



Presented at Icon Heritage Science Group's 'Historic document analysis using p-XRF: Pitfalls and Possibilities', The National Archives UK, 11th September 2017.

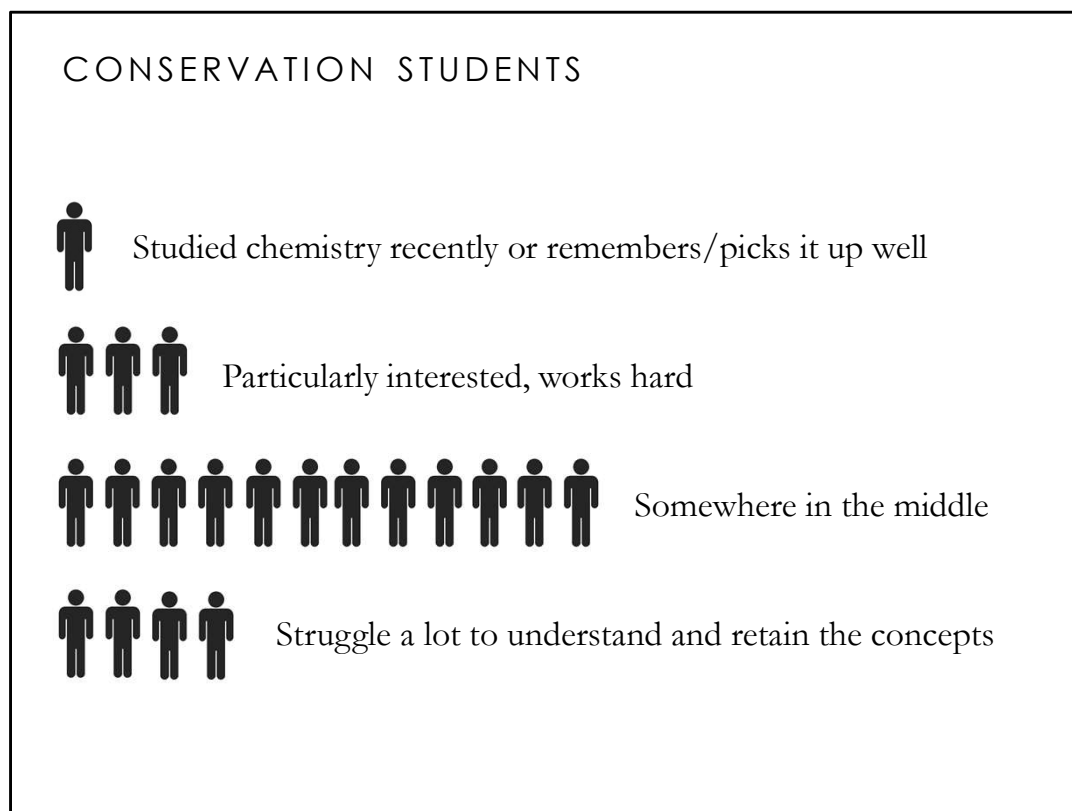
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To orient you to my perspective: I got a fine arts degree, then while I worked as a conservation technician at Columbia University I took undergraduate general and organic chemistry classes there. The American programmes require chemistry classes for admission but the UK ones don't, so when I came to West Dean I had much more chemistry knowledge than the average British student. As a teacher I fall somewhere in the middle; I know more chemistry than the students will need to learn, but less than a conservation scientist.

I taught conservation science for four years at Camberwell, and book conservation generally at West Dean, where I am still, and I've also taught short workshops to practicing conservators including a few on XRF at the V&A a few years ago.

I'd like to talk to you about how science is experienced by conservators, challenges in learning XRF spectrometry, and what scientists can do to help.



The classes range in size by year and programme but in a class of say 20 students, there would generally be

(click) one who was quite good with science,

(click) a few that either found it easy enough to pick up or who worked hard enough to do well,

(click) and maybe 3-4 at the other end of the scale who really struggled both to understand and retain the concepts and for whom English language might also be a problem.

(click) Everyone else would be somewhere in the middle. Generally people are drawn to conservation for the practical aspects, and for British students they might not have studied science since age 16. It's not unusual for this to be a second career so it might have been quite some time since then. Many find it intimidating. Basic math might also be uncomfortable.

I think one of the major problems with teaching it in a program with no prerequisites is that there is an amount of basic chemistry to cover before we can look at anything more directly relevant, like XRF for identification of materials. And from my own experience it's hard to get over the mountain of what seems like dry, unrelated, boring science before you know enough to get to the fun part. And then the fun part is hard.



Out in the world of professional conservators, there's a similar mix of science understanding because of having an older generation "grandfathered" in from before MA programmes with science were established, and because of new students being able to get through the programmes without a firm grasp on science. There may be people who went back to get the training afterwards as well, through courses like Chemistry for Conservators, or the odd conservator who also has a degree in chemistry and decided to find the lowest paying job possible.

ACCESS TO EQUIPMENT

Private practice:

- Conservator may have access but probably not much time

Institution

- Probably has a scientist if it has equipment
- May or may not allow conservators access to the equipment directly
- However, scientist would be a reliable source of information.

Institution without a scientist

- Less likely to have expensive analytical equipment like pXRF
- May be outsourcing analysis to another institution
- May start to as cost comes down and use becomes more widespread, particularly because of the “point-and-shoot” aspect of pXRF

click A private practice conservator, even one with a good deal of comfort with analysis, and connections to an institution with equipment, is unlikely to have the time or money for much research.

click The type of institution that has equipment is also likely to have a conservation scientist on staff. In that case the job roles are often sharply divided, which makes sense: the conservator takes the object or samples and a question to the scientist, and the scientist does the testing and sends back a report to the conservator. However, in this scenario, the conservator doesn't get any more experience using the equipment or chance to do their own research. Many job advertisements ask for science skills on the part of the conservator but then don't give much opportunity to implement them.

click A smaller institution without their own equipment is likely to send off for testing if it's on a smaller scale, but may be able to purchase equipment, particularly now that the prices are coming down. For example, Royal Collections Trust recently acquired a pXRF spectrometer for use by a conservator and volunteers.

BARRIERS FOR STUDENTS



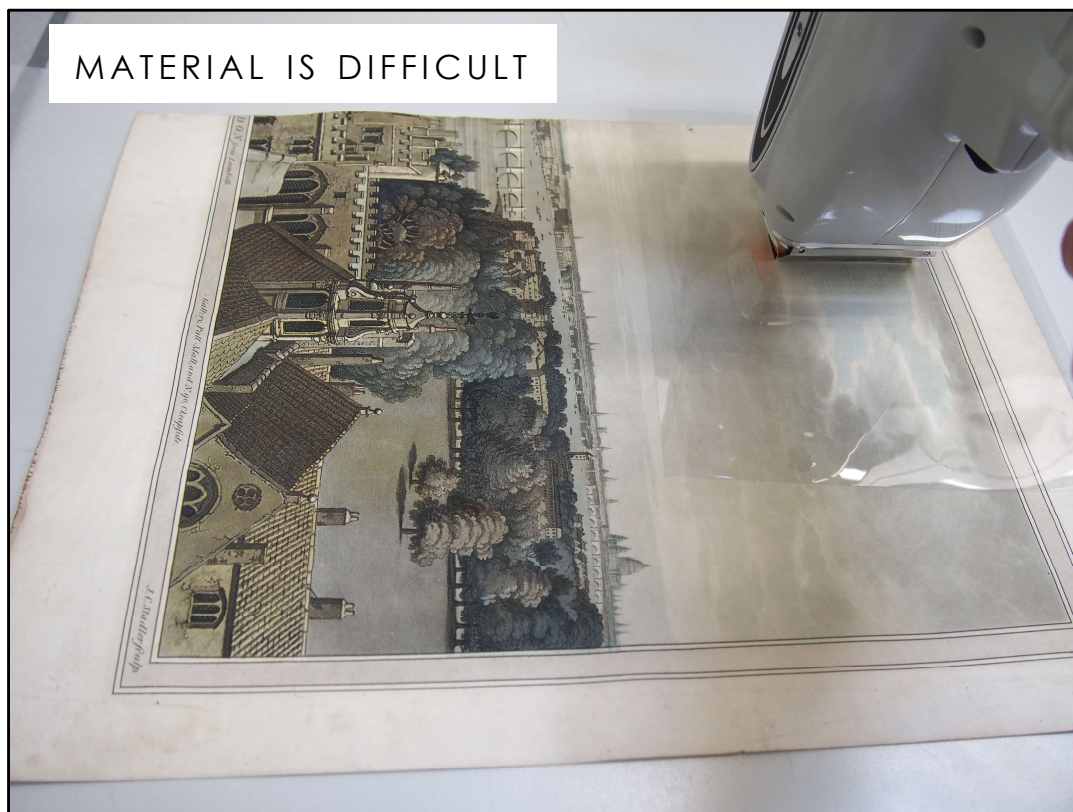
West Dean has a pXRF spectrometer but Camberwell doesn't. When I was teaching there, one time I was able to borrow West Dean's and bring it up to London so the Camberwell students could use it, and a few times I've taken students down to West Dean to use it on site for their MA projects, but generally we didn't have it at Camberwell. I would compromise in lessons by taking spectra at West Dean and giving the files to the Camberwell students to analyse (particularly since without any sample preparation, the actual taking of the data was pretty straightforward). The software we got from Bruker came with permission to install on as many computers as we wanted.



In the UK we haven't really decided on how important science is and have reached a compromise where all the programs teach it, but the students spend considerably less time on that than practical work, and grades are a little more generous than they need to be to really enforce science understanding. The result is that even at West Dean, where we have a spectrometer, we don't necessarily make sure everyone has used it independently although they would all at least see it used in class. Many choose to use it for their MA research at the end of the programme, but this might be the first time they've spent significant time with it. They have other assignments to complete and other interesting side projects so it takes motivation to spend "free time" in the lab.



David Dorning, who taught science at West Dean for many years before recently becoming the Head of Conservation, always wanted time to spend in the lab using the equipment for his own research in order to get more familiar with it and figure out more nuance to pass on to the students, but it never really worked out. I certainly don't have paid time for anything like that. We have a dedicated scientist now to run the lab and teach classes but this is her first year so we'll have to wait to see how it changes.



I found as a student, when I used pXRF for paper analysis in my MA research, there was little to draw on. I was looking at the selective discolouration of one section in a 17th century book, and drew a lot on Timothy Barrett's research in the US on the use of pXRF on paper, but there wasn't a lot out there generally on pXRF for this type of application. I wanted to hear other peoples' problems and how they interpreted data, so I could make sure what I was doing was sensible. There's a bit more out there now but it's still something that could be developed farther.

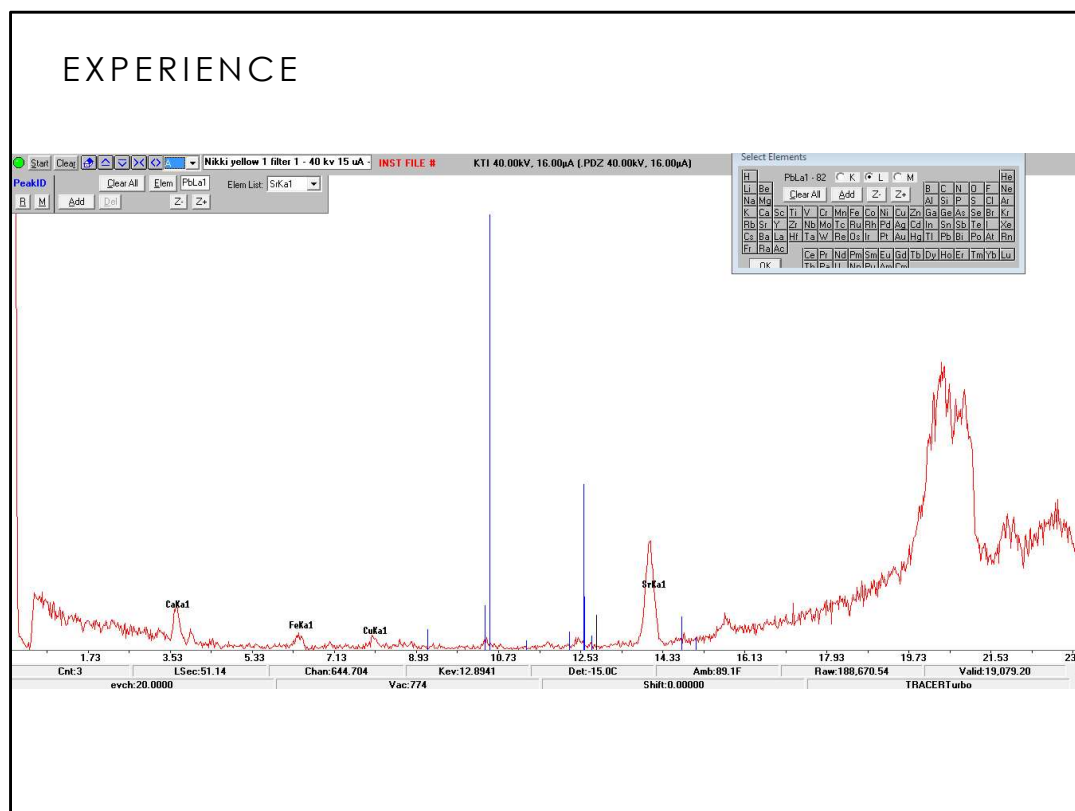
Generally our material being old, damaged, and composite provides extra problems that may not be encountered by scientists studying modern materials. And despite the portability of a pXRF spectrometer, we often have very thin or narrow samples next to other materials, or permission to use a spectrometer at a different site to where the object is located. Trying to identify a material under these conditions is particularly difficult as you all know, so even chemistry texts that discuss XRF may not be ideal resources for conservators.

LINKS TO SCIENTISTS/INSTITUTIONS

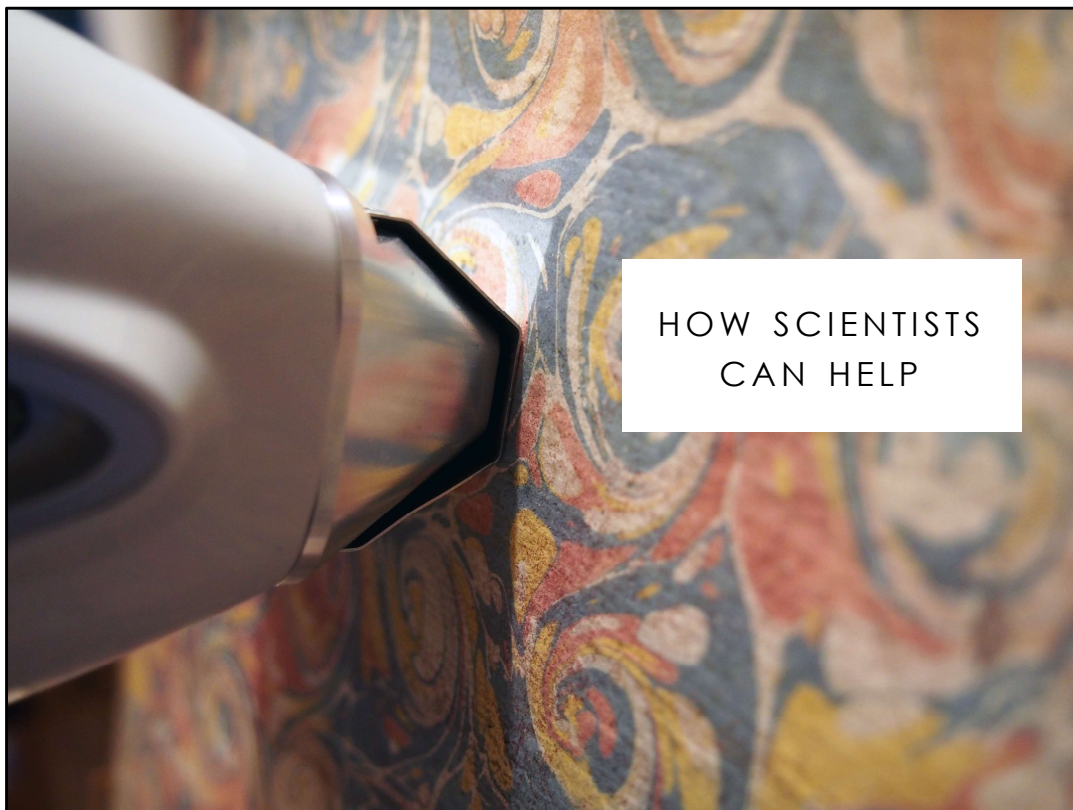


<http://paper.lib.uiowa.edu/methods.php>

Barrett worked with several institutions, with funding, to do his research. He had scientists who could figure out the maths to give quantitative data based on calibrated standards using destructive testing, which was beyond what I could figure out myself. He was able to machine a Perspex support that would safely hold a single page of a book in the air for reading just that page with the spectrometer. I made do by putting a little lead square behind the pages I scanned, to mask the radiation from penetrating farther, and then used that lead signal to try to account for the varying thicknesses of the paper, so that I could compare relative amounts of the various elements from one set of paper to the next. It felt a bit clumsy though. We often have the problem that those students with really quality research projects try to make connections with scientists in other institutions for help, but those scientists are too busy to follow through, or the analysis costs too much.






We generally lack both a broad scientific background and the day-to-day experience that working with the spectrometer would give. When I identify copper in my spectrum, maybe someone with more knowledge would be able to say just by looking at it that it's a level consistent with trace amounts that you'd find around generally. Or might be able to explain that chlorine found in paper is probably from the water used to make it. Or that these certain peaks tend to overlap so look for this one over here to confirm one element over another. Which peaks need to be identified, and which are small enough that they're probably just noise? The fact that some peaks line up perfectly with the guidelines and some don't----does that mean the identification is wrong or the calibration is off? One of the big things is even knowing what we should be able to tell from the data, and what a scientist would also struggle with. It always makes me feel better when a scientist says they don't know the answer either.



HOW SCIENTISTS
CAN HELP

TALK TO US!

Norman Billingham Jul 29 ☆  

to Kirstin 

Hi Kirstin

That's a slightly tricky question but Abby likes landing me with those

I'm a long way from expert, but as I understand it the ageing of wheat starch pastes is made up of two processes. The starch component undergoes hydrolytic cleavage at the glycosidic link, reducing its MW, but at the same time the protein component (gluten) crosslinks via formation of sulfur-sulfur (disulfide) bonds.

Oven ageing will accelerate both reactions up to a point but also tends to drive out the bound water so it will tend to slow things down as T gets higher and the paste gets drier. The scission reaction involves water directly but the crosslinking needs water mainly to keep the protein soft and mobile - it stops if the starch is too dry.

You also may need to be careful as going to high T will dry out the moisture from the paper too and it will presumably shrink at least a bit.

Total guesswork really but I think if it were me I'd probably start by ageing at around 60C on the basis that that's hot enough to accelerate things quite a bit but cool enough not to dry things out completely.

Any time you can give helps. It helps to hear about your research, in person or in print, it helps to have a scientist “on call” to ask small questions as they arise, it helps to have someone confirming we’re doing something right or pointing us in a better direction. It helps to keep the dialog open, to keep the vocabulary going. Tell us about the things you struggle with, so we don’t feel stupid when we struggle.

My scientist on call is Norman Billingham, who is a polymer chemist at Sussex University who also lectures occasionally at West Dean. He tells me his reasoning behind the answer, he uses language that isn’t too dumbed down but is also understandable, he tells me when he doesn’t know, and he’s interested in our problems. I think.



If you have pXRF or other equipment that could be useful to the students, let them come for an afternoon, either with a research project or just to see what the equipment can do, what you're working on. It will help them understand more, get excited about it, generate useful data for their research, and generally produce future conservators who will be better able to collaborate with you or communicate with you. If you're in an institution where there's a sharp line between the scientists and the conservators, try to soften it a bit, let the conservators use the equipment if they know how.

I can only imagine that the more conservators there are who are interested in and value science, the more advocacy there will be, the more projects proposed that involve analysis, the more opportunities for both of us.

PUBLISH THINGS WE UNDERSTAND!

Analytical Methods

AMC TECHNICAL BRIEFS

Raman spectroscopy in cultural heritage: Background paper

AMC Technical Briefs Committee, AMCTB No 67

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www.rsc.org/methods

In the last 30 years Raman spectroscopy has become an essential experimental tool for the analysis of a wide variety of artistic materials, often in a non-destructive, non-invasive manner. The Raman effect provides a quick and relatively straightforward molecular identification of a material under examination. A Raman spectrum can be considered as a fingerprint that could be used for compound identification when a database of reference spectra is available for comparison purposes.

Its use has become widespread because Raman spectroscopy is a non-invasive technique and, provided the correct experimental conditions are used by an expert operator, the materials under examination are not damaged in any way. Because of this, the technique has now become mainstream in heritage science. There is no single type of Raman instrument that can be used for all purposes; users now have a choice of instruments and operating conditions, depending on the analytical requirements and the type of an object to be analysed.

What is Raman good for?

Types of materials

When Raman experienced a renaissance in the 1980s, its main application to cultural heritage was for the analysis of traditional artistic materials, mostly pigments of mineral origin. This is still one of its main applications, although the technique is also used for the identification of a few natural/organic dyes (for example indigo and garancin), many modern synthetic dyes, most gums and semi-precious stones, minerals in general, and corrosion products. Other cultural heritage materials that have been examined more recently include plastics, parchment, paper, textile fibres, resins, bone and bone-like materials and varnishes. In the investigation of artistic materials the success and speed of the analysis often depends on what medium is mixed with the pigments (see "Pitfalls and drawbacks – fluorescence" below).

Types of objects

With conventional bench-top instruments coupled with a microscope, only relatively small, flat items that fit under the microscope can be analysed. For this reason, it is customary to use the technique with small samples or loose fragments or materials either individually or after mounting on a cross section. Paper- or parchment-based objects, such as small whole manuscripts, single illuminated pages and portrait miniatures are also easy to examine. Other items that can be analysed with relative ease include painted textiles, textile fibres (both natural and synthetic), gems set in jewellery and small, flat sculptures or other painted objects.

Types of instruments

Bench-top microscope

This is the most common Raman instrument found in a laboratory and is the instrument with the highest performance in terms of speed, signal intensity, spatial and spectral resolution, and freedom from disruptive vibrations (Fig. 1). A wide variety of lasers can be associated with such an instrument (see below). The use of a microscope also ensures that a very small area is analysed each time, less than a micrometre across and a few micrometres in depth, depending on the specifications of the microscope objectives used. This helps in limiting the interference of surrounding materials.

Probe

This is a really transparent piece of equipment that, contrary to the better-performing bench-top microscope, can be used on site during an excavation, or on unmovable objects such as wall-paintings, cave paintings, mosaics etc. When compared to a bench-top microscope, the drawbacks of a probe include reduced signal intensity, spatial and spectral resolution, a limited choice in terms of lasers, a less than ideal ability to view and evaluate with a proper microscope the sample under examination, and the presence of vibrations that can hinder the analysis.

Handheld

This type of instrument is easy to use and is especially suited for the analysis of inorganic materials, for example during a mineral survey in the field. However it has an even more limited spatial and spectral resolution compared to the probe, it may also be difficult to set the power intensity at the sample to a suitable level, and having no microscope objective at the end of the instrument, a handheld Raman probe does not allow the analyst to inspect and choose the target region carefully.




Fig. 1 A 17th century Chinese watercolour analysed with a bench-top Raman microscope.

to a Raman spectrum which can be mistaken for a different material.

The intensity of the Raman signal is inversely proportional to the excitation wavelength. For example, a sample will give a stronger Raman signal if it is analysed with a blue laser rather than a red laser.

There are of course exceptions to the following 'rules', but in general for a red or orange pigment it would be best to use a He-Ne laser (633 nm) or a krypton ion laser (647 nm) or any other true red solid state laser. It is not normally advisable to use a green laser, for blue pigments it is best to use a blue argon ion laser, 488 nm, or a green laser (argon ion, 514.5 nm; Nd:YAG, 532 nm, or any other solid state green laser). White and yellow pigments can usually be analysed with any type of laser. For red (solid state lasers usually between 780 and 785 nm) and near infrared lasers (Nd:YAG, 1064 nm, usually found on FT Raman spectrometers) are particularly suitable for dyes and organic materials, but tend to burn dark inorganic materials as the laser absorbs rather than scatter such laser radiation.

How to set up a protocol

It is advisable to do a preliminary test on the specimen under the microscope using a very low laser power (well below 1 mW). The laser power can be progressively increased as needed to obtain a good spectrum, always making sure that the sample is not being damaged by the laser irradiation. Commercial Raman microscopes usually come equipped with a set of neutral density filters; these allow fine-tuning of the laser power at the sample reducing it from 100% to below 1% of the maximum intensity. Please remember that laser-induced damage to the sample can occur even if no obvious change is visible under the microscope if the Raman bands change on the screen within a second or two from the start of the analysis, it is likely that the specimen is being adversely affected by the laser beam.

Pitfalls and drawbacks

Fluorescence

The laser beam can excite electronic transitions that may mask the Raman signal; if any Raman probe are visible at all, they appear as if they are just coming out of a very hazy or hilly haze. In some cases, fluorescence can be reduced by using a laser beam with a longer wavelength. Many organic dyes give rise to significant fluorescence and are not usually analysed by Raman. An oil-based binding medium often generates enough fluorescence to hide most of the Raman spectral features of the pigment or dye mixed with it (see Fig. 2).

Stability and focusing issues

One of the most frustrating practical aspects in the Raman analysis of relatively light objects is a loss of focus during the analysis, due to small movements of the object under the microscope. For manuscripts, for example, unless the page under observation is kept still, any air movement or floor vibration can alter the position of the page under the laser. It is

http://www.rsc.org/images/TB%2067_tcm18-247573.pdf

For example, I'm on the RSC's Analytical Methods sub-committee of the Heritage Science group. We've been working on a series of technical briefs about analysis of cultural heritage---they're 2-4 pages, written for conservators and curators to be able to understand but also technical enough to be useful. Some are on a technique more generally, some are on the applications for a specific material. They're peer-reviewed and published in Analytical Methods so it's a line for the CV as well as a great help to the conservators, once the corpus is developed more.

Blog posts and other more informal writing would also be good. If you're publishing something useful to us, in a resource we're unlikely to come across, get word to us somehow.

I know this is a lot to ask, and everyone is under time and money pressure—but that would be my wish list for the students.



Thank you!