

Killer wallpaper

Andy Meharg

School of Biological Sciences, University of Aberdeen, Cruickshank Building, St Machar Drive, Aberdeen, AB24 3UU, Scotland

Aniline dyes developed by William Perkin in the 1850s were the beginning of the end for a host of mineral pigments widely used in interior décor. Chromium, cadmium, mercury, lead, cyanide, antimony and arsenic salts were once commonplace as paint, wallpaper, food and fabric pigments. The arsenic pigments Scheele's green and Emerald green, the mercurial vermilion, green lead chromate, cadmium yellow, arsenical Naples's yellow, the cyanide salt Prussian blue, were the staple colours used to brighten up the Georgian and Victorian home. Whites were often lead white or arsenic trioxide. In the early days aniline dyes were far from safe with arsenious acid, used as a reductant in the dye manufacture, often present in high concentrations.

What were the health consequences of these metal pigments? There is little direct systematic evidence collected during the 19th century, but there is a vast amount of circumstantial evidence from newspaper and medical press articles suggesting mass poisoning of the Victorian world. A campaign was run by the Lancet to banish arsenic greens-copper arsenite (Scheele's green) and copper aceto arsenite (Emerald green)-as many illnesses and deaths were attributed to rooms wallpapered with arsenic stained papers. Arsenic greens were first synthesised in 1778 by the renowned Swedish chemist Karl Scheele-the discoverer of oxygen (independently from Joseph Priestly). By 1863 500-700 tonnes of arsenic green were manufactured in Britain.

Initially, deaths and illness attributed to green-papered rooms were thought to be caused by flecks of green dust detached from the wallpaper being breathed in. However, the cause of this arsenical illness was much more subtle. The German chemist Gmelin (responsible for the systematisation of organic chemistry) first noticed back in 1839 that in damp rooms with arsenic green wallpaper there was a "mouse-like" odour, which he thought was a gaseous derivative of cacadylic acid (dimethyl arsinic acid). It was only at the end of the 19th century that the Italian chemist Gosio isolated the gas and found that it had a garlic smell. Gosio had worked out that fungi living on wallpaper paste converted inorganic arsenic into a gas. Frederick Challenger identified Gosio's gas in the 1930s to be the highly toxic trimethylarsine. This gas had killed many, mainly children dying in their green decorated bedrooms. It was not until the turn of the 20th century that arsenic greens were finally phased out.

Trying to reconstruct past exposures, and the extent of arsenic use in wallpapers, is extremely difficult. Wallpapers are highly ephemeral and there are few collections of 19th century wallpapers to explore. My investigations into the use of arsenic, and other pigments, in wallpapers started with the most celebrated of British wallpapers, those of William Morris (1834–1996). His company Morris & Co. produced beautiful papers from hand printed, hand carved blocks from 1864 onwards. As Morris was central to the "Arts and Crafts" revival, and particularly to the resurrection of ancient dyeing techniques, his mythology suggests that he used natural pigments. This is from a Morris essay on pigments:

Of these dyes [aniline & synthetic] it must be enough to say that their discovery, while conferring the greatest honour on the abstract science of chemistry, and while doing a great service to capitalists in their hunt after profits, has terribly injured the art of dyeing, and for the general public has nearly destroyed it as an art.

However, a revealing letter of 1885 from Morris to his dyer Thomas Wardle suggested that he might have used arsenic greens in his famous and desirable designs. The letter piqued my interest, and early samples of Morris & Co. wallpapers were tracked down to the William Morris Gallery, Walthamstow, in the UK, once the childhood home of Morris. The Gallery had a scrap, 10 cm by 10 cm, of *Trellis*, Morris' first wallpaper design, and the third to be printed. It came from the home of Morris' general foreman George Campfield, and for this reason was thought to be of early origin. The scrap I received was a red rose on a green branch, see Figure 1. At this stage the only equipment readily available within our laboratory to analyse the paper was Energy Dispersive X-ray Analysis, EDAX, and the Museum allowed me to remove tiny flakes of pigments from Trellis for microanalysis. The results were immediate and impressive. The green branch was an arsenic-copper salt, the red rose vermilion. A highly toxic piece of art! This research was published in *Nature*.¹ The EDAX image, see Figure 2, shows arsenic distribution, using the Ka line, in a fleck of green pigment from the scrap of Trellis wallpaper.

Further investigations became problematic, since museums and archives were not keen on sending precious wallpaper samples through the post—particularly as most of the samples were large, unlike the scrap of *Trellis*. Also, routinely taking flakes of samples was not going to endear one to curators.

Some of the objects I wanted to look at could not be posted. Of particular inter-



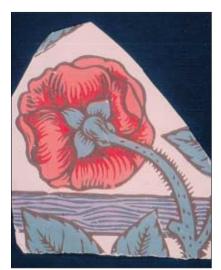


Figure 1. *Trellis* scrap from the William Morris Gallery.

est was an early Morris & Co. (actually at this stage Morris, Marshal, Faulkner & Co.)

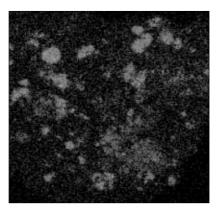
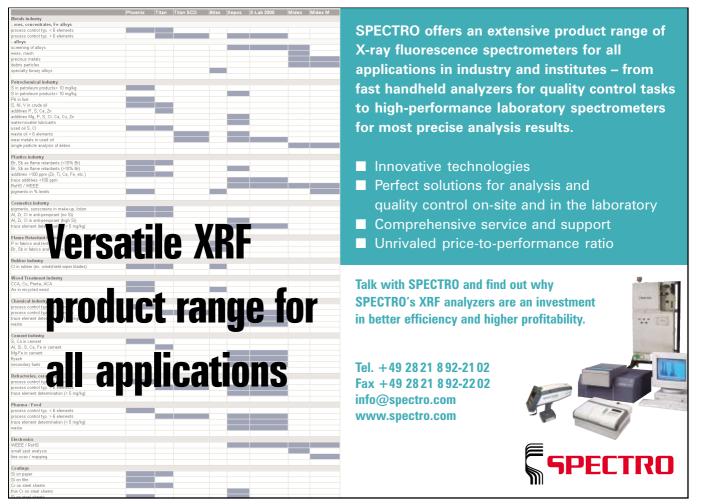


Figure 2. EDAX image showing arsenic distribution (light areas), using the Ka line, in a fleck of green pigment from the scrap of *Trellis* wallpaper.

commission, the *Green Dining Room* at the Victoria & Albert (V&A) Museum, built in the 1860s. Were the famous patrons of this most fashionable of London eateries, such as Whistler and Pointer, poisoned by trimethyl arsine, by this very green room?

Museums and galleries, while interested in studies into arsenic greens, would only allow investigations if they were undertaken at site with a portable X-ray fluorescence, XRF, instrument. Consequently, in collaboration with Niton Europe GmbH a trial was arranged at the V&A and the *Trellis* scrap was tested with a portable XRF spectrometer—reassuringly it was arsenic, see Figure 3, and mercury rich. The walls of the *Green Dining Room*, see Figure 4, proved to be highly contaminated, but not with arsenic. The XRF signal was saturated by the pigment lead chromate.

Impressed by the trial, and also considering the endless possibilities for furthering our group's interests in historical pollution, soil pollution and plant biogeo-



FASTLINK / CIRCLE 010 FOR FURTHER INFORMATION

ARTICLE

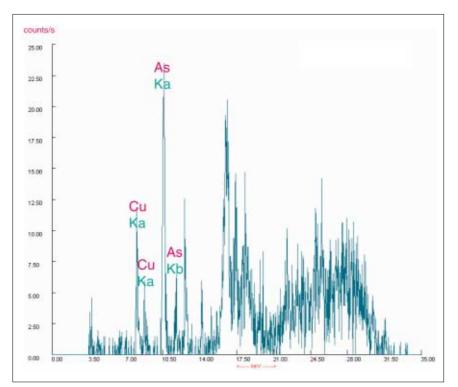


Figure 3. Portable XRF spectrum taken at the V&A from a flake from the Trellis.



Figure 4. Wall detail from the *Green Dining Room*, Victoria and Albert Museum, London.

chemistry, a Niton Portable XRF spectrometer was purchased, funded jointly by the Biotechnology and Biological Research Council and Aberdeen University. Among the early samples analysed in our laboratory was a suspiciously lurid green wallpaper sample from Charles Eastlake's 1860s classic Victorian authoritative handbook *Hints on Household Taste*. Within seconds we had established that arsenic greens mixed with cadmium yellow were responsible for the not very subtle colouration. Scraps of 19th century wallpaper started to show other interesting elemental contents. Silver showed up quite frequently; laserablation inductively-coupled plasma-mass spectrometry (ICP-MS), conducted in Joerg Feldmann's laboratory at Aberdeen University, soon identified flakes of silver and gold foil embedded in the pigments of many of the papers. These precious metals probably were dust generated from wallpaper gilding, suggesting the papers came from high-class manufacturers.

The wallpaper firm Sanderson now owns Morris & Co., and I was allowed to visit their Morris & Co. archive with the portable XRF. The archive contains a logbook of all Morris' wallpaper designs, kept in chronological order. I was able to establish that nine out the first eleven designs contained colourways that used arsenic pigments, with the use of arsenic stopping somewhere around 1872. Thus arsenic could be used to identify very early Morris & Co. papers. A visit to the William Morris Gallery helped me prove that a Morris wallpaper sample, Fruit from a collection of Morris & Co. artefacts by Edward Burne-Jones (the Pre-Raphaelite artist and founding member of Morris, Marshall, Faulkner & Co.), was, unexpectedly, an early printing as it contained arsenical pigments. The visit to the gallery also had another surprise. On the way in I noticed a display board outlining the discovery of a piece of wallpaper under the floorboards. Its design placed it firmly during William Morris' childhood. The green design on a white background arose my suspicion. I was able to confirm on the spot that Morris' house was also polluted with arsenic green, and probably trimethyl arsine.

Having examined the top end of the wallpaper market, I was keen to address what the poor were exposed to with respect to trimethyl arsine. The British Medical Journal in 1871 had noted, "In the majority of dwelling houses, from palace down to the navy's hut, it is rare to meet with a house where arsenic is not visible on the walls of at least some of the rooms". Enguiries at the National Trust for Scotland revealed that they had a building that contained 19th century wallpapers, the poor farm longhouse at Morlanich, Perthshire, built in the early 19th century. The residents obviously did not have a wallpaper stripper as peeling wallpaper on the walls revealed that it consisted of about twenty layers, including suspiciously green papers. With the portable XRF spectrometer I was able to



identify on-site that about six of the designs contained arsenic. To confirm that no trimethylarsine was present in the wallpapered rooms, air samples were taken and analysed by Joerg Feldmann using GC-ICP-MS. No arsenic gas was present, so the house is safe.

But it was not just wallpapers that were dyed green with arsenic—clothes were. *The Times* newspaper asked "What manufactured article in these days of high-pressure civilization can possibly be trusted if socks may be dangerous" following a revelation that high levels of arsenic were found in socks. W.S. Gilbert of Gilbert and Sullivan fame wrote in his 1869 *Bab Ballad, Only a dancing girl:*

No airy fairy she, As she hangs in arsenic green, From a highly impossible tree, In a highly impossible scene (Herself not over clean)



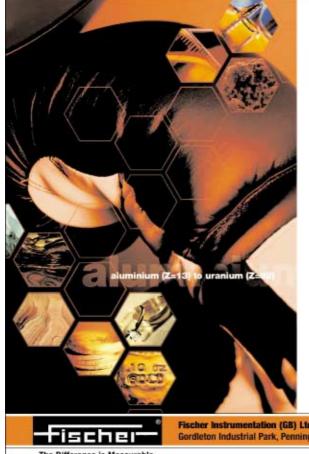
Figure 5. French fashion print from *La Mode*, 1848. The green dress is coloured using an arsenic-copper salt.

Medical reports of ill effects of arsenic green dresses abounded. Figure 5 shows an 1848 fashion plate from *La Mode*. The dress was probably dyed with arsenic green. XRF analysis showed that the ink used on the print to colour the dress green is a copper-arsenic salt.

The history of arsenic greens, illuminated by the portable XRF, and indeed the history of arsenic, is laid out in my forthcoming book.²

References

- A.A. Meharg, "Science in culture: The arsenic green", *Nature* 423, 688 (2003).
- A.A. Meharg, Venomous Earth: How arsenic is causing the world's worst mass poisoning. Macmillan Science, Basingstoke, to be published January 2005. http://www.macmillanscience.com/1403944997.htm



pulling no punches

There's no doubt that the remarkably small footprints of the Fischer XAN and XDAL energy dispersive spectrometers know how to make an impact.

And that can only be good news for those of you involved in the analysis of jewellery, gemstones and minerals, contamination of packaging materials, waste analysis to ppm accuracy or, to comply with RoHS, the detection of lead content in solder and components.

The Fischer spectrometry range can:

Tackle both quantitative element analysis and coating thickness measurement, with an astonishing range from Aluminium (Z=13) to Uranium (z=92),

Analyse coatings and bulk materials in solid, liquid and powder form. With its chamber, take large objects or measure many samples unsupervised due to a programmable XY table.

Tackle unprepared samples.

There's little else around that can compare with this package when it comes to XRF spectrometers. All these key features packed into a small footprint with starting prices affordable to the most cost sensitive laboratory.

Experience our fast and efficient solution:

Call: 01590 684100

Or visit www.fischergb.co.uk for the technical detail.

Fischer Instrumentation (GB) Ltd Gordleton Industrial Park, Pennington, Lymington, Hampshire SO41 8JD

The Difference is Measurable

FASTLINK / CIRCLE 011 FOR FURTHER INFORMATION