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

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ABSTRACT

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

1. Introduction

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

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

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

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

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

2. Experimental

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

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

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

Table 1
The 41 samples selected for this study.

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

2.2. Determination of emissions from reference plastic samples

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