Fluorescence Signalling in Historic Herbaria – Detecting Mercury-based Biocides in Museum Collections

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Introduction

Although it was generally known within the museum community that plant collections were historically conserved using toxic compounds of mercury and arsenic, it was not known that residues of these compounds still remained in significant quantities today. Master's research at De Montfort University (1996-98) determined that the Nation Museum Wales' (NMW) herbarium was severely contaminated with mercuric chloride and naphthalene residues - two of the most common biocides used historically and ubiquitous in many collections across the world - and could not be handled safely. As museum plant collections are unique research resources, access to them is essential – from both conservator and user perspectives. Due to the vast size of these collections (800,000+ specimens at the NMW) removal of the contaminated backing sheet was not an option (in terms of the time it would take), and routine chemical analysis to inform a rolling remounting programme was neither feasible in terms of time, nor economically viable.

This research aimed to develop a simple, cheap and rapid screening method to identify the presence of mercury on plant specimen backing sheets. Since a significant proportion of backing sheets have historic significance, a non- or micro-destructive method was preferable.

Figure 1: Specimens from the herbarium collection, National Museum Wales. The right hand image illustrates the fluorescence observed on the backing sheet under UV light (366 nm)

The research

- PhD research, in collaboration with the NMW, was carried out at the University of Lincoln (2003-2012).
- During initial Master's research (at De Montfort University), fluorescent spots, over a range of emission wavelengths, were observed on all of the backing sheets (Figure 1).
- Particle induced X-ray emission, using the linear accelerator at the Centre de Recherche et de Restauration des Musées de France, the Louvre (Paris), with funding from the EUArtech programme, determined the elemental compositional differences between the fluorescent and non-fluorescent areas on over 200 historic backing sheets from the NMW collection (Figure 2).
- X-ray photoelectron spectroscopy was carried out at the EPSRC facility at Cardiff University to determine the mercury speciation for both fluorescent and non-fluorescent areas.
- Laboratory simulations and accelerated aging experiments were carried out using modern materials to validate the research hypotheses.

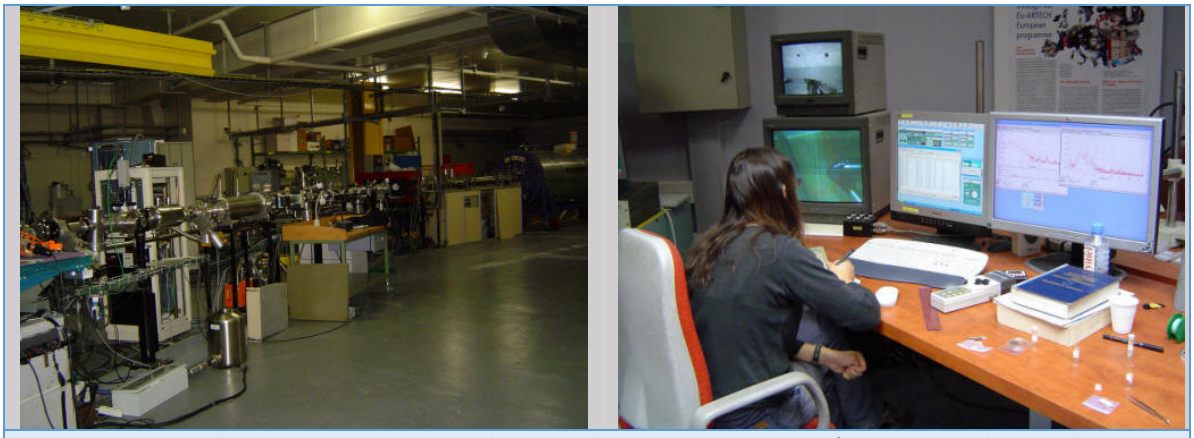

Figure 2: Linear accelerator at the Centre de Recherche et de Restauration des Musées de France, showing the PIXE control station (right)

Key findings of the research

- It has been demonstrated that the development of the fluorescence is directly linked to the presence of mercury.
- There is compelling evidence to support the hypothesis that the observed fluorescence within the herbarium collection is due to the reduction of Hg(II) to Hg(I) during the oxidative degradation of cellulose, occurring as part of the natural aging process.
- Both accelerated aging tests, and empirical observations, indicate that the fluorescence takes at least 30 years to develop, as the degradation of cellulose has to progress sufficiently to propagate the production of the fluorescent Hg(I) species.
- The application of naphthalene as a biocide is very common, and is likely to be present in the majority of herbaria in Britain and abroad. The presence of naphthalene increases the rate of fluorescence development on specimen sheets that have also been treated with mercuric chloride. The oxidative decomposition of naphthalene is a source of additional hydroperoxyl radicals, also produced during the oxidative degradation of cellulose. These hydroperoxyl radicals are responsible for the reduction of Hg(II).
- A hand-held UV-A lamp provides a rapid and effective method of identifying those samples within the collection that have been highly contaminated with mercuric chloride, and provides a means to prioritise which collections require immediate re-mounting. Furthermore, this will inform the implementation of standard procedures to protect personnel and visitors handling the collections, and enable the removal of a large amount of hazardous chemical from the herbarium environment.

Publications from Research

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