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A literature review of analytical techniques for materials characterisation of painted textiles—Part 2: spectroscopic and chromatographic analytical instrumentation

Keywords
textile; painted; analysis; conservation; spectroscopy; chromatography

Introduction
Part 1 of this two-part study introduced the investigation of painted textiles by broadly categorising them into two groups:

(1) those on which paint covers the entire surface of the textile; and
(2) those where the paint partially covers the textile.

Group (1) textiles, where the paint covers the entire surface, encompass, for example, medieval cloths and banners, thangkas, and theatre scenery, whilst Group (2)'s partially painted textiles include painted banners and flags that were made to be processed or flown, and paint-decorated textiles, and incorporate costume, hangings, Chinese textiles, ancient Egyptian textiles, furnishings and pictures.

Part 1 reviewed analytical methods used to identify the materials and to investigate the condition of painted textiles, reporting on the value of simple techniques such as low level microscopy and staining, which can be readily carried out by conservators.

In Part 2, the review will cover a wide range of more specialised spectroscopic and chromatographic techniques which characterise the chemical composition of materials. Advances in techniques that could be applicable to the study of painted textiles are also discussed, such as mapping in Fourier transform infrared spectroscopy (FTIR) and Raman, surface-enhanced Raman spectroscopy (SERS), surface-enhanced resonance Raman spectroscopy (SERRS) and secondary ion mass spectrometry (SIMS). The principles of detection methods are explained, including a discussion of their limitations and advantages as well as how they complement each other. There are remarkably few peer-reviewed publications on painted textiles, and even fewer specifically refer to the use of these analytical techniques. Therefore, additional selected articles from the wider literature using techniques not yet reported for the examination of painted textiles, have also been reviewed in the context of their potential application to painted textile study.

Analytical investigation techniques
1 Spectroscopic techniques using X-rays: X-ray fluorescence (XRF), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS or EDX)

These techniques all use X-rays to bombard samples causing electrons to be displaced from their atomic orbital positions. The energy they release is characteristic of a specific element, thus allowing it to be identified.

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1a **X-ray fluorescence (XRF) and X-ray diffraction (XRD)**

XRF provides elemental composition and atomic percentages of the elements present. It does not give information on the position of the elements in the sample, only the total amount of each present. Each element has its own unique X-ray signature, which means that the X-rays emitted from a sample can provide qualitative and quantitative compositional information about that sample.

XRD uses diffraction patterns to analyse materials by exploiting the dual wave/particle nature of X-rays to obtain information about their crystalline structure. As such a primary use of the technique is in the identification and characterisation of compounds based on their diffraction pattern. The depth at which XRD can operate ranges from a few micrometres to 100µm, depending on the density of the material. Additionally, by the use of a very small fixed incidence angle of the X-rays (glancing incidence measurement) thin layers of a few nanometres can be investigated.

In summary, XRF will give details of the chemical composition of a sample but will not indicate the crystalline structures present, whereas XRD can determine both qualitatively and quantitatively the elements present and also identify the crystalline phases of the mineral. Advantages of these two instrumental methods are that the elements, including, importantly, metals, can be identified, although quantitatively calibrated standards have to be run to determine amounts of elements in the samples. As both have portable versions, quite large objects can be analysed.

The use of hand-held instrumentation is limited in the published sources although their use is growing. Tonkin described the use of a hand-held XRF unit—a Bruker Tracer III–V—to provide portable X-ray Fluorescence Spectrometry enabling in-situ analysis for materials identification. Her work involves the comparison of the elements in the paints of an oil painted banner and an acrylic painted banner looking at modern paint films on textiles. Similarly, Kriznara et al. used portable XRF to identify elements in pigments used to paint sixteenth century Flemish panel paintings, and although useful, they concluded that the use of Raman spectroscopy and FTIR is usually required in addition to XRF to fully characterise materials.

1b **Energy-dispersive X-ray spectroscopy (EDX or EDS)**

SEM/EDX is the best known and most widely used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focussed, scanning (primary) electron beam. The analysis depth is commonly around 1–2µm and the lateral dimensions tend to be about 1µm. The quantitative results progressively improve as the element becomes heavier. As well as detecting materials at a single spot, the technique can also be used to create an elemental map, a map of the distribution of an element within an area, and this can be done for all the elements detected in that area. This technique is widely used for the study of stretched paintings.

SEM–EDX has been used to identify pigments and associated materials such as fillers made of calcium carbonate. It has also been used to detect causes of deterioration or sources of potentially harmful substances. For example, a polarised light microscope coupled with SEM with EDX was used by Wild to identify the unique morphology of different pigments to help determine the causes of loss to the cotton substrate associated with a green pigment. This also helped in determining whether the pigments were toxic or not, albeit that the author commented that any interpretation of results and conclusive identification relied on a skilled and practised eye.

2 See, for example, Mirtat Bouroushian and Tatjana Kosanovic, ‘Characterisation of Thin Films by Low Incidence X-Ray Diffraction’, *Crystal Structure Theory and Applications* 1, no. 3 (2012): 35–9.

3 Cf. Juan Manuel Madariaga, ‘Analytical Chemistry in the Field of Cultural Heritage’, *Analytical Methods* 7 (2015): 4848–76.

4 Leanne Tonkin, ‘Taking the Modern with the Traditional: Introducing the Challenges of Acrylic Emulsion Painted Banners’, in *Taking the Rough with the Smooth: Issues and Solutions for Decorated Surfaces*, ed. Alison Fairhurst (London: V&A Museum/Icon Textile Group, 2012), 6–16.

5 Anabelle Kriznara, Maria del Valme Muñoz, Fuensanta de la Paz Muñoz, Miguel Ángel Respaldizad and Mercedes Vegae, ‘Non-destructive XRF Analysis of Selected Flemish Panel Paintings in the Fine Arts Museum of Seville’, *Journal of the Institute of Conservation* 37 (2014): 156–51.

6 See, for example, Lubomír Vančo, Magdaléna Kadlečíková, Juraj Breza, Lubomír Caplovic and Miloš Gregor, ‘Examining the Ground Layer of St. Anthony from Padua 19th Century Oil Painting by Raman Spectroscopy, Scanning Electron Microscopy and X-Ray Diffraction’, *Applied Surface Science* (2013): 692–8; and Annelies van Loon and Jaap J. Boon, ‘Characterization of the Deterioration of Bone Black in the 17(th) Century Oranjewal paintings using Electron-Microscopic and Micro-Spectroscopic Imaging Techniques’.
Although X-ray spectroscopy techniques have been used in the identification of materials used in painted textiles for at least two decades, none have used mapping. The use of mapping to understand the distribution of elements (which is non-destructive and also non-intrusive if a portable instrument is used) would be undoubtedly beneficial to conservators. For example, a change in the amount of a specific material on a surface may indicate degradation or loss. Howard et al. used fast-scanning X-ray fluorescence microscopy using synchrotron radiation with a high definition XRF elemental mapping technique to investigate a self-portrait by Sir Arthur Streeton (1867–1943). The authors stated that one of the technique’s unique strengths is the ability to reveal metal distributions in the pigments of underlying brushstrokes, thus providing information critical to the interpretation of a painting. In 2014 Wang et al. reported on the value of EDX–ESEM on determining the pigments and gilding on clay-based polychromic sculptures in the Chongqing Temple, China—their findings not only identified materials used on the original sculptures but also more modern materials which showed that conservation work had been previously carried out on the objects.

The reported use of spectroscopic techniques using X-rays has demonstrated their value in determining the nature of the pigments under examination which has, in many cases, informed any subsequent conservation outcomes. Furthermore, developments in technology have resulted in improved accuracy of portable instrumentation and thus the authors conclude that these tools could be utilised more in the future.

2 Vibrational spectroscopy
Vibrational spectroscopy is a term used to describe the two analytical techniques, FTIR and Raman spectroscopy. These are both considered non-destructive techniques that provide information about the molecular composition of the materials being examined. These techniques measure the vibrational energy levels associated with the chemical bonds in a given material as each component spectrum is unique, like a fingerprint, and vibrational spectroscopy is thus used for identification and characterisation of materials.

2a Fourier transform infrared spectroscopy (FTIR)
FTIR is a vibrational spectroscopy technique and is described as an absorption technique which emits infrared (IR) frequencies from the near-IR region 14,000–4000cm⁻¹, the mid-IR region 4000–400cm⁻¹ and the far-IR region 400–10cm⁻¹. Both macro- and micro-FTIR are used extensively in conservation science—macro is used for bulk analysis and micro, by virtue of the attachment of a microscope, allows spectra to be collected from specific areas of a sample. Micro-FTIR can use transmitted, reflected and attenuated light to analyse a sample. Transmitted light is applied to very thin samples, reflected light is used when the sample is not suitable for transmission (when it is opaque), and when neither of these modes work, an attenuated total reflection (ATR) mode is used for both macro- and micro-analyses. Larkin describes the principles of FTIR in more detail and additionally compares and contrasts FTIR and Raman in a manner that is informative to scientists and non-scientists alike.

There are numerous papers on the use of FTIR for the identification of materials in cultural heritage science. The versatility of the technique can range from the use of a portable FTIR to macro- and micro-analysis and mapping. FTIR has been used to identify different aspects of a painted textile with, for example, Abdel-Kareem et al. using it to study the degradation of linen, where it was used to measure the ratio of carbonyl to carboxyl groups indicating that there was degradation when compared to the ratio shown by new linen. Abdel-Kareem et al. also showed that gum arabic was used in ink preparation and Schießl et al. identified an
animal glue size or priming layer on a fifteenth century painted cloth using FTIR. Here, the determination of size layers can prove difficult so it is important to be able to characterise the spatial location within the cross-section to distinguish, for example, whether a material is being used as a size or as a medium to disperse pigment.16

Lennard et al. used FTIR to determine the binding medium on the main part of the historic Formosa Republic Tiger flag they were tasked with analysing and reported that it appeared to be primarily oil, possibly modified with lead soap and/or resin.17 The addition of metal salts of organic acids as modifiers to artist paint formulations to assist with production, working, storage and drying properties is well documented.18 However, the lead soap encountered may have been formed in-situ as a reaction between the metal ions from the pigments and the fatty acids derived from the drying oil and not as a modifier. Whilst the authors state that a number of different techniques, including FTIR, were used to carry out additional pigment analysis, they do not explain which pigments were identified using FTIR so it is difficult to gauge the effectiveness of it in the determination of the pigments.

2b Attenuated total reflectance (ATR) FTIR
The use of ATR has revolutionised the application of FTIR. It is now one of the most popular techniques used in the analysis of materials as it is quick, non-destructive and need not require sample preparation.19 ATR can be used in the micro- and macro-mode and is therefore useful for detailed analysis as in micro-FTIR mapping. For macro-analysis an external arm with an ATR crystal (an internal reflection element) is extremely useful to view an object as a whole if it is flat enough to fit on the instrument examination area. ATR crystals enable the analysis of samples that are too opaque for transmission and too strongly absorbing for reflectance. Usually pressure of some sort is employed to hold the sample in place against the crystal as good contact is essential given that the produced evanescent wave rapidly decays. Typical crystals used are germanium (Ge), zinc selenide (ZnSe), thallium-bromoiode (KRS-5), silicone (Si) or diamond (C) and these vary in their depth of penetration into the sample—between approximately 0.5 and 2µm—and their spectral range. By understanding the mechanisms of how FTIR and ATR-FTIR work, it is clear that these are primarily surface techniques. Sometimes an object, depending on its size and geometry, can be analysed both in the macro- and micro-modes in its entirety, thus negating the need for a sample to be taken, which is truly non-destructive. Furthermore, if a sample does need to be taken this technique is non-destructive in that it can be subsequently used for further testing. However, while macro-FTIR is simple to use, it does require a level of skill and experience to interpret the findings, and for micro-FTIR good sample preparation is essential, especially for viewing cross-sections.

In a study of nineteenth century painted silk marching banners, Rogerson and Lennard used FTIR with ATR in determining and identifying the layers within the samples, and confirmed the presence of rubber, a layer which was first seen through optical microscopy.20 Nicole Rode used ATR-FTIR to study the white bloom on an early railway workers union banner and her analysis suggested the presence of a metal soap.21 Although FTIR alone was insufficient to confirm this, it was nonetheless instrumental in the first ever observation of metal soaps on painted banners in contrast to their much wider identification on easel paintings.22

Spring et al. reported on a study of the use of ATR-FTIR for the analysis of organic materials in paint cross-sections taken from old master paintings. They noted that the unique advantages of this technique are the high spatial resolution and gains in sensitivity in detecting trace materials, and
Rode, ‘Towards an Understanding of Whitening’ (see Note 8).

22 Vanessa Otero, Diogo Sanches, Cristina Montagner, Márcia Vilariogues, Leslie Carlyle, João A. Lopes and Maria J. Melo, ‘Characterisation of Metal Carboxylates by Raman and Infrared Spectroscopy in Works of Art’, journal of Raman Spectroscopy 45 (2014): 1197–206; Katrien Keune and Jaap J. Boon, ‘Analytical Imaging Studies of Cross-Sections of Paintings Affected by Lead Soap Aggregate Formation’, Studies in Conservation 52 (2007): 161–76.

23 Marika Spring, Camilla Ricci, David A. Peggie and Sergei G. Kazarian, ‘ATR-FTIR Imaging for the Analysis of Organic Materials in Paint Cross Sections: Case Studies on Paint Samples from the National Gallery, London’, Analytical and Bioanalytical Chemistry 392, no. 1–2 (2008): 37–45.

24 Larkin, Infrared and Raman Spectroscopy; Peter Vandenebeele, Howell G.M. Edwards and Luc Moens, ‘A Decade of Raman Spectroscopy in Art and Archaeology’, Chemical Reviews 107, no. 3 (2007): 675–86; Peter Vandenebeele and Luc Moens, ‘Raman Spectroscopy: New Light on Ancient Artefacts’, in Lasers in the Conservation of Artworks, Proceedings, ed. Johann Nimmrichter, Wolfgang Kautek and Manfred Schreiner (Berlin: Springer Verlag, 2007), 341–7; Giulia Lorenzetti, Jana Striova, Angela Zoppo and Emilio Mario Castellucci, ‘Confocal Raman Microscopy for in Depth Analysis in the Field of Cultural Heritage’, Journal of Molecular Structure 993, no. 1–3 (2011): 97–103.

25 See, for example, Neil Everall, ‘Depth Profiling with Confocal Raman Microscopy, Part II’, Spectroscopy (2004): 16–27; and Fran Adar, ‘Depth Resolution of the Raman Microscope: Optical Limitations and Sample Characteristics’, Spectroscopy Solutions for Materials Analysis (2010), http://www.horiba.com/scientific/products/raman-spectroscopy/raman-academy/raman-faq/what-is-the-spatial-resolution-of-a-raman-microscope/ (accessed 27 July 2017).

26 Averil Macdonald, Cordelia Rogersen, Alun Vaughan and Paul Wyeth, ‘Raman Microspectroscopy Interrogating 19th- and 20th-Century Painted Trades Union Banners’, in Wyeth and that the information derived from the location of these compounds is especially valuable. Importantly, the authors concluded that the value of using complementary techniques, including optical microscopy, SEM and EDX elemental mapping, played a crucial role in the interpretation of the FTIR images and Raman spectroscopy gave further characterisation of some of the components detected.

The use of FTIR is important in the identification of organic binders and preparation layers and arguably could be a valuable tool for the confirmation of less easily identified modern fibres. However, success with this technique depends on the skill of the analyst and the use of known standards to make accurate identification rather than relying solely on any online databases as these may not show subtle spectral detail or, indeed, the conditions of analysis. That said, such databases can be a useful starting point with which to narrow down the options for identification.

2c Raman

Raman is a vibrational spectroscopy technique that measures the radiation scattered from a sample. Raman spectroscopy uses laser light at a number of wavelengths in the ultra-violet UV (325nm), visible (780nm, 633nm, 532nm and 473nm) and in the near infrared (1064nm) regions of the spectrum. As such, the technique is able to detect minute quantities of a material. A comprehensive description of the principles of Raman spectroscopy is given by Larkin and details of its application to cultural heritage objects are expertly and concisely explained by Vandenebeele et al., Vandenebeele and Moens, and Lorenzetti et al.

Depth of penetration (the z plane) depends strongly on the confocal design of the Raman microscope being used, but also crucially on the excitation wavelength. At 532nm, the depth of penetration is 0.7µm but at 785nm this would be about 12µm. Raman is useful for analysing both organic and inorganic materials and some instruments have an external arm or are portable making them suitable for examining an object without sampling. Micro-Raman can give excellent results from a very small sample area although the power of the laser must be carefully controlled to avoid damaging the area under examination. Here the size of the sample compartment of the instrument dictates the size of the object which can be examined. It is widely used in cultural heritage studies and there are many articles related to its use. Reported problems with fluorescence associated with organic materials can be minimised by careful choice of wavelength, although this needs to be weighed against signal reduction caused by any wavelength change. This may be a particular issue that will need to be overcome for its use with painted textiles. Furthermore, the presence of the textile may also be an issue as frequently these materials fluoresce.

Raman has been used to identify pigments and ground layers in painted textiles, and Macdonald et al. investigated painted trades union banners manufactured by George Tutill & Co, George Kenning & Son and an unknown manufacturer. Analysis with Raman of a fourteenth-century double-sided banner identified the ground layer as calcium sulfate hydrate (gypsum) and a range of pigments, and Ernst used Raman to identify materials on thangkas. The main focus was to identify their pigments and these showed the usefulness of Raman to identify both organic and inorganic materials, albeit the author also discussed some of the challenges of the different laser wavelengths and the resulting fluorescence. Macdonald and Wyeth investigated the use of photobleaching to improve the reliability of pigment identification on painted textiles. The technique involves irradiating the sample with intense light for a few minutes and...
can be done using the Raman laser to decompose any fluorescent species. However, the authors concluded that the benefits of photobleaching to remove background fluorescence and facilitate pigment identification may be far outweighed by the potential longer-term damage caused to these valuable, fragile artefacts. 29

The usefulness of Raman spectroscopy in the study of historic paintings and objects is exemplified by the number of publications both within the conservation and heritage sector and in the wider scientific community. Indeed the Journal of Raman Spectroscopy has published special issues dedicated to the use of Raman in art and archaeology. 30 While many historical objects, paintings and pigments have been successfully characterised using Raman, recently attention has been focussing on techniques within Raman to improve analysis and also determine detection limits. 31 Vandenabeele and Moens published ideas on the definition of Raman spectroscopy detection limits with a view to defining the minimal amount of degradation product that can be detected on art and archaeological objects. When performing micro-Raman, the laser beam is typically focussed on a few cubic micrometres allowing the identification of minute inhomogeneities—therefore, it is critical to be aware of the measured volume in relation to the inhomogeneity of the sample. 32

Ropret et al. reviewed Raman mapping techniques on works of art and reported examples of their application. The authors point out that objects of cultural significance are generally hybrid organic–inorganic materials intrinsically characterised by micro- and macro-scale heterogeneities due not only to the artists’ techniques, but also to the effects of ageing, exposure to the environment and past conservation treatments. 33 More recent work on paintings and historical objects has benefitted from later developments in Raman, such as surface-enhanced Raman spectroscopy (SERS), and some examples are described below. As yet these have not been applied to painted textiles but the authors suggest that they have the potential to further the understanding of any inorganic and organic pigments used in particular.

2d Surface-enhanced Raman spectroscopy (SERS) and surface-enhanced resonance Raman scattering (SERRS)

A development of Raman that has flourished over the last four decades is surface-enhanced Raman spectroscopy (SERS). 34 In SERS the Raman scattering signal is greatly enhanced when organic molecules with large delocalised electron systems are adsorbed on the atomically rough noble metal surfaces. SERS enhancement is up to 10^6 the scattering efficiency of Raman and the presence of the noble metal also quenches fluorescence allowing lasers of shorter wavelength to be used, thereby increasing sensitivity. 35 In addition to SERS there is SERRS, surface-enhanced resonance Raman scattering. One major difference between SERS and SERRS is the huge additional enhancement effect found in SERRS, which enables detection of very small quantities of materials. 36

Harroun et al. studied house paint and wallpaper from an eighteenth century historic property. SERS was chosen as it was ideally suited to the analysis of pigments, both inorganic and organic, as the use of a noble metal substrate leads to greatly enhanced Raman signals, such that only minute (sub µg to pg) samples are required. The authors report that they were unsuccessful using normal Raman due to extreme limitations of sample size but were able to identify pigments in their samples with SERS. 37 Casadio et al. explored the use of SERS to identify the organic colourants used in a number of historic fibres, paints and glazes. They investigated a number of preparation techniques and Raman methodologies to achieve meaningful data. 38

In summary, Raman is an invaluable tool in the identification of materials. Careful choice of excitation wavelengths should be used to maximise its

29 Sarah Kleiner, ‘A Technical Study of a Late Fourteenth-Century Double-Sided Processional Banner by Spinello Aretino’, in Costaras and Young, Setting the Scene, 69–76.
30 Richard R. Ernst, ‘Science and Art—My Two Passions’, in Science and Art: The Painted Surface, ed. Antonio Sgamelotti, Brunetto Giovanni Brunetti and Costanza Miliani (Croydon: The Royal Society of Chemistry, 2014), 1–27.
31 Averil Macdonald and Paul Wyeth, ‘On The Use of Photobleaching to Reduce Fluorescence Background in Raman Spectroscopy to Improve the Reliability of Pigment Identification on Painted Textiles’, Journal of Raman Spectroscopy 37, no. 8 (2006): 830–5.
32 Danilo Bersanini and Juan Manuel Madariaga, ‘Applications of Raman Spectroscopy in Art and Archaeology’, Journal of Raman Spectroscopy 43 (2012): 1523–8.
33 Cf. Peter Vandenabeele, Luc Moens, Howell G.M. Edwards and Richard Dams, ‘Raman Spectroscopic Database of Azo Pigments and Application to Modern Art Studies’, Journal of Raman Spectroscopy (2000): 509–17; Polonca Ropret, Silvia A. Centeno and Peter Bukovec, ‘Raman Identification of Yellow Synthetic Organic Pigments in Modem and Contemporary Paintings: Reference Spectra and Case Studies’, Spectrochimica Acta A Molecular and Biomolecular Spectroscopy 69, no. 2 (2008): 486–97; Nadim Scherrer, Stefan Zumbühl, Françoise Delavy, Annette Fritsch and Renate Kuehnen, ‘Synthetic Organic Pigments of the 20th and 21st Century Relevant to Artist’s Paints: Raman Spectra Reference Collection’, Spectrochimica Acta. A Molecular and Biomolecular Spectroscopy (2009): 505–24; Natalia Navas, Julia Romero-Pastor, Eloisa Manzano and Carolina Cardell, ‘Raman Spectroscopic Discrimination of Pigments and Tempera Paint Model Samples by Principal Component Analysis on First-Derivative Spectra’, Journal of Raman Spectroscopy (2010): 1486–93; Lorenzetti et al., ‘Confocal Raman Microscopy’, Peter Vandenbeele and Luc Moens, ‘Some Ideas on the Definition of Raman Spectroscopic Detection Limits for the Analysis of Art and Archaeological Objects’, Journal of Raman Spectroscopy 43, no. 11 (2012): 1545–50.
34 Ropret et al. reviewed Raman mapping techniques on works of art and reported examples of their application. The authors point out that objects of cultural significance are generally hybrid organic–inorganic materials intrinsically characterised by micro- and macro-scale heterogeneities due not only to the artists’ techniques, but also to the effects of ageing, exposure to the environment and past conservation treatments. More recent work on paintings and historical objects has benefitted from later developments in Raman, such as surface-enhanced Raman spectroscopy (SERS), and some examples are described below. As yet these have not been applied to painted textiles but the authors suggest that they have the potential to further the understanding of any inorganic and organic pigments used in particular.

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In summary, Raman is an invaluable tool in the identification of materials. Careful choice of excitation wavelengths should be used to maximise its...
potential such that most inorganic pigments are clearly and easily identified at 532nm, whilst analysis of organic materials which fluoresce, such as coatings, are usually better carried out at 785nm. Sample preparation is also key to producing quality spectra and so sometimes samples are more easily analysed when not embedded in resin. If embedded, it is crucial to ensure that the spectrum of the embedding material is recorded and considered when interpreting results. Additionally, when mapping, a very flat surface is essential and therefore polishing should be carried out in a controlled manner and/or embedded samples cut using precision tools.\(^9\) While SERS and SERRS have dramatically increased the sensitivity of Raman, these techniques are complex to set up and require more extensive experience of sample preparation than for Raman alone.

3 Chromatographic techniques

Chromatography is a technique that separates the components of mixtures. All forms of chromatography work on the same principle as they all have a stationary phase (a solid) and a mobile phase (a liquid or a gas). The mobile phase flows through the stationary phase and carries the components of the mixture with it. Different components travel at different rates thus separating over time.

3a High performance liquid chromatography (HPLC)

HPLC is used with a variety of detection methods: photodiode array (PDA), ultra-violet (UV), visible (vis), refractive index (RI) and mass spectroscopy (MS). It is a chromatographic technique developed in the late 1960s and has since become one of the most commonly used techniques for both qualitative and quantitative analysis. Identification of the molecules and derivatives can then be achieved, based on retention time, molecular weight and spectral matching. Increasingly improved detectors and the introduction of ultraHPLC (uHPLC or UPLC) which can operate using very small quantities of sample by utilising small columns, and reduced solvent flow and spectral matching. Increasingly improved detectors and the introduction of ultraHPLC (uHPLC or UPLC) which can operate using very small quantities of sample by utilising small columns, and reduced solvent flow and rapid analysis, has facilitated the identification of samples in the nano (10\(^{-9}\)), pico (10\(^{-12}\)) and even femto (10\(^{-15}\)) gram range. In archaeological and other heritage science it has been used for the analysis of a number of materials including, for example, to identify natural organic dyes and pigments and binding media.\(^39\)

HPLC has the advantage of both retention time and spectral output for molecule verification when using UV-vis detection. Additionally the use of MS gives the molecular weight of the analytes. The technique is specialised both in sample preparation, instrument use and interpretation of results. It is destructive as the sample is dissolved in solvent and thus should be done using a sample that has otherwise been analysed non-destructively in order to maximise sample information and minimise sample taking.

Lennard et al. used ultra-violet spectroscopy (UV-vis) to determine the techniques and materials that had been used to colour the main part of the Formosa Tiger flag. While further analysis with HPLC–PDA was considered inconclusive—thus highlighting the challenges of identifying samples where the dye had almost completely faded—HPLC–PDA was able to confirm the presence of indigo dye in the modified section of the flag.\(^41\)

3b Gas chromatography (GC)

GC is an extensively used chromatographic technique which was developed in the 1950s. It is used for the qualitative and quantitative analysis of organic materials, frequently with a flame ionising detector (FID) which detects organics qualitatively and quantitatively. Mass spectroscopy (MS) is frequently used to determine specific molecules and their degradation products. Analysis is carried out using different types of MS such as thermal
desorption (TD) and pyrolysis (PY). When using MS, compounds and derivatives can be identified by comparison to a spectral library as each compound has a unique fragmentation pattern. Successful GC–MS depends on samples having suitable vapour pressures and thermal stabilities. It is an extremely sensitive technique and is therefore able to identify the constituents of very small amounts of sample material which makes it highly suitable for analysis of historical objects. There are many publications documenting the use of GC in historical object analysis.\textsuperscript{42}

GC has been used on a number of painted textiles to identify binding mediums. Bilson identified the binding medium on an Egyptian shroud to be an animal or fish glue with a small amount of unidentified wax using gas chromatography,\textsuperscript{43} and Prikryl et al. and Kleiner used it to analyse protein binders on paintings.\textsuperscript{44} GC–MS analysis by Rogerson and Lennard revealed that two different banner makers both used partially heat treated linseed oil throughout the painted regions of silk marching banners they were working on,\textsuperscript{45} and Rode used GS–MS to further categorise the bloom on a painted banner by identifying fatty acids—stearic, palmitic and myristic—and their proportions.\textsuperscript{46} Other examples of its use for paintings analysis are demonstrated by Russell et al., who applied GC–MS to the identification of organic pigments in modern paints, and Andreotti et al., who reported on GC–MS as a procedure to characterise glycerolipid, waxy, resinous and proteinaceous materials from one microsample.\textsuperscript{47}

\textbf{3c Thin layer chromatography (TLC)}

Thin layer chromatography is a simple method that has superseded paper chromatography. A thin stationary phase is made by coating an adsorbent gel of silica, alumina or cellulose onto a glass or plastic plate. The sample in solution is applied as a spot (0.1–1.0\textmu l) to the bottom of the plate and the plate is then placed in a tank with a mobile phase of solvent. The separation occurs as the solvent is carried up the plate by capillary action. The separated components are then detected by spraying the plate with a visualising agent.\textsuperscript{48} Although less used now as chromatographic instrumentation has become more available, it still offers the ability to separate components of a mixture and also to identify these by comparisons to standards. For example, using thin layer chromatography and video densitometry, Rezić et al. were able to determine the amino acid composition of the binding used in a banner as being a proteinaceous animal glue.\textsuperscript{49} Although chromatographic methods are destructive they can enable identification of small traces of a substance that are otherwise potentially undetected using other methods. This may prove useful in determining preparation layers on a textile before the paint is applied.

\textbf{4 Secondary ion mass spectrometry (SIMS)}

SIMS works by detecting and analysing the mass/energy of the secondary ions ejected from the sample surface by the primary ion focussed beam. By analysing these particles with a mass spectrometer the elemental, isotopic and molecular composition of the uppermost atomic layers of the material are identified. It is an extremely sensitive technique for the detection of elements down to parts per billion.

Mueller and Vervoort describe the theory and mechanism of SIMS very well,\textsuperscript{50} and SIMS is a well-established technique used for the characterisation of materials in the cultural heritage field, particularly pigments and oils, with, for example, Keune et al. reporting that the surface sensitivity of SIMS is advantageous when probing for paint constituent distributions.\textsuperscript{51} Its use in the areas of materials science and geochemistry, where there is developed methodology, is particularly well suited to the

\textsuperscript{41} Lennard et al., ‘Blue Flag with Yellow Tiger?’.

\textsuperscript{42} See, for example, Ursula Baumer and Patrick Dietemann, ‘Identification and Differentiation of Dragon’s Blood in Works of Art using Gas Chromatography/Mass Spectroscopy’, \textit{Analytical and Bioanalytical Chemistry} 397 (2010): 1363–76; and Lemonia Valianou, Shuya Wei, Mohammad S. Mubarak, Helen Farmakalidis, Erwin Rosenberg, Stergios Stassinopoulos and Ioannis Karapanagiotis, ‘Identification of Organic Materials in Icons of the Cretan School of Iconography’, \textit{Journal of Archaeological Science} 38, no. 2 (2011): 246–54.

\textsuperscript{43} Bilson, ‘The Conservation of a Roman Egyptian Painted Shroud Fragment’.

\textsuperscript{44} Petra Prikryl, Lenka Havlickova, Vera Pacakova, Janka Hradilova, Karel Stulik and Petr Hohta, ‘An Evaluation of GC–MS and HPLC–FD Methods for Analysis of Protein Binders in Paintings’, \textit{Journal of Separation Science} 29, no. 17 (2006): 2653–63; and Kleiner, ‘A Technical Study of a Late Fourteenth-Century Double-Sided Processional Banner’, 69–76.

\textsuperscript{45} Rogerson and Lennard, ‘Bilowing Silk and Bendable Binders’.

\textsuperscript{46} Rode, ‘Towards an Understanding of Whitening’.

\textsuperscript{47} Joanna Russell, Brian W. Singer, Justin J. Perry and Anne Bacon, ‘The Identification of Synthetic Organic Pigments in Modern Paints and Modern Paintings using Pyrolysis-Gas Chromatography–Mass Spectrometry’, \textit{Analytical and Bioanalytical Chemistry} 400, no. 5 (2011): 1473–91; Alessia Andreotti, Ilaria Bonaduce, Maria P. Colombini, Gwénaële Gautier, Francesca Modugno and Erika Ribechini, ‘Combined GC/MS Analytical Procedure for the Characterization of Glycerolipid, Waxy, Resinous, and Proteinaceous Materials in a Unique Paint Microsample’, \textit{Analytical Chemistry} 78 (2006): 4490–500.

\textsuperscript{48} Cf. Barbara H. Stuart, \textit{Analytical Techniques in Materials Conservation} (Chichester: John Wiley & Sons, 2007).

\textsuperscript{49} Iva Rezić, Dragica Krstic and Ljerka Bokic, ‘A Note on the Determination of the Binder Composition on an Historic Painted Textile’, \textit{Studies in Conservation} 51, no. 3 (2006): 223–8.
understanding of painted textiles, although currently there is no published research in this area.

5 Non-invasive spectroscopy

Non-invasive spectroscopy has been used in the identification and characterisation of paints and pigments for around 80 years. During the 1980s advances in fibre optic technology led to the development of fibre optic reflectance spectroscopy (FORS).\(^5\) FORS is able to collect data from the visible to the near infrared range (400–1655nm) and is a surface analysis technique that is able to produce spectra for materials such as dyes and pigments. As it requires little material to produce a result, it is ideal for identifying tiny quantities of pigments and dyes. As well as being non-invasive its advantage is that it is relatively portable allowing the object to be examined in-situ. Furthermore, advances in fibre optics have led to improved instrumentation which can measure fluorescence, visible and NIR spectra.

Oriola et al. reported on the use of near infrared spectroscopy (NIR) and multivariate data analysis to non-destructively assist with the characterisation of painted canvases of differing types. The use of NIR allowed spectra of the canvases to be recorded without sampling.\(^5\) These instruments have also been used in the study of silk artefacts.\(^5\)

Although there has been no reported use of these instruments for the study of painted textiles, their use in the analysis of pigments and dyes in easel paintings, frescos and on parchment, and in the analysis of fibre condition, suggest that they are ideal for the study of painted textiles, particularly banners where their large size is often a barrier to non-invasive analysis.

Bacci et al. used FORS in the 270–1700nm range to identify white pigments typically used in twentieth century painting and they concluded that this in-situ, non-invasive method for the identification of the pigments resulted in a simple and safe methodology for the investigation of objects of cultural significance.\(^5\)

Comelli et al. used a multi-analytical approach to the study of wall painting which included in-situ reflectance and fluorescence imaging techniques integrated with analysis of a cross-section of the painting, performed using micro-Raman spectroscopy and SEM. They concluded that although these in-situ instruments gave information regarding decorative elements of the works, for a more complete picture of the materials used additional information from the conservators and from precise information gained from detailed cross-section analysis in the laboratory would be required.\(^5\)

Multi-spectral visible and near-infrared imaging spectroscopy was used by Delaney et al. to identify materials on an illuminated manuscript. By using a variety of techniques to determine the robustness of their methodology the authors concluded that it worked well and that further advances of these techniques would improve the spatial and spectral quality of results.\(^5\)

This type of instrumentation gives information on materials such as pigments present on a painted surface. An advantage of using it in conservation is the fact that it is non-destructive and non-invasive and information from this type of analysis can help indicate where further and more detailed analysis may be required, e.g. where a cross-section sample should be taken.

**Discussion of analytical techniques**

It is evident from this review that these techniques provide potential to develop the study of painted textiles. In recent years the techniques favoured for the identification of pigments (organic and inorganic),
grounds, binders and varnishes have been Raman, surface-enhanced Raman spectroscopy (SERS) and surface-enhanced resonance Raman spectroscopy (SERRS). The most detailed chemical analytical work on painted textiles has been through the use of Raman and FTIR spectroscopy as carried out by Macdonald et al.⁵⁸ Examples from the literature on general dye and pigment analysis show that developments in instrumentation have caused some techniques to be superseded; for example, Raman and more recently SERS are now more often used instead of HPLC to determine organic pigments.⁵⁹ However it is important to be aware that these different techniques provide different information. For example, some techniques, such as Raman, will identify a material but for more detailed information on the components that make up the material further analysis is required, such as with chromatographic analysis, which would separate and detect components of a mixture. In order to gain this better understanding of materials used, it is crucial to understand the capabilities of instruments, including their limits of detection as well as depth and spatial limits.

Conclusions
Painted textiles are heterogeneous, complex and multi-layered in nature, and characterisation of the materials and the techniques used to create painted textiles is crucial to informing our understanding of these artefacts. The conservator has to understand the textile and painted elements, their complex interactions and their often opposing needs in order to make informed decisions about cleaning, stabilisation techniques and preventive care.

Published case studies demonstrate that it is common for the type of textile to be understood and the pigment to be identified but the identification of the binding medium, the preparation of painted textiles and the build-up of their paint layers is generally less well reported. By comparison, much work has been done—and continues to be done—in developing understanding of the materials and application techniques in paintings as well as developing research on modern paints.⁶⁰ By drawing on such research and working in conjunction with scientists, it is possible for textile conservators to benefit from such analytical techniques.⁶¹ However, the study of painted textiles presents particular challenges, particularly in the taking, preparation and study of samples as often there are only a very few, and thin, layers on a flexible surface.

Furthermore, available techniques and types of analysis may need to be adapted for specific use with painted textiles as, for example, analytical noise such as in the high fluorescence present in Raman, are often caused by the combinations and types of materials used. There are also problems encountered in FTIR with over-dominant signals in macro-analysis which result in materials not being identified.⁶²

Parts 1 and 2 of this review on the study of painted textiles have shown that while there are only a handful of papers that involve any analysis of painted textiles, it is clear that a wide range of techniques have been reported for their study (see Table 1) and that the ease of use and the level of skill required to execute the techniques are important considerations (see Table 2).

The questions asked of an object also influence the selection of the most appropriate techniques. Before any analysis on any item of cultural heritage it is important to consider 'what do I want to determine from the analysis?'. Whilst an understanding of the object under examination is important, not too many preconceived ideas of its material composition should be held as this can lead to the identification of only those materials believed to be present, missing others that may be there. Successful analysis depends on

58 Macdonald et al., ‘Raman Microspectroscopy Interrogating 19th- and 20th-Century Painted Trades Union Banners’; Macdonald and Wyeth, ‘On the Use of Photobleaching to Reduce Fluorescence Background in Raman Spectroscopy’.

59 Cf. Hannah Mayhew, David Fabian, Shelley Svoboda and Kristin Wustholz, ‘Surface-Enhanced Raman Spectroscopy Studies of Yellow Organic Dyestuffs and Lake Pigments in Oil Paint’, Analyst 138 (2013): 4493–9; Ambra Idone, Maurizio Aceto, Eliano Diana, Lorenzo Appollonia and Monica Galminti, ‘Surface-Enhanced Raman Scattering for the Analysis of Red Lake Pigments in Painting Layers Mounted in Cross Sections’, Journal of Raman Spectroscopy 45 (2014): 1127–32; Frederica Pozzi, Klaas Jan van den Berg, Inge Fiedler and Francesca Casadio, ‘A Systematic Analysis of Red Lake Pigments in French Impressionist and Post-Impressionist Paintings by Surface-Enhanced Raman Spectroscopy (SERS)’, Journal of Raman Spectroscopy 45 (2014): 1119–26.

60 See, for example, Joyce Townsend and Jaap J. Boon, ‘Research and Instrumental Analysis in the Materials of Easel Paintings’, in Conservation of Easel Paintings, ed. Joyce Hill Stoner and Rebecca Rushfield (London: Routledge, 2012), 341–65; Erma Hermens, ‘Technical Art History: The Synergy of Art, Conservation and Science’, in Art History and Visual Studies in Europe: Transnational Discourses and National Frameworks, ed. Matthew Rampley, Thierry Lenain, Hubert Locher, Andrea Pinotti, Charlotte Schoell-Glass and Kitty Zijlmans (Leiden: Brill, 2012), 151–66; Erma Hermens, ‘Rembrandt’s Entombment Sketch: The Passion in Paint, a Technical Investigation’, in Rembrandt and the Passion, ed. Peter Black and Emma Hermens (London/Munich/New York: Prestel, 2012), 101–34.

61 Cf. Lorna Lee, ‘Analysis—An Aid to Conservation’, in Painted Textiles: Postprints of the Forum Held at the Museum of London, 21 April 1997, ed. Vivian Lochhead (London: UKIC, 1997), 12 pp. not numbered.

62 Margaret J Smith, Karen Thompson, and Emma Hermens, ‘Breaking down
| Author                                      | Object                | Microscopy | X-radiography | SEM | SEM-EDX/EDS | XRD | XRF | FTIR/FTIR-ATR | Raman | GC | HPLC/TLC | IR-Reflectography |
|---------------------------------------------|-----------------------|------------|---------------|-----|-------------|-----|-----|----------------|-------|----|---------|------------------|
| Skelton and Lee-Whitman, 1986               | Painted silk          |            |               |     |             |     |     |                |       |    |         |                  |
| Lennard, 1989                               | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Bilson, 1992                                | Roman Egyptian shroud |            | ✓             | ✓   | ✓           |     |     |                |       |    |         |                  |
| Pollak, 1993                                | Painted silk dress    | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Reiter and Price, 1995                      | Painted silk dress    | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Martin, 1995                                | Painted silk dress    | ✓          |               |     |             |     |     |                |       |    |         |                  |
| McGlinchey, 1995                           | Painted silk          | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Rogerson and Eastop, 1999                   | Textiles inc painted  | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Villers, 2000                               | Painted cloth         | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Hale, 2000                                  | Painted cloth         | ✓          |               |     | ✓           |     |     |                |       |    | ✓       |                  |
| Schießl et al., 2000                        | Painted cloth         | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Takami and Eastop, 2002                     | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Takami and Wyeth, 2002                      | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Macdonald et al., 2003                      | Painted silk chair cover |          |               |     |             |     |     |                |       |    |         |                  |
| Rode, 2003                                  | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Macdonald et al., 2005                      | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Rogerson and Lennard, 2005                  | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Rezić et al., 2006                          | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Macdonald and Wyeth, 2006                   | Painted silk chair cover |          |               |     |             |     |     |                |       |    |         |                  |
| O’Connor and Brookes, 2007                  | Textile objects       | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Abdel-Kareem et al., 2008                   | Egyptian textiles     | ✓          |               |     |             |     |     |                |       |    |         |                  |
| McLeod, 2012                                | Indian Jain Painting  | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Tonkin, 2012                                | Banner                | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Wild, 2012                                  | Pichhva               | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Lennard et al., 2013                        | Flag                  | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Kleiner, 2013                               | Fourteenth century banner |       |               |     |             |     |     |                |       |    |         |                  |
| Thompson and Lennard, 2013                   | Theatre scenery       | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Ernst, 2014                                 | Thangka               | ✓          |               |     |             |     |     |                |       |    |         |                  |
| Smith et al., 2016                          | Banner                | ✓          |               |     |             |     |     |                |       |    | ✓       |                  |
Table 2 Spectroscopic and chromatographic techniques for use in the study of painted textiles.

| Method/Technique         | Preparation                        | Ease of use | Information gained                                      | Qualify | Quantify |
|--------------------------|------------------------------------|-------------|--------------------------------------------------------|---------|----------|
| XRD                      | Sample or small object             | Highly skilled | Identification of elements                              | ✓       | ✓        |
| XRF                      | Sample or small object             | Highly skilled | Identification of elements                              | ✓       | ✓        |
| FTIR macro and micro     | Sample loose, embedded or object   | Highly skilled | Finger print of organic and inorganic materials        | ✓       | ✓        |
| Raman (SERS and SERRS)   | Sample loose or embedded           | Highly skilled | Precise identification of material                      | ✓       | ?        |

Chromatography:
- HPLC: Sample extracted into solvent, Highly skilled, Identification and separation of material mixture
- GC: Sample extracted into solvent, Highly skilled, Identification and separation of material mixture
- Thin layer: Sample extracted into solvent, Skilled, Identification and separation of material mixture

Note: *These also come as portable instruments allowing them to be taken to an object and negating the need for sampling. ?Quantitative analysis is very dependent on the quality of the spectra and how the analysis can be carried out.

Table 3 Analysis of painted textiles—guide to materials characterisation.

| Support                  | Base or preparatory layer          | Ground and paint layers                                      | Varnish/Resin top layer                  |
|--------------------------|------------------------------------|--------------------------------------------------------------|-----------------------------------------|
| Ease of use, interpretation and access | e.g. silk, cotton, linen          | e.g. organic or inorganic pigments, oils                     | e.g. shellac, mastic                    |
|                          | Stain and solubility tests         | Stain and solubility for oils                                | Stain and solubility tests              |
|                          | Low level microscopy               | High level microscopy (fluorescence)                         | High level microscopy (polarised and fluorescence) |
|                          | SEM/EDX                            | SEM                                                          | Macro and micro FTIR/ATR               |
|                          | Macro and micro FTIR/ATR           | GC/MS; SIMS                                                  | HPLC                                    |

A literature review of analytical techniques for materials characterisation of painted textiles—Part 2: Spectroscopic and chromatographic analytical instrumentation
the interpretation and understanding of the data, to avoid misinterpretation and, more importantly, the publication of incorrect information. While manufacturers increasingly develop instruments that are ‘easy to use’, ultimately the value of analysis should be in its rigorous interpretation, something that can only be achieved by an understanding of the scientific principles behind the analysis.

Ideally a variety of techniques would be used as together they build a more complete understanding of the range of materials present, and this review demonstrates that no one analytical technique will be capable of identifying all materials; they are complementary. The review shows how useful such complementary techniques can be for understanding the material properties of painted textiles as illustrated, for example, by Franquela et al. who used both micro-Raman and micro-FTIR to characterise pigments, and Rode who used FTIR to first identify the presence of metal soaps on a banner and followed this with GC–MS to fully categorise it. Table 3 summarises how different techniques can be used to identify their different components. However, one caveat is that both sample size and accessibility ultimately influence the techniques which can be used, including whether or not in-situ analysis can be carried out using a portable analyser, such as hand-held Raman, fibre optic FTIR or hand-held XRF.

It is evident from the review of the publications describing the analysis of the materials and their deterioration that knowledge and understanding of painted textiles is variable. Conservators and curators may only wish to identify or confirm the presence of a particular material, and this has led to the publication of many extremely enlightening and informative technical papers, but the results do not always speak for themselves. In order to understand these issues better more research is needed on the materials, their interactions and the determination of the agents of deterioration in order to further develop the care of these textiles. One such gap readily identifiable is the study of their materials and condition related to their use—for example, it was not uncommon for banners to have undergone restoration for continued use, but little research has been carried out in this area. As banners have been carried in the wind and rain and often stored damp, this can have profound implications for any understanding of the agents of deterioration. In-depth examination and interpretation is required in order to better understand the interactions occurring at a banner’s interfaces and surfaces so as to help the conservator to more effectively preserve these socially significant cultural objects.

The most informative research relating to painted textiles comes from work involving close collaboration between conservators and scientists. Collaboration provides the opportunity to exploit the full capabilities of the analytical techniques and maximise any subsequent output from the often limited sample sizes or access to analysis itself.

From the discussions within this article it is clear that there is scope to use those newer analytical techniques already reported in wider cultural heritage studies. The objects themselves provide an invaluable source to learn more about their materials and to inform conservation. It is by comparing their similarities and differences within the different categories of painted textiles and with other painted objects, that the study of painted textiles can be advanced.

63 See, for example, María Luisa Franquela, Adrian Duran, Liz Karen Herrera, M. C. Jimenez de Haro and J. L. Perez-Rodriguez, ‘Comparison between Micro-Raman and Micro-FTIR Spectroscopy Techniques for the Characterization of Pigments from Southern Spain Cultural Heritage’, Journal of Molecular Structure 924 (2009): 404–12; Rode, ‘Towards an Understanding of Whitening’.

64 Cf. Debbie Lauwers, Anna Garcia Hutado, Vinka Tanevska, Luc Moens, Danilo Bersani and Peter Vandenabeele, ‘Characterisation of a Portable Raman Spectrometer for In Situ Analysis of Art Objects’, Spectrochimica Acta Part A—Molecular and Biomolecular Spectroscopy 118 (2014): 294–301; Camilla Ricci, Costanza Milani, Bruno Brunetti and Antonio Sgamellotti, ‘Non-Invasive Identification of Surface Materials on Marble Artifacts with Fiber Optic Mid-FTIR Reflectance Spectroscopy’, Talanta 69 (2006): 1221–6; François-Philippe Hocquet, Henri-Pierre Garnir, A. Marchal, M. Clar, Cécile Oger and David Strivay, ‘A Remote Controlled XRF System for Field Analysis of Cultural Heritage Objects’, X-Ray Spectrometry 37 (2008): 304–8.
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Abstract
Part 2 of this Literature Review of analytical techniques for materials characterisation of painted textiles focusses on the application of vibrational and X-ray spectroscopic and chromatographic techniques used in the analysis of painted textiles to inform understanding of their materials, methods of making and degradation. The principles of detection methods, technique limitations and advantages, and how they complement each other, are explained and advances in techniques applicable in the study of painted textiles are discussed, such as mapping in Fourier transform infrared spectroscopy and Raman, surface-enhanced resonance Raman spectroscopy, and secondary ion mass spectrometry. Most informative work relating to painted textiles comes from close collaboration between conservators and scientists in interpreting findings and this literature review provides a useful starting point to further develop the capabilities of analytical techniques to enhance the study and conservation of painted textiles.

Résumé
Partie 2 de cette révision bibliographique de techniques analytiques pour la caractérisation des matériaux de textiles peints se concentre sur l’application des techniques spectroscopiques et cromatographiques utilisées dans l’analyse des textiles peints pour comprendre leurs matériaux, leurs méthodes de fabrication et leur dégradation. Les principes des méthodes de détection, leurs limites et leurs avantages techniques, et la façon dont elles se complètent, sont expliqués. Les progrès dans les techniques applicables à l’étude des textiles peints, telles que la cartographie avec la spectroscopie infrarouge à transformée de Fourier, la spectroscopie Raman exaltée de surface et la spectrométrie de masse d’ions secondaires sont discutés. Les travaux les plus informatifs relatifs aux textiles peints proviennent d’une collaboration étroite entre conservateurs et scientifiques pour interpréter les résultats et cette revue littéraire constitue un point de départ utile pour développer davantage les capacités des techniques analytiques afin d’améliorer l’étude et la conservation des textiles peints.

Zusammenfassung
Teil 2 der Analyse der Literatur zu Analytischen Methoden der Materialcharakterisierung bemalter Textilien konzentriert sich auf die Anwendung von Vibrations- und Röntgenspektroskopie und Methoden der Chromatographie, die in der Analyse bemalter Textilien eingesetzt werden, um ihre Materialien, Herstellung und Verfallerscheinungen zu verstehen. Die Prinzipien der Analysemethoden, ihre Grenzen und Vorteile, sowie ihre jeweilige Ergänzung werden erklärt. Ebenso werden die Fortschritte in den Methoden diskutiert, die sich auf die Erforschung bemalter Textilien anwenden lassen, wie z.B. Mapping durch Fouriertransforminfrarotspektroskopie und Raman, Oberflächenverstärkte Resonanzamanspektroskopie und sekundäre Ionenmassenspektrometrie. Eine Großzahl informativer Werke bemalte Textilien betreffend entstammt der engen Zusammenarbeit zwischen Restauratoren und Wissenschaftlern bei der Interpretation der Resultate. Diese Literaturschau gibt einen nützlichen Anfangspunkt, um die Möglichkeiten der Analyse für das Studium und die Erhaltung bemalter Textilien weiter zu entwickeln.

Resumen
“Un estudio bibliográfico de técnicas analíticas para la caracterización de materiales de textiles pintados. Segunda parte: instrumentación analítica espectrosóptica y cromatográfica”
La segunda parte de esta revisión bibliográfica de técnicas analíticas para la caracterización de materiales de textiles pintados se centra en la aplicación de técnicas espectrosópticas y cromatográficas de vibración y rayos X utilizadas en el análisis de textiles pintados con el fin de poder conocer mejor estos materiales, sus métodos de fabricación y su degradación. Se explican los principios de los métodos de detección, las limitaciones y ventajas de las diferentes técnicas y cómo se complementan entre sí. También se discuten los avances de técnicas aplicables al estudio de los textiles pintados, como la cartografía de espectroscopia infrarroja transformada de Fourier y Raman, la espectroscopía de resonancias de superficie incrementada Raman o la espectrometría de masas de iones secundarios. Los estudios más informativos relacionados con los textiles pintados provienen de colaboraciones entre conservadores y científicos a la hora de interpretar los resultados. Este estudio bibliográfico proporciona un punto de partida útil para desarrollar el potencial de estas técnicas analíticas y así mejorar el estudio y la conservación de los textiles pintados.

Biographies
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Margaret Smith, BSc, MSc, PhD is a research scientist and lecturer at the Centre for Textile Conservation and Technical Art History, University of Glasgow. Previously, she was a research chemist for 21 years in academia and industry, where she gained extensive experience in analytical techniques and materials behaviour. Her research now focuses on painted textiles, including banners and barkcloth, and the physical and chemical aspects of tapestry deterioration. Her main research expertise lies in studying the degradation rates of materials, the effects of environmental conditions on those rates, and the interaction of different materials at surfaces and interfaces.

Frances Lennard, BA(Hons), PGDip, FHEA, ACR, FIIC is a lecturer of Textile Conservation and the convenor of the MPhil Textile Conservation programme at the Centre for Textile Conservation and Technical Art History, University of Glasgow. She is...
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