Smith *et al. Herit Sci* (2019) 7:74
https://doi.org/10.1186/s40494-019-0316-4

Heritage Science

COMMUNICATION Open Access

Ion milling: the perfect cross-section of a painted textile

M. J. Smith[1*], T. Schmidt[2], K. Thompson[1] and M. Dixon[3]

Abstract

The successful study and conservation of historical objects is greatly enhanced by accurate materials analysis. Here embedded cross-sections from a processional marching banner were viewed by scanning electron microscopy (SEM) pre and post ion milling The application of ion-milling to the resin embedded cross-sections of the painted textile improved the sample surface resulting in greatly enhanced SEM images by producing clear distinctions between layers. It also enabled clear images which show the areas where ingress of the ground paint layer had seeped into the textile support in some areas and not on others. This perhaps indicates deliberate differences in the preparation layer depending on the type of final painting layer or it could simply be due to a lack of accuracy in its application prior to painting. The analysis of cross-section samples from painted textiles often includes the textile itself making sample preparation more complex due to the possibility of fraying of the textile during sample polishing; the ion-milling technique prevented this from occurring. To enhance findings further analysis on these ion milled cross-section samples by the use of mapping spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and Raman would facilitate material identification of the layers.

Keywords: Painted textiles, Cross-sections, Ion-milling, SEM-EDX-mapping, Sample stratigraphy

Introduction

Analytical instrumentation has developed in the last few decades enabling the viewing and detection of materials in great detail (nano level). For this to be achievable the manner in which samples are presented for analysis has become important in order for high quality and reliable results to be produced. One area where research has demonstrated the value of developments in sample preparation is in the embedding of paint cross-section [1–4]. Traditionally sample fragments from paintings and painted objects are embedded as blocks in polymer resin. This confers stability on the fragile sample and also allows for easier handing. These blocks are then polished or cut by a microtome so the stratigraphy of the sample can be viewed. One challenge is the difficulty in achieving an extremely smooth and flat surface (in the order of low micrometres) when using hand polishing. Where the surface is microscopically 'rough', it may interfere with the quality of the analysis when carrying out micro mapping using spectroscopic instrumentation.

In the study of painted textiles, cross-sections have been analysed [5, 6] but these types of objects present additional challenges during polishing or cutting resulting from the differing hardness's of the textile, pigments and resin. Once the surface of the relatively 'softer' textile is exposed further use of mechanical polishing or cutting can easily damage it. This means that the sample may be better preserved for microscopic analysis by leaving a layer of resin but this can interfere with the quality of further analysis such as micro mapping using FTIR and Raman spectroscopic instrumentation.

It is in the area of historical painting sampling that preparation technology has developed in parallel with those used in pathology and nano-materials [2] and could be applicable to the study of painted textiles. Prati et al. [2, 7] investigated methods of embedding for studying samples for examination by micro Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR), including mapping. From this

*Correspondence: Margaret.Smith@glasgow.ac.uk
[1] Centre for Textile Conservation and Technical Art History, School of Culture and Creative Arts, University of Glasgow, Robertson Building, Glasgow G11 6AQ, UK
Full list of author information is available at the end of the article

research, they reported that three procedures were best for the purpose, embedding in potassium bromide (KBr), cyclododecane pre-treatment before embedding in resin and argon ion milling. All three of these limited contamination by the embedding medium and achieved good contact with the attenuated reflection (ATR) crystal. The use of ion-milling to produce high quality paint cross-sections was first proposed

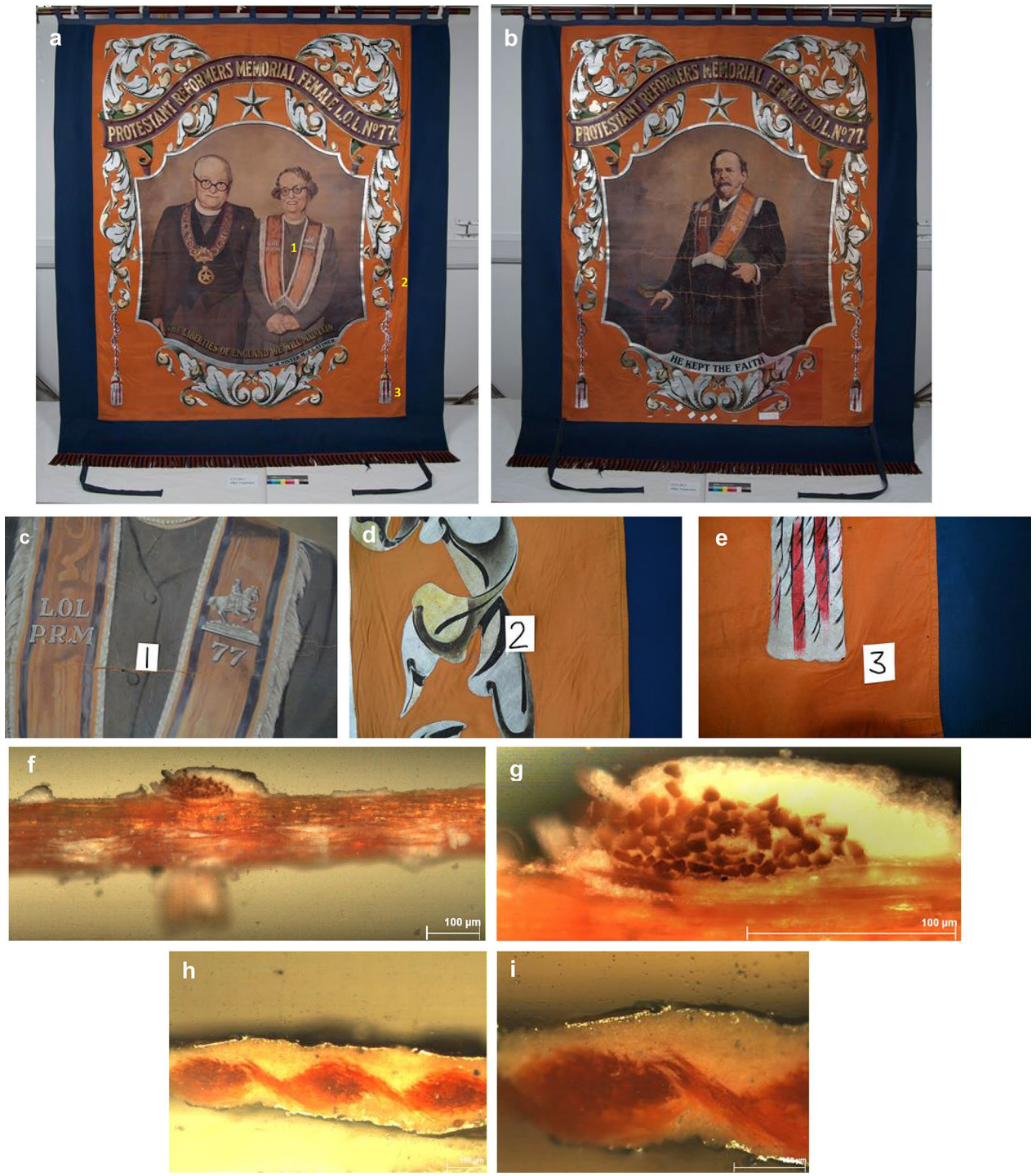

Fig. 1 **a** Banner front; **b** banner back; **c** sample 1 position; **d** sample 2 position; **e** sample 3 position; **f** sample 1 light microscopy dark field ×50 mag; **g** sample 1 light microscopy dark field ×100 mag; **h** sample 2 light microscopy dark field ×50 mag; **i** sample 2 light microscopy dark field ×50 mag

by Boon and Asahina in 2006 [8] who reported greatly improved SEM images of samples with 17th century lead white and modern acrylic paints. Weiszburg et al. [9] reported the successful use of focused ion beam-milled cross-sections to investigate gilt silver threads. However, such work has not been reported for use with painted textiles.

The aim of this work is to develop methodology to successfully ion mill resin embedded cross-sections of painted textiles causing no damage to the paint or textile layer to produce high quality results when analysed by SEM–EDX (energy-dispersive X-ray spectroscopy). It also has the potential to produce high quality samples for investigation by micro-FTIR and Raman mapping.

Experimental

The banner used in this study belongs to the Karen Finch Reference Collection housed at the Centre for Textile Conservation and Technical Art History, University of Glasgow. It represents a typical processional banner of the 19th and 20th centuries (for further details see [6]). Samples were taken from areas where there was previous damage and/or sampling had already been carried out. Figure 1 shows the front and back of the banner and the location of the samples. Reconstructions on silk were created to determine the appearance of cross-sections with a preparatory latex layer based on a publication by Labreuche [10] on the use of latex rubber in the preparation of painted canvases in the 19th c. and an 1861 patent [11] on the preparation of painted banners.

Embedded cross sections were prepared from samples by mounting them in curing resin (Technovit 2000LC, Kulzar). The resin blocks were prepared in silicone moulds and were cured in a UV curing unit (Technology Cu, Heraeus) for 30 min. The final polish was carried out using 12,000-mesh Micro-Mesh® polishing paper.

A total of five samples were ion milled, four samples were embedded and polished using a Hitachi IM4000Plus ion polisher and one was loose.

The following instrumental conditions were used for the resin embedded samples:

- Flat milling with sample rotation and periodic beam irradiation interruption.
- Beam-on for 1 rotation (25 rpm, means 2.4 s).
- Beam-off for 27.6 s (30 s period) total processing time 99 min (beam-on total 475 s).

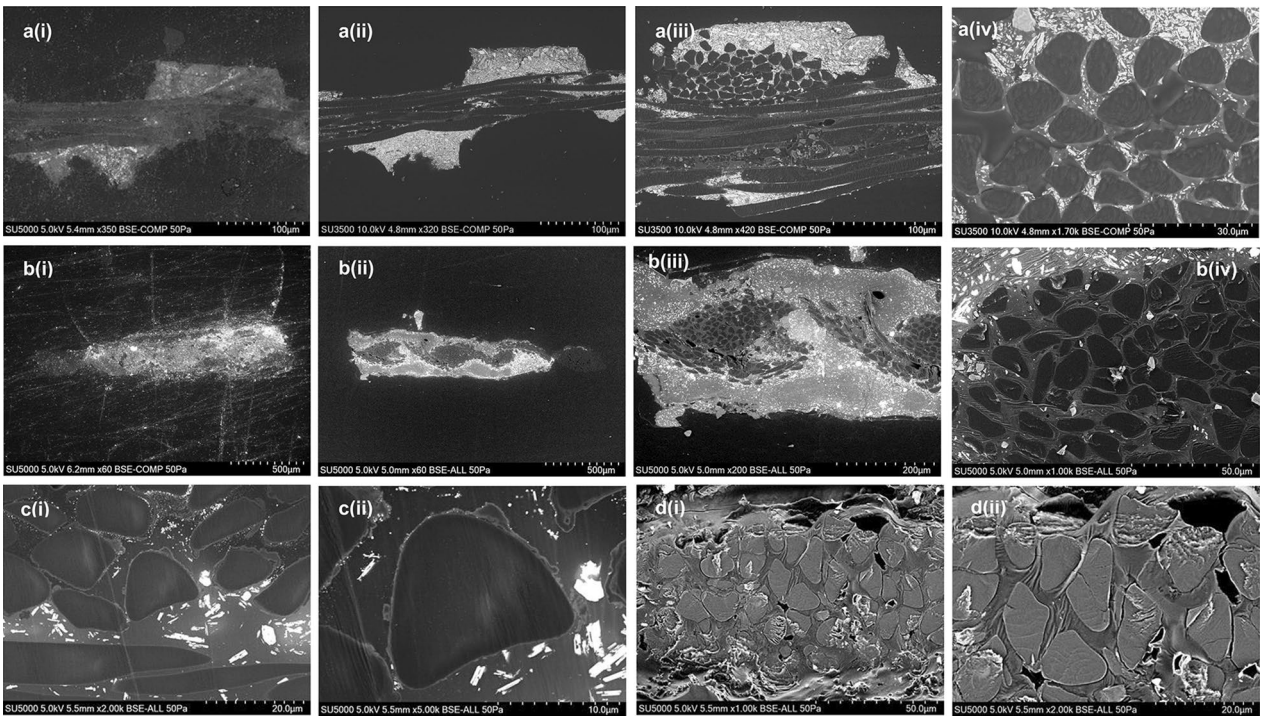

Fig. 2 **a** Sample 1 position 1 cross-section embedded **a(i)** polished with Micromesh mag ×350 **a(ii)** ion-milled mag ×320; **a(iii)** ion-milled mag ×420; **a(iv)** ion-milled mag ×1700. **b** Sample 2 position 5 cross-section embedded **b(i)** polished with Micromesh mag ×60; **b(ii)** ion-milled mag ×60; **b(iii)** ion-milled mag ×200; **b(iv)** ion-milled mag ×1000. **c** Sample 3 position 3 loose sample **c(i)** ion-milled mag ×2000; **c(ii)** ion-milled mag ×5000. **d** Reconstruction cross-section embedded **d(i)** ion-milled mag ×1000; **d(ii)** ion-milled mag ×2000

- Beam energy 4 keV, beam current ~ 135 μA, and irradiation angle 60° from vertical and zero excentricity.

The loose sample was held between two layers of epoxy resin. This was then held between two glass cover plates and was ion-milled using the following conditions:

- Cooling of the loose sample was required to prevent burning of the textile. It was precooled with the complete holder after assembly for 1 h to enhance cooling transfer.
- Acceleration electrode No. 1 energy setting; 4 keV oscillation ± 30°.
- Process time 4 h.
- Cryo-milling temp − 60 °C.

The sample was put into the IM4000plus with liquid nitrogen (N_2) Dewar attached. The instrument was set to − 60 °C and when the target temperature was reached the milling process was started and the temperature was maintained at − 60 °C with the liquid N_2 attached. The liquid nitrogen was refilled once to ensure there was always sufficient liquid N_2.

The embedded samples were examined under visible illumination using an Olympus BX41 microscope and Olympus Stream Start 1.8 image analysis software. SEM was carried out on Schottky Field-Emission FE-SEM SU5000. Micrographs conditions were back scatter detector V = 5 kV; spot Intensity 30; vacuum = 50 Pa.

Findings

The improvement in quality and clarity is best seen in SEM. Samples 1 and 2 from the banner were examined by SEM before and after ion milling, see Fig. 2a(i) and (ii), b(i) and (ii).

It proved difficult to ion mill the loose sample without causing damage to the textile layer thus cooling was used as described. Different milling regimes impart a range of thermal energy levels to the milled surfaces and care should be taken to note thermal artefacts, such as thermal shrinkage, formation of blisters and pseudo-pores in optical microscopy, and thermal fracturing [12].

From the improved SEM images, it can clearly be seen how the preparation layers have interacted with the textile in different areas of the design indicating variation in application methods and materials. For the areas were

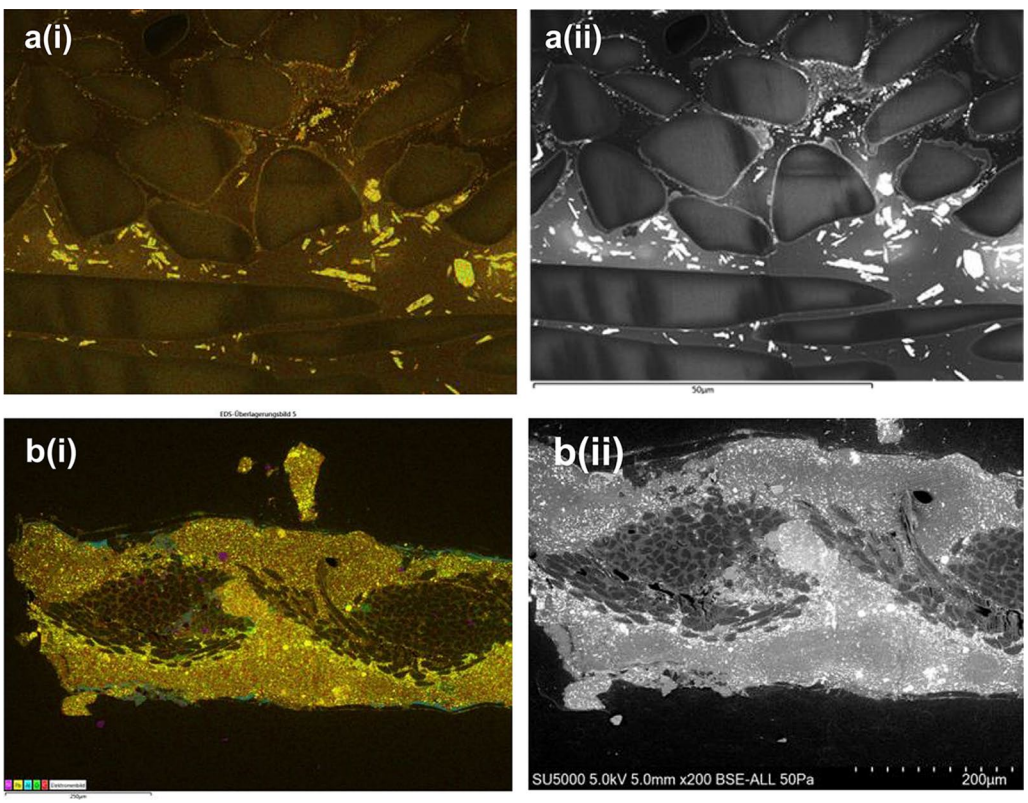

Fig. 3 SEM-EDX analysis. **a** Sample 3 position 3 loose sample ion-milled **a(i)** shows the presence of lead indicated in yellow and **a(ii)** for comparison showing the areas of the sample where an inorganic element is present. **b** Sample 2 position 2 cross-section **b(i)** shows the presence of lead indicated in yellow and **b(ii)** for comparison showing the areas of the sample where an inorganic element is present

metal paint/leaf were applied (sample position 2 and 3), a size layer [6] prevented the ingress of inorganic pigments such as lead white, through the textile, Fig. 2b(iv), c(i), (ii). However where pigment only was applied (2a(iv), the inorganic layers intermixed with the textile. This may indicate the lack of any size or a different method of application. Figure 2d(i), (ii) of the silk and latex coated reconstruction show how the presence of the latex layer prevents the ground paint layer reaching the textile.

Figure 3 shows the SEM images beside the SEM–EDX analysis (positions 2 and 3). SEM–EDX false colour maps are frequently used to show the presence of elements (and therefore the inference of inorganic paint pigments). Here when viewed beside the SEM images of the ion-milled samples it is clear where the inorganic lead white is situated.

Conclusions

The level of detail that can clearly be seen in the heterogeneous layers of the cross-sections where a textile is present is greatly improved by the ion-milling of the samples and revealed information about materials interaction not seen before in the study of painted textiles.

Abbreviations

ATR: attenuated total reflection; EDX: energy-dispersive X-ray spectroscopy; FTIR: Fourier transform infrared spectroscopy; KBr: potassium bromide; SEM: scanning electron microscopy.

Acknowledgements

Margaret Smith acknowledges funding from EPSRC (Grant Number EP/R033013/1) PISTACHIO: Photonic Imaging Strategies for Technical Art History and Conservation https://pistachio.gla.ac.uk/The authors acknowledge the ion-milling carried out by Hitachi High-Technologies Corporation.

Authors' contributions

MS had the idea to carry out the study, took, prepared and polished the embedded samples and carried out light microscopy. KT took, prepared and polished the embedded samples and carried out light microscopy. MD arranged for the analysis to be carried out. TS carried out the ion milling and SEM–EDX. All authors read and approved the final manuscript.

Funding

Margaret Smith is funded from EPSRC (Grant Number EP/R033013/1)

Competing interests

The authors declare that they have no competing interests.

Author details

[1] Centre for Textile Conservation and Technical Art History, School of Culture and Creative Arts, University of Glasgow, Robertson Building, Glasgow G11 6AQ, UK. [2] Hitachi High-Technologies Europe GmbH, Europark Fichtenhain A 12, 47807 Krefeld, Germany. [3] Hitachi High-Technologies Europe, Techspace One, SciTech Daresbury, Keckwick Lane, Daresbury, Cheshire WA4 4AB, UK.

Received: 17 June 2019 Accepted: 13 September 2019
Published online: 25 September 2019

References

1. van der Weerd J, Heeren RMA, Boon JJ. Preparation methods and accessories for the infrared spectroscopic analysis of multi-layer paint films. Stud Conserv. 2004;49:193–210.
2. Prati S, Sciutto G, Catelli E, Ashashina A, Mazzeo R. Development of innovative embedding procedures for the analyses of paint cross sections in ATR FITR microscopy. Anal Bioanal Chem. 2013;405(2–3):895–905.
3. Mazzeo R, Joseph E. Attenuated total reflectance microspectroscopy mapping for the characterisation of bronze corrosion products. Eur J Mineral. 2007;19:363–71.
4. Pouyet E, Fayard B, Salome M, Taniguchi Y, Sette F, Cotte M. Thin-sections of painting fragments: opportunities for combined synchrotron-based micro-spectroscopic techniques. Herit Sci. 2015;3:3.
5. Rogerson C, Eastop D. The application of cross-sections in the analysis of historic textiles. Conservator. 1999;23(1):49–56.
6. Smith MJ, Thompson K, Hermens E. Breaking down banners—analytical approaches to determining the materials of painted banners. Herit Sci. 2016;4:23.
7. Prati S, Rosi F, Sciutto G, Mazzeo R, Magrini D, Sotiropoulou S, Van Bos M. Evaluation of the effect of six different paint cross section preparation methods on the performances of Fourier Transformed Infrared microscopy in attenuated total reflection mode. Microchem J. 2012;103:79–89.
8. Boon JJ, Asahina S. Surface preparation of cross sections from traditional and modern paint using the Argon ion milling polishing CP system. Microsc Microanal. 2006;12(2):2006.
9. Weiszburg TG, Gherdan K, Ratter K, Zajzon N, Bendo Z, Radnoczi G, Takacs A, Vaczi T, Varga G, Szakmany G. Medieval gilding technology of historical metal threads revealed by electron optical and micro-Raman spectroscopic study of focused ion beam-milled cross sections. Anal Chem. 2017;89(2017):10753–60.
10. Labreuche P. India rubber painting grounds in Britain and France in the nineteenth century. Stud Conserv. 2011;56:14–30.
11. Tutill G. Treating materials for the manufacture of banners and flags. In: Office of the commissioners of Patents, London, UK, 1862.
12. Mastalerz M, Schieber J. Effect of ion milling on the perceived maturity of shale samples: implications for organic petrography and SEM analysis. Int J Coal Geol. 2017;183:110–9.

Publisher's Note