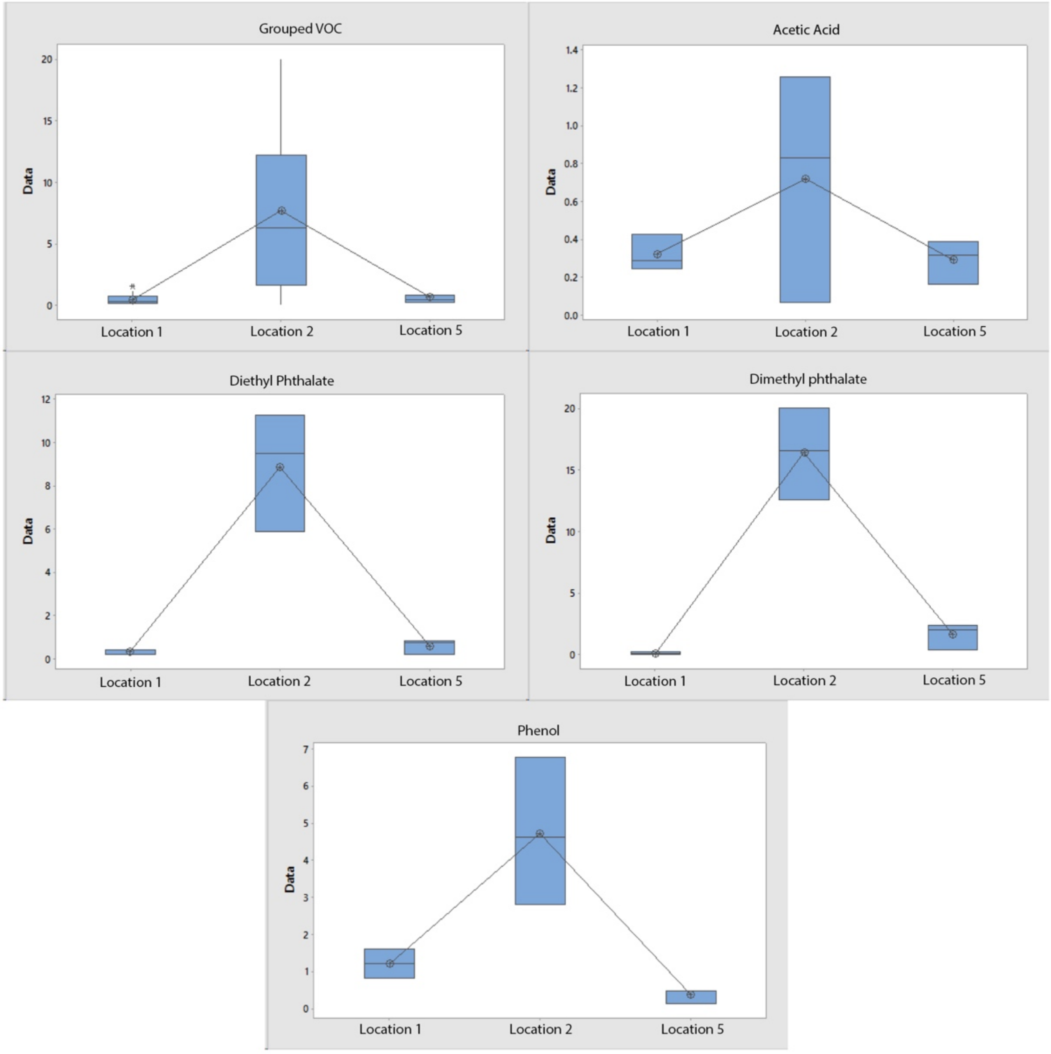


Figure 4-8 - Boxplots results taken directly from Minitab® of grouped and individual VOCs. They show the clear difference between locations 1, 2, and 5. In all cases, except for acetic acid there was a statistical difference between the VOC profiles at locations 1 (background) & 5 (away from the object) when compared to location 2 (high degradation area).

4.9 Conclusions

The work presented here perfectly highlights the multifaceted nature of SPME analysis. It was clear that relatively basic analysis of a historic polymer object was easy to achieve and yielded results of significant importance relating to degradation mechanisms and base polymer type. Yet despite this, when one aimed for a deeper understanding of the different underlying processes the method became quite complex. In certain situations, such as the distance from which to measure VOC profiles or when affected by temperature fluctuations, the method is highly limited and essentially fails to deliver the desired insight. In summation, this initial work has shown that –

- The most significant consideration to be made when determining VOC profiles is the location at which the fibres are placed relative to the object of study. One needs to judge if results should be specific to a selected object or simply report on the VOC profile in its surrounding background environment

- Research showed that an exposure time period of 7-Days led to a better representation of the equilibrium VOC profile around the object. However, it was also significantly more vulnerable to external factors which could potentially greatly limit the confidence of the results

- The best repeatability was seen via the exposure time period of 1-Day. This too suffered from some limitations, specifically in terms of relating profiles to concentrations.

- The long time periods of fibre exposure would not only lead to issues surrounding fibre placement competition, but also introduce the risk of contamination from background sources unrelated to the historic polymer object, such as the limonene which was found.

- Temperature contributed significantly to variation during the experiment due to its combination of chemical and physical factors. It is clear that increasing temperature increased the relative concentrations of VOCs exposed to the fibres, however this is balanced by the lower uptake by the fibre at higher temperatures, making for a complex relationship

This scoping research has answered the initial set of four research questions while the same time only part answering some of the additional five. Of those five additional questions the research has unearthed a number of previously unknown unknowns, specifically in relation to the exact role of temperature.

In the following chapters I will outline how we tackled the issues arising from this initial research. In Chapter 5 I outline how the high % RSD from open analysis forces us to return to laboratory-based techniques in our endeavours to understand the role of temperature and its effect on the efficiency of open SPME analysis.

Chapter 5 Methods of Preconcentrating VOCs before Analysis

5.1 Introduction

In moving forward with the project, the experience of the previous experiment indicated that in order to facilitate museum-based analysis one must understand how external factors, specifically temperature and background VOCs, impact SPME analysis. To do this required returning to a laboratory setting to allow for more repeatable analysis, as indicated by the lower % RSD found in previous laboratory-based SPME-GC/MS analysis.

Returning to the laboratory required a re-evaluation of the pre-concentration methods available – this chapter will outline these options and define the rationale for the eventual choice. This was a small piece of research, undertaken at an early stage of the project but crucial for determining future analysis methods.

5.2 What makes a good VOC pre-concentration method?

In essence, any method to capture VOCs and facilitate their exposure to a SPME fibre must, at the very least, meet one basic requirement – its VOC profile should not interfere erroneously with the VOC profile emitted from the sample. As such, methods for pre-concentration can vary greatly. As each of the options outlined below will have pros and cons, there are several other requirements which must also be met. They must be cost-effective as there will be a large volume of samples being analysed. They must be easy to use and require little preparation before beginning the analysis. They must facilitate a good working size of a sample – this means they must be able to hold a 3- dimensional object rather than simply a few milligrams of a powdered or shaved sample.

Finally, they must offer the repeatability needed to draw conclusions regarding the variables of interest.

For simplicity, the research into these methods focused on three main types which have been used successfully in the past. The three types are as follows –

- 5 l Tedlar® bags - Have been previously used for the analysis of VOC emissions from historic polymer objects
- Bespoke chamber – A specially made chamber to house sample before exposure to a SPME fibre. While specific to this project and therefore having never been utilized for SPME analysis before, the concept of designing a suitable chamber was deemed worthy of exploration
- 20 ml headspace vials – Commonly used for SPME analysis in a range of contexts

5.3 Assessment of Tedlar® bags

SPME has a long association with the use of Tedlar® bags with several review papers detailing the prolific research into areas such as breath analysis for detecting cancer (Saalberg *et al.*, 2016), asthma (Cavaleiro Rufo *et al.*, 2015), or general health biomarkers (Alonso *et al.*, 2013; Rattray *et al.*, 2014). Alongside this bio-analysis, Tedlar® bags have been used to study environmental surroundings (Kim *et al.*, 2009; Zhu *et al.*, 2013; Xu *et al.*, 2016).

The prevalence of its use in combination with SPME analysis has seen it feature in a number of different research projects focused on museum issues (Ryhl-Svendsen *et al.*, 2002; Ormsby *et al.*, 2006; Curran *et al.*, 2016; Bembibre *et al.*, 2017). It was this prevalence which led us to examine the material for our specific requirements.

The bag's construction material is Tedlar®, a type of polyvinyl fluoride film whose properties have been developed to be inert and impermeable (Dupont, 2020). One of the main positives of these bags is their availability in different sizes allowing some tailoring to the size of the sample object. The analysis presented here is based on the five-litre version as this was deemed to be the most convenient working size for smaller objects.

The bags were purchased from SKC, Inc.; a pack of ten bags costs £142 ex VAT (Sept 2019 quote). This is a significant drawback of this method of pre-concentration. These bags are not reusable as they adsorb VOCs onto their inner surfaces, leading to contamination of future analyses and at approx. £14 per bag, the cost of any medium to large research study becomes prohibitive. It was thought that future research during this project would require approximately 150 samples which would have required a £2100 capital outlay in Tedlar® bags alone. As this methodology is focused on use in Museums, whose budgets are limited as is, the cost of any research design needs to be considered.

Analysis of the bags was undertaken during the dissertation stage of the MRes SEAHA program based at UCL. This was a preparatory program which informed the development of this PhD project. While these tests did occur before the analysis described in Chapter 4 of this thesis, their main focus was the analysis of historic polymer samples. The insight gained on the relevance of the bags is still valid as the methodology and peripheral issues remain the same.

The set-up of Tedlar® bags is reasonably straight forward however it does take some time. The bags arrive sealed which means they must be cut open for use. Samples were placed into the bag and the bag was re-sealed using a heat press. Following this the bag is flushed with nitrogen gas three times, using the attached septum, before its final tightening. The main issue with this prep-work is its time (approx. 10

minutes per sample) and also the lack of control one has over the object when placed inside the bag. This lack of control could become an issue when dealing with valuable historic polymer objects which are often delicate. The bag removed the dexterity one needs to properly hold museum objects. Additionally, during setup the nitrogen in the bag is removed via a vacuum, the forces generated by this vacuum have the potential to damage objects if care isn’t taken.

The issues most pressing with the use of Tedlar® bags are best explained using the resulting chromatogram from small samples of acrylonitrile butadiene styrene (ABS) Lego ® samples (Figure 5-1).

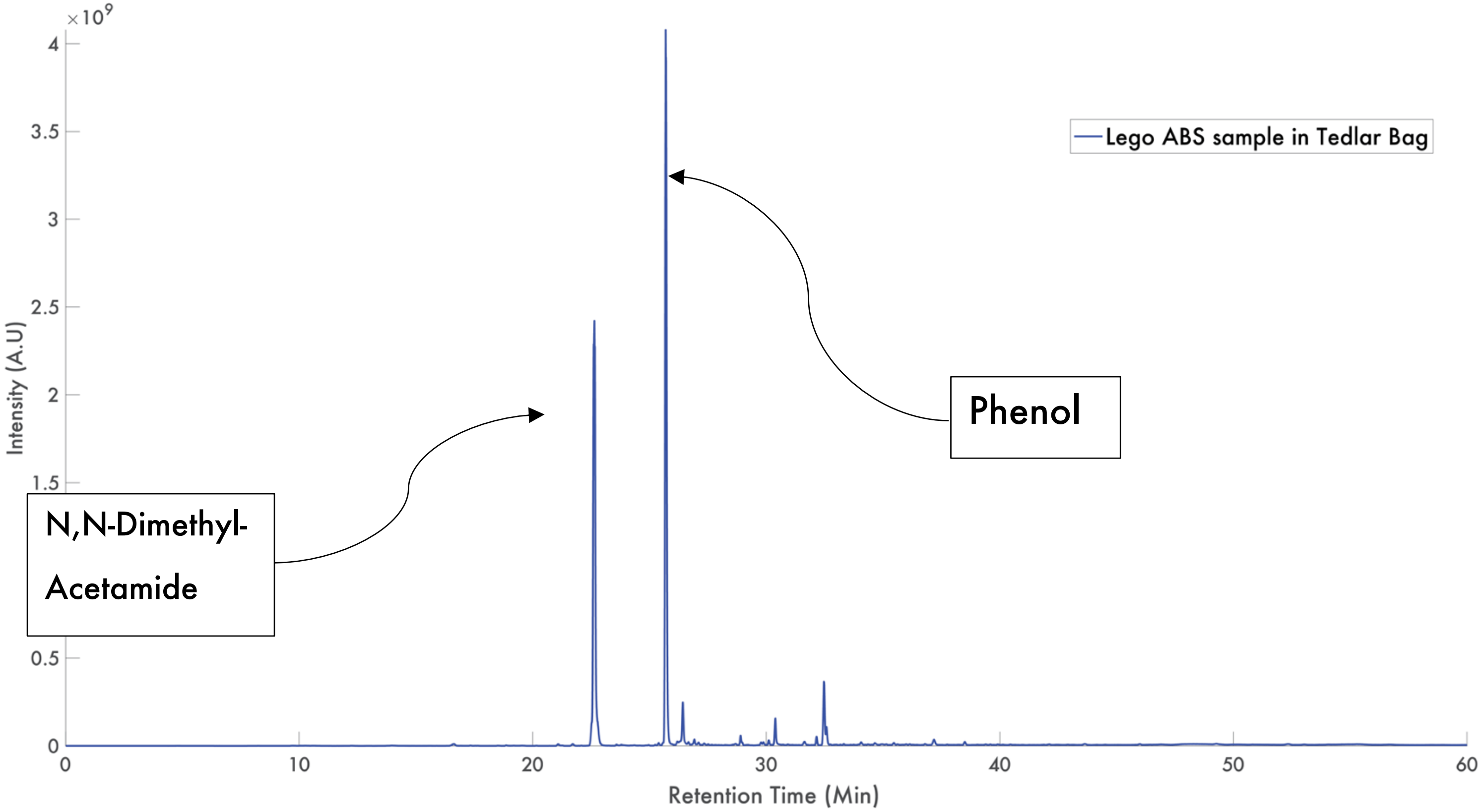
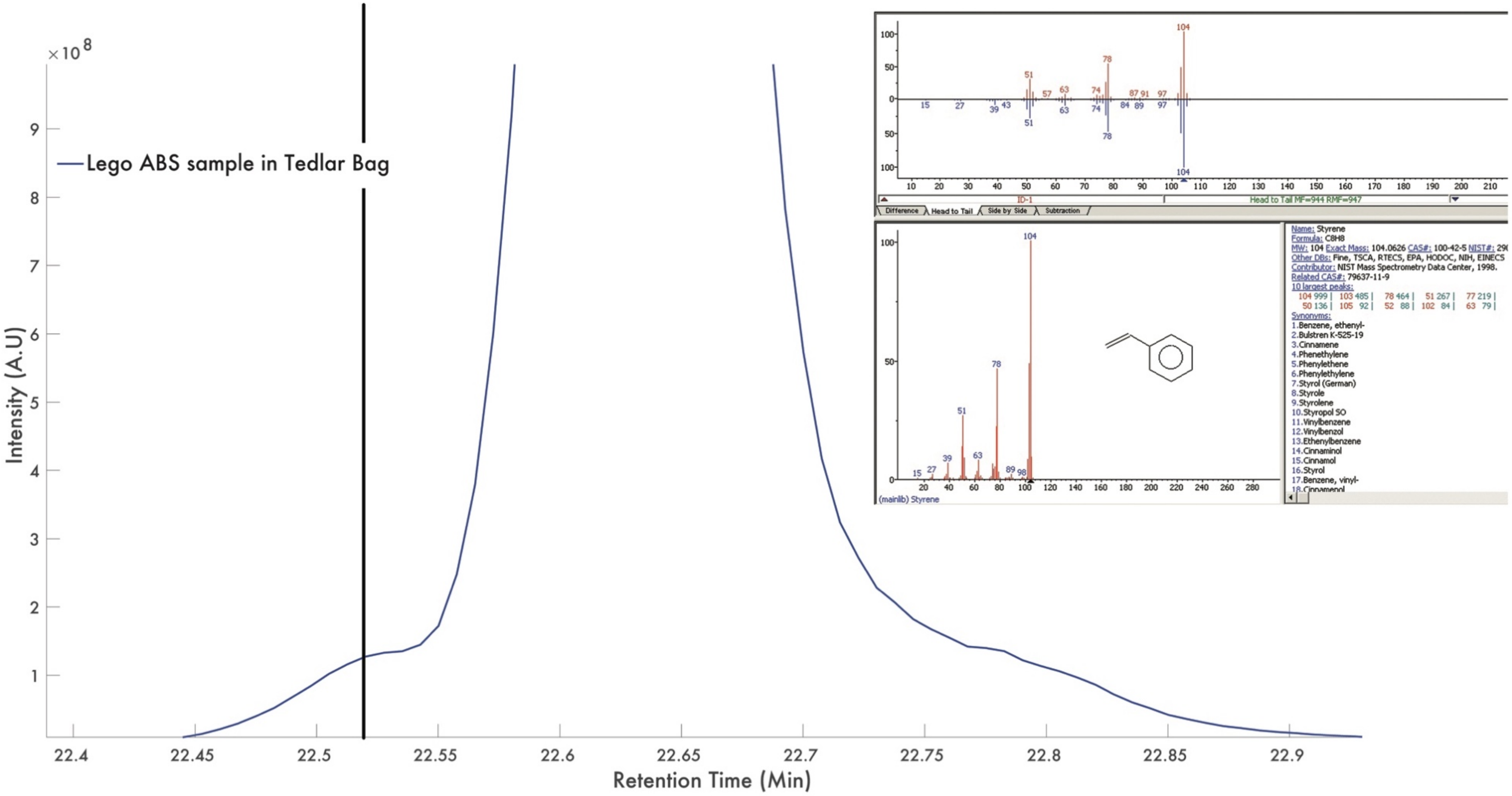


Figure 5-1 – An example of the VOC profile from an ABS polymer sample when using the Tedlar® bag system. Note that the profile is dominated by peaks at 25.6 and 22.6 minutes . These two peaks are from the bag itself and severely hinder the decoding of the polymer profile.

The two main peaks, at 25.6 and 22.6 mins respectively, are from the compound phenol and N,N-dimethyl-acetamide. These peaks have been documented to originate from the bag itself (Fortune *et al.*, 2012). These two compounds have a profound impact on the usability of Tedlar® bags for certain polymer objects. The fact the bag itself generates phenol means it would not be suitable to study CA objects as there is a possibility that the objects themselves emit this compound (see Chapters 4, 6,7 and 8). Furthermore, the location of N,N-dimethyl-acetamide is problematic for the study of ABS and polystyrene (PS) due to the fact that styrene appears at approx. 22.5 mins (Figure 5-2).



Head to Tail MF=944 RMF=947

Name: Styrene
Formula: C8H8
MW: 104 Exact Mass: 104.0626 CAS#: 100-42-5 NIST#: 29
Other DBs: Fine, TSCA, RTECS, EPA, HODOC, NIH, EINECS
Contributor: NIST Mass Spectrometry Data Center, 1998.
Related CAS#: 79637-11-9
10 largest peaks:
104 999 | 103 485 | 78 464 | 51 267 | 77 219 |
50 136 | 105 92 | 52 88 | 102 84 | 63 79 |
Synonyms:
1.Benzene, ethenyl-
2.Bulstren K-525-19
3.Cinnamene
4.Phenethylene
5.Phenylethene
6.Phenylethylene
7.Styrol (German)
8.Styrole
9.Styrolene
10.Styropol SO
11.Vinylbenzene
12.Vinylbenzol
13.Ethenylbenzene
14.Cinnaminol
15.Cinnamol
16.Styrol
17.Benzene, vinyl-
18.Cinnamenol

Figure 5-2 – Main image – Close-up view of the N,N-dimethyl-acetamide peak from the Tedlar® bag. The inset image is the NIST Library report from the point where the black line is placed. It shows the presence of styrene and shows it to have an RMatch value of 977. Due to the presence of N,N-dimethyl-acetamide it would not be possible to accurately calculate the peak area of styrene.

5.4 Assessment of bespoke chamber

The option to construct a reusable analysis chamber was mooted at the planning stage of this experiment with the idea being to design a standard SPME setup similar in concept to the Oddy Test (Heine *et al.*, 2018; Korenberg *et al.*, 2018). The main perceived benefits of a bespoke chamber would be a clear sample signal and consistency of analysis.

The conservation scientists at Tate had, for a previous study into anoxic picture frames, constructed four aluminium chambers which matched the design requirements needed for use with SPME (Figure 5-3).

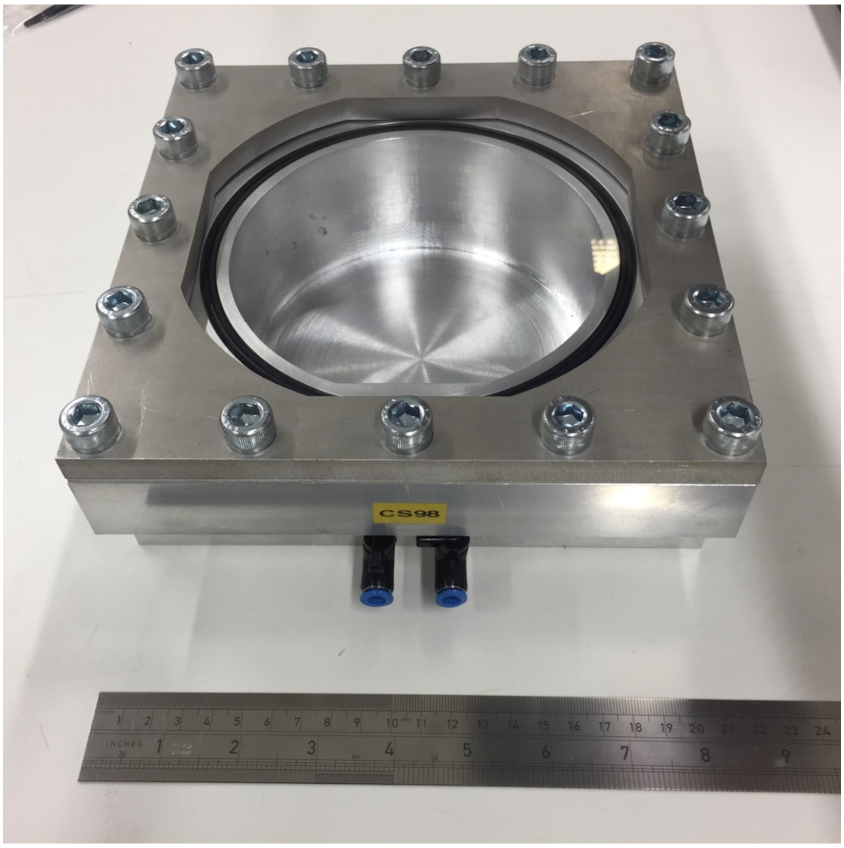


Figure 5-3 – An image of the anoxic chambers which were initially produced for Tate, by milling a block of aluminium. The image shows the large number of bolts needed to create an effective seal and the large rubber O-ring which formed this seal. While not clear on this photograph, there is a glass sheet between the main chamber body and the top cover.

These chambers had a small inner opening, where objects could be placed, which was sealed with a standard rubber O-ring and glass top which was secured to its base with 16 bolts. Gas inlet valves were tapped into the base and allowed the inner chamber to be flushed with the desired gas before being sealed. The aluminium and glass construction materials allowed for the entire unit to be placed into an oven, allowing for the examination of the role of temperature. The gas inlet valves would have allowed for tests with different gas environments or for air at a different specific humidity to be examined. A cleaning protocol was designed whereby the entire unit was cleaned first with deionised water, then rinsed with acetone and then placed into an oven at 150 °C for 24 hours.

In theory, this chamber provided us with all our desired requirements, however, in practice, the chambers performed poorly. The cleaning and setup of the chambers was both time consuming (in part due to the number of bolts) and posed a health and safety risk. As outlined above, the chambers were wet-cleaned twice followed by oven cleaning for 24 hours. Due to the mass of the chamber, which was approx. 1.7 kg, combined with the high heat, they needed to be left to cool for a further 24 hours before being useable. This introduced the possibility of contamination from VOCs in its surrounding environment (such as limonene from cleaning products which was discussed in the previous chapter). Further to this, the chambers needed to be placed in the open to cool, this introduced a risk of burning to other lab users. The chamber is made from a solid billet of aluminium, it is therefore heavy and would be difficult to manoeuvre for many people.

Even if the above issues were mitigated somehow, the chamber's performance when performing SPME analysis was exceptionally poor. Figure 5-4 shows the resulting chromatogram produced by SPME-GC/MS analysis of the empty chamber after cleaning. It highlights the extraordinarily complex background from what should be simple aluminium.

Tate Chamber after cleaning protocol with no object		**Large O-Ring used to seal chamber lid**	
Rank - RT (min)	**ID**	**Rank - RT (min)**	**ID**
40.72	Pentadecane	40.85	Pentadecane
33.37	Tridecane	36.98	Tetradecane
36.89	Tetradecane	45.42	Nonadecane
30.13	Dodecane	22.65	N,N-dimethylacetamide
26.18	NI	25.72	Phenol
45.30	Nonadecane	26.13	NI
29.67	Hexadecanol-2-methyl-1	51.35	Nonadecane
28.91	Nonanal	16.60	Hexamethyl-cyclotrisiloxane,
36.41	Isothiocyanato-Cyclohexane	33.46	Tridecane
10.59	Acetic Acid	36.50	Isothiocyanato-Cyclohexane

Table 5-1 – Top 10 NIST library results for peaks found in the TIC from the chamber (Figure 5-4) and the large rubber O-ring which is used to seal the top of the chamber. Note the colour coded compounds which are found in both datasets. This is evidence that the large O-ring is responsible for the majority of the contamination seen within the chamber. NI - not identified.

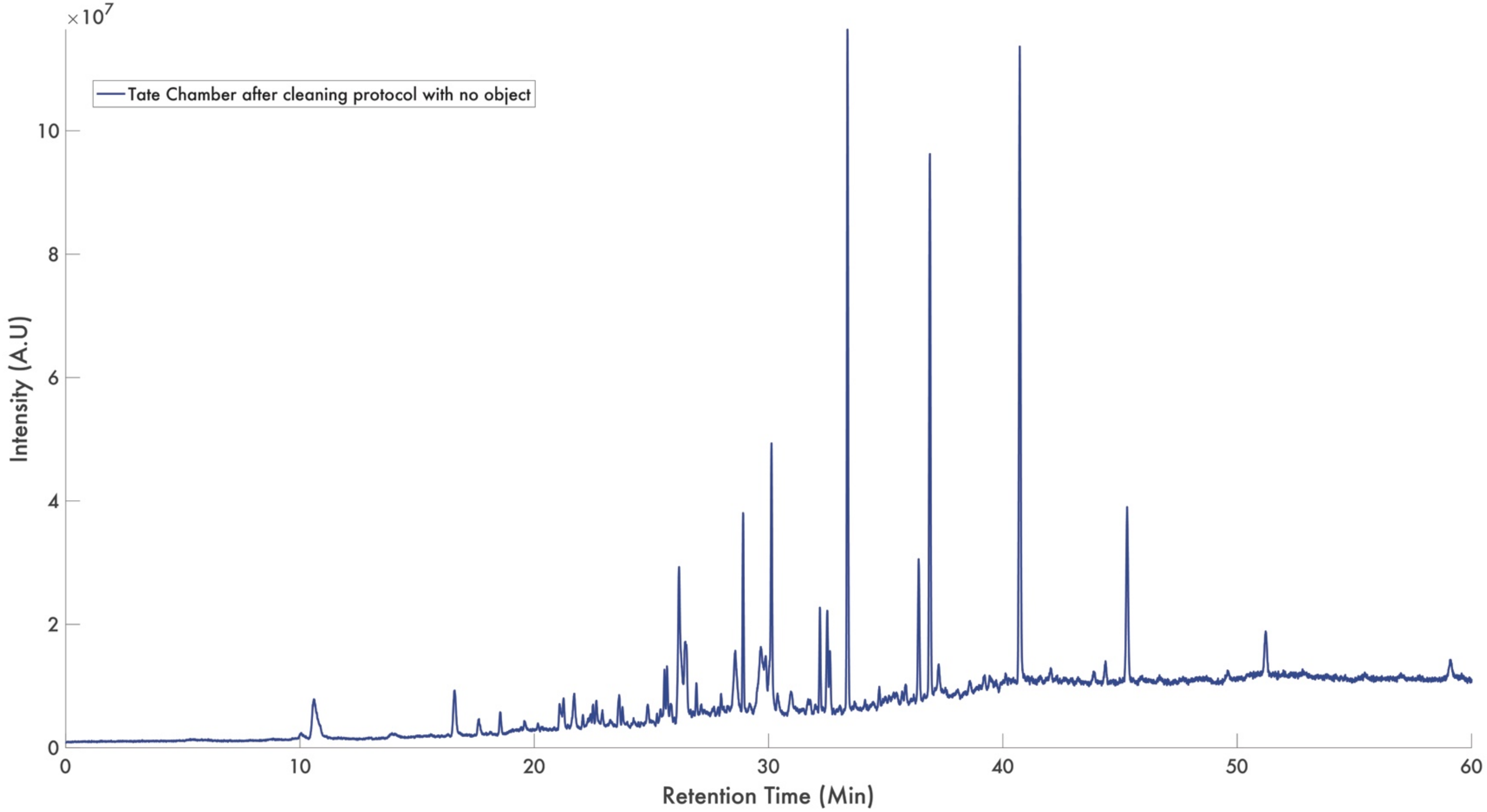


Figure 5-4 - TIC from empty Tate chamber after cleaning. Despite the clean and oven treatment, the background VOC profile is very cluttered, and it would be difficult to determine an object's VOC profile from the background.

As discussed in chapter 4, when dealing with an adsorption fibre (such as the CAR/DVB/PDMS fibre used during these tests) the presence of additional VOCs, which are not relevant to the object will skew any resulting profile from that object.

It would be difficult to judge what compounds pertain to the chamber and that of an object given the profile shown in Figure 5-4. However, in an effort to judge where this profile was originating from, SPME samples were taken from the O-ring and gas valves. Figure 5-5 shows that many of the major VOCs originate from the O-ring.

On the basis of these results, the use of the chamber in future analysis was discounted. However, towards the end of the PhD project a set of low emitting O-rings, which had been produced in partnership with Arkema and manufactured specifically for these chambers, were delivered. These new O-rings provided a significant improvement on the profile of an empty and clean chamber. However, despite this, the complexity and cost of chamber/O-ring manufacture, coupled with the associated health and safety concerns, and time-consuming setup still renders the bespoke chambers unsuitable for further use.

The pursuit of a purpose-built reusable chamber capable of holding larger samples/objects is still valid and worthwhile. During the testing of these chambers, commercially bought glass jars were also tested. However, these had a similarly complicated VOC profile. If these jars could be adapted to use the new O-rings, then they would remove many of the obstacles faced by the chambers – most noticeably the cool-down time and overall cost. While it was not possible to explore this during the PhD, future projects could greatly benefit from doing so.

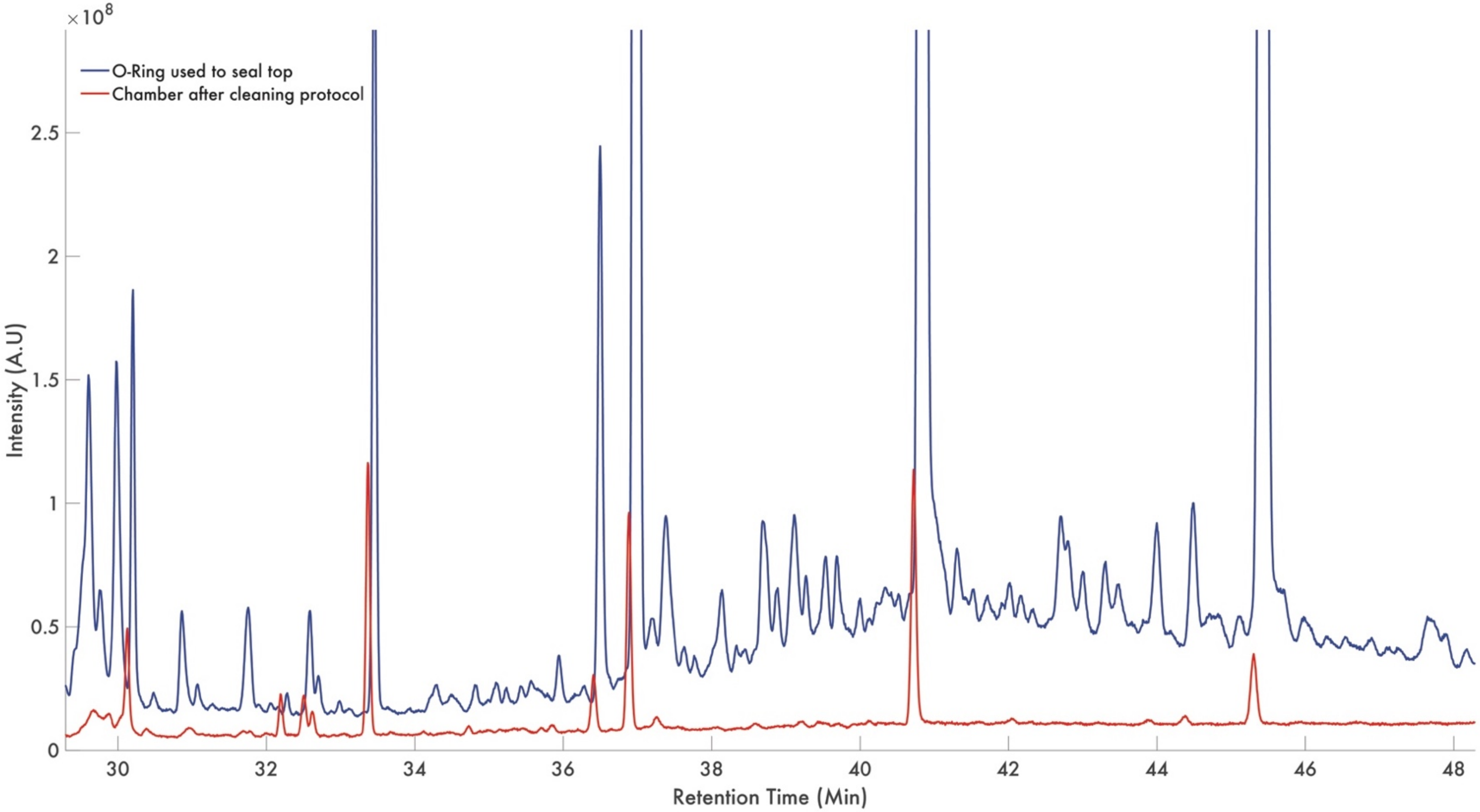


Figure 5-5 – A close-up image of the VOC profile from the Tate anoxic chamber (red) with the VOC profile from the large black O-ring highlighting that the major components of the chamber profile originate from the O-ring. The discrepancy in the intensity of both signals is due to both TIC's not being normalized, and, the measurement from the chamber where O-ring was not fully exposed to the interior of the chamber and therefore not fully exposed to the SPME fibre as was the case in the specific O-ring analysis.

5.5 Assessment of 20 ml headspace vials

The use of 20 ml headspace vials has been recommended for the development of SPME GC/MS methodologies on several occasions (Roberts *et al.*, 2000; Gröning *et al.*, 2002; Wang *et al.*, 2005; Risticevic *et al.*, 2010) as well as being used extensively within a heritage context (Lattuati-Derieux *et al.*, 2004; Strlič *et al.*, 2009; Curran *et al.*, 2016; Sawoszczuk *et al.*, 2017).

While the major limitation of the vials is their size, it was felt that a solid 3-dimensional sample, which differed significantly to the samples used in previous analysis of historic plastics (Curran *et al.*, 2016), would still fit inside the 7 mm diameter opening of the vial. By using solid cuboid-shaped samples rather than shaved or powdered samples we limit the surface to weight ratio and keep it in line with what is found in real-world artworks.

Vials, and their associated caps and septa (product code CRMA20-HSVST201-CP), were supplied by VWR at a cost of £80.77 ex VAT per 125. This makes the vial option the most cost-effective for medium to large research studies.

There is very little setup time required for the vials. They are placed into an oven at 150 °C for 24 hours, on removal they take approx. 45 minutes to cool to room temp. The silicone/PTFE liners create an effective seal and also do not cause undue VOC interference (Figure 5-6). The small footprint of the vials means they are easily stored in their dedicated trays on a lab benchtop, inside an oven or fridge allowing for a range of different temperatures to be measured. Furthermore, while not utilised during this project, they are also compatible with SPME autosamplers from a range of different manufacturers, allowing for high-throughput analysis.

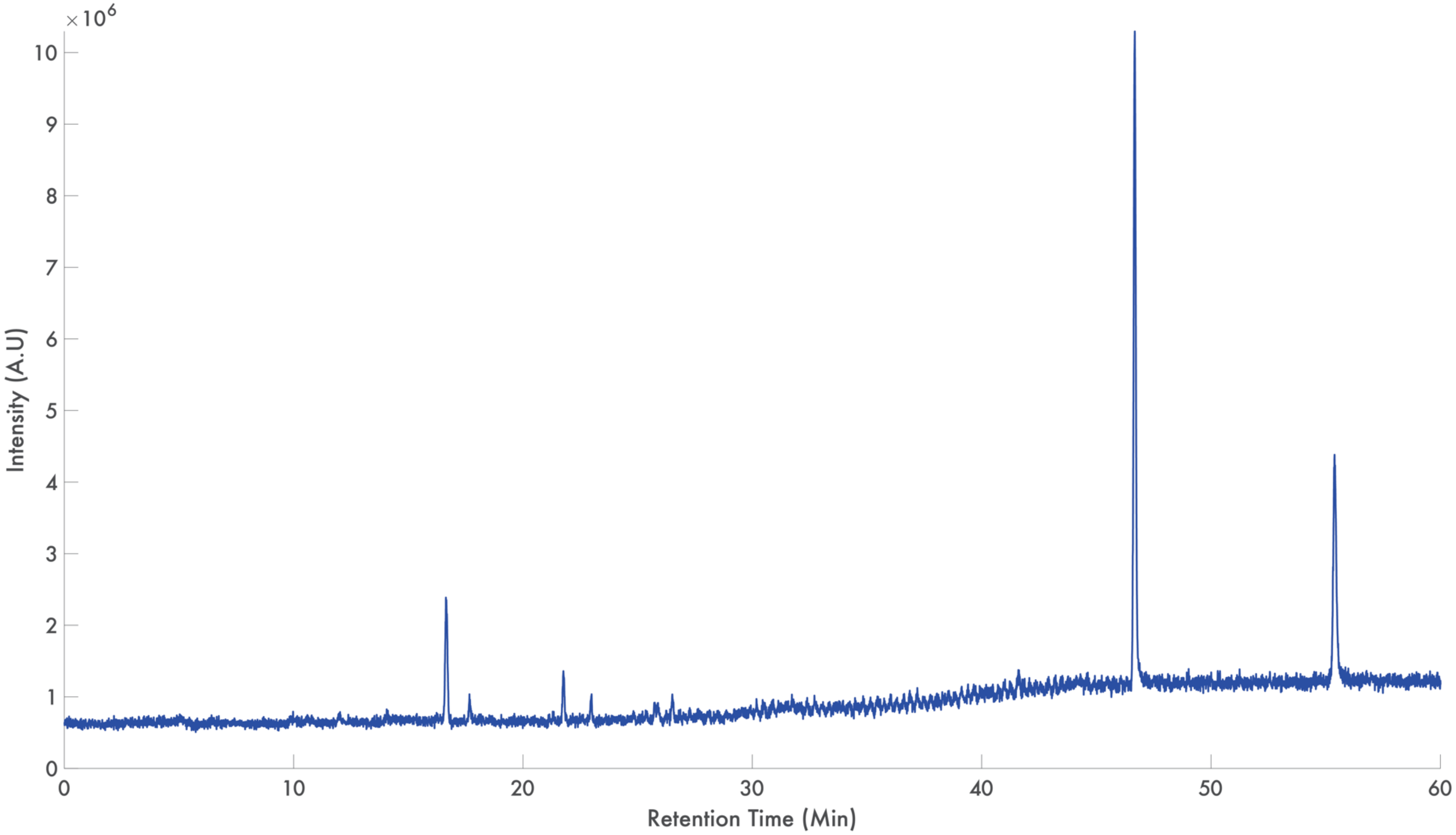


Figure 5-6 - TIC from a blank vial showing carry over from previous analysis along with column artefacts. This figure highlights that the environment inside the vial is inert and does not cause contamination to the sample TIC.

To quantify the repeatability achievable while using the vials we analysed our MISA Group 17 standard five times in a row. The standard was allowed to equilibrate in the vial for approx. 45 minutes before the initial test. Between each analysis run, the cap and septa were replaced, and the sample allowed to equilibrate once again for 45 min before further testing. The consistency of the depth to which the fibre entered the vial was controlled. As with the regular standard protocol, the fibre was exposed to the standard for 20 s.

Standard Number	Compound Peak Area (arbitrary units)		
	Benzene	Ethylbenzene	Toluene
Standard 1	1.75E+10	1.16E+10	1.67E+10
Standard 2	1.97E+10	1.15E+10	1.62E+10
Standard 3	1.84E+10	1.13E+10	1.59E+10
Standard 4	1.87E+10	1.09E+10	1.51E+10
Standard 5	1.37E+10	8.57E+09	1.24E+10
Average	1.76E+10	1.08E+10	1.53E+10
Standard Dev.	2.31E+09	1.26E+09	1.69E+09
Rel. Standard Dev	13.10%	11.68%	11.06%
Without Standard 5			
Average	1.86E+10	1.13E+10	1.60E+10
Standard Dev.	7.89E+08	2.67E+08	5.92E+08
Rel. Standard Dev	4.24%	2.36%	3.70%

Table 5-2 – Shows the results and statistical analysis of the standard when measured using the 20 ml headspace vials. The result in yellow highlights what the effect of user error can be on the final result.

Table 5-2 and Figure 5-7 show the resulting peak areas of a series of compounds found in the MISA Group 17. In general, the peak area of ethylbenzene would be used to normalize analysis runs. The % RSD of the set of five is within the scope of values seen in the literature. However, it is worth noting that as this method is manual, a certain amount of variability is introduced by the user. It was noted that during the exposure of the fibre during *Standard 5* that the fibre did not extend in a smooth single motion, as would be normally the case. This could explain the difference between measurement five and the remaining four. Removing the fifth analysis would render the % RSD (for ethylbenzene) to 2.36, which is remarkably low. Whichever % RSD is used, the outcome remains the same – 20 ml headspace vials offer the best repeatability of any pre-concentration method that was tested[6].

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[6] Note – Repeat measurements are not given for the other two methods examined. This is due to their overall poor performance in other areas which would rule out their use regardless of repeatability concerns.

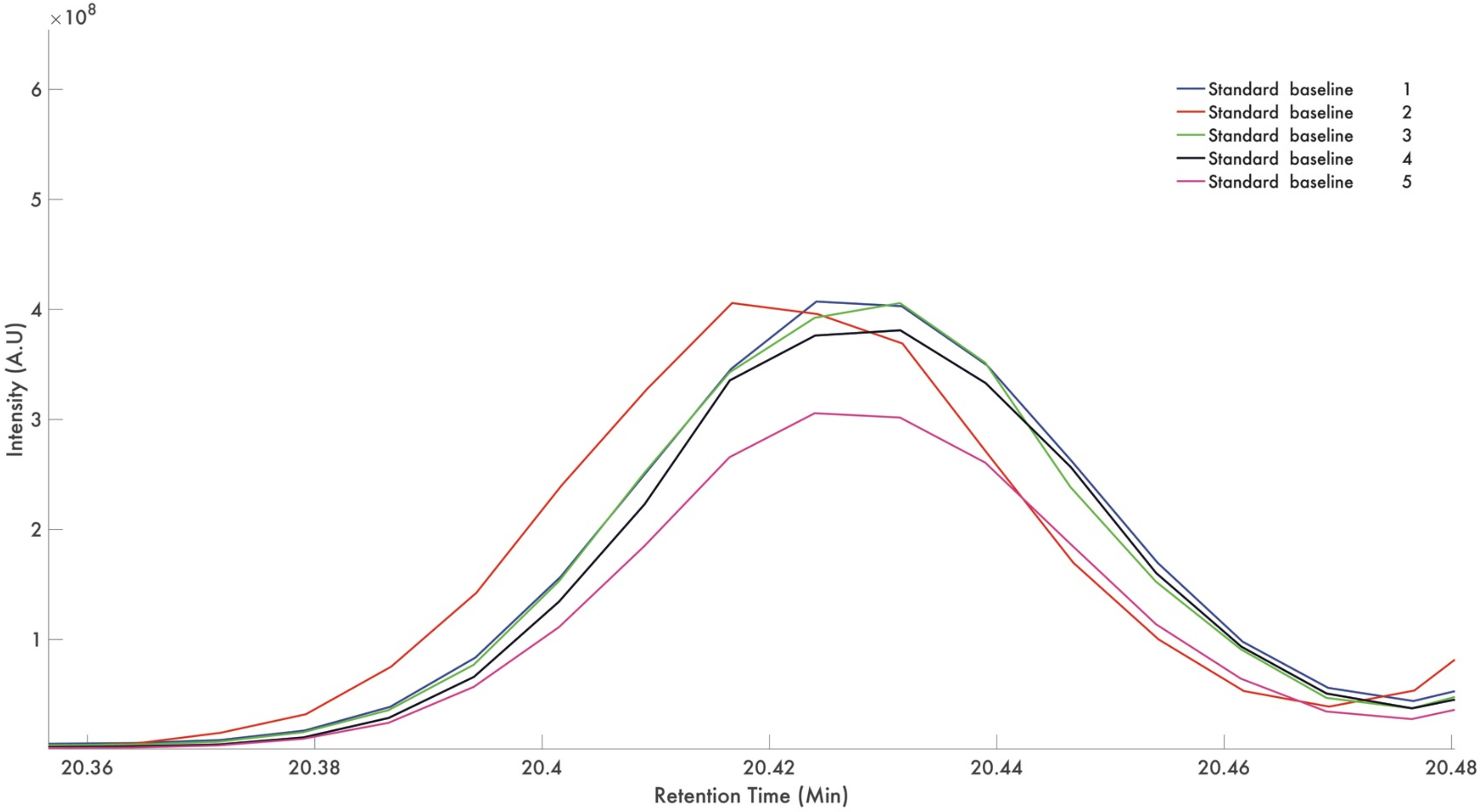

Figure 5-7– A close up of the ethyl benzene peak from the standard. Note the light pink/purple line which is lower than the other four. This was due to user error when performing the analysis of the standard. It highlights the importance of consistency when performing manual SPME GC/MS analysis.

5.6 Conclusions

It is clear from the research above and outlined in a traffic light system in Table 5-3, that the traditional setup of 20 ml headspace vials offers the best consistency from the three options. The limiting factor is still their 7 mm opening diameter. Given that samples are unlikely to be taken from historic polymer objects, unless they are sub-milligram in weight, this opening diameter is not as limiting as could be initially thought. However, it does mean that additional time and attention to detail must be allocated in order to produce samples of the correct size. Secondly, as will be shown in the next chapter, care must be taken that the samples produced are themselves compositionally consistent.

The investigation into the bespoke chambers yielded some positive results. With more development they could be a viable option. However, as this project was focused on SPME performance rather than VOC capture they were not investigated further. There is potential in their development, especially in the idea of larger glass jars, these topics will be discussed further in Chapter 9.

In the next chapter, the benefits of this preparatory research will be highlighted, had one of the other systems been used it is doubtful that conclusive determinations could have been made.

Methodology	Tedlar® Bag	Bespoke Chamber	20 ml Vial
Metric			
Cost	🟥	🟥	🟩
Max Object Size	🟨	🟨	🟥
Ease of Use	🟨	🟥	🟩
Contamination Issues	🟨	🟥	🟩

Table 5-3 – A traffic-light system for judging the different methods of VOC pre-concentration from samples. Note that the different metrics used may be a combination of a number of individual issues – e.g while the cost of an individual Tedlar® bag is low they are single use and over the course of the project this would be a large expense, hence its red stop label.

Chapter 6 The Effect of Temperature for Data Collection when Analysing Historic Polymer Samples via SPME Analysis

6.1 Introduction

The scoping experiment which was reported on in chapter 4 of this thesis was highly influential in the overall direction of the PhD project. It highlighted key areas which required further understanding for SPME to be correctly implemented within a heritage context.

Chief among these issues was the relationship between the temperature at which the historic polymer is analysed with the resulting VOC profile. The following chapter outlines the efforts made to understand the constraints placed upon researchers when examining historic polymers within collections. It is generally the case that heritage institutions will permit a small range between an upper and lower limit regarding the temperature and relative humidity of stores or galleries. This introduces an added variable to the data interpretation– temperature. A hint of the extent of the influence temperature has on the resulting chromatogram was seen in chapter 4, however the monitoring undertaken in that experiment was not sufficient to provide deep insights into its role in altering the resulting VOC profiles.

This chapter aims to explore this relationship in an effort to quantify and if possible correct for it.

6.2 Experimental outline & objectives

During the data processing phase of the initial experiment at Tate Britain, it became clear that external stressors were causing unexpectedly large variations to the VOC profile measured at the different points-of-interest. This is best exemplified by focusing on two graphics – the first are the results of the VOC diethyl phthalate (Figure 6-1) and the second is the external temperature variation throughout the experiment (Table 6-1). The variation between the peak intensities in the chromatograms found during 1-Day Set 1 and 7-Day Set 3 is almost two orders of magnitude. While the duration of exposure clearly had an effect on the resulting chromatograms, the analysis was accompanied by an external temperature change of almost 17° C. However, a critical factor is that the exact values of temperature where the SPME fibres were placed are unknown as the values presented here are external. Despite the limited buffering provided by the building fabric (because the room has an air brick), they are not what the object itself would have experienced and as such one cannot extrapolate patterns given the present dataset.

1-Day	Average Temp	Min Temp	Max Temp
Set 1	8.4	4.6	13.6
Set 2	13.4	8.4	20.1
Set 3	10.1	5.6	14.3
7-Day	**Average Temp**	**Min Temp**	**Max Temp**
Set 1	11.5	3.1	21.6
Set 2	13.0	8.3	25.0
Set 3	22.2	14.2	31.3

Table 6-1 - Values of temperature during the dates when the fibre was exposed to the museum environment. Note the difference between 1-Day Set 1 and 7-Day Set 3 which is almost 17 degrees. All temperatures are in ° C

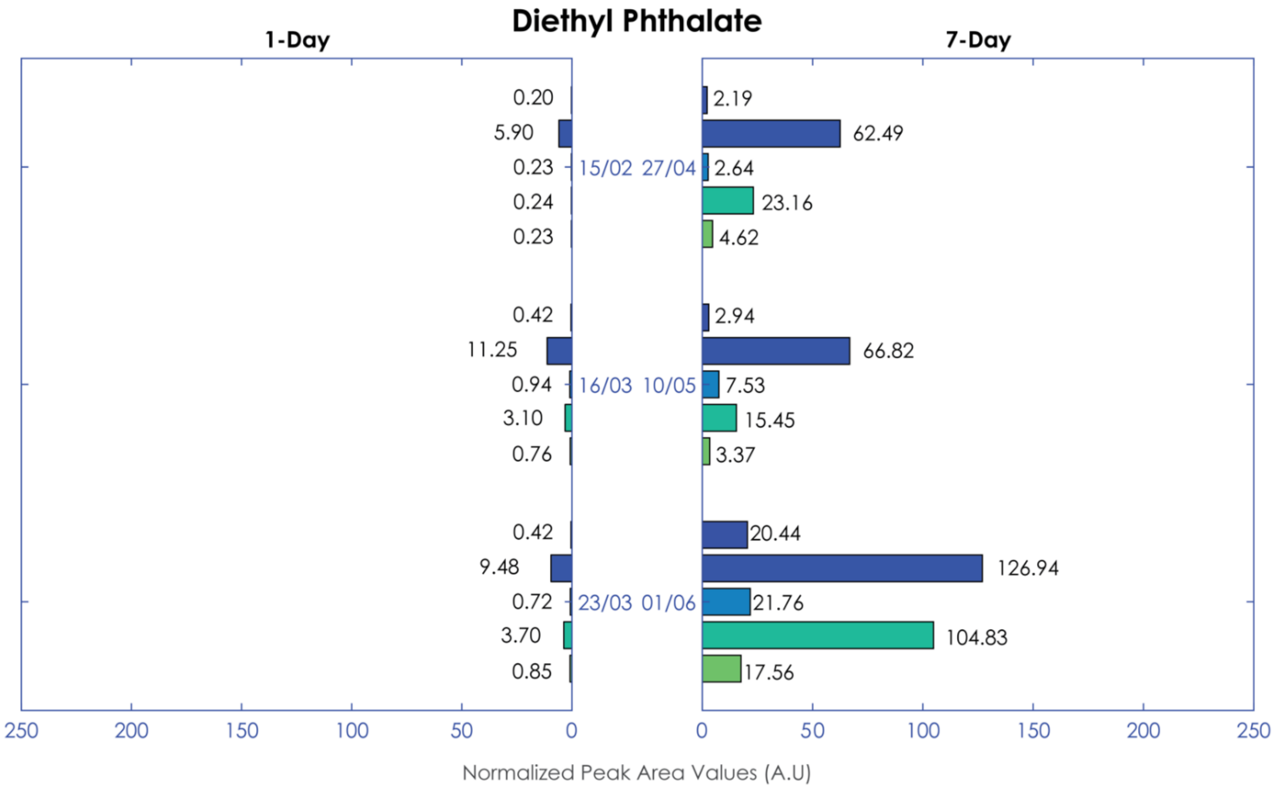

Figure 6-1 - Normalized peak area values for the VOC diethyl phthalate which were recorded during the initial SPME GC/MS investigation of the storage environment for T02143, *Two Cones* . Note the difference from the 1-Day exposure performed on 1 Feb (Top left) versus the values for the 7-Day exposure performed on 1 June. One explanation for the difference between the two sets is the almost 14°C change in temperature between the two dates.

In order to judge the effect of temperature for SPME fibre exposure correctly, an experiment was devised which would analyse the VOC emissions from four different polymer samples at three different temperatures. Further to these conditions, the samples would also undergo different degrees of accelerated ageing at a fixed temperature.

Table 6-2 outlines the combinations which were tested.

Organizing the experiment in this way allowed for a number of research questions to be answered in the most efficient manner. These were:

- How do degradation and identification marker VOCs behave upon ageing? (i.e. Do VOC emissions of plasticisers decrease upon ageing while VOCs from degradation products increase?)
- For each polymer sample type is it possible to differentiate an unaged sample from an aged sample when the data was collected at the same temperature?
- For each polymer sample type, that underwent accelerated ageing to the same degree, is it possible to distinguish the data sets by the temperature at which the SPME fibres were exposed?
- Is it possible to differentiate an unaged sample from an aged sample when the data was collected at different temperatures?

The answers to these questions are essential in order to judge how feasible long-term monitoring of historic polymer objects is, because the ability to track objects as they degrade in uncontrolled environments is an essential requirement.

Date of analysis	Sample Name	Target Temp	Average Temp	Max Temp	Min Temp	Ageing Time	Plasticiser Type	Sample Type
17/10/2018	CA-CW 0-WK H-Temp	25	25.6	26.4	24.7	0	DEP	Industrial
06/10/2018	CA-CW 0-WK M-Temp	20	17.6	18.3	16.6	0	DEP	Industrial
15/11/2018	CA-CW 0-WK L-Temp	4	7.8	11.5	6.4	0	DEP	Industrial
16/10/2018	CA-CW 4-WK H-Temp	25	23.9	24.5	22.1	4	DEP	Industrial
07/10/2018	CA-CW 4-WK M-Temp	20	18.2	22.2	16.7	4	DEP	Industrial
16/11/2018	CA-CW 4-WK L-Temp	4	6.8	7.5	6.3	4	DEP	Industrial
23/01/2019	CA-CW 12-WK H-Temp	25	22.7	24.3	16.7	12	DEP	Industrial
24/01/2019	CA-CW 12-WK M-Temp	20	17.9	22.1	16.1	12	DEP	Industrial
27/01/2019	CA-CW 12-WK L-Temp	4	n/a	n/a	n/a	12	DEP	Industrial
14/12/2018	CA-NewCW 0-WK H-Temp	25	22.7	24.5	16.6	0	DEP	Industrial
15/12/2018	CA-NewCW 0-WK M-Temp	20	17.3	20.8	16.2	0	DEP	Industrial
13/12/2018	CA-NewCW 0-WK L-Temp	4	10.9	24.0	6.2	0	DEP	Industrial
01/03/2019	CA-NewCW 8-WK H-Temp	25	20.7	24.3	6.0	8	DEP	Industrial
03/03/2019	CA-NewCW 8-WK M-Temp	20	17.6	21.9	16.5	8	DEP	Industrial
02/03/2019	CA-NewCW 8-WK L-Temp	4	8.4	19.4	5.9	8	DEP	Industrial

*Please see next page for remainder of table and caption

Date of analysis	Sample Name	Target Temp	Average Temp	Max Temp	Min Temp	Ageing Time	Plasticiser Type	Sample Type
31/07/2018	CA-DEP 0-WK H-Temp	25	24.3	24.9	23.5	0	DEP	Bespoke
04/08/2018	CA-DEP 0-WK M-Temp	20	23.7	27.0	19.0	0	DEP	Bespoke
01/08/2018	CA-DEP 4-WK H-Temp	25	24.3	25.1	23.9	4	DEP	Bespoke
05/08/2018	CA-DEP 4-WK M-Temp	20	23.2	26.3	18.9	4	DEP	Bespoke
02/08/2018	CA-TPP 0-WK H-Temp	25	24.4	27.2	23.3	0	TPP	Bespoke
06/08/2018	CA-TPP 0-WK M-Temp	20	22.6	26.0	19.2	0	TPP	Bespoke
03/08/2018	CA-TPP 4-WK H-Temp	25	26.0	29.8	22.4	4	TPP	Bespoke
07/08/2018	CA-TPP 4-WK M-Temp	20	23.8	27.4	19.5	4	TPP	Bespoke
21/01/2019	CA-TPP 10.5-WK H-Temp	25	23.6	24.3	22.5	10.5	TPP	Bespoke

Table 6-2 – Samples used during the experiment. CA-TPP samples were plasticized with triphenyl phosphate while CA-DEP samples were plasticized with diethyl phthalate. For each date of exposure five samples from the corresponding sample set were analysed via SPME GC/MS. Samples are grouped by extent of ageing. The ageing conditions were 70 °C and 50 % RH. 'Target Temp' refers to the desired temperature for SPME fibre exposure while the 'Average', 'Min', and 'Max' temp values represent the actual value 'felt' by the sample during the period of exposure . All temperatures are in °C.

6.2.1 Temperature settings

The temperature at which the objects were examined was controlled in a laboratory setting either via overall room air conditioning or for cooler levels by storing the polymer samples within a fridge. While exposure within a laboratory environment is not the same as within an open uncontrolled[7] heritage one, in order to judge the effects of temperature all conditions were controlled to reduce the overall variability in the experiment, as such reverting to laboratory-based analysis was deemed to be the correct direction for the project. Three different temperature settings were chosen based on feedback from Tate preventive conservation staff regarding typical environmental conditions for collections storage. These levels would be circa 25 °C (High) and 20 °C (Middle) which represent the range of typical museum environments and the third level of 4 °C (Low) which is typical of 'cool' storage which is often used for polymer objects (PAS 198, 2012). However, in reality, these exact levels were difficult to achieve via air conditioning and while the fridge was set to 4 °C its temperature was slightly higher than this. The exact temperature values experienced by each sample can be seen in Table 6-2.

Environmental conditions were monitored during the exposure periods via a series of custom-made sensors. The room and GC/MS area were monitored separately. Additionally, a sensor was placed into a vial and sealed. This facilitated measurements which the sample itself would have 'felt'. Temperatures reported in Table 6-2 are from the sensor placed into the vial. Further details regarding the sensors can be found in Chapter 3-9.

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[7] In this context 'uncontrolled' relates to the macro environment which the object finds itself within – Most museum environments are controlled to some degree, however, there are still microclimates within these environments and some museums have no environmental control whatsoever. Within a laboratory environment one can account for these microclimates with tighter tolerances.

6.2.2 Sample types

Two main types of samples were utilized during this study –

- Bespoke cellulose acetate samples - Two types of CA were specifically produced for this research. The first was plasticized with 20 % w/w diethyl phthalate (DEP) (a common plasticiser type in historic CA), the second with 16 % w/w triphenyl phosphate (TPP). An outline of their manufacturing process was detailed previously in Chapter 3.

- Industrial samples – Two samples of CA which were industrially manufactured were used. These were likely manufactured in the 1960s and were initially thought to be plasticized with DEP. As was discussed in a previous chapter, these industrial samples were likely manufactured in the late 1960s by Mazzucchelli 1849. CA-CW was an imitation 'tortoiseshell' type of CA, while CA-NewCW was simply a blue coloured CA material.

Industrial samples were cut (via a small band saw) from a larger sheet – each sample was approx. 30 mm X 5 mm. A table of the average weights (for the set of 15 samples) for each material type can be seen in Table 6-3; A full list of samples and their weights can be seen in Appendix 1.

For each sample set at each temperature , five fibres were analysed. The results for the normalized peak areas of the VOCs of interest were averaged from these five measurements.

Sample	**CA-CW**	**CA-NewCW**	**CA-TPP**	**CA-DEP**
Average	1993.28	1325.02	544.02	619.74
Standard Dev.	123.03	57.63	55.06	57.05

Table 6-3 – Average sample weights before any accelerated ageing had taken place for the four sample types tested during the experiment. Note that the two industrial samples (CA-CW & CA-NewCW) were thicker and therefore weighed more. All values are in mg.

6.2.3 Accelerated ageing

Both the bespoke and industrial samples underwent accelerated ageing during this study. The accelerated ageing conditions used during this project were a temperature of 70 °C and relative humidity of 50%. Samples were placed into a small Pyrex® glass bowl which sat on top of a shelf in a desiccator with a saturated sodium bromide salt solution underneath the shelf. This was placed in an oven as outlined in section 3.6, the first aging campaign lasted 4 weeks while the second lasted 8 weeks.

Furthermore, due to the significant deterioration of the bespoke TPP samples that developed during the second ageing campaign, these were removed after 6.5 weeks (giving a total ageing time of 10.5 weeks). A full account of the ageing campaigns each sample set underwent can be seen in Table 6-2.

6.2.4 Analysis methods – SPME

Analysis via SPME GC/MS followed the method outlined in section 3.2. Each of the five samples for the respective set was placed into a 20 ml headspace vial 24 hours before analysis. If the exposure was to be undertaken at the high or middle-temperature level, then the vials were placed on the tray holder atop the GC/MS machine. If the exposure was to be conducted at the low-temperature level, then the vials were seated in a plastic sample tray and placed into the middle level of a fridge (Figure 6-2.)

Figure 6-2 – Exposure setup inside the fridge during the experiment. This shows the vial which contained a temperature and relative humidity sensor along with a vial which has a SPME fibre placed inside it.

In order to be as consistent as possible two wooden depth markers were constructed. The larger of the two (Figure 6-3) was used to consistently place the SPME needle at the same depth inside the headspace vial. The smaller (Figure 6-4) was used to deploy the SPME fibre by the same distance during both exposure to the vial headspace and when desorbing into the GC/MS.

Figure 6-3 –Exposure setup for both 25 °C and 20 °C. To the left of the vial with a SPME fibre is a T/RH sensor which is monitoring the GC/MS area. Next to this is a vial which contains a sample. Also shown here is the larger of the two wooden depth markers. To the right of this is the vial containing another T/RH sensor.

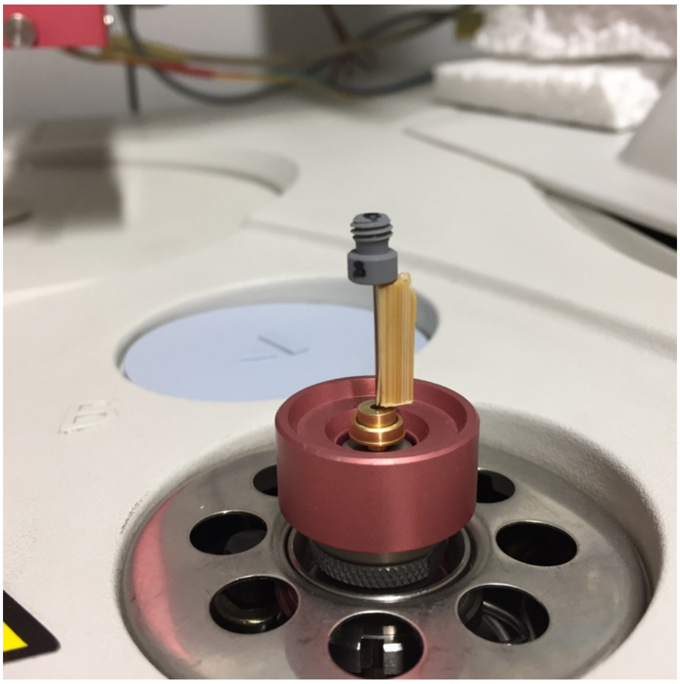

Figure 6-4 – This image shows the smaller of the two wooden depth markers. This facilitated the consistent placement of SPME fibre into both the GC/MS port and analysis vial (not shown).

6.2.5 Analysis methods – Complementary techniques

To complement the data obtained via SPME GC/MS samples were also characterised with ATR-FTIR spectroscopy and colour measurement. Data was obtained from a single sample from each sample set at each stage of artificial ageing – for example, sample 2A from the CA-CW sample set was analysed using ATR-FTIR before artificial ageing and after each of the two ageing stages. The weights of all samples were recorded at each stage of ageing – these can be seen in Table 6-4.

CA-CW	Unaged	4 Weeks	12 Weeks	Change		CA-TPP	Unaged	4 Weeks	10.5 Weeks	Change
Average	1993.28	1957.48	1879.46	113.82		**Average**	544.02	529.44	424.17	120.33
St. Dev	123.03	113.04	114.24	28.88		**St. Dev**	55.06	52.26	20.63	44.68
CA-NewCW	**Unaged**	**8 Weeks**	**Change**			**CA-DEP**	**Unaged**	**4 Weeks**	**Change**	
Average	1325.02	1264.00	61.02			**Average**	619.74	595.79	23.95	
St. Dev	57.63	55.02	5.57			**St. Dev**	57.05	54.69	2.82	

Table 6-4 –Data expended from Table 6-3 to show the resulting average weight after accelerated ageing. Note the different periods ageing between the different sample types. All values are in mg.

6.3 Results

6.3.1 Initial observations – temperature settings

As was discussed in section 6.2.1 there were three temperature settings which the samples would be subjected to. Two of these settings were to be achieved via the air conditioning unit for the laboratory. However, as can be seen in Table 6-2 the exact levels which were desired (25 °C and 20 °C) were not achieved. This was because the air conditioning unit was not able to regulate the large volume of the laboratory in its initial setting due to the added interference from additional heat sources such as the GCMS itself. Unexpected changes to the operation of the air-conditioning during the night were also only discovered midway through the experiment. Better results were achieved when these two issues were mitigated.

When values are presented in this chapter, they will reflect the average value "seen" by the sample over the pre-exposure and analysis duration. The different levels will be discussed as High, Middle, or Low and refer to the target temperature of 25 °C, 20 °C, and 4 °C respectively.

6.3.2 Initial observations –artificial ageing conditions

Figure 6-5 & Figure 6-6 show part of the overall ageing period for both cycles and highlight the conditions inside the ageing vessel. As can be seen from these figures, the ageing conditions the samples experienced were highly consistent.

Unfortunately, approximately mid-way through the second ageing cycle the oven was turned off by one of the other laboratory users. The oven remained off for approx. 48-hours before its discovery. Conditions inside the ageing vessels reverted to the desired level shortly after the oven reached its correct temperature. Samples were checked for damage caused by the rapid change in temperature, but no damage was visible at the time. Therefore, for convenience, during the remainder of this chapter the samples will be referred to by their overall aging length, in reality the total duration samples spent under accelerated ageing conditions is two days less than stated.

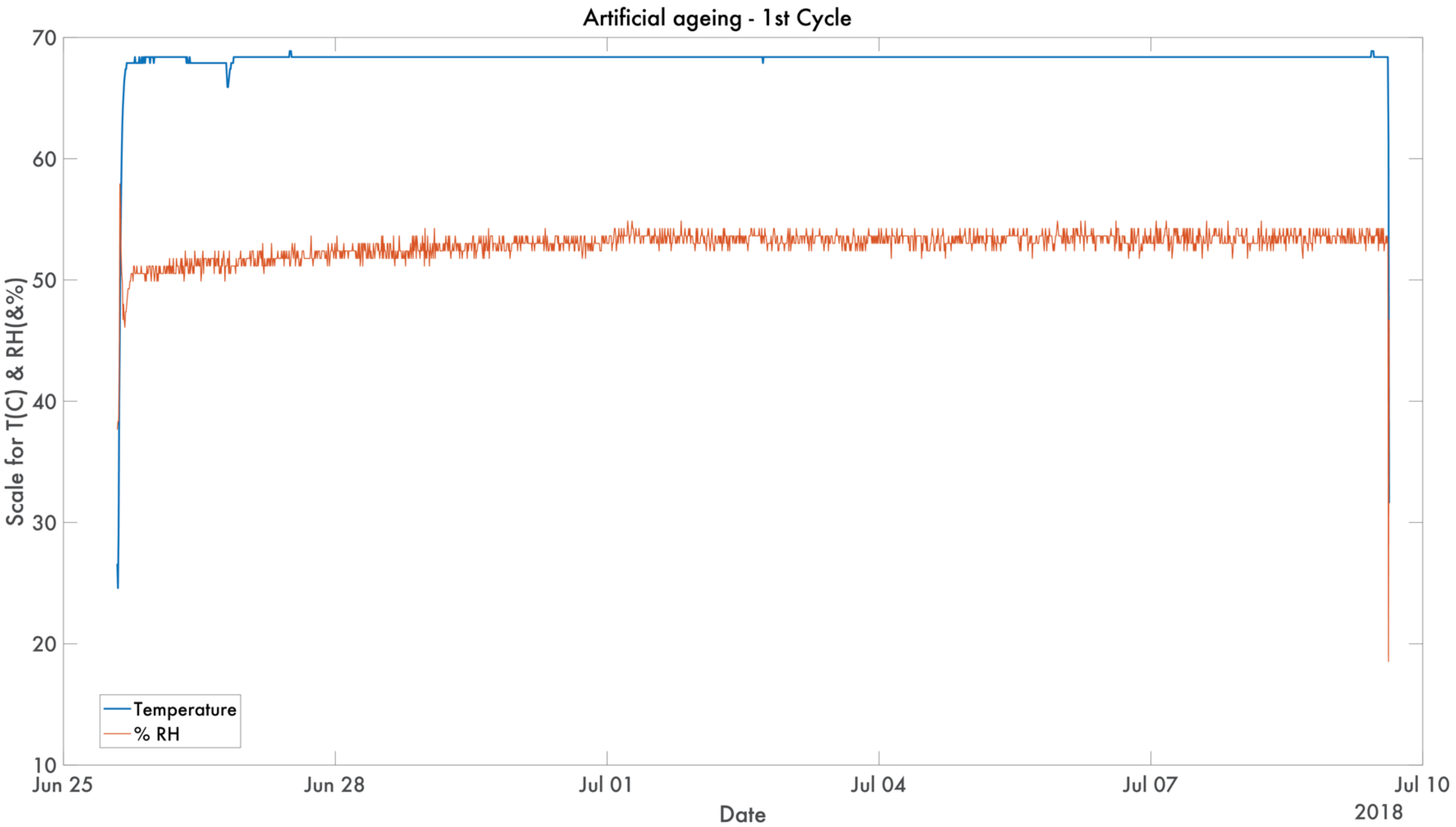

Figure 6-5 – A sample of the data from inside the ageing vessel during the 1ST cycle of ageing. It shows that the target for both temperature and RH were achieved. It also shows that during the ageing process the conditions were consistent.

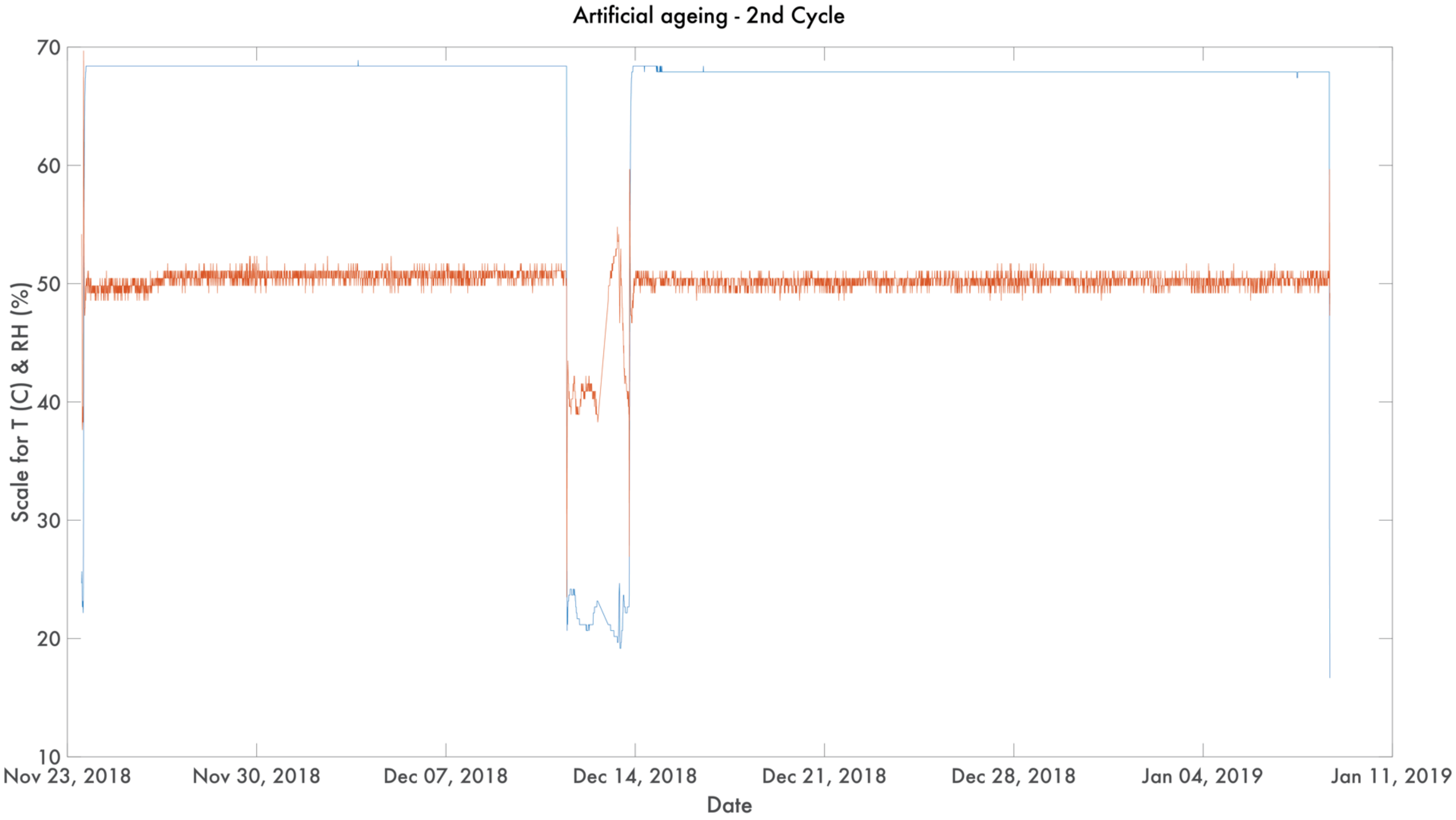

Figure 6-6 – A sample of the data from the second ageing cycle showing that it too performed as necessary. The graph also highlights the error where the oven was switched off for approx. 48-hours. No damage to the samples was observed during the rapid changes in conditions.

6.3.3 Initial observations –overview of VOC profiles

The results of the experiment will be reported in the following sub-chapters; however, it is important to describe initial parameters for both the framework of analysis and for the initial state of the polymer samples.

This experiment consisted of three different temperature levels and in many cases three different degrees of ageing. Therefore, it is prudent to choose one initial setting from which all others will be compared. For the following discussion the 'base' for each sample type will be taken as the unaged sample with the SPME fibres exposed at the target temperature of 25 °C (note that actual analysis temperatures can be found in Table 6-2). This base level was chosen as no alterations to the sample were made in order to record its VOC profile – the laboratory is not actively cooled, nor is the sample itself altered via artificial ageing. Any deviations to this initial VOC profile are due to either a change in exposure temperature or through the effects of artificial ageing or a combination of both.

The unaged sample-set CA-CW produced a typical VOC profile for samples comprising of cellulose acetate. The profile contains both plasticisers and the early signs of degradation to the sample. Figure 6-7 shows a typical TIC from one of the five samples analysed for this combination of temperature and ageing.

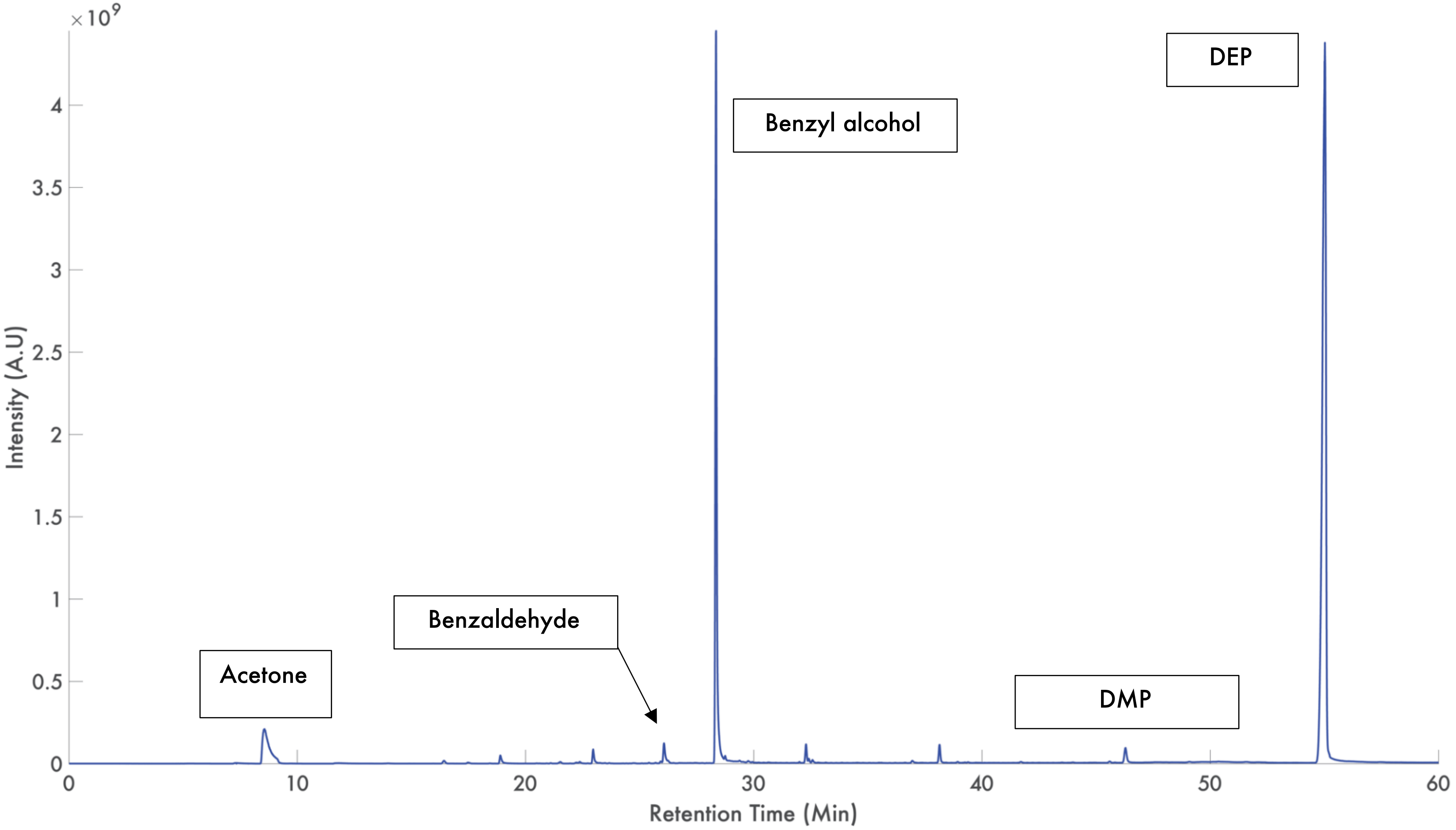

Figure 6-7 – TIC from an unaged sample from the CA-CW 0-WK H-Temp analysis set conducted at a target temperature of 25 °C.

Analysis shows that this naturally aged sample emits the characteristic VOCs one would expect from a sample of cellulose acetate. There is clear evidence of the inclusion of three types of plasticiser (two phthalates and triacetin) which were widely used (Giachet *et al.*, 2014; Bao, 2015). The addition of camphor is perhaps the most interesting finding as this plasticiser is normally associated with cellulose nitrate (Mazurek *et al.*, 2019) – further discussion regarding this compound can be found later in the chapter.

The additional presence of benzyl alcohol, benzaldehyde, and nonanal all suggest that the sample is actively degrading, as these are degradation products of cellulose (Strlič *et al.*, 2009; Fenech *et al.*, 2010; Gibson *et al.*, 2012) which given the age of the sample is an understandable finding.

The additional presence of acetone is explained by the sample's close proximity to the bespoke samples during storage before the analysis took place. However, the amount of acetone found is somewhat concerning given that, as was discussed in Chapter 4.7, its presence on the fibre will distort the overall relative amounts of the other, more pertinent, compounds.

Analysis of the remaining three sample types revealed a similar initial picture to that of the CA-CW sample Figure 6-8. The main features of each sample type are their respective plasticisers and a certain number of degradation products.

The most remarkable details regarding the initial state of the test sets are, in the first instance, the uniformity of the cellulose acetate samples. Despite each sample having a slightly different chemical make-up the compounds emitted by the sample sets overlapped significantly. Secondly, all samples show signs of degradation, however, the stereotypical degradation identifier of acetic acid is only present in the sample plasticized with TPP and in the industrial sample CA-NewCW. This suggests that this degradation mechanism does not propagate from the initial moment of sample degradation but rather comes after a delay or is below the limit of detection for some time. Thirdly, these samples again highlight the ease of use and useful data SPME GC/MS can provide when used in a laboratory setting. With little sample preparation, the analysis has provided enough evidence not only to identify the plasticisers present, but also it informs the researcher on the active degradation mechanisms.

Finally, these samples also highlight a significant limitation of SPME GC/MS analysis – contamination via any of cross-infection, GC carry-over, and external sources. The presence of acetone and camphor in all samples, including those bespoke samples where camphor was known not to have been incorporated, shows the sensitivity of the methodology but also its vulnerability to contamination. Without any analytical context or further analysis, the presence of those compounds could not be discounted as having originated from the sample itself. This poses the obvious issue of mischaracterising polymers in objects due to the detection of spurious compounds. The clear antidote to this vulnerability is to avoid blindly assigning polymer types based solely on set VOC criteria but rather on a more nuanced approach where data from SPME GC/MS analysis is combined with contextual awareness regarding polymer type. The movement towards non-analytical identification has greatly advanced since the beginning of this doctoral project with initiatives at the V&A Museum (van Aubel, 2017) and the Dutch-based collective SBMK's 'Plastic Identification Tool' (www.sbmk.nl/nl/tool/plastics) providing excellent resources regarding context, to complement the information provided by VOC analysis.

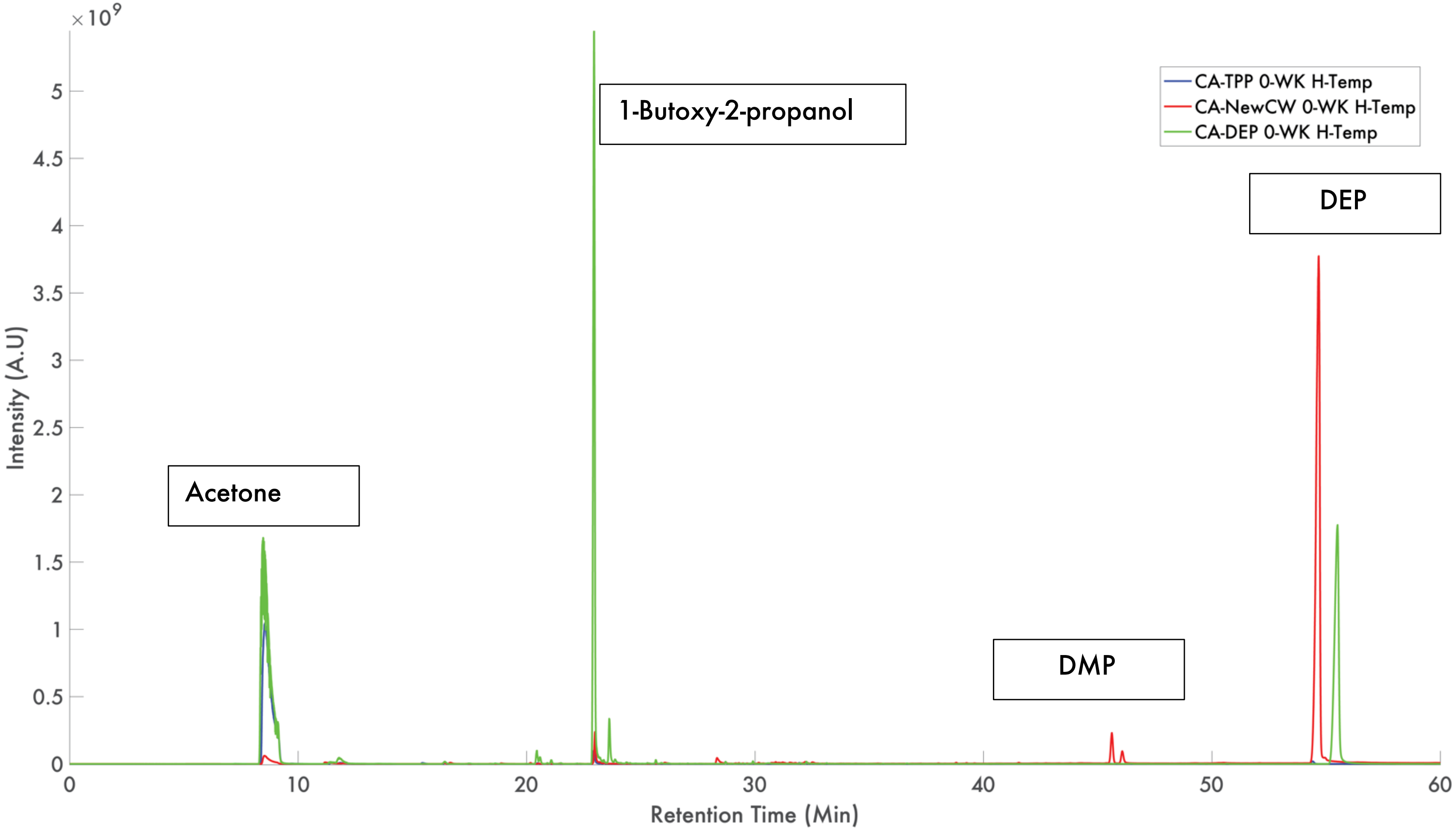

Figure 6-8 – TIC's from three different polymer sample types showing the strong cross over between the VOCs each emits. The figure shows that for some polymer types a set of VOCs or a VOC profile may possibly be used in order to track the change of that sample over the course of ageing.

CA-CW 0-WK H-Temp					
Rank	RTMin	m/z Identifier	NIST R Match	Normalised Area	Compound
1	55.02	149	949	89.75	Diethyl Phthalate
2	28.35	79	963	37.42	Benzyl alcohol
3	8.57	58	964	8.40	Acetone
4	46.29	163	956	1.27	Dimethyl Phthalate
5	26.07	77	953	1.21	Benzaldehyde
6	38.14	103	951	1.05	Triacetin
7	32.29	95	936	0.96	Camphor
8	22.96	57 & 87	910	0.86	1-Butoxy-2-propanol
9	18.90	-	-	0.61	n/a
10	28.75	57 & 79	703	0.24	Nonanal
15	22.37	104	869	0.11	Styrene
19	17.48	91	893	0.09	Toluene

Table 6-5 - A list of the top ten compounds (by peak area) and additional compounds of interest found from the analysis of a single sample taken from the CA-CW 0-WK H-Temp set. RT Min refers to retention time (in minutes) while the normalized area is unitless. All compounds were identified via the NIST library. Compounds which are reported as "n/a" could not be identified due to poor matching or similarities between multiple candidates.

CA-DEP 0-WK H-Temp					
Rank	RT Min	m/z Identifier	NIST R Match	Normalised Area	Compound
1	22.96	57 & 87	899	33.62	1-Butoxy-2-propanol
2	55.50	149	947	27.90	Diethyl Phthalate
3	8.37	58	969	3.23	Acetone
4	23.62	-	-	1.85	n/a
5	20.46	769	58	0.57	4-hydroxy-4-methyl-2-Pentanone
6	23.86	-	-	0.18	n/a
7	16.41	207	886	0.15	Cyclotrisiloxane
8	25.66	105	853	0.12	1,2,3-trimethyl-Benzene
9	23.38	-	-	0.12	n/a
10	29.91	57	879	0.08	Dodecane
11	32.25	95	821	0.07	Camphor
12	28.71	57	846	0.07	Nonanol

Table 6-6 - List of VOCs found from an unaged bespoke sample of cellulose acetate plasticized with Diethyl phthalate. Note that the presence of camphor in the sample is due to contamination while the sample was being stored. Compounds which are reported as "n/a" could not be identified due to poor matching or similarities between multiple candidates

CA-NewCW 0-WK H-Temp					
Rank	RT Min	m/z Identifier	NIST R Match	Normalised Area	Compound
1	54.67	149	954	187.00	Diethyl Phthalate
2	45.62	205	946	6.68	Butylated hydroxytoluene
3	22.99	59	911	5.02	Hexylene glycol
4	46.08	163	957	3.02	Dimethyl phthalate
5	28.33	79	939	1.75	Benzyl alcohol
6	8.52	58	989	1.20	Acetone
7	54.94	149	894	1.11	Diethyl Phthalate
8	32.20	69	747	0.43	Camphor
9	16.65	56	895	0.36	4-Penten-2-ol, 4-methyl-
10	32.51	105	768	0.27	Benzoic acid, ethyl ester
16	26.05	77	882	0.14	Benzaldehyde
18	11.17	60	983	0.14	Acetic acid

Table 6-7 - List of VOCs found from an unaged sample of industrially manufactured cellulose acetate where the exact components are unknown. However, SPME analysis shows that there were at least two different plasticisers used. Note that diethyl phthalate is featured twice due to peak splitting and the software 'seeing' as two separate peaks

CA-TPP 0-WK H-Temp					
Rank	RT Min	m/z Identifier	NIST R Match	Normalised Area	Compound
1	8.54	60	974	35.49	Acetone
2	22.95	57	903	0.70	1-Butoxy-2-propanol
3	54.40	149	873	0.22	DEP
4	15.44	-	-	0.10	n/a
5	59.59	73	736	0.10	n-Decanoic acid
6	16.46	87	207	0.09	Cyclotrisiloxane
7	28.70	57	866	0.07	**alkanes with approx. 10 carbons
10	31.93	57	852	0.04	**
11	23.39	57	907	0.03	**
12	11.45	60	-	0.03	acetic acid
13	29.89	57	854	0.03	**
14	32.23	95	798	0.03	Camphor
19	17.51	91	723	0.01	Toluene
21	33.07	57	809	0.01	**
32	22.38	104	759	0.00	Styrene

Table 6-8 – List of VOCs found from an unaged sample of cellulose acetate plasticized with TPP. Note that compounds which have been identified using the m/z value of 57 and named as ** are all alkanes with approx. 10 carbons. It is difficult to accurate attribute these alkanes to a specific compound - in order to definitively determine the compound a Retention Index standard would need to have been carried out. Compounds which are reported as "n/a" could not be identified due to poor matching or similarities between multiple candidates

6.3.4 Effect of accelerated ageing on samples

In line with data treatment in previous chapters and as the VOC profiles generated via SPME GC/MS can be complex due to the number of VOCs collected the data treatment presented in the following sections will focus on those VOCs which impart the greatest amount of information regarding the sample. The criteria for inclusion are based on the overall rank of the VOC within its sample's profile combined with its ability to inform on degradation mechanism or base polymer type.

6.3.4.1 Analysis of CA-CW Samples

Analysis of the VOC profile from the CA-CW samples was typified by two central observations which were in keeping with the logical assumptions one could make about the ageing process of polymers. The first observation was the diminishing amount of plasticiser found in the VOC profile. The second was an increase in the amount of degradation products found. Further to these was the lack of any detectable acetic acid formation over the course of the aging period.

After the initial 4-week ageing cycle there was a significant change to the level of plasticiser found to be emitted from the object. In general, after an ageing cycle the plasticisers (DEP, DMP, & Triacetin) saw a decrease to their normalized peak areas. For DEP the initial decrease on ageing was comparatively small when compared to the second ageing cycle (Figure 6-9), however, this second campaign lasted 8-weeks, twice as long as the first. It is therefore clear that ageing, and especially accelerated ageing, has a dramatic effect of the levels of plasticiser emitted from the objects. Yet despite this, the overall degree of substitution (DS) for the polymer (discussed further later in this chapter and seen in Table 6-17), which was measured using FTIR ratios, changed very little[8]. However, analysis showed that not all VOCs behaved in a

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[8] A more in-depth analysis regarding this change in DS will follow in the next chapter as the data covered is more applicable to the remit of that chapter.

similar manner. Figure 6-10 and Figure 6-11 show a subsection of the TIC highlighting a number of peaks over the course of the different ageing cycles. Benzyl alcohol initially increases after the first ageing cycle, however, after the second cycle its peak area falls to below its initial starting position. This could be due to the reaction mechanism for that degradation product slowing down or stopping. However, it could also be due to the compound being oxidised into benzaldehyde, something it is known to do at ambient room temperatures (Sankar *et al.*, 2014).

This feature of the profile highlights the danger of assigning any type of a degradation level based on a single VOCs or on single-point exposure. It demonstrates that any classification of polymer degradation must be formed via tracking a sample over the course of a set period of time.

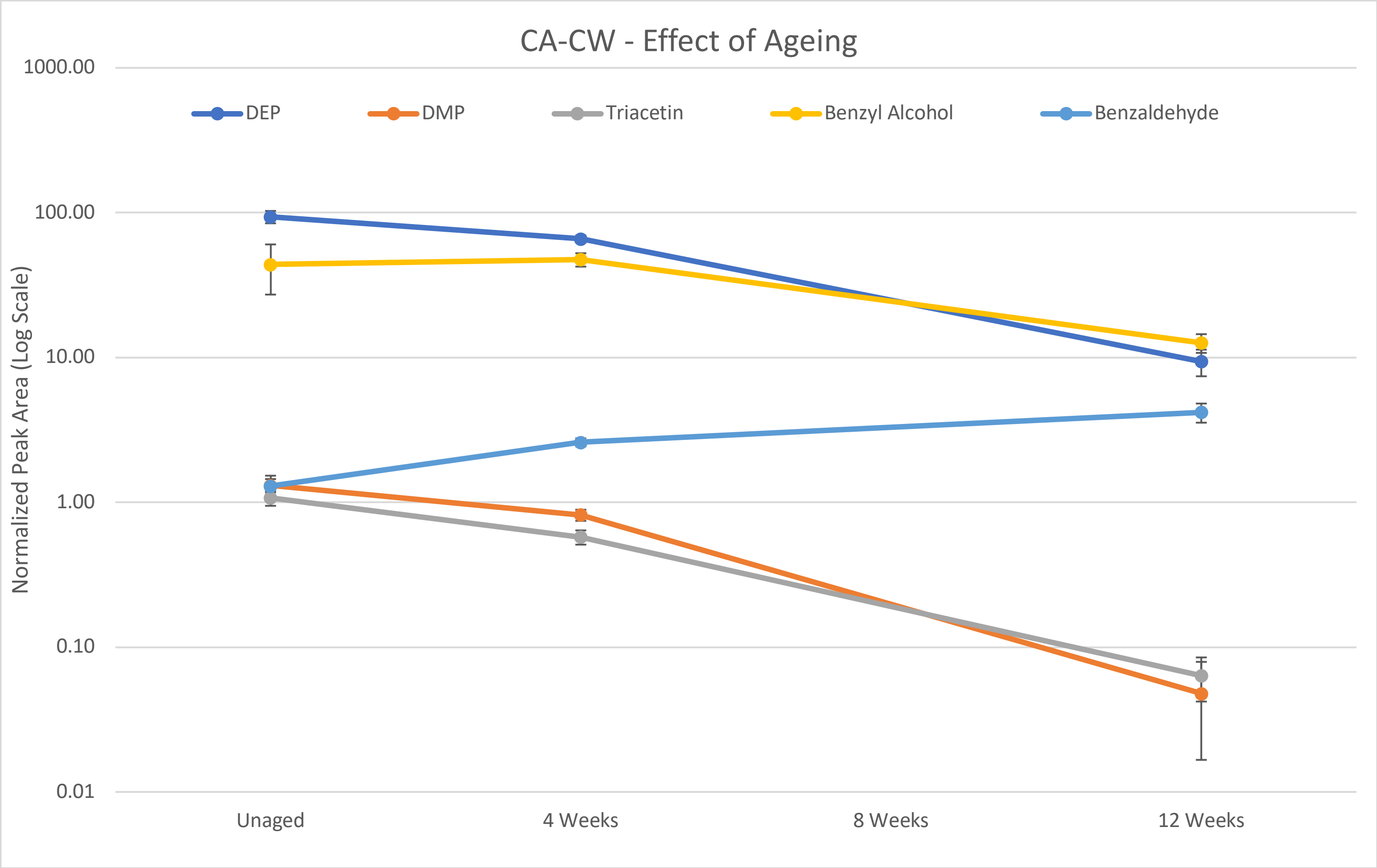

Figure 6-9 – A line plot from CA-CW of the five main VOCs of interest to be found using SPME GC/MS aalysis. This plot tracks their normalized peak area over the course of the different aging cycles.

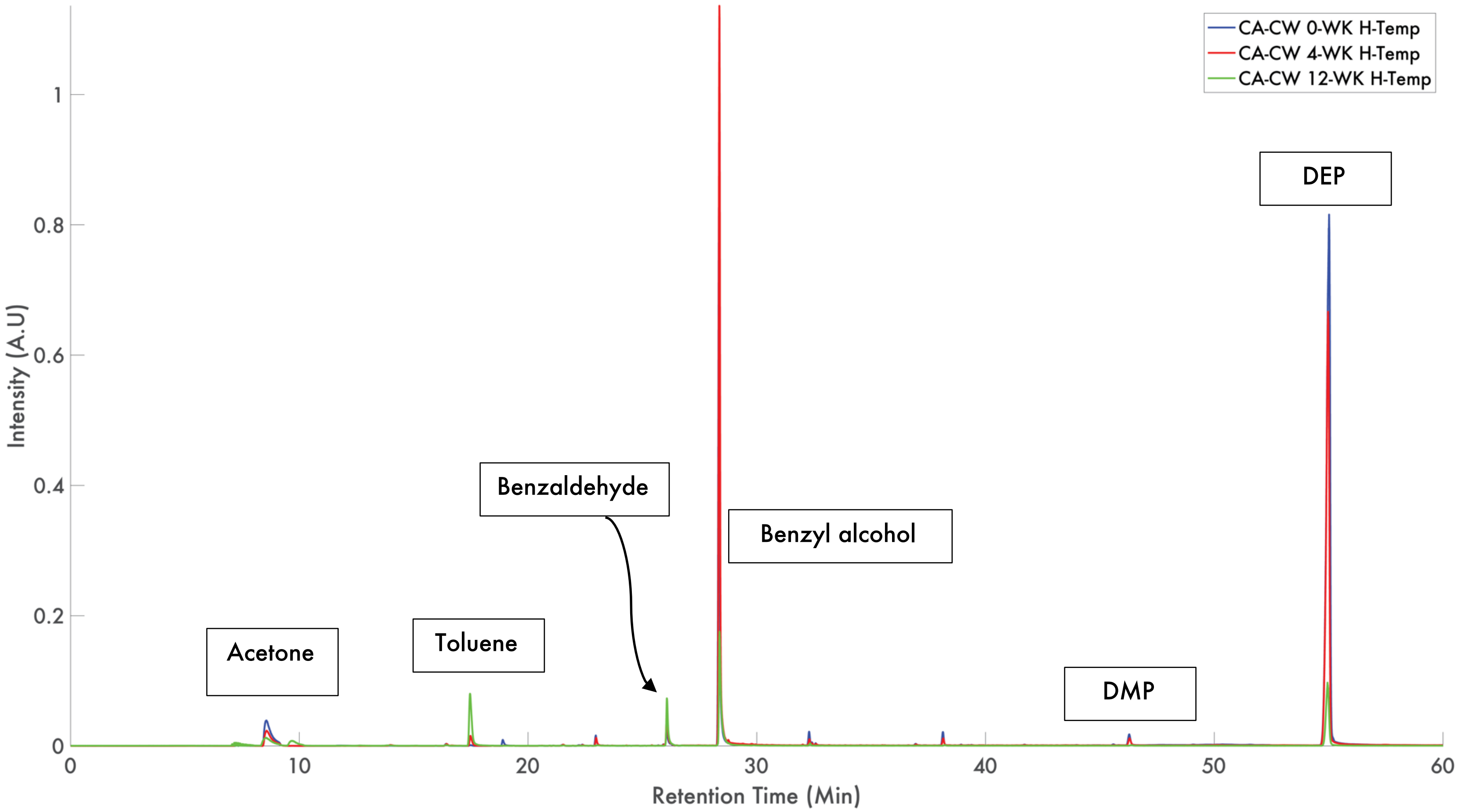

Figure 6-10 – TIC's of a sample from CA-CW at the three different ageing stages. Notice that the plasticisers decrease after ageing while in general the degradation products increase. Note also that the peak circa 8 minutes is that of acetone rather than acetic acid, which would normally be found in this area of the chromatogram.

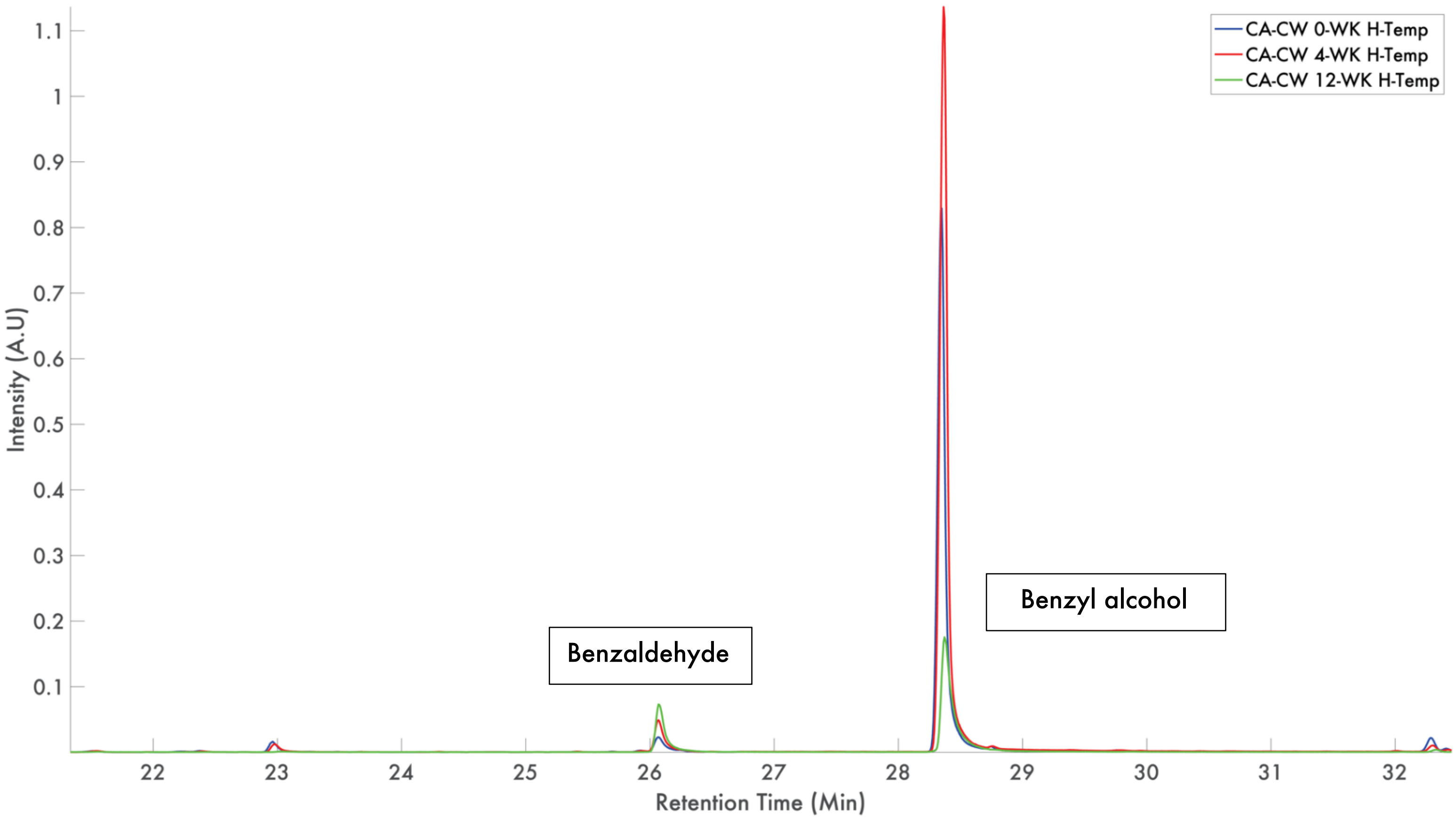

Figure 6-11 – A close up of some VOC peaks from CA-CW during the three ageing stages. Notice that the peak at circa 28.5 minutes, which is that of Benzyl alcohol, initially increases after the first ageing cycle but then decreases on the second cycle suggesting two potential pathways 1) that its degradation mechanism slows down or stops and 2) that it oxidizes into benzaldehyde. Furthermore, this figure gives a clear visual to the phenomenon of degradation products increasing, such as that of Benzaldehyde.

6.3.4.2 Analysis of CA-NewCW Samples

Results from the analysis of the CA-NewCW samples were somewhat inconsistent compared to the other sample types. Table 6-9 details the normalized peak areas of the five target VOCs at the initial state and following an eight-week exposure to the accelerated ageing conditions. While the expectation that the amount of plasticisers found to be present on the fibre would decrease upon ageing hold true, the VOCs associated with degradation markers were found to have also decreased after undergoing accelerated ageing. In essence, upon ageing, all VOCs were reduced, according to their normalized peak areas. There is a precedent for seeing a reduction in peak area, as was shown earlier in the case of benzyl alcohol; in that case, it was a single VOC (which had initially increased before decreasing) rather than all degradation marker VOCs. One potential cause for the reduction in VOCs seen was due to an imbalance in the standards used to normalize peak areas too; this would be where one standard was significantly higher or lower than the previous, thereby skewing the results in one particular direction. This was investigated and found to have had no significant role in altering the profile of the VOCs. A full account of this analysis can be found in Appendix 2. Despite these atypical changes (compared to real-world ageing) the samples have provided two clear datasets from which temperature effects can be extrapolated.

Target Compound	Normalized area at 0-Week	Normalized area at 8-Week
Diethyl Phthalate	206.55	26.97
Dimethyl phthalate	4.61	0.43
Benzyl alcohol	2.43	0.44
Benzaldehyde	0.34	0.10
Acetic acid	1.07	0.31

Table 6-9 – Normalized peak areas for five target VOCs showing a decrease after accelerated ageing. While the two phthalate plasticisers behave as would be expected; in the case of degradation markers this is not what one would expect.

6.3.4.3 Analysis of CA-TPP Samples

Analysis results from the samples CA-TPP will be presented in the following chapter. This is due to its unique degradation profile which differed significantly from the three previous samples. However, in a brief summary - in terms of degradation trends, the CA-TPP samples matched closely with those of CA-CW whereby the normalized peak area for degradation products such as phenol and acetic acid was found to rise on ageing. Triphenyl phosphate was used as the sole plasticiser, however, this compound is not volatile enough to be detected directly via SPME analysis and as such, it was not possible to track its progress with ageing.

6.3.4.4 Analysis of CA-DEP Samples

The initial 4 weeks of ageing did little to change the VOC profile of the CA-DEP samples. As before, the relative amounts of the plasticiser decreased from an average normalized peak area of 27.34 to 19.07. In the case of the nonanal peak from these samples, there was only a slight difference which was just above the threshold for a statistically significant change.

By comparison to other analytical methods it is possible to confirm that little change had occurred after the accelerated ageing period. Table 6-10 details the colour analysis on CA-DEP samples after completion of the ageing cycle. The table shows that it did not lead to a large change, above the ΔE_{00} 1.5 *"just noticeable difference"* suggested by Pretzel (2008), in the colour of the CA-DEP samples.

Sample		L	a	b
CA DEP 2A 0-Week H-Temp		52.90	1.45	5.03
CA DEP 2A 4-Week H-Temp		46.15	2.19	8.48
Change from 0-WK -> 4-WK		6.76	-0.74	-3.45
ΔE_{00} 0-WK -> 4-WK		**7.28**		
CA DEP 7A 0-Week H-Temp		64.56	0.94	4.05
CA DEP 7A 4-Week H-Temp		64.26	1.11	7.26
Change from 0-WK -> 4-WK		0.30	-0.17	-3.21
ΔE_{00} 0-WK -> 4-WK		**2.58**		

Table 6-10 - Results from the colour measurement performed before (0-WK) and after (4-WK) accelerated ageing on two samples CA-DEP (Sample 2A and 7A). While samples did change above the 1.5 threshold that indicates a detectable colour change, they are not significantly above it and this change equated to only slight yellowing of the samples, comparable to that shown in Figure 7-4. One aspect to note is that the samples themselves differ greatly showing that not all samples responded to the ageing process in the same manner. The values presented here are the average values of five repeat measurements on each sample. ΔE_{00} values were calculated using an online calculator (http://colormine.org/delta-e-calculator/cie2000).

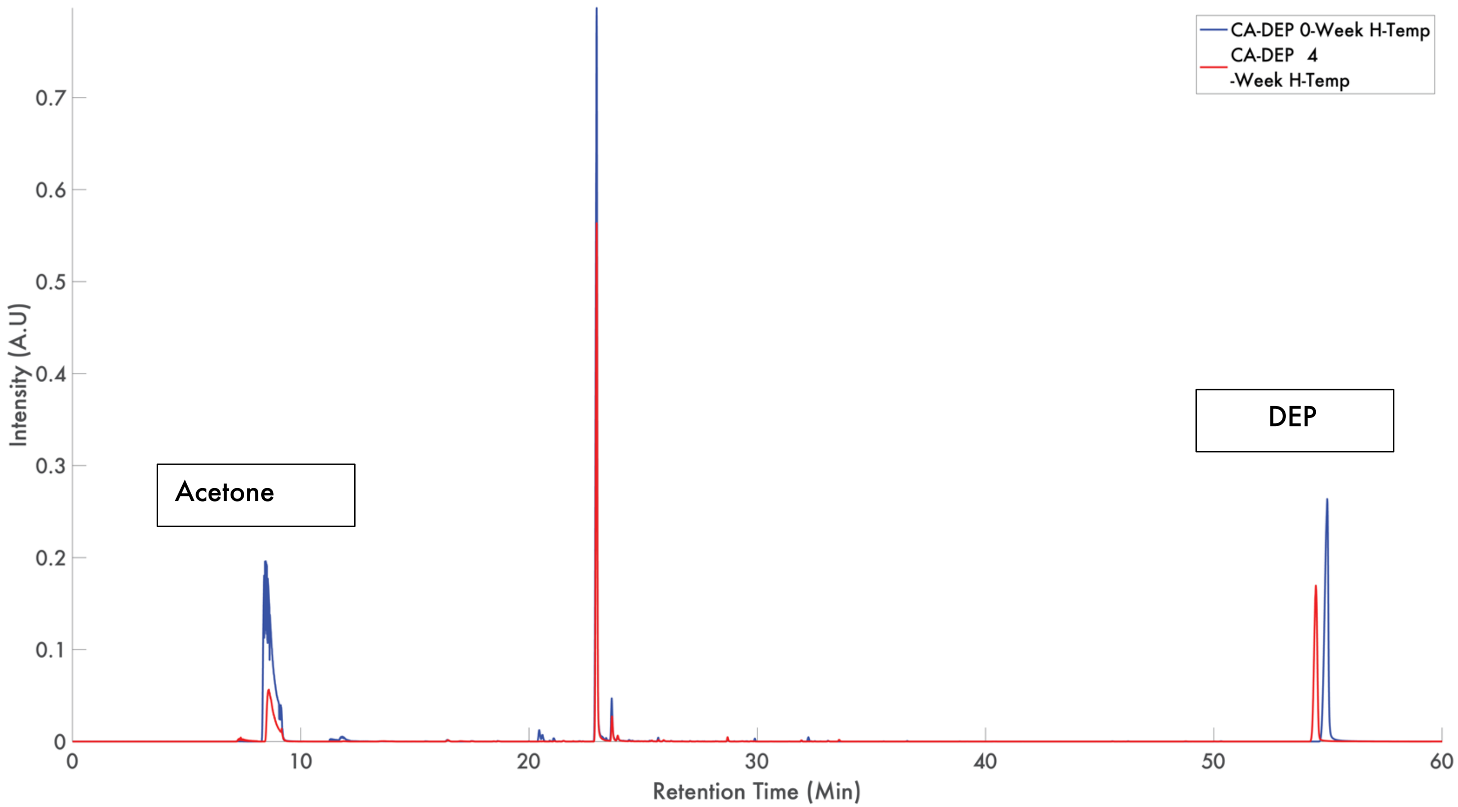

Figure 6-12 - TIC of two CA-DEP samples before (0-wk) and after (4-wk) accelerated ageing. While the sample did undergo a statistically significant change for certain VOCs, not all relevant VOCs changed to the same degree. This TIC shows that the sample changed very little after accelerated ageing.

6.3.4.4.1 Summary of ageing effects

Returning to the research questions outlined in section 6-2; we are now in a position to comment on the initial two questions regarding the behaviour of the VOCs profile upon ageing and the ability to differentiate samples based on the amount of accelerated ageing when the temperature remains constant and when it varies.

It is clear from the above that not all samples behave in a similar manner. While broad intuitive trends can be extrapolated, i.e. that plasticisers generally decrease on ageing while degradation products increase, they are only general trends and the evidence provided here shows that they cannot be accepted as a general rule on which to base the relative age of a sample. The circumstances by which degradation mechanism rates decrease *with* ageing or entirely new degradation products form as new mechanisms occur mean that utilizing any single VOC for relative age discrimination is useless. The research points towards examining historic polymer samples via VOC profiles, where the information gained from two or more VOCs is combined to give a clearer understanding of the current condition of the object.

The research, therefore, highlights the need & usefulness of continued measurements of samples. This concept of repeated measurements over a long time period will be examined further in chapter 8.

The following section will examine if this condition holds true when the temperature is changed as any real-world analysis will not have a guarantee of long-term environmental stability. Within this limitation, the ability to accurately judge the ageing levels or the ability to track degradation could potentially be of vital importance in building a case for a specific collection management strategy.

6.3.5 Effect of exposure temperature on resulting VOC profiles

As was outlined earlier in section 6.2 the variation in temperature, inside a heritage environment, over the course of multiple months can be as great as 10 °C. With the goal of producing a methodology robust enough for monitoring, over the course of an object's lifetime within a museum, these temperature fluctuations must be accounted for. Furthermore, if the role they play is consistent or clearly defined then it may be possible to perform a correction in order to account for it, furthering the practicalities of SPME analysis for historic polymer objects.

6.3.5.1 Analysis of temperature effects on CA-CW

As can be seen in Table 6-2, only CA-CW was investigated at all three temperature and ageing conditions. This allows for a great deal of information regarding the robustness of the methodology and the samples to be gathered.

The most significant results are that the relative amount of our key VOCs, recorded by the SPME fibre, consistently decrease as the temperature decreases regardless of the level of accelerated ageing which the sample had undergone (Table 6-11 and Figure 6-13 and Figure 6-15). Further to this is the insight that even the temperature change between High and Medium settings, which in reality was only a few degrees was sufficient to significantly alter the resulting VOC profile.

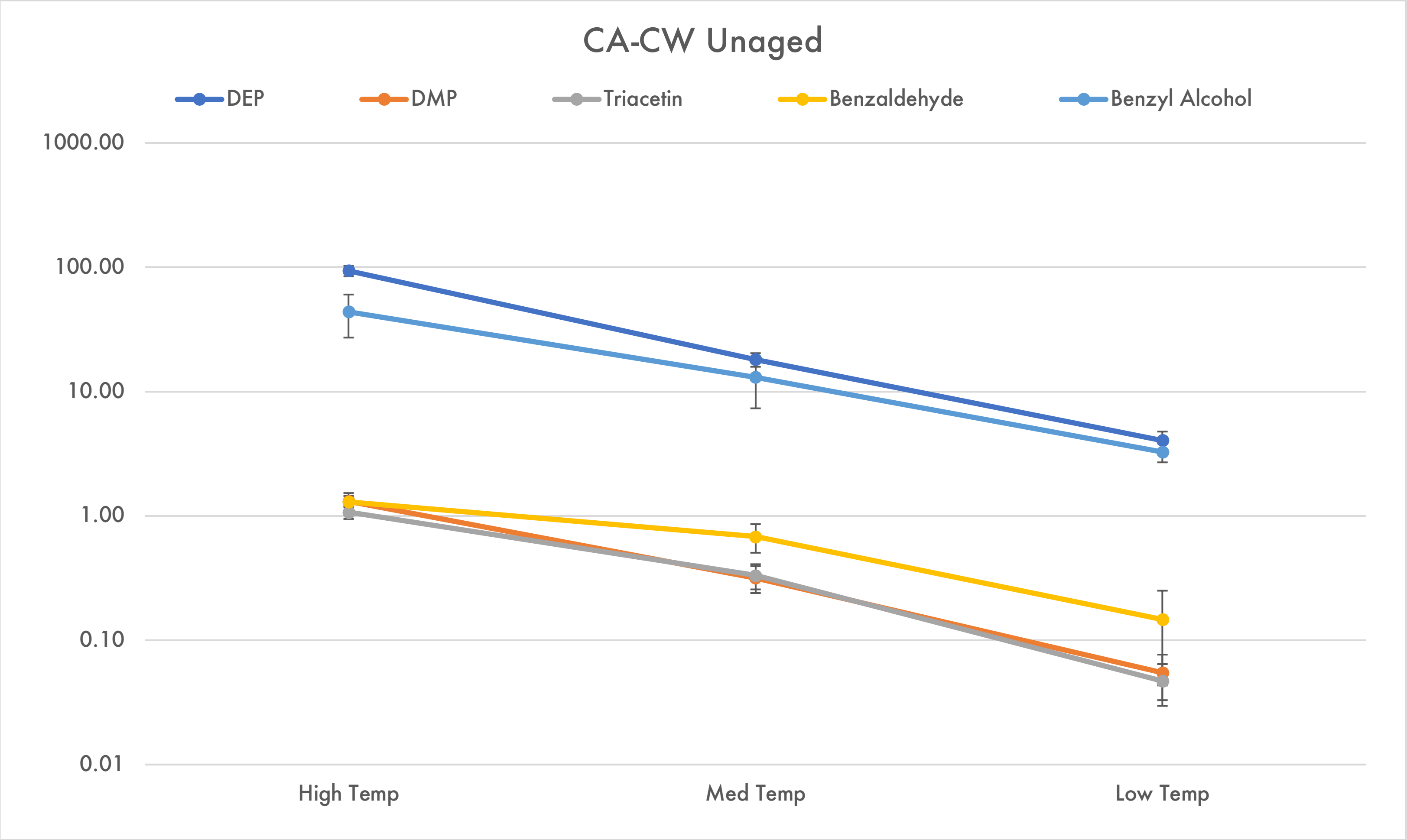

Figure 6-13 – The trend for the normalized peak areas from the key VOCs from CA-CW is shown to be decreasing as temperature also decreases. Despite all of the sample sets being of similar ageing status, the levels of identification markers (such as DEP) and degradation markers (such as Benzaldehyde) all decrease in line with decreasing exposure temperature. Note that the normalized peak area (y-axis) is in a log scale.

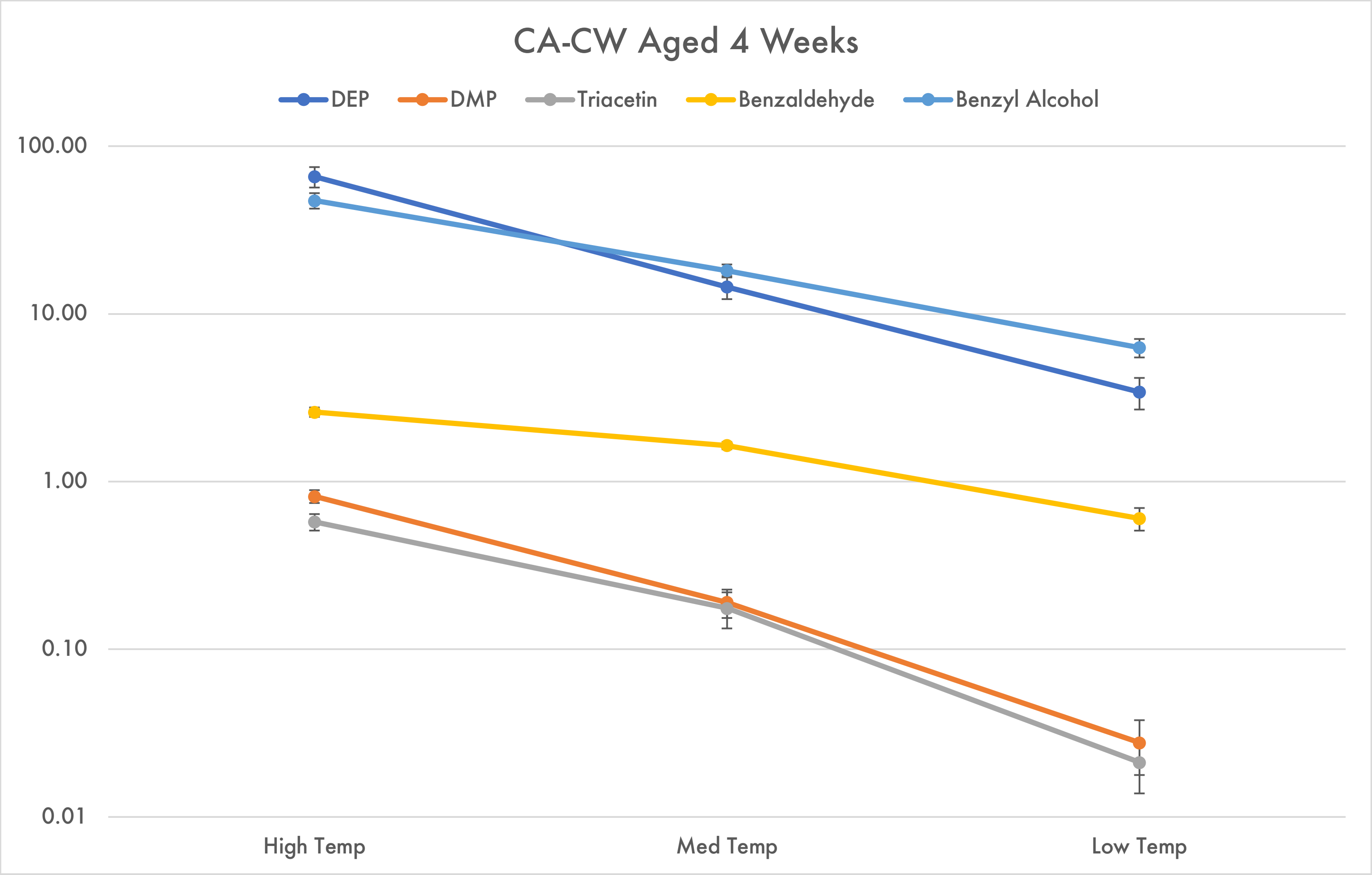

Figure 6-14 - A similar line plot to Figure 6-15, however, in this case, the samples have experienced four weeks of accelerated ageing in a sealed chamber held at 70 °C and relative humidity of 50 %. Note that the normalized peak area (y-axis) is in a log scale.

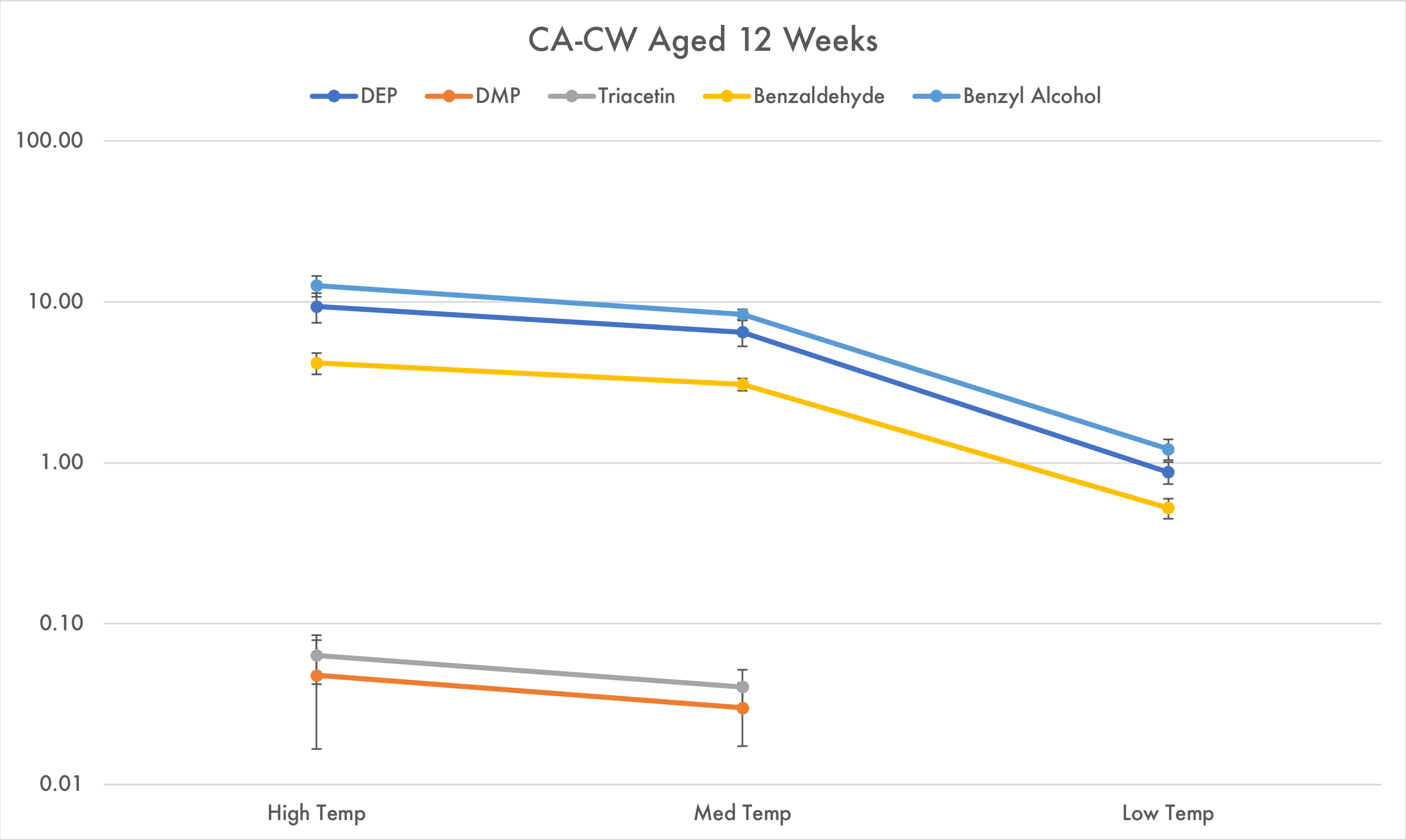

Figure 6-15 - CA-CW samples after twelve weeks of accelerated ageing. Again, notice the downward trend in overall VOC normalized peak area. Note that the normalized peak area (y-axis) is in a log scale.

The above figures highlight the consistent decrease of VOCs (at all ageing conditions) when the exposure temperature is reduced. Figure 6-15 in combination with Table 6-11 also highlights that even as degradation products increase in the overall VOC profile emitted from the sample, those too are affected by temperature and decrease with temperature. One feature which defies the overall trend is the level of acetone which was found to be greater when moving to the lowest temperature level (not shown on graphs). However, as was previously mentioned, this is easily explained within the context of the experiment. At the lower temperature samples were conditioned and exposed to the SPME fibre within the fridge. This fridge held the bespoke samples, manufactured for this experiment and for others, which utilized acetone as a solvent for the cellulose acetone and the plasticisers used. Therefore, there would be a higher level of acetone surrounding these samples than during the other forms of analysis.

		High Temp	Med Temp	Low Temp
DEP	Unaged	93.62	18.11	4.04
	4 Weeks	65.83	14.50	3.42
	12 Weeks	9.37	6.48	0.87
DMP	Unaged	1.31	0.32	0.05
	4 Weeks	0.82	0.19	0.03
	12 Weeks	0.05	0.03	Not Found
Triacetin	Unaged	1.07	0.33	0.05
	4 Weeks	0.58	0.18	0.02
	12 Weeks	0.06	0.04	Not Found
Benzaldehyde	Unaged	1.30	0.68	0.15
	4 Weeks	2.60	1.64	0.60
	12 Weeks	4.18	3.07	0.52
Benzyl Alcohol	Unaged	43.78	13.08	3.27
	4 Weeks	47.43	18.10	6.29
	12 Weeks	12.62	8.38	1.22

Table 6-11 – Highlights the normalized peak areas from samples of CA-CW of key identification and degradation markers over the course of both the accelerated ageing the samples underwent and the change in exposure temperature. Notice the general trend of lower normalized peak areas as ageing increases and while temperature decreases. Specific temperatures for each analysis set can be seen in Table 6-2. Note that these values are the average values of the five repeat samples used during testing.

6.3.5.2 Quantifying changes to CA-CW

While the VOC profile decreased individual VOCs did not all decrease by a similar level. Table 6-12 highlights the ratios of a selection of VOCs, which show that the change between each temperature setting is not the same for each VOC. Furthermore, the ratio is not consistent with relation to accelerated ageing, this is exemplified best via the ratios for DEP. When moving from the unaged to 4-week aged results both the ratio for specific temperature change (Table 6-13) and VOC change is reasonably consistent, however, for the 12-week aged samples the VOC ratio is significantly higher. Furthermore, we see in Table 6-13, which shows the changes, as a ratio of the high temperature, to the exposure temperature during the different ageing sets, that the results for the ratio for temperature at the 12-week ageing set is in line with the previous two. This informs us that the results seen in Table 6-12 are not brought about from radically different temperature changes, but rather the combined interaction between matrix properties, temperature, and VOC emission leading to the individualistic nature of the response.

DEP	High Temp	Medium Temp	Low Temp
Unaged	1	0.19	0.04
4 Weeks	1	0.22	0.05
12 Weeks	1	0.69	0.09
Benzaldehyde			
Unaged	1	0.53	0.11
4 Weeks	1	0.63	0.23
12 Weeks	1	0.74	0.13
Benzyl Alcohol			
Unaged	1	0.30	0.07
4 Weeks	1	0.38	0.13
12 Weeks	1	0.66	0.10

Table 6-12 - Ratios based on normalised peak areas from CA-CW samples. The values for the High Temperature have been set to 1 and the others defined relative to these. This table highlights the inconsistent changes VOCs undergo. Notice that each VOC responds to changes in exposure temperature differently, despite similar changes in temperature over the course of different sample sets.

	High Temp	Medium Temp	Low Temp
Unaged Temp Ratio	1	0.69	0.31
4-WK Temp Ratio	1	0.76	0.29
12- WK Temp Ratio	1	0.79	n/a

Table 6-13 – This table illustrates that the difference in temperatures between the different sample sets was not sufficiently different to cause the inconsistencies seen in peak ratios in Table 6-12. In this table the 'High Temp' is set to 1 and all other values in that experiment are a ratio against its value.

While it is clear from Table 6-11 that the more accelerated ageing a sample receives, the lower its plasticiser level goes, the use of a lower exposure temperature (which occurs when the exposure is conducted in the fridge for the lower temperature setting) would lead to the erroneous conclusion that the sample has lost more plasticiser than it had, thereby suggesting the sample was aged to a greater degree.

A further issue relates to the absence of certain VOCs at lower temperatures. This can be seen for both DMP and triacetin whose presence at the lowest exposure temperature was not found despite its detection at the higher temperatures. This has a direct impact on the interpretation of samples which have been exposed at lower temperatures. This not only distorts the '*health*' of the sample by suggesting its plasticiser content is lower than it is, but it can also impact on the context of the sample. For example Giachet *et al.* (2014) have noted in their research that animation cells, constructed with CA before 1983, typically did not feature DMP. Within the context of these animation cells, measuring the VOC profile at a lower storage temperature could have a dramatic effect by misattributing them to a different period.

6.3.5.3 Effects of temperature on CA-NewCW

CA-NewCW, another example of an industrially made sample, behaved in a similar manner to CA-CW. As before, the levels of key VOCs decreased as the temperature decreased (Figure 6-16 & Figure 6-17, Table 6-14) Also, as before, the level of acetone is seen to rise on a decrease in temperature, further validating the explanation relating to the analysis conducted inside a fridge used to house the bespoke samples.

Target Compound	Ageing	High Temp	Med Temp	Low Temp
Diethyl Phthalate	Unaged	206.55	66.63	13.87
	8 Weeks	26.97	17.75	2.87
Dimethyl phthalate	Unaged	4.61	1.43	0.32
	8 Weeks	0.43	0.27	0.03
Benzyl alcohol	Unaged	2.43	1.02	0.21
	8 Weeks	0.44	0.29	0.21
Benzaldehyde	Unaged	0.34	0.13	0.12
	8 Weeks	0.10	0.13	0.04
Acetic acid	Unaged	1.07	0.17	0.11
	8 Weeks	0.31	0.29	0.07

Table 6-14 – Shows the average normalized peak areas of two identification markers (the phthalates) and three degradation markers from the CA-NewCW sample set. Note that the value of each VOC decreases as the exposure temperature decreases. The values are the average values of the five repeat samples used during testing.

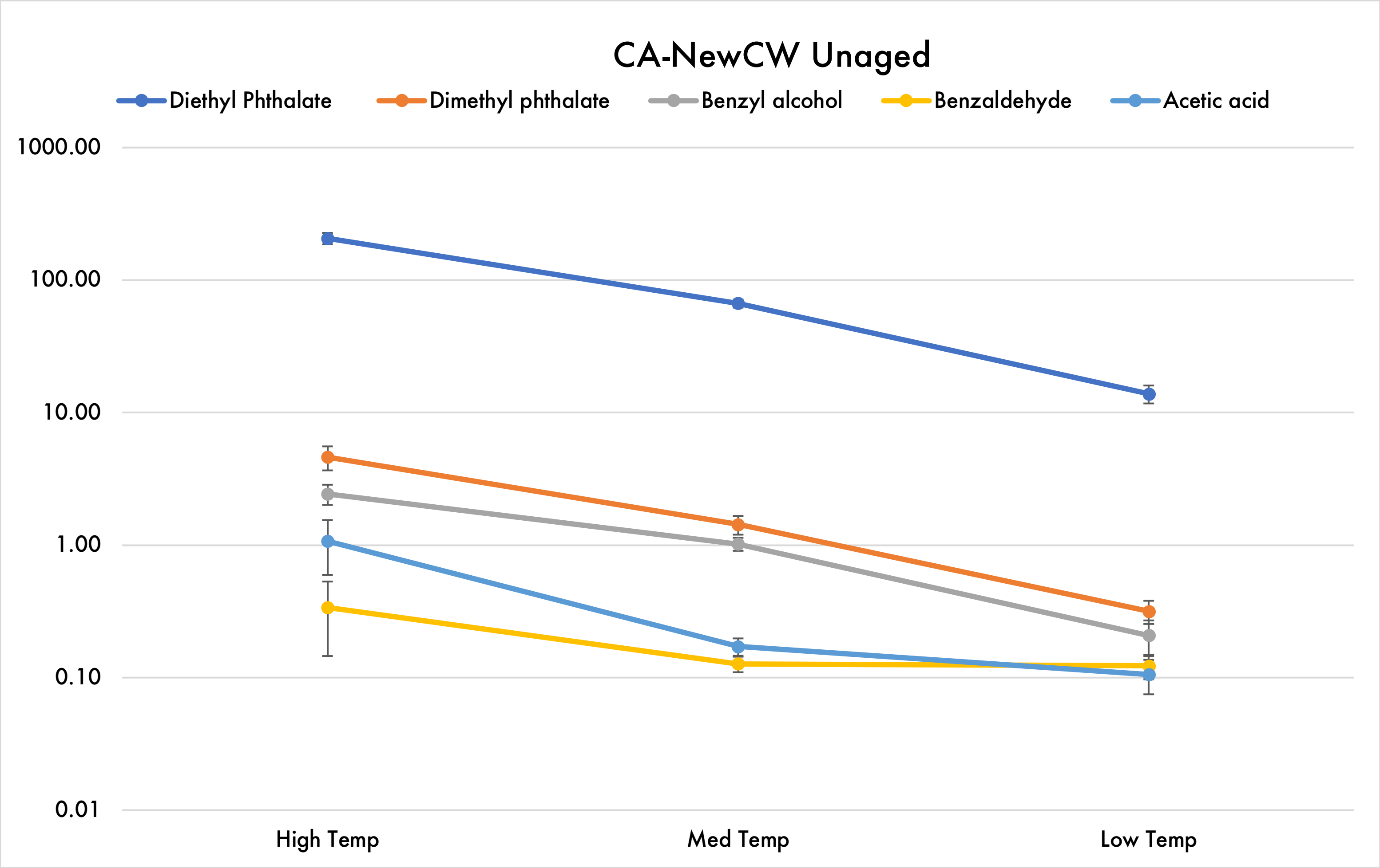

Figure 6-16 - A similar set of line plots to Figures 6-13 - 6-15, however, in this case they are the CA-NewCW samples. These samples have not experienced any accelerated ageing.

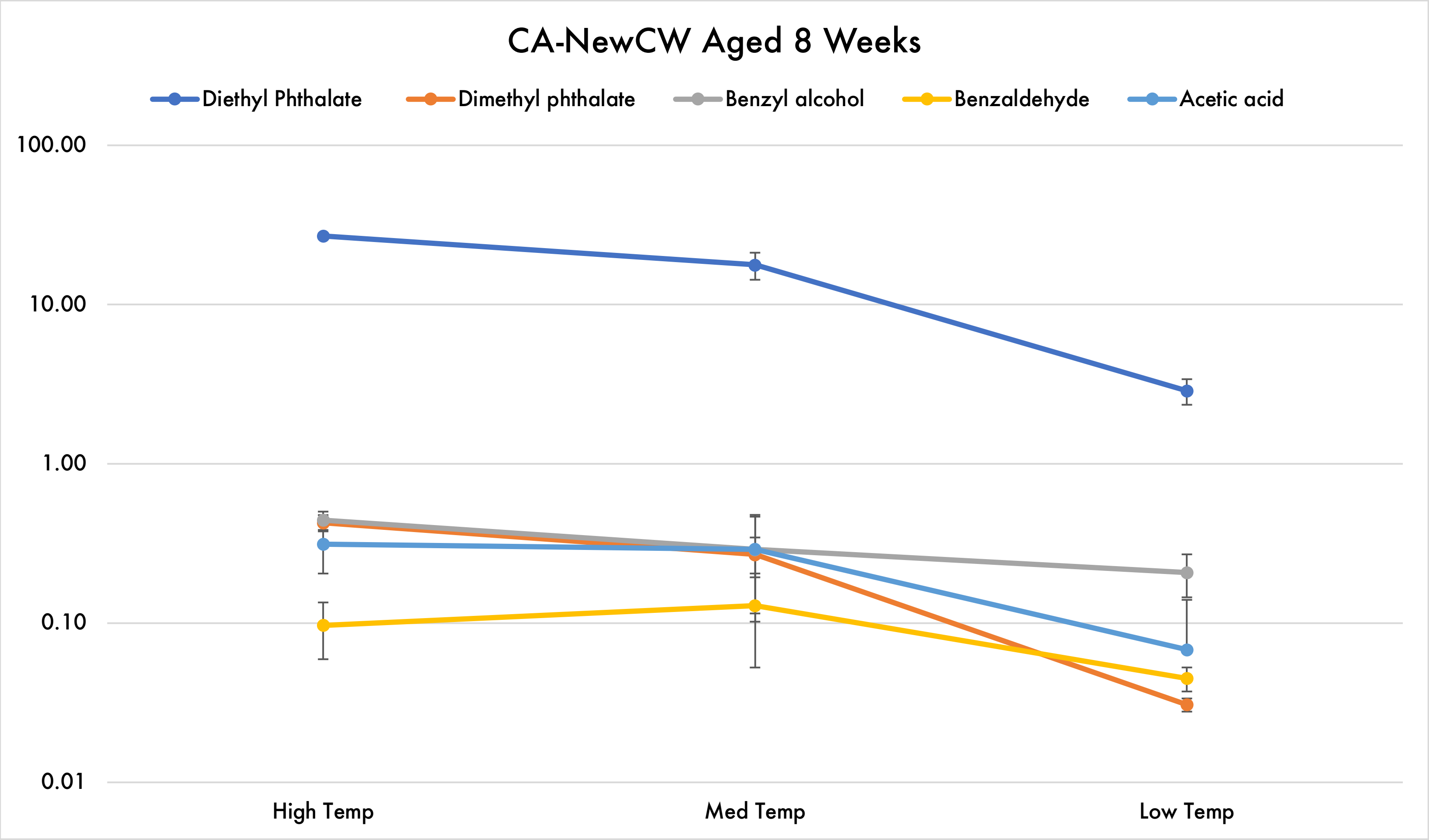

Figure 6-17 - Line plot CA-NewCW samples after undergoing ageing for eight weeks. The three sample sets displayed here have each been analysed at a different temperature. It is clear that as the temperature of analysis is reduced the resulting VOC profile is also sees a reduction in overall intensity.

Despite the clear similarities in the overall trend between the two industrial samples, there is a significant difference between how the two sample sets behaved during this experiment. Table 6-15 shows the ratios of peak area between the different temperature analysis levels. As before these show that each VOC reacts differently to the change in temperature and that this behaviour is not consistent when moving between different ageing levels. This table (6-15) shows that when compared to the ratio results from the CA-CW sample set (see Table 6-12) there is no continuity between the two data sets despite the two samples being industrially made cellulose acetate of a similar age.

DEP	**High Temp**	**Medium Temp**	**Low Temp**
Unaged	1	0.32	0.07
8 Weeks	1	0.66	0.11
Benzaldehyde			
Unaged	1	0.38	0.36
8 Weeks	1	1.33	0.46
Benzyl Alcohol			
Unaged	1	0.42	0.09
8 Weeks	1	0.65	0.47

Table 6-15 - Ratios based on normalised peak areas from CA-NewCW samples. As before, this table highlights the inconsistent changes VOCs undergo. Furthermore, it also highlights that the ratios are not consistent with the other cellulose acetate sample which was examined.

	High Temp	Medium Temp	Low Temp
Unaged Temp Ratio	1	0.76	0.48
8-WK Temp Ratio	1	0.85	0.41

Table 6-16 – Temperature ratios for the different analysis sets for CA-NewCW. This highlights that the temperature changes were not significantly different between each other. In this table the 'High Temp' is set to 1 and all other values in that experiment are a ratio against its value.

6.3.5.4 Quantifying changes due to temperature differences.

The insight provided by examining the ratios (Tables 6-12 & 6-15) experienced by individual VOCs, has a profound impact on the interpretation of any future unknown datasets examined. The first issue is the lack of consistency between the VOCs within a single sample set meaning a general conversion factor can't be implemented over the entire dataset. Additionally, the fact that the ratio for individual VOCs does not hold constant when moving between different sample sets means that any future analysis cannot use an individual VOC conversion factor to account for changes in temperature. This makes long term monitoring with any major degree of accuracy, with relation to quantitative analysis, extremely difficult. Each individual sample would need to be monitored as close to the conditions for the first measurement as possible. Even with this condition met, tracking relative amounts of key identification and degradation marker VOCs becomes difficult.

Another consideration is the difference between datasets collected at the high and medium temperature settings. This range is well within the parameters seen in real museums (The American Society of Heating Refrigerating and Air-Conditioning Engineers, 2011; Lukomski *et al.*, 2017) and highlights the real world challenge to monitoring open collections. Furthermore, it adds weight to the argument for collections being kept at the lower limit of their acceptable temperature range (see section 4.4 in PAS 198, 2012) for as much time as possible to limit the rate of degradation.

6.3.5.5 Issues frustrating quantitative analysis with variable temperatures

Within conservation, there is an adage, put forth by Stefan Michalski of the Canadian Conservation Institute, which states *"Double the life for each five-degree drop"*. The basis for this presumption come from formulas derived from the Arrhenius equation (Michalski, 2002). In essence, this tells us that as the temperature drops one would naturally see a reduction in the rate of chemical mechanisms which produce the VOCs. Therefore, one would naturally expect a lower normalized peak area of VOCs from any resulting analysis pertaining to a lower temperature.

Coupled with this phenomenon are the physical principles governing the uptake of compounds onto the fibre. Pawliszyn (2009, pp.20) notes that the distribution constant is temperature dependent and that lowering the temperature will increase this constant. Equations 1-15 and 1-16, which are taken from (Wei *et al.*, 2016) show the mathematical basis for this finding. The consequence of this insight is an increase of the amount of sample extracted onto the fibre at equilibrium.

The combined influence that temperature has on the resulting chromatogram, through both the rate of the reactions and the extent of adsorption onto the SPME fibres again highlights the difficult and complex nature of long-term uncontrolled open environment monitoring via SPME. The direct implications are that any numerical corrections, such as conversion factors are unlikely to be effective. This then directly impacts any explicit statement of concentrations surrounding the object. While statements of concentration can be calculated, they may lack the accuracy which is needed for long term monitoring.

Returning to the original research questions for this experiment, specifically the third research which asked if it possible to distinguish the data sets by the temperature at which the SPME fibres were exposed? It is now clear that changing the exposure temperature significantly affects the overall VOC profile. If a sample set is measured at a lower temperature to its predecessor, then its profile will have a lower normalized peak area. This allows researchers to distinguish data sets based on the relative levels of their VOC profiles. However, due to the individualistic response of the VOCs within the VOC profile, it is not possible to retroactively 'correct' for changes in temperature by way of a conversion factor.

6.3.6 Ability to differentiate samples exposed at different temperatures based on degradation level

We now know that the VOC profile emitted from historic polymer objects is altered via two pathways – through additional ageing and through changing the temperature used for data collection. Furthermore, while the above work has merit in an academic sense by virtue of its discoveries regarding the relationship between VOC profiles and temperature, in a real-world historic environment the goal is to monitor artworks whose profile may initially be unknown. As such the ability to clearly answer the final research question of whether it is possible to differentiate an aged sample from an unaged sample when each has been investigated at a different temperature is of vital importance in judging the level of change an object may have undergone between dates for sampling.

Both Table 6-11, which relates to the CA-CW samples and Table 6-14, which relates to CA-NewCW, are complex to decipher, especially when the relative abundances of the five VOCs chosen are inter-dependent on each other. It is not easy to visually distinguish the differences between the different sample conditions via these tables alone. Therefore, another tool must be utilised to investigate if it is possible to differentiate the samples based on ageing duration and exposure temperature. One tool which has been widely used within the heritage community is multivariate analysis (Strlič *et al.*, 2009; Lau *et al.*, 2013; Visco *et al.*, 2017) where it is used to gain a deeper understanding of an object though the lens of multiple different variables. These methods have also been applied to SPME analysis in other fields of research whose central research themes overlap with this research, albeit within a different context (Oliveri *et al.*, 2012; Souza-Silva, Jiang, *et al.*, 2015; Giannetti *et al.*, 2017; P. Silva *et al.*, 2017). Within this analysis Principle Compound Analysis (PCA) will be utilized for its ability to maximise the variability explained while reducing the number of dimensions needed.

PCA was conducted, via Matlab, on the datasets for both the CA-CW and CA-NewCW samples. The datasets contained the information outlined in Table 6-11 (pertaining to CA-CW) and Table 6-14 (pertaining to CA-NewCW). Before PCA was conducted the dataset was standardized to Z-scores. In doing so, the variance of each variable (VOC) was standardized so that its standard deviation was equal to 1. This is because PCA is sensitive to the scaling of the original variables and as can be seen in Table 6-11 peak areas can vary over orders of magnitude. Had the Z-score not been utilized then the resulting plots would have been automatically scaled to favour those VOCs with higher relative values.

Figure 6-18 shows the resulting PCA biplot from the analysis of the five VOCs of interests for the CA-CW samples. The first item to note are that when combined PC-1 and PC-2 account for over 95% of the variability in the datasets. This implies that by only looking at a biplot of the combination of these two principal components we can understand the majority of the variability of the entire dataset and that looking at further principal components would not yield any further insights.

The second item of note is PCA loadings (shown in the graph as solid blue lines) which indicate which variable influences a principal component. In the case of CA-CW, these loadings are broken into two groups – PC-1 is strongly influenced by plasticisers while PC-2 is influenced by degradation markers such as benzaldehyde. This, in turn, allows for interpreting the placement of the scores (read samples) on the biplot. Those scores which are placed positively on the PC-1 axis have a greater abundance of plasticisers than those with a negative placement. Likewise, with PC-2, those scores which have a positive PC-2 value have greater levels of degradation products relative to those which have a negative value.

Principal component analysis is a method which converts the correlations, if any, among the different variables which in this case is the VOCs, into a 2-D graph. The axes of the PCA graph are ranked by the amount of variability each contains, with principal component 1 explaining the largest share of variability. Samples which are highly correlated cluster together within the 2-D space. However, as the axes are ranked by importance, differences between clusters which appear to be similar in size in each axis direction do not reflect the true amount of difference between the clusters. For example, if Cluster A is equidistant to Cluster B on the PC-1 axis and to Cluster C on the PC-2 axis then in reality the differences between Cluster A and B are greater than the differences between Cluster A and C due to PC-1 explaining a greater proportion of the overall variability of the datasets. It is these properties which will be exploited in order to gain a better understanding of how the interplay between the five VOCs affects the different groupings of samples.

In the initial interpretation of the biplot, the most striking feature is the grouping of the low-temperature exposure sets. These three datasets, which differ in accelerated ageing time are indistinguishable from each other. This is relevant to practical conservation in two ways. The first being that VOCs analysis of historic polymer objects, when they are housed under cool-storage conditions, should not be done at temperatures this low. This is due to the suppression of VOCs being emitted from the objects at these low temperatures, which in turn masks their true degradation levels. The second practical takeaway is that storing objects at these cool temperatures has a dramatic effect on their emission and as such would lead to a longer lifespan (Michalski, 2002).

The most striking aspect of the resulting PCA of CA-CW (Figure 6-18) is that compounds cannot be differentiated based on single VOCs analysis alone. For example, PCA shows that unaged (Black) and 4-week samples (Pink), both examined at the medium temperature level, cannot be separated based on their respective levels of plasticisers. However, if one adds the influence of degradation products then the two sample sets are separable. A more dramatic example, at least in terms of the real-world categorisation of samples, again involves the unaged samples (Black) at the medium exposure temperature setting. When compared (in terms of their plasticiser content) to the 4-week sample measured at the higher temperature (Red) it is the unaged sample that ‘appears’ to be aged to a greater degree based on the premise that more ageing leads to more plasticiser loss. In this example the difference in temperature is skewing the interpretation of the theory that samples aged for longer will exhibit lower levels of plasticiser. It is only when degradation products are taken into account that we are able to see that the 4-week sample has a greater degradation profile.

As was discussed in the literature review in Chapter 1 both VOC analysis and SPME have been widely used in other fields, specifically, the medical industry where they have helped in the development of *VOC profiles* (relevant VOCs which when grouped together in fixed proportions provide researchers with more information about the sample than if each VOC was interpreted separately) to diagnose specific diseases (Di Francesco *et al.*, 2005; Saalberg *et al.*, 2016). The concept of VOC profiling is also appearing within heritage science with the development of profiles for watercolours (Thomas, 2012), Asian lacquers (Schilling *et al.*, 2016) and for classifying the degradation of polymer artworks (Curran *et al.*, 2018). This precedent shows that the concept of using a specific profile rather than single VOCs is the most efficient method at accurately determining the subtle differences between similar samples.

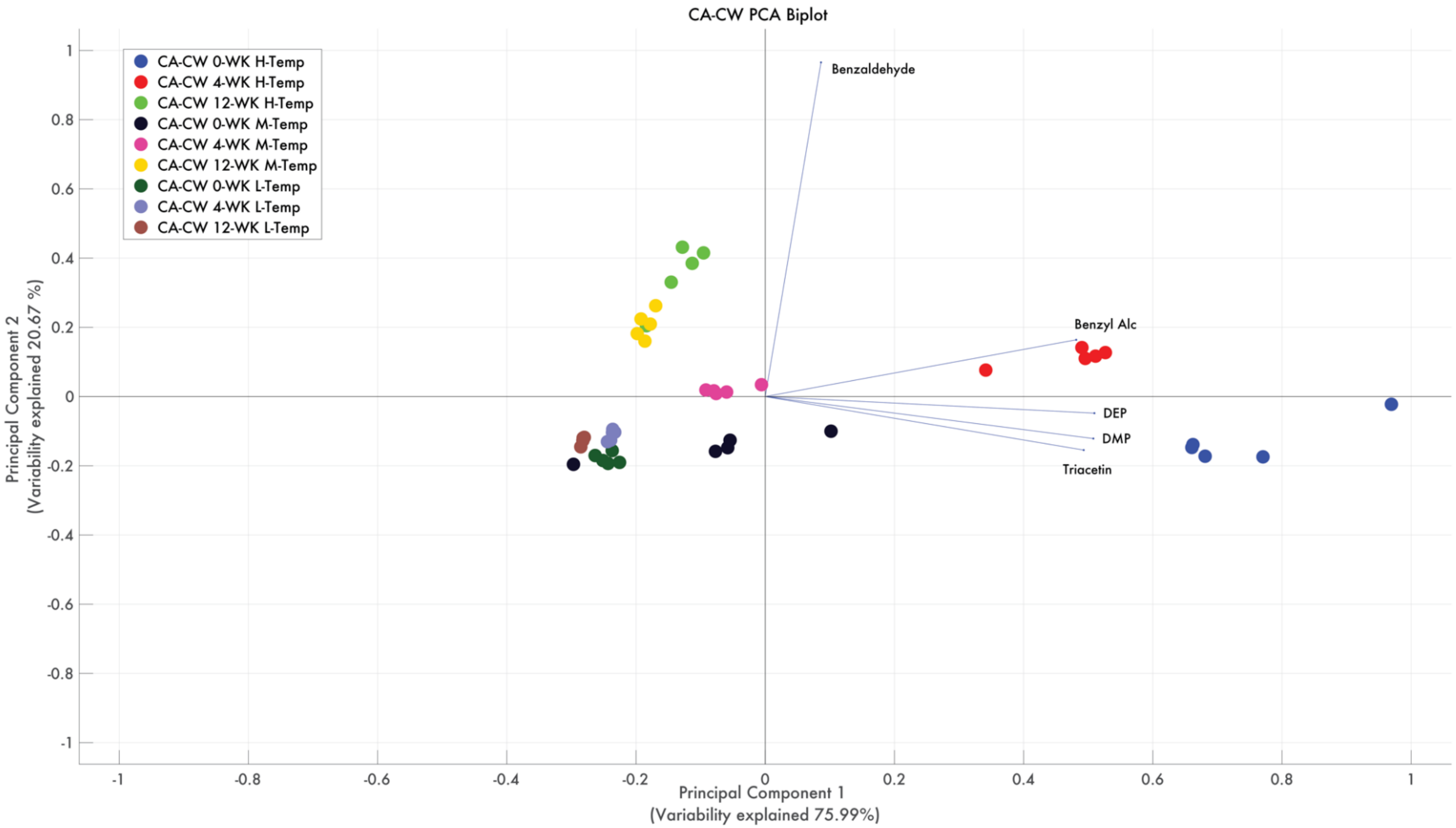

Figure 6-18 – PCA biplot of the CA-CW samples. The blue lines represent the loadings and show that PC-1 is mostly influenced by the three plasticisers found to be present while PC-2 is mostly influenced by the degradation products. However, as both benzyl alcohol and benzaldehyde are positive in the PC-1 axis they therefore contribute somewhat to the variability explained by PC-1

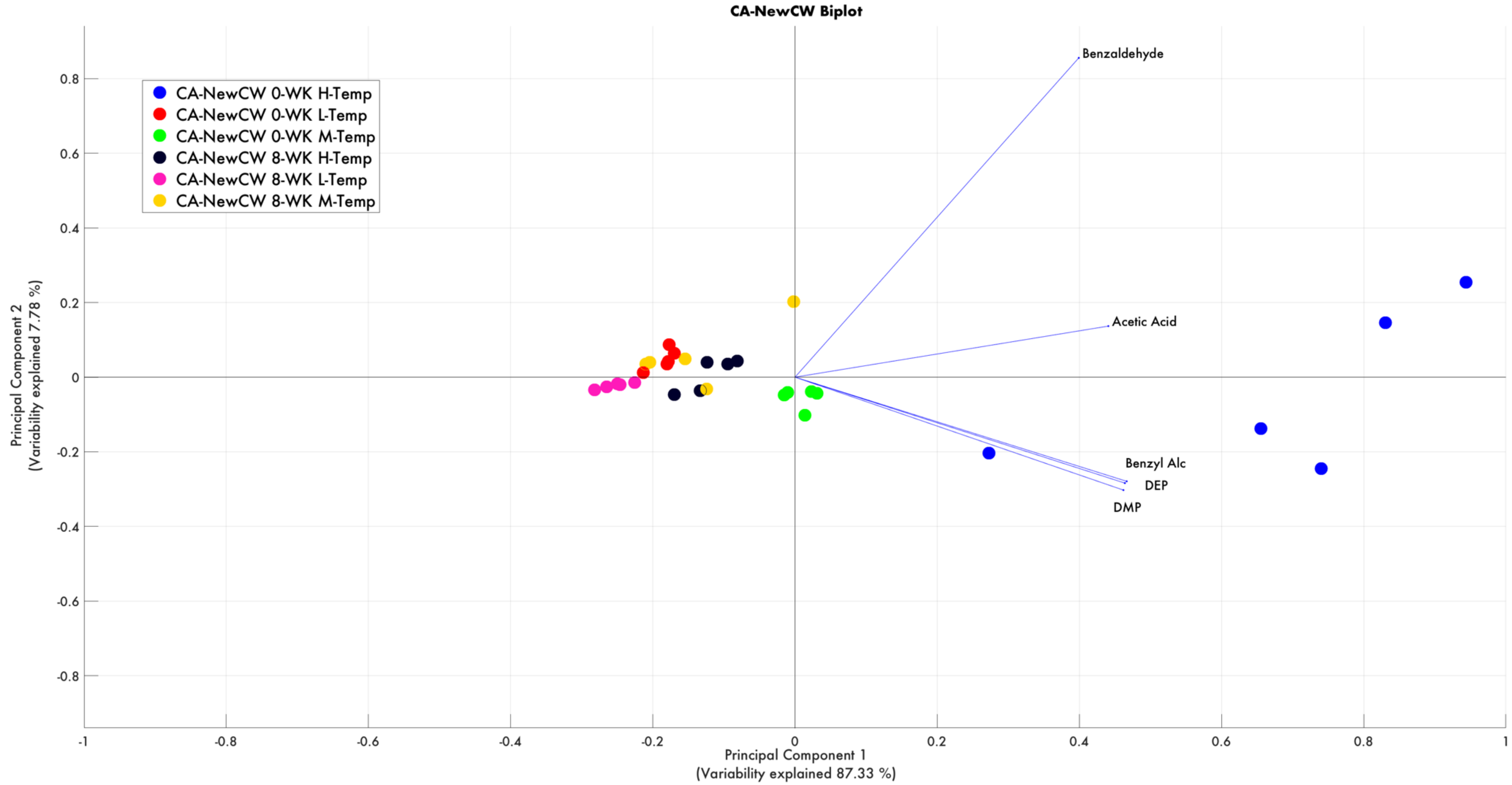

Figure 6-19 – PCA analysis of the CA-NewCW dataset. Note that only the unaged samples at high (blue) and medium (green) temperatures are separated. As in the previous PCA analysis, PC-1 is influenced by plasticiser and degradation products. PC-2 is mostly influenced by degradation products.

However, there is an issue in relation to the effectiveness of the SPME methodology for long-term monitoring presented by the PCA findings.

This issue stems from examining the 12-week samples at the high (Green) and medium (Yellow) temperature for CA-CW. Even with PCA providing VOC profiling of samples these two sample sets are almost indistinguishable from each other. In one sense this is a positive aspect – it means that when samples have reached a certain point of aging their VOC profiles are somewhat resilient to fluctuations in temperature for data collection. More explicitly stated – anything degraded will be classified as degraded.

Yet, the counter point to this is that the exact degree of degradation at which this effect becomes noticeable is difficult to determine and as such tracking changes over long time periods still requires stable conditions for the SPME methodology to work efficiently. The root of the issue is that when sufficient aging has occurred the amount of plasticiser emitted from the sample is depressed. When this happens the lack of difference in the VOCs making up the loadings of PC-1 (in these examples it is plasticiser content) between the two data sets is not enough to separate them with confidence. The methodology does not have sufficient information to work with. This issue is seen in the results from the PCA analysis of the CA-NewCW datasets. In this analysis, only the unaged samples from the high (Blue) and medium (Green) temperature settings are separated. All other samples, even those from the low temperature setting are clustered together[9]. And therefore, in this case one cannot tell if they are grouped due to ageing level or exposure temperature, or a mixture of both.

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[9] Note that the colour coding of the samples on the PCA figures is to distinguish sample types and can have the effect of producing groupings which would not be discernible otherwise.

The difference in appearance between the two PCA plots is a visual representation of the issues which were discussed earlier in section 6.3.4. The fact that most of the variation in the CA-NewCW samples is explained by PC-1, which corresponds to the intensity of all investigated VOCs, means that the samples are clustering more according to overall emission rates than any more subtle factors. This reflects the fact that all VOC levels were found to be lower after ageing in these samples. Had the degradation products not decreased on ageing the resulting biplot may have been similar to that of CA-CW.

The combination of SPME analysis and PCA has also provided greater information than the complementary techniques used such as FTIR. In the case of the CA-CW dataset the SPME/PCA combination was able to separate out the majority of the samples based on their ageing and show that emissions from plasticiser had lowered. However, when samples were examined via FTIR in order to calculate their degree of substitution and the amount of plasticiser lost the results were not as informative.

	CA-CW 2	CA-CW 7	CA-CW 11
Initial average DS	2.29 (.009)	2.27 (.023)	2.30 (.013)
Initial average Plasticizer %	14.73 (0.84)	15.94 (0.24)	16.96 (0.57)
DS Value - 4 WK	2.28 (.016)	2.30 (.037)	2.34 (.014)
Plasticizer % 4WK	15.90 (0.56)	17.28 (1.02)	19.58 (0.39)
DS Value - 12 wk	2.24 (.014)	2.24 (.042)	2.29 (.008)
Plasticizer % 12WK	12.48 (0.80)	12.83 (0.95)	14.19 (.59)

Table 6-17 - Values for the degree of substitution and the change in plasticiser % from the CA-CW samples used for FTIR analysis. Note that these values are unitless. Also note that after 12-weeks of ageing the plasticiser content appears to have increased slightly, something that contradicts SPME analysis. Note that the values in brackets are the standard deviation values for their respective sample.

Table 6-13 details the FTIR results when both the degree of substitution (DS) and the change in plasticiser were calculated using peak ratios[10]. Via FTIR analysis the change to the DS only shows a slight change, which when examined via a simple t-test is not statistically different. Analysis after 12-weeks of accelerated ageing shows a slight change with the plasticiser increasing. If one solely relies on FTIR analysis, then one would not be able to judge which of the samples had been subjected to accelerated ageing. However, SPME not only provides this information but also information regarding the types of plasticiser present and the types of degradation products present. This again highlights why the development of a consistent SPME GC/MS methodology for historic polymer artworks is so worthwhile – the information it provides cannot

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[10] Please note that a more in-depth explanation of how these values were calculated will follow in the next chapter as they will be utilized further there.

be matched by other techniques currently utilized by heritage professionals.

6.4 Conclusions

This investigation into the role temperature for data collection plays in the SPME GC/MS data analysis has not only given answers to the original four research questions but it has also served as an example of the type and quality of information one may gain from undertaking such analysis.

In terms of specific research questions, the analysis of data has shown that –

- In general, as the extent of accelerated ageing increases then the relative amount of emitted plasticiser decreases while the amount of degradation products increases.
- However, in the case of certain degradation products SPME analysis is sensitive enough to indicate when the degradation mechanism producing a specific VOC has slowed or stopped, if that is the case.
- SPME analysis, when the fibres are exposed the same temperature, is sensitive enough to show the difference between unaged and aged samples.
- The methodology is also robust enough to be able to distinguish between samples which have similar ageing levels but have had the SPME fibres exposed at different temperatures.
- However, as the degree to which each VOC is altered by the change to the exposure temperature is different, it is not possible to apply a conversion factor to the resulting datasets to account for these changes.

- As the relative amounts of VOCs which make up the total emitted from a sample are intra-dependent and as there is a large volume of data to process it can be difficult to differentiate unaged samples from aged when the SPME fibres have been exposed at different temperatures. Furthermore, differentiation cannot be achieved via the data from a single VOC.
- However, when pertinent VOCs are grouped together to form a VOC profile and Principal Component Analysis is applied to this profile it is possible to differentiate the samples into their ageing and temperature groupings. This works best when the samples behave as one would normally assume i.e on ageing plasticiser emissions decrease while volatile degradation products increase.

This research has also highlighted a number of practical issues with the experimental design implemented. Most noticeably, in some instances, accelerated ageing can mask the data which was originally desired. This can lead to a decrease in certain VOCs which in turn can skew any future analysis. There can be issues with cross contamination, either from cleaning products or from other objects. These alien VOCs can skew the interpretation of the TIC and may lead to misidentification of the base polymer. Additionally, bespoke samples can have issues with homogeneity which again can skew any future analysis.

Despite these challenges SPME analysis, especially when combined with PCA, has shown itself to be a very powerful tool. It provides significant information regarding how degradation and identification markers change during ageing. It also does this without the need for overly complicated sample preparation. Furthermore, it also outperforms current analysis techniques, such as FTIR, by providing a deeper and more consistent insight into the condition of the samples which is both non-invasive and non-destructive.

Chapter 7 Observations of Phenol during the Degradation of Cellulose Acetate

7.1 Introduction

Cellulose acetate is one of the oldest forms of a semi-synthetic modern polymeric material, having first been utilized as a replacement for the more unstable cellulose nitrate from the mid-to-late 1900s onwards (Schilling *et al.*, 2010). Within a museum context, the material is synonymous with problematic degradation patterns and troublesome storage requirements. It is noted as being one of the four most vulnerable polymers found within the collections of many different museum types (Littlejohn *et al.*, 2013). Much of this instability arises from two sources – in the early forms of the material it stems from *their "poorly stabilized and largely experimental formulations*" (Shashoua, 2008). The second source is the base chemistry formulation whereby acetic acid is formed via the deacetylation of the polymer leading to an autocatalytic reaction.

Many in the conservation community will be aware of the term 'Vinegar Syndrome'. Initially discussed in chapter 1, this degradation mechanism was extensively studied by the Image Permanence Institute, for movie films. In those studies, the release of acetic acid and controlling that release is shown to have major implications on the degradation of the polymer (Bigourdan *et al.*, 1998, 2000). However, over the past few years, there has been a growing body of research suggesting a third variable can contribute significantly to the often-rapid degradation of cellulose acetate – the presence of the plasticiser triphenyl phosphate (TPP).

First described by Shinagawa, Murayama and Sakaino (1992) the decomposition of TPP leads to both diphenyl phosphate (DPP) and phenol. The authors of that study suggest that the presence of this new DPP compound has a 'significant effect on the [cellulose triacetate] degradation'. The authors also note that the exact mechanism had yet to be outlined but followed the model laid out in Figure 7-1.

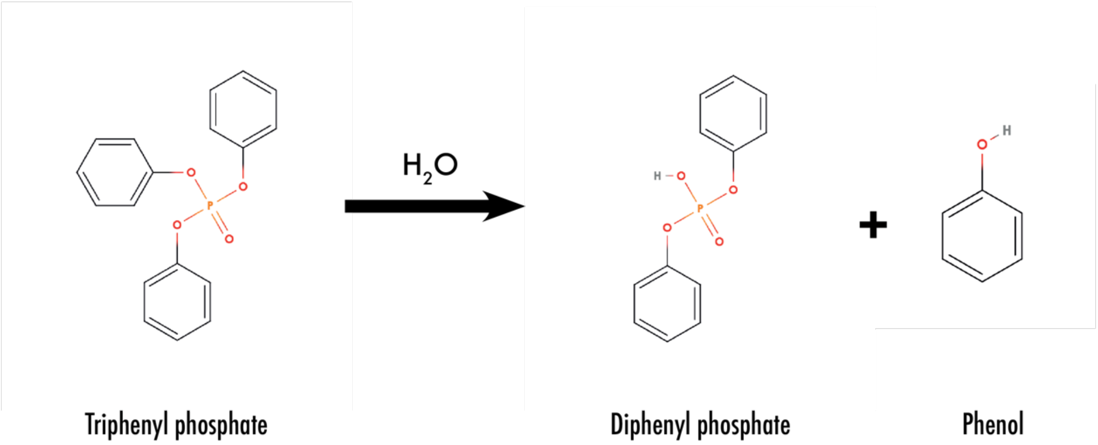

Figure 7-1 – The basic graphical representation of the mechanism for the production of phenol from TPP as set out by Shinagawa, Murayama and Sakaino (1992). Figure – Mr. Kearney

It is worth noting that the lack of a clear mechanism is not the only limiting factor of this theory. In the doctoral research conducted by McGath (2012), pH measurement was used to infer the production of DPP from TPP by way of hydrolysis. A sample of TPP was exposed to 100% humidity and 90 °C with pH measurements taken periodically. However, McGath was unable to replicate the reduction in pH seen by Shinagawa, and therefore concluded that no DPP (and consequently phenol) had been produced. This has left the issue of TPP-plasticized CA somewhat ambiguous in the conservation community. Additionally, Tulsi Ram (1990, pp. 24) notes that *"the presence of TPP is not contributing to the degradation of CTA at ambient temperatures."* Though this statement was in relation to the formation of phosphoric acid and not phenol.

Despite these communications, current literature features several studies which have reported on the higher rates of degradation of CA in conjunction with the presence of TPP. Tsang *et al.* (2009) noted a clear correlation between the condition of the CA objects and the presence of TPP, as did Groom (1999). In addition to this, they also observed direct evidence of the phenomenon of cross-contamination, which was also discussed by Curran *et al.* (2014). This occurs when objects that had not been plasticized with TPP were placed in direct contact with those that had been. Consequently, they exhibited higher degradation than those which were not in contact with a TPP-plasticized object.

Furthermore, while examining the best workflow for solid phase microextraction (SPME), utilizing a CA sculpture from the artist Naum Gabo, this author noted the high levels of phenol being emitted from one part of the object compared to other areas (Kearney *et al.*, 2018, 2020).

While much of the research has been focused on the production of acetic acid and monitoring this 'vinegar syndrome', the prospect of a manufacturing additive (TPP has a fire retardant role as well as acting as a plasticiser (Mazurek *et al.*, 2019)) having a greater role in the degradation of the polymer is of significant value to warrant further research. If the evidence points towards TPP's excessive influence on the stability of CA, a case can be made for screening for it before accession into collections and for the examination of objects already present.

SPME analysis offers a unique opportunity to study this issue due to its sensitivity to small concentrations of compounds, its selectivity to a wide range of compounds and its inherent non-invasive & non-destructive methodology. Should the conclusions from this research prove Shinagawa *et al.* (1992) correct then a new method for the screening, via the presence of phenol, of historic polymer samples for a predisposition for rapid degradation will have been validated. This would, in the future, provide conservation scientists with an additional tool to study and prolong the lifespan of CA-containing objects.

In an effort to explore both the effect of TPP on the degradation of CA and to explore its ability to produce large levels of phenol we examined a number of CA samples in conjunction with objects which displayed a similar degradation pattern to those reported in the literature. Our central research questions were –

- Can phenol be detected from triphenyl phosphate plasticized cellulose acetate when analysed via SPME?
- Are phenol levels linked to degradation?
- Do cellulose acetate samples, plasticized with triphenyl phosphate exhibit higher levels of degradation than those which are plasticized with other products?

7.2 Methodology

7.2.1 Sample Composition

Three main types of samples utilized during this study were –

- bespoke cellulose acetate samples whose manufacture and composition has been set out in chapter 3
- industrial samples – A sample of CA which was industrially made was used. This was likely manufactured in the 1960s and was plasticized with DEP
- museum Teaching collection – A sample from two different objects, which form part of the teaching collection at the Victoria

and Albert Museum, were analysed. Their exact composition was unknown before analysis.

FTIR spectroscopy was used as a validation tool to confirm the composition of each of the samples. This was most pressing for the industrially made type and the two object samples acquired from the Victoria and Albert Museum.

The spectra from each sample were compared to reference spectra of both TPP & DEP using the FTIR methodology set out in Chapter 3. Furthermore, the criterion in order to confirm the presence of TPP was a peak match at circa 782 cm^{-1} (Skornyakov *et al.*, 1998)

Figure 7-2 shows the FTIR spectra between 800 & 650 cm^{-1} and shows that the only sample not to contain TPP in its spectrum was the industrial sample CA-CW.

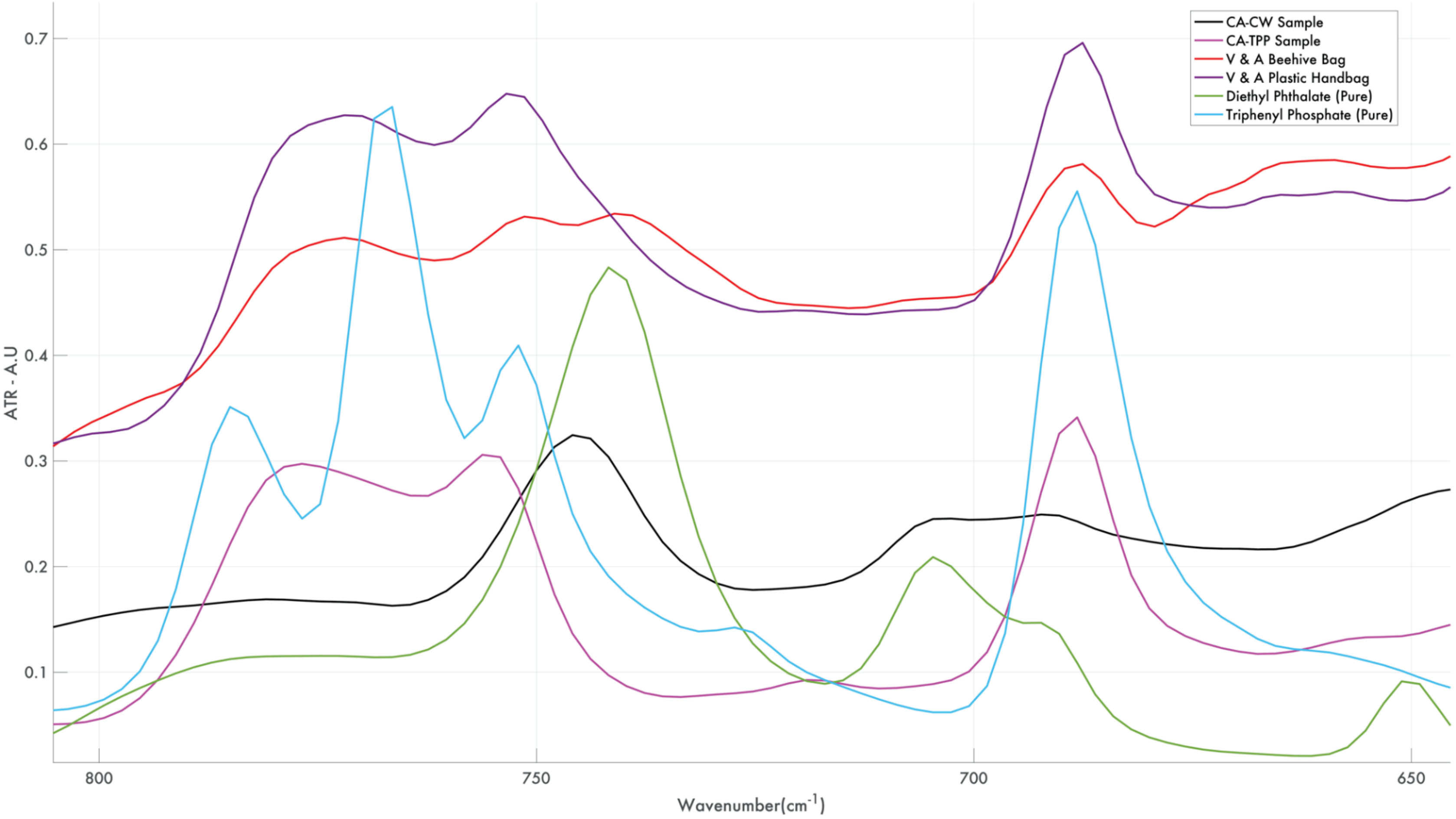

Figure 7-2 - A close up of FTIR data highlighting the area where TPP would be found circa 782 cm^{-1}. Note that both the V & A samples (Red and Dark Purple) and the CA-TPP (Light purple) sample have peaks matching that corresponding to TPP (Blue) while CA-CW (Black) has peaks accociated with DEP (Green).

7.3 Results

7.3.1 Initial Results

Both bespoke samples and the industrial sample were examined using SPME GC/MS, before accelerated ageing took place, in order to provide a benchmark for future ageing and to confirm that phenol was not present in any of the resulting chromatograms. The insert to Figure 7-3, highlights the lack of phenol in any of the samples. Only the CA-DEP and CA-CW samples contain DEP. However, TPP is not present in any chromatogram as it is not possible to detect it using SPME due to its high boiling point (370 °C).

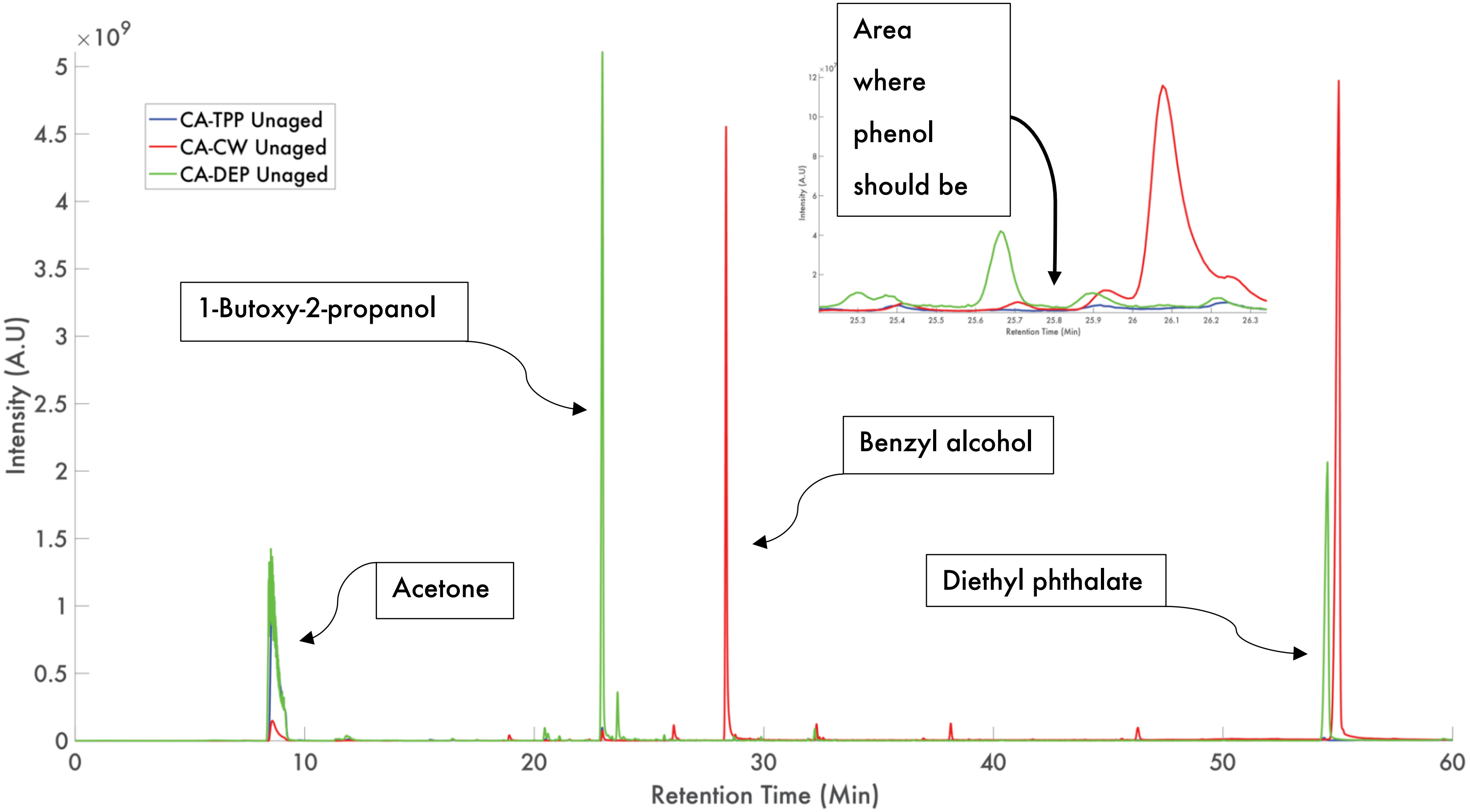

Figure 7-3 – Shows the resulting TIC from the unaged samples of CA-TPP (Blue), CA-CW (Red), and CA-DEP (Green). The major peaks are listed – the peak corresponding to 1-Butoxy-2-propanol (m/z identifier 57 & 87; NIST R.Match 917) is thought to be from a cleaning produced used during the experiment prep as this compound is a common surfactant. The inserted image highlights the region where one would expect phenol to be found – none of the peaks present here are from phenol.

7.3.2 Condition after Four Weeks of Ageing

Samples appeared to have changed only slightly after completion of the first ageing cycle of 4 weeks, as can be seen from Figure 7-4 showing minor colour change between unaged and aged samples. SPME analysis confirmed this, as well as confirming the lack of any phenol formation. Despite the only slightly changed appearance, SPME analysis has the resolution to detect even minor changes. Normalized peak areas of benzaldehyde emitted from the CA-CW sample showed it increased from 1.12 to 2.75 indicating the possible further degradation of the sample[11]. Correspondingly, we see a reduction in the amount of DEP plasticiser found, decreasing from 104.53 to 65.48 after the ageing cycle. The loss of a volatile plasticiser such as DEP at the high temperature of our aging conditions is to be expected, however plasticiser loss at room temperature is also an important degradation mechanism in CA objects in museums.

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[11] It is also likely that some of this increase is from the oxidation of benzyl alcohol

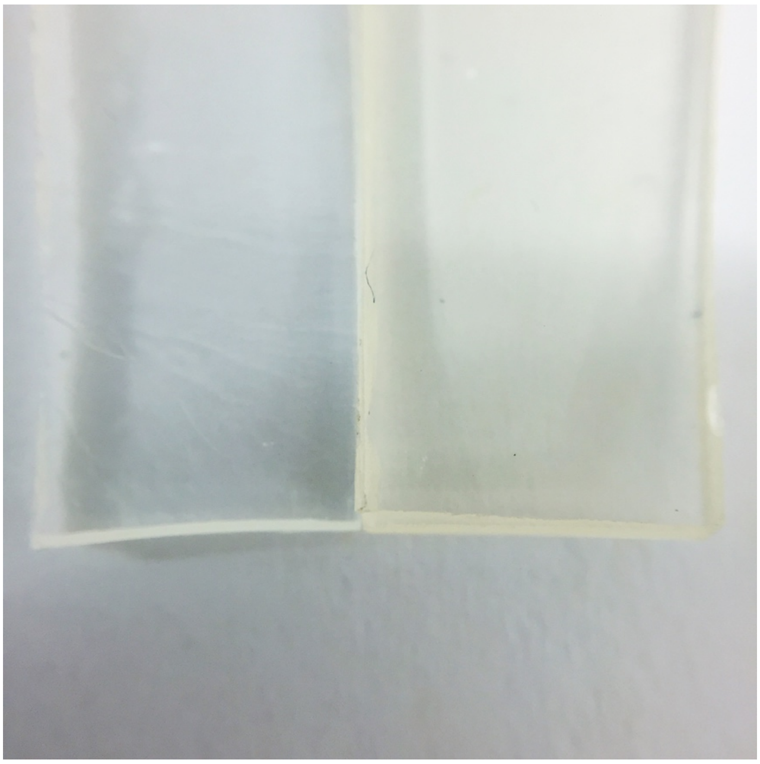

Figure 7-4 – An image of an unaged (left) and aged (right) samples of CA-TPP following the first ageing cycle. Note the slight yellowing of the sample on the right which has undergone accelerated aging.

A point to note is the lack of acetic acid formation in the CA-CW samples during this period. Despite evidence for increased degradation and a reduction in plasticiser, no evidence of acetic acid was found.

In essence, the results after the first ageing cycle displays a picture consistent with degradation patterns reported (long period of perceived stability before rapid degradation (Image Permanence Institute, 2001; Knight, 2014), however, the lack of acetic acid, or at least a level of acetic acid below the limits of detection for this methodology is seemingly at odds with the work by Knight (2014) who suggests that acetic acid should be constantly produced from the initial moment of degradation; however, this will be discussed further later.

7.3.3 Condition after further ageing

Samples were checked regularly during the accelerated ageing process. During the inspection after 6.5 weeks, it was discovered that the TPP-plasticized samples had rapidly degraded since the previous check (see Figure 7-5). The level of degradation was such that while the second ageing cycle was due to last a total of 8 weeks, the TPP samples were removed at this point (6.5 weeks).

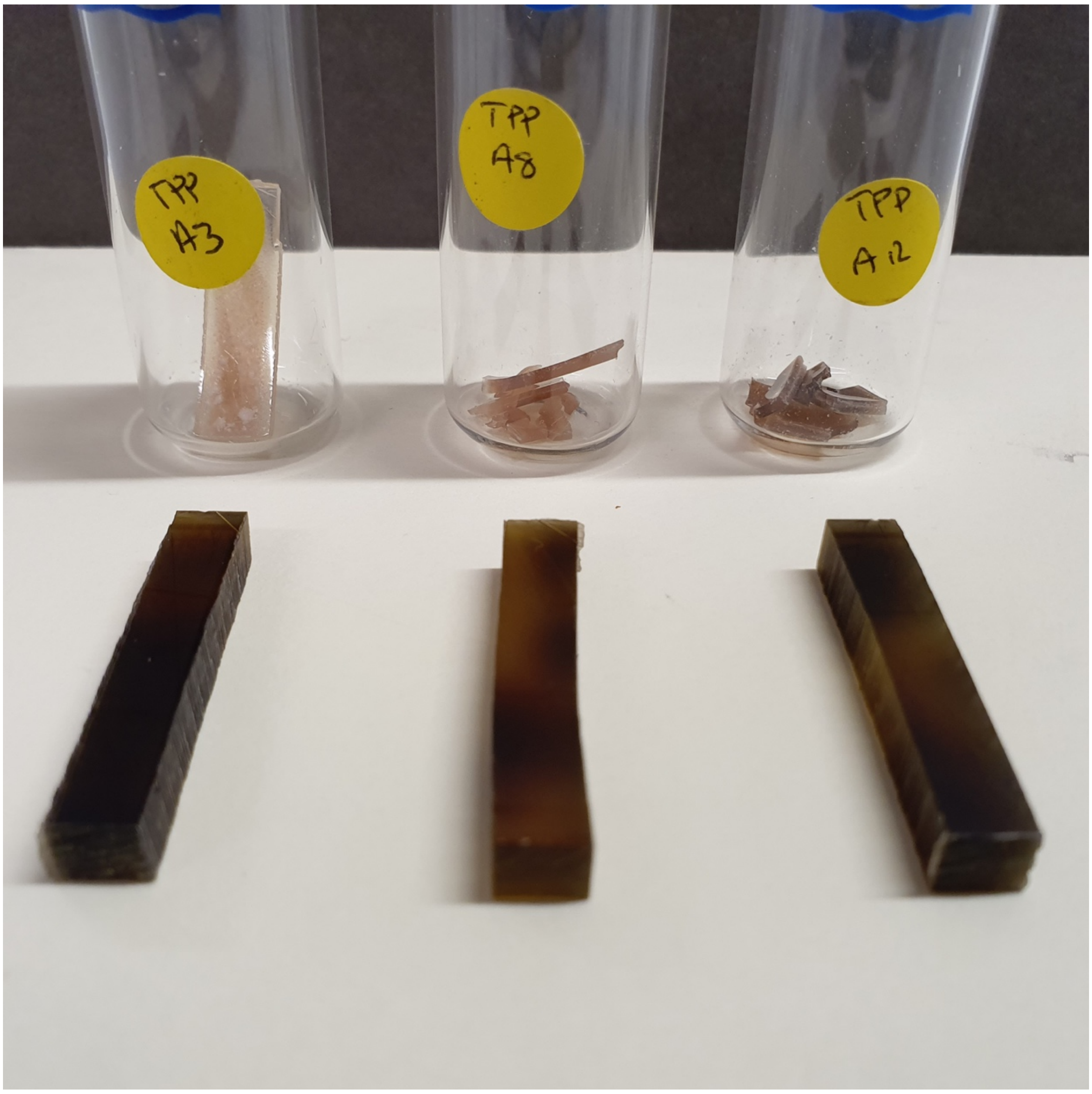

Figure 7-5 - A photograph of the different samples used during the experiment. Top left to right there is CA-TPP samples after a total of 10.5 weeks of ageing, the samples below are of CA-CW after 12 weeks of ageing. Note the difference in condition between the two sample sets with the CA-TPP samples having degraded to a much greater degree than the CA-CW. CA-TPP samples have crystals forming on their surface and have also cracked into a number of different pieces. In their original forms the CA-TPP samples were clear, while the CA-CW were a brown 'tortoise shell' which can be seen here.

On removal from the oven, a number of aspects were observable – some samples had begun to crack, while others were more stable.

Secondly, degradation was not uniform, with some samples having a much deeper change in colour (see Figure 7-5).

Table 7-1 shows the colourimetry results from three individual samples of TPP which had undergone 10.5 weeks of ageing. The table highlights not only the very considerable colour change induced by the ageing, where the lowest ΔE_{00} was 29.02, but also the variation between the three samples. The samples performed reasonably similarly to each other during the first ageing cycle, however, after a further six and a half weeks of ageing sample 12A was significantly darker than the other two samples. In terms of ΔE_{00}, sample 12A had a value of 52.98, which is over 20 units higher than the next sample, very large compared to the perceptible change (pc) limit of 1.5 that was suggested by Pretzel (2008, pp. 4).

Sample		**L**	**a**	**b**
CA TPP 3A Unaged		59.65	1.50	5.48
CA TPP 3A 4 WK		56.02	1.77	6.76
CA TPP 3A 10.5 WK		29.96	6.72	13.41
Change after 4 WK		3.63	-0.27	-1.28
Change after additional 6.5 WK (10.5 WK Total)		26.06	-4.95	-6.65
Total Change		**29.69**	**-5.21**	**-7.93**
ΔE_{00} Unaged -> 10.5 WK		**29.02**		
CA TPP 8A Unaged		57.34	1.68	6.08
CA TPP 8A 4 WK		51.74	1.89	7.01
CA TPP 8A 10.5 WK		25.24	11.36	18.07
Change after 4 WK		5.60	-0.21	-0.93
Change after additional 6.5 WK (10.5 WK Total)		26.50	-9.47	-11.06
Total Change		**32.10**	**-9.68**	**-11.99**
ΔE_{00} Unaged -> 10.5 WK		**30.87**		
CA TPP 12A Unaged		69.04	1.24	6.02
CA TPP 12A 4 WK		62.40	1.54	7.56
CA TPP 12A 10.5 WK		9.58	11.53	10.56
Change after 4 WK		6.64	-0.30	-1.53
Change after additional 6.5 WK (10.5 WK Total)		52.82	-9.99	-3.01
Total Change		**59.46**	**-10.29**	**-4.54**
ΔE_{00} Unaged -> 10.5 WK		**52.98**		

Table 7-1 - Shows the results from colour analysis of the CA-TPP samples. Note the difference in ΔE_{00} values between the three samples. Note that 3A, 8A, and 12A are individual samples from the overall larger batch of samples which were subjected to accelerated ageing.

An additional observation noted was the presence of liquid (Figure 7-6) on the surface of many of the samples. While these were liquid on direct removal from the oven, they formed into white needle-like crystals when samples were placed into a fridge for storage.

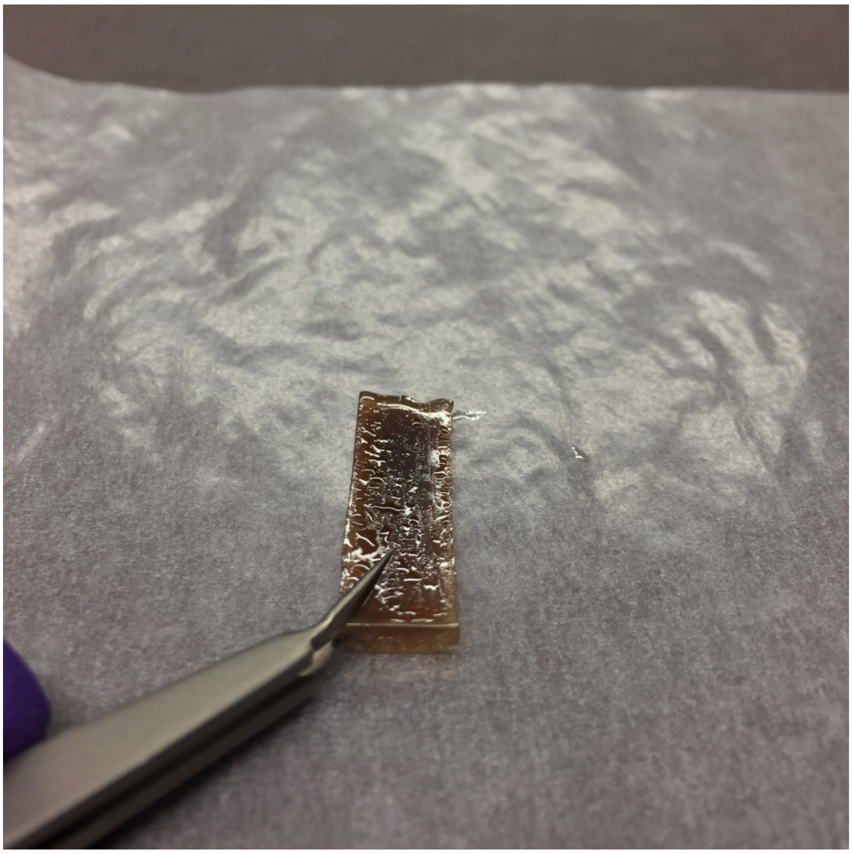

Figure 7-6 – An example of the liquid found on the surface of the samples shortly after removal from the oven. Once placed in the fridge this liquid formed into white crystals.

SPME GC/MS analysis of the TPP samples showed a significant change in the profile since the initial ageing cycle (Figure 7-7). The presence of phenol and its corresponding intensity was the biggest change between the two sets. Phenol (m/z identifier 94) was the most abundant compound detected from the five repeat measurements of TPP samples. The normalized peak area for the five repeats ranged from 36.90 to 49.14. The detection of phenol, and to such an intensity, gives further weight to the observations by both (Shinagawa *et al.*, 1992; J. S. Tsang *et al.*, 2009)Shinagawa et al. (1992) and Tsang *et al.* (2009) and contradicts the work by McGath (2012). In addition to the detection of phenol, acetic acid was also detected, it was also the second most abundant compound found. Again, this is in keeping with the degradation profile associated with cellulose acetate samples.

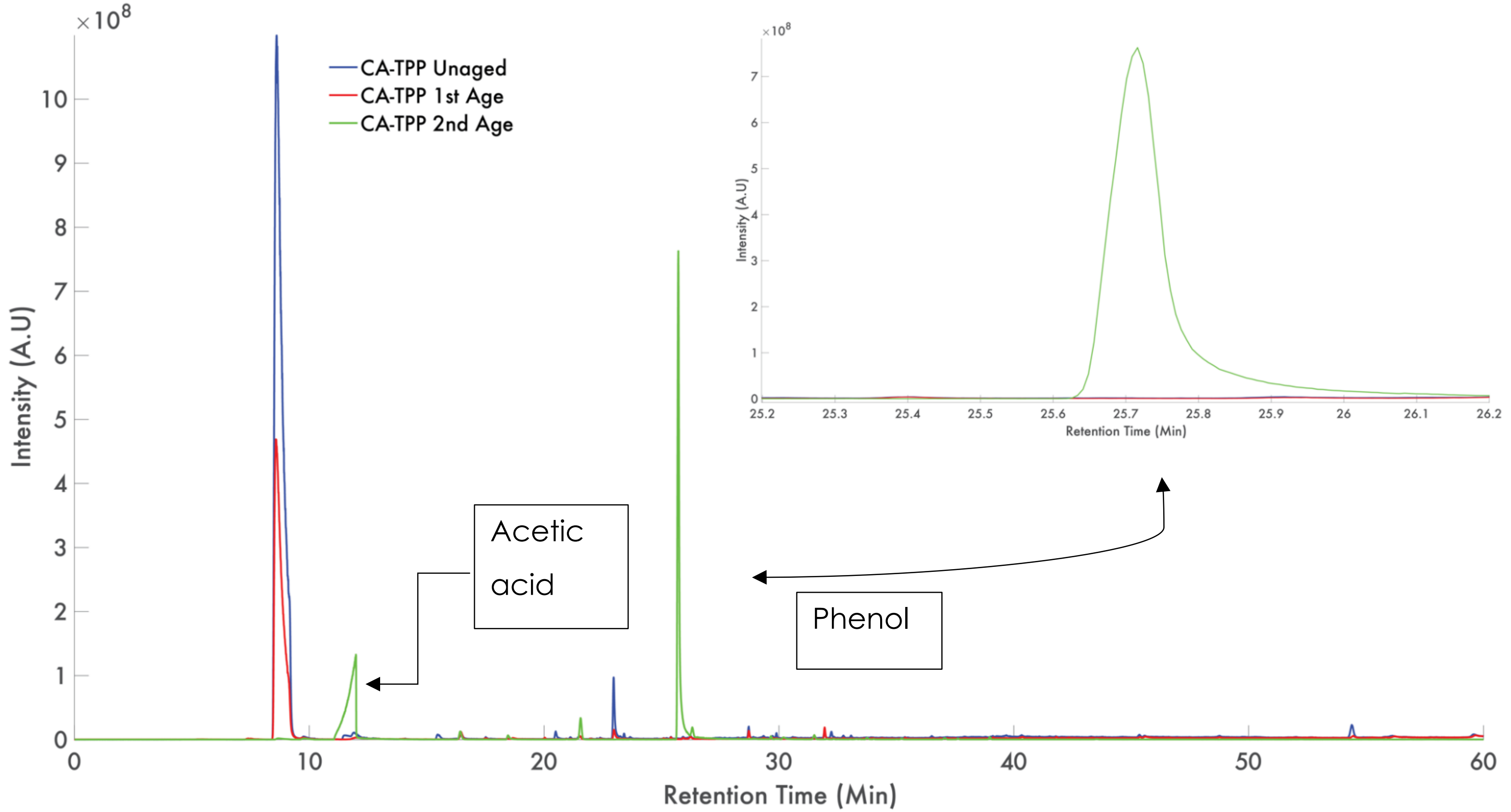

Figure 7-7 – The TIC from the CA-TPP samples for the three different ageing sets. Phenol is formed after the second ageing cycle. The inset image shows that it is only present in this analysis set. Furthermore, acetic acid generation has also increased after the second ageing cycle.

While not a quantifiable metric, upon opening the desiccator that held the samples during ageing, there was an intense smell of phenol. Despite the presence of acetic acid, there was no noticeable smell associated with it.

Figure 7-7 shows the progression of the TPP sample after each stage of accelerated aging. Between the unaged and 4-week aging sets there is little change to the sample. Yet there is significant change to the VOC profile following a further aging round (leading to a total age time of 10.5 weeks), with the emergence of phenol being the biggest difference between the three different sets. In contrast to these results were those from the CA-CW industrial samples that were plasticized with DEP and showed no sign of phenol nor any acetic acid Figure 7-8. Further to this, sample no. 5 shown in Figure 7-8, while not part of the samples used in this thesis. However, it was manufactured in a similar way to the CA-DEP samples used but has been aged for 120 days under the same conditions as the other aged samples. It has no obvious signs of degradation, which is in contrast to the samples of CA-TPP which were aged to a lesser degree yet show serious signs of degradation. These observations indicate that phenol production is the result of the presence of TPP and not associated with the DEP plasticiser and leads to accelerated degradation rates.

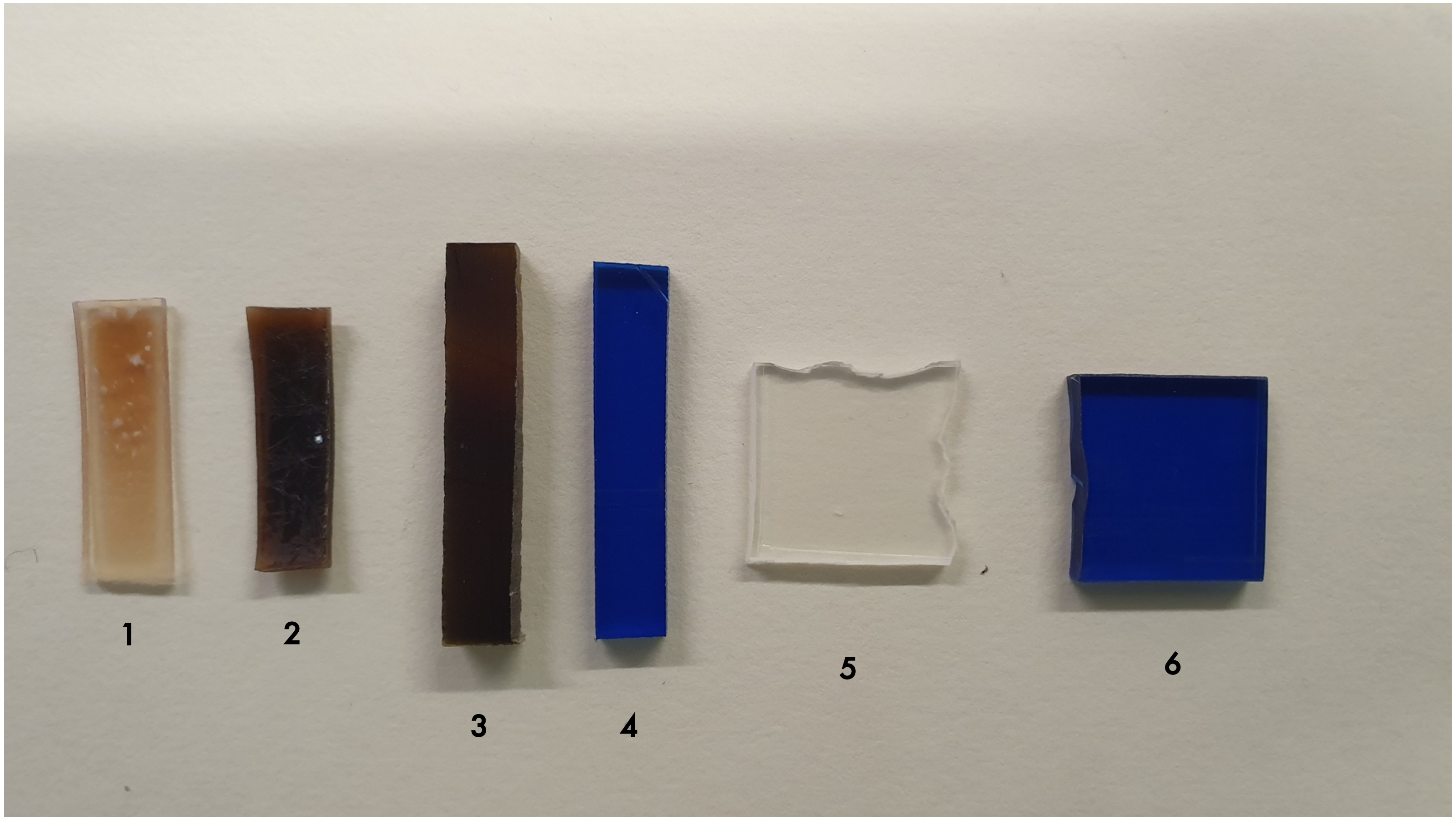

Figure 7-8 - A photograph of the different samples used during the experiment. 1 - CA-TPP 2; 2 - CA-TPP 7: 3 - CA-CW 2: 4 - CA-NewCW 6. The two extra samples on the far-right hand side are samples of 5 - CA-DEP and 6 - CA-NewCW respectively. Both samples 5 & 6 have undergone a total of 120 days aging at the same conditions than the others and show no visible signs of degradation. This illustrates the degree to which the CA-TPP samples have aged in comparison to similar samples which contained no TPP.

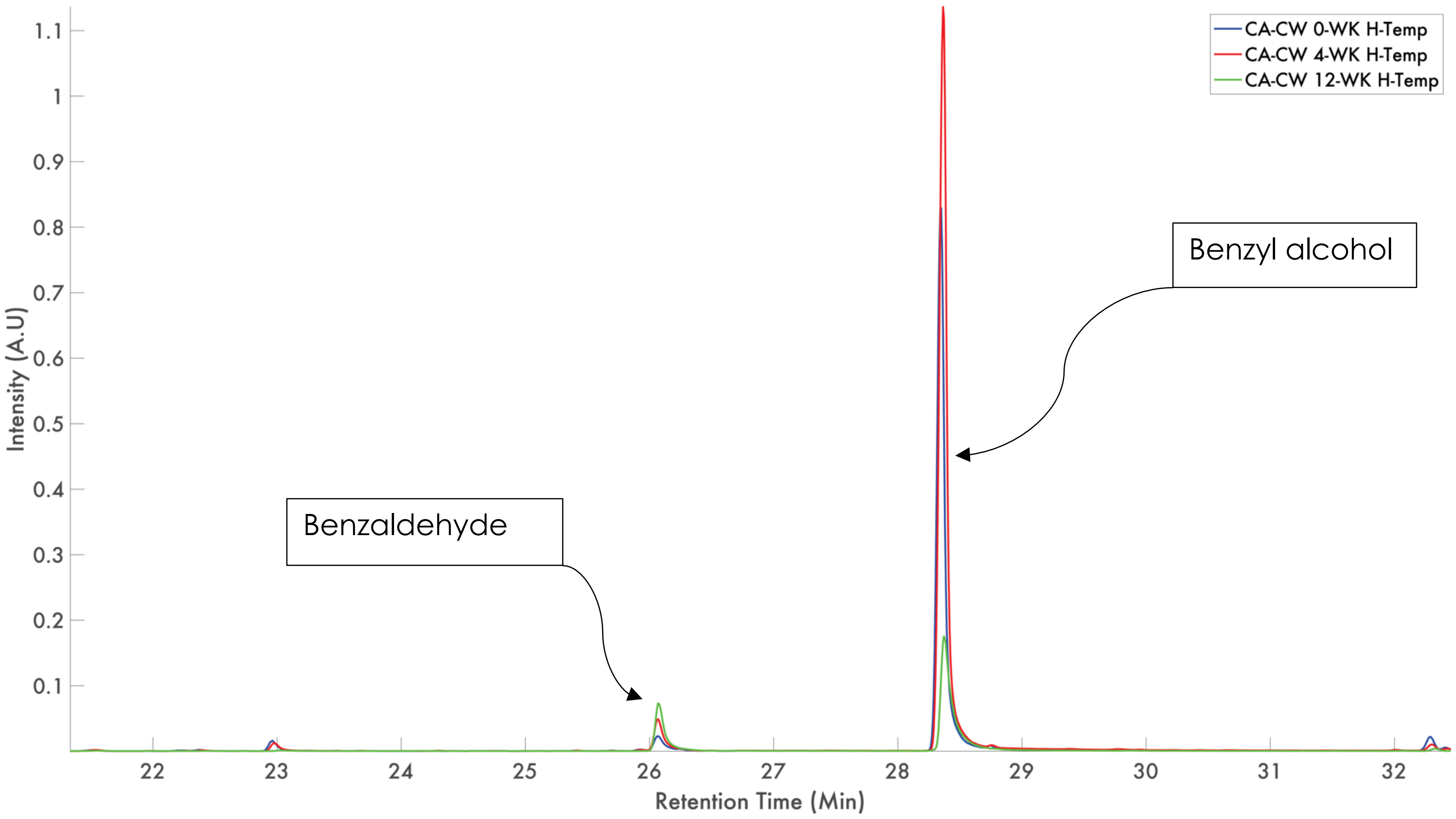

Figure 7-9 – A close up image from the TIC of CA-CW samples aged for different periods. This figure shows the progression of degradation from the industrial CA-CW samples. Over the course of the ageing cycles there is an increase in Benzaldehyde while Benzyl alcohol decreases. There is no evidence of phenol formation which would be seen circa 25 minutes. Note that this image is the same as that found in Chapter 6 Figure 6-10

7.3.4 Further insights into degradation & cross validation via FTIR

FTIR analysis of the samples provided a means to track their degradation during the different ageing cycles. It also acts as a secondary method to confirm the observations found via SPME GC/MS analysis.

Figure 7-10 shows the FTIR results from sample 8A from the CA-TPP set over the course of the different ageing cycles. There is a noticeable increase in the peak at circa 3400 cm^{-1}, corresponding to the O-H bond, that can be associated with the deacetylation of the cellulose acetate (Rowen *et al.*, 1947). This is further backed up by the reduction in the peak intensity for the C=O band at circa 1750 cm^{-1} (Giachet *et al.*, 2014). When compared to the FTIR spectra of the CA-CW samples (Figure 7-11) these changes do not appear despite being both naturally older and having been exposed to 1.5 weeks more of accelerated ageing than the TPP samples.

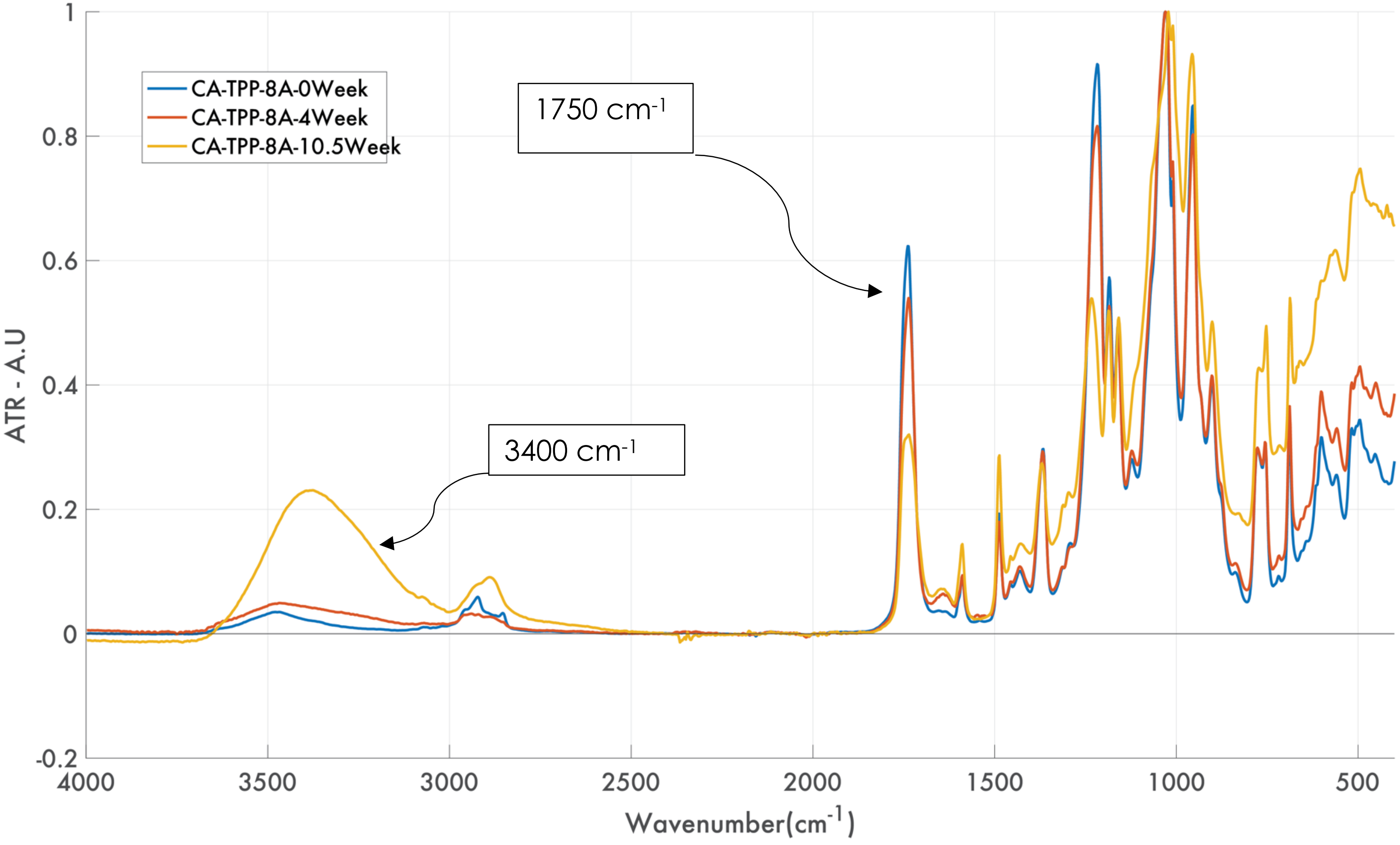

Figure 7-10 – FTIR spectra from the CA-TPP sample showing the progression of the degradation with an increase in the band at 3400 cm^{-1} and a decrease at 1750 cm^{-1}, both indicating degradation of the polymer.

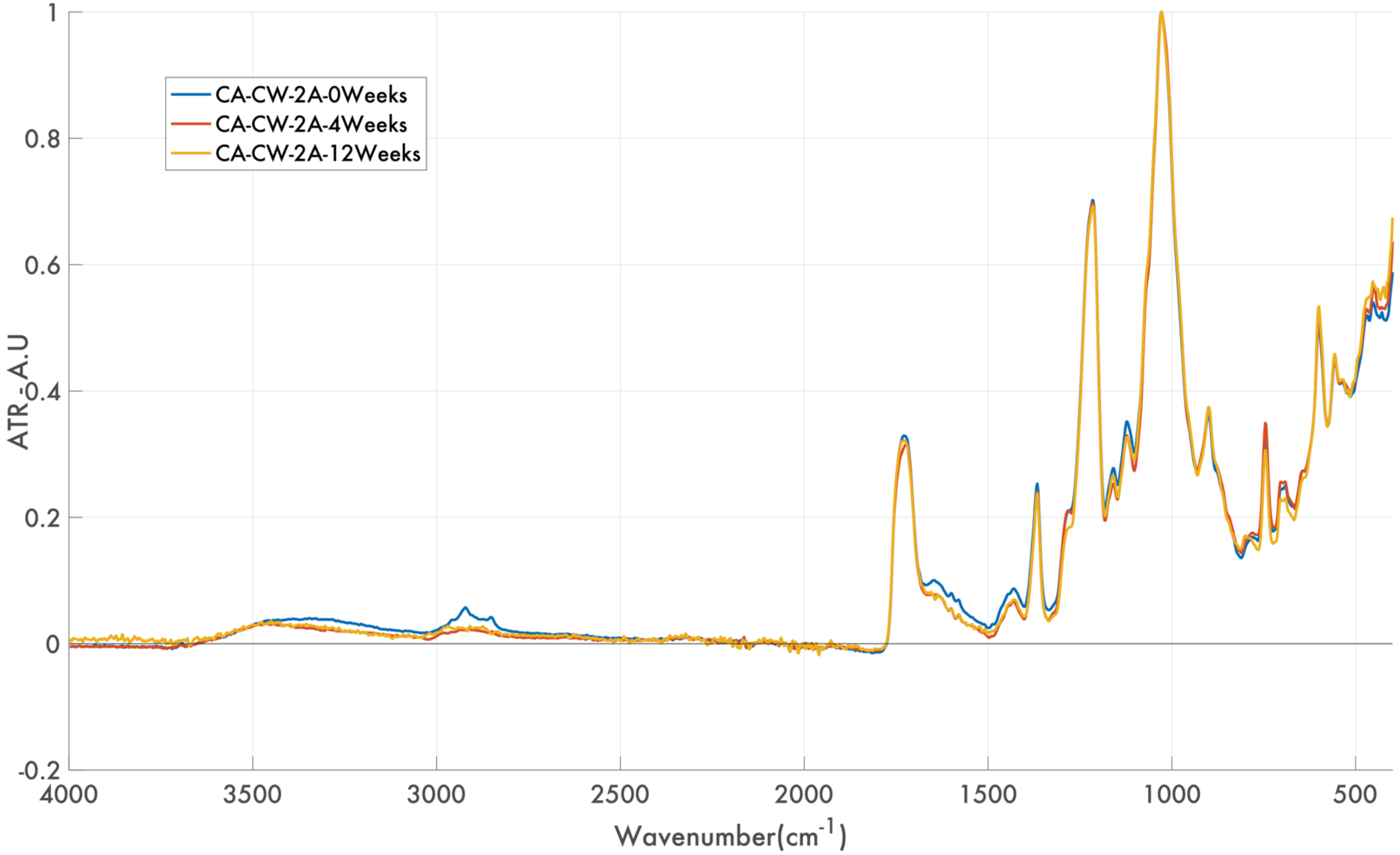

Figure 7-11 – In contrast to Figure 7-10 above, there is no similar features of degradation found in the FTIR spectra from the CA-CW sample.

In an effort to quantify the change to both the degree of substitution (DS) and the plasticiser loss, ratios of relevant FTIR peaks were calculated as per the method in Chapter 3.3.1. For the work presented in Table 7-2 the intensity of the peak at circa 1215 cm^{-1} was divided by the peak intensity at circa 1030 cm^{-1}. The results from this work place our samples into the '*cellulose diacetate'* category that was described by da Silva *et al.* (2017) and Mazurek *et al.* (2019).

The loss of plasticiser was also quantified via FTIR. As the characteristic peak for each plasticiser is different – in the case of DEP the intensity of the peak at circa 748 cm^{-1} was used, for TPP the peak intensity at 782 cm^{-1} was taken. In both cases, the peak intensity at 602 cm^{-1} was used as the reference peak. In the case of the TPP samples, this data was further processed into a plasticiser content percentage by way of a calibration curve developed by Dr Da Ros.

Two important aspects to note are that the values presented in Table 7-2 are taken from the surface and as such do not represent the bulk measurement of either DS or plasticiser change. Other researchers, such as Da Ros *et al.* (2021) have noted a correlation between DS calculated via surface FTIR and NMR where bulk measurements have been taken, however, they do not correlate exactly as plasticiser loss will be more readily lost from the surface, for example. This can be seen in the DS values given in Table 7-3 which were calculated by Dr Da Ros via NMR analysis on samples provided to her from the samples discussed here. While the values do not align the overall data tends do. Similarly, for a plasticiser, the measurements from the surface can be skewed because of poor material homogeneity or as will be argued later by surface deposits of plasticiser. Therefore, the values presented are known to not describe total change throughout the samples, but they are extremely helpful in understanding the degradation behaviour of the samples. The second aspect to note is that they are the average values of five measurement locations on the sample, and as such, there is the possibility that one location could differ greatly compared to the average, or as in the case with the TPP sample TPP-8, it differs significantly after 10.5 weeks of ageing from the other two samples tested.

Sample	TPP - 3*	TPP - 8	TPP - 12		CA-CW 2	CA-CW 7	CA-CW 11
Initial average DS	2.46 (.003)	2.47 (.004)	2.46 (.007)	Initial average DS	2.29 (.009)	2.27 (.023)	2.30 (.013)
Initial average Plasticizer %	12.47 (0.66)	14.02 (0.28)	11.92 (0.24)	Initial average Plasticizer %	14.73 (0.84)	15.94 (0.24)	16.96 (0.57)
DS Value - 4wk	2.38(.004)	2.39 (.005)	2.38 (.013)	DS Value - 4 WK	2.28 (.016)	2.30 (.037)	2.34 (.014)
Plasticizer % 4WK	7.83 (0.13)	8.97 (0.24)	7.21 (0.46)	Plasticizer % 4WK	15.90 (0.56)	17.28 (1.02)	19.58 (0.39)
DS Value - 10.5 Weeks*	2.35 (.144)	2.06 (.020)	2.38 (.002)	DS Value - 12 wk	2.24 (.014)	2.24 (.042)	2.29 (.008)
Plasticizer % 10.5WK	19.67 (8.07)	8.53 (0.69)	44.66 (0.66)	Plasticizer % 12WK	12.48 (0.80)	12.83 (0.95)	14.19 (.59)

Table 7-2 (A) – Details for the (average) results from degree of substitution and plasticiser calculations, via FTIR analysis, for samples which underwent accelerated ageing. Note that the values in brackets are the standard deviation values for their respective sample. Furthermore, note that each column represents an individual sample taken from a larger batch of samples of that material type. This single sample was measured five times producing the average value described here.

Sample	CA-DEP 2	CA-DEP 7	CA-DEP 12		CA-NewCW 3	CA-NewCW 8	CA-NewCW 12
Initial average DS	2.46 (.002	2.46 (.003)	2.46 (.002)	Initial average DS	2.24 (.029)	2.45 (.004)	2.45 (.009)
Initial average Plasticizer %	21.29 (1.24)	21.03 (0.56)	18.83 (0.61)	Initial average Plasticizer %	16.05 (1.07)	17.14 (0.31)	17.77 (1.38)
DS Value - 4wk	2.39 (.007)	2.38 (.006)	2.38 (.005)	DS Value - 8 Wk	2.45 (.011)	2.43 (.004)	2.44 (.008)
Plasticizer % 4WK	17.46 (0.68)	16.95 (0.54)	16.39 (0.38)	Plasticizer % 8WK	20.51 (0.52)	17.99 (0.14)	21.22 (0.45)
	Additional ageing not carried out on CA-DEP samples				**Additional ageing not carried out on CA-NewCW samples**		

Table 7-2 (B) – Continued table from 7-2 (A) above.

The results highlight the correlation in DS between CA-TPP and CA-DEP samples before accelerated ageing began. Both samples appear to be at the same starting position at the beginning of the experiments, which makes sense given that both were made from the same commercial CA. Contrasting with this is the DS values for CA-CW & CA-NewCW, which may have started life with a smaller DS or have seen a reduction in DS over their 50 year lifetime.

After the initial accelerated ageing cycle both CA-TPP and CA-DEP samples react similarly, with a decrease to a DS of approximately 2.3 from the initial starting point of approx. 2.4. However, the industrial samples did not experience this level of reduction. This was reflected in the SPME GC/MS results which showed only a small progression of degradation in the bespoke samples, and little to no progression from the industrially made CA-CW samples. It's worth noting that GC/MS results also highlighted the presence of dimethyl phthalate and triacetin in the CA-CW samples, both common plasticisers used in conjunction with CA. Their presence may be further stabilizing the commercial CA during the degree of artificial ageing used here and would not be quantified in the plasticiser ratio values given in Table 7-2. The results of NMR analysis which was carried out by Dr Da Ros and shown in Table 7-3 highlights the samples before and after the initial 4 weeks of aging. In it is shown a similar trend to that found using FTIR whereby CA-TPP samples change to a greater extent than those of CA-CW.

Sample	Before Aging	After 4 WK
CA-TPP	2.34 (0.04)	2.3 (0.01)
CA-CW	2.11 (0.01)	2.10 (0.01)

Table 7-3 – Results from NMR analysis of the DS for samples. Note that the values here are an average of three analysis runs and the values presented in the brackets are the standard deviations. This table shows that CA-TPP samples started at a higher DS and changed to a greater degree than CA-CW samples after four weeks of ageing.

The results from the second ageing cycle show a marked difference for the bespoke CA-TPP samples, whose DS decreased, to a low value of 2.06. Again, in contrast to this, the three CA-CW samples emerged from the accelerated ageing with a value of circa 2.24. Most significant is the relative change in the DS between the two samples. The CA-TPP 3 sample saw an 17% reduction in DS while the greatest change of DS for the CA-CW samples was approx. 2%.

The decrease of DS is clearly associated with the extreme degradation witnessed in both appearance and via SPME GC/MS analysis. Therefore, it is not the absolute value which is important in this circumstance but rather the relative change which the sample has undergone. This links with ideas put forth by Knight (2014. pp. 4) who noted "*Similar behaviour is seen in the degradation of paper, where the degree of polymerisation may be halved with only a small loss in tensile strength, but a further small decrease in DP causes a considerable loss of strength*". In essence, changes in DS leading to a change in DP, which were described in Chapter 1 as having only a minor role when compared to the damage due to the acid produced, might occur for a significant time before a critical threshold is reached and the object changes from appearing structurally sound to losing all structural integrity. The lack of (detectable) acetic acid from the CA-CW samples limits the accelerated degradation of the base polymer. Furthermore, the degradation of TPP into phenol is facilitating, to some degree, the increased degradation rate of CA, leading to the physical degradation pattern seen in our samples and the corresponding increase in acetic acid one associates with CA degradation.

As was mentioned previously, ATR-FTIR spectroscopy is a surface measurement. This fact provides insight into the counter-intuitive result of discovering more plasticiser present at the end of the second ageing cycle than at the beginning. Two of the three CA-TPP samples displayed this increase, however, as shown in Figure 7-6, samples had a liquid that turned into crystals once cooled atop their surface. Tulsi Ram (1990, pp. 24) suggests a mechanism by which this can occur (at least in the case of cellulose triacetate) – *"Degradation of CTA polymer under ambient conditions is accompanied by its ability to pick up more water in the deacetylated regions which facilitates exudation of the solid TPP to the surface."*

FTIR analysis of the liquid found on the surface of the samples after their removal from the oven showed that the compound was either TPP or DPP. It is natural then that TPP is presenting as an increase when using ATR-FTIR analysis. Furthermore, surface measurements can also account for DS values which seem to increase after aging, as was seen in sample CA-CW 7 & 11. However, both of these changes were within a margin of error and should be read as no change to the DS after ageing.

7.3.5 Confirmation of phenol presence

There are now clear examples within the literature and from this research for the degradation profile of TPP-plasticized CA. An initial steady stage period, followed by rapid degradation presenting with lower acetic acid emissions, high phenol emissions and the presence of white needle-like crystals on the object's surface. To further confirm this hypothesis, two objects from the teaching collection at the Victoria and Albert Museum were examined for the presence of phenol. These objects were chosen due to exhibiting rapid (over the course of a few months rather than years) & catastrophic degradation and white crystal formation (Figure 7-12).

Figure 7-12 – Image on the left was from the object known simply as 'Plastic Handbag' while the image on the right is of the 'Beehive Handbag'. Both objects show signs of crystal formation, with the Plastic Handbag showing a significant amount of crystallization. Both objects presented similar degradation patterns marked by rapid and catastrophic decomposition. Objects are part of V&A teaching collection and not accessioned objects. Photos taken in 2014.

ATR-FTIR spectroscopy confirmed that both objects were cellulose acetate. SPME-GC/MS confirmed the presence of high levels of phenol in combination with DEP in both samples.

The positive confirmation of phenol from these samples again highlights the correlation between high levels of degradation and high levels of phenol. Objects which had degraded rapidly and for no apparent reason, have now been shown via SPME analysis to be emitting phenol. Through this research we have shown that similar objects which emit this compound degraded at a faster rate than those without. Both the analysis of the reference samples and of the historic polymer objects were conducted without the need for physically interaction between them and the analysis technique. While these samples were analysed in a lab, when combined with the information garnered from previous research (See Chapter 4) it is possible to say that this same level of information could be collected *in situ* without the need for laboratory experimentation.

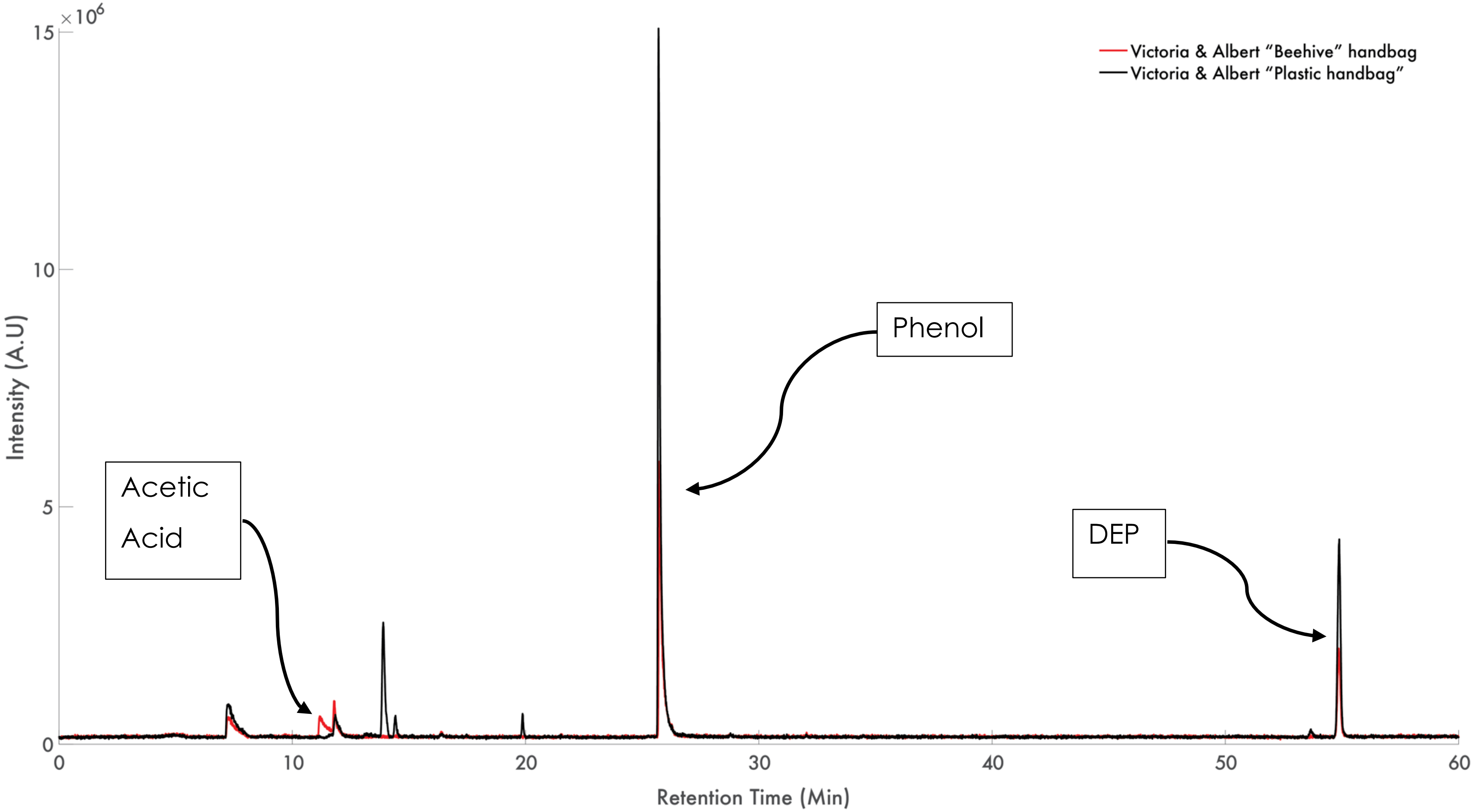

Figure 7-13 – SPME GC/MS results from the two V&A samples showing a large phenol peak accompanied by acetic acid and DEP. There are also two unknown compounds which were not identifiable via the NIST library. However, the peak at circa 6 minutes did return a hit for formic acid (which would fit with the samples), however, its confirmation is not possible given the m/z value range utilized during the methodology.

7.4 Conclusions

The implications of the findings from this chapter highlight the complexity of dealing with modern polymeric materials within museum collections. There are a number of positive outcomes to draw from this research. These could have dramatic implications on the storage and care of historic polymer objects within collections. The major outcome is that this research has definitively linked the plasticiser triphenyl phosphate with both the emission of phenol from cellulose acetate and more worryingly with an increased degradation rate of the polymer.

We have also shown that SPME GC/MS is an effective method to track the emission of phenol from CA objects. In doing so an extra data point is available to conservation professionals to triage incoming (or existing) objects in a quick and non-invasive method.

These findings show that the implementation of SPME analysis within historic environments has the potential for a profound impact on collections management. It offers professionals an additional method to triage incoming (or existing) objects in a quick and non-invasive method to discover the most vulnerable within their collection and quickly implement mitigation strategies. It allows for the deployment of vital resources to objects most in need of them rather than a blanket adoption of costly storage methods. Finally, if the environmental conditions are correct (a discussion this will follow in Chapter 8) it may be possible to track the progression of objects and their reaction to any mitigating procedures invoked. In doing so, though, the use of SPME is a way to justify certain conservation strategies to higher management who may only wish to see solid data points rather than anecdotal evidence.

When these points are collated then there is a clear case to be made for the testing of cellulose acetate objects, or objects thought to be manufactured with cellulose acetate, for the presence of triphenyl phosphate. For objects already exhibiting degradation patterns similar to those outlined above, there is an argument to be made for the allocation of time to conduct continued close monitoring. This could potentially be in the form of SPME GC/MS analysis to monitor the emission of phenol, or FTIR to monitor changes in the degree of substitution.

Furthermore, due to the nature of the degradation profile, there is a justification for those objects exhibiting early stages of the profile to be removed from their surroundings and stored separately, possibly in cold storage to further limit the emission of VOCs and to limit any cross-contamination risks they pose.

Chapter 8 Case Studies

8.1 Introduction

The previous four chapters have all been concerned with either methodological or theoretical aspects of the implementation of SPME within a heritage context. In each chapter our understanding of how to correctly deploy SPME has improved. These chapters have provided information on how long to deploy SPME fibres for and where, with relation to the object or point-of-interest, should the fibre be placed. They have also informed on the need to closely monitor the environmental conditions. These considerations were made with the intention of improving the resulting analytical findings.

However, at this stage of the method development, there is no substitute for testing the practical application of the methodology. The re-evaluation of where the methodology stands, in light of the new information gained could allow for further refinement or for new priorities to be set.

This chapter will describe two case studies involving the use of SPME in a museum context, performed in collaboration with the heritage partner of this project: Tate. It will also discuss the results of a workshop for heritage professionals.

The first will outline how useful SPME is within the general context of use within heritage. It also has the aim of comparing the performance and results profile to other techniques used (or in current development) for the analysis and monitoring of VOCs from historic polymer objects or from packaging typically used in the storage of museum objects. This case study experiment was also designed to utilize the design of a typical storage crate used by Tate so as to judge its suitability to be used as a pre-concentration device for larger objects.

The second case study concerns the long-term monitoring of three historic polymer objects housed in the sculpture conservation studio at Tate Britain. The aim was to investigate if, given the additional information gained from the previous research, it is now possible to implement a long-term monitoring programme in a heritage environment.

The final section of this chapter will report on the findings of a workshop whose aim was to introduce the current SPME method to a wider heritage professional audience. The goal was to gather feedback on the practicality of the method, current research productivity within the field and, information regarding the institutional barriers which the methodology may face before implementation.

8.2 Case Study 1 – Investigating a storage crate

An important aspect of any new methodology is placing it in context with similar techniques which might be utilized to gain a similar result. The field of research into historic polymer objects is a relatively new one - as was discussed in Chapter 1 many of the traditional methods used have been adapted to work with these materials. Few methodologies or techniques have been developed with historic polymers at the forefront or even as a secondary aim. It was therefore of great interest to examine the place of SPME in the context of the wider field of scientific techniques either already developed or in the early stages of their research.

To maximise the knowledge gained from any research into this aspect of the methodology, a new crate of the design currently used by Tate to store sculptures was made available. By utilizing a storage crate, it was not only possible to conduct the experiment within a closed and controlled environment, but it also provided information regarding the condition and suitability of the storage crate itself.

Four different techniques were chosen to complement SPME. These were a commercial total volatile organic compound (tVOC) sensor which would be connected to a raspberry pi computer (Adafruit SGP 30, pimoroni.com), AD-Strips from the two principal suppliers, and a passive Dosi-tube (GAS81D Acetic Acid Passive Dosi-Tubes, a1-cbiss.com, 0.5 ppm – 100 ppm sensitivity range). The final technique was an electronic gas sensor which is currently in development. This was based on lead-coated piezoelectric quartz crystals (L-PQCs) and was developed at UCL by Sarah Hunt, who is a fellow SEAHA student (Hunt *et al.*, 2017). Hunt's sensor is in fact a composite sensor which can house a number of individual sensors. During this case study three individual sensors were simultaneously utilized and shall be known collectively as *Sensor 1*.

The case was specifically commissioned by Tate for this and future Tate-led experiments and was manufactured to their required specifications, in the materials used in 2019 for the storage of sculptures. The internal dimensions of the case were 590 x 800 x 600 mm (H x W x D). A schematic of the case can be seen in Figure 8-1. The case was constructed from 25 mm birch-faced plywood with an internal lining of 50 mm white Plastazote LD24 or LD15 foam which was not glued in place (both foam types were specified as suitable in the Tate spec sheet sent to the manufacturer).

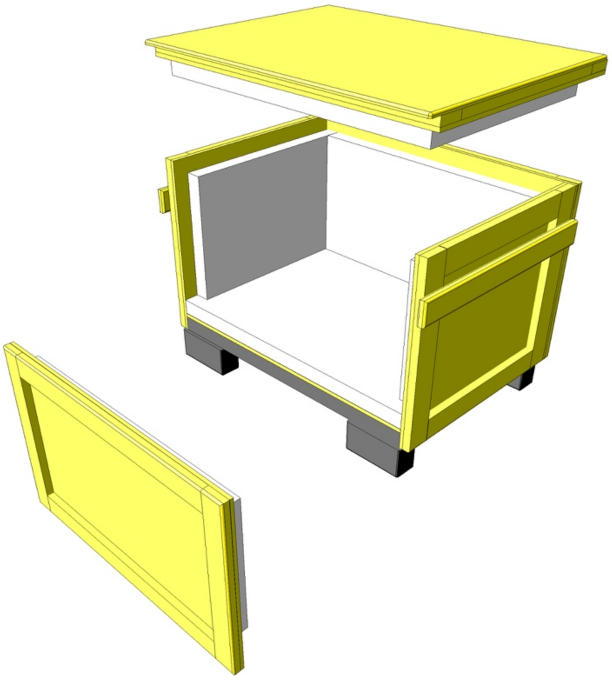

Figure 8-1 Schematic of the sculpture crate used by Tate, designed by Roger Murray. This was the specification drawing given to the manufacture however the side panel is not removable as is suggested here. Image: Roger Murray, Tate 2019.

One aspect to note is that the material for the case is not treated in any way or subjected to any testing before use. The wood used in its construction is specified to be compliant with IMP15 wood regulations (IPPC Secretariat, 2009), but the specific wood used in construction is not stated. The paint is specified as being a yellow colour conforming to the 'BS 08-E51' standard (specifying the colour). The crate is not specified as conforming to any other specific British or International standard such as how air-tight it should be, the specific wood used or any method of construction.

As the case was quite large, three different areas were chosen for placement of the different sensors. Aluminium platforms were constructed by Roger Murray, Senior Sculpture Conservation Technician at Tate, to hold the sensors. These platforms were placed at three different levels – top (approx. 50 mm from the top), middle and bottom. They were also placed at a diagonal from the top left corner to the bottom right corner (Figure 8-2 and Figure 8-3)

Figure 8-2 – Image of the three levels inside the crate. The levels were constructed from aluminium sheets and the bottom layer (on the right of this image) had no struts and was placed on top of the Plastazote. Note that the wires from the sensors were forced into the Plastazote when the crate cover was placed on top and as such the seal was not compromised.

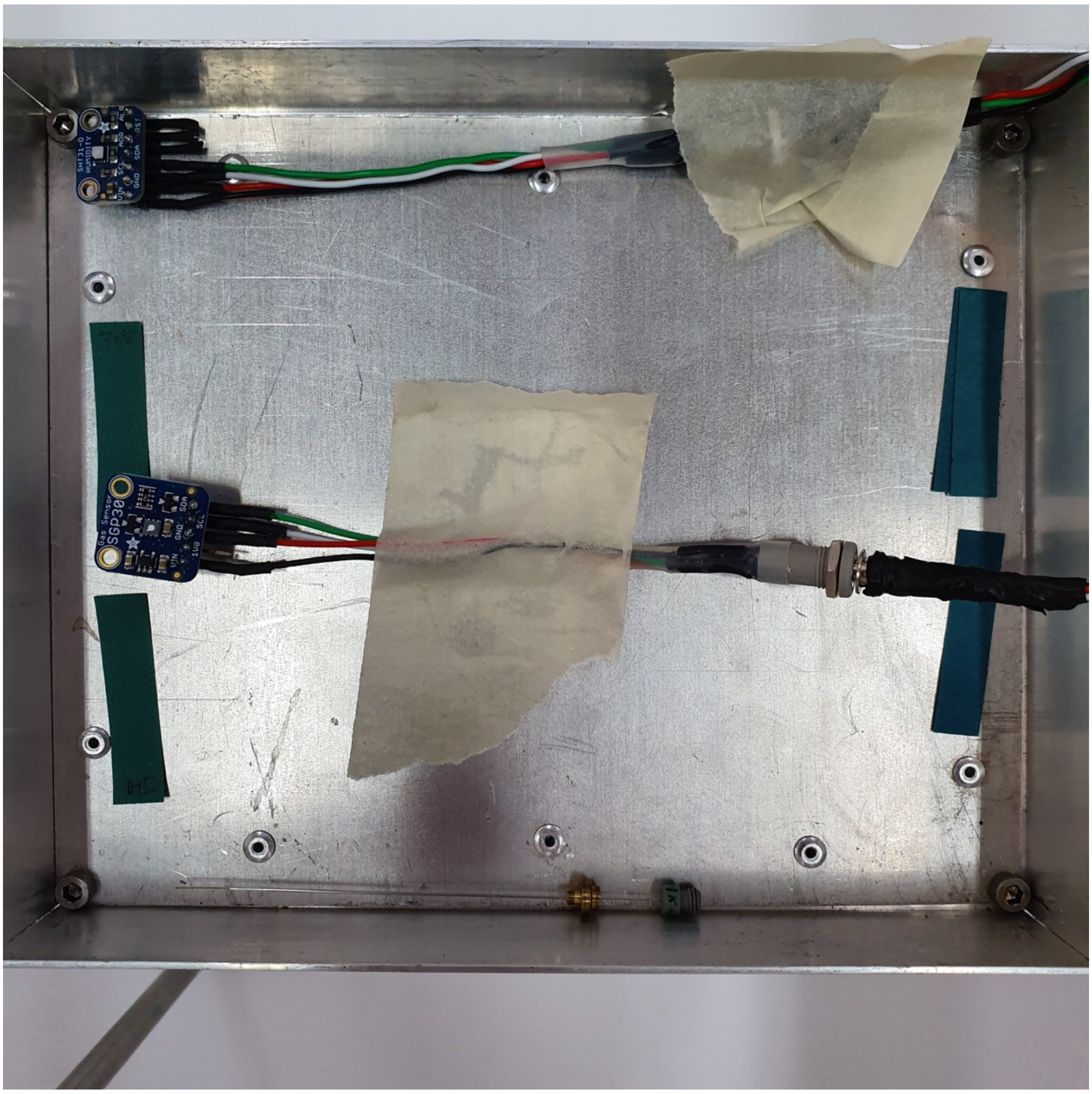

Figure 8-3 – A close up image of one of the middle level showing four AD-strips (blue paper strips on left and right sides), a temperature and RH monitor (Top sensor), a gas sensor (Bottom sensor), and a SPME fibre (bottom). Not shown here is the Dosi-tube which was also placed on this middle level

The experiment was designed in two stages – during the first stage the SPME fibres, AD-strips, Dosi-tube, tVOC sensor, and *Sensor 1* were used to examine the crate. During the second stage, tests were conducted on the air tightness of the crate. Throughout the entire experiment temperature and relative humidity sensors measured the internal environment at the bottom and middle levels.

The SPME fibres, tVOC sensor, and Dosi-tube were exposed to the closed internal environment for approx. 48-hours. *Sensor 1* was first exposed to the ambient conditions beside the crate for 1 hour. Following this the sensor was placed into the crate, sealed and exposed for 5 hours. To facilitate the removal of *Sensor 1* the crate was briefly opened at the end of the first day. After removal the crate was sealed again, and the remaining experiments allowed to continue their exposure to the internal atmosphere.

Following the completion of these experiments, it was decided to carry out a second separate test using both SPME and the tVOC sensor – this was done in order to confirm certain aspects of the initial VOC profile as well as to remove any error which may have arisen from opening the crate to remove *Sensor 1*. Additionally, the air exchange rate was also tested during this second round. The gas from two 16 g CO_2 canisters was released into the crate and the lid then replaced. Two CO_2 data loggers were used – one outside the crate to act as a reference, the second inside to measure the concentration of CO_2 over the course of two days.

The second round of analysis also provided an opportunity to measure temperature and relative humidity at all levels. At this stage, a small sample of the Plastazote® foam was removed from the case and analysed via SPME under laboratory conditions.

8.2.1 Results

Analysis from the three SPME fibres inside the crate highlighted a complex VOC profile comprising a mixture of compounds originating from the crate itself, the Plastazote® lining, and the compounds found inside the room (Figure 8-4). This result confirms that the use of a crate for pre-concentration of VOCs within a controlled environment is not ideal. As can be seen from Figure 8-4 the large number and intensities of the compounds would interfere with the signal from any object present. As discussed in Chapter 5 the complex background not only hinders clear identification of VOCs from samples but also interferes with the correct ratios within a VOC profile due to competition on the fibre.

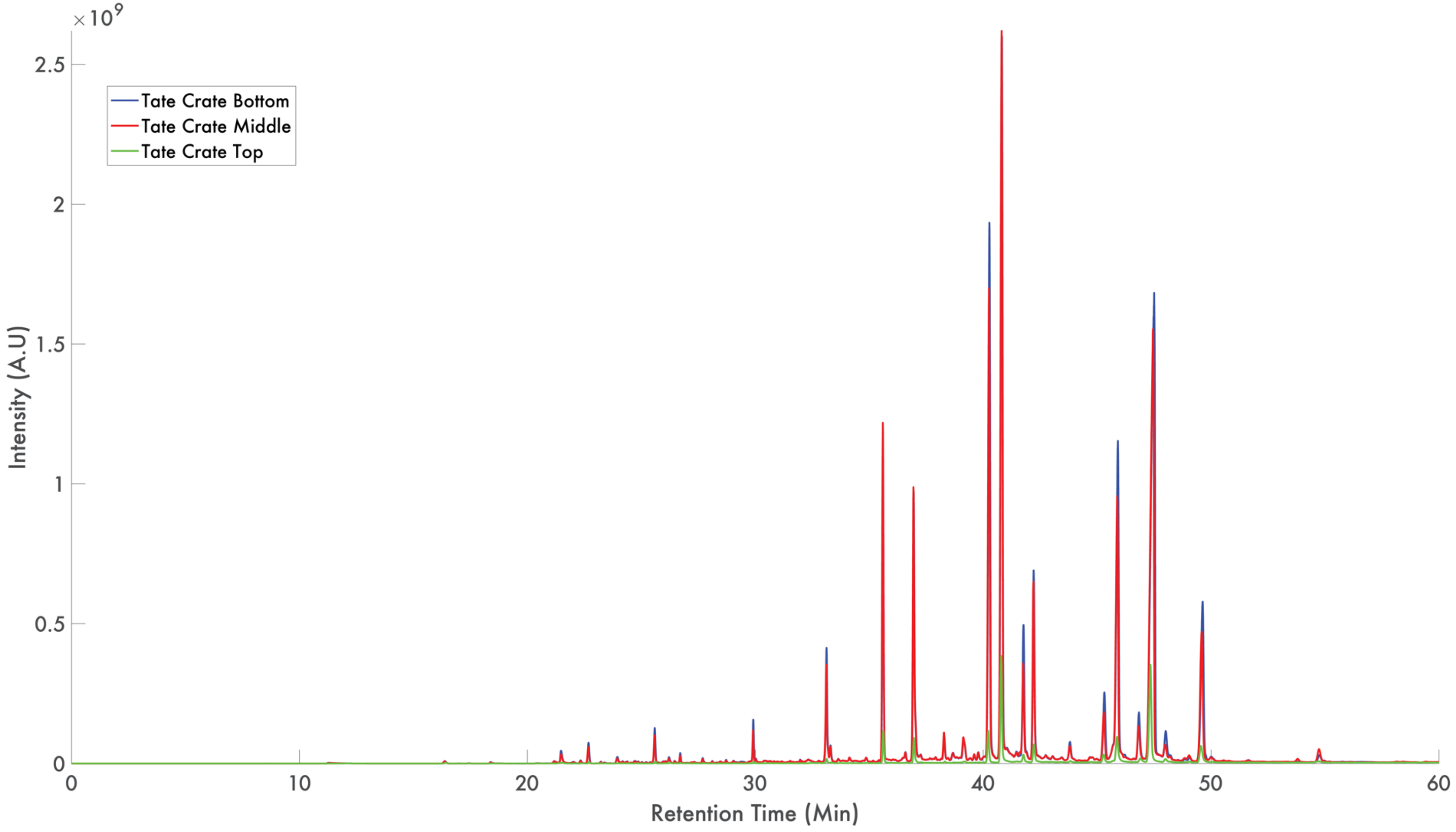

Figure 8-4 – TIC image from all levels showing the complex background which objects would be presented with upon placement inside the crate.

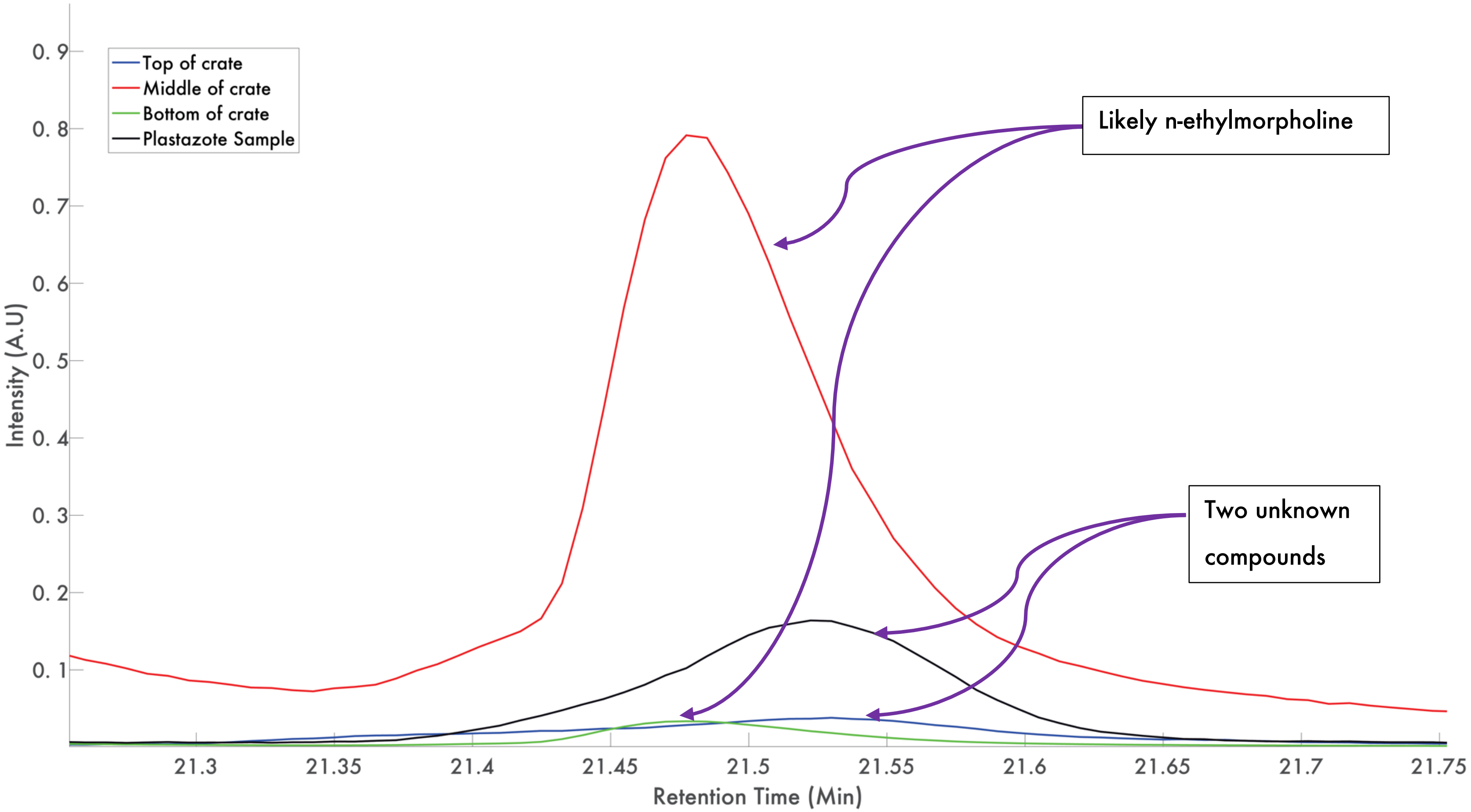

Figure 8-5 – Close up image of results from all levels showing peaks centered around 21.5 minutes. These peaks could be mistaken for a single compound, however, there are two present.

Speaking specifically about the atmosphere inside the crate, it is clear that both the room and the Plastazote contribute significantly to the overall interior atmosphere which objects would be exposed to (Figure 8-4). What is unclear is how these VOCs would affect the objects as no test analogous to an *Oddy Test* for the effect of VOCs on selected metals (See Chapter 1.5.2), has been designed or carried out on this specific crate or more importantly been carried out with influence upon polymers being the main focus. However there has been work done that shows that off-gassing by materials can affect otherwise healthy objects within their vicinity (Curran *et al.*, 2014).

Despite the complex nature of the TIC it is possible to deconstruct most of the TIC from the crate into its respective sources. This is best exemplified by examining the peak at approx. 21.45 minutes (Figure 8-5). On first observation, it would appear that this peak is the same compound for each sample. However, on inspection of the m/z values for each sample at this retention time, one discovers that there is, in fact, three different compound types present. The first two compounds (whose identification is unclear), are seen at the top level of the crate along with being a feature of both the room and the Plastazote. Another compound (most probably n-ethylmorpholine) is found in the middle and bottom of the crate.

There are also a number of terpenes present in the TIC (See Table 8-1). This is to be expected as the crate is constructed with plywood (Hodgson *et al.*, 2002; Fransman *et al.*, 2003; Wilke *et al.*, 2012). Their presence is likely the partial cause of the strong indistinguishable odour which was noted upon opening the crate.

Retention Time	Compound
22.68	α-pinene
25.58	3-carene
26.21	Limonene
26.45	o-cymene

Table 8-1 – A list of terpenes found and their respective retention times.

Analysis from the crate also highlighted the presence of acetic acid. While the intensity of the acetic acid peak was low it still poses a risk to objects when contained in such an airtight container.

The results from SPME analysis are comprehensive and deliver a good understanding of the complex atmosphere surrounding any object placed inside the crate. However, not all of the techniques utilized performed as robustly as SPME or provided a similar level of detail. Table 8-2 highlights the top 20 compounds found in the chromatogram from the bottom of the crate. A number of things should be noted in this table. The first is that as can be seen in Figure 8-4 results from SPME analysis at each height are similar to each other, therefore, for clarity a table listing the compounds from one level is presented. Additionally, differently substituted *Ethanones* feature heavily in the chromatogram. It is unlikely that the order of these compounds is correct in the list provided in Table 8-2 as it would be very difficult to ascertain the correct variation of *Ethanone* using our methodology. As such the "top-hit" on the NIST library is presented in the table.

Rank	RT Min	Normalised Area	Compound	Main m/z Value	Nist R-Match Value
1	47.50	145.62	1-[4-(1-hydroxy-1-methylethyl)phenyl]-Ethanone,	163	881
2	40.82	109.14	1-(2,3-dihydro-1H-inden-5-yl)-Ethanone,	145	907
3	40.27	79.58	2,3-dihydro-1,1-dimethyl-1H-Indene-4-methanol,	161	790
4	45.91	63.44	1,1'-(1,4-phenylene)bis-Ethanone,	147	930
5	36.95	36.02	, 1,4-bis(1-methylethenyl)-Benzene	158	968
6	49.63	35.70	1-[4-(1-hydroxy-1-methylethyl)phenyl]-Ethanone,	163	929
7	35.61	31.42	1,3-bis(1-methylethenyl)-Benzene,	158	935
8	42.21	27.28	1-[4-(1-methylethenyl)phenyl]-Ethanone,	145	896
9	41.77	20.79	2,3-dihydro-1,1-dimethyl-1H-Indene-4-methanol,	161	820
10	33.13	13.20	Tridecane	57	974
11	45.32	12.46	α,α′-Dihydroxy-m-diisopropylbenzene	179	895
12	46.83	8.38	1,1'-(1,4-phenylene)bis-Ethanone,	147	929
13	48.00	4.67	α,α′ -Dihydroxy-m-diisopropylbenzene	179	843
14	39.14	4.30	Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	71	867
15	29.91	4.28	Dodecane	57	950
16	25.59	3.93	3-Carene	93	934
17	43.81	3.72	-	193	-
18	38.29	2.83	1-[4-(1-methylethyl)phenyl]-Ethanone,	147	926
19	22.69	2.60	α-pinene	93	940
20	21.48	2.08	N-Ethylmorpholine	57	919

Table 8-2 – A list of the top 20 peaks, ranked by normalized peak height found at the bottom level of the crate. Note that Ethanone, or variations of it, are found in a number of different peaks. It is not possible to definitively say which form is correct using our methodology, however, it is possible to say that this type of compound features heavily in the TIC.

Readings from the commercial tVOC sensor proved highly unstable. The exact sensor used was chosen due to its relatively low cost (£19.80) and its claimed ability to register tVOC concentrations in the parts per billion range. The sensor also worked on the same I^{2}C connection protocol as the SHT-31 temperature and relative humidity sensor that worked very well throughout its use during the PhD project.

However, two aspects of the sensor hindered its usefulness in this experimental context. The sensor measured total VOCs, yet the exact VOCs it was sensitive to was difficult to determine. The information sheet from the manufacturer stated it was tested against ethanol but did not give any further details on other compounds which it may be sensitive too, nor those it cannot detect. Secondly, the gas sensor continually failed and stopped working during testing before the crate experiment. It was intended that the gas sensor would log for an entire week, however, during the first round it only logged for the first two days, and during the second round of testing, it failed almost immediately.

While the sensor was running, it did provide an insight into the case which SPME was unable to provide. Figure 8-6 shows the results of the tVOC sensor connected to the Raspberry Pi processer over the initial two days of the first experiment round. The level of the tVOCs continues to rise over the course of the two days indicating that no air exchange, or a very small one, is taking place. In turn the VOCs are trapped inside the crate with any further emission from the case allowed to build up. This creates a situation whereby the emission exceeds the leakage rate and the overall concentration seen by the sensor gradually rises over time. This insight was also backed by the specific air-exchange experiment (results not shown here) carried out during the second round of testing in which the CO_2 level registered on the CO_2 logger never went below its maximum level of 5000 ppm during the two-day testing period. This suggests that the air-exchange rate is very low.

When this information is combined with the that from SPME regarding the presence of acetic acid, it is clear that these crates could pose a risk to objects in their own right. Furthermore, the very low air exchange rate would allow any VOCs emitted from an object to also build up creating an unsuitable environment for the object inside.

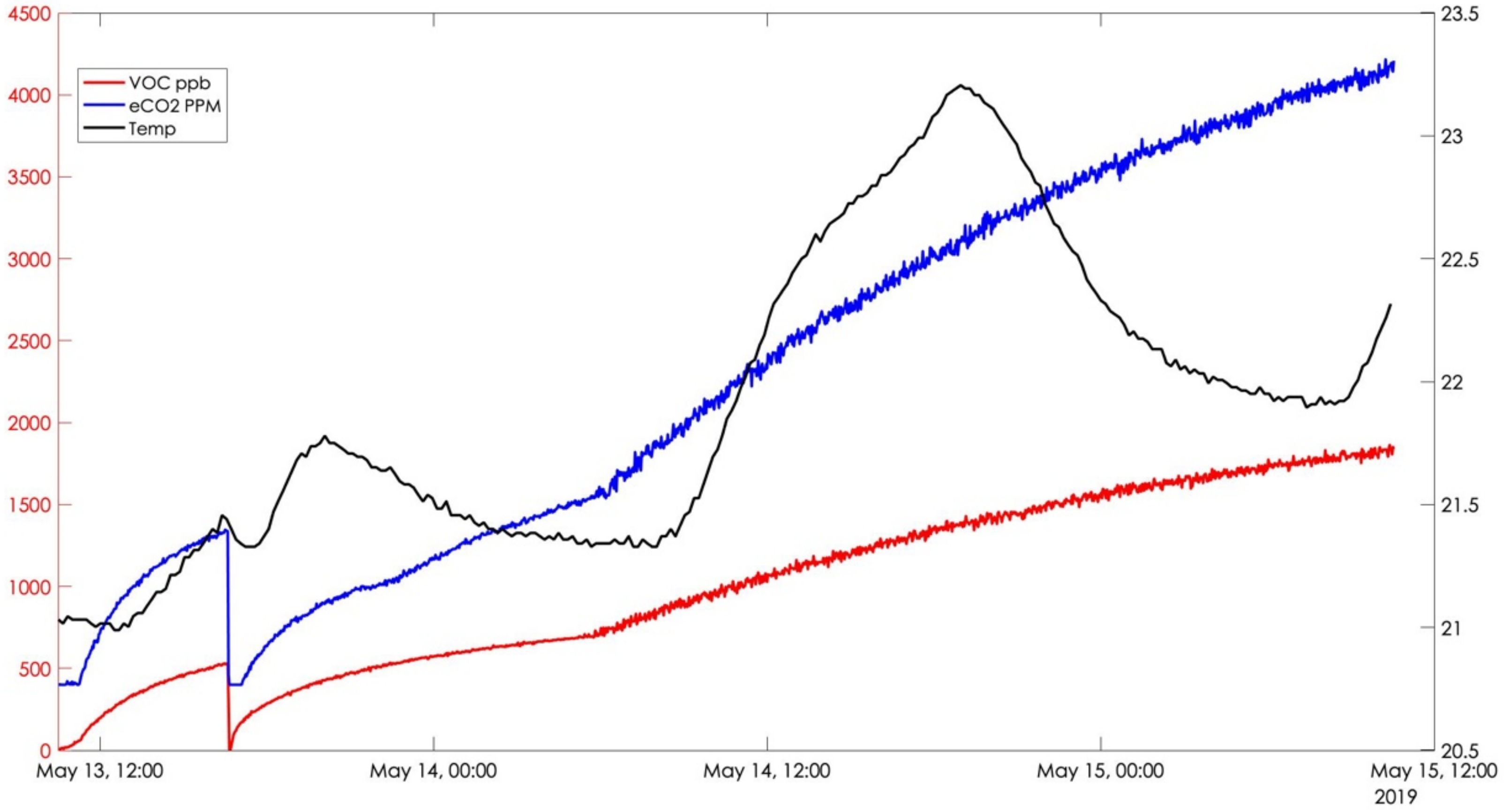

Figure 8-6 - Results from the tVOC gas sensor, at the middle level, showing a steady increase in the concentration of tVOCs (Red line) during the time the sensor was running. Note the reaction to the sensor (sharp lowering of concentration) at the beginning of the time period to the case being opened to remove Sensor 1.

The tVOC gas sensor was included as an example of a cheap and widely available alternative which any heritage professional might deploy if access to more expensive and complex equipment was unavailable. However, its instability and its lack of selectivity means that this sensor is not a serious alternative to the other techniques available. Furthermore, it is unclear as to why the CO_2 level also rises as there should not have been a source of CO_2 inside the crate. However, the manufacture states the sensor is not a specific CO_2 sensor and in reality, calculates an equivalent carbon-dioxide (eCO_2) concentration based on their own proprietary algorithm, so it is likely that this leads to misattribution of other compound(s) as CO_2. Despite this, the basic principle of the emission rate exceeding the leakage rate still stands.

Analysis results from the DOSI-Tube showed a just detectable colour change and therefore implied a just-measurable and therefore low acetic acid level. This was further confirmed by A-D strips which, based on the work by Hackney (2016) and ongoing work by Dr Joyce Townsend, Tate, would register a '*zero/low*' concentration level. Figure 8-3 illustrated A-D strips from two suppliers, and a colour difference after their exposure is obvious: both would be interpreted in this range.

Analysis via *Sensor 1* was in line with SPME and showed a minor concentration of acetic acid. These sensors are sensitive to acetic acid and to other acids, and also react to changes in relative humidity, this reaction results in a change in mass on the surface of sensor that induces a frequency change in the piezoelectric crystal. As can be seen in Figure 8-7 the sensors are initially stable (before the black horizontal line) when monitoring outside the crate. Upon placement into the crate the frequency begins to rise in line with a rise in RH; as such it is not possible to discern if this change is due to the presence of an acid or simply the rise in RH. However, as the RH levels off (after the orange line) the frequency still changes indicating that a compound is altering the mass of the QCM. As described by Hunt "*the rate of change is slow and the magnitude of frequency change small, therefore, I believe the concentration of acetic acid (or other compounds capable of reacting with the lead oxide) to be low concentration, however, I am unable to quantify this.*" (Hunt, 2020, Personal communication)

As such, this sensor does indicate the presence of *something* but does not give the same level of understanding which is afforded by SPME. Nor does the sensor provide the ability to discern the origin of these compounds, something which SPME is capable of doing.

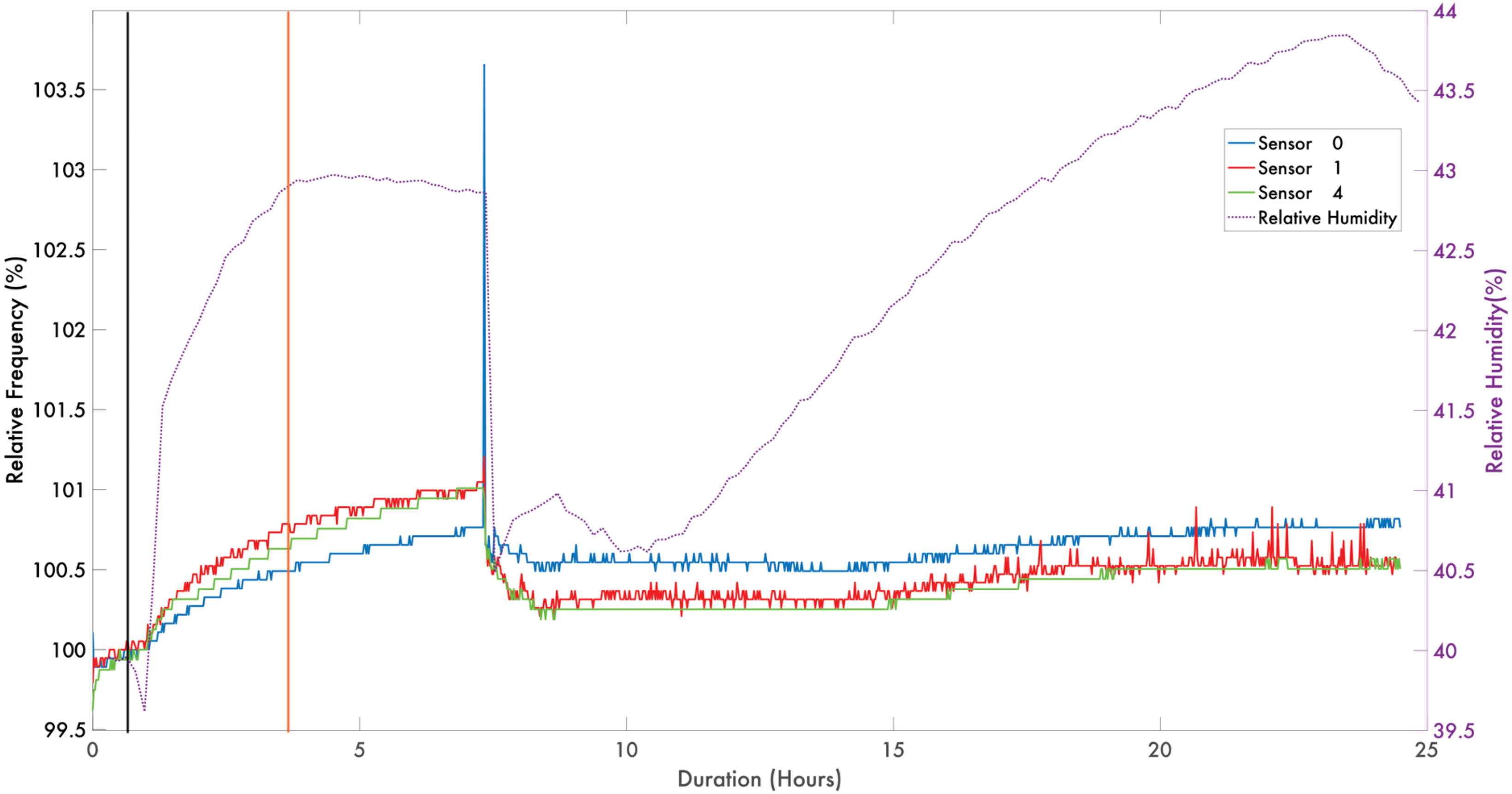

Figure 8-7 – Results from three sensors which formed *Sensor 1* showing a frequency change (between black and orange horizontal lines) which is partly caused by a change in RH and exposure to a compound capable of reacting with the sensor. Sensors removed from crate at approx. 7.5-hour mark.

8.3 Case Study 2: Long-term monitoring

The previous work reported on in Chapter 4 of this thesis utilized data collected over a time period of three and a half months. During this time the environmental conditions of the room housing the object were not directly monitored. Furthermore, the room itself was used for storage of a very limited number of artworks and was not entered during normal day-to-day activity. The room has a reasonably small footprint of approx. 5.5 sq. meters (with a ceiling height of approx. 4 meters) and is very much smaller than the main studio area within the sculpture conservation section.

While the results from this previous research were invaluable to both the direction of the project overall and the progression of knowledge regarding the use of SPME within heritage, the initial research did have some limitations. Having conducted further research surrounding the deployment of SPME, it was the objective of the following research to expand on the knowledge base and to rectify many of the limitations mentioned above. The aim, in doing so, was to investigate if it would be possible to carry out long-term monitoring of objects in which the variations previously seen could be accounted for.

Three historic polymer objects were chosen to be monitored in the main studio of the sculpture conservation section over a period of six months[12]. The three objects were chosen based on their condition and availability for the entire time period. The objects varied in condition from good to very poor. Table 8-3 provides details on the objects and images of the objects.

Naum Gabo, *Circular Relief* c.1925 (Tate T02142) and *Model for 'Spheric Theme'* c.1937 (Tate T02173)

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[12] As will be shown later in the chapter, due to scheduling conflicts, analysis from only five of the six months were taken.

Object Number/Name	**Object Condition**	**Tate Image**
Naum Gabo, *Circular Relief* c.1925 (Tate T02142) Clear cellulose acetate sheet and heat-formed clear Perspex strips	Poor - Object showing serious signs of degradation - cracking, warping, & discoloration of the CA components. Object is no longer available for display, and an authorised replica is displayed instead	 (view from above)
Naum Gabo, *Model for 'Spheric Theme'* c.1937 (Tate T02173)Opalised cellulose acetate	Good - some signs of degradation but in general the condition is good and it can be displayed	

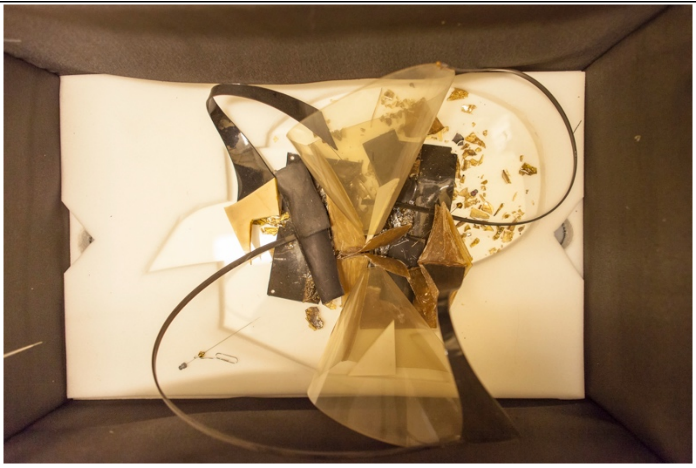
Naum Gabo, *Construction in Space, Two Cones* ’ 1927, replica 1968 by the artist (Tate T02143) Cellulose Acetate	Very poor condition. Object has significant loss due to cracking. Some areas have extensive colour changes. Object is no longer available for display, and an authorised replica is displayed instead	

Table 8-3 – Details regarding the three objects studied. All works © Nina & Graham Williams.

The objects were chosen to be monitored in the open studio as one object (T02142) was unable to be moved from its normal location. The two other objects were brought to the same bench for testing[13]. Additionally, it was felt that monitoring in this location would provide even greater realism to the analysis methodology as most objects would not be able to be housed in the smaller storage area for testing or for any remedial conservation work needing to be carried out. One initial downside of this, noted at the start of the experiment, was for accidental movement of the objects during the monitoring programme. To counteract this, a sign was placed around the objects noting they were not to be moved.

T02143, *Two Cones* and T02173 were both housed in polyethylene storage crates lined with Plastazote foam.– In the case of T02143, *Two Cones* there had been intentionally no lid to its crate which was covered by thick Vilene fabric to permit some air circulation; T02143, *Two Cones* had air vents on two sides and while it did have a lid, this was not tightly fitting. A similar lid but with a better fit was provided or

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[13] During analysis one object was accidentally transferred by staff to the storage area. This will be highlighted later in the chapter.

T02143, *Two Cones* for the duration of the experiment. The T02142 was placed on a lab bench and had a 5-sided Perspex cover with small air vents cut into its side however, this cover was not designed to act as an air seal. (see Figure 8-8 to Figure 8-11).

SPME fibres were exposed to the objects for 1 day each month, with analysis following the steps laid out in Chapter 3. Each object was analysed by a single fibre, with an additional fibre placed close to the bench which housed the objects to analyse the room's background VOC profile. The location of the fibre placement was also chosen based on the concept of 'easiest placement' rather than on any specific point-of-interest. The concept of 'easiest placement' is based on a number of considerations such as a damage risk to the object from movement, limiting the movement of the storage crate when facilitating fibre placement, ease of access to points of interest on the object (e.g. access from the front rather than back of storage crate), and to facilitate placement of environmental monitoring sensors – access to a power supply. This was again done in an effort to judge the feasibility of the methodology in a real-world analysis situation. Furthermore, the concept had the advantage of requiring less time to setup and therefore, as supervision from Tate staff was required while working on Tate objects it was more congenial to their workflow.

Environmental conditions (Temp & RH) were extensively monitored during the analysis period. Three different loggers were utilized to gain insights – a TinyTag logger was used to measure the overall conditions in the studio as well as to provide information regarding object T02173. Due to its small size and open crate, monitoring this object in this way was judged to be sufficiently representative. Two Raspberry Pi Zero W minicomputers with an SHT-31D Temp/RH sensor attached were used to monitor T02143, *Two Cones* and T02142. Figure 8-11 shows the placement of the sensors relative to the SPME fibres for each object.

The same fibre was used at the same location for each analysis run over the monitoring programme.

Figure 8-8 – A view of T02142 showing its placement on its bench along with the clear plastic cover over it. The sensor and SPME fibre were placed through cutouts on the bottom left of the plastic cover.

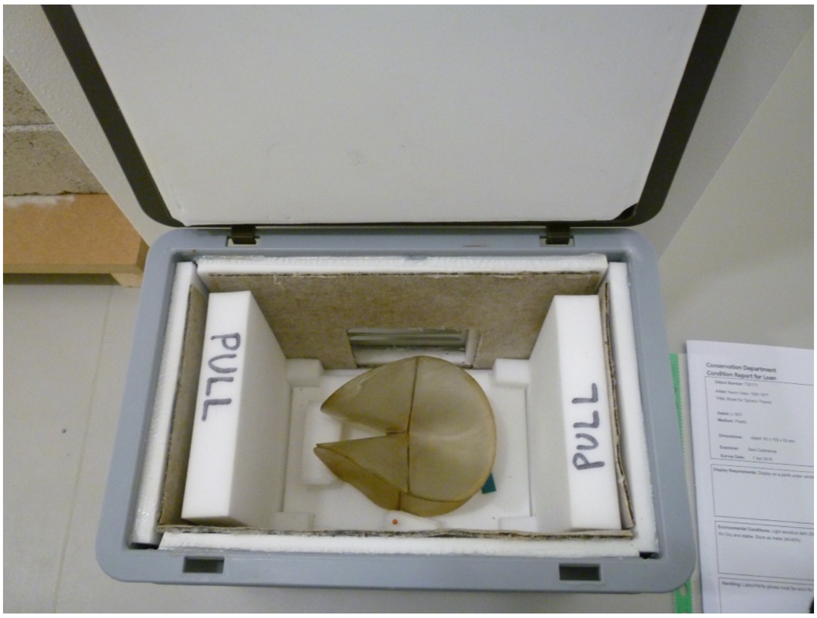

Figure 8-9 – A top view of T02173 showing it in its crate.

Figure 8-10 – T02143, *Two Cones* shown on its shelf in the small strong room within the sculpture conservation section. This image highlights the cloth cover which has been place on top of the crate allowing for ample air exchange between the object and the wider area.

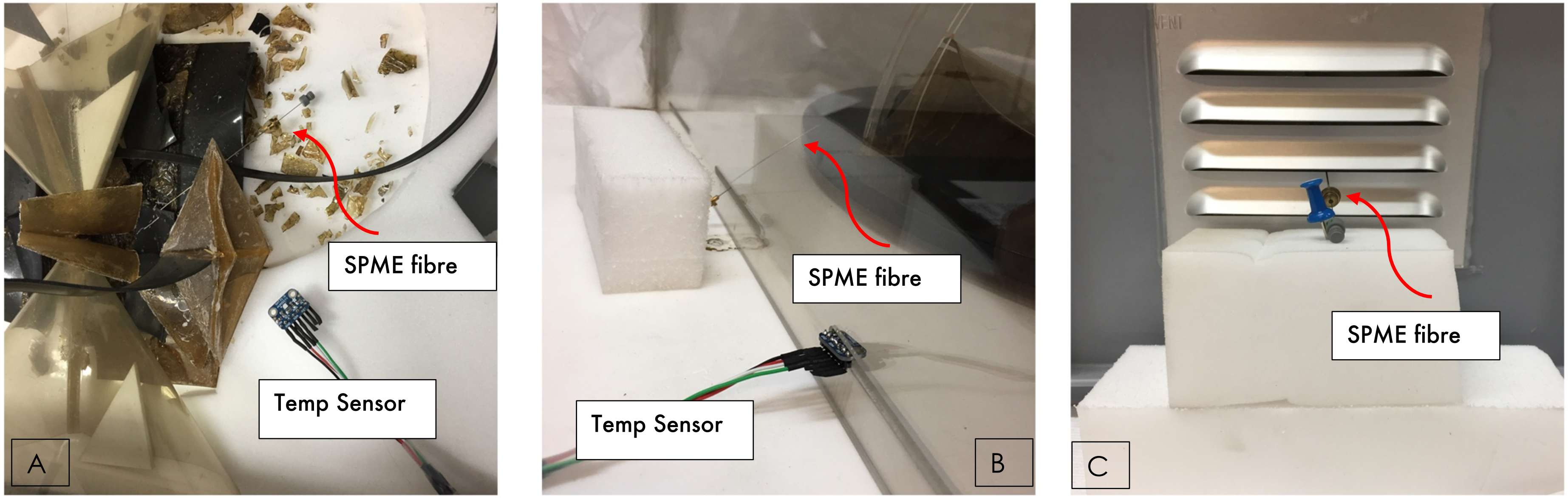

Figure 8-11 A-C - Images showing the location of fibre (Red arrows) and senor placement on A - T02143, *Two Cones*, B - T02142, and C - T02173. Note that T02173 is in a small crate and there was no place to place a sensor inside the crate.

8.3.1 Results

Both Chapters 2 and 4 have shown that temperature plays a major role in the resulting VOC profile, so it is important to place any further analysis in the context of any temperature variation. Table 8-4 shown below, indicates that the temperature experienced by the fibres during the 1-day analysis period, at each of the six-month monitoring dates, did not vary significantly. Typically, at any one location, the temperature variation, on the day of analysis, between the maximum value to the minimum value was less than 2.5 °C.

Studio

Analysis Month	Avg	Max	Min	Range
Nov	19.4	20.6	18.4	2.2
Dec	18.9	19.6	18.4	1.2
Jan	18.4	19.4	17.6	1.8
Feb	21.2	22.5	20.7	1.8
April	20.7	21.8	20.0	1.8

T02142

Analysis Month	Avg	Max	Min	Range
Nov	Not Logged			
Dec	19.2	20.0	18.6	1.4
Jan	19.2	20.4	18.2	2.1
Feb	22.1	23.3	21.5	1.7
April	Data Logger Failed			

T02143, *Two Cones*

Analysis Month	Avg	Max	Min	Range
Nov	18.1	19.4	17.8	1.6
Dec	19.3	20.4	18.7	1.7
Jan	18.7	19.8	17.7	2.1
Feb	18.7	19.9	18.5	1.4
April	18.1	18.9	17.7	1.2

Difference Between Studio and T02143, *Two Cones*

Lab Avg	Two Cones Avg	Difference
19.4	18.1	1.3
18.9	19.3	-0.4
18.4	18.7	-0.3
21.2	18.7	2.5
20.7	18.1	2.6

Table 8-4 - Table of results showing the temperature variations seen at each sensor. Note that the grey highlighted values are from when T02143, *Two Cones* was removed from the initial test site and placed inside the smaller storage area. This was done by mistake sometime after the January measurement and rather than compound the mistake by further movement the remaining analysis was carried out in the smaller storage area. All figures above are in °C.

As with the analysis of T02143, *Two Cones* carried out in Chapter 4, a VOC profile of the four major VOCs present was chosen as the focus in order to simplify the overall data processing. These VOCs were phenol, acetic acid, diethyl phthalate and dimethyl phthalate.

Given the small temperature variation seen by all objects during the analysis period, one would presume that the corresponding VOC profile would also not have any significant vacation. However, this is not the case and significant variation is seen for all objects. Table 8-5 outlines the normalized peak area values for T02143, *Two Cones* and T02142.

<table>
<tr><th colspan="6">T02143, <i>Two Cones</i></th></tr>
<tr><th>Analysis Month</th><th>Phenol</th><th>Acetic Acid</th><th>DEP</th><th>DMP</th><th>Avg. Temp</th></tr>
<tr><td>Nov</td><td>1.32</td><td>0.11</td><td>2.61</td><td>4.81</td><td>18.14</td></tr>
<tr><td>Dec</td><td>3.58</td><td>2.29</td><td>6.10</td><td>13.70</td><td>19.32</td></tr>
<tr><td>Jan</td><td>0.66</td><td>0.12</td><td>1.02</td><td>2.07</td><td>18.70</td></tr>
<tr><td>Feb</td><td>2.19</td><td>0.57</td><td>3.54</td><td>5.05</td><td>18.69</td></tr>
<tr><td>April</td><td>0.55</td><td>0.02</td><td>1.92</td><td>1.75</td><td>18.11</td></tr>
<tr><td colspan="6"></td></tr>
<tr><th colspan="6">T02142</th></tr>
<tr><th>Analysis Month</th><th>Phenol</th><th>Acetic Acid</th><th>DEP</th><th>DMP</th><th>Avg. Temp</th></tr>
<tr><td>Nov</td><td>0.22</td><td>0.01</td><td>6.44</td><td>0.71</td><td>Not Logged</td></tr>
<tr><td>Dec</td><td>2.56</td><td>0.95</td><td>132.88</td><td>14.12</td><td>19.24</td></tr>
<tr><td>Jan</td><td>2.65</td><td>1.53</td><td>59.07</td><td>11.62</td><td>19.16</td></tr>
<tr><td>Feb</td><td>0.71</td><td>0.03</td><td>13.25</td><td>1.39</td><td>22.11</td></tr>
<tr><td>April</td><td>3.83</td><td>0.10</td><td>223.89</td><td>18.60</td><td>Not Logged</td></tr>
</table>

Table 8-5 - Normalised peak areas for the four main VOCs of interest from two objects. Note the undulating pattern of the results which does not correspond to fluctuations in temperature (or in the case of T02143, *Two Cones* could be explained completely by its movement to the smaller storage area)

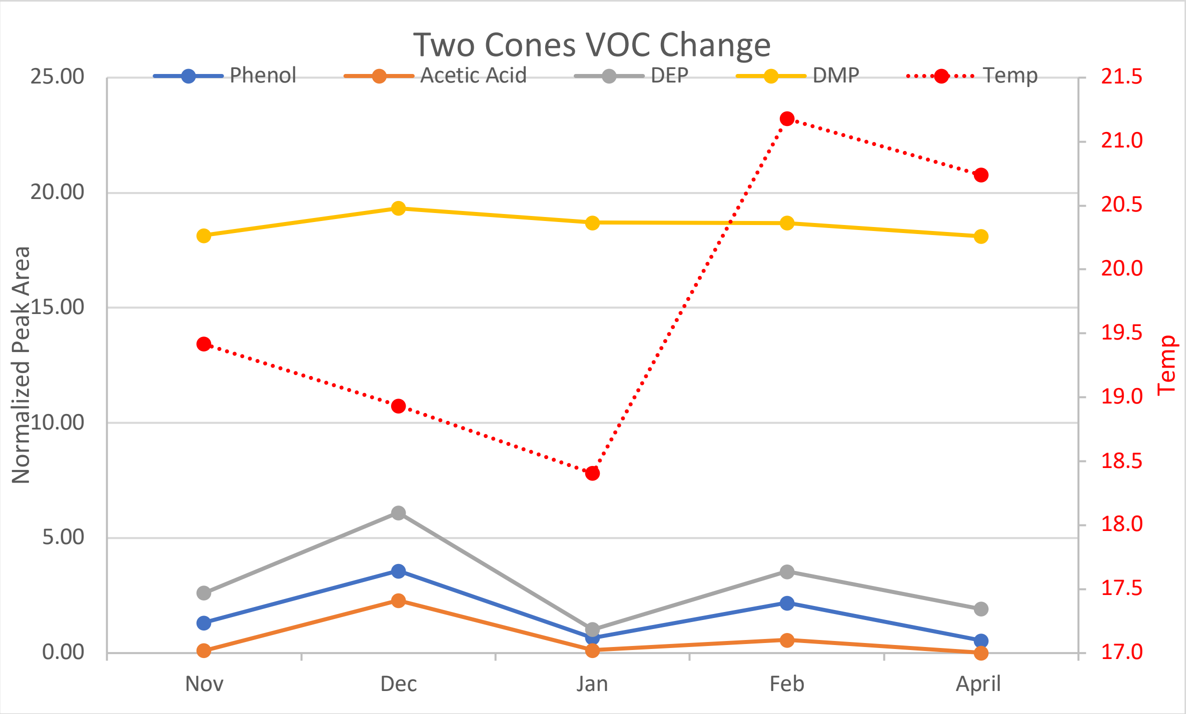

Figure 8-12 & Figure 8-13 - A graphical line plot of the data presented above in Table 8-5 shows how the four key VOCs behaved and how the temperature changed during the analysis months. Note the two vertical scales on each graph showing the normalized peak area on the left and the temperature on the right. Also, note the log scale of the peak area due to the greater range between the VOC datasets for Figure 8-13.

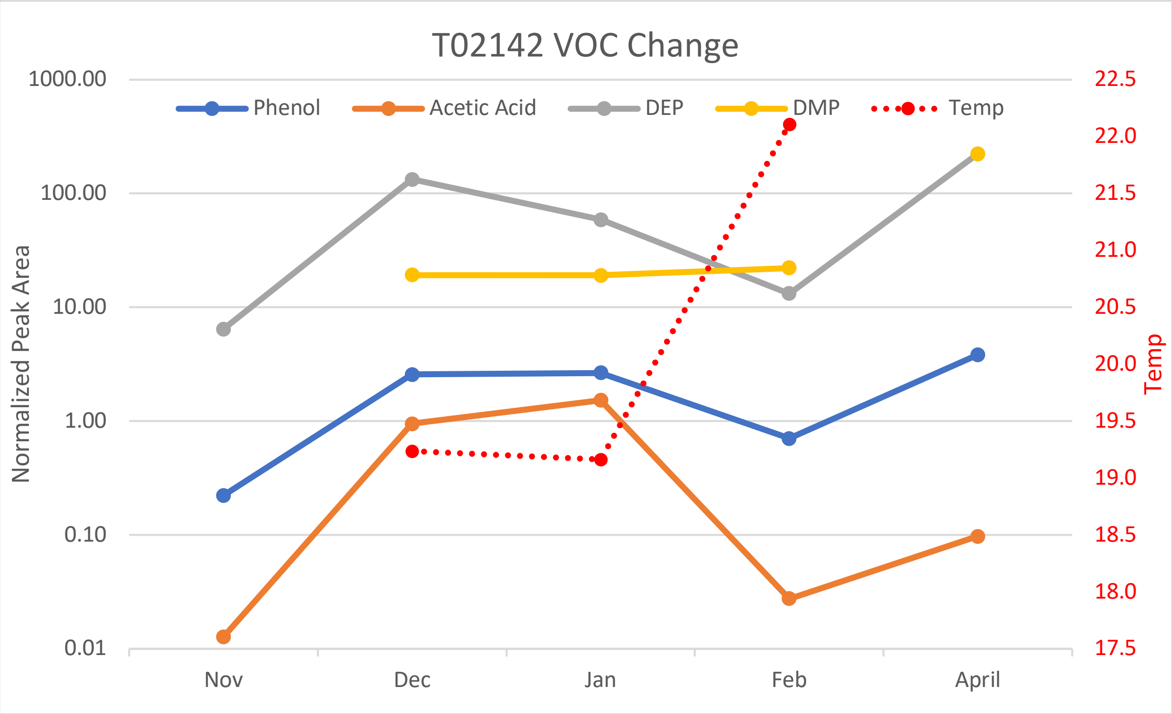

Figure 8-13

The initial point to focus on is the difference between the VOC profiles recorded for T02143, *Two Cones* and those of the other two objects despite the fact that all three have cellulose acetate as their main construction material (Figure 8-14), and in all three cases as the only material showing visible degradation.

The profile from T02173 was extremely difficult to distinguish from the background due to their similarity. This is best exemplified by comparing the TIC's from February, see Figure 8-15 and in the comparison made in Table 8-6. The VOC with the largest normalised peak area from T02173 is found at 23.36 minutes and was identified, via the NIST library, as being decane. While there is a suggestion that this compound is associated with the degradation of cellulose (Gibson *et al.*, 2012), it is more of note that this compound is also present in the VOC profile from the background. Its presence in both VOC profiles (and to such prominence) somewhat removes the ability to associate its original source to either profile.

T02173			**Room**		
	RT min	**m/z Value**	**Rank**	**RT min**	**m/z Value**
1	23.36	56.54, 70.62	3	23.37	56.6, 70.62
2	25.64	104.72, 119.82	5	25.64	104.78, 119.82
3	26.69	56.54, 70.62	1	26.69	56.6, 70.62
4	24.01	70.62, 56.54	17	24.02	70.62, 56.6
5	27.58	118.8, 90.7	6	27.59	118.87, 90.7
6	27.04	104.72, 119.82	17	27.04	104.78, 119.82
7	27.37	104.72, 133.91	8	27.37	104.78 133.91
8	25.25	56.54, 104.72	26	25.25	56.6, 84.71 104.78*
9	22.06	56.54, 70.62	40	22.06	56.6 70.62
10	24.50	104.72, 119.82	34	24.52	104.78 119.89

Table 8-6 - Shows the top ten peaks from T02173 when ranked by normalized peak area. These values are then matched to corresponding peaks found in the room (with their rank in that TIC). VOCs were matched based on both retention time (RT Min) and m/z values. Note that only the first two m/z values are presented here. The table highlights that the room played a significant role in the outcome of the TIC from the object.

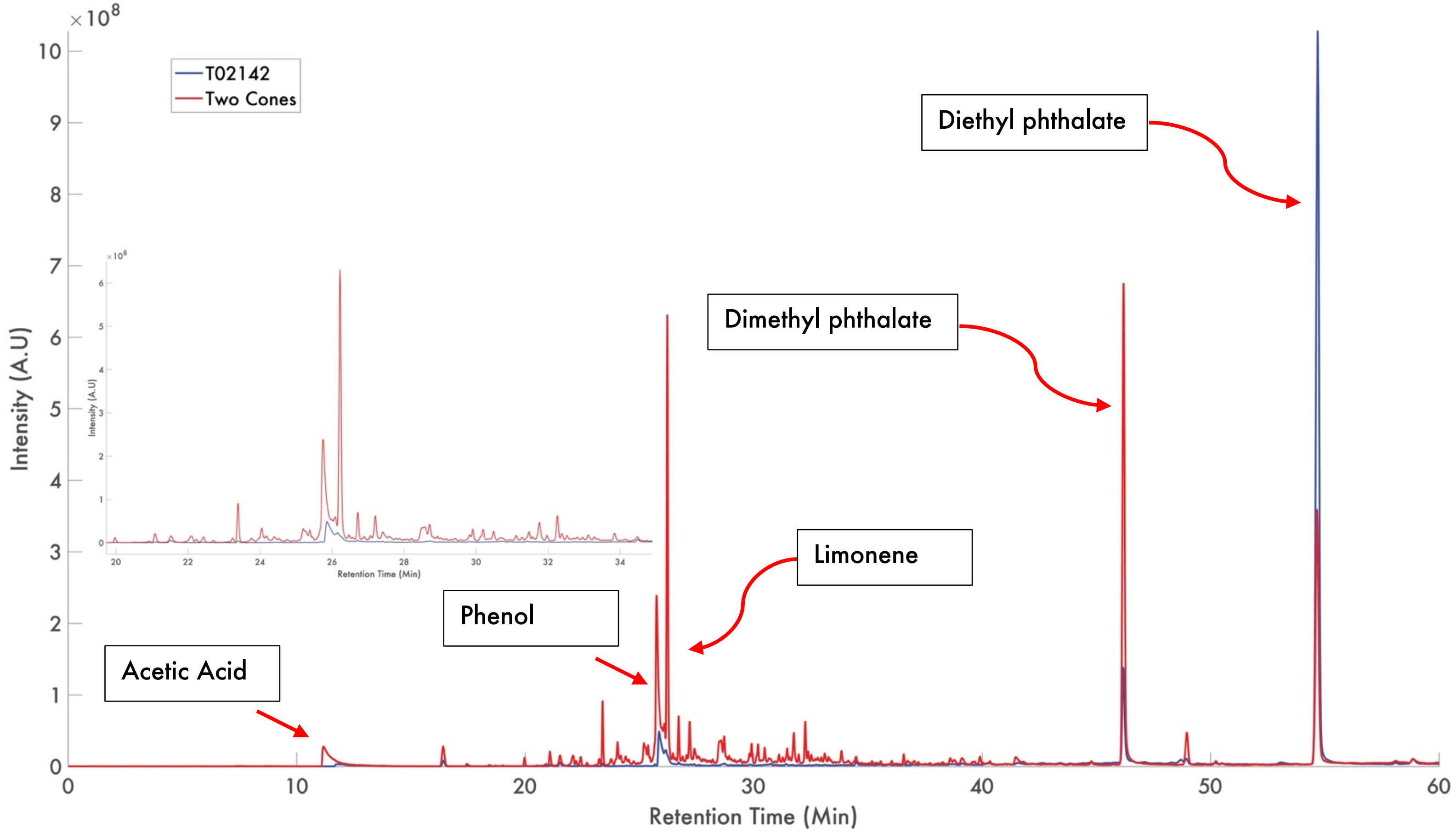

Figure 8-14 – SPME analysis results showing T02143, *Two Cones* (Red) and T02142 (Blue). This figure highlights the difference in VOC profile between the two objects. While both objects have the four main VOCs present, the area between 20 minutes and 35 minutes (See insert) have significant differences. Overall, the interpretation of TIC from T02143, *Two Cones* is less hindered by the background than the other two samples.

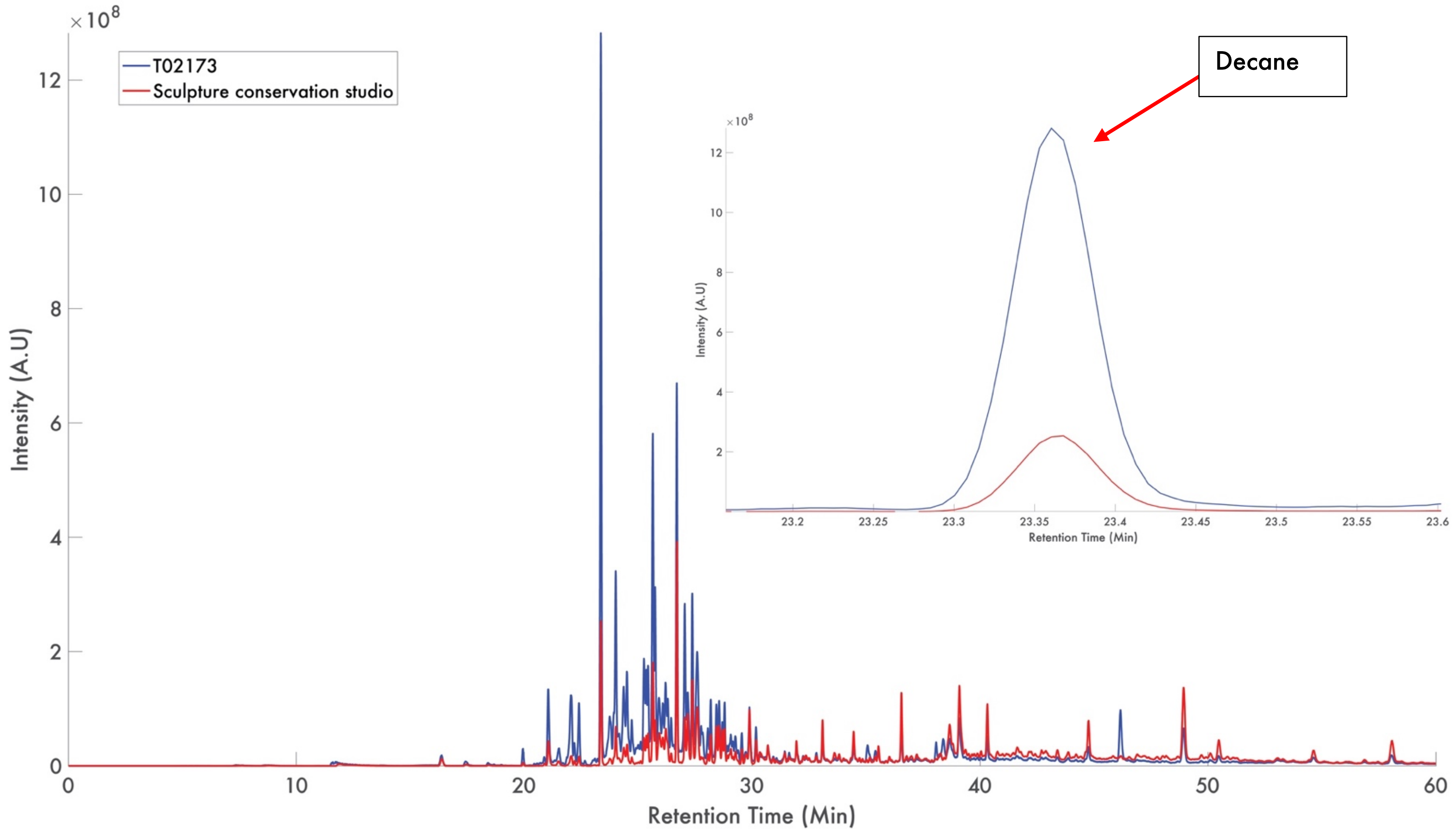

Figure 8-15 – SPME results showing the background room profile in comparison to T02173. This sample was most like the background with its largest peak of decane (see insert) likely originating from the room. This result again highlights the importance of correct fibre placement.

It is, therefore, clear that one of the limiting factors of the VOC profile seen at T02173 is its similarity to the background VOC profile from the room. This can be explained by the positioning of the SPME fibre, shown in Figure 8-11 as the rationale for fibre positioning was 'easiest placement', in the case of T02173, which had been placed into a small storage crate with little free room surrounding it, the easiest location to place the object was through the open grills at the front of the crate. This location, however, means that the fibre was also exposed to the open air.

The result from the other two objects is somewhat mixed. On the one hand, for each month SPME fibres were capable of picking up degradation and identification markers from their respective objects. Additionally, phenol was detected at T02142; this is a clear indication of the degradation of TPP and as was discussed in Chapter 7 gives the object a higher risk of rapid degradation than if it was constructed with other forms of CA. As was described in Chapter 2 (see Figure 2.1), these were the criteria which would need to be met in order for a *successful* analysis campaign. However, on the other hand, it is very clear from Table 8-5 that the fluctuating values frustrate any deeper understanding from monitoring over the course of six months.

There does not seem to be a definitive correlation between the environmental fluctuations and those seen in the VOC profile. Chapter 6 has shown us that even temperature changes of circa five degrees can equate to large changes in the observed VOC normalized peak area. However, the up/down temperature pattern does not always correlate to a similar pattern in the VOC profiles. This is best illustrated by attempting to correlate the VOC profile from T02142 to the temperature changes during the monitoring programme. In December the temperature was less than a degree higher than in January, however, the normalized peak area in January was less than half the value in December.

It is clear, therefore, that in addition to temperature effects, other factors have significant impacts on the resulting VOC profiles. One might postulate that the next likely cause is air movement causing the removal of VOC '*build-ups*' from around the object. For example, the main conservation studio which houses the object is utilized by up to six persons who each go in and out of the two main entrances several times a day. This is contrasted with the relative undisturbed airflow during the weekend when the studio is unoccupied. As each object was placed into an open storage crate designed to allow a certain degree of air movement this would likely factor into the variability of VOC profile. What is not clear is what the object "sees" – how variable is the concentration that the object is exposed to?

Currently, the effects of air movement have not been researched, as such, this case study identifies another knowledge gap with relation to the monitoring of historic polymer objects. The case study also demonstrates the challenges one faces when trying to perform long-term monitoring of historic polymer objects. The results from this work suggest that currently, those challenges exceed our knowledge base and our ability to compensate for even known influencers (e.g GCMS performance via the use of a standard.)

8.4 Workshop

Just as important as placing the proposed SPME methodology in context with other analytical techniques is placing it in the workflow context of heritage professionals who will be the target end-users. Through their feedback, the methodology can be refined and based on this feedback it also allows for certain aspects of the technique to be accentuated in future tutorials or peer-reviewed papers to maximise both its usefulness and impact.

In order to gain this feedback, a workshop was run in conjunction with Anna Pokorska who is a fellow SEAHA doctoral candidate whose work focuses on the light stability of historic polymer objects. The workshop acted as a focus group with heritage professionals who were introduced to the methodology by way of a worked example. This was followed by a short group discussion revolving around the methodology and the wider field of plastics in heritage. A questionnaire was also handed out before the discussion which afforded the participants the opportunity to give anonymous feedback after having seen the presentations (An example of the questionnaire can be found in Appendix 3).

Fourteen museum professionals attended the half-day workshop. Their backgrounds varied from conservators to management. Attendees were gathered from leading UK institutions, a list of which can be seen in Table 8-7.

Attendee Institution
British Library
British Museum
National Trust
Tate
The Museum of Design in Plastics
The Science Museum
The Welcome Collection
Victoria and Albert Museum

Table 8-7 – A list of insitutions that attended the workshop.

8.4.1 Results

The overall reception to the methodology was positive with eleven of the respondents choosing 'Useful' or 'Very useful' when asked their opinion of VOC analysis relative to other analytical techniques (Figure 8-16). This was likely due to nine of the fourteen attendees having undertaken some form of VOC analysis prior to the workshop. None of the respondents chose 'Not useful' or 'Somewhat useful' when describing their opinion of the technique. This is a powerful demonstration of the interest museum professionals hold for methods which offer greater information to them regarding their collection.

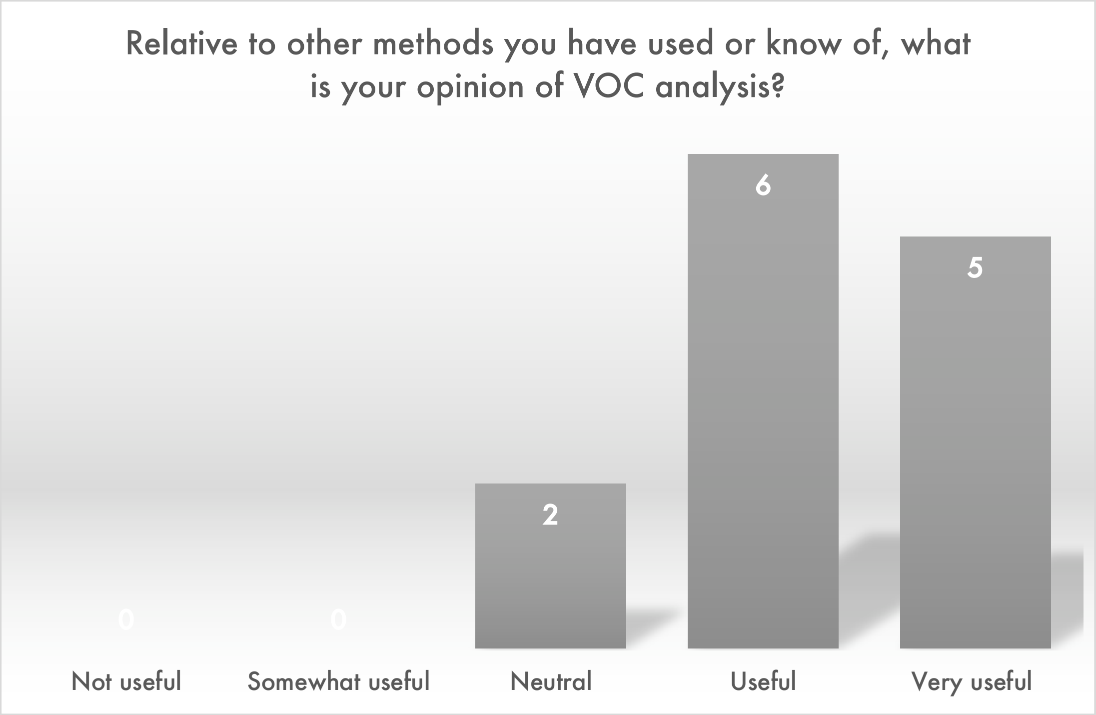

Figure 8-16 – Results from the survey which indicate that a majority of those at the workshop had a positive opinion of VOC analysis.

This sentiment was also highlighted during the discussion when participants were asked about their feelings on the evolution of the conservation of historical polymer objects over the past 15 years. Respondents voiced their opinion that experienced conservators might think that they know plastics but that might not be entirely accurate and that previous research has given a firm grounding of basics but also the realisation that additives "*make each object chemically different and we can't look at it like [for example] stone*". SPME has the ability to offer this next level of insight into their collections and as has been demonstrated in the previous chapters of this thesis can do so via a non-invasive and non-destructive methodology. However, there were mixed feelings regarding the ease of use of the method – seven respondents felt the method was either 'Not difficult', 'Somewhat difficult', or held a 'Neutral' view. Six respondents felt the methodology was either 'Difficult' or 'Very difficult' (Figure 8-17). Respondents also felt that the methodology would require "specialist knowledge" to be implemented and that staff "resourcing is an issue".

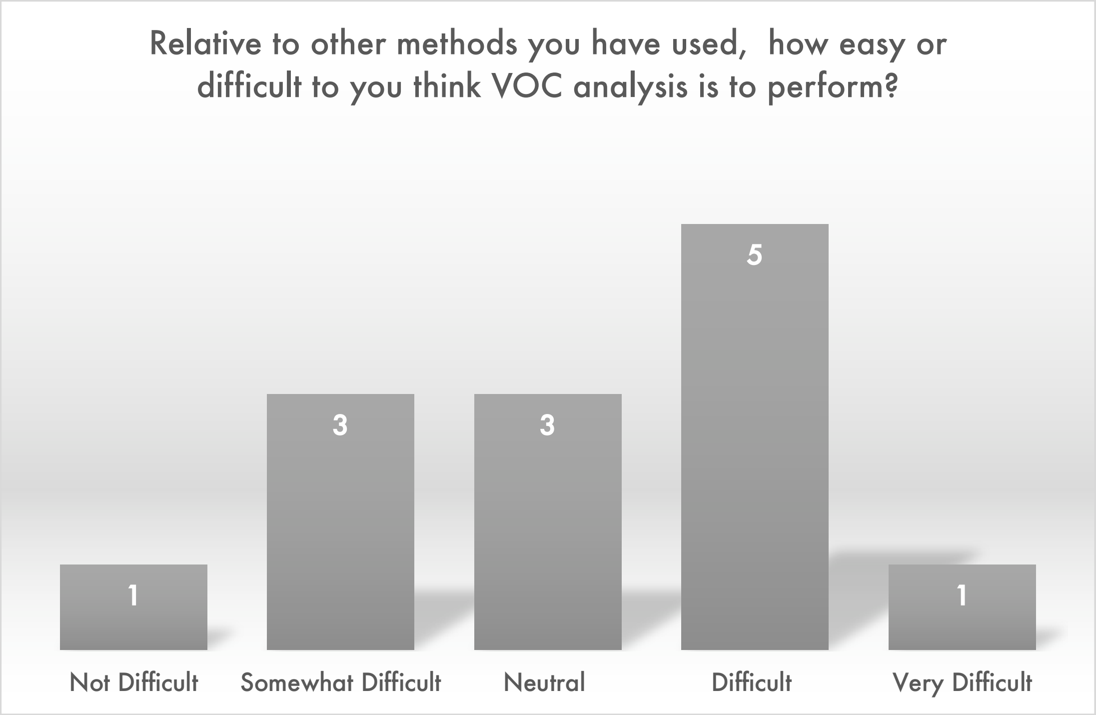

Figure 8-17 – Highlights that there were some concerns regarding the difficulty of the methodology.

Finally, the question regarding what information would be of most use to heritage processionals garnered a range of different views (Figure 8-19). There were suggestions on providing information on the identification of plastics within large collections, the lifespan of collections, what are the best options for storage, how pragmatic one can be regarding large collections given the individualistic nature of historic polymer objects, and when to allocate additional resources to higher-profile objects. SPME has the potential to impact all of these aspects as it has the ability to provide vital information which can be used to build a case to senior management for specific issues. An issue which was identified by 3 respondents during the discussion was the results from the experiment into the influence of temperature (See Chapter 6). While this experiment was not a formal part of the worked example demonstrated, questions were asked about its results and positive comments were made as to the usefulness of such information when justifying storage requirements which require high energy costs.

This theme of limited resources was acutely highlighted by way of eleven of the respondents saying that access to equipment was preventing them from utilizing VOC analysis within their institution. This is an important aspect to understand in order to allow the methodology to proliferate. The use of SPME GC/MS would require significant investment in both staffing and equipment. Currently, there is no mitigating solution to this issue, and it is likely the single greatest barrier to wider use of both VOC analysis and more specifically SPME GC/MS within the heritage community. It should also be noted that the institutions who attended this workshop are, relative to the rest of the heritage industry in the UK, very well-funded at both a national governmental level and through individual donors. It is therefore even less likely that smaller institutions would have the resources to commit to such capital outlay. As one respondent put it when asked about the potential use of SPME in their institution – *"Only in isolated occasions for high profile projects. Day to day work of managing 160 million items does not allow for this level of analysis as standard."*

Later in the discussion, the topic of resources returned when one respondent asked a question regarding the potential for a technique which provided a similar level of information that SPME delivers without the need for costly resources. In essence, they were asking for a product similar to electronic noses developed for the medical industry and described in Chapter 1. When this was described to the participants and a roadmap of the requirements needed to achieve its development were outlined there was still interest in pursuing it further from some participants. Chapter 9 will further discuss this and other potential resource mitigation strategies and directions for moving forward with implementing SPME and VOC analysis within heritage institutions.

Respondents were more positive regarding the speed with which results could be formulated by way of SPME analysis. When asked in the questionnaire how long they would be willing to wait for results from VOC analysis many responded with a timeframe of months rather than days (Figure 8-18). When asked in the discussion about the time given for the identification of plastic types found in the collection the question was met with a spontaneous eruption of laughter – due in part to the severe lack of time allocated to the task. As was shown previously (and demonstrated during the worked example during the workshop), the integration of bespoke computer code allows for results from SPME to be achieved in a significantly shorter timeframe than months; and with some experience in using the methodology, initial results on degradation and identification markers from large datasets can be obtained within hours.

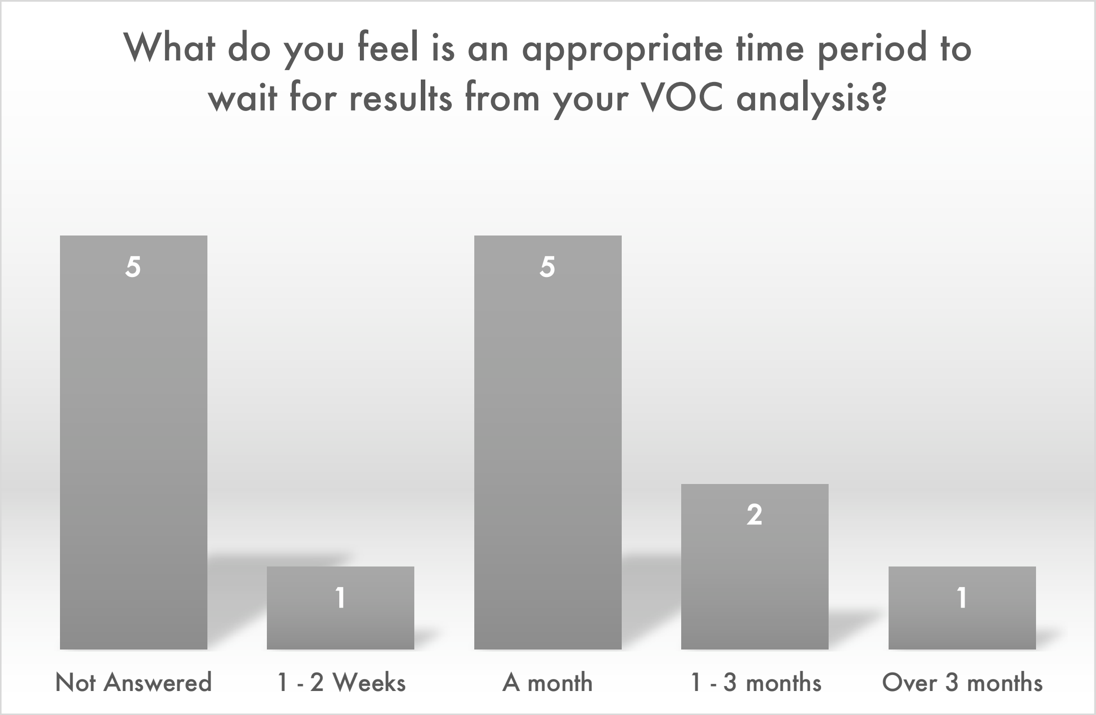

Figure 8-18 – A clear indication that an appropriate timeframe is in 'months' rather than days/weeks.

There was disagreement within the group during the discussion regarding computer coding. One respondent suggested that "*coding* *skills were not often [found] in museums"*, however, this was countered by another respondent who suggested that the groundwork for coding has been achieved in other industries but that the heritage industry was behind in its implementation. They also suggested that through collaboration computer models could be designed which allow for greater efficiency and insight.

It is clear that heritage professionals have been slow to develop computer coding skills compared to other industries. This may be due to demographics which suggest a lack of experience during professional training – a recent survey by ICON highlighted those working in conservation were *"typically white, female and middle-aged."* (Aitchison, 2013, pp. 8). This is not the typical demographic which is predisposed to IT subjects - as of 2018 those working in IT services in the UK were 83.5 % male (Office of National Statistics, EMP04: Employment by occupation - April to June 2018 Dataset) However, there are signs that this viewpoint within heritage is rapidly changing – examples being the 2019 'Hackathon' organised by UCL SEAHA students and two podcasts by on the subject of IT by 'The C Word' (http://thecword.show/2019/10/16/s06e03-the-one-with-the-arduino/ & http://thecword.show/2017/06/21/s01e09-museum-pi/.) Therefore, the concern over coding skills is likely to be short-lived and not as large an obstacle to SPME's implementation as was implied during the discussion.

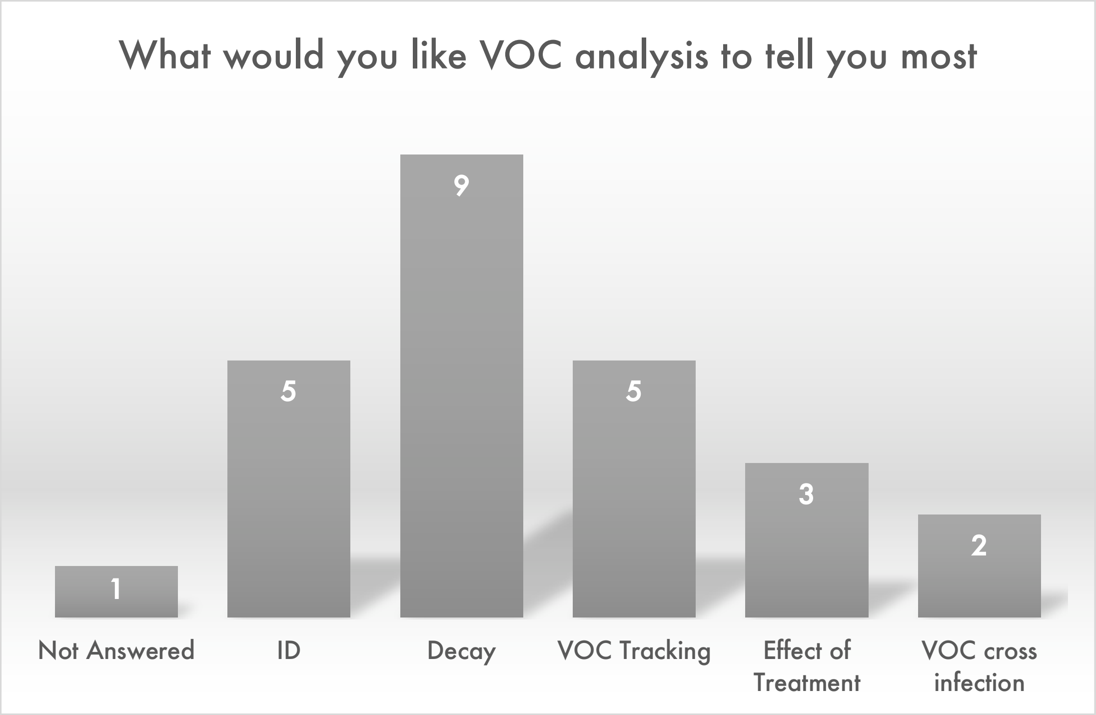

Figure 8-19 – Results highlighting that issues surrounding decay were most valued by respondents

8.5 Overall Conclusions

The information gained from these two case studies and accompanying workshop highlight not only the challenges faced by the methodology but also the great potential it possesses. While the main goal of the long-term monitoring programme was not achieved, the work highlighted SPME's ability to inform on an object's condition with relative ease. It is a positive step forward and builds on the work which has come before. The case study also highlighted another research area which must be understood to a greater extent in order to facilitate the long-term monitoring of historic polymer objects.

The insight gained from the case study involving the storage crate allows researchers to place the method in context with its peers. It allows for SPME to be selected based the additional information gained via its use over these peers. However, it was through the workshop where one gains the greatest insight into SPME's potential role within the heritage community. Their feedback clearly identifies the need for additional analytical tools – tools specific to the study of historic polymer objects. Yet despite this need, there is also the major challenge of acquiring additional resources (both in staffing and finance) to avail of the potential SPME analysis offers.

The final chapter of this thesis will outline further where SPME analysis stands after the completion of this PhD project and what future work could elevate it further.

Chapter 9 Conclusions & Future work

9.1 Introduction

The philosophical impetus for this research has hinged on two basic concepts – the first was the quote from Madden and Learner who asserted that our understanding of modern polymeric materials, from a conservation point of view, was rudimentary (J.Paul Getty Trust, 2014). The second was the postulation by Freinkel that stressed the importance plastics have and will play in our social history (Freinkel, 2012).

As a profession, there has been a number of attempts to address the former so as to allow for greater care and protection to the objects which would manifest the latter. The POPART and NANORESART projects are two high-profile examples. Yet, as this project has shown, there are significant gains to be made through the pointed study of single issues.

This project aimed to address the concept of monitoring modern polymeric materials, in a heritage context with the belief that in doing so more impactful insights would be unveiled. The research presented here demonstrates the fruitfulness of the endeavour while clearly signposting the road forward.

9.2 R.Q-1: When using SPME, what is the most efficient and effective methodology to monitor the condition, via emitted VOCs, of historic polymer objects in a heritage environment?

At the beginning of this work, in Chapter 2, four research questions were presented that highlighted the main knowledge gaps. The initial research question revolved around the adaptation of a methodology (which had shown great promise in laboratory settings) to work within a heritage framework.

The initial exploratory work outlined in Chapter 4 showed that the SPME method could easily be transported from the lab and work in an open heritage environment. Basic information regarding polymer type and degradation profiles could be achieved with little preparation. The results from the fibre exposed to the room environment crystalized the ease with which information about the types of VOCs emitted could be collected.

However, the similarities between this 'Room' fibre and a fibre placed at the opposite side of an object's storage crate highlights the poor degree to which this 'Room' information can be extrapolated to the condition of any single object. This should not be taken as a fault of the methodology, rather it should be an acknowledgement of its limitations. This research has definitively shown that any methodology, whose aim is the study of a specific object, must work as close to that object as possible.

The research presented in Chapter 4 also highlighted the major insights into the degradation pattern of the object that can be achieved with SPME analysis. The discovery of two degradation mechanisms present within a single object highlights both the complexity of historic polymer objects as well as the effectiveness of SPME's ability to analyse these materials.

Despite this impactful step forward both Chapter 4's work on the single Gabo sculpture and Chapter 8's case study work on a number of sculptures indicates that a certain level of variability can be introduced by external forces in open analysis.

Working within a more controlled environment was shown to be more consistent. However, the limitations of the sample size are seen in the research presented in Chapter 6. While working under these constraints was an acceptable limitation in the context of the research in Chapter

6, moving forward it would be beneficial to utilize larger testing chambers.

Chapter 5's initial work into the type of apparatus to use underlines the issues regarding background noise from fixtures and fittings. Yet a way forward in low-emission O-rings was hinted at. Time constraints and the overall remit of this thesis prevented a more in-depth exploration of these O-rings.

Moving forward the profession will need to confront the limitation of open analysis environments. Through the development of a bespoke low-emission chamber, which has the capacity to house small to medium-sized objects, the profession can mitigate any of these limitations. Additionally, through the development of such a chamber, whose internal atmosphere can be altered, new avenues on research into the effect of air exchange rates, changes to humidity, or VOC matrix mixture combination and concentrations can be investigated.

9.3 R.Q 2 - Can a correlation be made between VOC emissions and visible forms of deterioration in plastic artworks?

The research conducted during this project has shown that this initial question is more nuanced than it first appears. In reality, there are two aspects to this question – can the VOCs, which SPME can easily detect, be linked to degradation markers and what concentration surrounds the object.

The first aspect of this question was clearly answered during the work carried out in Chapter 6. While the main focus of that research was examining the role of temperature, a natural by-product of the research was an investigation into the effect of ageing on cellulose acetate.

That investigation definitively showed that as the object ages the relative amount of plasticiser it emits decreases while at the same time the amount of degradation product emitted increases. The critical insight, which SPME was able to provide, was that these changes are independent of each other and between samples. Sample A does not change by the same degree to which sample B might change under similar conditions, similarly, a specific VOC associated with active degradation may not change by the same degree as a similar VOC type. Furthermore, the insights which SPME was able to highlight were confirmed by cross-referencing them against a more traditional method of analysis – FTIR, thus proving that SPME is just as capable at detecting change as that method while at the same time providing information on the exact type of degradation occurring.

Furthermore, the immense benefit of SPME's ability to detect specific VOCs was shown in the research in Chapter 7 through the role the plasticiser triphenyl phosphate plays in the overall degradation of cellulose acetate. By detecting the emission of phenol from objects plasticised with TPP and showing that these samples were dramatically more degraded than those without TPP/Phenol, SPME analysis has identified a clear risk to collections. Additionally, SPME can detect this risk easily; thereby provided an additional way which CA objects could be screened upon entry to a collection.

Yet the greatest challenge was in relation to assigning a concentration value to these VOCs. Chapter 1 and 4 highlighted the difficultly in accurately determining the concentration of VOCs from SPME analysis and the number of considerations which must be dealt with in order to provide such a value. While it is true that there are methods which allow for values to be assigned, there are limitations to their relevance. These limitations, as were discussed in Chapter 4, are again best described by Pörschmann, Kopinke and Pawliszyn (1998) with their assertion that *"[the] term 'concentration' in SPME analysis should be rep laced by the more appropriate term 'activity'"*.

There is a second elephant in the room regarding concentration values – as it stands any value assigned is meaningless due to the lack of research into the effect specific concentrations have on modern polymeric materials in a heritage context. The supply of a certain value for a specific VOC does not impart any additional information to the end-user bar that it is present. Furthermore, due to the lack of research in the area noting that the concentration of a VOC associated with a degradation mechanism has doubled does not imply that its state of degradation has or will double.

Moving forward this area of research will be of critical importance. The profession must research the effect of specific concentration levels on objects. Doing so will allow for greater authority to be imparted in any collections care recommendations. At the very least 'activity' levels could be easily studied using the SPME methodology outlined in this research. This would at least give a consistent relativistic grading system which collection care managers could base decisions on.

9.4 R.Q 3 - How can we translate previous work carried out using plastic samples in a laboratory context to complex plastic objects within collections? & R.Q 4 - Can the detection of VOC emissions from plastic objects of specific polymer types, stored in heritage collections, be used as a non-destructive method for understanding ongoing degradation processes and changes in material properties?

This research forms a constituent part of an ongoing larger research stream investigating the potential methods to monitor historic polymer objects in much the same way as we currently monitor temperature and relative humidity. Previous research had shown the potential of SPME however, its adaptation to three-dimensional objects of art and design had been untested. The research presented here has conclusively shown that the ease of SPME analysis which was outlined by Curran *et al.* (2016) can be transferred to large artworks.

However, as was seen during Chapter 4 and the case studies of Chapter 8 tracking these changes is difficult in an open analysis environment condition. Chapter 6's work in attempting to quantify the degree to which temperature alters the emission of VOCs again showed the individualistic nature of these emissions.

Yet this research also provided a potential way to mitigate some of these difficulties. By adopting the methodology widely utilized outside of heritage of constructing VOC profiles and using multivariate analysis some sense was able to be made of the numbers. Promising results were made via principal component analysis when the temperature was controlled. In the case of one sample, a clear pattern was observed as it aged in all but the lowest temperature analysis; each sample was resolved into its respective age group based on the loadings of the first two principal components.

While temperature clearly impacted the behaviour of the VOCs in the profile, through the use of PCA these variations were accounted for and patterns were observable. Analysis at the lowest temperature was shown to be dramatically different from the other two. While this leads to difficulties in monitoring, this research has clearly benefited collection managers in providing concrete evidence that cool storage temperatures have a dramatic effect on an object's lifespan. Additionally, the use of VOC profiles opens the profession to the potential development of electronic noses (that were discussed in Chapter 1) which are specific to a heritage application. This would lower the entry cost to VOC analysis and also provide more information to the community regarding links between specific compounds and degradation patterns.

Moving forward it would be clearly advantageous for the profession to continue the development of VOC profiles. Doing so for materials other than cellulose acetate is needed and the methodology provided by this research provides a workflow to achieve these new profiles. Furthermore, there is a clear path to develop these profiles while simultaneously achieving the other work suggested – the development of a larger chamber allows objects with larger and more complex geometry to be studied while the development of acceptable concentration levels would provide data on how VOC profiles might change as the object ages.

Taken as a triad, the completion of these additional projects would provide researchers with a standard methodology to tests objects, a data processing system to monitor the progression of changes, and a framework judge the severity of the object's immediate environmental surroundings.

In conclusion, this research has begun to consign Madden and Learner's statement to the past and provided a clear trajectory to follow to increase the lifespan of historic polymer objects long into the future.

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Appendices

Appendix 1 - Initial weights and changes over ageing periods for samples used in Chapter 6

CA-CW –

CA-CW	Unaged		4 weeks	12 weeks	Total Change to Set A
Sample Number	Set A	Set B	Set A	Set A	
1	2093.50	2008.10	2048.77	1964.04	129.46
2	1984.90	1989.80	1955.15	1892.63	92.27
3	1861.40	2124.70	1844.94	1679.76	181.64
4	1977.40	1890.00	1942.66	1875.91	101.49
5	1946.40	1916.30	1903.90	1835.70	110.70
6	1938.30	2191.50	1900.37	1824.44	113.86
7	2073.10	2162.30	2045.33	1975.20	97.90
8	1806.90	2163.50	1787.26	1734.66	72.24
9	1954.50	2049.60	1936.27	1875.57	78.93
10	2064.50	2118.20	2026.92	1949.53	114.97
11	1986.30	1987.70	1964.02	1894.99	91.31
12	2056.80	1936.90	2009.85	1934.15	122.65
13	1778.60	2029.10	1748.12	1680.14	98.46
14	2288.70	2116.90	2224.50	2125.85	162.85
15	2087.90	2068.00	2024.12	1949.32	138.58
Average	1993.28	2050.17	1957.48	1879.46	113.82
St. Dev	123.03	91.84	113.04	114.24	28.88
% Rel Std	6.17	4.48	5.77	6.08	25.37
Max	2288.70	2191.50	2224.50	2125.85	181.64
Min	1778.60	1890.00	1748.12	1679.76	72.24
Range	510.10	301.50	476.38	446.09	109.40

All weights are in mg

CA-NewCW –

CA-NewCW	Unaged		8 weeks	2nd Ageing	Total Change to Set A
Sample Number	Set A	Set B	Set A	Not Carried out	
1	1270.7	1363.55	1216.58		54.12
2	1235	1340.61	1183.78		51.22
3	1297.75	1215.02	1241.38		56.37
4	1294.15	1434.4	1238.61		55.54
5	1362.19	1430.83	1298.62		63.57
6	1304.72	1415.47	1236.27		68.45
7	1403.96	1262.43	1339.76		64.20
8	1352.31	1214.68	1289.73		62.58
9	1263.08	1162.99	1204.08		59.00
10	1268.6	1319.06	1213.44		55.16
11	1369.63	1358.15	1301.91		67.72
12	1423.05	1143.4	1360.59		62.46
13	1413.32	1320.8	1350.19		63.13
14	1334.15	1365.35	1273.64		60.51
15	1282.68	1266.35	1211.39		71.29
Average	1325.02	1307.54	1264.00		61.02
St. Dev	57.63	90.24	55.02		5.57
% Rel Std	4.35	6.90	4.35		9.13
Max	1423.05	1434.40	1360.59		71.29
Min	1235.00	1143.40	1183.78		51.22
Range	188.05	291.00	176.81		20.07

All weights are in mg

CA-DEP –

CA-DEP	Unaged		4 weeks	12 weeks	Total Change to Set A
Sample Number	Set A	Set B	Set A	Not Carried out	
1	631.09	533.94	605.81		25.28
2	488.26	539.52	467.18		21.08
3	584.74	698.08	564.07		20.67
4	574.96	648.57	552.74		22.22
5	697.19	613.81	668.94		28.25
6	542.66	568.51	523.46		19.20
7	548.26	481.93	527.98		20.28
8	647.40	668.13	624.98		22.42
9	678.90	578.13	652.51		26.39
10	646.62	627.04	619.07		27.55
11	659.13	554.00	633.22		25.91
12	652.85	636.17	629.34		23.51
13	638.35	654.74	613.45		24.90
14	674.60	591.87	646.84		27.76
15	631.10	572.74	607.24		23.86
Average	619.74	597.81	595.79		23.95
St. Dev	57.05	56.65	54.69		2.82
% Rel Std	9.21	9.48	9.18		11.76
Max	697.19	698.08	668.94		28.25
Min	488.26	481.93	467.18		19.20
Range	208.93	216.15	201.76		9.05

All weights are in mg

CA-TPP –

CA-TPP	Unaged		4 weeks	10.5 weeks	Total Change to Set A
Sample Number	Set A	Set B	Set A	Set A	
1	594.12	478.65	577.35	426.52	167.60
2	493.34	591.09	481.87	417.76	75.58
3	484.8	488.77	473.2	410.67	74.13
4	564.52	507.85	548.51	449.22	115.30
5	536.76	467.14	522.98	427.87	108.89
6	548.58	530.72	533.81	429	119.58
7	649.37	681.96	629.31	436.89	212.48
8	526	522.8	513.79	n/a	n/a
9	512.77	496.43	499.51	408.67	104.10
10	577.85	519.02	560.62	461.3	116.55
11	650.29	650.83	629.92	446.18	204.11
12	555.85	505.1	540.09	n/a	n/a
13	496.13	526	483.62	396.95	99.18
14	517.69	485.4	506.39	419.05	98.64
15	452.24	502.31	440.59	384.08	68.16
Average	544.02	530.27	529.44	424.17	120.33
St. Dev	55.06	60.49	52.26	20.63	44.68
% Rel Std	10.12	11.41	9.87	4.86	37.13
Max	650.29	681.96	629.92	461.30	212.48
Min	452.24	467.14	440.59	384.08	68.16
Range	198.05	214.82	189.33	77.22	144.32

All weights are in mg

Appendix 2 - Analysis of the standard & its relationship to the peak area values for CA-NewCW

One issue to note is the discrepancy between the standards used to normalize the unaged samples and the samples aged for 8 weeks. For the unaged standard the peak area of ethylbenzene was 2.27×10^9, while the peak area for the standard used to normalize the aged samples was 1.25×10^{10}. As was discussed in chapters 1 & 3 the standard is utilized to allow for comparison between samples over the course of long time periods; the theory being that the standard measures the performance of the GC/MS at that moment in time. This holds only if the standard has been carried out correctly.

It is possible to retroactively determine the performance of the standard used for the aged samples by comparing its relative standard deviation to both the relative standard deviation of the unaged and also with the relative standard deviation of repeated measurements of the SPME standard. In the first instance, we see that the %RSD of the standards performed during the working week in which the aged samples were analysed was 19.76%, while during the week of the unaged samples was higher at 28.51%. Secondly, the standard utilized for the aged samples was also in keeping with our own standard repeatability tests (Chapter 3) which showed that user error would lead to a %RSD of circa 11%.

Unaged Samples			**Aged Samples**	
Date	**STD Peak Area**		**Date**	**STD Peak Area**
13/12/2018	2.81E+09		28/02/2019	7.32E+09
13/12/2018	1.39E+09		28/02/2019	9.54E+09
14/12/2018	2.27E+09		28/02/2019	7.34E+09
15/12/2018	3.06E+09		28/02/2019	8.45E+09
19/12/2018	2.08E+09		01/03/2019	1.25E+10
19/12/2018	1.42E+09		02/03/2019	7.46E+09
19/12/2018	2.45E+09		03/03/2019	8.13E+09
19/12/2018	1.36E+09			
Average	2.10E+09		**Average**	8.67E+09
St. Dev	6.00E+08		**St. Dev**	1.71E+09
% Rel Std	28.51		**% Rel Std**	19.76

Peak area analysis from the peak of ethylbenzene which is used as an external standard to both track the performance of the GC/MS machine and to allow for intra-day comparison of the relative abundance of VOCs emitted from samples.

If it holds that the performance, read in peak area, improves then as the standard increases so too do the samples. Therefore, between the two dates, a rise or fall in a sample's normalized peak area is based on the quantity in the sample rather than the performance of the GC/MS or the method.

Returning to the CA-NewCW samples, its VOC profile had been shown to be lower for the aged samples which we interpret to be an actual decrease in the sample rather than something untoward occurring with the running of the sample.

One further way to check for errors in the method is the examine the %RSD of the five samples which make up the average normalized peak area of the VOC profile. If we use the largest peak, that of diethyl phthalate, the unaged samples registered a %RSD of 9.98% while for the aged samples was 3.75%. This shows that the decrease was unlikely to be caused by a poorly sealed vial driving the overall average down.

This leaves two possible pathways for the levels to decrease –

1. The VOCs have actually been lowered via a reduction in degradation mechanisms driving their respective degradation processes, or
2. The accelerated ageing process itself has caused the VOCs to be driven off and we are left with hardly any volatiles to measure.

As was mentioned previously, as all VOCs of interest in the VOC profile were reduced, and as it is unlikely that all degradation processes were stopped/slowed it is possible to discount this theory.

This suggests that rather than a degradation mechanism slowing down or reaching an endpoint it is likely due to some aspect of the accelerated ageing process. While not reported on in this thesis, this phenomenon has been seen previously by this researcher where a PVC sample emerged from accelerated ageing with significant yellowing (with a ΔE_{00} of 53). However, SPME analysis highlighted a reduction in aldehydes which contain carbonyl groups associated with the yellowing of CA (Shashoua, 2008, p. 184). It is clear therefore that in certain cases accelerated ageing can have unintended consequences which frustrate experimental insights.

Appendix 3 - Example of Questionnaire used in workshop

Please take some time to fill in this questionnaire as best you can.

Q 1 – Have you previously worked with VOC analysis?

No

Yes

If yes, what type of VOC analysis and what type of material was analysed?

Q 2 – What would you like VOC analysis to tell you most (e.g. degradation markers, ID markers, ability to track objects' progression etc)?

Q 3 – Relative to other methods you have used or know of, what is your opinion of VOC analysis?

1. Not useful
2. Somewhat useful
3. Neutral
4. Useful
5. Very useful

Q 4 – Relative to other methods you have used, how easy or difficult to you think VOC analysis is to perform?

1. Not difficult
2. Somewhat difficult
3. Neutral
4. Difficult
5. Very difficult

Q 5 – Is access to equipment stopping you from using VOC analysis?

No

Yes

Q 6 – What do you feel is an appropriate time period to wait for results from your VOC analysis?

Q 7- Do you see any potential for this technique at your institution in the future?

Q 8 –

How and when is the light stability of plastic objects currently assessed in your institution? (e.g. during the acquisition process, condition surveys or prior to display)

Q 9 – What guidelines or materials, if any, do you use to inform those assessments?

Q 10 – Do you think you have sufficient knowledge or information on light stability of plastics, or access to such to assess objects in your collection?

Q 11 – Are there any challenges involved in making these assessments?

No

Yes

If yes, what are they?

Q 12 – What would be helpful in overcoming these challenges?

Q 14 – Are you aware of light-damaged plastic objects in your collections?

No

Yes