

## The Development of a SPME-GC/MS Method for the Analysis of VOC Emissions from Historic Plastic and Rubber Materials

Katherine Curran<sup>a</sup>, Mark Underhill<sup>a</sup>, Lorraine T. Gibson<sup>b</sup>, Matija Strlic<sup>a</sup>

<sup>a</sup> UCL Institute for Sustainable Heritage, University College London, 14 Upper Woburn Place, London WC1H 0NN, United Kingdom

<sup>b</sup> Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

**Corresponding Author:** Katherine Curran: k.curran@ucl.ac.uk

### Abstract

Analytical methods have been developed for the analysis of VOC emissions from historic plastic and rubber materials using SPME-GC/MS. Parameters such as analysis temperature, sampling time and choice of SPME fibre coating were investigated and sampling preparation strategies explored, including headspace sampling in vials and in gas sampling bags. The repeatability of the method was evaluated. It was found that a 7 d accumulation time at room temperature, followed by sampling using a DVB/CAR/PDMS fibre, with a sampling time of 60 min at room temperature was a suitable strategy for the detection of VOC emissions from a wide range of historic plastic and rubber artefacts. For 20 mL vials, a sample size of 50 mg was found to be appropriate and grinding the samples improved the repeatability of the analysis and yielded higher levels of emissions. A non-destructive adaptation of the method that could be used directly on historic objects in a museum environment is also presented. The detected emissions improve understanding of ongoing degradation processes within historic plastic and rubber materials, in addition to providing information on material composition.

### Keywords

Volatile Organic Compounds; SPME-GC/MS; Heritage; Plastic; Modern Materials;

## Figure Captions

**Figure 1.** Selected VOC emissions detected from 3 different plastic objects depicted as the peak areas detected using the CAR/PDMS fibre relative to those detected using the DVB/CAR/PDMS fibre. The error bars show the average range between maximum and minimum values. Hydrocarbons 1 and 2 are two hydrocarbons detected in the VOC emissions of polyethylene samples which could not be identified based on their mass spectra.

**Figure 2.** Variation in Peak Areas for the two selected external standard compounds over 9 months of the experiment. The Peak Area Ratio was calculated by dividing the area of the ethyl benzene peak by the area of the xylene peak.

**Figure 3.** Close-up of a region of a chromatogram showing SPME-GC/MS analysis of VOC emissions from samples of a NR object. Samples were sealed in vials for different accumulation times before analysis.

**Figure 4.** Peak areas of selected VOC emissions from SPME-GC/MS analysis of 4 different plastic objects after sampling at both room temperature and at 40 °C. The results have been log transformed and are the average of 3 repeats and the error bars show the maximum and minimum values.

**Figure 5.** Peak areas of selected VOC emissions detected from a PS object using different sampling times.

**Figure 6.** Peak areas of selected VOC emissions detected from a CA object using different sampling times.

**Figure 7.** Non-destructive analysis of a PUR foam doll using a SPME fibre in a manual holder

**Figure 8.** Chromatograms showing the results of the analysis of (a) a sample from a CA doll and (b) the non-destructive analysis of a similar doll: a. acetic acid, b. N,N-dimethylacetamide, c. phenol, d. tetramethylsilane, e. dodecamethylpentasiloxane, f. dimethylphthalate, g. diethylphthalate.

## 1 Introduction

The analysis of VOC emissions from polymer-based materials can provide an insight into their composition and degradation and has found a wide range of applications such as quality control monitoring in the plastics processing industry and in the assessment of indoor air quality in homes and offices. [1] [2][3][4]

In the field of cultural heritage, there is a growing interest in the use of VOC analysis as a tool for the characterisation of historic objects with recent work including the on-site detection of VOC emissions from historic wax objects in the Musee d'Orsay in Paris [5] and the analysis of historic paper samples. [6][7] [8] A significant advantage of VOC analysis for heritage applications is that it has the potential to be entirely non-invasive, while also providing detailed chemical information. This would make the technique unique among other options for heritage material characterisation, which typically require close contact between the instrument and the object.

Headspace solid-phase microextraction gas chromatography mass spectrometry (HS-SPME-GC/MS) is a reliable, easy-to-use analytical technique that enables the detection and identification of a wide range of VOCs. First reported by Pawliszyn et al. in the early 1990s [9], it involves the adsorption of volatile analytes onto a coated fibre placed in the headspace of an object, followed by desorption at high temperature and analysis using GC/MS.

While a large number of plastic and rubber objects are found in modern art and design collections, in 20<sup>th</sup> century social historical collections and in sound and cinematic archives, the conservation of these objects is complicated by the wide range of material types and formulations present. [10][11][12] In addition, plastics have often been found to degrade more rapidly and suddenly than many traditional heritage materials, often displaying visible signs of degradation within 5-25 years of acquisition. [13]

A variety of techniques are in use for the characterisation of these materials and processes. Most routinely, IR (including NIR) and Raman spectroscopy are in use, however, it is often very difficult to do more than identify the base polymer material. Although non-invasive imaging methods are in development,[14][15] it is unlikely these will improve beyond the point-based analysis methods, as they are based on the same analytical principle. For more detailed analysis, e.g. of plasticisers or antioxidants, pyrolysis-GC/MS is often used [16], however, this is by definition a destructive method of analysis.

There is therefore a need for new tools for understanding the composition and monitoring the degradation of plastic and rubber objects in museum and library collections using a non-destructive and potentially non-invasive approach. The analysis of VOC emissions from historic plastics and rubbers is one such tool, and a study of VOC emissions from historic plastics was published recently.[17] VOC analysis can be seen as combining the non-destructiveness of spectroscopic techniques, with the ability of chromatographic methods to unambiguously identify specific components in complex materials.

The goal of this work was to develop an analytical method that is suitable for the characterisation of a wide range of polymer-based materials relevant in cultural heritage collections, including cellulose acetate (CA), cellulose nitrate (CN), polyvinyl chloride (PVC), polyurethane (PUR), polystyrene (PS), phenol formaldehyde (Bakelite) (PF) and natural rubber (NR). The influence of parameters such as fibre coating, sampling time and temperature, as well as sample preparation were explored. The analytical method was developed by SPME-GC/MS analysis of samples from plastic and rubber objects in headspace vials. From this laboratory-based approach, the next step is to adapt the

method for the analysis of real plastic and rubber artefacts, to explore how VOC analysis can be used as an entirely non-destructive method of chemical analysis suitable for heritage collections. To demonstrate how this can be achieved, VOC emissions from objects in a reference collection of historic materials were analysed by placing the objects in Tedlar® bags and sampling them using the analytical method developed here, slightly adapted for a non-destructive approach. The observed differences in the results of the analysis of plastic and rubber objects and samples from the same objects will be discussed.

## 2 Experimental

### 2.1 Source and identification of historic plastic and rubber objects

The polymer types to be analysed were selected due to their ubiquity in museum environments, based on surveys completed as part of the Preservation Of Plastic ARTefacts (POPART) project [18] and other reports from the Victoria and Albert (V&A) Museum [12], the Science Museum, London [11], the British Museum [19] and a study of plastics in archives [10]. For the purposes of this work, 21 different objects were used, comprising 11 different polymer types and are listed in Table 1.

The samples were collected from 3 different sources: the Historic Plastic Reference Collection (HPRC) at the Institute for Sustainable Heritage (ISH), University College London, the SamCo collection from the Preservation of Plastic Artefacts (POPART) project [20], and the RESINKIT™ company, Woonsocket, RI, USA. Samples from objects were also artificially degraded at 80 °C and 65 % RH using a Vötsch 0030 climate chamber for 2,4,6,8 or 10 weeks.

Prior to studying VOC emissions, most samples were analysed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) using a Bruker Alpha FTIR Spectrometer with an ATR Platinum Diamond single-reflection module #CFBFA32D. 24 scans were collected over the wavenumber range 4000 to 375  $\text{cm}^{-1}$  with a band width resolution of 4  $\text{cm}^{-1}$ . The exception was the samples provided from the POPART SamCo reference collection as they had been previously characterised using FTIR, Raman spectroscopy and pyrolysis GC-MS giving unambiguous identification of the samples' polymer type.

**Table 1.** Plastic objects used in this work

Entry no.	Reference no.	Plastic or Rubber type	Notes
1	HS91	Cellulose acetate	Doll
2	HS251	Cellulose acetate	White object
3	HS2	Cellulose nitrate	Jewellery box
4	HS3	Cellulose nitrate	Jewellery box
5	HS5	Poly(vinyl chloride)	Doll
6	HS137	Poly(vinyl chloride)/ Poly(vinyl acetate) copolymer	Vinyl record
7	HS89	Polyurethane foam	Doll
8	HS244	Polyurethane ether	Foam
9	HS328	Polyurethane ester	Thermoplastic
10	HS 145	Polystyrene	Green cup
11	HS50	Poly(ethylene terephthalate)-glycol modified	Transparent ResinKit
12	HS324	Glass reinforced polyester	Green fibreglass
13	HS1	Polyethylene	White object
14	HS24	Polyethylene	Doll
15	HS117	Polyethylene	Red orange squeezer
16	HS320	Phenol formaldehyde	Brown wood substitute
17	HS44	Poly(methyl methacrylate)	Transparent ResinKit
18	HS210	Poly(methyl methacrylate)	Purple object
19	HS26	Polypropylene	Transparent ResinKit
20	HS92	Poly(isoprene) rubber	Swimming cap
21	HS216	Natural rubber	Yellow object

## 2.2 Sampling

For destructive sampling, an Everise Rotary Tool (Code: N60GR) was used to grind samples providing a final sample mass of approximately 50 mg, which was inserted into a 20 ml Chromacol headspace sample vial (20-HSV T229) and sealed with a Chromacol 18 mm Magnetic Screw Cap with a 1 mm Silicone/PTFE Liner - Not Prefitted (18-MSC-ST101). HS-SPME-GC/MS analysis was performed using a DVB/CAR/PDMS SPME fibre (50/30  $\mu\text{m}$ ) (Supelco, 57298-U) or a CAR/PDMS fibre (75  $\mu\text{m}$ ) (Supelco 57343-U).

For non-destructive sampling, whole objects were placed in 5 L Tedlar<sup>®</sup> Sample Bags with a single polypropylene fitting (Cat No.: 232-05) from SKC (Dorset, England). HS-SPME-GC/MS analysis was performed using a DVB/CAR/PDMS SPME fibre (50/30  $\mu\text{m}$ ) (Supelco, 57328-U) in a fibre holder for manual use (Supelco, 57330-U). Objects were placed in Tedlar bags by cutting open the bags using a scalpel, placing the object inside and then resealing using a Packer Poly Sealer (Typ: PBS-400-C) heat sealer.

Samples were placed in closed vials or bags and left at room temperature unless otherwise stated. The SPME fibre was not exposed to the headspace above the sample at this time.

The laboratory temperature was monitored and the average value was found to be 25 °C over a 6-month period.

### 2.3 HS-SPME-GC/MS analysis

Analytes were recovered from the fibre by heating in the injection port of a Perkin Elmer Clarus 500 gas chromatograph equipped with a Combipal PAL System (CTC Analytics) autosampler coupled to a Perkin Elmer Clarus 560D mass spectrometer. A VOCOL column (Supelco, 20 % phenyl- 80 % methylpolysiloxane) was used (60 m in length and 0.25 mm diameter) to separate the VOCs using the oven programme as follows: initial temperature of 50 °C (hold for 5 min), ramp rate of 10 °C/min to 100 °C, then 5 °C/min to 200 °C, then 2 °C/min to 220 °C, which was held for 20 min. The carrier gas was helium with a constant flow of 1 cm<sup>3</sup> min<sup>-1</sup>. The injector temperature was 250 °C and the injector was used in splitless mode with a 1 min injection.

The interface and source temperatures were 200 °C and 180 °C respectively. Mass spectra were collected under electron ionisation (EI) mode at 70 eV and recorded from  $m/z$  45 - 300 with a scan time of 0.4 s and an interscan delay of 0.05 s. VOC peak identification was performed using the NIST 2005 Mass Spectra Library V2.1.

A MISA Group 17 Non-Halogen Organic Mix was purchased from Sigma Aldrich (48133 Supelco). It contains 2000 µg/ml each of benzene, ethylbenzene, styrene, toluene and ortho-, meta- and paraxylene in methanol. 1 ml of this was diluted up to 50 ml in methanol. On a daily basis, 1 ml of this solution was transferred into a 20 mL Chromacol headspace sample vial (20-HSV T229) and the headspace analysed in the same way as for solid samples, as a standard. This provided daily data on instrumental and column drift, as well as the performance of the SPME fibre. The daily run consisted of cleaning the SPME fibre, analysis of a blank (an empty vial containing no sample), analysis of a standard, followed by analysis of 6 samples. After each batch of 6, another blank and standard were analysed.

For some of the experiments, different parameters to those described above were used e.g. more than 50 mg of sample was used in some cases. This reflects the fact that these experiments were performed at an earlier stage of the research, before the optimal parameters had been identified. However, each experiment is consistent within itself and the findings can be used confidently for method development.

## 3 Results

### 3.1 SPME fibre

It was necessary to select a SPME fibre coating that was suitable for the widest possible range of analytes. A range of SPME fibres with different coatings are commercially available and 2 were selected for the study: a 50/30 µm DVB/CAR/PDMS fibre, a general purpose fibre which has been shown to be suitable for the analysis of VOC emissions from historic paper and wax objects [5] [6] and a 75 µm CAR/PDMS fibre, for gases and low molecular weight compounds and with a known affinity for polar compounds such as organic acids. The results of the analyses of samples from 3 different objects, composed of PS, CA and PE are shown below (Figure 1). 50 +/- 5 mg samples of ground plastic were used and for each fibre, each object was analysed in duplicate. The samples were analysed using a 60-min sampling time at room temperature.

Overall, the DVB/CAR/PDMS fibre was shown to be 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. In particular the enhanced collection of volatile hydrocarbons from polymers such as polyethylene was very evident.

The expected higher collection of organic acids by the CAR/PDMS fibre was demonstrated (Figure 1); however, although organic acids are known degradation products of several plastics such as CA and PE, significant quantities of acetic acid were also detected using the DVB/CAR/PDMS fibre, and overall the ability of the DVB/CAR/PDMS fibre to detect a wider range of analytes was deemed to be more important. This is due to the fact that this work aimed to understand the range of VOCs that were relevant to provide an understanding of the composition and condition of plastic materials in collections. These results are consistent with previous work on the analysis of VOC emissions from historic paper, in which the DVB/CAR/PDMS fibre was also used. [6]

### 3.2 Inter- and Intra-day Repeatability

The inter-day repeatability was monitored and ensured by using a standard solution prepared as described in the Materials section and analysed using a sampling time of 20 s at room temperature and the DVB/CAR/PDMS fibre. It was necessary to use a short sampling time for analysis of the standard solution, as the use of longer sampling times e.g. 1 min, 5 min, 30 min led to contamination, with analytes from the standard being carried over to later analyses.

The changes in two peak areas corresponding to ethyl benzene and two co-eluting isomers of xylene were studied over a 9 month period, which included 177 measurements. Analysis of standards took place on each day that analysis of plastic samples took place. The two peaks were chosen as their retention times differed by only 0.1 min and thus the separation achieved between the two peaks would give a useful indication of changes in chromatographic resolution. Over the period of study, considerable variation in the areas of these two peaks was observed with a RSD of 60.2% for the ethyl benzene peak and RSD of 58.9% for the xylene peak. The retention times were very consistent (RSD = 0.16%) and the ratio of the peak areas was also very consistent (RSD = 3.2%). These values can be seen below in Figure 2 and demonstrate the importance of understanding this variation in order to make meaningful comparisons over time as the performance of SPME sampling and of the chromatographic system changes.

The intra-day variability can be studied by examining the variation in peak areas following analysis of multiple external standard samples on the same day. Table 2 below shows the relative standard deviations of the areas of the ethyl benzene and xylene peaks from 5 analyses on the same day, four times. The results show that there is a significant intraday uncertainty due to variation in instrument performance, SPME fibre condition, laboratory temperature or inherent variations in sample preparation e.g. the extent to which a vial cap is sealed.

A comparison between these values and the values in Table 5 (below) which shows the results of analysis of VOC emissions from plastic samples, demonstrates that the repeatability of analysis of VOC emissions from plastic samples is comparable to the overall intraday repeatability. This is a satisfactory result as it demonstrates that the method of analysis for plastic samples developed here yields analysis that is almost as repeatable in many cases as analysis of a standard solution.

**Table 2.** Variation in peak area from 5 repeated analyses of external standard samples on a single day.

Date	Relative Standard Deviation (%)	
	Ethyl benzene	Xylene
14 <sup>th</sup> December 2012	6.8	6.6
4 <sup>th</sup> February 2013	16.3	15.3
29 <sup>th</sup> April 2013	12.0	10.8
17 <sup>th</sup> June 2014	12.8	11.7

### 3.3 Assessment of the repeatability of sealing the vials

Given that plastic samples were to be kept in sealed vials to allow population of the headspace for 7 days, an experiment was run to explore leakage of volatile analytes from the capped vial during this period. It was assumed that some leakage could occur, however what was deemed important was whether or not such leakage was repeatable. To ensure that the tested samples were equal and repeatable, a solution of 15  $\mu$ l of each of toluene, benzene and hexane in 150 ml methanol was used instead of a solid sample. On two consecutive days (two batches), 5 ml of this solution was placed in 10 vials (20 vials total). These were sealed and left for 7 d before sampling at room temperature for 20 s using the DVB/CAR/PDMS fibre. Again a shorter sampling time was used for this solution, as the use of longer sampling times for analysis of solutions was found to lead to contamination. The results are shown in Table 3. It was clear that vial leakage did not have a significant effect on the repeatability of analysis even after one week, when compared to the intra-day variation observed using the standard (Table 2).

**Table 3.** Results of vial leakage test.

	Analyte	Relative Standard Deviation (%), N=10
<b>Batch 1</b>	Hexane	12.8
	Benzene	8.3
	Toluene	10.7
<b>Batch 2</b>	Hexane	5.5
	Benzene	9.9
	Toluene	14.3

### 3.4 Internal Standard

The use of an internal standard was explored to see if the repeatability of analyses could be improved. Dimethyl phthalate- $d_6$  was chosen as a substance that was unlikely to be present in any real plastic objects, although chemically very similar to a commonly detected plasticiser and volatile enough to be detectable using SPME-GC/MS (b.p. = 282 °C). A solution of 5 mg of the phthalate in 10 ml methanol was prepared. In an initial experiment, 5 vials were treated by placing 50  $\mu$ l of the solution into the neck of the vial, and leaving it at a tilt overnight to allow the solution to coat the vial wall without pooling at the bottom of the vial. After being left open overnight to allow the solvent to evaporate, the vials were sealed, left for 7 d to allow VOCs to accumulate and then



analysed using the CAR/PDMS fibre and a 60 min sampling time. This 60 min sampling time was chosen as it was found to yield detectable quantities of a wide range of analytes from plastic samples (see section 3.8 below). The results showed that the peak area of the phthalate signal varied considerably, with a calculated relative standard deviation (RSD) of 46.4%. A repeated experiment gave an RSD value of 44.6%.

In order to study the impact of weighting the peak areas of VOC emissions from plastic samples using an internal standard, 3 vials were pre-prepared with the phthalate solution as described above. Before sealing the vials, a piece of a PS object (mass = 250 +/- 25 mg) was placed in each vial, before leaving them sealed for 7 d and analysing as described above. In this experiment, nonstandard conditions i.e. 250 mg of sample were used, however they still provide a valid assessment of the use of an internal standard. The ratio of the peak area of the styrene emission from the PS object to the peak area of the phthalate-d<sub>6</sub> was measured. The peak area ratio varied from 0.62 to 4.37 i.e. by almost an order of magnitude. This was still the case, even after normalising for sample mass, given that 250 +/- 25 mg of sample was used in all cases.

Given that there was significant variation in the peak areas of the phthalate-d<sub>6</sub> and that weighting the peak areas of VOC emissions from plastic samples using the internal standard did not produce results of satisfactory repeatability, the use of an internal standard was not pursued further. The reasons for the variability are not known, they may be related to the way in which the samples were prepared (grinding samples produced more repeatable results, see section 3.7). Alternatively, the phthalate may have interacted differently with different plastic samples, possibly being absorbed more by one than another, due to differences in surface area or surface roughness.

### 3.5 Accumulation time

The accumulation time refers to the time required for VOCs to accumulate in the headspace. The SPME fibre was not exposed to the headspace during this time. To examine this, pieces of 4 plastic objects – an NR object, a CA object, a PUR object and a PS object, were stored for 1, 2, 7, 14, 21 or 28 days in sealed sample vials prior to analysis. Sample masses of 250 +/- 25 mg were again used and the CAR/PDMS fibre was used to sample the headspace.

The fibres were analysed using a 60 min sampling time. The results from the NR object are shown in Figure 3. It can be seen, that even after a 1 d accumulation time, detectable quantities of VOCs are emitted from the plastic samples. After 7 d accumulation time, a significant increase in the VOC peak intensities was measured after which time decreases in peak area are observed. The reasons for these decreases are not known, it may be due an inherent variability due to sample preparation, as grinding the samples was found to improve repeatability (see section 3.7).

Similar results were observed for other objects and therefore a 7 d accumulation time was considered suitable. A 7 d accumulation time has been used for the majority of the experiments described in this paper, with the exception of the study of sampling temperature (section 3.6) and the study of sample preparation (section 3.7) which used a 14 - 16 d and a 21 d accumulation time respectively, as these experiments were done at an early stage of the research. However, these experiments are consistent within themselves and are therefore valid.

A 7 d accumulation time was also found to be suitable for the non-destructive analysis of plastic objects in Tedlar® bags i.e. detectable quantities of a wide range of emissions were found after 7 d. This does not necessarily imply that the maximum concentration of VOCs in the bag had been reached after 7 d, and it may be interesting to explore longer accumulation times. However, the permeability of Tedlar® bags also needs to be taken into account as the recovery of several VOCs has

been found to decrease after 6 d, and stability of VOCs for longer periods is not guaranteed. [33] A comparison of the results from analysis of plastic samples and the non-destructive analysis of plastic objects is given below in section 3.10.

### 3.6 Sampling temperature

Room temperature sampling was preferred as this would be most suitable for determination of VOCs emitted from objects held in heritage collections. However, it was hypothesised based on previous research studying historic paper that at elevated temperature larger quantities, or a wider range of analytes, could be emitted from objects and detected.[6] In order to test this, 4 samples were studied, 2 different polyesters (Poly(ethylene terephthalate – glycol modified (PETG) and Glass reinforced polyester (GRP)), PMMA and PF. These plastic types were chosen as their VOC emissions were expected to be low, and thus they were the plastic types most likely to benefit from increased sampling temperature. Six sub-samples (mass 250 +/- 25 mg) of each material were sealed in vials and VOCs were allowed to accumulate in the headspace at room temperature in all cases for 14 – 16 d. This varies from the accumulation time of 7 d described in section 3.5, as this experiment was done at an earlier stage of the research. However, this experiment was consistent within itself. Triplicate analyses of each sample were performed both at room temperature and at 40 °C, using a 60 min sampling time and the CAR/PDMS fibre.

A comparison of selected analytes from each sample is shown below (Figure 4). The peak areas have been log-transformed in order to plot and compare them more easily. The results show that there is no significant advantage to be gained from heating the samples to 40 °C. No additional peaks were detected at the higher temperature and there were no significant increases in the peak areas of detected analytes.

All further analysis was performed by sampling at room temperature. This has clear advantages for a heritage application, as potentially damaging heating of artefacts can be avoided. The use of room temperature sampling for 60 min as described in this paper, differs significantly from the use of either sampling at 60 °C or at room temperature for 15 d as used in previously published work on the analysis of heritage artefacts using SPME-GC/MS. [17][6]

### 3.7 Sample preparation

Heterogeneity of the degraded objects (chemical as well as structural, e.g. porosity) could affect repeatability, therefore grinding of samples was explored as a homogenisation strategy. Three objects were selected, composed of PS, PMMA and NR. Six samples of each object were analysed using SPME-GC/MS, 3 samples of ground material, and 3 solid pieces of each. 250 +/- 25 mg samples were used, except in the case of the ground PMMA sample where 100 +/- 10 mg were used due to a lack of sample. The samples were sealed in vials for 3 weeks at room temperature before analysis using the DVB/CAR/PDMS fibre and a 60 min sampling time at room temperature. The accumulation time varies from the 7 d described in section 3.5, as this experiment was done at an earlier stage of the research. However, this experiment was consistent within itself.

The results of the analysis of the PS and PMMA objects are shown in Table 4, which shows a comparison between peak areas for selected VOCs from both ground samples and solid pieces. The results show that grinding greatly improves the repeatability. For example, in the case of the emission of styrene from PS samples, the RSD of the peak areas from the solid pieces is 6.3% while that of the peak areas from the ground samples is 62.7% (Table 4).

The variation in the peaks presented in Table 4 is representative of the variation of other peaks within those chromatograms.

Grinding the samples also leads to more intensive emissions, as would be expected with a significant increase in surface area. This is particularly clear for the PMMA samples for which, despite the fact that the ground samples have less than half the mass of the solid samples, the peak areas are significantly larger. For example, the average peak area of the methyl methacrylate emissions from the ground samples is an order of magnitude larger than that from the solid pieces.

Destructive sampling including grinding is clearly not a suitable approach for the analysis of artefacts in real heritage collections. On the other hand, for the purposes of exploring material degradation, it is crucial to be able to distinguish between changes in detected VOC emissions that are directly related to deterioration, and those that are the result of differences in surface area. The analytical method including homogenisation as proposed here should be used to develop a fundamental understanding of how VOC analysis can be used to assess changes in the condition of plastic and rubber materials in collections. Building on this knowledge e.g. by identifying emissions indicative of the onset of advanced decay ('threshold' emissions) or of the existence of a particular degradation pathway ('marker' emissions), at which conservation action is advisable, the non-destructive method described below can then be employed directly in museum collections, to identify at-risk objects, or to prioritise conservation work.

**Table 4.** Relative Standard Deviation (RSD) of selected analytes from ground samples and pieces of 3 different sample objects

Plastic	RSD of Peak Area (%) N = 3	
	Ground Sample	Piece
<b>Polystyrene</b>		
Ethylbenzene	4.1	72.0
Styrene	6.3	62.7
1-methylethylbenzene	5.1	85.1
<b>PMMA</b>		
Ethyl acrylate	14.8	77.4
Methyl methacrylate	9.3	90.0
<b>Natural Rubber</b>		
Hexanal	1.7 <sup>a</sup>	4.9
Dodecadienone	3.5 <sup>a</sup>	6.1
Hexenal	4.1 <sup>a</sup>	4.5

<sup>a</sup> Only two ground samples of the Natural Rubber object were analysed, the values quoted are therefore the difference between the two peak areas as a percentage of the mean peak area.

The other aspect of sample preparation is sample mass. Overall, a sample size of 50 +/- 5 mg of ground sample was found to ensure satisfactory emissions and low sample consumption for most materials and was thus used for further experiments.

### 3.8 Sampling time

In order to identify for what length of time the SPME fibre should be exposed to the headspace, an experiment was performed using 3 different objects, composed of PE, PS and CA. These objects were chosen as they were expected to emit different quantities of VOCs, with the CA known to emit significant quantities of acetic acid and the PE sample known to emit lower levels of VOCs. Six

samples of each object were analysed using the DVB/CAR/PDMS fibre, with two samples of each analysed using 5 min, 30 min and 60 min sampling times respectively.

The results showed that a 60 min sampling time was sufficient. This was particularly evident for the PE object, from which no VOC emissions were detected after 5 or 30 min sampling. VOC emissions were detected from the two other samples at the shorter sampling times, such as acetic acid and dimethyl phthalate emissions which were detectable from the CA object even after 5 min. However, a wider range of compounds was detectable using a 60 min sampling time. These results are shown in Figure 5, in which it can be seen that emissions of additives such as the antioxidant butylated hydroxytoluene (BHT) and the plasticiser dimethyl phthalate (DMP) from the PS samples were not detectable after 5 min or 30 min respectively and in Figure 6 in which it can be seen that 60 min was required in order to detect significant emissions of benzoic acid methyl ester, a degradation product of DMP. [21]

A longer sampling time was also explored, with two samples each of the PE, PS and CA objects mentioned above analysed using a 120 min sampling time. It was found that there was an increased number of analytes detected from the samples after using a 120 min sampling time. For example degradation products such as nonanal and hexanal, in addition to the plasticiser camphor were detected from the PE object using a 120 min sampling time, which were not detected using a 60-min sampling time. It should be noted however that the instrument performance was much better on the day on which the analysis using a 120 min sampling time was run, compared to the day on which the 60 min analysis was done. The peak intensities for the standards were an order of magnitude higher on the day on which the analysis using the 120 min sampling time was run, which may account for the better results.

Increasing the sampling time also led to a problem with contamination. Analytes detected from samples using a 120 min sampling time were sometimes found in the samples that were analysed at a later point in the run. For example, styrene was detected from the CA samples which were run after the PS samples. Styrene had not been previously detected from samples of this CA object, and it is likely that the styrene is a contaminant from the PS samples, which is a serious concern.

Considering that the use of a 60 min sampling times achieved satisfactory results, that this enabled us to synchronise sampling time with a chromatographic run (of the same length), and bearing in mind the risks of misleading contamination, an optimal balance was achieved between an efficient experimental time and the ability to detect VOC emissions from low emitting materials such as PE and emissions of minor components such as additives or degradation products. Therefore, 60 min was selected as optimal for further experiments. A 60 min sampling time has been used for the analysis of plastic samples in all of the experiments described above and below. As noted previously, a shorter sampling time (20 s) was used for the analysis of standard solutions, due to problems with contamination.

### *3.9 Physical Sampling uncertainty*

In order to test the sampling uncertainty, 3 different plastic objects were studied, composed of PE, PETG and IR. As it was hypothesised that the inhomogeneity of real objects would have a significant impact, each object was sampled in two different ways. Firstly, samples were taken from 5 different locations on the object and analysed individually. Secondly, the object was sampled from the same 5 locations, and the samples were mixed together and then analysed as 5 separate aliquots. 50 +/- 5 mg of material was used in all cases, and the sampled material was either ground or cut into small pieces. An accumulation time of 7 d was used and the samples were analysed using a 60 min

sampling time. The relative standard deviations of selected analytes from each plastic object are shown below in Table 5.

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**Table 5.** Repeatability of selected analytes from 3 different sample objects

Sample	Analyte	Relative Standard Deviation (RSD) (%) N=5	
		Sample from specific location	Mixed sample
Polyethylene	Undecane	13.9	13.7
	Nonanal	16.3	12.0
	Dodecane	14.5	15.5
	1-[2-(Isobutyryloxy)-1-methylethyl]-2,2-dimethylpropyl 2-methyl propanoate	28.0	22.1
Polyethylene terephthalate (glycol-modified)	Acetone	17.2	9.1
	Camphor	36.3	84.0
Polyisoprene rubber	Pentanal	53.5	12.9
	1-ethyl-5-methylcyclopentane	29.5	24.1
	Hexanal	33.7	20.5
	Dimethyl phthalate	51.8	12.5

Interestingly, the results are not unequivocal. For the IR object, there is an improvement in repeatability of several analytes when using the averaged sample, compared to the analysis of individual samples from different locations of the object. This shows that inhomogeneity may be a significant source of variation when working with real objects. The effect is only significant for the IR object (a swimming cap), while the other two objects appear to be more homogeneous. This may indicate a greater degree of inhomogeneity in commercial mass-produced items such as the swimming cap than in standard plastic samples (the other two samples were taken from a Resinkit). The other two samples show smaller reductions in RSD, although variability of all emissions detected from all three objects (except camphor for PETG) is similar to the intra-day repeatability, as discussed above.

The PETG object was found to emit only two analytes that were not also present in the blanks. For the camphor peak, the repeatability was very poor, with RSD 84.0% for the averaged sample. One of the samples emitted almost no camphor, which is the reason for this high variation, however even excluding this sample, RSD = 58.6%.

The reason for this variability is not known. It seems unlikely that it is due to the inhomogeneity of the object, given that all 5 “mixed” samples were composed of a relatively homogeneous mixture of pieces from different locations on the object. It also seems unlikely that the results are due to the inhomogeneity of the surface area, given that the object was cut into small pieces. These results show that, although in several cases the repeatability of the analysis is reasonably good, it is not possible to always obtain analysis at this level of repeatability, considering the complexity of the objects under study.

### 3.10 Non-Destructive analysis of objects from a historic reference collection

To explore how the method described here can be used to provide information about the composition and degradation of plastic materials in collections, the VOC emissions from 3 objects from a reference collection, a CA doll, a PUR foam doll and a CN jewellery box were analysed. Samples of the objects were analysed and in addition, a non-destructive approach was used to show how the method could be adapted for use with real collections. 50 +/- 5 mg samples of ground material was placed in a vial for 7 d at room temperature followed by sampling using the DVB/CAR/PDMS fibre for 60 min at room temperature. In one case a sample of an object that had been artificially degraded at 80 °C and 60% RH was also analysed.

The non-destructive approach involved placing the object in a 5 L Tedlar® bag, followed by SPME-GC/MS analysis. The same accumulation time (7 d), sampling time (60 min) and fibre choice (DVB/CAR/PDMS) were used and both accumulation and SPME sampling were done at room temperature (see Figure 7).

Tedlar® Bags are made from poly(vinyl fluoride) [22] and have been used previously for the study of VOCs in many fields including environmental science and health. [23][24] Two compounds were detected from analysis of empty Tedlar bags: phenol and *N,N*-dimethylacetamide – a finding that has been published previously.[25]

The results show that the developed method is suitable for the analysis of a wide range of objects, and can be used to provide evidence of degradation and information regarding object composition. Emissions of acetic acid were detected from the CA doll. The deacetylation of CA to yield acetic acid is a well-known degradation reaction and the impact of the produced acetic acid on the degrading object and other materials in the vicinity has become known as the “vinegar syndrome”. [26][27] Emissions of furfural were detected from a sample that had been artificially degraded at 80 °C and 65% RH for 2 weeks. Furfural is a known degradation product of cellulose and its presence may provide evidence of degradation of the polymer backbone, in addition to deacetylation.[28][29] The detection of phenol from the CA doll may provide evidence of the degradation of the plasticiser triphenyl phosphate (TPP). TPP is a commonly used plasticiser in CA and is known to degrade into diphenyl phosphate, a strong acid, and phenol.[30] Analysis of this object using Py-GC/MS analysis confirmed the presence of TPP. Further information as to the composition of this doll is provided by the detection of the plasticisers dimethyl- and diethyl phthalate.

The CA doll that was analysed non-destructively was a different doll to the one from which the sample was taken, as very little remained of the sampled doll. However, both dolls are of the same model, are visually very similar and are of a similar age. The results from the analysis of the whole doll are comparable to the analysis of the ground sample, with acetic acid and phthalate plasticisers such as dimethyl- and diethylphthalate being detected. Phenol was also detected, however as phenol was detected from analysis of empty Tedlar bags, it is difficult to assign this peak to the doll with confidence. However, there are some differences, with some VOCs such as 2-octanone, 1-chlorooctane and propanoic acid being detected from the ground sample and not the whole object, while 4-methyl octane, xylene, undecane and benzaldehyde were detected from the whole object but not the ground sample. The reasons for these differences are likely due to the fact that, while the ground sample was taken from one part of the doll, and was thus composed of CA only, the whole doll contained other materials, such as nylon. This represents a typical issue in heritage collections, where many objects are composed of several different modern materials. The results of the analysis of both the ground sample and the doll are shown below in Figure 8. It can be seen that the 3 dominant VOCs detected from the doll, acetic acid, dimethyl- and diethylphthalate are present in both cases. Significant differences in peak intensities between the sample and the analysis of the

object were found, with more intense emissions detected from the ground sample. For example, the acetic acid peak in the chromatogram of the CA sample has a peak intensity that is 5 times higher than that in the chromatogram of the CA object. This may be due to variation in instrument performance on the days of analysis, increased emissions due to grinding or competitive sampling from the VOCs emitted by the Tedlar bag. Silane- and siloxane-based VOCs detected are likely to be the result of deterioration of the SPME fibre or the GC column.

In the case of the PUR foam doll, there are significant differences between the results of the analysis of the whole object and a ground sample of the same object, with several VOCs detected from the whole object and not the sample. For example, 2-methyl-furan and organic acids such as propanoic and pentanoic acids were detected from the doll but not from a sample of the foam. This is likely due to the fact that analysis of the whole doll incorporates analysis of foam in a wide range of conditions, in addition to the coating on the foam, while the ground sample analysed was of foam in a reasonably homogeneous and good condition (visually assessed) and contained no coating. The organic acids detected may be degradation products of the polyurethane foam. Development of carboxylic acid functionalities following photooxidation of PUR model samples have been previously observed and organic acids such as lauric and myristic acid have been detected from thermally degraded PUR samples. [31] [32] The chromatogram resulting from the analysis of the doll is dominated by 2-butanone, which may also be a product of oxidation. In this case, the peak intensities of the VOC emissions detected from the sample were lower than those emitted from the object, with for example the 2-butanone peak in the chromatogram of the sample having a peak intensity that is an order of magnitude lower than that in the chromatogram of the object.

Similar results were obtained from the analysis of both the CN jewellery box and a ground sample of the same object. The chromatograms are both dominated by the presence of a large camphor peak, in addition to camphor derivatives such as fenchone and camphenilone. In this case, the peak intensities of the camphor emissions from both the sample and the object were similar. However, the peak intensities of other emissions such as camphor derivatives were higher by one or sometimes two orders of magnitude in the chromatogram of the sample. Significant camphor peaks have been detected from all CN objects analysed as part of this work, and elsewhere [17] raising the possibility of using camphor as a marker for CN objects in collections.

The results show that VOC detection can be used as a non-destructive method for the analysis of plastic objects, although in order to trap the headspace, the objects need to be enclosed in a sampling bag (or a sealed vessel) before sampling. However, the analyses provide detailed information about degradation products and object composition, from the information on the base material to minor constituents in an object. This is in contrast to analysis using spectroscopic techniques, from which unambiguous identification of components e.g. plasticisers is difficult. Py-GC/MS has been used previously to identify plasticisers present in objects [16] however, this approach is necessarily destructive. VOC analysis therefore emerges as a valuable tool that combines advantages of both approaches.

#### 4 Conclusions

A method has been developed that is suitable for the analysis of VOC emissions from a wide range of plastic and rubber materials relevant to heritage collections. The uncertainty and repeatability of the analytical procedure have been critically assessed, which enables much better evaluation of results, both those presented in this paper and results already published in the literature. The following can be concluded:

- Sample equilibration and SPME sampling at room temperature analysis was found to be suitable. No additional or increased levels of VOC emissions were detected at elevated temperatures during



SPME sampling. Room temperature analysis is particularly suited to heritage applications.

- After a sample is sealed into a vial, a 7 d accumulation time was found to be sufficient in order to populate the headspace in the vials and provide detectable quantities of analytes from a range of different materials.
- The DVB/CAR/PDMS fibre was found to be more appropriate than the CAR/PDMS fibre due to its greater selectivity towards non-polar analytes.
- Grinding samples significantly improved the repeatability of analysis, and made it comparable to the repeatability of analyses of liquid samples. Use of non-homogenised samples (non-averaged samples) led to a greatly increased uncertainty, which could reflect locally heterogeneous composition/degradation – this could itself be explored in further research.
- A  $50 \pm 5$  mg sample size was found to be adequate for most plastic objects.
- A SPME sampling time of 60 min was found to be necessary in order to detect VOC emissions from low emitting materials and minor components such as additives or degradation products, and optimal in view of sampling running simultaneously with chromatography and to avoid contamination.
- Repeatability: In some cases, RSD of peak areas is less than 25%. However, given the complexity of real historic artefacts, it is not possible to be fully confident of this in all cases.
- The described method has been modified for use as a non-destructive tool for the analysis of VOC emissions from plastic objects in collections
- Use of internal standards (added to a solid sample in a vial prior to SPME sampling) is not advisable as such standards probably interfere with the sample and as a result, repeatability of the analyses is decreased

The developed method was found to be suitable for the non-destructive detection of degradation products, starting materials and additives such as plasticisers and antioxidants from historic plastic and rubber artefacts. The use of VOC analysis for the study of objects composed of modern materials combines the advantages of other analytical approaches, i.e. the non-destructive nature of spectroscopy and the ability of Py-GC/MS to detect specific additives. Further research in this area is ongoing.

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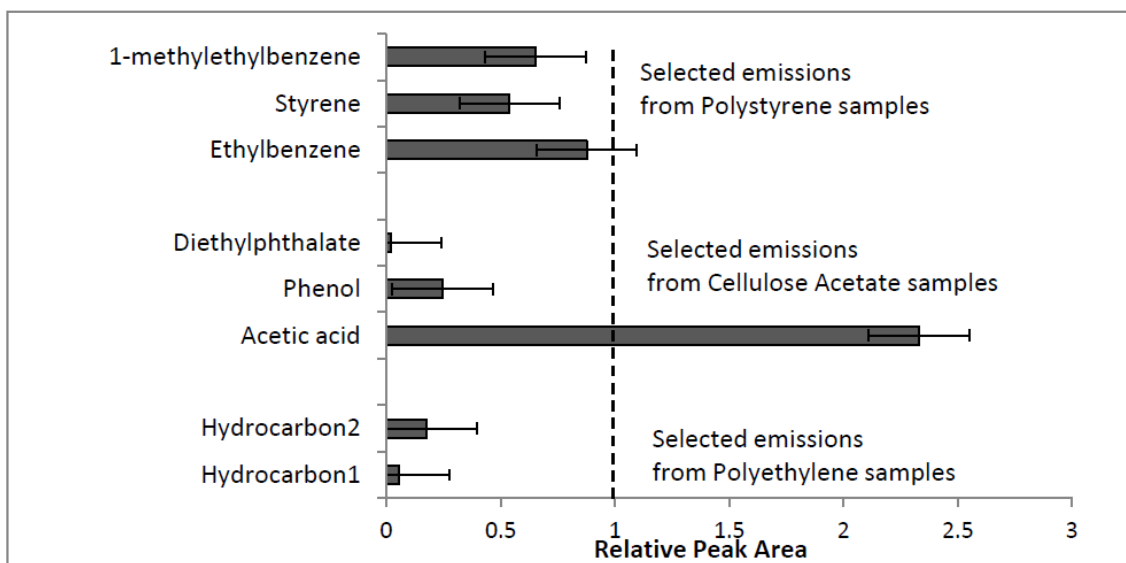
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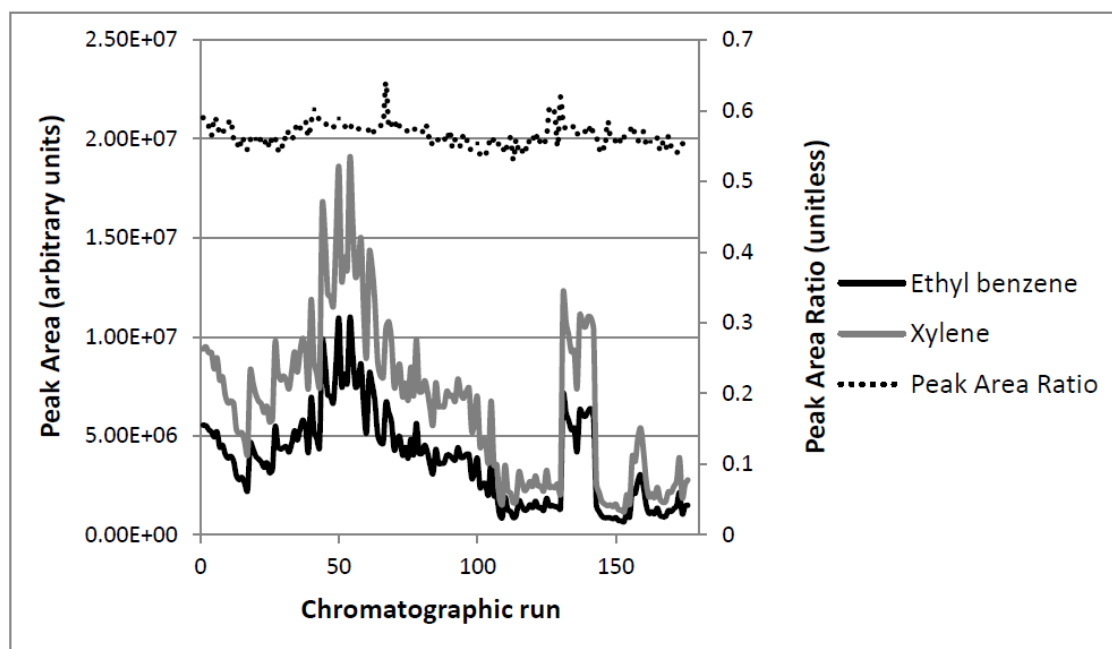
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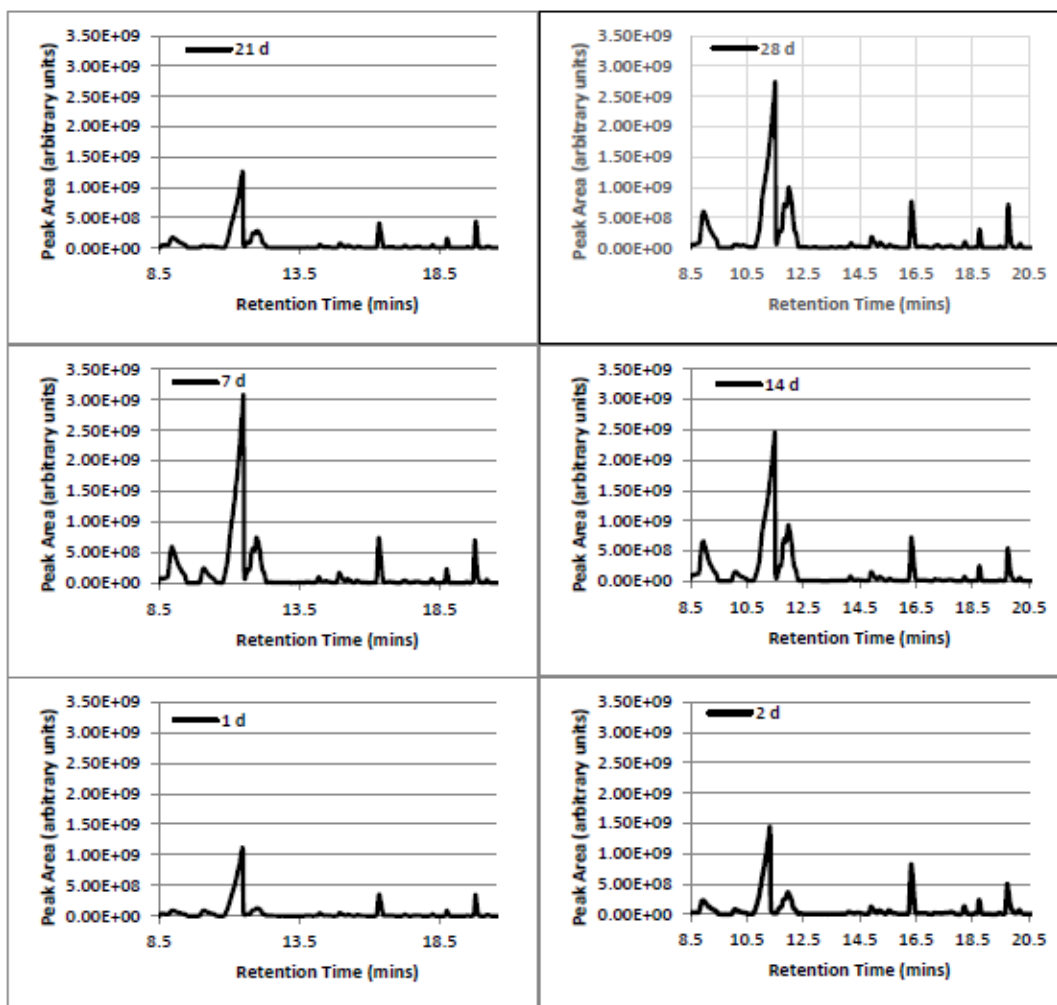
**Figure 1.** Selected VOC emissions detected from 3 different plastic objects depicted as the peak areas detected using the CAR/PDMS fibre relative to those detected using the DVB/CAR/PDMS fibre. The error bars show the average range between maximum and minimum values. Hydrocarbons 1 and 2 are two hydrocarbons detected in the VOC emissions of polyethylene samples which could not be identified based on their mass spectra.

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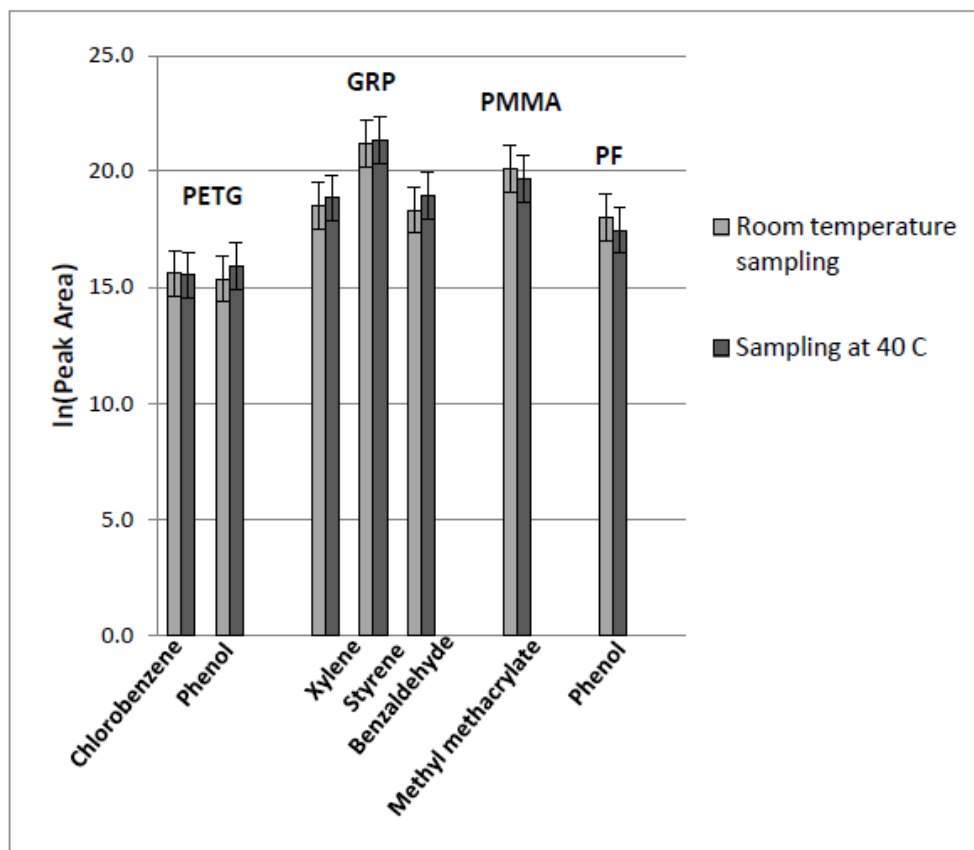
**Figure 2.** Variation in Peak Areas for the two selected external standard compounds over 9 months of the experiment. The Peak Area Ratio was calculated by dividing the area of the ethyl benzene peak by the area of the xylene peak.

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**Figure 3.** Close-up of a region of a chromatogram showing SPME-GC/MS analysis of VOC emissions from samples of a NR object. Samples were sealed in vials for different accumulation times before analysis.

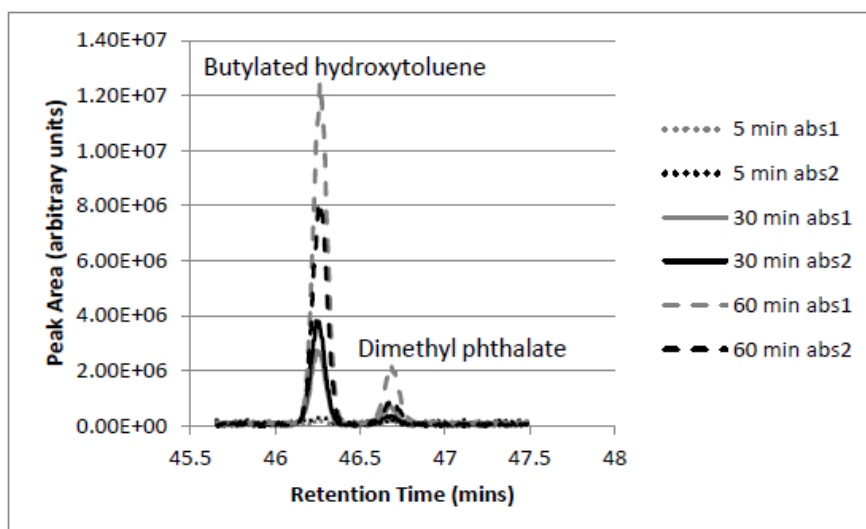
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**Figure 4.** Peak areas of selected VOC emissions from SPME-GC/MS analysis of 4 different plastic objects after sampling at both room temperature and at 40 °C. The results have been log transformed and are the average of 3 repeats and the error bars show the maximum and minimum values.

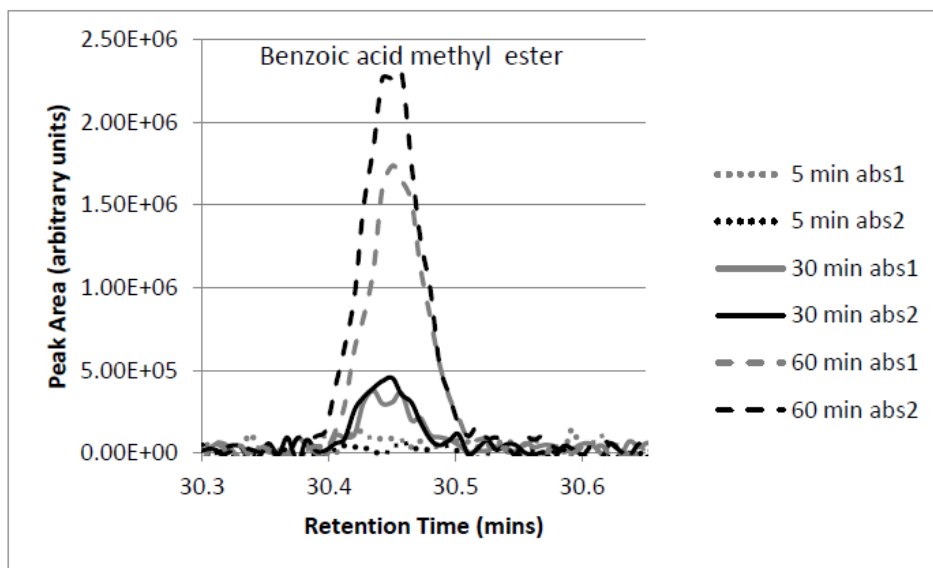
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**Figure 5.** Peak areas of selected VOC emissions detected from a PS object using different sampling times.

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**Figure 6.** Peak areas of selected VOC emissions detected from a CA object using different sampling times.

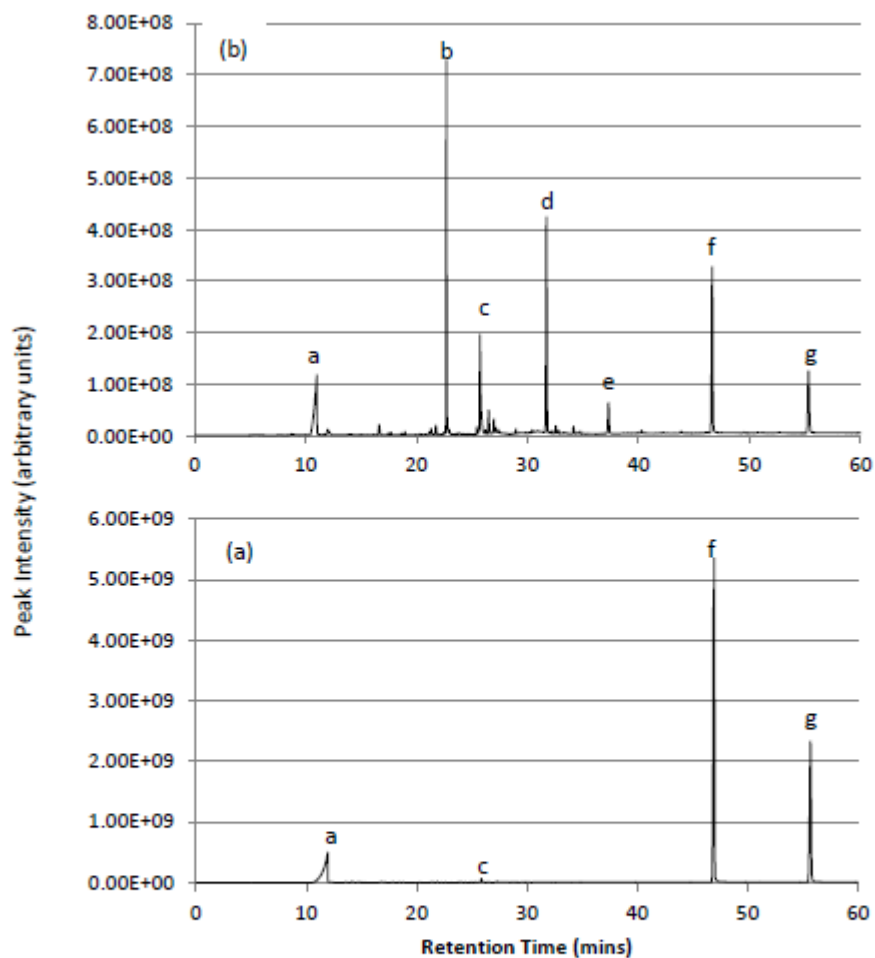
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**Figure 7.** Non-destructive analysis of a PUR foam doll using a SPME fibre in a manual holder

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**Figure 8.** Chromatograms showing the results of the analysis of (a) a sample from a CA doll and (b) the non-destructive analysis of a similar doll: a. acetic acid, b. N,N-dimethylacetamide, c. phenol, d. tetramethylsilane, e. dodecamethylpentasiloxane, f. dimethylphthalate, g. diethylphthalate.

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### Highlights

- A method for analysing VOC emissions from historic plastic and rubber collections is proposed
- Analysis temperature, sampling time, sampling preparation strategies and choice of SPME fibre coating were investigated
- The repeatability of the method was assessed
- A non-destructive method suitable for analysing VOC emissions from plastic or rubber objects in real heritage collections is presented

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