

Trends in Spectroscopy and Imaging for Heritage and Archaeology: a meta-analysis of the last decade with a UK and Ireland focus

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A report that uses publications in the field since 2010 to look at trends, users & patterns of use of various spectroscopic and spectral imaging techniques in heritage and Archaeology.

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(i) Introduction

This report uses metadata and survey data to outline trends in the use of spectroscopy and spectral imaging for heritage studies and archaeology since 2010, with a focus on the situation in the UK and Ireland. Spectroscopic techniques have been applied to a wide variety of topics in these two disciplines, with multiple techniques often complementing each other (Table 1). Metadata analyses provide an overarching view of publication trends and the various applications of these technologies in the UK and Ireland. Complementing that analysis, surveys of people applying these techniques offers impressions of future research directions, user assessments of instrumentation, an overview into how equipment is used, and insight into the main forums of discussion/dissemination.

Topic	Instruments
Bone Characterisation	Vis-NIR, FTIR, Raman, XRF, Spectral Imaging
Ceramic Composition	FTIR, Raman, XRF
Construction Material Characterisation	Vis-NIR, Raman, XRF, Spectral Imaging
Design Reconstruction	FTIR, Raman, Spectral Imaging
Document Conservation	Spectral Imaging
Glaze/Enamel Chemistry	XRF
Material Degradation	Vis-NIR, FTIR, Raman, Spectral Imaging
Metal Characterisation	Raman, XRF, Spectral Imaging
Mineral Characterisation	Vis-NIR, FTIR, Raman, XRF
Misc. Organics Characterisation	FTIR, Raman
Painting Process and Sequence	Spectral Imaging
Paper Characterisation	Vis-NIR, FTIR, Spectral Imaging
Particle Characterisation	Raman
Pigment Chemistry	Vis-NIR, FTIR, Raman, XRF, Spectral Imaging
Plastic Conservation	Vis-NIR, FTIR
Residue Analysis	Raman, XRF
Resin Chemistry	Raman, XRF
Sediment Characterisation	XRF
Shell Characterisation	FTIR
Aerial Site Mapping/Identification	Spectral Imaging
Textile Characterisation	Vis-NIR, FTIR, Raman, Spectral Imaging
Wood Characterisation	FTIR, Raman, XRF

Table 1: Key heritage and archaeology research topics and the spectroscopic techniques used to address them

For an overview of typical processes for using the various types of spectroscopy discussed here please see Appendix A.

(ii) *Methods: gathering metadata and surveys*

Data on global and just UK and Ireland heritage and archaeology research papers was gathered using online database searches. Global data was gathered via specific searches the online Web of Science (WoS)¹ database offered by Clarivate Analytics. WoS offers analytics for any search that breaks down information on, for example, how many papers were published in any one year, which countries or regions authors were based in (at the time of publication), and the specific journals where papers were published. To this end, 12 specific WoS searches of “all databases”² (for list of search terms see Appendix B) for papers between 2010 and 2019 were carried out.

To build a picture of UK and Ireland trends a slightly different approach was taken in order to maximize coverage of publications since 2010 and to provide a greater degree of detail. In this case the Google Scholar³ database was employed; again using specific relevant search terms for publications since 2010. Fourteen searches were made (see Appendix B for search terms), and a “deep dive” made through the results, recording the details of any paper with at least one author based in the UK or Ireland (e.g. years, authors, topics, instruments used). Each deep dive search involved the author checking every result until they became repetitive or irrelevant; this process usually meant 200-300 papers were looked at for each search term. The details of papers appearing in the WoS search that did not come up in the Google Scholar search were also recorded.

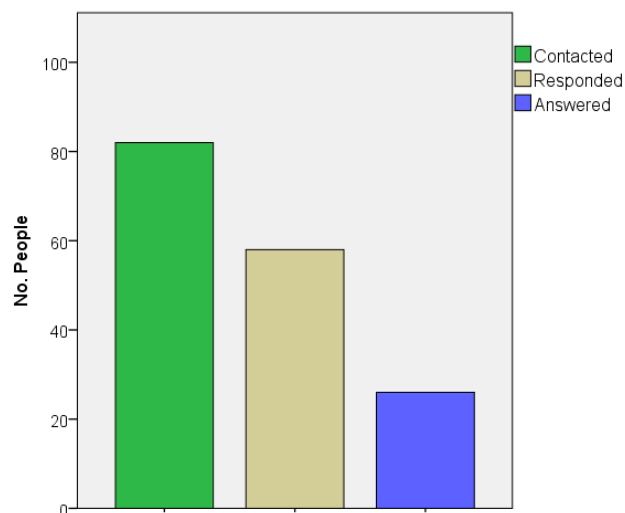


Figure 1: Visualisation of survey contacts and responses

Survey questionnaires were sent to active heritage scientists and archaeologists in universities and national heritage charities. The surveys asked about their use of spectroscopy or imaging

¹ www.webofknowledge.com

² WoS offers the option to restrict searches to specific databases or types of database

³ scholar.google.co.uk


in their research, their opinions on future trends or developments, opinions on the key points of relevant spectroscopic instruments, their access to equipment (i.e. whether their institution own instruments, whether they borrowed from another department or institution, and general lending patterns), and where key discussions of results and methodology tend to take place (see Appendix C). Individuals were identified via the searches above, with the most active researchers contacted via email to ask whether they would participate. In addition, researchers involved in current relevant heritage or archaeological projects listed on the UK Research and Innovation (UKRI) project database⁴ were contacted; as were individuals from national heritage foundations or governmental bodies identified as using spectroscopic methods.

In total, 82 researchers were sent initial emails, and of these 58 responded, either to say they would participate in the survey or to decline (some directed me to other scholars, who were then contacted – these individuals are included in the current figures) (Fig. 1). Twenty-six researchers from a variety of institutions answered the survey questions before the end of the project (Fig. 1), so almost one-third of those contacted initially eventually took the survey.

⁴ gtr.ukri.org

(iii) Trends in Spectroscopy and Spectral Imaging: specific techniques

(iii-i) Visible-Near Infrared Spectroscopy (Vis-NIR)



Vis-NIR Spectroscopy

- Pigment Chemistry**
- Paper Characterisation**
- Textile Characterisation**
- Construction Materials**
- Material Degradation**
- Plastics Conservation**
- Bone Characterisation**

(image courtesy of Analytik Ltd.)

Globally, since around 2015, there has been a relatively large increase in the use of vis-NIR in heritage studies (Fig. 2a). Applications of this technology in archaeology have also grown yet only slightly and thus remain quite rare. In the UK and Ireland the general trend in application appears flat, with noticeable spikes in output likely reflecting the outcomes from specific projects/work groups (Fig. 2b).

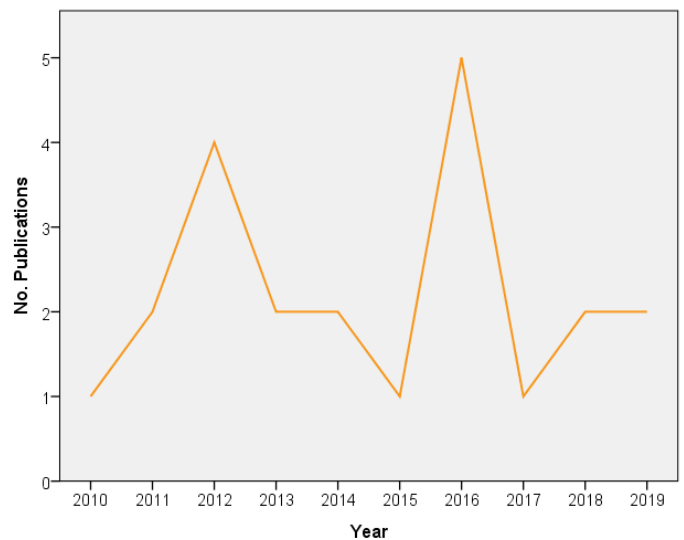
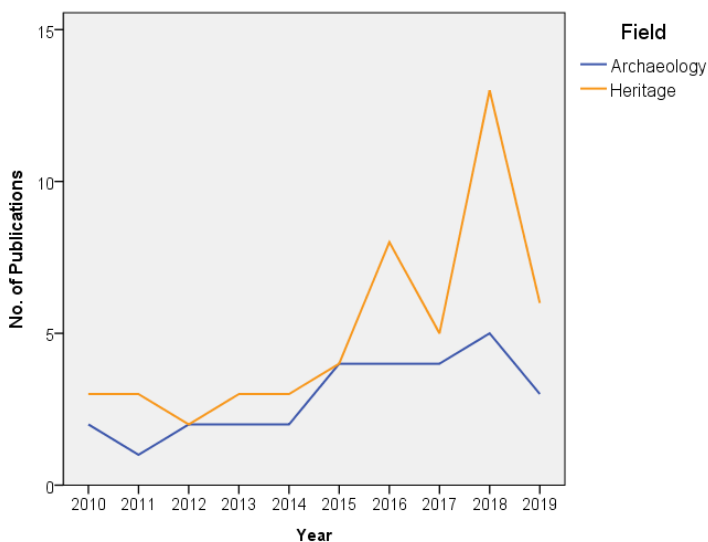


Figure 2: (a) global trends in and heritage and archaeology publications using vis-NIR since 2010 (left); (b) UK and Ireland trends in heritage publications using vis-NIR since 2010 (right)

Scholars based in 24 countries have been involved in work using vis-NIR since 2010. The noted spike in heritage interest was primarily driven by Italian scholars, where 58% of heritage papers using vis-NIR involved Italian laboratories or included scholars based in Italy. The next largest centres of such research were the UK and USA, with 18% of publications involving one or more authors based in one of those two countries.

Scholars from 22 nations applied vis-NIR to archaeological questions, with a fairly even spread among those nations. Around 28% of publications involved scholars from Chinese institutions, while Belgium (17%), France (14%), Germany (14%), New Zealand (14%), and Sweden (14%) were also relatively active in using these techniques.

Ten UK and Ireland based heritage and archaeology scholars responded to the survey questions. Of these, 8 thought that there was good scope for growth in the use of vis-NIR in their respective specialisms. Indeed, the International Conference for Near-Infrared Spectroscopy held its first ever session dedicated to heritage and archaeology in 2019, further highlighting growing global interest in the technique (see Fig. 1a). One respondent noted a growth in publications over the past 5 years, and suggested that cheaper equipment and more refined models for the interpretation of spectra has made vis-NIR a more accessible technique.

Despite the general positivity, two respondents noted that the potential for new entrants into the field was somewhat limited. Lack of funds, training, and facilities outside of existing large centres of research (e.g. the British Library, the Bodleian Library) were cited as barriers to an expansion of expertise.

Heritage

Topic	Number of Publications
Construction Material Characterisation	1
Material Degradation	1
Paper Characterisation	2
Pigment Chemistry	13
Plastic Conservation	1
Textile Characterisation	3

Table 2: Uses of vis-NIR in heritage publications involving UK or Ireland based scholars since 2010 (for list of papers see supplement)

While vis-NIR is used to study various types of material, far and away the most common application in heritage studies has been investigations of pigment chemistry (including binders) (Table 2). The predominant targets of analysis were either paintings or illuminated manuscripts, with the typical aim of characterising artists' palates, their techniques, or the compositions/origins of the pigments themselves. More recently, historical maps (Kogou et al, 2016) or textile dyes (Tamburini & Dyer, 2019) have also been analysed. Pigment chemistry is the only topic with a consistent publication output year-on-year since 2010, while applications to novel materials (e.g. paper, textiles, earthen building materials) generally do not extend beyond 2014.

Eight survey respondents used vis-NIR in heritage science, and they had a variety of interests and applications:

- Tracking artefact degradation via changes to colour spectra
- Identifying the presence of certain pollutants on artefacts
- Identifying plastic types and their compositions
- Investigating pigments and binder chemistry
- Characterising the physical state of paper, canvas, or tapestry

The crucial importance of vis-NIR spectroscopy's non-destructive nature and ability to carry out *in situ* analyses were stressed by all. Delicate, expensive, and/or large heritage items obviously require great care to study, and non-destructive analysis that can be brought to the items in museums and collections was variously described as "essential", "extremely useful", or "highly desirable". One respondent also noted the relative ease in training new users, along with the fact that such instruments tend to be more robust and require less maintenance than other equipment.

Further, the lower cost of portable instruments was highlighted, although the quality of spectra was suggested by one respondent to be lower. Even so, another respondent noted that portable vis-NIR (and other) technology was catching up with lab-based equipment.

Archaeology

Since 2010 only two papers have been published that involved UK or Ireland based authors applying vis-NIR to archaeological questions. Both applications investigated the mineral compositions of certain materials but in radically different settings. Anderson et al (2014) applied vis-NIR to plasters and natural sediments to help source Neolithic period wall plaster. On the other hand, Blasco-Martin et al (2019) used NIR spectroscopy to successfully identify the materials used to decorate ivory artefacts from Iron Age Iberia.

A newly emerging use of vis-NIR is the application to archaeological bone samples. The

technique is described by one survey respondent as offering a fast and reliable screening method for identifying bone collagen content, a proxy for preservation and the suitability of a sample for further analysis (e.g. DNA analysis, paleoproteomics, radiocarbon dating) (Sponheimer et al, 2019). The two archaeologists surveyed about vis-NIR both noted that the technique offers deeper penetration than FTIR. One further argued that this technique should become standard practice in museums with a bone collection; suitable samples could be quickly and easily identified, thus preserving those that may otherwise needlessly be subjected to destructive analyses.

(iii-ii) Fourier-Transform Infrared Spectroscopy (FTIR)



FTIR Spectroscopy

Pigment Chemistry

Material Degradation

Wood Characterisation

Textile Characterisation

Plastic Conservation

Bone Characterisation

(image courtesy of Analytik Ltd.)

There has been a relatively steady increase in the use of FTIR in heritage studies since 2010, with some large spikes for heritage publications in recent years (Fig. 3a). Applications of this technology in archaeology have grown only slightly; whether the jump in interest in 2018 (which falls off in 2019) is sustained remains to be seen. In the UK and Ireland the general trend in FTIR application to archaeological questions appears flat, but use in heritage studies shows a broad increase (Fig. 3b).

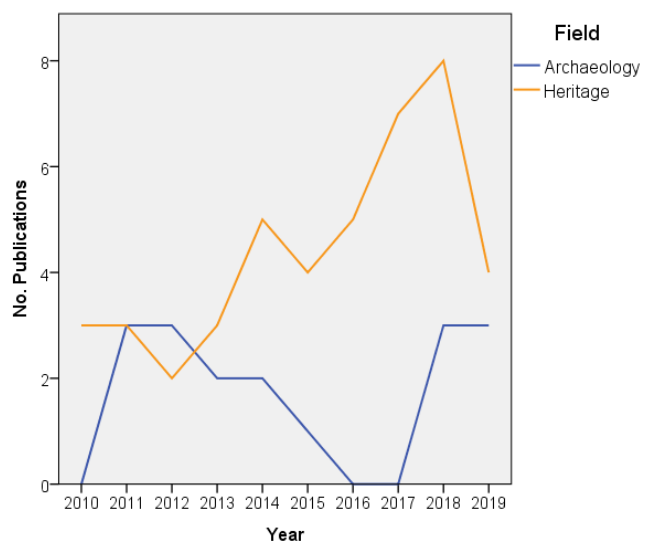
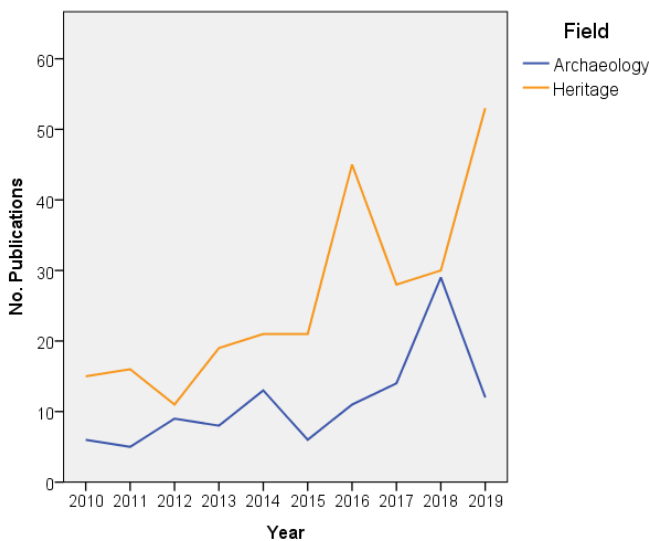


Figure 3: (a) global trends in and heritage and archaeology publications using FTIR since 2010 (left); (b) UK and Ireland trends in heritage and archaeology publications using FTIR since 2010 (right)

Scholars based in 47 countries carried out research using FTIR since 2010. Researchers from Italy, Spain, and Romania have driven the bulk of heritage research using FTIR, where respectively 32%, 15%, and 10% of heritage publications using that technique involved scholars based in those three countries.

In archaeology, scholars from 39 countries were involved in research using FTIR. Italy (23%), the UK (15%), and the United States (12%) were the top three research centres, although scholars based in China (11%), Spain (10%) and Germany (9%) have also been involved in a relatively high number of publications.

Ten UK and Ireland based heritage and archaeology scholars who use or have used FTIR spectroscopy responded to the survey. Six indicated that there was scope for growth in FTIR use within their respective fields, either in terms of use on specific materials or a scope for application to a wider range of materials. Three respondents saw the technique as at limit, but did qualify that their opinions related to their specific applications of FTIR rather than more broadly (one person did not give an opinion). Similarly, the three respondents that did not expect FTIR use to grow in future all applied FTIR to archaeological bone; an application perhaps more suited to vis-NIR moving forward (see vis-NIR Spectroscopy section). One respondent from the heritage sector noted the increase in interest since 2015 reflected in Fig. 3(a).

Some respondents highlighted potential limits to the perceived growth potential in their specialist areas. For example calibration issues for archaeological pigments were mentioned by one archaeologist, as was the lack of baseline work for archaeological wood by another. The small size of particular research communities was also suggested as a limiting factor by one scholar who uses FTIR to characterise archaeological shell.

Heritage

Topic	Number of Publications
Design Reconstruction	2
Material Degradation	5
Mineral Characterisation	1
Paper Characterisation	2
Pigment Chemistry	21
Plastic Conservation	4
Textile Characterisation	4
Wood Characterisation	5

Table 3: Uses of FTIR in heritage publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

Since 2010 almost half of UK and Ireland based heritage publications that used FTIR were investigating pigment chemistry (Table 3). Most such studies investigated paintings (e.g. museum pieces, wall murals, illuminated manuscripts), however inks (Bardon et al, 2013), dyes (Wertz, 2017; Wertz et al, 2017; 2018), or pigments on other types of material (e.g. a cabinet – Burgio et al, 2018; a medieval parade shield – Sanders et al, 2012) were also targeted. Pigment chemistry was the only single category that has had a consistent publication output since 2010.

Studies into material degradation and conservation techniques are also well represented, variably crossing four of the categories in Table 3 (material degradation, plastic conservation, wood characterisation, textile characterisation). In addition to wood and plastics/polymers, FTIR spectroscopy has been used to track proxies for degradation in glass (Rodrigues et al, 2018a; 2018b), paint (Vichi et al, 2019), organic materials like bone, antler or ivory (Simpson, 2011), and wool (Kissi et al, 2017). Cumulatively these applications represent a significant portion of the work with FTIR since 2010.

Three survey respondents used FTIR in heritage science, and they had variety of interests and applications:

- Identifying plastic and other polymer types and their material composition
- Characterising varnishes and binding materials
- Tracking artefact degradation via changes to colour spectra
- Identifying the presence of certain pollutants on artefacts
- Experimental uses to track glass or rubber degradation

Respondents stressed the importance of FTIR spectroscopy's non-destructive or non-invasive analyses, clearly essential for valuable and fragile heritage items. Portability of instruments was described as useful or desirable, facilitating on-site analysis of items too valuable or large to move to a laboratory and quick surveys of many objects (although at a cost of lower signal strength relative to lab-based instruments). One respondent also highlighted FTIR's relative ease of use and low maintenance costs.

Archaeology

Topic	Number of Publications
Bone Characterisation	7
Ceramic Composition	1
Mineral Characterisation	2
Misc. Organics Characterisation	2
Pigment Chemistry	2
Shell Characterisation	1
Wood Characterisation	2

Table 4: Uses of FTIR in archaeology publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

The most common use of FTIR in archaeology has been to characterise the preservation levels of archaeological bone samples via investigating their crystal structure or the relative levels of particular proxies indicating decay (e.g. collagen levels) (Table 4). FTIR has also been used sporadically on other materials with similar aims, for example shell (Loftus et al, 2015), wood (Ascough et al, 2011; Vaiglova et al, 2014), or charred cereal grains (Styring et al, 2013).

Seven survey respondents used FTIR to study archaeological material. They had variety of interests and applications:

- Identifying the presence of organic material in rock art pigments
- Characterising the compositions of archaeological sediments
- Identifying molecules characteristic of decay in wood, seeds, or animal materials (e.g. leather)
- Identifying the levels of aragonite to calcite recrystallisation in archaeological marine shell
- Gauging the level of proxies for archaeological bone degradation (e.g. collagen levels, phosphate levels)

Survey respondents emphasised the flexibility, ease of use, and relatively low cost of FTIR spectrometers. FTIR can be applied to a variety of archaeological materials both in the lab and in the field. Portability was not universally desired or required though, but opinion was strongly related to the particular uses the respondents were putting the techniques to. Lab-based work using powdered samples would not really require portability, however characterising soils/sediments during excavation, examining rock art *in situ* and pre-

screening samples in museum collections or the field makes instrument portability essential.

(iii-iii) Raman Spectroscopy



Raman Spectroscopy

Pigment Chemistry

Material Degradation

Design Reconstruction

**Textile
Characterisation**

Ceramic Composition

**Characterising Organic
Materials**

(image courtesy of Analytik Ltd.)

Globally, since 2010, the use of Raman Spectroscopy in heritage and archaeology research has grown significantly. In particular a noticeable jump in both heritage and archaeology occurred in 2016, with sustained interest since then (Fig. 4a). In the UK and Ireland however only the growth of Raman usage in heritage research matches the global pattern (Fig. 4b). The employment of this technology in archaeological work has been sporadic and not particularly widespread in terms of overall publication numbers.

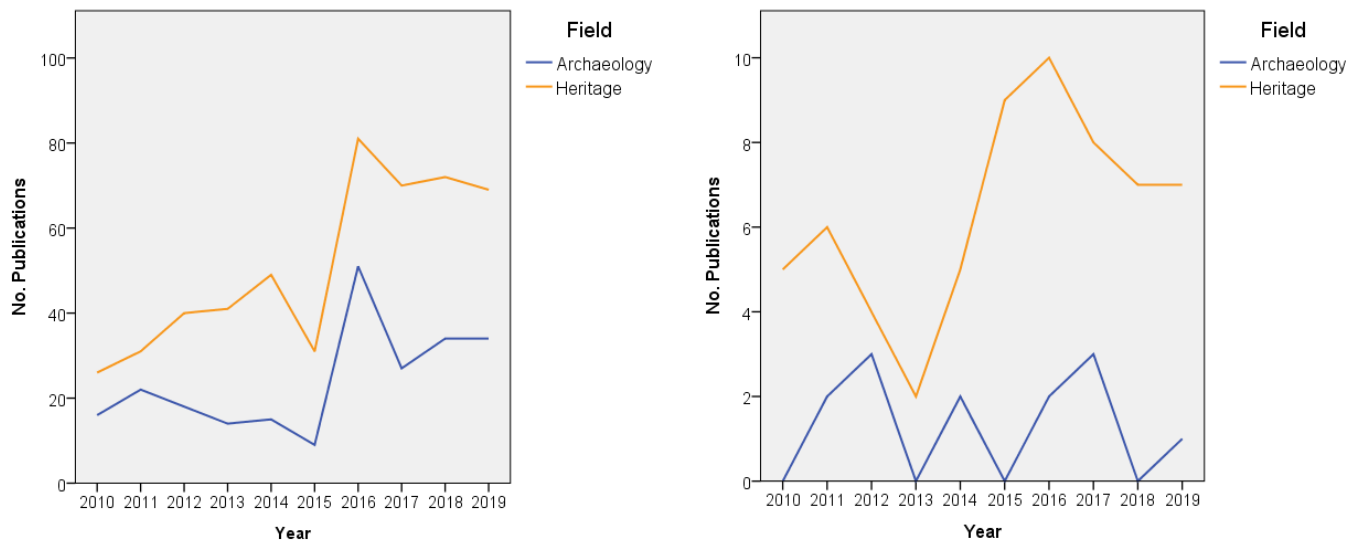


Figure 4: (a) global trends in and heritage and archaeology publications using Raman Spectroscopy since 2010 (left); (b) UK and Ireland trends in heritage and archaeology publications using Raman Spectroscopy since 2010 (right).

Since 2010, scholars from 51 countries have participated in published heritage research using Raman Spectroscopy. That research has been heavily concentrated in Italy and Spain, whereby 33% and 23% (respectively) of publications have involvement from scholars based in those two nations. Researchers from the UK (11%) and the USA (11%) were also relatively common.

In archaeology researchers from 44 nations have been involved with publications utilising Raman. As above, Italy and Spain were the top two centres for such research, with 25% of papers having Italian scholars' involved and 17% Spanish. Researchers based in the UK (13%), France (13%), China (10%), the USA (10%), and Belgium (10%) also made significant contributions to archaeological papers using Raman Spectroscopy.

Ten UK or Ireland based scholars that have recently used Raman Spectroscopy responded to the survey questions. Of these, 6 saw scope for growth in interest into the future, with one heritage research fellow saying that *"there is certainly a growth in interest in technical study of fine art"*. Only one respondent saw the Raman market as saturated, while three had a neutral or non-specified view of future trends.

Even though the majority of respondents had a generally positive view of the future interest and use of Raman several still highlighted particular issues that they thought could or would be barriers to expansion. The first issue, mentioned by four respondents, involved concerns over damage to target items, particularly paintings, manuscripts or rock art; damage could be caused by laser intensity or the need for very close/direct contact with a piece in some cases. Another concern, again raised by three of the respondents, was a lack of expertise and facilities outside of a few centres. Without investment in those areas any scope for growth

will be limited.

Heritage

Topic	Number of Publications
Construction Material Conservation	1
Design Reconstruction	2
Material Degradation	3
Metal Characterisation	1
Mineral Characterisation	1
Particle Characterisation	1
Pigment Chemistry	49
Resin Chemistry	1
Textile Characterisation	2
Wood Characterisation	1

Table 5: Uses of Raman Spectroscopy in heritage publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

Since 2010 almost 80% of UK and Ireland based heritage publications that used Raman spectroscopy were studying pigment chemistry (Table 5). The most common applications of Raman were to paintings or manuscripts, to characterise artist’s palates or date/provenance pigments. There have been several applications to novel materials, for example textile dyes (Hadian et al, 2012), inks (Paintanida et al, 2013), or pigments on ceramics (Rosi et al, 2011), but these were singular attempts clustering at the start of the study period.

Recent novel applications include those on metal (Di Martino et al, 2019), construction materials (Columbu et al, 2018), and wood (Berenguer et al, 2019). Whether such research becomes more common in the future remains to be seen, but investigations of pigment chemistry will remain the staple use of Raman for the foreseeable future.

Eight survey respondents used Raman Spectroscopy in heritage science, studying a range of materials:

- Characterising pigments on paintings and illuminated manuscripts
- Analysing paints on sculptures and frescoes
- Identification of materials within ceramics
- Identifying gems or other inorganic material
- Investigating traces of corrosion or material degradation over time

The non-invasive nature of Raman Spectroscopy was highlighted by respondents, obviously important when dealing with sensitive artefacts. Portability of instruments was universally

described as important or essential, especially for very delicate items like manuscripts, or very large artefacts. However, one heritage researcher described portability as “*both a blessing and a curse*”, noting that cheaper portable systems may be applied incorrectly by the inexperienced, thus causing damage to artefacts.

Archaeology

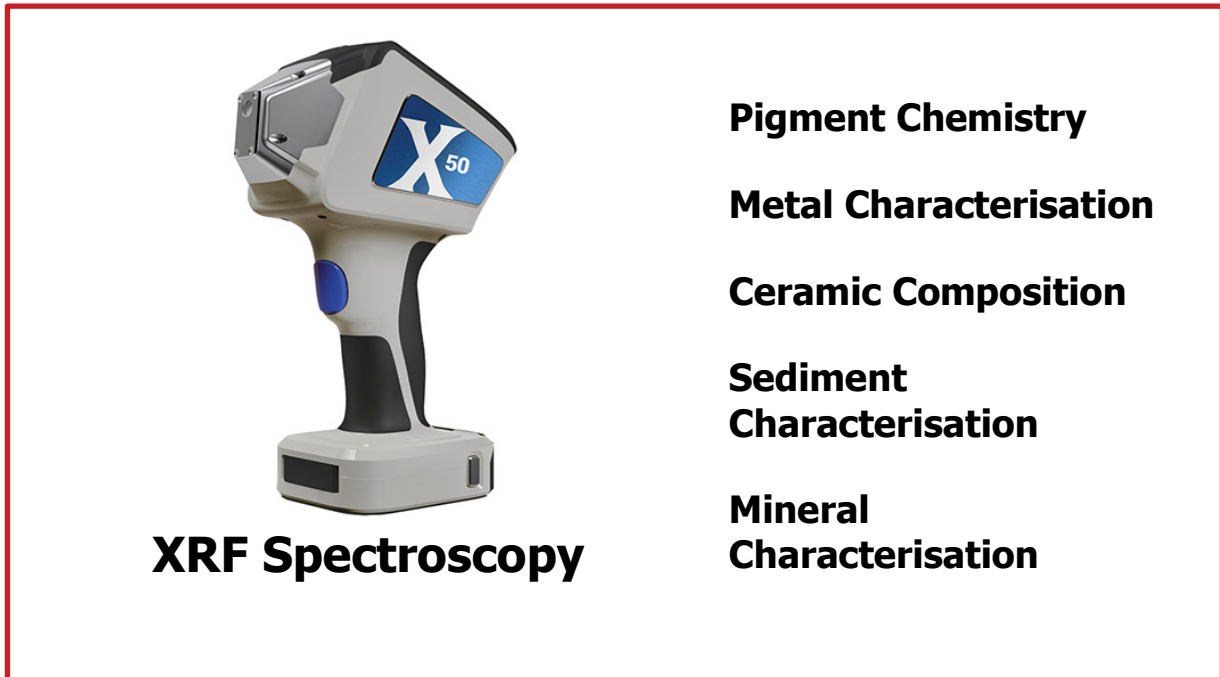
Topic	Number of Publications
Bone Characterisation	1
Ceramic Composition	2
Construction Material Characterisation	1
Mineral Characterisation	1
Misc. Organics Characterisation	2
Pigment Chemistry	4
Residue Analysis	2

Table 6: Uses of Raman Spectroscopy in heritage publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

As noted above, the use of Raman Spectroscopy in UK or Ireland based archaeological work has been uncommon since 2010 (Fig. 4b). Analyses of pigments on rock art (Bonneau et al, 2012), textile dyes (Hadian et al, 2012), or Mesopotamian cuneiform tablets (Chiriu et al, 2017) make up the largest single topic of work (Table 6). Raman has also been employed to investigate Roman medicine residues (Stacey, 2011), preserved human brain tissue (O’Conner et al, 2016), or to characterise lime coffins from the Spanish Civil War (Schotsmans et al, 2017). Raman Spectroscopy thus has versatile applications for archaeological research, but the expertise required to deploy and interpret findings means collaboration with specialists is often necessary.

Only two survey respondents used Raman to address archaeological questions, and both used the instruments to investigate pigments (on ancient/archaeological walls or on rock art). Both stressed the need for portable instruments because their work required *in situ* analyses. Both also talked about the limitations of current equipment, noting that the instrument needed a flat surface and needed to be placed very close to the object of study; archaeological materials are rarely flat, and close proximity risks severe damage to rock art. Such issues may contribute to why Raman has not found a wider niche in archaeological science.

(iii-iv) X-Ray Fluorescence Spectroscopy (XRF)



(image courtesy of Analytik Ltd.)

Mirroring the outputs of other techniques, XRF saw a rapid spike in global research interest after 2015 in both archaeology and heritage studies (Fig. 5a). This spike has broadly been maintained but only time will tell whether the drop off in 2019 was an anomaly or a reset to previous levels of use. In the UK and Ireland any particular positive or negative trend in the numbers of heritage or archaeology publications is hard to pick out (Fig. 5b). A minor elevation in the amount of published work may be visible, but the overall numbers are relatively low.

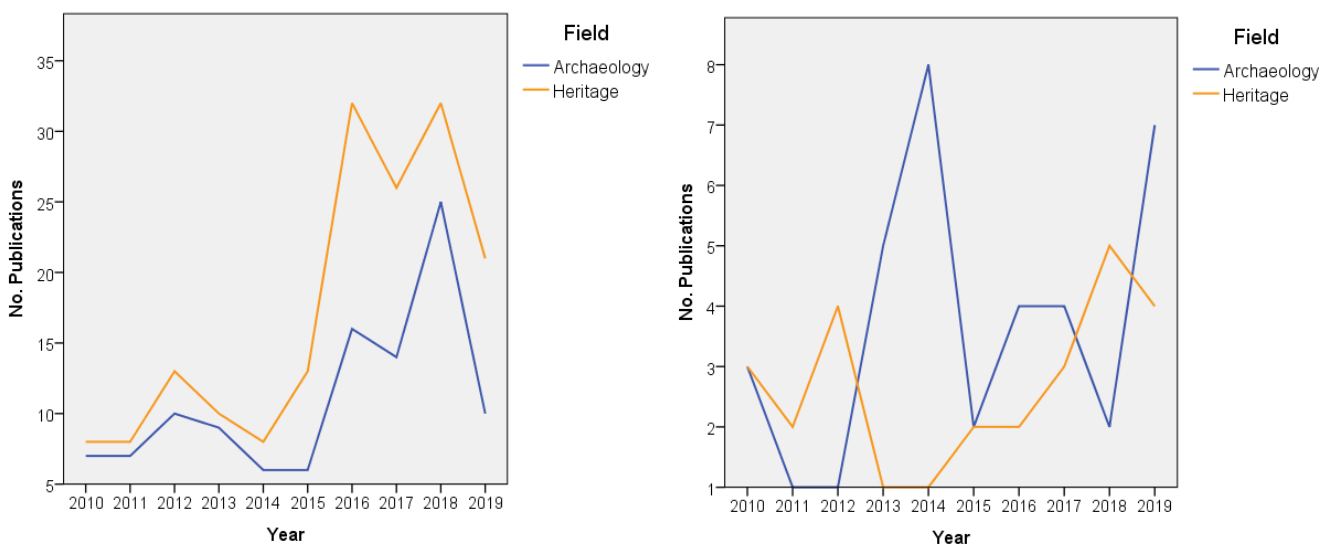


Figure 5: (a) global trends in and heritage and archaeology publications using XRF since 2010 (left); (b) UK and Ireland trends in heritage and archaeology publications using XRF since 2010

(right)

A hub for XRF work in heritage science, similarly with other techniques, appears to be Italy, with 30% of papers involving Italian laboratories and/or authors. Authors based in Spain (19%) and France (16%) also contributed to a relatively large amount of research using XRF. Overall, scholars from 38 countries contributed to papers that used XRF spectroscopy in heritage research.

In archaeology too researchers from 38 nations applied XRF spectroscopy since 2010. Italy was again a centre of research using XRF, with 27% of publications involving scholars or labs from Italy. The United States (26%) was another hub of archaeological research using XRF. Scholars from Spain (11%), China (11%), France (10%), and the UK (9%) also published a relatively high proportion of work.

Seven UK or Ireland based researchers who use XRF responded to the survey questions. All seven respondents foresaw growing interest in and development of XRF techniques in their respective specialisms. Potential limits or issues that would affect future growth were also mentioned; (i) calibration and noise remain an issue for portable XRF (pXRF) systems, which one respondent's group were working to improve, and (ii) that pXRF use in the field to test sediments was already at limit (with scanning XRF use for compositional work being specified as the growth area).

Heritage

Topic	Number of Publications
Ceramic Composition	1
Construction Material Characterisation	1
Metal Characterisation	2
Pigment Chemistry	20
Resin Chemistry	1
Wood Characterisation	2

Table 7: Uses of XRF in heritage publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

Since 2010 around three-quarters of publications from UK or Ireland based scholars using XRF investigated pigment chemistry (Table 7). Other uses were sporadic, with pigment chemistry being the only topic regularly covered throughout the target period. The bulk of the pigments sampled were from paintings or illuminated manuscripts, but XRF was also used to investigate pigments on mosaics (Smirniou et al, 2010), dining ceramics (Rosi et al, 2011), a shield (Sanders et al, 2012), or a cabinet (Burgio et al, 2018).

A recent novel application has been to lacquer-ware for resin analysis (Risdonne et al, 2018).

Investigation of the layering allowed the production process of a shrine to be outlined.

Four survey respondents used XRF in their heritage research, sharing a number of interests and applications:

- Characterising pigments on paintings and illuminated manuscripts
- Verifying the composition of metal alloys or precious metals
- To check ceramic composition

Depending upon their specialism respondents variably saw the portability of XRF systems as either desirable (but not necessary) to being essential. For portable heritage objects made of ceramic or metal a portable system may not be needed, but for very sensitive items like illuminated manuscripts *in situ* analysis is the only option. One respondent did note however that the cost of portability was a lower resolution for the resulting data.

Archaeology

The most common use of XRF in archaeology has been investigations of ceramic composition (Table 8), narrowing down origins of ceramic types and their subsequent exchange networks or uses. Other core areas of work using XRF are the characterisation of metals and the investigation of archaeological sediments. XRF application to metals is commonly targeted at copper or bronzes, although a recent critique of pXRF use on metals has been published (Pearce, 2018). Applications on sediments have a variety of aims, for example to reconstruct landscape and land use (Abrahams et al, 2010), to identify metalworking areas (Slater and Doonan, 2012; Grattan et al, 2014), or to characterise the different activities occurring in living spaces (Cannell, 2016).

Topic	Number of Publications
Bone Characterisation	2
Ceramic Composition	14
Construction Material Characterisation	1
Metal Characterisation	7
Mineral Characterisation	4
Pigment Chemistry	2
Residue Analysis	1
Sediment Characterisation	6

Table 8: Uses of XRF in archaeology publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

Three scholars using XRF in archaeology responded to the survey, applying XRF to:

- Characterise rock art pigments
- Investigate archaeological sediments
- Investigating the compositions of metals, ceramics, or lithics to illuminate artisans' technical choices or provenance

The respondents highlighted multiple strengths of XRF spectroscopy, particularly regarding pXRF. The non-destructive nature of the analysis is very important, facilitating work that preserves artefacts for future analyses and allows duplicate measurements to be made, which improves precision. One respondent also noted the ease of sample preparation and XRF's effectiveness when used alongside other techniques (e.g. "*isotopes, radiometric, magnetic*"). Portability was seen as essential for certain applications, such as the pre-screening of samples in the field or in museum collections and the *in situ* analysis of rock art pigments.

(iii-v) Spectral Imaging



Spectral Imaging

Pigment Chemistry

Document Conservation

Painting Process/Sequence

Archaeological Site Identification

(image courtesy of Analytik Ltd.)

Worldwide, since 2010, the use of multispectral imaging in both heritage and archaeology appears to have steadily grown; in heritage studies more so than in archaeology (Fig. 6a). Steep growth in the use of hyperspectral imaging in heritage science is also in evidence, although use in archaeology has, overall, remained flat (Fig. 6b).

UK and Ireland publications trends generally track global ones (Fig. 7). Use of spectral imaging in heritage studies has seen a significant increase since 2010, whereas deployment in archaeology remained relatively flat.

Researchers based in 39 countries have used multispectral imaging in heritage studies since 2010; the figure for hyperspectral imaging is 29 countries. Scholars based in Italy or the USA were those driving the use of multispectral imaging, with 30% and 20% of papers (respectively) involving scholars or labs based in one of those two countries. The same was true for hyperspectral imaging, with the USA (29%) and Italy (27%) acting as hubs for the deployment of that technology in heritage studies.

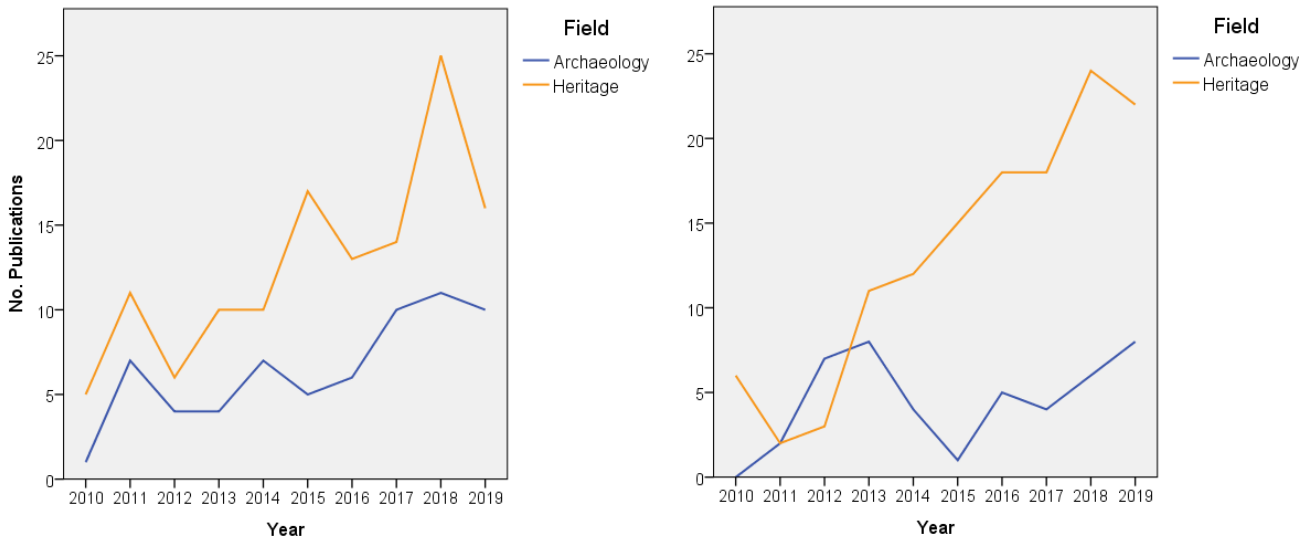


Figure 6: (a) global trends in and heritage and archaeology publications using multispectral imaging since 2010 (left); (b) global trends in and heritage and archaeology publications using hyperspectral imaging since 2010 (right)

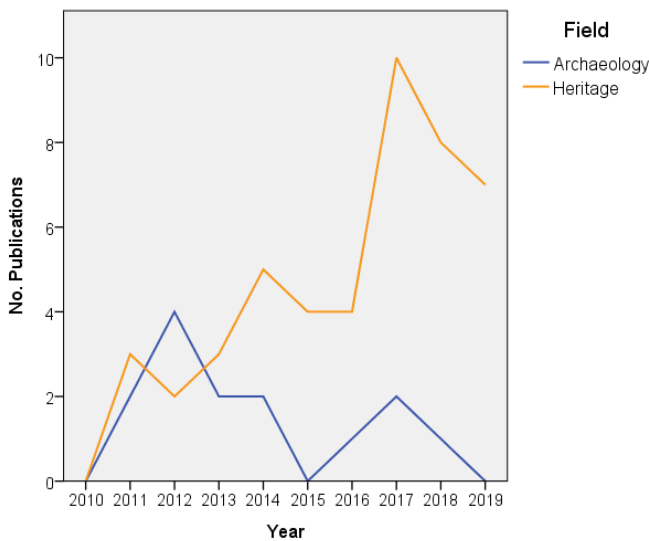


Figure 7: UK and Ireland trends in heritage and archaeology publications using any kind of spectral imaging since 2010

In archaeology scholars from 30 nations used multispectral imaging in their published research; for hyperspectral imaging the figure was 26 countries. A high proportion of papers that used multispectral imaging involved laboratories or scholars from Italy (26%), Cyprus (20%), and the USA (18%). The use of hyperspectral imaging was more evenly spread, with scholars from Cyprus (20%), Italy (13%), the UK (11%), Germany (11%), and the USA (11%) being involved in a relatively large proportion of work.

Seven UK or Ireland based heritage and archaeology researchers who used spectral imaging responded to the survey. Five of these seven saw scope for a growth in the use of spectral

imaging in their respective specialties. One respondent noted that spectral imaging offers more information and better results than other techniques limited to the visible spectrum, although another argued that combining spectral imaging with other techniques led to the most useful results.

This general positivity came with a number of caveats however. The high monetary cost of hyperspectral imaging systems was highlighted as a barrier by several respondents; while lack of training or expertise outside of a few centres was also mentioned. One respondent saw shorter term growth focused on basic research into the scientific underpinnings of the technique, potentially leading to more affordable instruments suited to heritage work in the longer term.

Heritage

Since 2010, in the literature from scholars based in the UK and Ireland, uses of hyperspectral imaging in heritage science have overwhelmingly been examinations of pigment chemistry (Table 9). Almost all cases were targeting paints and pigments from on canvas, paper/parchment, or walls. However a recent novel application has been to a leather codex from pre-Colombian Mesoamerica (Snijders et al, 2016).

For multispectral imaging uses were more varied, although studies of pigment chemistry were still the most common topic (Table 9). As with hyperspectral imaging, targets of analysis were primarily paintings or paper/parchment, yet Gibson et al (2018) have also applied multispectral imaging to papyrus on Egyptian mummies, revealing subsurface text. Textiles (Tamburini and Dyer, 2019) and pigments on marble sculptures (Pollard, 2018) have also been investigated. The characterisation of painting process and the tracking of document degradation were other relatively common uses of multispectral imaging.

Topic	No. Hyperspectral Publications	No. Multispectral Publications
Construction Material Characterisation	1	1
Design Reconstruction	-	2
Document Conservation	-	4
Material Degradation	1	-
Metal Characterisation	1	-
Painting Process and Sequence	1	4
Paper Characterisation	1	-
Pigment Chemistry	13	10
Textile Characterisation	-	1

Table 9: Uses of spectral imaging in heritage publications involving UK or Ireland based

scholars since 2010 (see supplement for list of papers)

Six survey respondents had used spectral imaging in heritage studies, with a variety of interests and applications:

- Characterisation of pigments on manuscripts or paintings
- Conservation of paper and parchment
- Benchmarking spectral imaging systems
- Examining under-texts, faded texts, or erased texts
- Fraud detection
- Tracking retouching and painting processes

Respondents noted that spectral imaging offers more information than ultraviolet or infrared photography alone can manage. One respondent also said that such deeper analytical capabilities allow the closer tracking of deterioration of paintings or paper/parchment over time. The non-destructive nature of spectral imaging was also highlighted, with one respondent commenting that it offers equivalent information to more invasive chemical analyses.

Depending on the end use, opinions about instrument portability varied between it being “essential” to just “desirable” (making do with simply transportable equipment). Clearly, artefacts that cannot be moved are likely to require portable instruments for analysis. Either way, two respondents noted that the positive points of portability had to be weighed up against a loss in overall resolution.

Archaeology

Topic	No. Hyperspectral Publications	No. Multispectral Publications
Bone Characterisation	1	-
Site Identification	5	8

Table 10: Uses of spectral imaging in archaeology publications involving UK or Ireland based scholars since 2010 (see supplement for list of papers)

In UK and Irish archaeology almost all use of spectral imaging is for site identification, the only exception was where near-infrared hyperspectral imaging was used to characterise bone collagen preservation (Vincke et al, 2014) (Table 10). Remote site identification has been carried out by instruments carried by unmanned aerial vehicles (UAVs) (Cowley et al, 2017;

Khan et al, 2017; Moriarty et al, 2018), analysis of photographs from current or historical survey (e.g. Aqduş et al, 2012; Stott et al, 2013), or Landsat data (Kinsey et al, 2014). Such analyses generally aim to identify vegetation proxies/crop marks that expose underlying archaeological features.

Only one archaeologist with experience of using spectral imaging answered the survey. They used spectral imaging to carry out annual reconnaissance surveys, using vegetation growth patterns to locate buried sites. They noted that traditional visible survey and aerial photography (using balloon or aeroplane flights) were seeing diminishing returns, with spectral imaging able to “*see the unseen*”. Work remains experimental, combining spectral imaging cameras with UAV surveys.

(iv) *Instrument Use Patterns*

Over two-thirds (18 of 26) of survey respondents used spectroscopic instruments owned by their laboratories or their home departments/institutions. Eight researchers borrowed from or collaborated with other departments in their home institution, another institution, or a private entity. Table 11 summarises where instruments used by respondents were located; there is some overlap because some laboratories had certain equipment and borrowed others.

Department / Institution	Number of Responses
Museum / Heritage Foundation Labs	7
Chemistry or Applied Sciences Departmental Labs	6
Archaeology Departmental Labs	4
Heritage of Conservation Departmental Labs	4
Earth or Environmental Science Departmental Labs	3
Engineering or Electrical Science Departmental Labs	2
Private Entity	2
Geography Departmental Labs	1

Table 11: University departments or institutions where survey respondents indicated that relevant instruments were owned or from where they were borrowed

Sharing of equipment was reported as primarily being through cross-disciplinary or inter-institutional collaborative projects. Respondents either took equipment out to sites in order to carry out analyses or took their own samples to partner laboratories, although one regularly worked with postgraduate projects to secure access to the relevant technology. Only two respondents (or their host institutions) had independently rented equipment from commercial entities.

One online space facilitating equipment sharing was highlighted in the survey, namely the Kit-Catalogue⁵ hosted by the National Heritage Science Forum (NHSF). Here, members of the NHSF can publically share what equipment they are willing to share with research partners. Each instrument has its own entry, and the catalogue offers information about potential uses of any instrument, its location, and make/model. However, availability is limited by the fact that only NHSF members may put up equipment and only equipment that a laboratory is willing to share will be present.

⁵ equipment.heritagescienceforum.org.uk

(v) Spaces for Discussion

Survey respondents offered a variety of opinions about where discussions of spectroscopy or spectral imaging took place in their respective specialist areas (see Table 12). For those that gave a definitive opinion, both papers and conferences were seen as the central forums through which results were disseminated and techniques or developments discussed. One respondent noted however that not all conferences produce proceedings, and thus very useful discussions can be lost.

Locations of Discussion	No. Responses
Papers	3
Papers <i>and</i> Conferences	8
Conferences	2
Conferences <i>and</i> Informal Discussion	2
Informal Discussion	2

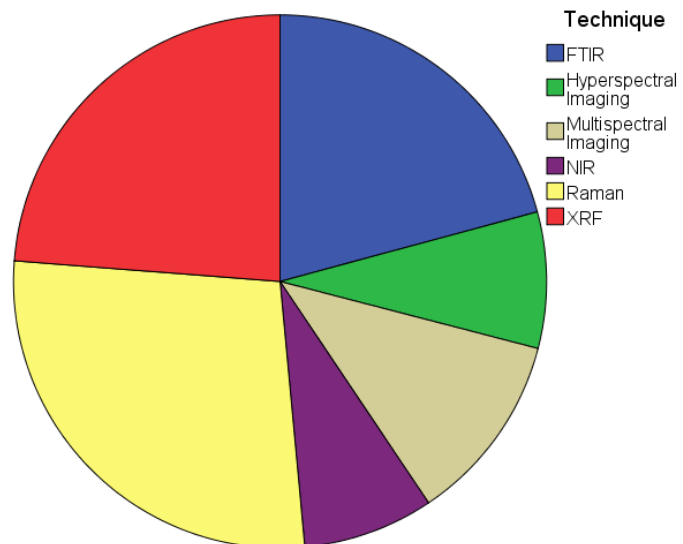
Table 12: Spaces noted as the main sites of discussion for spectroscopic and/or imaging research

A minority of respondents indicated that informal discussions or behind the scenes meetings were the main sites of discussion (Table 12); all four of those mentioning such forums either worked in museums/heritage foundations or were discussing collaborative work with museums and heritage foundations. One museum researcher noted that *“the most efficient and useful discussions happen at one-to-one meetings, or at discussions on the side-line of conferences/meetings”*. One academic researcher also highlighted that informal discussions with curators can be key to getting projects off the ground. Unfortunately many of these fruitful discussions can be lost, and much useful work in museums or foundations goes unpublished; as one researcher at a heritage foundation laboratory said *“we probably publish only about 10% of what we do”*.

(vi) Conclusions

Overall, in UK and Ireland heritage and archaeology, Raman spectroscopy has, narrowly, been utilised the most (Fig. 8). FTIR and XRF have also seen a significant proportion of use since 2010. As a whole, spectral imaging has also seen relatively frequent application. Finally, relative to other techniques NIR has not seen significant application since 2010.

Figure 8: Proportions of UK and Ireland based publications using the various techniques discussed in this report



In the UK and Ireland there is scope for growth in the interest and application of all the techniques discussed in here, but more-so for heritage science than for archaeology. In heritage science the use of all the types of technology discussed has seen an increase over the past 10 years, and in the cases of spectral imaging, Raman, and FTIR significant increases in interest since c. 2015 can be noted. Even so, the vast majority of work has been focused on very specific applications, and although some experimental work may provide new trajectories or opportunities novel applications are unlikely to overtake more traditional ones in the foreseeable future.

Barriers or limitations to such growth are not insignificant however. Costs and a lack of baseline research in archaeological applications need to be overcome before particular techniques can move into wider use; this has already largely been addressed the case for XRF, as reflected in the relatively high application globally and in the UK/Ireland. In heritage studies funds for equipment and a lack of training outside of specific research centres will remain a limiting factor. Even so, the development of better and more affordable portable equipment does appear to have stimulated increasing deployment of spectroscopic techniques over the past 10 years.

Collaboration and equipment sharing facilitates growth in application and interest in spectroscopic techniques. But the tendency in heritage science for equipment and expertise

to become concentrated at a few centres limits regional institutions' ability to carry out wider research. Expansion of the NHSF's Kit-Catalogue would expand opportunities for research, as would the setting up of forums to capture the more informal discussions, developments and results that are not publically available currently.

(vii) Future Work: Earth and Environmental Sciences

Originally this project was to include similar overviews of the uses of spectroscopy in earth and environmental science, and to that end several researchers working in those areas were surveyed. Unfortunately the scale of that work was too wide for the time allotted to this particular project, therefore such an overview will have to be presented in future work. The handful of interviews that were carried out highlighted novel uses of portable FTIR for *in situ* screening for organic and metal pollutants, the utility of portable XRF for pre-screening core samples in the field, the rising use of vis-NIR for calibrating aerial surveys, and the continued growth of paleoclimate studies (using XRF and other techniques) since 2010.

(viii) Acknowledgements

Thanks go to the Cambridge Social Sciences Partnership, who funded this project through their Cambridge Grand Challenges Fellowship. Also, thanks go to the staff at Analytik, who were all very welcoming and provided a great deal of advice and support. Finally, I would like to thank all those who responded to my survey questions, along with those who aided the project by suggesting other researchers to talk to or directly facilitated contact with others.

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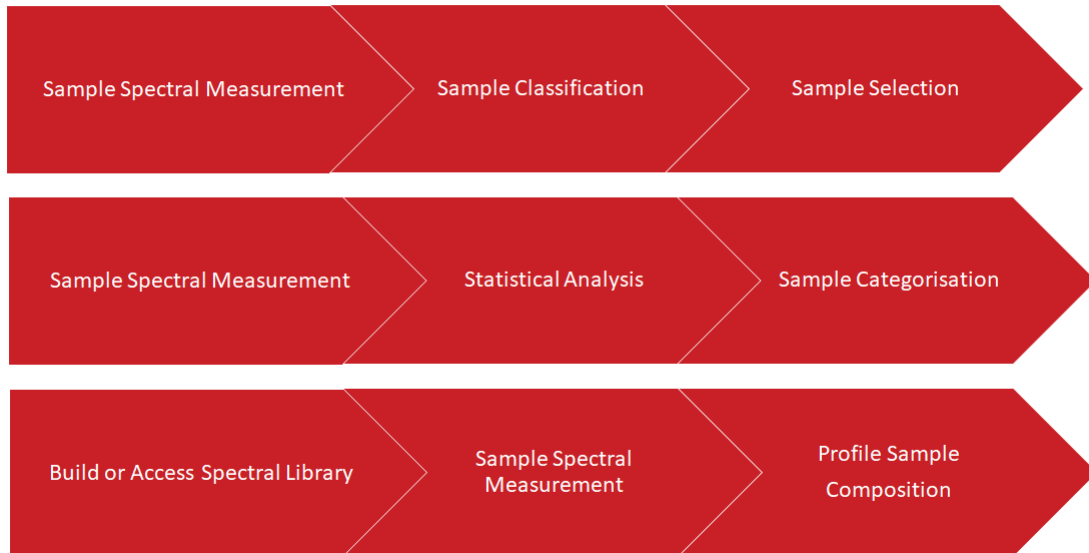
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Appendix A: Typical Application Methods of Relevant Techniques

Overview of Technology Processes All - Appendix



Broadly speaking, there are 3 approaches to using the spectral techniques as tools in Heritage and Archaeology research.

The first approach is to use the spectra to classify samples. This can be used, for instance, to choose the best samples for further study.

The second is to measure a large number of specimens and then to use statistical analysis to categorise them based on similarities within groupings (PCA, ...).

Another common approach is to build or access spectral libraries and then use these to compare with samples measurements to profile them in terms of composition and origin.

Appendix B – Database Search Terms

Web of Science Searches

- “FTIR spectroscopy” AND “archaeology”
- “FTIR spectroscopy” AND “heritage”
- “NIR spectroscopy” AND “archaeology”
- “NIR spectroscopy” AND “heritage”
- “Raman spectroscopy” AND “archaeology”
- “Raman spectroscopy” AND “heritage”
- “XRF spectroscopy” AND “archaeology”
- “XRF spectroscopy” AND “heritage”
- “multispectral imaging” AND “archaeology”
- “multispectral imaging” AND “heritage”
- “hyperspectral imaging” AND “archaeology”
- “hyperspectral imaging” AND “heritage”

Google Scholar Searches

- XRF studies of archaeological ceramics
- XRF studies of archaeological metals
- geoarchaeology XRF studies
- archaeology FTIR studies
- archaeology NIR studies
- archaeology hyperspectral imaging
- archaeology multispectral imaging
- archaeology raman studies
- heritage NIR spectroscopy
- heritage FTIR spectroscopy
- heritage raman spectroscopy
- heritage multispectral imaging
- heritage XRF studies

- heritage hyperspectral imaging

Appendix C – Survey Questions

(i) How do you use [TECHNIQUE] in your research?

(ii) What is the future direction of research with these techniques in [RELEVANT FIELD]? Is there a growth in interest and use or is it already at limit?

(iii) What are the unique points of this instrumentation for [RELEVANT FIELD] research? Is portability a necessary or desired attribute? If so, what analysis does portability allow that lab based techniques do not?

(iv) If you have your own equipment, do you or [INSTITUTION] allow equipment be shared? If so, is use restricted to within your institution or shared more widely? If not, was the relevant instrumentation from intra- or inter-institution collaboration/loan?

(v) In your view, where is the efficacy of such analyses mainly discussed (e.g. papers, conferences, informal fora)?

(vi) If I were trying to locate the publications in your area of research what handful of key terms would you recommend I use to maximise relevant coverage?

(vii) Do you use other types of spectroscopy or spectral imaging?

(viii) Would you like to hear more at the conclusion of the project?