THE BRITISH MUSEUM

Technical Research Bulletin

VOLUME 3 2009

Assyrian colours: pigments on a neo-Assyrian relief of a parade horse

Giovanni Verri, Paul Collins, Janet Ambers, Tracey Sweek and St John Simpson

Summary The colours present on a fragment of a neo-Assyrian carved stone relief (British Museum 1847,0702.27: ME 118831) depicting a parade horse, which retains extensive evidence of original polychromy, were investigated using visible-induced luminescence imaging and Raman spectroscopy. The horse harness was found to have been extensively painted with elaborate patterns including alternating bands of Egyptian blue and red ochre, two pigments commonly encountered in contemporary contexts. Although the blue pigment is still visible in some areas of the relief, its overall distribution across the object is obscured by surface dirt and/or the degradation products from the original materials. However, even in discoloured areas, the spatial distribution of the pigment was revealed by illuminating the object with visible light and by recording the luminescence of Egyptian blue in the infrared range (*c*.800–1000 nm). This non-invasive technique allowed the spatial distribution of Egyptian blue to be mapped thoroughly and rapidly.

The survival of some of the original polychromy on the relief poses constraints on its cleaning and raises questions about the survival of these and other pigments on Assyrian (and other) sculptures. However, the comparison of the distribution of pigments on this relief with that on contemporary Assyrian wall paintings from Til Barsib is highly instructive, as it confirms for the first time that similar colour schemes were used on reliefs and wall paintings.

INTRODUCTION

Although many ancient civilizations are known to have made extensive use of polychromy on sculpture and carved stone, much of this colour has since been lost. This is particularly evident when direct comparisons can be made between wall paintings and ceramics, which often remain brightly decorated, and sculpture from the same period, which is frequently denuded of virtually all colour [1]. For example, although classical sculpture has been prized for centuries for its pure whiteness, it has been recognized that ancient Greek and Roman stone artefacts were often originally brightly coloured [1, 2]. Similarly, pigments such as Egyptian blue, malachite and vermilion have been identified on external limestone reliefs and tomb façades at the Achaemenid sites of Persepolis and Naqsh-e Rustam [3, 4]. There are a number of possible reasons for the loss of the original polychromy. The paints used in antiquity would generally have comprised two components: a coloured pigment and an organic binder. The pigment would have either been based on an organic material derived from a plant or animal extract or an inorganic pigment that comprised a naturally occurring mineral or a simple compound produced synthetically. The organic binders available included gums, egg, milk or glues derived from animal sources. Metal adornments, such as gilding and silvering, were also commonly used on ancient sculpture; often the only surviving traces of these are the means by which they were attached [1]. Although organic materials, particularly the binders, but also the organic colorants, are highly susceptible to decay, paint often survives surprisingly well in stable burial conditions. As described here, drawings and watercolour illustrations of objects made at the time of excavation clearly show newly excavated carved stone pieces with obvious traces of polychromy that are no longer visible on the same objects. Much of the difference between colour survival on carved stone and that on wall painting and ceramics may be explained by a combination of the highly destructive effects of an unstable environment on freshly excavated materials and the conditions prevailing during their subsequent display and storage. However, the main culprits, for classical sculptures at least, seem to be the over-zealous cleaning procedures that have been undertaken for centuries, often for aesthetic reasons. These aggressive cleaning practices can be traced back at least as far as the rediscovery of ancient Roman sculpture during the Renaissance. Although scattered traces of polychromy must have been present on newly excavated ancient sculptures, their general white appearance determined the beginning of a new fashion that highly valued the colour of bare stone. Later, the paradigmatic white of neo-classicism influenced cleaning regimes and these were even extended to objects from other ancient cultures. Another factor that may have contributed to pigment loss was overenthusiastic moulding for the purposes of creating casts, whether for academic, display or purely commercial reasons.

Scientific examination of ancient artefacts may reveal the presence of original materials and may shed light on painting practices in antiquity. In particular, imaging techniques are useful to characterize the spatial distribution of the remaining traces of painting materials within a painted scheme [1]. Such imaging techniques, the selection of which depends on the physical and chemical properties of the compounds under investigation, generally include visible, infrared (IR), ultraviolet and photo-induced luminescence. A particular photo-induced luminescence imaging technique, visible-induced luminescence (VIL), plays a key role in the characterization of one very common ancient pigment – Egyptian blue. This contribution discusses the analysis of a neo-Assyrian relief using VIL imaging and Raman spectroscopy.

THE RELIEF

The sculpted gypsum head of a caparisoned horse (British Museum 1847,0702.27: ME 118831) comes from the palace of the neo-Assyrian king Sargon II (reigned 721–705 BC) at Khorsabad, ancient Dur Sharrukin, in northern Iraq. Sargon founded Khorsabad in 717 BC but construction at the site was halted in 705 BC when the king was killed in battle and his successor Sennacherib (704–681 BC) moved the capital to Nineveh. In the tradition of some earlier Assyrian royal builders, Sargon had the lower walls of the principal rooms and courtyards in his palace decorated with carved slabs of gypsum. The sculpture considered here was originally part of a narrative frieze, a hunting scene, which adorned a small room in the north west wing of the palace, perhaps the private quarters of the king. The slabs of gypsum are divided into three horizontal registers. The top register depicts a banquet and was divided from the hunting scene in the lower register by a wide band of inscription. French excavations of 1842–1844 had uncovered the room (numbered as VII), and the surviving reliefs were recorded in excellent drawings by Eugène Flandin, Figure 1 [5; Plate 109]. In 1845, Alexander Hector, a merchant who had settled in Baghdad, visited Khorsabad and removed some reliefs and carved inscriptions from various areas of the palace. The British Museum purchased 50 of these fragments, including this head of a horse, from Hector in 1847; they entered the collections only a few weeks after the arrival of the first Assyrian reliefs from Henry Layard's excavations at Nimrud and were displayed from 1852 to 1964 on the east side of the Assyrian Transept. While in this location, they were described in the 1884 *Guide to the Exhibition Galleries* as "chiefly fragmentary figures from a more extensive series, some on a large scale, and retaining remains of colour. The horses' heads, facing the window, are richly and carefully finished" [6]. Between 1928 and 1935 the Oriental Institute of the University of Chicago undertook extensive excavations at Khorsabad, in the process of which room VII was re-examined and the surviving panels removed to Chicago [7].

Although surviving colours are sparse and our present understanding of painting schemes on Assyrian reliefs is limited, it is generally agreed that many Assyrian reliefs were originally painted, either over their entire surface or, perhaps more often, in specific areas [3]. Indeed, remains of some colour are known to have been visible on the panels from room VII when they were first excavated; Flandin records the presence of red, black and blue, the last colour used on birds and fir trees. He makes no reference to paint on the horse discussed here, although colours must have been apparent, as traces of red and blue are still visible to the naked eye.

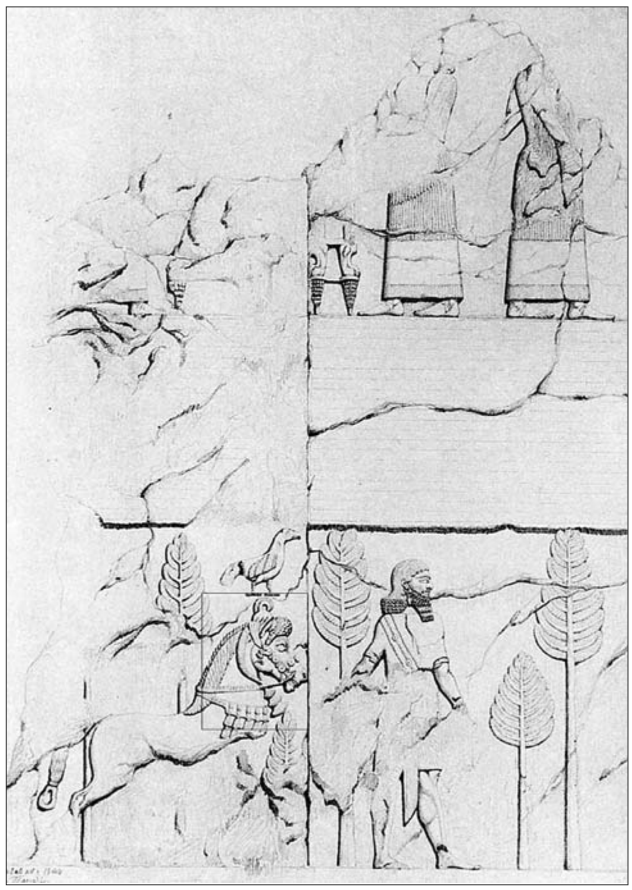

FIGURE 1. Drawing by Eugène Flandin of a relief representing a hunting scene from the palace of the neo-Assyrian king Sargon II (721–705 BC) at Khorsabad. Drawn during a French excavation in 1842–1844 before the reliefs were fragmented. The box outlines the original position of the head of the caparisoned horse now in the British Museum

METHODOLOGY

VIL imaging of Egyptian blue

Much of the work described here was only possible because of a relatively new imaging technique for the study of Egyptian blue, which has been developed at the British Museum and the Courtauld Institute of Art, London [8–10]. Since it is of such importance to the interpretation of this object, and of great potential use in similar studies, the technique is briefly described here; full details of the experimental procedure are included in the experimental appendix.

Egyptian blue – one of the earliest synthetic pigments – is a calcium copper tetrasilicate ($CaCuSi_4O_{10}$) that has the same composition and structure as the rare natural mineral cuprorivaite. This bright blue inorganic compound was extensively used throughout the Mediterranean from the Fourth Dynasty in Egypt (*c.*2500 BC) until the end of the Roman period in Europe [11]. When excited by radiation in the blue, green or red region of the electromagnetic spectrum, Egyptian blue shows an intense and broad emission (full width at half peak height of *c.*120 nm) in the IR region, centred at about 910 nm [12, 13]. The emission from Egyptian blue can be recorded by using visible excitation sources and a camera with some sensitivity to IR radiation in the *c.*800–1000 nm range of the electromagnetic spectrum. Commercially available fluorescent lamps, which were used as light sources in this study, emit mainly visible radiation with only a small component of IR radiation. In the monochrome VIL images, Egyptian blue appears as 'bright white', while all other materials appear grey. Grey levels higher than those for a 99% reflectance standard, which is placed alongside the object under investigation and included in the image, can only be due to luminescence from the Egyptian blue. Grey levels less than the reference standard are considered to result from reflected 'stray' IR radiation. The presence of a low level of stray IR radiation from the fluorescent lamps is, in this instance, considered beneficial, as it allows the location of the fluorescing materials to be correlated with the scheme of the work of art. Light-emitting diodes (LED), which emit no stray IR radiation, were also used in this study [10].

In summary, this technique allows an image to be produced in which every region containing Egyptian blue, even down to single crystals in some instances, is clearly visible as a 'bright white' area simply by illuminating an object with fluorescent lamps in an otherwise darkened room and using an adapted digital camera. It should be mentioned that, although other pigments, such as cadmium red and yellow, show luminescence properties in the same spectral range, the experimental configuration used in this study is only sensitive to Egyptian blue and the chemically related Chinese pigments Han blue and Han purple.

Technical examination of the relief

The relief was first examined closely with the aid of low magnification. It was then imaged in visible-reflected and VIL modes. Based on the data from the visual examination and the VIL images, small samples (of one or two grains) of each pigment present were then taken and analysed using Raman spectroscopy as detailed in the experimental appendix.

RESULTS AND DISCUSSION

Figure 2a shows the current appearance of the relief. Despite the presence of surface dirt, traces of blue and red pigments can be observed in several locations, such as the tassel strapped on the horse's neck and the elaborate feathered decoration on the headstall of the animal. A brown coloration is also present over much of the object. This brown material seems to be composed of a homogeneous patina and dirt that has accumulated on the surface. There is also a small splash of bright red paint on the mane, which has a different hue to the red on the tassels and proved to be of modern origin (see below).

Attempts to determine the original distribution of the red and blue pigments were complicated by the dirt, the brown coating and the discontinuous distribution of the surviving pigments. In Figure 3a, a detail from the relief, the present distribution of the red and blue particles can be seen. Figures 2b and 3b, the VIL images of the relief and corresponding detail, give far better impressions of the distribution of the blue pigment. In these images the bright white areas correspond to the presence of Egyptian blue. Since even single particles of the blue pigment can be revealed using this method, it is possible to define its distribution within the scheme of the composition very clearly. Unfortunately, no analogous method currently exists for mapping the red pigment, so its distribution must be extrapolated from visual examination.

Raman analysis confirmed the blue pigment to be Egyptian blue, and showed the red to be mostly haematite (Fe_2O_3), probably representing the use of natural red ochre. Both pigments were in common use throughout the ancient world at this period and have been recorded from other Assyrian and later Achaemenid contexts [3, 4]. The bright red paint splash on the mane was found to be lead chromate, confirming it to be modern contamination, almost certainly from nineteenth- or twentieth-century cataloguing of the object; the same paint was used to add the accession number at the top right of the relief. The Raman analysis of the brown material did not provide conclusive results, but Fourier transform infrared spectroscopy suggests the presence of copper oxalate. Although this may represent the degraded remains of an original organic binder, it could also result from relatively recent surface treatment or exposure to the elements.

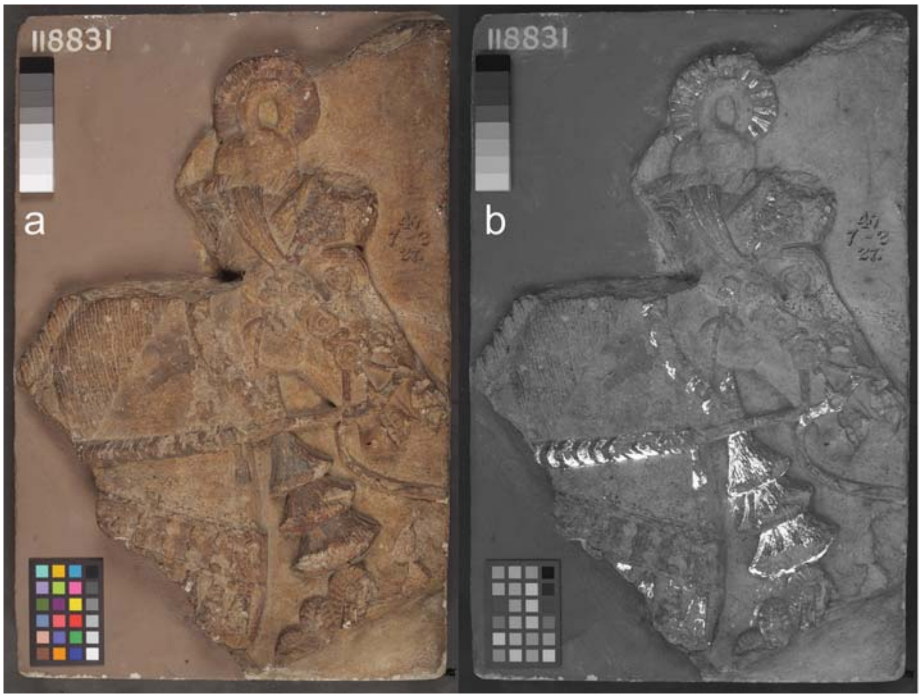

FIGURE 2. Head of the caparisoned horse (British Museum 1847,0702.27: ME 118831): (a) visible image, in which remnants of blue and red pigments can be observed; (b) VIL image showing the particles of Egyptian blue as 'bright white' areas

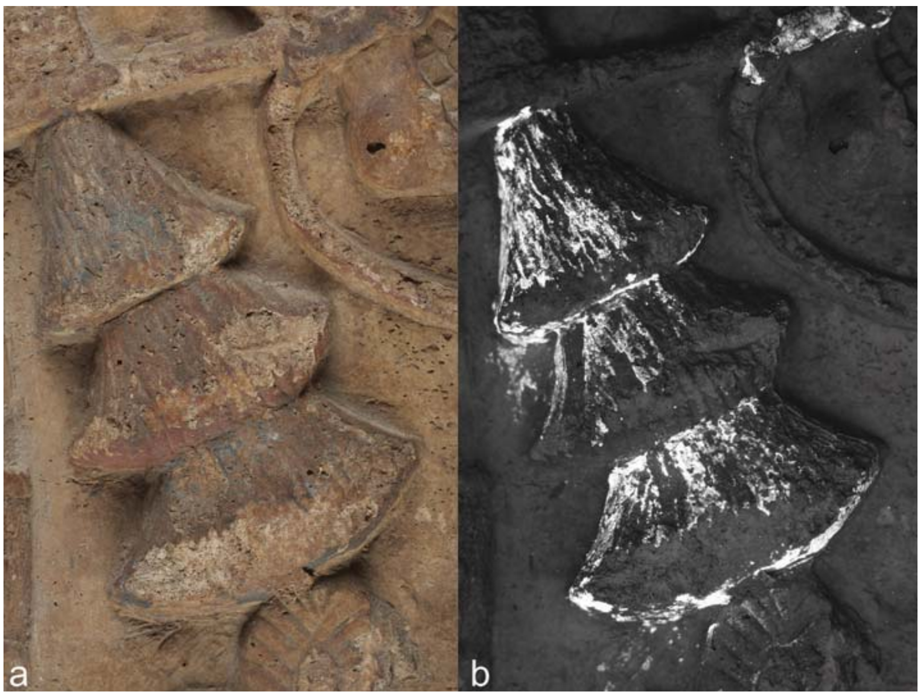

FIGURE 3. Detail of the horse shown in Figure 2, showing the surviving polychromy on the tassel: (a) visible images; (b) VIL image of the same detail, showing the 'bright white' areas that correspond to the presence of Egyptian blue and confirm its original use in alternating red and blue stripes. Note the single brush strokes and spattered paint containing particles of Egyptian blue

The alternating red and blue pattern of colour decorating the horse's head, the tassel and the trappings finds its closest parallel in a wall painting from an Assyrian royal residence at Til Barsip (modern Tell ʿAhmar). Located on the west bank of the River Euphrates in modern Syria, Til Barsip was excavated by French archaeologists between 1929 and 1931 [14]. Wall paintings, mostly polychrome on white lime plaster, were discovered *in situ* in one area of the building identified as the royal apartments. Some fragments of the paintings are housed in the Musée du Louvre and Aleppo Museum, but they are known principally from careful colour scale copies made soon after their discovery by the architect Lucien Cavro, many of which have been published by Parrot [15]. The relevant painting was uncovered in room XXIV; it is a large composition, some 22 metres long by 1.5 metres high, painted at eye level, above a band of bitumen that lined the base of the wall. The French excavators dated it to the time of Tiglath-pileser III (reigned 744–727 BC), although a recent study of the textile patterns in the scene by Albenda has led her to date the painting convincingly to the reign of Sargon II [16; pp. 69–74]. The painting depicts an enthroned Assyrian king, approached by tribute bearers or prisoners of war. Behind the king stand officials, a chariot and two spare horses. The leading horse is coloured blue (Figure 4) [15], while its trappings and the tassel, like those of the Khorsabad horse, are decorated in a pattern of alternating red and blue stripes. These stripes on the tassel of the Khorsabad horse can be better observed in the VIL image of the detail, Figure 3b. In this case, the red stripes appear dark, while the blue stripes appear bright white. The top and bottom sections of the tassel were painted applying strokes of haematite over Egyptian blue, while the middle section was painted using Egyptian blue over haematite. The blue strokes can be clearly observed in the middle section.

This combination of colours is familiar in elite jewellery from ancient Mesopotamia: red cornelian and blue lapis lazuli were among the most popular ornamental stones used for beads, most famously in the 'Royal Graves' at Ur (*c.*2500 BC) and the same colour symbolism extends back into deeper antiquity, judging from personal ornaments excavated in sixth-millennium BC graves at Tell es-Sawwan [17, 18]. In Mesopotamia these rare imported stones were synonymous with splendour and were attributes of gods and heroes; they were believed to possess healing properties and were placed in the foundations of buildings for ceremonial or magical reasons. In addition, monumental architecture could be decorated with the same colours, perhaps to provide magical protection; at Nineveh, for example, the battlements were striped red, blue and white (unpainted) [19].

FIGURE 4. Wall painting from an Assyrian royal residence at Til Barsip (modern Tell 'Ahmar). The colour patterns are very similar to those found on the relief depicting a horse's head. Image by Lucien Cavro [15]

CONCLUSIONS AND FURTHER INVESTIGATIONS

The combined use of VIL imaging and Raman spectroscopy allowed the identity and distribution of the original colours on a neo-Assyrian relief to be determined. Egyptian blue and haematite were identified on a sculpted gypsum head of a caparisoned horse excavated from the palace of the neo-Assyrian king Sargon II (reigned 721–705 BC) at Khorsabad, ancient Dur Sharrukin, in northern Iraq. The painted scheme on the relief was found to be nearly identical to contemporary wall paintings from an Assyrian royal residence at Til Barsip (modern Tell 'Ahmar), Syria and allowed comparisons to be made with contemporary textiles, jewellery and monumental architecture.

The same methodology will be applied to other reliefs in the British Museum in order to extend the understanding of Assyrian and Achaemenid polychromy and to assess the potential effects that moulding and casting the reliefs in the nineteenth century may have had.

EXPERIMENTAL APPENDIX

VIL imaging

The individual components in the equipment used are as follows. For excitation, two identical fluorescent radiation sources (Philips TLD 58W/35) are placed symmetrically at approximately 45° to the focal axis of the camera. The luminescence emission from Egyptian blue is captured using a Canon 40D camera from which the IR-blocking filter has been removed; the camera is operated in fully manual mode. The sensitivity range is selected by placing a Schott RG830 filter in front of the lens. A reference grey scale, comprising a set of Lambertian black, grey and white tiles, is placed in the same plane as the object under investigation. These Spectralon® references have uniform reflectance properties across the ultraviolet, visible and infrared spectral ranges under investigation; crucially for this study, they show no luminescence properties. A visible (*c*.400–700 nm) image of the objects was also always made for comparison. All images were acquired as 'raw' images and transformed into 4256 × 2848 pixel resolution images in 16-bit TIF (tagged image file) format [10].

Raman spectroscopy

Raman spectroscopy was carried out using a Jobin Yvon LabRam Infinity spectrometer using green (532 nm) and near IR (785 nm) lasers with maximum powers of 2.4 and 4 mW at the sample respectively, a liquid nitrogen cooled CCD detector and an Olympus microscope system. Samples of a few grains were collected using a clean scalpel, placed onto a microscope slide and measured without any further treatment. The resultant spectra were identified by comparison with a British Museum in-house database.

ACKNOWLEDGEMENTS

One of the authors (GV) is a postdoctoral science fellow in the Department of Conservation and Scientific Research at the British Museum supported by a grant from The Andrew W. Mellon Foundation.

AUTHORS

Giovanni Verri (gverri@thebritishmuseum.ac.uk) and Janet Ambers (jambers@thebritishmuseum.ac.uk) are scientists and Tracey Sweek (tsweek@thebritishmuseum.ac.uk) a conservator, all in the Department of Conservation and Scientific Research. Paul Collins (pcollins@thebritishmuseum.ac.uk) and St John Simpson (ssimpson@thebritishmuseum.ac.uk) are curators in the Department of the Middle East at the British Museum.

REFERENCES

1. Brinkmann, V., 'Research in the polychromy of ancient sculpture', in *Gods in color: painted sculpture of classical antiquity*, ed. V. Brinkmann and R. Wünsche, Stiftung Archäologie and Staatliche Antikensammlungen und Glyptothek, Munich (2007) 21–28.
2. Wallert, A., 'Unusual pigments on a Greek marble basin', *Studies in Conservation* 40 (1995) 177–188.
3. Stodulski, L., Farrell, E. and Newman, R., 'Identification of ancient Persian pigments from Persepolis and Pasargadae', *Studies in Conservation* 29 (1984) 143–154.
4. Ambers, J.C. and Simpson, St J., 'Some pigment identifications for objects from Persepolis' (2005) www.achemenet.com/ressources/enligne/arta/pdf/2005.002-Ambers-Simpson.pdf (accessed 25 March 2009).
5. Botta, P.E. and Flandin, E., *Monument de Ninive*, Imprimerie Nationale, Paris (1849) Plates 107–114.
6. *A Guide to the Exhibition Galleries of the British Museum, Bloomsbury*, Trustees of the British Museum, London (1884).
7. Loud, G., *Khorsabad, Part I: excavations in the palace and at a city gate*, University of Chicago Press, Chicago (1936).
8. Verri, G., *An investigation of corrected UV-induced fluorescence for the investigation of polychromy*, MA dissertation, Courtauld Institute of Art (1997) (unpublished).
9. Verri, G., 'The use and distribution of Egyptian blue: a study by visible-induced luminescence imaging', in *The Nebamun wall paintings: conservation, scientific examination and display at the British Museum*, ed. A. Middleton and K. Uprichard, Archetype Publications, London (2008) 41–50.
10. Verri, G., 'The spatial characterisation of Egyptian blue, Han blue and Han purple by photo-induced luminescence digital imaging', *Analytical and Bioanalytical Chemistry* 394(4) (2009) 1011–1021 [DOI: 10.1007/s00216-009-2693-0].
11. Riederer, J., 'Egyptian blue', in *Artists' pigments: a handbook of their history and characteristics, Vol. 3*, ed. E. FitzHugh, National Gallery of Art, Washington DC (1997) 23–40.
12. Pozza, G., Ajo, D., Chiari, G., De Zuane, F. and Favaro, M., 'Photoluminescence of the inorganic pigments Egyptian blue, Han blue and Han purple', *Journal of Cultural Heritage* 1 (2000) 393–398.
13. Accorsi, G., Verri, G., Bolognesi, M., Armaroli, N., Clementi, C., Miliani, C. and Romani, A., 'The exceptional near-infrared luminescence properties of cuprorivaite (Egyptian blue)', *Chemical Communications* (2009) 3392–3394 [DOI: 10.1039/b902563d].
14. Thureau-Dangin, F. and Dunand, M., *Til-Barsip*, Librairie Orientaliste Paul Geuthner, Paris (1936).
15. Parrot, A., *Nineveh and Babylon*, Thames and Hudson, London (1961) Plate 347.
16. Albenda, P., *Ornamental wall painting in the art of the Assyrian Empire: Cuneiform Monographs 28*, Styx-Brill, Leiden (2005).
17. Pittman, H., 'Jewelry', in *Treasures from the royal tombs of Ur*, ed. R.L. Zettler and L. Horne, University of Pennsylvania Museum, Philadelphia (1998) 87–122.
18. El-Wailly, F. and es-Soof, B.A., 'The excavations at Tell es-Sawwan. First Preliminary Report (1964)', *Sumer* 21 (1965) 17–32.
19. Reade, J.E., 'Assyrian architectural decoration: techniques and subject-matter', *Baghdader Mitteilungen* 10 (1979) 17–49.