

*Abstract*

Raman spectroscopy and secondary ion mass spectrometry were used to investigate chemical and structural changes in soda and soda-lime glass exposed to organic pollutants under ambient and accelerated ageing conditions. Raman spectroscopy reveals modification of the glass structure non-destructively, in situ, and as a function of depth. The pollutants caused growth of crystalline salts and structural changes in the glass surface, with formic and acetic acid more corrosive than formaldehyde.

*Keywords*

Raman spectroscopy, secondary ion mass spectrometry, organic pollutants, deteriorated glass, soda silicate glass

## Understanding glass deterioration in museum collections: a multi-disciplinary approach

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### Introduction

Study of glass within the National Museums of Scotland (NMS) showed that a significant proportion of the historical glass collections were weeping and growing crystalline corrosion products, with some crizzling (Eremin et al. 2005, Robinet et al. 2004). Growth of sodium formate resulted from unstable glass compositions, high concentrations of organic pollutants and fluctuating relative humidity (RH).

The presence of formates on corroding glass is not unique to the NMS. Schmidt (1992) attributed formate formation to formaldehyde emission by plywood shelving. Formates also occurred on the surface of glass objects from The Corning Museum of Glass, analyzed by the authors, probably because of prolonged storage (over 25 years) on composite wood shelves in an enclosed wooden storage area. Formate formation may be more widespread than currently appreciated as there are few published analyses of corrosion products on historical glass.

Glass alteration has two aspects: the visible crystalline corrosion products forming at the surface and the less visible modified glass structure. The latter is more complex and may have greater impact on the object preservation.

Raman spectroscopy has been used to characterize the crystalline deposits forming on glass objects (Eremin et al. 2005, Robinet et al. 2004). It is here assessed to investigate the molecular structural change and measure the alteration depth, known as the depletion depth, of corroded glass objects. Examination of the structural change in a glass can be undertaken from a section, either free or embedded in a resin. However, sectioning requires sampling of the artefact. As an alternative, Raman spectroscopy can measure spectra non-destructively, in situ from intact artefacts, and even record the spectra at various depths for transparent glass. In addition, general compositional information, such as soda or potash silicate glass, can be obtained (Coupry et al. 1993). As alteration layers have less structure, the Raman scattering from these is weaker than from the original glass and alteration layers thinner than 3  $\mu\text{m}$  cannot be detected. To observe nanometre scale changes, the glass is examined by secondary ion mass spectrometry (SIMS). SIMS provides an excellent method of obtaining detailed

high precision information on the concentration of elements as a function of depth (Fearn et al. 2004). When operated in depth profiling mode, SIMS combines high depth resolution with trace element detection. SIMS can also resolve concentration variations occurring over a few nanometres for all elements of the periodic table, over depths of tens of nanometres to several microns.

The effects of cleaning deteriorated glass artefacts remains poorly understood, and for vulnerable objects it is unclear if cleaning is beneficial or accelerates deterioration. A study assessed the effects of cleaning a previously deteriorated glass artifact on degradation in ambient conditions. Pieces of the artifact were cleaned with distilled water, cleaned with non-ionic detergent or left untreated. After 7 weeks ageing, the samples surfaces were examined with focused ion beam microscope (FIB).

## Experimental

### *Analysis*

Raman spectra were recorded on a LabRam micro-spectrometer using a 532 nm line of a doubled diode laser. Measurements were carried out through a  $\times 100$  objective and 100  $\mu\text{m}$  confocal hole. The site of the laser spot was  $\sim 3 \mu\text{m}$  diameter at the waist and  $\sim 5 \mu\text{m}$  along the vertical axis.

Depth profiles were obtained using a modified Atomika quadrupole SIMS tool (Atomika) equipped with a floating low energy ion gun (Dowsett et al. 1997), and a Cameca 4f. Before analysis samples were wiped with dry ethanol to remove any corrosion products on the surface, as the salts cause loss in depth resolution. Samples were sputter depth profiled using a  $\text{N}_2^+$  at 5 keV, and an  $\text{O}^-$  beam at 10.5 keV, depending upon the instrument used. Secondary ions of Na, Al, Si, K and Ca were collected. Charge compensation was performed in all analyses using an electron flood gun, and surface coating the samples. The depths of the final sputtered crater were measured using a Zygo NewView white light interferometer and stylus profilometry.

A FIB microscope was used to image the surface of glass samples of cleaned and corroded deteriorated glass. The surface was imaged by bombardment with ions from a liquid Ga ion source. These ions were accelerated at 30 keV and focused to a beam size of  $\sim 5 \text{ nm}$  with a beam current of 5–500 nA to give an ion image.

### *Artificial ageing experiments*

Artificial corrosion experiments were set up using glass samples produced with similar bulk composition to analysed degrading historic glass.

The initial experiments were undertaken at ambient temperature over 5 months using glass fragments from an unstable soda glass decanter (72 per cent  $\text{SiO}_2$ , 14.5 per cent  $\text{Na}_2\text{O}$ , 6.5 per cent  $\text{PbO}$ , 5 per cent  $\text{K}_2\text{O}$ , 0.6 per cent  $\text{CaO}$ ). RH was fixed at 40 per cent or 100 per cent and the pollutants, formic acid, acetic acid and formaldehyde, either single or mixed, were set at two concentrations, 150/100 ppm and 5 ppm.

A second series of experiments investigated the effect of glass composition, manufacturing technique and pollutant type and concentration using soda glass (72 per cent  $\text{SiO}_2$ , 18.5 per cent  $\text{Na}_2\text{O}$ , 3.5 per cent  $\text{K}_2\text{O}$ , 3 per cent  $\text{CaO}$ , 1 per cent  $\text{Al}_2\text{O}_3$ ) and cast and blown soda-lime glass (67.5 per cent  $\text{SiO}_2$ , 19 per cent  $\text{Na}_2\text{O}$ , 1.5 per cent  $\text{K}_2\text{O}$ , 6.5 per cent  $\text{CaO}$ , 2.5 per cent  $\text{Al}_2\text{O}_3$ , 1.5 per cent  $\text{MgO}$ ). Experiments were undertaken for 4 weeks under ambient or accelerated conditions, the latter was set up following the accelerated corrosion method used in museums to assess the corrosiveness of materials (Robinet and Thickett 2003) with a glass fragment replacing the metal coupon in the silicon stopper.

### *Cleaning Tests*

Glass fragments from a replica bottle with a soda glass composition (67 per cent  $\text{SiO}_2$ , 21 per cent  $\text{Na}_2\text{O}$ , 4 per cent  $\text{K}_2\text{O}$ , 4 per cent  $\text{MgO}$ ,  $< 1$  per cent  $\text{CaO}$ ) are being used to assess the effects of cleaning. This bottle was displayed in the

Museum of Scotland from 1998 to 2004. During this time, crystals of sodium formate developed on the surface despite low levels of organic pollutants and an environment of 45–60 per cent RH in the case and gallery. Fragments of the bottle were cleaned with distilled water or non-ionic detergent followed by distilled water. Samples were left for 7 weeks at 60 °C in a low humidity environment before examination.

## Results and discussion

### *Raman spectroscopy of a corroded 19th century soda glass decanter*

Raman spectroscopy provides information about the structure of the silicate tetrahedra and their degree of polymerization based on the vibration of the covalent bonds of the different tetrahedral species. Raman spectra from alkaline silicate glasses have bands in the region 900–1200  $\text{cm}^{-1}$ , which correspond to the stretching of silicate tetrahedra containing non-bridging Si–O bonds (Furukawa et al. 1981, McMillan 1984). Raman analysis of a 19th century corroded glass decanter shows a significant change between the structure of the altered and original glass (Figure 1). The altered glass is characterized by a decrease of the band at 1100  $\text{cm}^{-1}$ , from loss of silica tetrahedra with one non-bridging Si–O bond owing to leaching of sodium ions out of the glass structure. Spectral mapping of a section of the altered glass shows that the structure of the altered layer is uniform.

Using the confocal system of the Raman spectrometer, spectra can be recorded from the altered surface down to the original glass without contact with the object or sample (Figure 2). Intermediate spectra occur close to the interface, for example the spectrum at 34  $\mu\text{m}$  depth in Figure 2. These spectra do not correspond to an intermediate structure but are linear combinations of the altered and original glass spectra resulting from measurement of a volume rather than a layer. This volume is determined by the size of the confocal hole and the objective used.

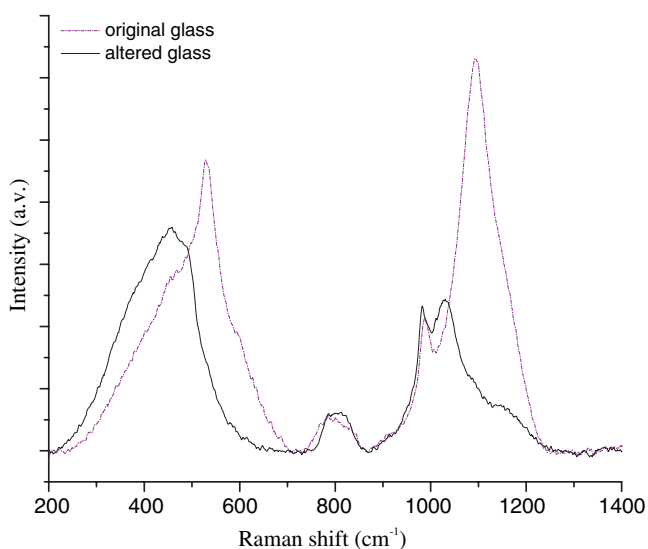


Figure 1. Raman spectra of the altered and original glass taken from a section of the soda glass decanter

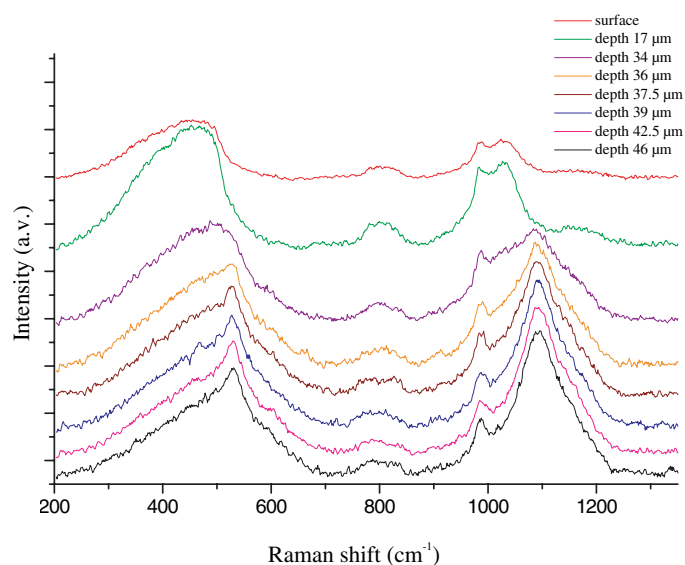


Figure 2. In situ Raman spectra of the soda glass decanter from different depths

The depth of alteration, the depletion depth, is defined as the depth at which the spectrum of the original glass is reached. The measurements made in situ on the decanter indicate a depletion depth of 36–37.5  $\mu\text{m}$ . This agrees with the measurements by Raman spectroscopy and scanning electron microscopy from a section of the same object. This method is promising for the analysis of glass objects in situ in museums to determine the extent of structural alteration of objects. The influence of the corrosive environment on modification of the glass structure is investigated by Raman spectroscopy of artificially corroded samples.

*Artificial ageing experiments*

The 5 month ambient experiment and the accelerated experiments (Figure 3) on the soda glass produced micron-depth alteration layers, ideal for Raman spectroscopy analyses. The less reactive soda-lime glass had alteration depths below the Raman detection limit and could only be measured by SIMS (Figure 4). For the SIMS analysis, the alteration depth was defined as the depth at which the elemental profiles reach the bulk level.

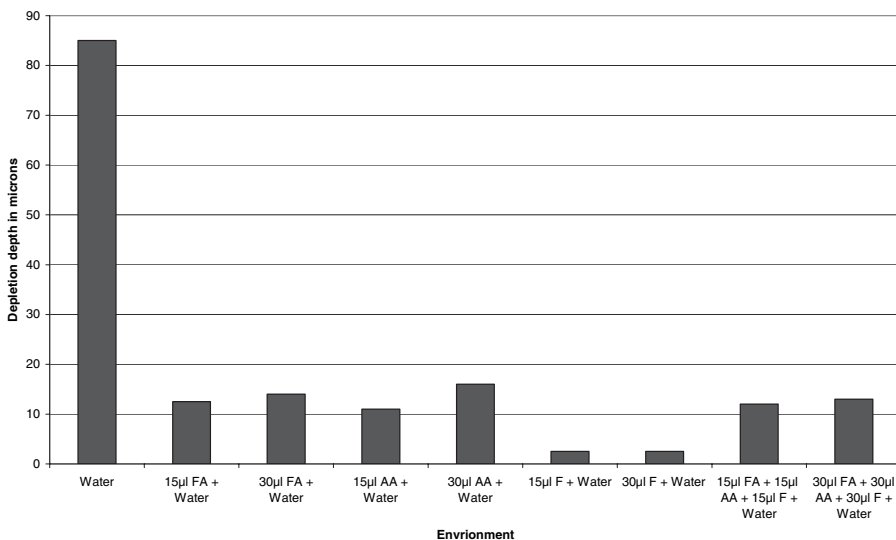


Figure 3. Depletion depths measured by Raman spectroscopy on soda glass corroded under accelerated conditions for 4 weeks at 60 °C and saturated humidity; FA, formic acid; AA, acetic acid; F, formaldehyde

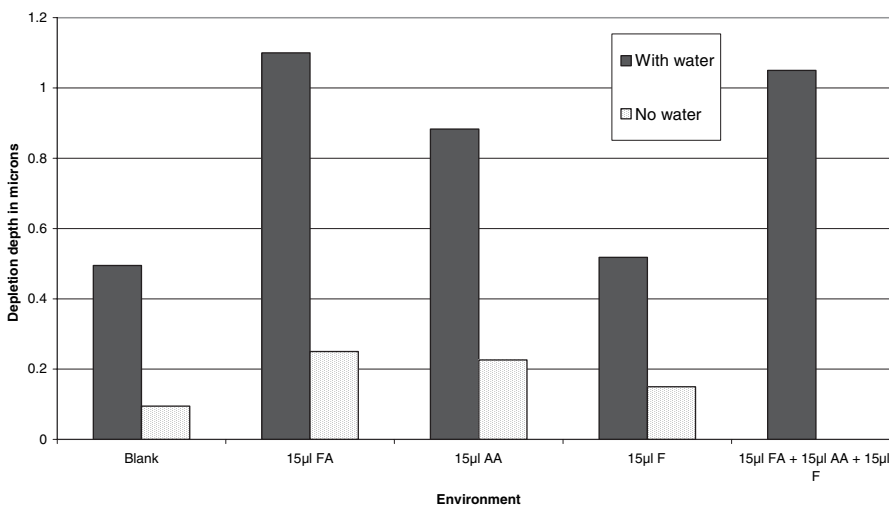


Figure 4. Depletion depths measured by SIMS on soda-lime glass corroded under accelerated conditions for 4 weeks at 60 °C, and saturated (water) or low humidity (no water); FA, formic acid; AA, acetic acid; F, formaldehyde

A low humidity environment was probably present inside the tubes even in the absence of water, due to the ambient air introduced during the set up and possibly from the glass itself. The low humidity might explain the sodium depletion of the blank soda-lime glass (Figure 4). A depletion depth of about 0.001 µm was measured on the soda-lime glass before the experiments. All fragments have some depletion from manufacture and subsequent ‘natural’ ageing.

The results from the ambient and accelerated experiments follow the same trend except for soda glass exposed to water vapour alone. As expected, soda glass is more reactive than soda-lime glass. In the case of soda-lime glass, the cast fragments appear more reactive than the blown fragments. Although the three

pollutants produced similar alteration of the glass, acetic and formic acids are more detrimental to the glass than formaldehyde. For a given pollutant, the depletion is always greater in the presence of high humidity (Figure 4). However, even at very low humidity pollutants still react with the glass to cause sodium depletion. The increase in pollutant concentration or the combining of pollutants does not appear to have greatly increased corrosion. However, the pollutant levels used in the experiments were much higher than the levels in museums and concentration may have more impact at low pollutant concentration. After exposure to formic acid vapour, Raman analysis showed that in a few instances sodium formate crystals occurred several microns under the surface. The pressures generated by these crystalline products are potentially dangerous to the object, particularly where fluctuating relative humidity causes repeated deliquescence and recrystallization.

Water vapour usually causes less depletion when on its own than when combined with pollutants (Figure 4). In the case of the accelerated experiment (Figure 3), water produces a deep (~85  $\mu\text{m}$ ) opaque layer at the surface of the soda glass, which cracked and flaked off on drying. The structure of this altered layer is very different from the one produced by organic pollutants in a humid atmosphere. The difference observed between the ambient and accelerated experiments may be due to a change in the surface pH. The glass exposed to water vapour only in accelerated conditions reached a surface pH of 14, well over the 9–10 at which the silicate matrix breaks down. For this reason the alteration process and the kinetics were different from those of the other experiments.

During the initial artificial experiments several contamination problems were encountered. Calcium chloride salt solutions were originally used to control the RH at 40 per cent in ambient experiments. Sodium and potassium chloride corrosion crystals formed at the glass sample surface in the presence of formic acid vapour. Formic acid is likely to have reacted with calcium chloride to form hydrochloric acid, which subsequently reacted with the glass. This was not observed for the acetic acid and formaldehyde atmospheres. In subsequent experiments, salt solutions were replaced by 'Artsorb' pellets to control the RH.

Polystyrene boxes were initially tested for use as containers for setting up the artificial experiments. After two days exposure of a glass fragment to formic acid vapour, a layer of polystyrene was identified at the glass surface. All experiments are currently done in 2 litre glass desiccators. The zinc metal grid generally present in these desiccators is removed as it can react with glass in direct contact at very high RH.

The clear plastic boxes originally used to store and transport the glass samples after experiments can also cause contamination, with polystyrene found on the surface of some samples. Glass bottles were used as an alternative.

#### *Cleaning experiments*

The FIB images of the glass surfaces are shown in Figure 5. The surface of a typical 'as-made' blown soda glass from a similar bottle is given in Figure 5a to show the appearance of a freshly blown surface, as the deteriorated bottle was not examined prior to corrosion. The samples which were not cleaned developed corrosion salts distributed non-uniformly across the glass surface and some etch pits, as shown in Figure 5b. The sample cleaned with distilled water, shown in Figure 5c, developed some etch pits and some corrosion salts whilst the sample cleaned with a non-ionic detergent, shown in Figure 5d, developed etch pits but no salts.

### **Conclusion**

Raman spectroscopy proved an excellent technique for the examination of glass corrosion in museums. Analyses can be undertaken non-destructively directly on objects and is unique in providing depth information for clear glasses. Raman can identify both the crystalline surface deposits and changes in the glass structure.

Organic pollutants result in growth of crystalline products and contribute to structural change in the glass. This change is different from that caused by water

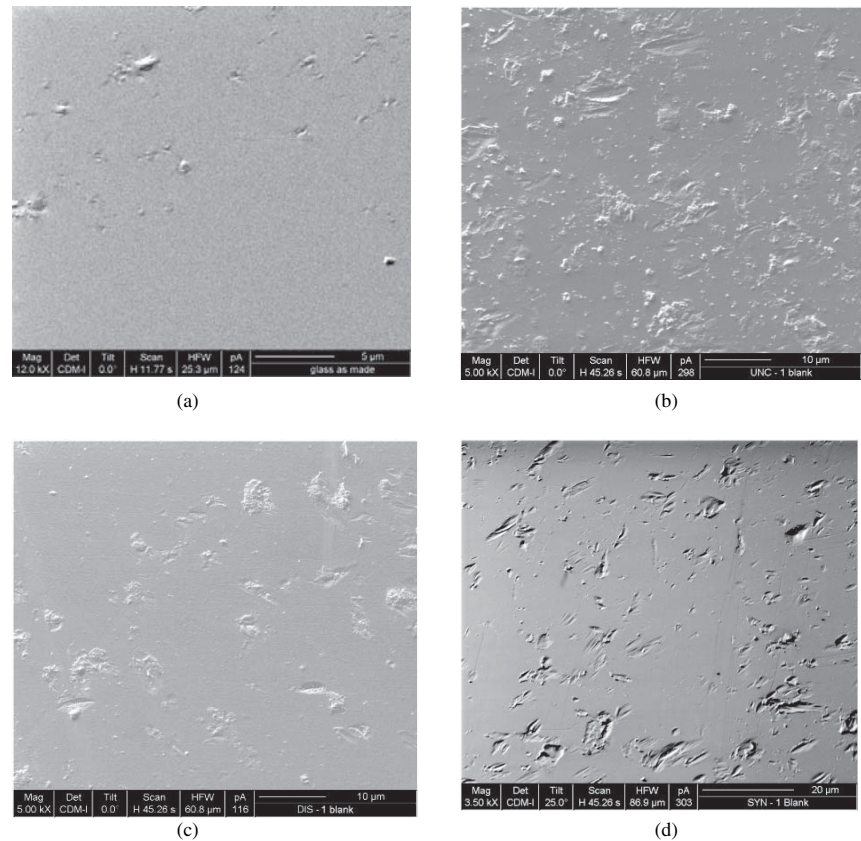


Figure 5. FIB ion images of the surface of soda glass, (a) 'as manufactured', (b) uncleaned, (c) cleaned with distilled water, and (d) cleaned with a non-ionic detergent. Samples (b), (c) and (d) were left for 7 weeks at 60 °C in a dry environment before examination

vapour alone due to a difference in surface pH. The organic acids have more effect than formaldehyde, which should therefore not be considered as the main danger for museum glasses.

Study of the alteration processes of organic pollutants on historic glass is ongoing. The application of spectral deconvolution techniques to the Raman spectroscopy data as well as the use of complementary techniques such as solid-state nuclear magnetic resonance will increase understanding of the processes.

A qualitative assessment of cleaned and untreated surfaces from deteriorated glass has been undertaken with FIB microscopy. Further work should examine how these surfaces react in corrosive environments and assess any chemical and/or structural alteration due to cleaning.

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