

SCIENTIFIC PAPER

MICRO-SPECTROSCOPY: A POWERFUL TOOL TO UNDERSTAND DETERIORATION

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Identification of accretions on object surfaces is vital to understand their deterioration processes. The presence of certain species can give a strong indication of the cause of that deterioration. The increasing availability of high spatial resolution vibrational spectroscopy allows analysis of the very small scale accretions found on certain object types. This paper discusses the utility and advantages of such an approach through a series of case studies. In each instance such techniques have been instrumental in elucidating the deterioration mechanisms and slowing the process down.

1 Introduction

Preventive conservation aims to slow the interaction of the environment with cultural heritage artifacts and collections. English Heritage presents a wide variety of collections in over 130 historic buildings where climate control options are very limited. Many artifacts have impure compositions, due to refining technologies and microstructures that are often unknown in detail. These affect the way in which they react. They are aged which further affects their reactions and have often undergone multiple conservation treatments. The environments in historic buildings can be complex, with temperature, relative humidity and light levels constantly varying. Particulate composition is often variable and affects deterioration and the gas phase is multi-component mix, especially inside showcases. All of these mean that assigning a cause to an observed particular deterioration can be difficult, especially for chemical deterioration. This is an essential first step to remediate environments that are causing deterioration. However, the deterioration products often occur on a micro-scale and can be intimate mixtures. High spatial resolution vibrational spectroscopy is becoming increasingly available to conservation scientists through infra-red and Raman microscopes. These tools can be used to analyse many deterioration products, providing invaluable information to help elucidate causes of deterioration. The benefits of such analyses are illustrated through a series of examples.

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2 Experimental

Analyses were carried out with a range of infra-red and Raman spectrometers and microscopes:

- Nicolet Avatar 360 FTIR with an Inspect IR microscope
- Thermo Fisher Scientific Nicolet iS10 FTIR with Continuum microscope
- Perkin Elmer 2000 FTIR with Durascope with single bounce diamond ATR
- Horiba Jobin Yvon Infinity Raman microscope with 532 nm laser
- Renishaw System 1000 Ramascope with 630 nm laser

Although macro attenuated total reflectance (ATR) is not often considered a micro technique the information depth is determined by the ratio of the refractive index of the diamond and the sample. The information depth for ATR is given by:¹

$$d = \lambda / 2 \pi (n_p^2 \sin^2 \Theta - n_s^2)^{0.5}$$

where:

- λ is the wavelength
- n_s is the refractive index of the sample
- n_p is the refractive index of the ATR prism (diamond is 3.44)
- Θ is the angle of incidence and reflection of the beam

Hence the technique recovers information from a very limited spatial resolution in one dimension.

With the accessory used (SensIR Durascope), it is normally between 0.5 and 2.0 μm in the wavelength range of interest. The lateral resolution is 1 mm.

3 Results

3.1 Deposits on Glass

Some compositions of glass are unstable and susceptible to environmental deterioration. If the glass has too little silica (less than 64 mol%) and too little bivalent stabilizer (calcium and lead), then hydroxonium ions from atmospheric water undergo ion exchange with sodium or potassium in the glass. This results in a surface layer rich in silica and depleted of these elements. Sodium or potassium salts often form on the glass surface.²

Deposits were observed to re-occur in a dehumidified (Munters MG50 dessicant wheel dehumidifier) showcase storing weeping glass from the eighteenth and nineteenth centuries. Analysis of the deposits with FTIR microscopy indicated them to be sodium methanoate.

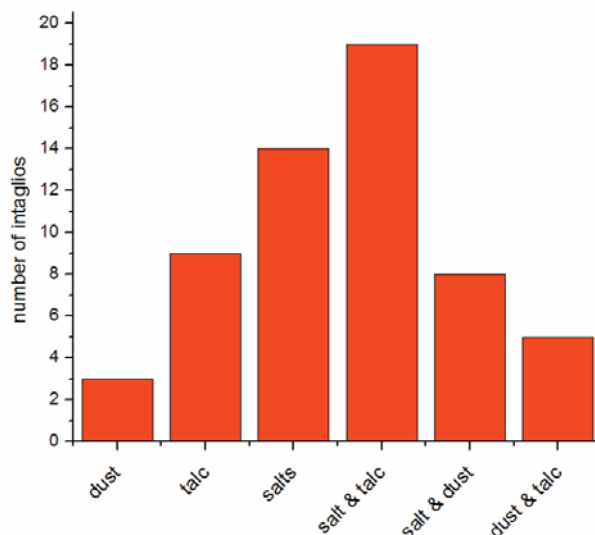


Figure 1: Types of 'deposits' analysed on Tassie intaglio surfaces.

Analysis of the water/IMS (industrial methylated spirit) swabs used to clean the glass surfaces with ion chromatography indicated a methanoate deposition rate of 16 $\mu\text{g}/\text{cm}^2/\text{year}$ (microgrammes per square centimeter per year). Analysis of the sodium removed indicated an increase in gel layer thickness of 13 $\mu\text{m}/\text{year}$ from SEM-EDX determination of the glass sodium concentrations. This figure extrapolates to complete loss of some of the glass in under 75 years, as some of the vessels are under a 1 mm thick. Diffusion tube measurements of the atmosphere indicated methanoic acid values between 152 and 337 $\mu\text{g}/\text{m}^3$, with much higher methanal concentrations between 473 and 1072 $\mu\text{g}/\text{m}^3$.³ No reaction rates of glasses with methanoic acid at different concentrations have been published on which to base air quality targets.⁴ However the gas concentrations of methanoic acid are quite low and seem unlikely to be able to cause such dramatic leaching. The presence of copper in glass is reported to dramatically increase the effect of methanal, probably through oxidizing the methanal to methanoic acid at the glass surface.⁵ Enhanced deposit formation was indeed found to correlate with glasses containing copper (analysed with XRF). The plywood shelving in the case is almost certainly the source of both methanoic acid (from the wood) and methanal from the adhesives used in the plywood.⁶ Replacement of the plywood shelving from the cases with an inert material was recommended to remove the source of carbonyl pollutants.

James Tassie patented a high lead glass formulation for portrait intaglios, popular in the eighteenth century. A conservation survey highlighted deposits on a collection of several hundred intaglios stored in cardboard and glass specimen boxes at The British Museum. There were con-

cerns that the boxes were emitting methanoic acid as this is known to accelerate glass deterioration. Analysis with FTIR microscopy identified several instance of potassium salts, formed from the glass, and several other instances of deposits of dust or casting materials (Figure 1). These were

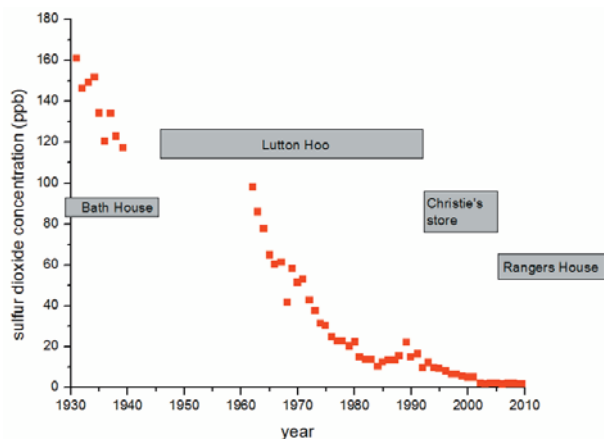


Figure 2: Sulfur dioxide concentration in London, bars show dates for location of the Werner collection of enamels. Data collection was interrupted by the Second World War.

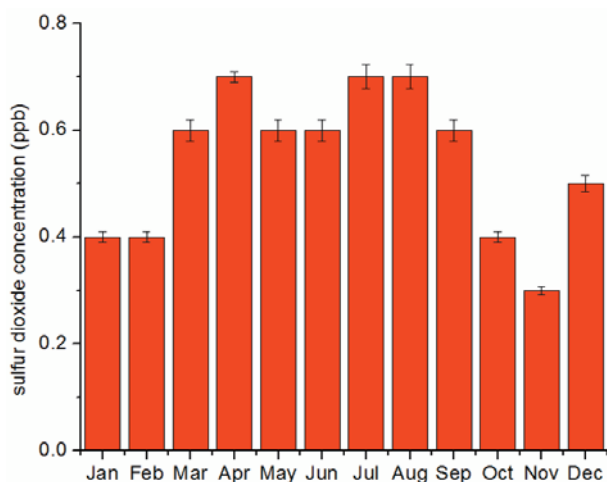


Figure 3: Sulfur dioxide concentrations measured in Rangers House.

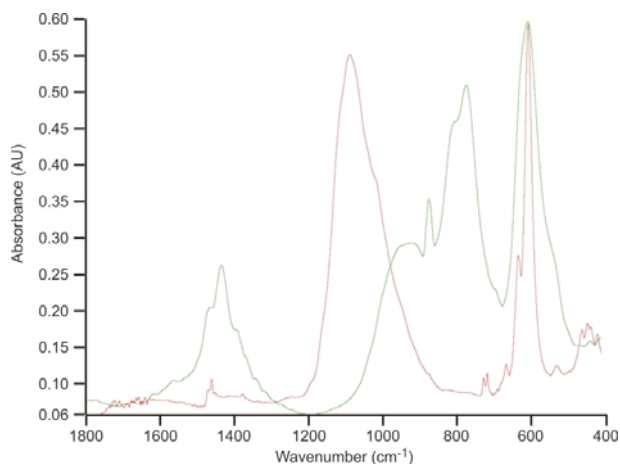


Figure 4: ATR FTIR spectra of carbonated sodium hydroxide (green) and sodium sulfate (red).

not related to deterioration, but were indistinguishable by eye, even under magnification.

This illustrates the limitations of visual examination alone, with many objects characterized as deteriorating that were in fact stable. No methanoate salts were detected, indicating the storage boxes were not accelerating the glass deterioration.

English Heritage presents the Werner Collection at Rangers House on the outskirts of London. The collection is on a hundred year loan and was installed in 2002. A program of assessing and improving the showcases and environments provided within them has been ongoing since installation. Microscopic examination of two enamel plaques revealed crystalline deposits over the blue and purple enamels. Several other enamel colours on the same plaques did not have these deposits on the surfaces. Since the sealant used on the MDF (medium density fibreboard) panels in the showcase is known to be inadequate at blocking methanoic acid emissions from the MDF, again the concern was that the showcase environment was accelerating the deterioration. Analysis with FTIR microscopy and Raman identified the deposits as sodium sulfate. The average sulfur dioxide concentration in London has dropped to below 3 ppm (parts per million) over the past three decades. It was thought that the sodium sulfate was likely to be formed in the past, when concentrations were orders of magnitude higher. Figure 2 shows the average annual concentrations in London updated from published figures (with no data between 1940 and 1960) for London in 1996, with averages calculated from government automated monitoring stations.⁷ The location of the enamels through this period is marked. Bath house and Christies are in central London, Rangers House in outer London and Luton Hoo in the countryside.

The sulfur dioxide concentrations in the room housing the showcase with the enamels were monitored through the MIMIC project using diffusion tubes, as well as concentrations inside the showcases.

These analyses revealed values below 1 ppb throughout the year and concentrations below detection inside the case, strengthening the thought that the deposits were not formed recently. To verify this, sodium hydroxide pellets were exposed in the case and room for six months. After exposure they were analysed by infrared with diamond ATR. For the sulfate band of sodium sulfate at 1100 cm^{-1} , the information depth was calculated to be 1.93 μm using an equation derived from Kramers-Kronig theory.⁸ This gives a very high

level of surface sensitivity and a low detection limit of the formation of sulfate on the sodium hydroxide surface, (Figure 4).

No sulfate was detected and the sodium hydroxide had reacted to form sodium carbonate on its surface. This confirmed that the sodium sulfate salts were formed prior to display at Rangers House and that remediation of the showcase environment was not required.

3.2 Past Environments of Iron Artefacts

A project studying the deterioration of archaeological iron identified a large concentration of heavily deteriorated objects from an unconditioned store. There was no monitoring information from the store and an assessment of the damaging RHs was required. This is a common issue in preventive conservation. Environmental monitoring has grown immensely over the past two decades, but many large institutions still do not have every space containing collections monitored. The objects were stored in cardboard boxes, as was common practice at the time of their excavation in the early 1970s. Spot RH measurements with dataloggers placed quickly inside the boxes, yielded an RH that was probably the average of that experienced over the past thirty days or so due to the buffering of the cardboard. However, unconditioned buildings often suffer a wide annual cycle of both temperature and RH, hence the last month's average may not be representative. Monitoring data for an adjacent room was also kindly supplied by the Victoria and Albert Museum, who share the storage facility. Unfortunately room conditions can vary widely due to differences in building fabric, building services, ventilation and aspect. Temperatures tend to be less variable than RHs and in these rooms the maximum temperatures reach 24-31 °C in late summer. This is generally accompanied by the maximum RHs experienced.

When the objects were examined, small white crystals were observed on the surface of most of them. These crystals were analysed with Raman micro-spectroscopy and found to be sodium hydrogen carbonate. This material was used as an abrasive for air abrasive cleaning in the 1970s and its use confirmed from the conservation records. Sodium hydrogen carbonate is reported irreversibly to convert to sodium carbonate on exposure to sufficiently high RH, dependant on the temperature. Unfortunately the published literature only gives a series of bands of RH for the transformation derived from exposures above saturated salt solutions.⁹⁻¹¹ A series of experiments were

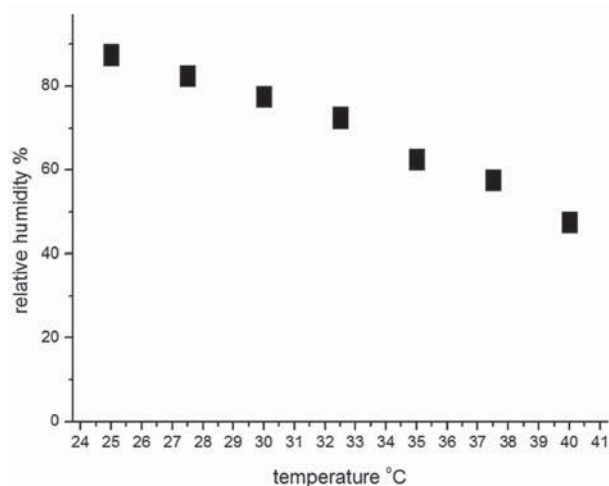


Figure 5: Critical RH and temperature ranges for conversion of sodium hydrogen carbonate to sodium carbonate. The boxes indicate the range for both RH determined by the glycerol solutions used and temperature determined by the ovens operation. Reference 11 gives a range of 27-75% RH for this process at 30 °C.

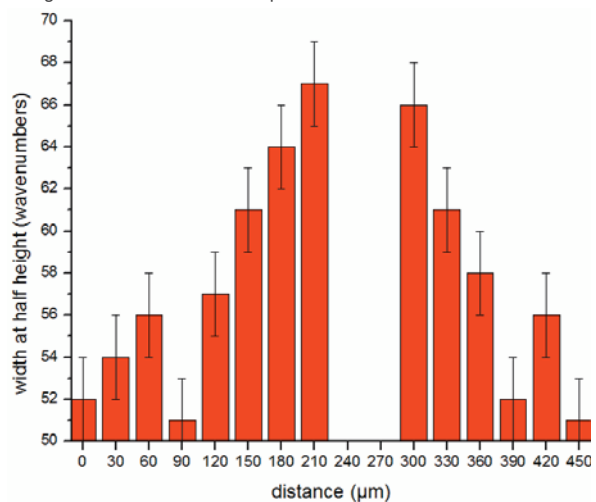


Figure 6: Carbonyl peak widths at half height for Mastic around a gravel derived particle, no signal is present at 260 µm as this is the particle.

undertaken exposing sodium hydrogen carbonate crystals to a series of RHs at 5% intervals and at different temperatures to elucidate the boundary conditions of the transformation and hence determine a maximum RH that the crystals could possibly have been exposed to. The crystals were analysed as previously described. Results are shown in Figure 5.

The boundary conditions form the maximum RH to which the crystals have been exposed. The maximum temperature was estimated at 30 °C, giving a maximum RH of 80%. This information was valuable in assessing the effect of RH on the deterioration. As sodium carbonate was not detected on the iron objects, the sodium hydrogen carbonate had probably not been exposed to RHs greater than 80%.

3.3 Damage from Dust

Direct damage from dust is an area that has not received a great deal of attention in the conservation literature. The contribution of dust to metal corrosion in historic houses has been assessed: exposing silver, copper, lead and steel coupons at 45°, the amount of corrosion on the top side and underside (much lower dust deposition <10%) was analysed with potential sweep voltametry.¹² Kenwood House in North London presents the Iveagh Bequest of paintings and furniture. The house is surrounded by a gravel path, as it was when it was occupied by the Iveaghs. Very large amounts of gravel are walked into the house by visitors and dust levels are well above those expected from the visitor numbers. Analysis of the dust deposited at 2m height with SEM-EDX confirmed about 75% of it originated from the gravel, which has quite a distinctive chemical signature. The dust contained silica, alumina, iron, calcium and strontium, FTIR microscopy confirmed a silicate. Many gravels have lime, CaO, added to them and SEM-EDX analysis confirmed large amounts of calcium in the deposited dust. The potential high alkalinity of the dust poses a risk to the varnish on the fine art collection. Steel strips coated with mastic were exposed at 2 m height. A method for analysing the strips with FTIR (Amplif-IR on Perkin Elmer 2000), using broadening of the carbonyl absorption, has been developed and correlated with more sensitive measurements such as mass spectrometry.¹³ This method would struggle with the very dusty strips exposed at Kenwood House. The dust has absorptions in the same region used for the analysis. The method was miniaturised using an FTIR microscope in direct reflectance mode, also known as transfectance. The infra-red beam passes through the mastic layer and is reflected from the steel, passing

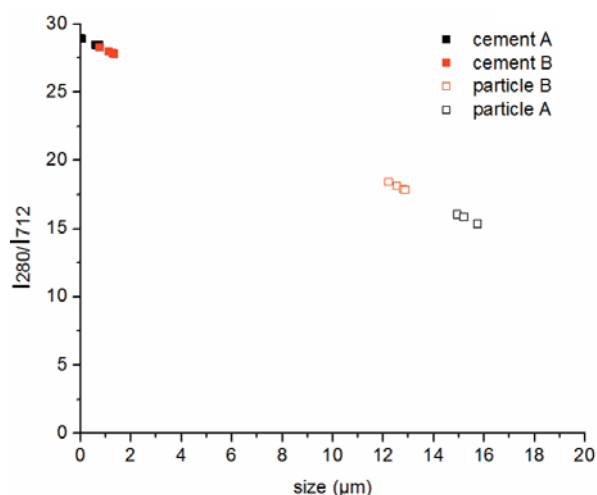


Figure 7: Calcite crystallite size determined from Raman micro-spectroscopy on two dust particles A and B and the associated cementing matter.

through the mastic a second time, before returning to the detector. Trials proved that high quality spectra could be produced from the mastic coated steel strips. Gravel derived dust particles collected from Kenwood house were placed on a mastic coated steel strip. The strips were exposed in acrylic boxes with one face open and covered with Tyvek to exclude dust less than 1µm in diameter. This arrangement allowed the samples to be exposed to the environment in Kenwood house without being contaminated with further dust.¹⁴ The environment has fluctuating temperatures, relative humidities, light levels and pollutant gas concentrations. After six months exposure, 30µm square analytical areas around dust particles on the exposed strips were analysed. Results from a typical series of analyses across the area around a gravel-derived dust particle are shown in Figure 6.

There is a dramatic effect around the gravel-derived dust particle, with very significant broadening of the mastic carbonyl absorption. At distances more than 120 µm away from the particles the width at half height falls to a value between 51 and 57. This value is greater than the unexposed mastic and is due to exposure to light and oxidising pollutants without any influence of the dust. The width at half height has increased to over 70 cm⁻¹, close to the particle, compared to a width of between 50 and 55 cm⁻¹ across the unaffected (but naturally aged, light oxidising pollutants and RH) mastic. This increase is approximately equivalent to the change expected from a light exposure to 3.8 Mlux h (data from light aging carried out in MIMIC project).¹⁵ This is equivalent to an extra 2.2 years of exposure under the lighting conditions in the rooms at Kenwood House that have paintings and equivalent to an increase in deterioration rate by a factor of just over four. Analysis of mastic coated steel strips exposed for four months in different locations in Kenwood House all showed a correlation of increased broadening of the mastic carbonyl bands adjacent to some dust particles.

3.4 Cementation of dust

A Leverhulme Trust funded project allowed The University of East Anglia, English Heritage, The National Trust and Historic Royal Palaces to investigate coarse dust cementation in historic houses. This effect had been commented on since the eighteenth century and increases cleaning resources (often a very major component of overall collection maintenance costs) and can cause additional damage when cemented material has to be removed from fragile materials such as degraded silk.^{16,17} The cementing material is extremely

small. Dust samples were collected from Dover Castle in South England as it experiences very high RHs. Dover houses significant Second World War collections. Confocal micro-Raman identified the cementing crystals as calcite, probably formed from dissolution and recrystallisation of the calcite dust particles. The literature suggests that the peak height ratio $280\text{ cm}^{-1}/712\text{ cm}^{-1}$ is proportional to the calcite grain size.¹⁸ The calibrations reported are for larger grain sizes than the cementing material. A calibration was performed with spray-dried and ground calcite of well characterized particle and grain size. Results from the calibrations and the analysis of cementing material and calcite dust particles are shown in Figure 7.

The cementing calcite has a very small crystallite size, whilst the calcite particles it originated from have much larger crystallite sizes. Analysis of soluble salt ions on the surface, indicated deposition rates of $134\text{ }\mu\text{g}/\text{m}^2/\text{day}$ of sulfate; $37\text{ }\mu\text{g}/\text{m}^2/\text{day}$ of chloride; $183\text{ }\mu\text{g}/\text{m}^2/\text{day}$ of sodium and $22\text{ }\mu\text{g}/\text{m}^2/\text{day}$ of magnesium ions. Calculations with the Pfizer model parametrised for this set of ions verified that the amount of calcium required for the cementing conditions would be soluble in the salt solution present.¹⁹ SEM-EDX analysis confirmed calcium, carbon and oxygen in the cementing material.

Microcrystalline calcite has been identified as the cementing material present.

4 Conclusions and Discussion

Analysis of deposits on glass and enamels has clarified whether they are signs of ongoing deterioration. Alternative sources are deposits from the atmosphere and previous use of the artefacts. The rapid identification of methanoate based salts allows identification of problems with display and storage materials and can direct appropriate interventions to improve the environment.

The lack of conversion of sodium carbonate residues from abrasive cleaning of archaeological iron objects has determined the upper limit of the RH that these objects could have been exposed to in the twenty years since that treatment was applied. This has helped to reconstruct the past environment of actively deteriorating objects.

The effect of gravel-derived airborne dust on oil paintings was assessed by exposing metal strips coated with mastic resin. Infra-red microscopy identified dramatically increased local deterioration of mastic varnishes.

The very fine cementing matter between dust particles and fibres has been identified as calcite, and the crystallite size determined, allowing thermodynamic calculations to verify the cementing mechanism and causes.

These examples show that FTIR and Raman micro-spectroscopy can be extremely powerful tools for understanding deterioration processes and gathering information required to understand and control those mechanisms. Their ability to characterize the compounds present is often instrumental in making informed conservation decisions.

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