

Volatile Organic Compound (VOC) emissions from plastic materials used for storing and displaying heritage objects

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Abstract

Volatile organic compound (VOC) emissions from plastic materials used in storage and display (e.g. Plastazote or Tyvek) were analysed. Polymer types of 42 material samples provided by UK heritage institutions were identified using attenuated total reflectance Fourier transform-infrared spectroscopy. These samples were also analysed for VOC emissions using headspace solidphase micro-extraction gas chromatography/mass spectrometry. Acetic acid was detected from 28 of the samples, including Moistop and Plastazote. A calibration was developed to estimate the concentrations of acetic acid emitted, which were found to be between 222 – 346 ppb. Additional detected VOCs include other polymer oxidation products such as aldehydes, and limonene, which is likely absorbed from the museum environment. These results indicate that plastic materials can oxidise in a museum environment to emit acidic VOCs and the way in which they are used in heritage institutions needs consideration.

Introduction

The damaging impact of volatile organic compounds (VOCs) on historic materials is well known. VOCs such as carboxylic acids and aldehydes can cause metal corrosion,

degradation of calcareous natural history specimens and the embrittlement of organic materials (Grzywacz 2006).

The sources of these VOCs are often the materials in which objects are stored or displayed and tests such as the Oddy test have been developed to identify potentially damaging materials (Oddy 1973). Previous work in this area includes analysis of VOC emissions from showcases, wood and wood products, resins, foams, adhesives and insulation materials (Schieweck and Salthammer 2011; Hatchfield and Carpenter 1986; Thickett 1998; Baer & Banks 1985).

Plastics are a well-known source of damaging VOCs. For example objects composed of both cellulose acetate (CA) and cellulose nitrate (CN) are known to emit acetic and nitric acid respectively, which can damage other materials in their vicinity (Allen et al. 1987; Shashoua 2009). In the case of CA, this is known as the vinegar syndrome. Carboxylic acids and aldehydes have been detected from a range of other polymeric materials, including poly(ethylene) (PE), poly(propylene) (PP), poly(styrene) (PS) and polyurethane (PUR) (Hakkarainen et al. 1997; Larkin et al. 2000; Gurman et al. 1987; Thiebaut et al. 2007).

Many specialised plastic materials are used in the storage and display of historic objects (e.g. Tyvek, Plastazote and Melinex). Previous work by this author showed acidic emissions from some such materials had a degrading impact on historic paper (Curran et al. 2014). However, only a small number of materials were studied. This paper expands on that work, with a particular focus on the detection and quantification of acetic acid (AA) emissions.

Method

Source and characterisation of samples

Plastic samples were provided by the National Records of Scotland, the Museum of London and The National Archives. 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 cm^{-1} with a resolution of 4 cm^{-1} .

Analysis of VOC emissions

VOC analysis was performed according to a previously published method (Curran et al. 2016) using headspace solidphase micro-extraction gas chromatography/mass spectrometry (HS-SPME-GC/MS). 50 ± 5 mg of each material cut into small pieces was analysed. 1 ml aliquots of aqueous AA solutions were analysed by the same method after equilibration for 24 hours at room temperature. Vapour phase AA concentrations were calculated using experimental conditions and Maple 14.01 from Maplesoft.

AA peak areas were weighted using an external standard (MISA Group 17 Non-Halogenated Organic Mix 2000 mg/ml in methanol; 48133 Supelco, diluted 1/50 in methanol). 1 ml aliquots of the diluted standard were analysed according to Curran et al. (2016).

The environmental conditions (temperature and relative humidity) of the laboratory were recorded using an Onset Hobo data logger (U12-011) placed beside the GC/MS.

Results

Polymer identification

Using ATR-FTIR spectroscopy, a range of different polymer types were identified including PE, PS and poly(butyl terephthalate) (PBT). The most common polymer type was PE. The samples and polymer identifications are shown in Table 1.

Table 1. Samples used in this research and polymer types identified by FTIR

Sample name	Source	Commercial source	Polymer type
Vacuum bags	NRS ^a	Protective Packaging	Poly(ethylene)
Extruded LD45 grey	NRS ^a	Preservation Equipment	Poly(ethylene)
Extruded LD45 white	NRS ^a	Preservation Equipment	Poly(ethylene)
LD45 black perforated	NRS ^a	Polyformes	Poly(ethylene)
LD45 grey	NRS ^a	Paulamar Company Ltd	Poly(ethylene)
LD45 black	NRS ^a	Paulamar Company Ltd	Poly(ethylene)
Tyvek 1	NRS ^a	Preservation Equipment	Poly(ethylene)
Tyvek 2	MOL ^b	N/A	Poly(ethylene)
Tyvek 3	TNA ^c	Preservation Equipment	Poly(ethylene)
Biodegradeable Bag	NRS ^a	Ferrari Packaging Ltd	Poly(ethylene)
Ethafoam	MOL ^b	N/A	Poly(ethylene)
Reflective Mylar	MOL ^b	N/A	Poly(ethylene)
Marvelseal	MOL ^b	N/A	Poly(ethylene)
Plastazote 1 black	MOL ^b	N/A	Poly(ethylene)
Plastazote 2 grey	MOL ^b	N/A	Poly(ethylene)
Plastazote 3 white	MOL ^b	N/A	Poly(ethylene)
Plastazote 4 blue	MOL ^b	N/A	Poly(ethylene)

Plastazote 5 black	TNA ^c	Kewell Converters Ltd	Poly(ethylene)
Jiffy foam	MOL ^b	N/A	Poly(ethylene)
Coroplast with UV inhibitor	NRS ^a	N/A	Poly(propylene)
Correx	MOL ^b	N/A	Poly(propylene)
Charcoal cloth	MOL ^b	N/A	Poly(ethylene terephthalate)
Bondina 30 gsm	NRS ^a	Conservation by Design	Poly(ethylene terephthalate)
Bondina 100 gsm	NRS ^a	Conservation by Design	Poly(ethylene terephthalate)
Reemay	NRS ^a	Conservation by Design	Poly(ethylene terephthalate)
Vivak	TNA ^c	Bayer	Poly(ethylene terephthalate) - glycol modified
Base for medals, coins, finds	MOL ^b	N/A	Poly(styrene)
White Gatorfoam (inside)	MOL ^b	Alcan Composites	Poly(styrene)
Standard Foamboard 5mm (inside)	TNA ^c	Conservation by Design	Poly(styrene)
Bump ons	MOL ^b	N/A	Polyurethane
UV filter material	MOL ^b	N/A	Poly(methylmethacrylate)
Moistop	MOL ^b	N/A	Poly(butylene terephthalate)
Coloured film backing plastic	MOL ^b	MACTac- A Bemis Company	Poly(butylene terephthalate)
Melinex 75 micron	TNA ^c	Preservation Equipment	Poly(butylene terephthalate)
Coloured film 798-01 frosted	MOL ^b	MACTac- A Bemis Company	Poly(vinyl chloride)
Coloured film 798-02 dusted	MOL ^b	MACTac- A Bemis Company	Poly(vinyl chloride)
Coloured film 738-00	MOL ^b	MACTac- A Bemis	Poly(vinyl chloride)

offshore blue		Company	
Coloured film 748-00 refreshing mint	MOL ^b	MACtac- A Bemis Company	Poly(vinyl chloride)
Coloured film 708-00 sparkling yellow	MOL ^b	MACtac- A Bemis Company	Poly(vinyl chloride)
Coloured film 758-00 romantic rose	MOL ^b	MACtac- A Bemis Company	Poly(vinyl chloride)
Coloured film 778-00 luxurious Gold	MOL ^b	MACtac- A Bemis Company	Poly(vinyl chloride)
Lexan 9030	TNA ^c	theplasticshop.co.uk	Polycarbonate

^aNational Records of Scotland ^bMuseum of London ^cThe National Archives

The FTIR spectra of three samples, showing common polymer types among the materials studied are shown in Figure 1. The Tyvek sample, composed of PE shows characteristic peaks at 2947 and 2914 cm^{-1} (CH stretch), at 1472 and 1462 cm^{-1} (CH deformation) and at 730 and 716 cm^{-1} (CH rocking). Coroplast, composed of PP shows peaks at 2949, 2917, 2867 and 2838 cm^{-1} (CH stretch), at 1456 and 1375 cm^{-1} (CH deformation) and peaks at 1167, 998 and 973 cm^{-1} (C-C skeletal). Charcoal cloth, composed of poly(ethylene terephthalate) (PET) shows characteristic peaks at 2959, 2916, 2848 cm^{-1} (CH stretch), a strong peak at 1728 cm^{-1} (C=O) and peaks at 1240 and 1159 cm^{-1} (C-O-C groups) (Socrates 2001).

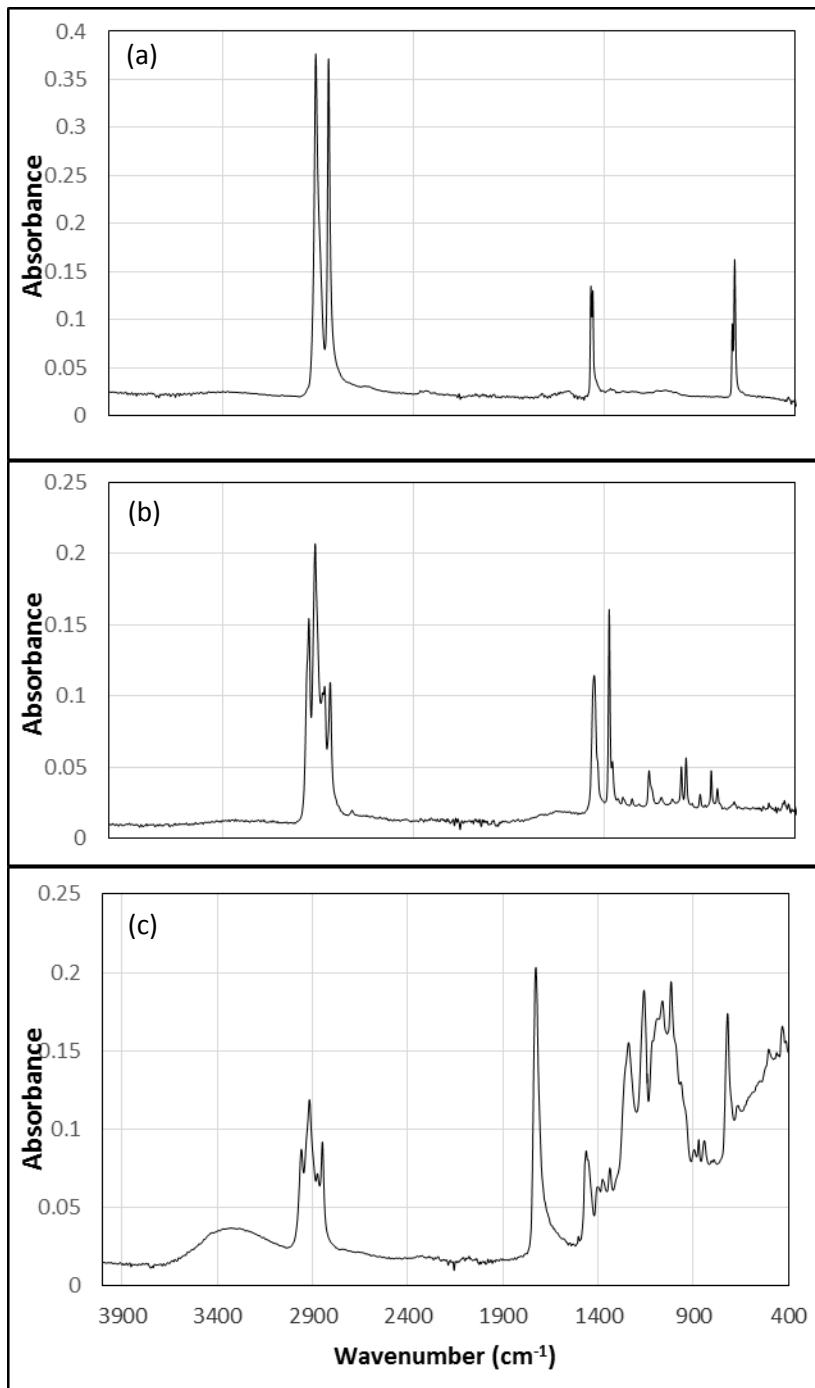


Figure 1. FTIR spectra of (a) Tyvek 2 composed of poly(ethylene), (b) Coroplast with UV inhibitor composed of poly(propylene) and (c) Charcoal cloth composed of poly(ethylene terephthalate)

VOC analysis of packaging materials using SPME-GC/MS

Using HS-SPME-GC/MS analysis, many different VOCs were detected from the samples. An example of a chromatogram showing emissions from Jiffy Foam is shown in Figure 2.

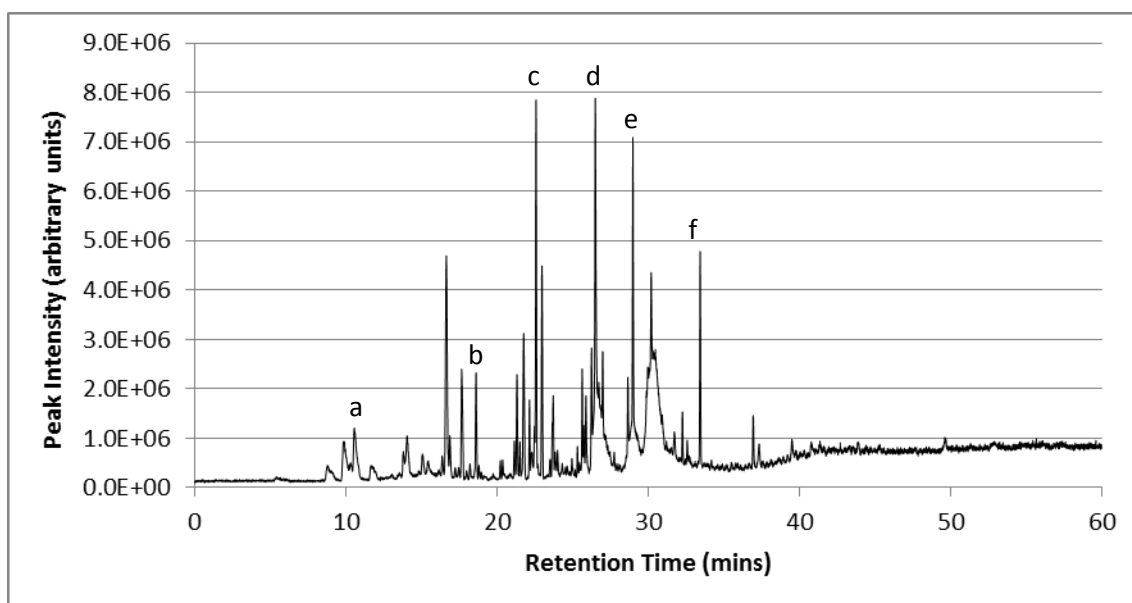


Figure 2. Chromatogram showing volatile organic compounds detected from Jiffy foam (PE) using HS-SPME-GC/MS analysis: (a) acetic acid, (b) hexanal, (c) styrene (d) limonene, (e) nonanal, (f) tridecane

Of the VOCs detected in this research, the one that gives the most cause for concern is AA, which was detected from many different materials. To better understand the significance of these results, a calibration was developed to estimate the concentrations of these emissions. Using the same HS-SPME-GC/MS method as was used for the material samples, a set of aqueous AA solutions of known concentrations were analysed. Using equations developed by Hodgkins (2011), the vapour phase concentration (VPC) above each solution was calculated. As the VPC is dependent on environmental conditions, the temperature of the laboratory at the time of analysis of each solution, recorded using a data logger, was incorporated into the calculations. The relative humidity was assumed to be 100%, as each analysis was done as a headspace measurement above an aqueous solution that had been allowed to equilibrate. The relationship between the AA peak areas detected using HS-SPME-GC/MS (weighted using standards to account for inter- and intra-day variation) and the calculated VPC of each solution is shown in Figure 3 and Table 2. The concentrations of emitted AA from the tested materials were estimated using this calibration and are shown in Table 3. These were found to range between 222 – 346 ppb.

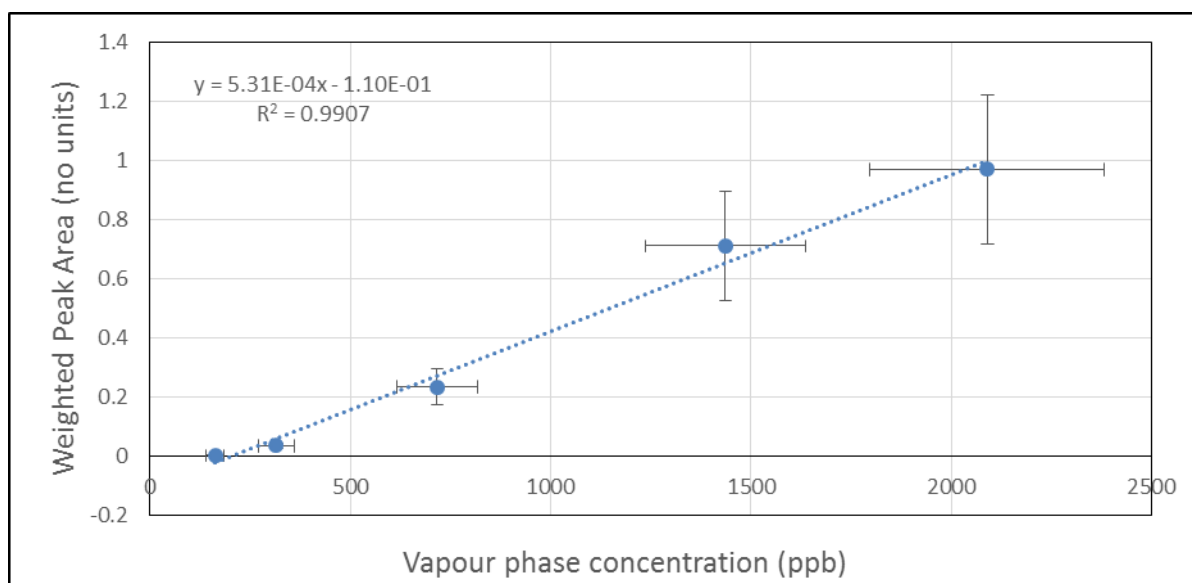


Figure 3. The relationship between the area of the acetic acid peak detected using GC/MS above each acetic acid solution, weighted using a standard and the calculated vapour phase concentration. The points show the average of 5 repeated analyses (except for the lowest concentration which shows two repeats). The error bars show relative standard deviation.

Table 2. Aqueous acetic acid solutions used for calibration

Sample	Solution concentration (M)	Weighted acetic acid peak area (no units)	Acetic acid vapour phase concentration (ppb)
Test solution A	0.015	0.97 ^a	2090.5 ^{a,b}
Test solution B	0.01	0.71 ^a	1436.6 ^{a,b}
Test solution C	0.005	0.23 ^a	717.0 ^{a,b}
Test solution D	0.002	0.03 ^a	315.8 ^{a,b}
Test solution E	0.001	0.002 ^c	163.1 ^c

^a Average of five repeats

^b Calculated using Hodgkins (2011)

^c Average of two repeats

Table 3. Calculated vapour phase concentrations of acetic acid emitted from samples

Sample	Weighted acetic acid peak area (no units)	Acetic acid vapour phase concentration (ppb)^{a,b}
Moistop	0.063	346 +/- 81
Bumpons	0.050	321 +/- 71
Reflective Mylar	0.044	308 +/- 66
Marvelseal	0.038	297 +/- 62
Jiffy foam	0.026	272 +/- 51
Extruded LD45 white	0.024	268 +/- 50
Coloured film 798-01 frosted	0.022	264 +/- 48
LD45 grey	0.020	261 +/- 47
UV filter material	0.020	260 +/- 47
Extruded LD45 grey	0.019	259 +/- 46
Coloured film 748-00 refreshing mint	0.018	257 +/- 45
Plastazote 3 white	0.018	256 +/- 45
Coloured film 798-02 dusted	0.015	251 +/- 43
Coloured film 738-00 offshore blue	0.014	248 +/- 42
Plastazote 4 blue	0.011	242 +/- 40
Standard foamboard 5 mm (inside)	0.010	241 +/- 39
Coloured film 708-00 sparkling yellow	0.009	239 +/- 38
LD45 black	0.009	238 +/- 38
Coloured film 758-00 romantic rose	0.006	233 +/- 36
Plastazote 2 grey	0.005	231 +/- 35
Bondina 30 gsm	0.005	231 +/- 35
Reemay	0.005	231 +/- 35
Plastazote 5 black	0.005	231 +/- 35

Coloured film backing plastic	0.004	229 +/- 34
Vivak	0.003	227 +/- 34
Bondina 100 gsm	0.003	226 +/- 33
LD45 black perforated	0.001	223 +/- 32
Vacuum bags	0.001	222 +/- 31

^a Calculated using the calibration developed in this work

^b Errors are calculated using the relative standard deviations for both the peak areas and calculated concentrations of the acetic acid solutions.

More is needed to provide a full calibration. For example, each material was only analysed once and repeated analyses would give more confidence. The relative standard deviation of the peak areas detected using this HS-SPME-GC/MS method has been shown previously to be 22.6% (Curran et al. 2016). However, given that the AA peak areas of the samples in Table 3 are of the same order of magnitude as those from Test Solutions D and E, it seems reasonable to estimate that the VPC emitted from these samples are also of the same order of magnitude of those above Test Solutions D and E. In addition, it is possible that the relative humidity above the solutions was lower than 100%, in which case the concentrations described here are slightly too low. However, calculations using the ambient relative humidity (average 49%) gave similar values: 273 – 428 ppb, so we are confident that the values described here are in the right range. Blank vials were analysed several times during each HS-SPME-GC/MS run, none of which showed any evidence of AA – demonstrating that it is not present in the laboratory environment.

No AA emissions were detected from the remaining samples, which include Coroplast, all three samples of Tyvek, one of the Plastazote samples, the PS base for medals, the charcoal cloth, Correx, Ethafoam, Melinex, Lexan, the biodegradable bag and the “gold” coloured film. This does not necessarily mean that no acid was present, as Figure 3 shows, a detected peak area of zero could correspond to a concentration of approximately 221 ppb. However, at present we have no evidence that acid was emitted from these samples.

The detected concentrations are significant as guidelines from the Getty Conservation Institute define AA levels of 200 – 480 ppb as “High” (Grzywacz 2006). Guidelines from the Canadian Conservation Institute advise that the length of time for which an artefact can be exposed to concentrations of 400 ppb “with minimal risk of deterioration” is 1 year (Tetreault 2016).

AA was detected from four out of five of the Plastazote samples analysed. It is less likely that these are due to absorption from the atmosphere in which the samples were stored, as these came from two different organisations, the MOL and TNA. AA is a known product of the oxidation of PE (Hakkarainen et al. 1997). AA was detected from other PE samples, including all the LD45 samples, the vacuum bags, Mylar, Marvelseal and Jiffy foam. No AA was detected from any of the Tyvek samples.

Several of the polyesters emitted AA, including two samples of Bondina, Reemay and Vivak. The highest concentration detected from any of the samples was from Moistop which is PBT. The fact that all of the coloured films were found to emit AA may be due to the PBT backing plastic used, which emitted AA when analysed in isolation, rather than the coloured PVC layers.

AA was detected from one of the PS samples (Standard Foamboard) although not from the other PS samples. It was also detected from the only PUR sample analysed (Bumpons). AA has previously been detected from other PS and PUR objects as part of unpublished research ongoing in this laboratory. Proposed mechanisms for the formation of carboxylic acids from the oxidation of PS and PUR have been published (Wilhelm and Gardette 1997; Mailhot and Gardette 1992). No AA was detected from the PP samples, although only two PP-based materials were analysed.

Other VOCs detected include aldehydes such as hexanal, heptanal and nonanal. Aldehydes were detected from several of the PE samples from which AA was also detected including Plastazote samples 2 – 5, Jiffy foam, Mylar and the vacuum bags. Aldehydes are also products of PE oxidation and work by Strlic et al. (2011) suggests a slight negative effect of hexanal on the degradation of historic paper. However, aldehydes were also detected from PE samples from which no acid was detected, including Plastazote 1, and Tyvek sample 3. No aldehydes were detected from the two PP samples, indicating that oxidation of these materials had not taken place.

Limonene was detected from many samples, including Plastazote samples 1 and 4, Tyvek samples 1 and 2, Correx, Jiffy foam. In some cases, limonene was one of the largest peaks in the chromatogram. Limonene can be found in cleaning products and has been detected before during analysis of library and archive spaces (Gibson et al. 2012). Limonene was detected from materials from both the NRS and MOL. Oxidation of limonene has been linked to negative health impacts (Lipsa et al. 2016).

The results from this research do not necessarily imply that similar concentrations of AA are found in the vicinity of these materials when used in a museum context. Further research is needed to translate the concentrations detected from small samples analysed in vials, as in this work, to the concentrations found in museums. Our results suggest that these materials degrade via oxidation over time and that consideration needs to be given to the length of time over which they are used, particularly when used in close contact with artefacts as microclimates can be created. It is also possible that the VOCs detected have been absorbed onto the materials tested here from museum objects or from other materials, such as wood or cardboard present in the areas in which they are stored. AA and aldehydes are known degradation products of cellulose (Strlič et al. 2011). Further work to understand whether detected VOC emissions originate from the materials themselves or are absorbed from the surrounding environment is ongoing.

Conclusions

Specialised plastic materials are widely used for the storage and display of historic objects. No material lasts forever, and many of the polymers used for such materials are known to oxidise to produce volatile products such as acids and aldehydes.

This work shows that acetic acid is emitted at room temperature from a range of material samples composed of PE, PET, PBT, PS and PUR including Plastazote, Moistop and Mylar. Using a calibration developed in this work, the concentrations of emitted acids were found to range from 222 – 346 ppb. These are significant as they fall within the “High” level defined by the Getty Conservation Institute. Other volatile oxidation products such as aldehydes were also detected from these materials.

These results do not provide evidence that hazardous quantities of acids are emitted from such materials in a museum context. However, they do indicate that they can oxidise in a museum environment and that the way in which they are used needs consideration.

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