Exploring the Potential for Surface-Enhanced Raman Spectroscopy (SERS) in Monitoring the Off-Gassing in Storage of Objects Containing Poly(vinyl chloride)

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BACKGROUND

Deterioration Process

Poly(vinyl chloride) (PVC) is a “malignant” plastic, known to deteriorate when points of instability in its polymer’s structure are exposed to heat, light, and oxygen (Shashoua, 2008). This results in:

• dehydrochlorination of the polymer
• breakdown through hydrolysis and migration to the surface of the phthalate plasticizers (typically di(2-ethylhexyl) phthalate (DEHP)) to modify the PVC to the polymer’s properties

In addition to physical problems, the potential to generate hydrochloric gas and release phthalates can cause issues:

• the process is autocatalytic, so the accumulation of gases in storage spaces could accelerate the loss of an object
• it can cause the deterioration of other objects through the effects of the released gases
• it could pose health risks for museum staff and researchers who would be exposed to elevated levels of phthalates

Therefore, in order to inform decisions regarding safe storage and access, it is important to monitor PVC objects for off-gassing.

Selection of Technique

GC-MS is the most commonly used technique in off-gassing studies of plastics, demonstrating a high degree of sensitivity and accuracy. However, GC-MS is not always readily available, and this lack of access prompted the study to investigate if there were viable alternative techniques of Raman could be a viable alternative, especially as it is already used to study other aspects of plastics.

Surface-enhanced Raman spectroscopy (SERS) was used; this utilizes a substrate coated in metal nanoparticles to enhance the Raman signal, thereby potentially making it possible to detect off-gassing.

EXPERIMENTAL DESIGN

Outline of Goals

This study was an investigation to see if SERS has the potential to monitor off-gassing in storage of objects containing PVC.

Hypothesis

Based on the deterioration pathways, we expected the following:

• dehydrochlorination

Raman peaks: 600-800 cm⁻¹, 1500-1650 cm⁻¹, C=O (Stromberg et al., 1958; Smith and Dent, 2005)

• phthalate plasticizers

Raman peaks: 1040, 1581, 1601, 1726 cm⁻¹ (Netryaiberg and Berg, 2002)

This indicates that 1500-1650 cm⁻¹ is especially significant for Raman detection of PVC objects.

RESULTS

Object Materials Collected SERS Spectra

Snake Oil by Hany Armanious (component with no visual deterioration): polyethylene (PET) with PVC and oil paint

MSDS confirmed HCl as degradation product

Snake Oil by Hany Armanious (component with visual deterioration): PET with some PVC and oil paints

ATR-FTIR identified four plasticizers in the pool of liquid (Blake, 2015)

Second derivative (change in slope) - note the differences in the 1500-1650 cm⁻¹ region

Raman spectra of 200-1300 cm⁻¹ (overlaid) and 1300-2300 cm⁻¹ (offset)

Blue-Blank Purple-Empty Bag

Red- Snake Oil green

Khalil: Snake Oil brown

Green- Plastic landscape

Plastic landscape by Tony Coleing: PVC with lead stabilizers

Fig. 1: Heat-sealing to create the bag with the object inside.

Fig. 2 (from far right): Nitrogen tank feeding through a portable low oxygen pest eradication chamber, into a hose, and to the bag with the object.

Fig. 3: Using the OxyBaby to measure the oxygen levels in the bag. Once 0.3% oxygen was reached, the bags were sealed shut.

Fig. 4: Substrate (at the red arrow), placed in close proximity to the object.

Fig. 5: Objects sitting in sealed bags with the substrates for 24 hours.

DISCUSSION

Despite flushing the atmosphere inside the bags with nitrogen, the spectra were complicated by the fact that the substances are easily contaminated by other sources encountered before use. Unused substrates from both manufacturers had peaks in their Raman spectra, and Raman mapping showed variation across individual substrates, so there was no standard background from which to subtract. For typical use of the substrates, signals would presumably be high enough to overwhelm this background contamination, but that was not the case in this study.

While acknowledging that SERS may produce slightly different spectra from traditional Raman, there do appear to be some matches in the spectra to those identified in the hypothesis as significant:

• 600-800 cm⁻¹ (dehydrochlorination): While parts of the lower region of Raman may prove indicative of deterioration (noticeably around 250 cm⁻¹ where the peak for the brown component of Snake Oil has a different shape than the green one), peaks from 600-800 cm⁻¹ did not consistently appear in the spectra.

• 1040, 1726 cm⁻¹ (phthalate plasticizers): Peaks at these locations did not consistently appear in the spectra.

• 1500-1650 cm⁻¹ (both): This region: the middle of the fingerprint region for many materials is crowded, but some peaks do seem indicative. There is a peak at 1610 cm⁻¹ for the brown component of Snake Oil that does not appear in the spectrum of the less deteriorated green component. Other differences between the two spectra are more clear in the second derivative (specifically at 1572 and 1640 cm⁻¹).

This suggests off-gassing products from PVC have been detected.

CONCLUSION

Future studies would benefit from concurrent analysis with GC-MS, as well as investigating the possibility of amplifying the off-gassing peaks against the background contamination by increasing the time the objects are monitored in the bags or making bags with less air space.

Some of the expected peaks for PVC off-gassing did still appear to be visible against the background contamination, particularly on the gold substrates. If the suggestions for improving these results are effective, SERS could provide an alternative method of determining the rate of off-gassing and subsequently the rate of deterioration of objects containing PVC.

This will improve recommendations for storage in terms of both human health and object longevity.