Characterisation of VOCs Surrounding Naum Gabo’s Construction in Space ‘Two Cones’, (Tate) by in situ SPME GC-MS Monitoring

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Introduction

Currently, there are few options for in situ non-destructive monitoring of the stability of modern polymeric materials within heritage collections. Past research has focused on exploiting the information contained in volatile organic compounds (VOCs) emitted from an object to understand decay mechanisms or identify the polymer composition (Lattuati-Derieux et al. 2013; Hakkarainen, Albertsson, and Karlsson 1997). The fundamental shortcoming of many previous studies utilising VOC capture is that often they use destructive analysis, elevated temperatures, artificially aged samples or combinations of these during analysis. While these studies have given us a wealth of information regarding decay profiles and key VOCs emitted from specific polymers, they often lack real-world applicability.

Previous work by Curran et al. (2016) has shown that it is possible to capture relevant VOC data from three-dimensional polymer objects at room temperature using solid phase microextraction gas chromatography/mass spectrometry (SPME-GC-MS). However, this required pre-concentration of VOCs within Tedlar sealable bags, which introduces risks to the object from poor handling during bagging, and severely limits the size of objects which can be studied. The novelty of the method described here lies in using SPME to undertake a systematic and repeated non-destructive and non-invasive monitoring programme of multiple points-of-interest (POI) around a naturally aged three-dimensional polymer object within its normal storage environment.

The central questions this research aimed to answer were –

- Can key VOC markers for polymer composition or decay be efficiently and confidently detected using SPME-GC-MS in a museum storage environment?
- Can differences between the intensity of key VOC markers be detected from different POIs around the object?
- Can insights into object material condition be detected using SPME-GC-MS?
- What is the potential impact for conservation practice and VOC monitoring?

Materials and methods

Two experimental campaigns were carried out on the constructivist sculpture Construction in Space ‘Two Cones’ (Tate T02143, 1936, this replica 1968) by the artist Naum Gabo. The work is available for study because it is deemed too deteriorated for display, and currently suffers, among other issues, from warping, crazing, and crystal growth (Figure 1(b)). As such an authorised replica is being used instead for display (Lawson and Cane 2016). The sculpture is principally constructed from cellulose acetate (CA) and is currently loosely packed within a polymer storage crate lined with activated charcoal cloth wrapped around Plastazote foam, a Plastazote base, covered by fabric to prevent dust accumulation, but not enclosed. During each campaign, POIs around the object (see Figure 1(a,b) for locations) were examined by placing an exposed 50/30 μm DVB/CAR/PDMS SPME fibre at each POI. A fifth SPME fibre was placed within the room housing the object to measure the background VOCs present. The two experimental campaigns differed in the length of time the SPME fibre was exposed to the object. One campaign was exposed to the object for 24 hours, the other for 7 days. Three replicate measurements were made during each campaign, on different dates. Peak areas were normalised to the peak area of ethylbenzene from a MISA Group 17 Non-Halogen Organic Mix (Sigma Aldrich 48133 Supelco) standard.
Results

The results have shown that an exposure time of 24 hours is adequate for the capture of VOCs relating to polymer composition and decay markers (Table 1). VOCs such as acetic acid and phenol, which relate to decay mechanisms, and the plasticisers diethyl phthalate and dimethyl phthalate, were found at each of the POIs examined, though the concentration levels varied at each location.

Another significant result was the apparent differences between POI associated with areas of decay and those POI slightly further away. At both exposure times, the concentration of the four key VOCs, mentioned above, was significantly higher close to an area with visible signs of decay as opposed to the fibres placed inside the storage crate but slightly away from the object—giving two distinct sets of results from the four fibres places around the object.

Possibly the most significant insight was the clear difference between the two areas of decay examined, suggesting different decay mechanisms present on a single object. The area where fibre two was placed had a significantly higher ratio of phenol to acetic acid than where fibre four was placed (Figure 2). This feature was present for both 24 hours and 7 days exposure times, though the ratio was less at 7 days (Table 1). Despite this difference in ratio, the overall concentration of acetic acid was higher at fibre four than at fibre two. Visually, the area centred around fibre two appeared to be more heavily decayed and contained more crystal growth on the polymer surface than fibre four, which had virtually no crystal growth. FTIR analysis was performed on a crystal which had formed on the SPME fibre housing, however, definitive identification was not possible. Results suggested some form of phenyl phosphate plasticiser (tri- or diphenyl phosphate could not be distinguished). These results are also backed up by previous analysis on the object (Townsend, Angelova, and Ormsby 2016) which did show the presence of triphenyl phosphate (TPP). The high levels of phenol could be explained by the work by Shinagawa, Murayama, and Sakaino (1992) who proposed that the decay of TPP, via hydrolysis, led to diphenyl phosphate and phenol. Our results are also in keeping with those of Tsang et al. (2009) who noticed that CA plasticised

Table 1. Normalised peak area results from 24-hour exposure.

| Acetic acid | Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 | Phenol | Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 |
|-------------|---------|---------|---------|---------|---------|--------|---------|---------|---------|---------|---------|
| Set 1       | 0.29    | 0.07    | 0.01    | 0.27    | 0.16    | Set 1  | 0.83    | 2.81    | 0.09    | 0.13    | 0.14    |
| Set 2       | 0.43    | 1.26    | 0.17    | 3.38    | 0.39    | Set 2  | 1.60    | 6.77    | 0.32    | 1.31    | 0.49    |
| Set 3       | 0.24    | 0.83    | 0.26    | 2.07    | 0.32    | Set 3  | 1.21    | 4.61    | 0.44    | 1.21    | 0.48    |
| Dimethyl    | Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 | Diethyl Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 |
| Set 1       | n/d     | 12.56   | 0.36    | 0.78    | 0.43    | Set 1  | 0.20    | 5.90    | 0.23    | 0.24    | 0.23    |
| Set 2       | n/d     | 16.58   | 0.94    | 14.06   | 2.01    | Set 2  | 0.42    | 11.25   | 0.41    | 3.10    | 0.76    |
| Set 3       | n/d     | 20.01   | 1.77    | 14.20   | 2.41    | Set 3  | 0.42    | 9.48    | 0.72    | 3.70    | 0.85    |

Table 1. Normalised peak area results from 24-hour exposure.

| Acetic acid | Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 | Phenol | Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 |
|-------------|---------|---------|---------|---------|---------|--------|---------|---------|---------|---------|---------|
| Set 1       | 0.04    | 0.15    | 0.05    | 0.28    | 0.09    | Set 1  | 1.05    | 3.53    | 0.59    | 3.31    | 1.46    |
| Set 2       | 0.08    | 0.16    | 0.08    | 0.21    | 0.06    | Set 2  | 1.79    | 3.53    | 1.10    | 2.38    | 1.00    |
| Set 3       | 2.75    | 1.59    | 1.49    | 3.06    | 2.17    | Set 3  | 10.98   | 10.44   | 6.09    | 7.30    | 6.75    |
| Dimethyl    | Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 | Diethyl Fibre 1 | Fibre 2 | Fibre 3 | Fibre 4 | Fibre 5 |
| Set 1       | 0.16    | 19.23   | 1.88    | 15.44   | 4.28    | Set 1  | 0.60    | 13.69   | 0.78    | 7.24    | 1.38    |
| Set 2       | 0.24    | 19.60   | 3.10    | 13.03   | 3.25    | Set 2  | 0.80    | 13.99   | 1.00    | 6.14    | 1.01    |
| Set 3       | 4.33    | 101.21  | 58.74   | 205.94  | 49.49   | Set 3  | 20.44   | 126.94  | 21.76   | 104.83  | 17.56  |
with TPP appeared to decay at a faster rate than CA without. Our results, therefore, heavily suggest that we are detecting two distinct decay mechanisms from the two different areas. The higher levels of acetic acid seen at fibre four are generated by the deacetylation of CA, while hydrolysis of TPP leads to higher levels of phenol.

Taken together, these results suggest that SPME is an efficient methodology for monitoring polymer object decay. Our research also provides evidence that monitoring of VOCs emitted from polymer objects either needs to be targeted at specific POIs close to the object, or else generally, with the understanding that VOC ‘hot spots’ may be missed.

Our work highlights the capabilities of SPME-GC-MS to detect potential differences in decay mechanisms from a single object. Our work also adds further evidence to the theory that CA plasticisers with TPP decay at a faster rate than other forms of the material.

There is also a potential impact for collection care, as our research suggests that current storage practices, such as open storage and charcoal inhibitors for highly decayed polymer objects are insufficient for eliminating VOC build-up in certain areas. Our research points towards the need for better control of the ventilation of troublesome polymer objects kept at room temperature – this would likely take the form of an invasive procedure such as a continuous air flow over the object or periodic flushing of the atmosphere around the object.

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