Case Study 9: Lost polychromy and gilding of Neo-Assyrian ivories

Summary

Antique objects are known to have been brightly coloured. However, the appearance of these objects has changed over time and paint traces are rarely preserved. But today, only specific alteration phenomena like cracks and discolorations can be observed on the ivory surfaces. Where has the colour gone? Can it be reconstructed from the remaining traces on the objects, and what might we learn about them?

Elephant-ivory carvings by highly skilled Phoenician craftsmen, from the Neo-Assyrian archaeological site of Arslan Tash in Syria and dated to the 8th century BC, were excavated in 1928 and are now in the collections of the Louvre Museum and the Badisches Landesmuseum.

Figures 1 & 2, showing two similar and beautifully formed bed decorations, directly compare ion beam analysis (IBA) with synchrotron X-ray fluorescence (sy-XRF) techniques. Figure 1 (IBA: Albéric et al, Talanta 2015 [1]) shows imaging with a detailed reconstruction of the lost polychromy, where Figure 2 (sy-XRF: Reiche et al, Analytical Chemistry 2013 [2]) shows only qualitative and partially ambiguous imaging.
Although care must be taken to avoid beam damage in both IBA and sy-XRF analyses, implying limits to the fluence used: for both instruments the data collection is sufficiently efficient for powerful analysis. The synchrotron X-ray beam is fixed in space, and usually the sample is mechanically scanned (rather slowly!) for imaging applications, but for this work (Figure 2) a CCD X-ray camera together with capillary X-ray optics were used to form images without mechanical scanning. For IBA of course, imaging with scanning ion microscopy is as easy as it is for scanning electron microscopy.

Figure 2:
Imaging the lost gilding on a Birth of Horus ivory by sy-XRF
Decorative carved elephant-ivory, excavated 1928 from the neo-Assyrian site of Arslan Tash
Left: Optical images with selected area on wing and (below) possible reconstructions of the lost gilding; Right: sy-XRF false-colour maps of selected area
From the Badisches Landesmuseum (Karlsruhe) collection: Al_EI_KB, inventory number 72/39
From Figures 1c, 8 and 9 of Reiche et al, Analytical Chemistry 2013.

For both XRF and IBA, qualitative 2D chemical images of elements ranging from Na to Pb on the surface of the ancient ivory carvings provide evidence of lost polychromy and gilding. But quantitative particle-induced X-ray emission (PIXE) data of specific areas allow discrimination between traces of sediments and former polychromy. Different shades of blue can be differentiated from particular Pb/Cu ratios. The characterization of gilding based on Rutherford backscattering (RBS) data demonstrates the exceptional technological skills of the Phoenician craftsmen who carved the Arslan Tash ivories, allowing more precise reconstructions of the original polychromy than in the previous XRF work.
Figure 3 shows the IBA instrumentation used at the Louvre Museum to analyse treasures in air from their collection (Pichon et al, NIMB 2015 [3]). PIXE, RBS, EBS, NRA and IBIL are excited simultaneously by the focussed and scanned proton (or alpha-particle) beam which exits the vacuum system through an ultra-thin Si$_3$N$_4$ window. The X-ray spectra collected at the synchrotron are entirely comparable to PIXE spectra. But in IBA the particle backscattering spectra are also available (see Figures 4 & 5), and these enable full quantitation of layered samples where the sample structure is not known: this XRF cannot do.

Figure 4 shows how the RBS signal from the gold surface layer determines the thickness of the gilding layer unambiguously, indicating that they were applied with a beating technique; not only that, but the (non-Rutherford) EBS signals of C and O are plainly visible and quantifiable although where these elements come from is currently unknown.

XRF is almost entirely blind to light elements: it is possible to accurately obtain the average atomic number of the sample using the ratio of elastic to inelastic (Rayleigh & Compton) scattering, see Campbell et al, 2016 [4] and Hodoroaba & Rackwitz, 2014 [5]; but this does not work for multilayered samples of unknown structure, and in any case can only determine one unknown element. Figure 5 shows an EBS spectrum from a gilding-free region in another ivory of the same collection which shows how the ivory is modified near the surface, presumably as a result of nearly three millennia in the ground. This sort of depth-resolved analysis allows better discrimination between regions that look similar with XRF or PIXE imaging (that is, without light element sensitivity or depth resolution).
There are two features of Figure 4 that invite comment. The signal for He comes from the helium atmosphere surrounding the sample, used to minimise both absorption of low energy X-rays and the energy loss of the backscattered particles. It also promotes efficient cooling of the sample, important to help avoid the beam damaging these treasures.

There is also a large misfit between the calculated and measured data near 2.5 MeV. This is a well-known effect due to the surface roughness of the sample, that the code used cannot simulate. However, these sorts of rough samples can now be simulated accurately, as Paneta et al (2014) [6] have shown in their Figure 3, using the algorithm of Molodtsov & Gurbich [7]. Probably, if roughness were correctly modelled (for Figure 4) the low energy part of the spectrum would also be correctly modelled. Correct modelling is essential to reliable quantification.

The work described above uses both atomic (PIXE) and nuclear (RBS & EBS) techniques simultaneously, but does not interpret them synergistically. In many cases the information obtained with the atomic and nuclear techniques is independent, but in many other cases it is not. Figures 6 & 7 show an example where the PIXE data cannot be interpreted without the BS data, and neither can the BS data be interpreted without the PIXE. The first recorded photograph, by Joseph Niépce in 1827, is shown in Figure 6.
In Figure 7 the PIXE data are shown, not as an energy spectrum, but as a histogram of the characteristic line areas (number of photons) together with the fitted line areas. The corrosion involves oxidation of the tin content to a depth of about $10^{20}$ atoms/cm$^2$ (~10 $\mu$m). In principle, the PIXE cannot be quantified without knowing the depth profile, but the EBS does not distinguish between Pb and Sn. But given that the boundary condition on the Pb/Sn surface ratio is fixed by RBS, these data jointly determine the depth profile. It is now possible to handle atomic and nuclear data synergistically: Pascual-Izarra et al, NIMB 2007 [8] is the first example of this so-called “Total-IBA” [9] analysis, with the data collected at the Louvre Museum.

Uses of PIXE and Total-IBA methods (together with many complementary techniques) have included: the search for hard-solders and platinum-group-element inclusions in ancient Egyptian gold jewellery [10]; the determination of various technological features (including composition, and degradation processes) in medieval ceramics from the Alcazar Palace [11] in Seville; the provenancing of obsidians from Neolithic Çatalhöyük (central Anatolia) [12]; the characterisation of...
prehistoric pigments from Abri Pataud (in the Dordogne) [13]; and the investigation of pigments and varnishes in paintings (see also de Viguerie et al, *Analytical Chemistry* 2009 [14], and Beck et al, *NIMB* 2008) [15].

**Keywords**

Complementary Techniques

IBA: ion beam analysis (including PIXE, RBS, EBS, and “Total-IBA”)
PIXE: particle-induced X-ray emission
RBS: Rutherford backscattering
EBS: elastic (non-Rutherford) backscattering
Total-IBA: synergistic use of multiple IBA techniques
XRF: X-ray fluorescence (in this case sy-XRF, or synchrotron XRF)

**Cited Literature**


