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Analysing objects to produce more sustainable conservation environments

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Abstract

Preventive conservation mainly determines conditions from an artifacts material type. Within most material groups there are a wide range of documented different responses to RH and pollution conditions. If sufficient knowledge exists, which is just becoming available for some cultural heritage materials, and suitable analytical methods have been developed, then analysing the artefact can be used to determine the required environment. Some glass compositions are unstable and different RH conditions have been recommended for stable and unstable glasses. Measurements have shown approximately, a three times larger carbon footprint to generate the tighter RH environment for unstable glasses, compared to that for stable glasses. Sampling from art glass is extremely difficult.

Keywords: glass, IRRAS, ATR-FTIR, NIR, OCT, ion chromatography, non-invasive techniques.

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It has been recognized for some time that certain glass compositions make those objects much more environmentally sensitive (Brill 1975, Bimson 1968). Recent research (Koob et al 2018) has recommended very strict RH conditions (40-42% RH) for such unstable glasses. Maintaining this tight RH range for unstable glass is energy or carbon intensive, but only a small portion of glass objects require it. A wider band (40-50% RH) is recommended for other glass objects. Several methods can be used to analyse glass objects and determine those pieces with composition or behaviour that predicts such instability. Conservation examination by eye or using low magnification microscopy can determine the early stages of degradation of some glasses. However, visual detection of the gel layer depends on differences in refractive index, which are not always present. Efflorescences can be confused with either dust deposition or remnants of casting (Thickett and Pretzel 2010). This can lead to instances of deterioration going unnoticed (Thickett and Ling 2021, Lombardo 2022). Additionally, the authors have undertaken several analyses for new displays highlighting unstable glasses, thought to be stable via conservation examination. Instrumental analysis can be advantageous, either the glass composition or the early stages of deterioration can be determined in some way. The value of glass objects means non-invasive methods are highly preferred. Sampling will be visible in most objects. The thickness of alteration layer that will sensitize a glass to low RH conditions (cause it to crack when RH is low) is unknown. It is also likely that the degree of alteration in the layer and residual stress will also affect this. For glasses (15% K, 48 Si, 15 Ca, 4 P, 3 Na, 3 Mg, 1.5Al, 1 Mn, 1 Fe) corroded in sodium carbonate solution at 30°C, cracking was observed when alteration layers thicker than 2-3 μm were present.

X-Ray fluorescence can analyse the elements of interest, however the production of alteration layers may affect results, which are very surface sensitive. A range of other non-invasive techniques: absorption- reflection Fourier Transform infra-red spectroscopy (FTIR); attenuated total reflection (ATR FTIR); near infra-red spectroscopy (NIR); confocal Raman micro-spectroscopy; surface ion analysis and optical coherence tomography (OCT) have been assessed for this purpose. Each has been applied to two sets of objects: 19th century cover glasses from daguerreotypes and Limoges enamels.

Methods and materials

Two sets of objects were used to compare different analytical methods. A set of Limoges enamel plaques, part of the Wernher Collection and displayed at Rangers House, London, and a set of cover glasses from six daguerreotype packets of Charles Darwin's family from 1842 and one replacement from 1996. Both sets of objects present some level of degradation. In the case of the Limoges enamel plaques, previous analysis has shown degradation of some colours with alteration layers of some depth (Thickett et al 2017), while the cover glasses present very thin alteration layers (Thickett et al 2022).

Infrared spectroscopy, infrared reflection-absorption (IRRAS) microscopy and reflectance spectroscopy have all been used to characterise the alteration layer thickness. As the alteration layer forms, Si-O-Si bonds break to Si-OH and Si-O-Na bonds, which can be observed at characteristic wavenumbers (around 1100 cm^{-1} and 970 cm^{-1}) in infrared spectra (MacDonald et al 2000). In this work, a Nicolet Inspect IR microscope was used for external reflection FTIR running off a Nicolet Avatar 360 bench. This fixed-focus instrument collected a spectrum from a 100 μm-diameter circle at 1 cm^{-1} resolution. Previous work has shown the beam capable of penetrating 1.78 but not 2.04 mm of enamel

glass (Thickett et al 2017). ATR FTIR analysis was performed on an IR microscope (Continuum on Thermo Is-10 FTIR) with a Germanium ATR head. The Germanium ATR head collects information from a 150 x 150 μm area and calculations have shown that at 1100 cm^{-1}, the information depth is approximately 0.5 μm. Near infra-red spectroscopy was performed with an Analytik Labspec 4 spectrometer with large area fibre optic head, following the method of Zaleski et al (2019).

Confocal micro-Raman spectroscopy was performed with a Horiba Jobin Yvon Infinity using a 532nm Nd-YAG laser and 100 μm confocal aperture. This has an information depth of 3.8μm which can be tracked through the depth of transparent samples using the microscope.

Surface ion analysis was performed by swabbing a known area, extracting and analysing sodium and potassium concentrations with ion chromatography. Sampling was performed by wetting a cotton wool swab with 1 ml of 3:1 water/IMS and rolling the swab over a 5 by 5 cm rectangular area. The sample was then extracted in 5 ml of water at a resistivity of 18.2 MΩ-cm. The extracts were filtered and analysed using a Dionex ICS 1100 ion chromatograph with an Ionpac CS12 column and 18 mM methane sulfonic acid eluent.

Ultra highresolution (UHR) OCT operating at a central wavelength of 810 nm has a depth resolution of 1.2 μm in glass, with a depth range of a few millimetres is capable of collecting a 3D image cube of a 5 x 5 mm area at a transverse sampling resolution of 10 μm in 10 s (Read et al2019).

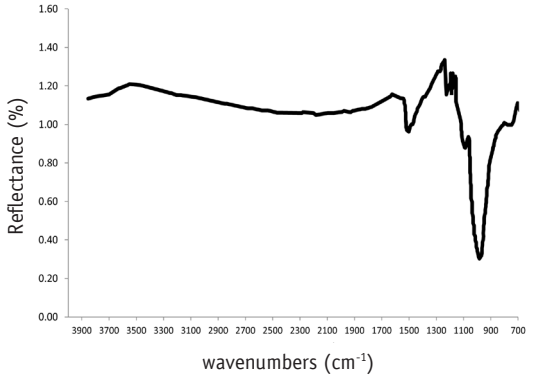

Fig. 1 IRRAS spectrum of blue enamel.

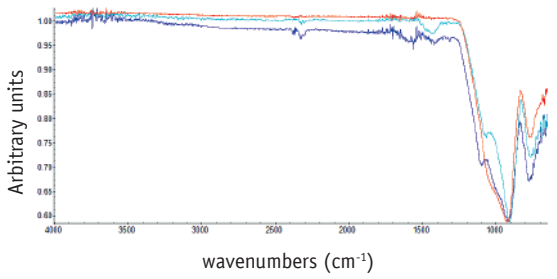

Fig. 2 Ge ATR-FTIR spectra from plates.

Results

Figure 1 shows a typical external reflection (IRRAS) FTIR spectrum for one of the enamel plaques and Figure 2 ATR spectra for the plates (right).

The beam is known to penetrate the full depth of the enamel glass during IRRAS (Thickett et al 2017). The relative contributions from each depth segment (upper alteration layer, unaffected glass, lower alteration layer) are unknown. Clear splitting was observed in all the enamel spectra taken. At the early stages of glass deterioration, the alteration layers are very thin. No splitting could be observed in the daguerreotype plates. It is possible that peak fitting, multivariate calibration or chirped algorithm calibration (Shalaby et al 2020) may improve sensitivity, but this was beyond the scope of this work. Clear splitting is observed on both interior and exterior surfaces. All surfaces of all the cover glasses showed clear splitting, including the 1996 replacement glass. Most of the spectra include a shoulder at around 1020cm^{-1}, indicating unreacted glass. This probably indicates the alteration layers are less than 0.5μm deep, the

information depth of the system at this wavelength.

The 100-μm diameter analytical IRRAS area can accommodate some curvature of the surface. More curved surfaces could be analysed with more highly focused FTIR microscopes, but longer collection times would probably be needed. The ATR head has to be pressed against the glass to achieve optical contact and good spectroscopy. This was certainly easier with flat objects but may be impossible with highly deteriorated and fragile glass surfaces, although the question of stability may be already answered for glass objects in such condition. The ATR head can deal with the degrees of curvature expected for the vast majority of glass objects. With this technique, once the alteration layer extends beyond 0.5 μm, no further change in spectra is expected.

Figure 3 shows the NIR spectrum of a purple enamel glass and more degraded plate.

The isolated bound water peak at 1910 nm is clearly visible in the enamel spectrum. No peak above background noise level was observed for the cover glasses.

The Raman spectrum from the surface layers of the enamels showed displacement of peaks at 500 and 1070 cm^{-1}. These are clearly shifted from 530 and 1100 cm^{-1} in the deeper un-degraded glass. No peak shifts were observed with the plates. The information depth of the micro Raman system is too large to detect the thinner alteration layers present on the plates.

Figure 4 shows the concentrations of ions swabbed from the cover glass surfaces.

The concentrations are well above detection and limit of quantification, even for the least degraded replacement glass. The method (swab area, extraction volume, and ion chromatography) can also be altered to improve the detection limit (Thickett et al 2022).

The increase in alteration layer thickness can be estimated from the ion concentration, original glass composition and density (Thickett and Ling 2021). The composition of the replacement glass has been measured

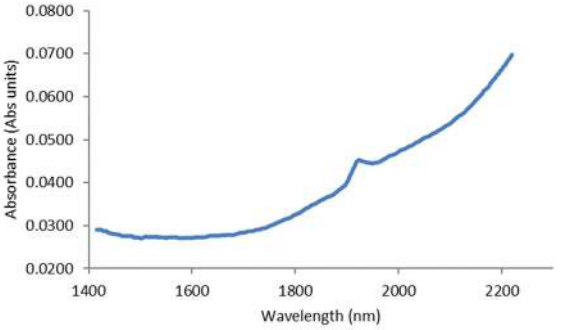

Fig. 3 NIR spectrum of enamel.

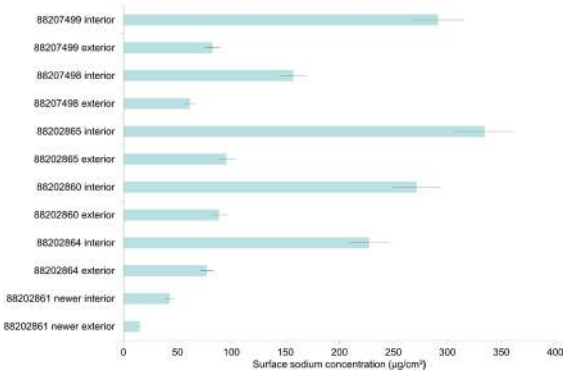

Fig. 4 Ion concentrations on plate surfaces.

(Thickett et al 2022) and the density was calculated from physical measurements. This indicated an alteration layer thickness of 0.08 μm.

Reconstructed virtual cross-section images (known as B scans) produced by the UHR OCT of the blue enamel is shown in Figure 5.

The alteration layer is clearly visible on the upper face of the enamel, but not continuous. Separation of the glass from the metal has occurred over about half of the contact area. A thin alteration layer is also visible on the inner face, in contact with the metal.

No alteration layer is detected in the images of any plates. The salts are clearly observed (points marked A) and the relative refractive indices can be determined

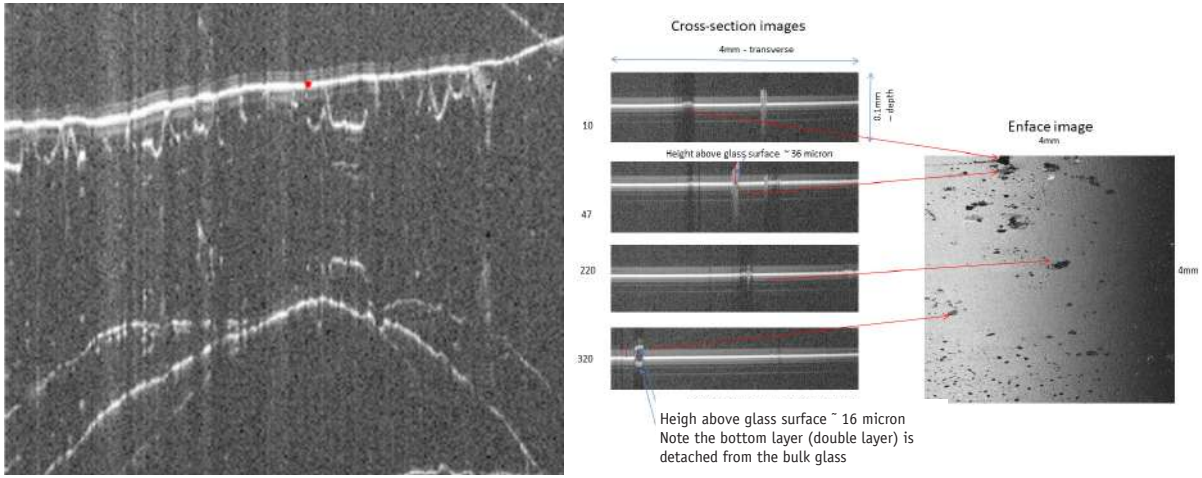

Fig. 5 Z scan from UHR OCT of enamel; enface and Z scan of plate.

Tab. 1

	Portable	Enamels	Cover Glasses	Issues	Impact of cleaning
R-A FTIR	Y	Y	N	Scattering can give distorted spectra	Some, dust will contribute to spectra
Ge ATR-FTIR	-	Y	Y	Limited to surface 0.5μm.	N, avoid dust/salts by visualization under magnification
NIR	Y	Y	N		N
Raman	-	Y	N	Glass must be transparent to laser wavelength	N, avoid dust/salts by visualization under magnification
IC	N	Y	Y	Can be wicking under mask for curved surfaces. Cleaning resets.	Y, removing sodium and potassium negates analysis
OCT	Y	Y	N		

from the height above the surface and the apparent depth. Even with the improved UHR OCT, the alteration layer is not seen in the early stages of glass deterioration, despite observing leached salts.

Tab. 1 summarizes the results for the techniques investigated.

For this approach to be effective, portability is important to analyse large numbers of objects quickly. Whilst portable ATR-FTIR microscopes and Raman exist, the sensitivity of the microscope control required can limit their use. Whilst ion chromatography is generally not portable, samples are taken with a swab, and these can readily be transported to the instrument.

Conclusions

Both ATR-FTIR and surface ion analysis have been proven able to detect the very early stages of glass deterioration and determine a glass object's stability. Whilst the other techniques worked for relatively degraded glass, they could not detect the early stages. Significant research is required to determine the critical alteration layer depth for different glass types degrading under different conditions. Some empirical observations have been made for weeping glass and ion chromatography (Verhaar et al 2020). However, these results only apply to the glass compositions present (which were not described in detail) and the environments experienced. The Horizon Europe project GoGreen will investigate further aspects of such analyses for glasses and limestones.

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