

A new method for coating heritage lead observed in real-time using synchrotron techniques

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Introduction

The use of synchrotron-based analytical techniques is becoming more frequent in the field of heritage science, as a means of characterizing cultural heritage artefacts, and in the development of more effective methods for treating and preserving these artefacts. Here, we used synchrotron XRD as a real-time monitor of the growth of protective lead coatings, and to determine the outcome of a new growth process.

Previously, aqueous solutions of sodium carboxylate – $\text{CH}_3(\text{CH}_2)_n\text{COONa}$, hereafter referred to as NaC_n – have been used to grow carboxylate layers on lead [1, 2], but the solubility of high molecular weight NaC_n ($n > 10$) in water is very low. Therefore, our recent work has been focused on depositing the coating by reaction with an ethanolic solution of the corresponding carboxylic acid HC_n . Ethanol is a more effective solvent for the higher molecular weight acids (up to HC_{20}) and the resulting coating has a greater water resistance, whilst still being easy to remove – an important criterion for any protective coating used on heritage artefacts. The coating is also aesthetically justified; only a slight darkening of the lead is observed, provided the coating is thin. But what actually grows?

Experimental details

X-ray diffraction experiments were performed at beamline BM28 (XMaS) at the European Synchrotron Radiation Facility, Grenoble, France.

The sample was a 12.5 mm diameter lead coupon mounted on a moveable electrode in an electrochemical cell [3] which was filled with a 0.05 M solution of tetradecanoic acid (HC_{14}) in ethanol. The cell was mounted at 10° to the incoming beam. A laptop controlled the movement of the electrode and triggered the X-ray shutter when the sample was raised.

The electrode remained in its lowest position (a few centimetres from the window) for the majority of the experiment. Since the X-ray penetration depth in liquids is very short, the sample was periodically raised close to the window (within approx. $100 \mu\text{m}$) to allow diffraction spectra to be recorded. This ensured that the deposition of the coating was not hindered by the proximity of the sample to the window. The cell window itself was constructed from $7 \mu\text{m}$ thick Kapton® film to allow the X-ray beam to reach the sample (see Figure 2).

The diffraction measurements were carried out in reflection mode with a beam energy of 8 keV. The images were captured using a MarCCD 165 X-ray detector (Mar USA, Inc. – now Rayonix, LLC). The camera was mounted at an angle of 40° to the beam at a distance of 130 mm from the sample; signals from 2θ angles between 8° and 72° were acquired.

The growth was carried out overnight and diffraction spectra were recorded every two minutes throughout the experiment. The cell was emptied approximately one hour before the end of the experiment and the sample drying was observed.



Fig. 3: The (thicker) coatings are clearly visible on the sample surface after it has dried. The incomplete coverage of the coating is likely due to the sample touching the window slightly when it was raised into the diffraction position.

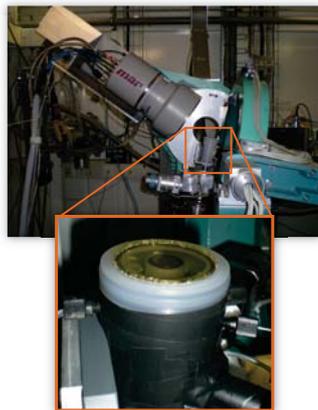


Fig. 2: As a result of the configuration used, the centre of diffraction is outside the field of view of the camera. Consequently, the diffraction cones intercept the camera plane at an angle producing elliptical arcs, rather than complete rings.

Fig. 1: Corrosion of the lead pipes in historic organs is caused by volatile organic compounds (VOCs), such as acetic acid, emitted by the woods used in their construction. Thousands of organs across the EU, including the Stellwagen organ in Lübeck, Germany, are at risk.



Processing using esaProject

The images captured by the MarCCD camera have been processed using esaProject (© EVA Surface Analysis) [4], a software package that has been developed to extract spectra from a variety of data file formats and perform subsequent analysis. The batch processing capabilities of the software allow all the images in a sequence to be normalized, re-projected and have the spectra extracted in single operation.

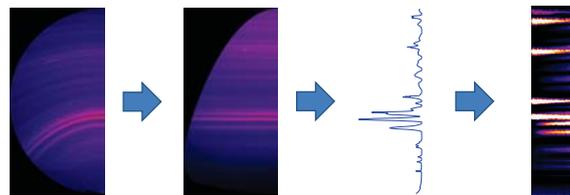


Fig. 4: (a) the unmodified image from the MarCCD camera; (b) the re-projected image; (c) the spectrum extracted from the re-projected image; (d) a series of spectra can be formed into a spectrum sequence.

Results

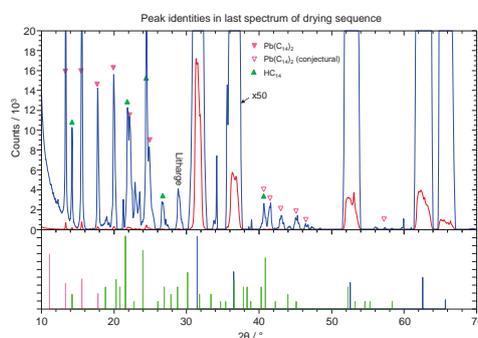
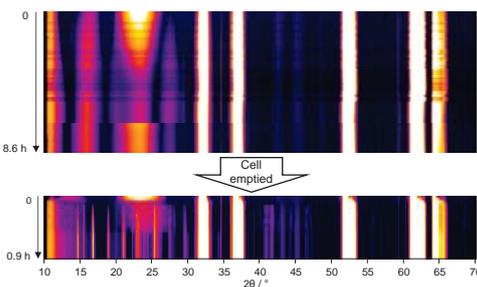


Fig. 5 (above): The peaks seen in the low-order region match those in the ICDD reference spectrum for lead tetradecanoate, confirming the presence of the carboxylate. However, it appears that the reference is incomplete as there are several other peaks that, based on previous measurements, are believed to be attributable to the carboxylate.

Fig. 6 (right): The time sequence of spectra obtained over the course of the experiment clearly illustrates the development of the carboxylate layer, and makes the differences in the layer structure before and after the cell was emptied immediately apparent.

During immersion, the low-order scattering region was dominated by a diffuse but structured background which is likely due to the formation of a gel on the surface of the sample. It is not until the cell is emptied that we see the formation of the lead tetradecanoate (plus a small amount of tetradecanoic acid), as illustrated in Figure 6.

This is in contrast with the growth of lead decanoate on a lead coupon immersed in an aqueous solution of sodium decanoate; in this case, the formation of the carboxylate layer is visible while the sample is still submerged.



Conclusions

The growth of a carboxylate coating on lead has been observed in real-time using synchrotron-based X-ray diffraction. Although, spectra were recorded during the entire deposition process (approx. 10 hours), it was not until the cell was emptied and the sample dried that the diffraction peaks corresponding to the coating were observed.

The fact that the lead tetradecanoate layer does not form until the surface dries in air suggests that it may be possible to apply the coating by 'painting' the solution onto the surface. This could be significant as the ease of application is another important criterion against which a protection system is assessed.

These details could not have been determined by examining the end product alone; an in-situ, time-resolved study was required in order to monitor the sample as the layer was growing. This allowed all stages of the layer formation to be observed, including the intermediate formation of the gel layer which would not have otherwise been seen.

In future work, we will be using real-time and off-line exposure to oak VOCs on XMaS to assess the protection afforded by the coating.

References

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