Case study: Enclosed Gardens of Mechelen

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Introduction

The brass elements in Enclosed Gardens are mostly pristinely preserved, however a small selection are heavily corroded. The factors that induced the corrosion are still unknown, thus, identifying the reason for the exceptionally poor conservation state of these metal objects and of the glass beads considered is fundamental to correctly preserve the altarpieces and prevent potential future hazards. A thorough characterization of the original materials and their corrosion products is therefore crucial. However, the complex three-dimensional shape of the objects under examination and the small amounts and high heterogeneity of the degradation products pose a complex analytical challenge, creating the need for a versatile technique such as 0-PTIR.

O-PTIR exploits the photothermal effect of the sample induced by the irradiation with a tunable IR laser, which is then measured using a visible laser. The collected data is similar to transmission FTIR spectra, allowing for direct comparison with the literature. One of the main advantages of the technique is not needing any complex sample preparation, unlike traditional FTIR. Indeed, small objects can in fact be analyzed in a completely non-invasive and non-destructive manner.

Objectives

To decipher the factors that induced the degradation of the corroded glass beads and sequins found in the Enclosed gardens.

Materials and methods

O-PTIR measurements were collected on the mIRage Infrared Microscope (Photothermal Spectroscopy Corp.). Spectra were collected in reflection mode, 2 cm⁻¹ spectral data point spacing, through a 40x, 0.78 NA, 8 mm working distance Schwarzschild objective (spot size of approximately 450 nm). The pump IR source was a pulsed, tunable four-stage QCL device, scanning from 800 to 1900 cm⁻¹. The probe was a CW 532 nm visible variable power laser. The power of both lasers was optimized before the analysis to not cause damage to the sample. Specifically, the QCL laser power was set to 100% (less than 3 mW on the sample) while the probe laser power was set to 0.25% (\approx 80 µW on the sample). To obtain a good signal-to-noise ratio to interpret the spectral difference, five spectra were averaged at each point resulting in a total measuring time of approximately 1 minute per point. The data treatment was performed using the Quasar 1.0.0 software. Spectral maps were generated by normalizing the spectra by the min-max method (using the most intense band) and plotting the integrated area of selected peaks (with a linear baseline computed using two wavenumbers at the feet of the peak).

Raman spectroscopy measurements were performed by an Xplora Plus Microscope (Horiba) with a 100mW 785 nm laser (the effective power used was always ≤1% to avoid beam damage), considering

the effective range of 50–2000 cm⁻¹. At each point, five 10 second accumulations were collected. Additionally, a lower wavelength laser (540 nm) was tested but showed intense fluorescence bands and was therefore not further employed.

SR- μ FTIR measurements were performed at the SMIS beamline at Synchrotron Soleil (France) using a Thermo Fischer NEXUS FTIR spectrometer Nicolet 5700 attached to a microscope Continuum XL Small fragments of the corrosion products were extracted and squashed in a diamond compression cell. Measurements were done in transmission mode accumulating 256 scans at 4 cm⁻¹ spectral resolution with a spot size of 10x10 μ m², the wavenumber range is between 800 to 4000 cm⁻¹.

The XRPD analysis was carried out with a custom-built diffraction setup in reflection geometry at a fixed incident angle of 10 degrees between the X-ray source and sample. The X-ray source generates a beam of monochromatic Cu-Ka radiation (8.04 keV) with a photon flux of 2.9 x 108 photons s⁻¹ and a focal diameter of 0.15 mm. Multiple point measurements with an exposure time of 10 s pt⁻¹ were performed to account for the heterogeneous nature of the samples. A 2D single photon counting PILATUS 200K detector was used to register the emerging diffraction signals. The analysis of the data was performed with the in-house developed software package XRDUA while the structural information was obtained from the American Mineralogist Crystal Structure Database.

The microscopic observation of the samples was performed by optical and scanning electron microscopies. The optical microscopy (OM) observation was performed with a Nikon Eclipse LV100 microscope. The samples were also examined with a Field Emission Gun – Environmental Scanning Electron Microscope (FEG-ESEM) equipped with an Energy Dispersive X-Ray (EDX) detector (FEI Quanta 250, USA; at AXES and EMAT research groups, University of Antwerp), using an accelerating voltage of 20kV, a take-off angle of 30°, a working distance of 10 mm and a sample chamber pressure of 10⁻⁴ Pa. Imaging was performed based upon secondary electrons (SE), back-scattered electrons (BSE). Different EDX maps were collected, using a beam current of ≈0.5 nA, at different resolution, with pixel size values from 0.5 to 2.7 μ m and dwell time from 0.1 to 10 ms/pixel. From these EDX maps several EDX spectra were extracted for quantification. The dwell time of these spectra lies in the range of 1-7 s per spectrum.

Results and discussion

MA-XRF, µXRF and µCT were first employed to identify the areas of interest on the sequin, wires and beads. These exploratory analyses allowed to: 1) highlight the presence of elements, in the corrosion products on the surface of the metal objects (sequin and wires), traceable to the composition of the glass (i.e. K) and 2) identify elements, present in the corrosion products on the surface of the glass beads, likely ascribable to the brass composition (i.e. Cu and Zn).

These results support the hypothesis of a direct chemical interaction between the glass and the metal objects. In particular, the systematic presence of K, often mixed with Zn (Fig. 1 and Fig. 2), on the surface of the corroded brass elements, is likely a result of a glass-induced corrosion process of the metal.(1) Alkaline cations such as K⁺ (and Na⁺), can in fact leach out from the silica network during the degradation of glass and then reprecipitate, possibly in the form of mixed salts when in contact with a corroding metal(1–3). Zn and K mixed salts (possibly carboxylates), have been recently described by Fischer et al.(4) as products of a glass-induced metal corrosion on the surface of historical brass objects.

The hypothesis of K^{+} originating from the glass beads is clearly supported by the chemical composition of the glass, since both glass beads are made of a potash rich glass (Fig. 3), and by the poor conservation state of the beads.

In a similar fashion, the enrichment of Cu and Zn in the corrosion products on the surface of the weathered glass beads (Fig. 3), and in particular in areas where the contact with the metal would have been more probable (on the central shaft and inner rim, Fig. 4), also supports the hypothesis of an interaction between brass and glass.

Nonetheless, it needs to be mentioned that the presence of K⁺ in the corrosion products of a copper alloy is not sufficient, on its own, to confirm a chemical interaction with glass. This cation, in fact, often occurs in airborne particulate matter(5) and might therefore be present on the metal due to deposition and soiling.(6) Similarly, Cu and Zn might be also present in the bulk composition of the glass, in particular linked to coloring agents(4), and therefore might not be associated to a chemical interaction with brass.

Indeed, in figures 5-7, an overview of the results of O-PTIR and complementary analyses on three different samples (representative of the three categories of objects considered: metal sequin, metal wires, glass beads) are presented. In particular, Fig. 5 shows the analysis of a small area ($30x62 \mu m$) on the surface of the corroded sequin, while Fig. 6 and Fig. 7 contain the results of point analyses on the surface of a glass bead and a corroded wire respectively.

the molecular signature of glass is clearly identified in a particle on the surface of the metal sequin (Fig. 5B spectrum 1 and Fig. 5C) due to the very broad and intense (slightly saturated) band between 1250 and 980 cm⁻¹ (Si-O-Si and Si-O region(7)). A very similar spectrum is observed in a visually nondegraded area on the surface of a potash glass bead (Fig. 6A spectrum 1), which supports the hypothesis of a direct contact between the brass object and this type of glass. The chemical information obtained with O-PTIR goes beyond but clearly agrees with the complementary SEM-EDX elemental analysis (Fig. 5D and Fig. 5B), showing higher Si and K contents in the areas identified as glass. The additional bands in the 1650–1300 cm⁻¹ region hints to the presence of other species (e.g. spectra 2, 3 and 4 in Fig. 5B) overlapping and in close contact with the glass particle. It is noticeable that similar spectral features can be observed in this region on the surface of the glass beads (Fig. 6A spectrum 1), indicating that the related compounds might be associated to the degradation of glass. In particular, the spectrum agrees with the presence of carboxylate (formate and/or acetate) species (bands at ≈1600-1500 and ≈1500-1400 cm⁻¹ related to C-O asymmetric and symmetric stretching respectively) as well as with the presence of carbonates (bands at ≈1450-1350 cm⁻¹ related to C-O stretching). (8) These compounds have been previously linked to the degradation of glass (9). In addition, the bands at \approx 1625 and \approx 1320 cm⁻¹ may be linked to the presence of oxalates, which are usually found linked to different types of degradation processes on cultural heritage materials.(10) Interestingly, the spectral features of oxalates appear in all spectra in Figure 5, suggesting a presence of these corrosion products in all points analyzed. The results demonstrate that the mentioned compounds may coexist in the same region.

Spectrum 2 of Fig. 5B is one of the spectra most commonly encountered in the green-bluish areas of the sequin, glass beads and wires alike (Fig. 6A spectrum 2, Fig. 7A spectrum 2). This compound is more abundant in areas containing Cu and O and close to no Zn and K (Fig. 5C,D). The intense peaks in the 1650–1580 cm⁻¹ and 1400–1320 cm⁻¹ regions indicate the presence of a carboxylate and, in particular, of a Cu formate(11).

Basic copper formates are extremely rare as corrosion products on historical metal objects, unless the degradation is catalyzed by the contact with weathered glass(1). The alkaline liquid film formed during the degradation of glass, in fact, favors both the solubilization of the metal alloy and the conversion of formaldehyde (off-gassed during the ageing of wood and other organic materials(12)) to formic acid through the Cannizzaro reaction(4), ultimately leading to the precipitation of the basic form of the metal formate. In the context of this study, the diffuse presence of basic copper formate on all the samples in analysis (the spectral markers of this compound are visible in all spectra from figure 5, 6 and 7) decisively confirms the existence of a chemical interaction between weathered glass and brass. The strong connection between this formate corrosion product and glass is further supported by the close contact observed between these two materials in Fig. 5C, visualized thanks to the high spatial resolution allowed by the O-PTIR analysis.

Spectrum 3 in Fig. 5B is tentatively assigned to a carbonate species, in particular the band at \approx 1400 cm⁻¹ is likely related to the stretching and the one at \approx 842 cm⁻¹ to the bending of the CO₃²⁻ group(13). Given the overlap of the bands with the signal from other species, the identification of the precise type of carbonate cannot be done unambiguously only by OPTIR. Based on the SEM-EDX results (Fig. 5D), this could correspond to a type of potassium carbonate resulting from the degradation of the potash glass(14).

Spectrum 4 in Fig. 5B is characterized by an intense and broad absorption at around 1440 cm⁻¹. The explanation for the broad and complex nature of the band can be found in the overlapping of the signals from several species, such as the ones in spectrum 2 and spectrum 3 of Fig. 5B, with additional metal carbonates and/or a mixed metal carbonates.(13) The co-presence of different species is in agreement with the overlapping of Zn, K and Cu signals observed in these areas with SEM-EDX (Fig. 5D).

IR spectra with similar bands were observed in areas rich in Zn, K and Cu also on a glass bead (Fig. 6A spectrum 3) and on two corroded brass wires (Fig. 7A spectrum 1), although with slightly different features. In particular, a carbonate with a CO_3^{2-} asymmetric stretching vibration at 1422 cm⁻¹ and two bending vibrations at 876 and 845 cm⁻¹ was observed in a white corrosion product on the surface of the glass bead (Fig. 6A spectrum 3), while a carbonate with a CO_3^{2-} asymmetric stretching vibration shifted to 1480 cm⁻¹ and either one bending vibration at 878 cm⁻¹ or two bending vibrations at 880 and 842 cm⁻¹ was observed on two different brass wires (Fig. 7A spectrum 1).

In all cases, a more detailed interpretation of these complex mixtures of carbonates is further complicated by the overlap with the signals of Cu formate. Nonetheless, the existence of a spatial correlation between the carbonate signals identified by OPTIR and the Zn, K and, to a minor extent, Cu identified by SEM-EDX on the sequin, glass bead and corroded wires (Fig. 5, Fig. 6 and Fig. 7), suggests that mixed carbonates might be present in all the samples. Although further studies would be necessary to fully characterize the nature of these carbonates, the identification of generic mixed carbonates most likely containing K, Zn and possibly Cu on these samples is in itself remarkable. In order for these corrosion products to be formed, Zn²⁺, K⁺ (and Cu²⁺) and solubilized atmospheric CO₂ would have to be simultaneously present in an alkaline solution (similarly to what described by Eggert et al.(1). Such a condition would have been likely met, in the Enclosed Gardens, only in the case of a direct contact and interaction between weathered potash glass (such as the one of the glass-beads in analysis) and the brass alloy.

On the surface of the glass bead, an additional species was also observed in an area rich in Ca, K, Cu and S (Fig. 6 spectrum 4). The high S content together with the intense bands at 1120 cm⁻¹ (SO_4^{2-}

stretching) and 1630 cm⁻¹ (OH bending) suggests the presence of sulfates/hydrated sulfates (such as gypsum(15) or syngenite(16)), possibly mixed with a metal (probably Cu, Ca, K or a mixture of these metals) carboxylate (additional peaks at ~1600 cm⁻¹ related to the C-O asymmetric stretching of COO- and 1473 and 1448 cm⁻¹ related to the C-O symmetric stretching of COO⁻ and to C-H vibrations). Sulfates and hydrated sulfates are often encountered as degradation products on the surface of potash-lime glass due to the interaction with atmospheric agents(17), while the presence of metal carboxylates in the degradation products might further support the hypothesis of a glass-induced corrosion of brass (Cu often forms complex mixed carboxylates in these conditions(1)).

Conclusion

Clear markers of glass-induced metal corrosion processes were identified thanks to 0-PTIR on the surface of both metal and glass objects. In particular basic copper formate ($Cu_2(OH)_3(HCOO)$ and, possibly, a mixed Zn, K carbonate were found intimately mixed in the corrosion products.

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Tables, figures and graphics



Fig. 1. Elemental analysis of the corroded sequin (sample 1S): a) MA-XRF elemental maps; b), c) SEM-EDX elemental maps.



Fig. 2. µXRF analysis of the visually degraded areas of the corroded brass wires analyzed: a) SUM spectrum, in evidence the presence of K and Ca; b) elemental scatter plot for Zn and K (integrated K Lines; red = sample 1W, yellow= sample 2W, blue = sample 3W).



Fig. 3. μ XRF analysis of different areas of the glass beads: a) SUM spectrum; b), c), d) elemental scatter plots (red = sample 1B; blue = sample 2B). The points showing higher levels of Cu and Zn correspond to areas with green-blue corrosion products.



Fig. 4. µCT scan results: reconstructed volume and localization of highly attenuating corrosion products (red rectangles) on the inner rim and central shaft of the two glass beads a) sample 2B, b) sample 1B.



Fig. 5. High-resolution O-PTIR molecular imaging of degradation products on the surface of the degraded brass sequin (1S). A) OM photomicrograph of the area in analysis, in evidence the location of the representative spectra shown in B (numbered points) and of the imaged area (white rectangle); B) representative spectra of the imaged species and integration range (in grey); C) corresponding integration maps (30x62 µm with a pixel size of 2 µm) with tentative interpretation (integration range in cm⁻¹); D) complementary SEM-EDX elemental imaging of the scanned area.



Fig. 6. O-PTIR point analysis of degradation products on the surface of a glass bead (sample 1B). A) Locations analyzed (OM photomicrograph) and corresponding spectra; B) complementary SEM-EDX elemental imaging of the region of interest.



Fig. 7. O-PTIR point analysis of degradation products on the surface of a corroded brass wire (sample 2W). A) Locations analyzed (OM photomicrograph) and corresponding spectra; B) complementary SEM-EDX elemental imaging of the region of interest (white rectangle in Fig. A).