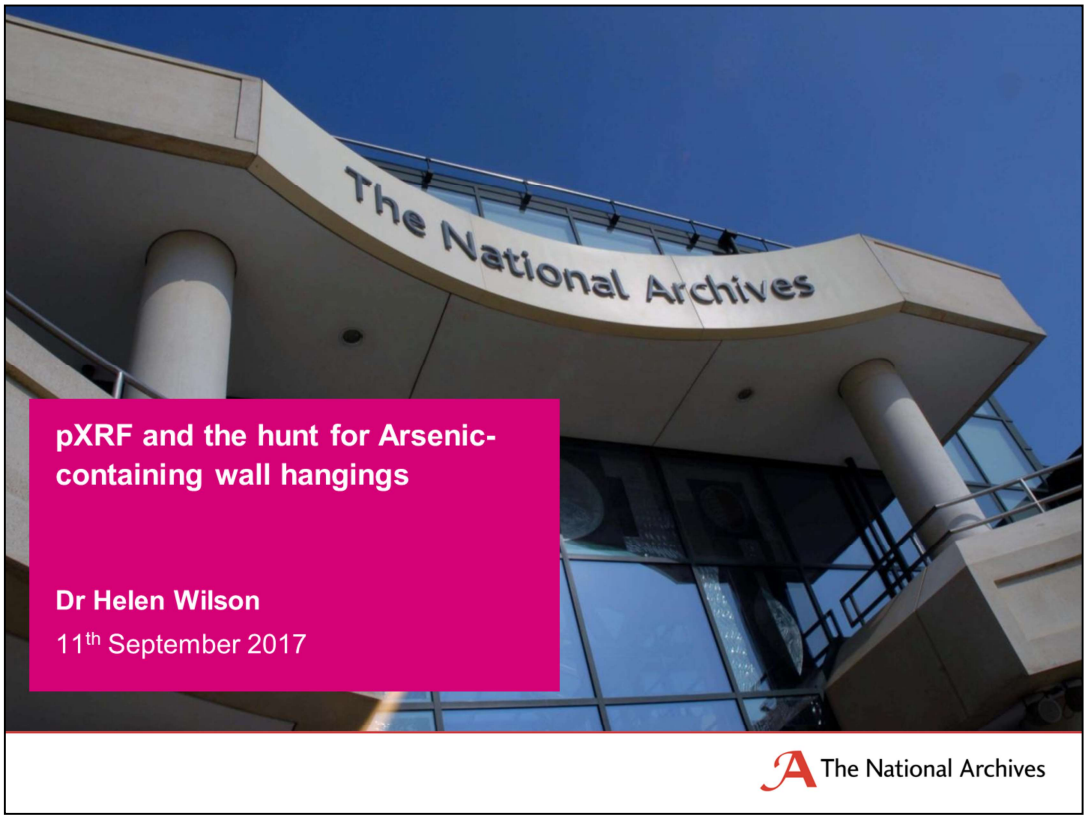
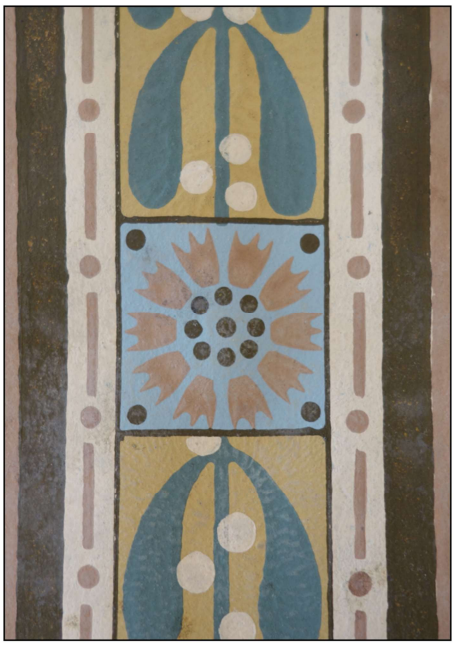


Presented at Icon Heritage Science Group's event: 'Historic document analysis using p-XRF: Pitfalls and Possibilities', 11th September 2017, The National Archives, UK.

Contents

- Board of Trade design registers
- Research question
- Why pXRF?
- Data collection challenges
- Analytical method
- Interpreting and reporting the data
- 'Bitten by Witch Fever'
- Any questions?



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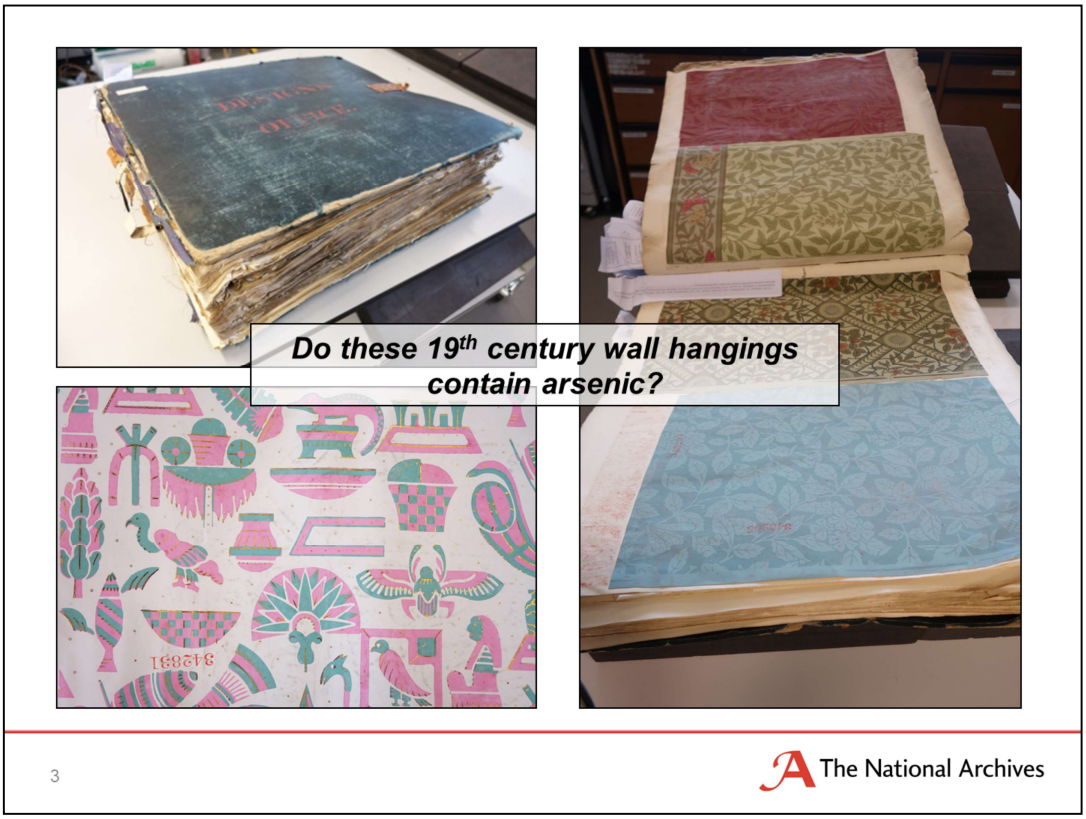


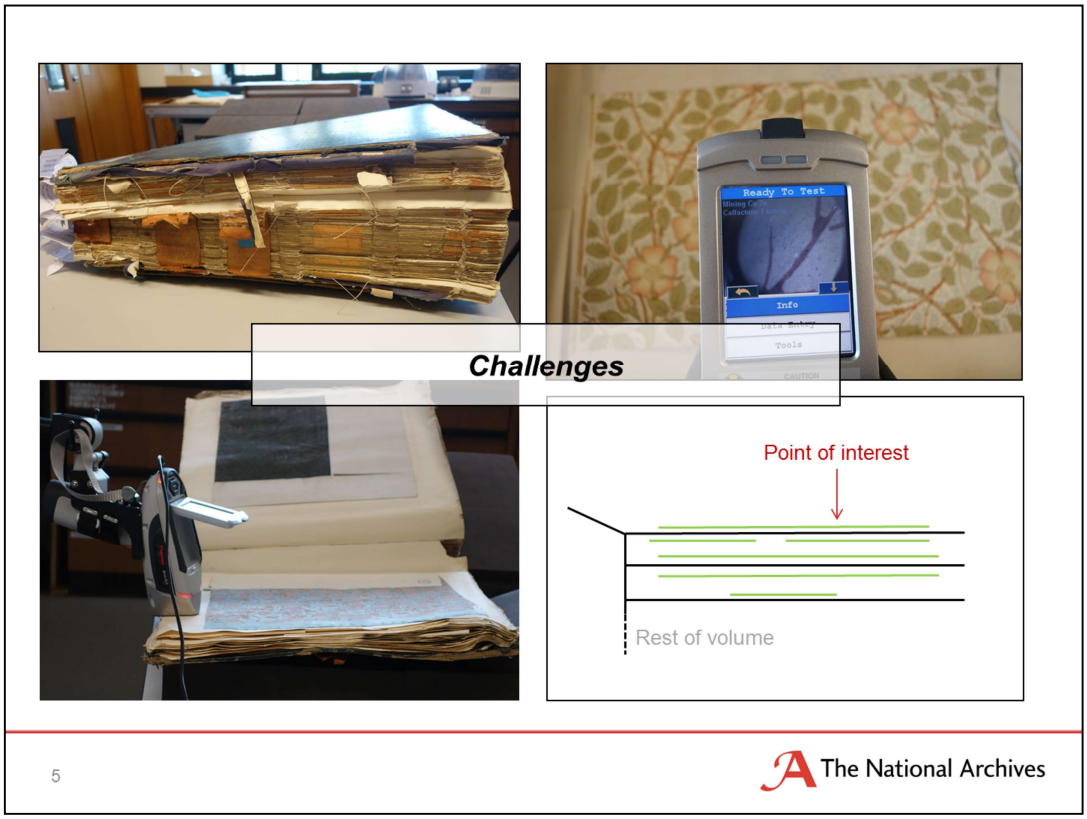
The Board of Trade design registers …

This volume (BT 43/103) contains hundreds of colourful wall hanging representations that were registered between 1879 and 1881. These include samples of original wall hangings, produced using the materials and methods of the time. Apart from the existance of low levels of inactive mould, the designs are in general, in an excellent state of preservation with bright, bold colours that can be reliably assumed to be close to if not exactly as they were when fresh off the production line.

Consequently, these volumes provide a fascinating and rich source of historic material…an opportunity to evidence and better understand the tastes, fashions, resources, and technology of the time and the implications thereof on society.

The National Archives' Collection Care department was enlisted to identify whether arsenic was present in any of 279 selected designs. The results were to feature in a book, 'Bitten by Witch Fever' by Lucinda Hawksely (Thames & Hudson Ltd, 2016), supporting written historical evidence that arsenic-containing pigments were used in wall hangings of this time.

We had a short time in which to analyse these wall hangings. pXRF was chosen to gather the evidence due to its ability to rapidly and non-destructively identify elements present in a surface. Additionally, once a method has been established it is easy to set-up, and its portability and the flexibility in terms of alignment ensured that it would be effective for analysis of a large volumes with various angles… moving machine rather than document meant there was less handling of document, less risk of damage to the document,



Challenges to pXRF analysis in the BT volumes:

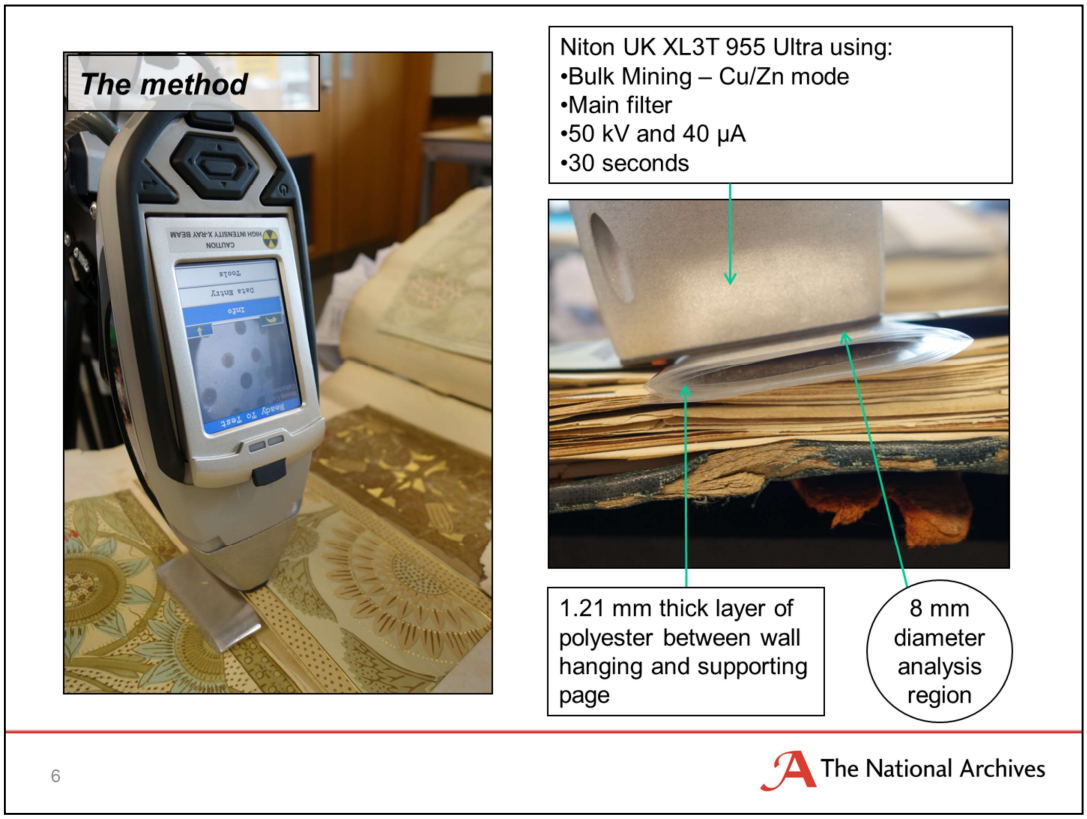
Large volume, handling issues

Elements, particularly heavier elements, present in the wall hanging samples that are adhered to the other side of the support page, as well as to some of those lying on pages beneath this page are likely to be detected. [PHOTO/DIAGRAM]

Elements from lower layers of paint within the same sample will be detected

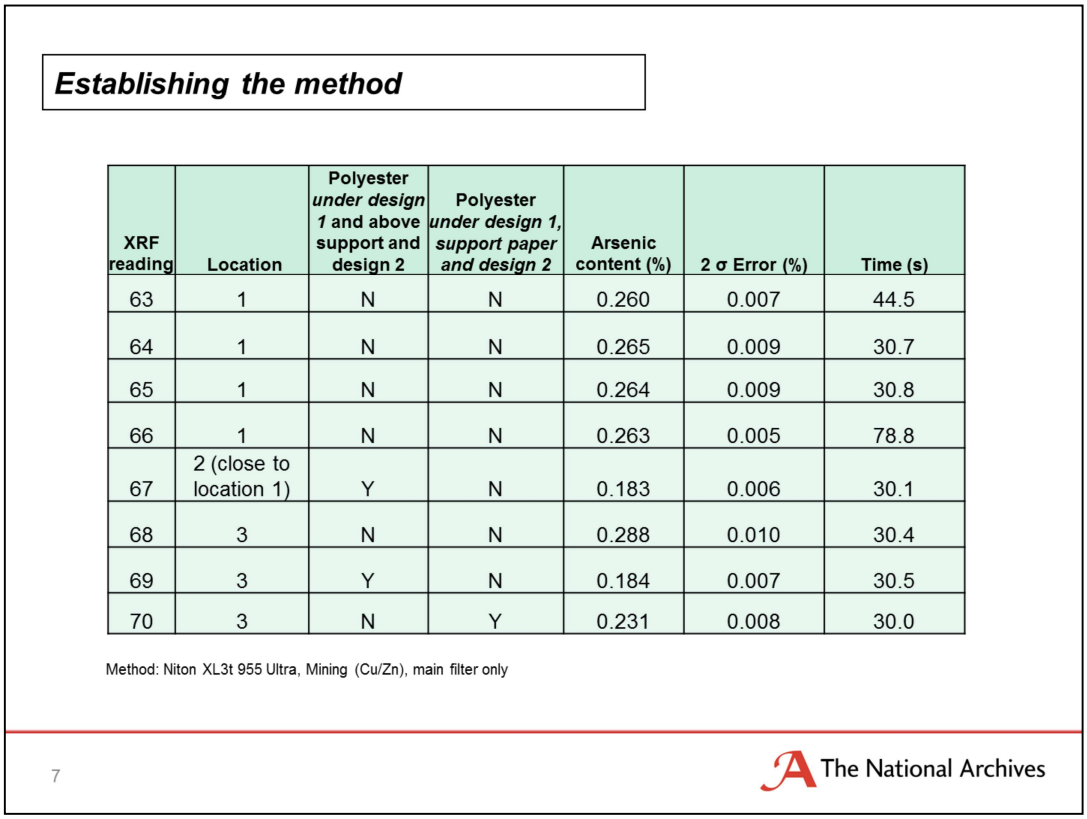
Often it was difficult to find an area in which only the colour of interest was being measured. [PHOTO]

Nature of the volume meant that angles of measurement varied between one sample and another which added more time than I had anticipated to the analysis.



Method:

Non-destructive analysis to determine the arsenic content in the yellow and/or green-based pigments in BT43/103 designs was undertaken using a Niton UK XL3T 955 Ultra handheld X-ray Fluorescence Analyser (XRF analyser). A 1.21 mm thick layer of polyester was placed between the region of interest in a design and the supporting page in the volume. A maximum of two colours were analysed per design. Selected supporting papers were also analysed. The analyser measures an 8 mm (diameter) area using an X-ray tube with a gold target and a Peltier cooled detector. Operating conditions were 50 kV and 40 µA for 30 s using the main filter on 'Bulk - Mining - Cu/Zn' mode. The % arsenic content as well as details such as the colour, location, and description of the area of analysis was recorded in a spreadsheet during analysis.



Establishing the method

XRF reading	Location	Polyester *under design 1* and above support and design 2	Polyester *under design 1, support paper and design 2*	Arsenic content (%)	2 σ Error (%)	Time (s)
63	1	N	N	0.260	0.007	44.5
64	1	N	N	0.265	0.009	30.7
65	1	N	N	0.264	0.009	30.8
66	1	N	N	0.263	0.005	78.8
67	2 (close to location 1)	Y	N	0.183	0.006	30.1
68	3	N	N	0.288	0.010	30.4
69	3	Y	N	0.184	0.007	30.5
70	3	N	Y	0.231	0.008	30.0

Method: Niton XL3t 955 Ultra, Mining (Cu/Zn), main filter only

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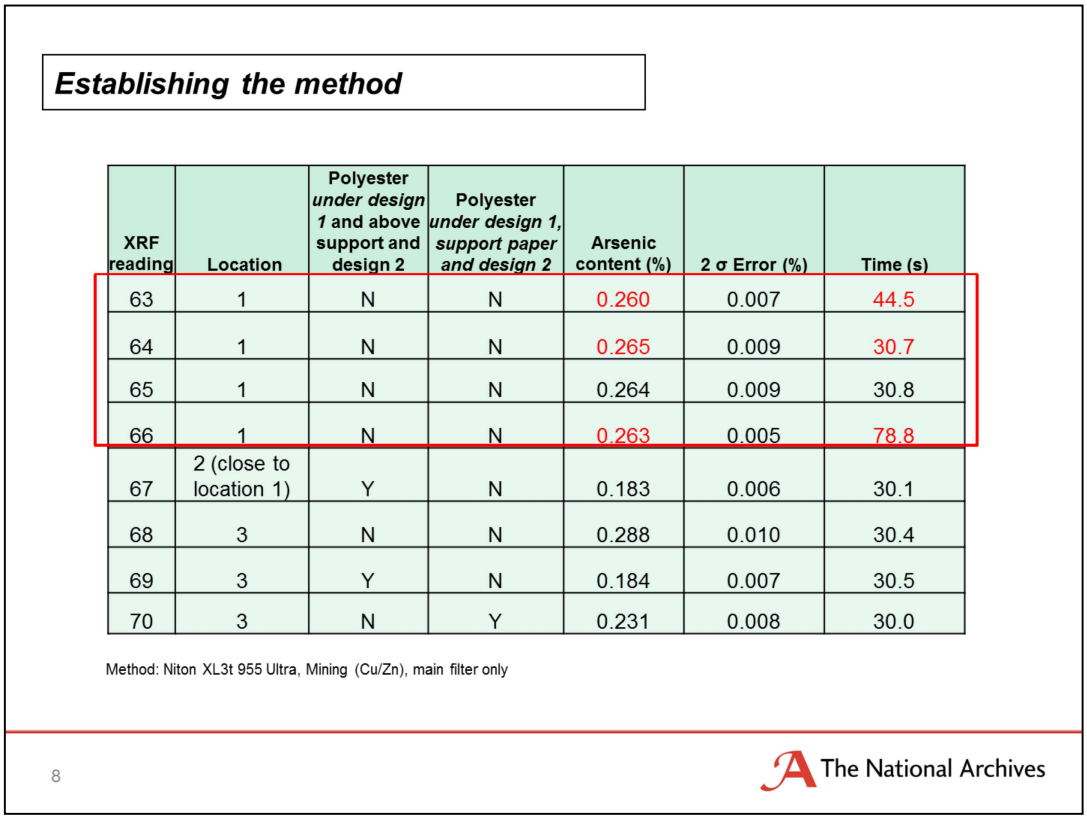
To establish this method, I worked with a conservator to ensure we found the approach that best balanced the needs of the research, resources available, and preservation of the document. This was particularly important for example, when deciding whether the analyser could be in direct contact with the painted surfaces, and if so, for how long.

To establish the settings, I analysed an area of a design that was particularly rich in arsenic under various conditions. Here is some of the data that I gathered:

Readings 63-66 led to decision to analyse on Mining (Cu/Zn) Main filter (30s) for 30s. Arsenic was only detected during analysis with the main filter hence the other filters were not used.

Readings 68-70 led to decision to use the folded polyester under the design where possible as the impact of elements in the lower designs would be minimised. Polyester 0.07mm per sheet, folded to a 1.21mm thickness.

I selected the mode and filter options for the ability to detect arsenic.



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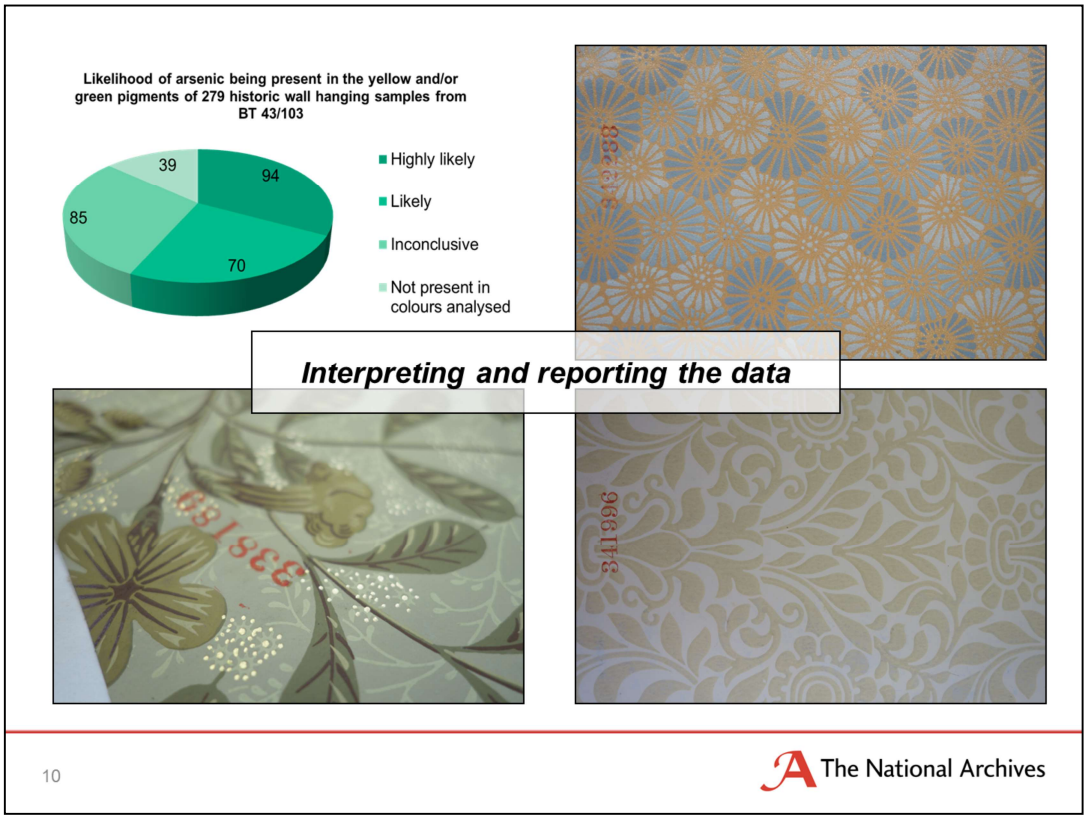

Data interpretation:

Due to the semi-quantitative nature of the results, we chose to not share the % arsenic values with the author and publishers. In particular because despite warnings about the semi-quantitative nature of the results, discussions suggested that there was a strong possibility that they would take the data literally, inadvisably publishing and comparing % arsenic contents of different wall hangings. Instead we provided a report in which the likelihood of the wall hangings containing arsenic was indicated. This we did using the following scale:

highly likely (0.1% or greater reported arsenic content) e.g lower LHS image, likely (0.05 – 0.1% reported arsenic content), inconclusive (up to 0.05% reported arsenic content), not present e.g. RHS images.

The boundaries to these categories are based on assumptions related to the level of error in the results that I anticipated could arise due to the presence of arsenic in samples below that of interest. These boundaries could change with more in-depth research. In such cases it is likely that some of the 'inconclusive' results would be re-categorised as 'likely'.

This possibility was included in the report that we provided the publishers.

Beautiful book with high quality reproductions of many of the wallpaper designs analysed.

The data that we provided was converted from likelihood of arsenic being present to possibility of toxicity of the papers. Despite the serious health risk that this suggests these papers pose the low quantities present, the low exposure levels (occasional viewing), the stable nature of the paint layers, the controlled environmental conditions (preventing exposure to particularly damp air), and a strict document handling policy in which readers are advised to wash hands after handing The National Archives' collection material, make the risk to readers and other users of the document, low.

A condition of the use of this data was that the method of data acquisition be reported. As a result it is detailed on the last page.

...Any questions?

12 *For more information: http://blog.nationalarchives.gov.uk/blog/x-rays-wallpapers-hunt-arsenic/*

The National Archives

Any questions?

The work from this project has been published as a blog on The National Archives' blog (http://blog.nationalarchives.gov.uk/blog/x-rays-wallpapers-hunt-arsenic/)