

The analysis of waxes in heritage collections gives us insight into early human technologies, material innovation, use, their meaning and opacity. For

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Fig. 1 Left: a fragment from unpigmented wax seal, likely medieval, showing the separation of beeswax into layers. Right: a micro-X-ray tomography cross-section of a similar seal fragment, showing the extent of layer fragmentation through the bulk of the material. Images courtesy of David Mills, Queen Mary University of London.

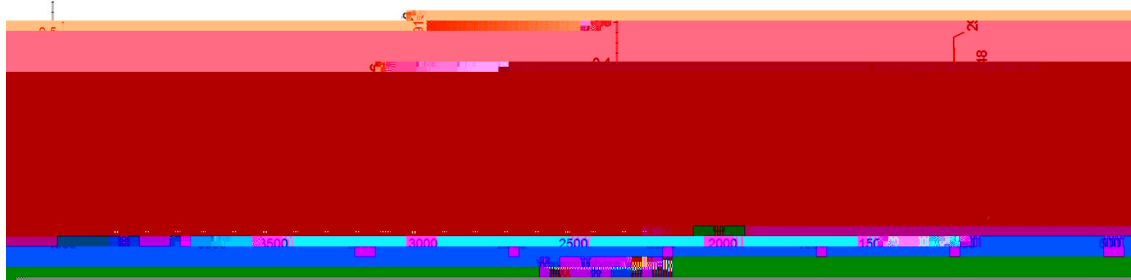
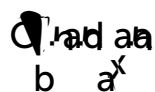


Fig. 2 ATR-FTIR spectrum of unbleached contemporary beeswax.

incorporated. The presence of these additives affects the stability and longevity of the final material. Wax seals, for example, often display a fragile, layered, pastry dough-like structure as a result of the kneading method used to incorporate pigments and resins into the beeswax prior to sealing (Fig. 1).



Beeswax is a complex mixture of long-chain wax esters, hydrocarbons, fatty acids, and other organic components, the relative proportion of which can vary depending on the wax's origin (*e.g.* on the species and feeding habits of the bees). The long organic molecules in wax can crystallise in two forms, an orthorhombic structure composed of esters and non-functionalised polymethylenes, and a monoclinic one, containing alcohols and fatty acids. This crystalline, organised portion of the wax comprises approximately two thirds of the total mass; the rest of the wax structure is amorphous.

Because of its relative prevalence, beeswax is the most extensively studied wax in the context of heritage science. For this reason, the analysis methods outlined below (some of the techniques described are destructive whereas others are non-destructive) will focus on this material, but may be applicable to other types of wax. The most common scientific techniques used for the characterization of beeswax are Fourier-transform infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS), although many other complementary techniques can also be used. Both methods are primarily used to determine if an object is composed of, or contains, wax, as well as to differentiate the types of wax present. In some instances, these methods have been employed to understand the ageing behaviour of waxes.

FTIR spectra of beeswax are dominated by the hydrocarbons, fatty acids, and esters (Fig. 2). The hydrocarbon signals are seen as very strong —CH_2 asymmetric and symmetric stretches at *ca.* 2920 and 2850 cm^{-1} , respectively, —CH_2 scissoring at *ca.* 1470 cm^{-1} , and

backbone —CH_2 rocking as a doublet at *ca.* 720 cm^{-1} ; a carbonyl stretch *ca.* 1735 cm^{-1} (esters), commonly with a shoulder at *ca.* 1710 cm^{-1} (free fatty acids), as well as a GO ester stretch present at *ca.* 1170 cm^{-1} .¹ In aged wax, the carbonyl shoulder (1710 cm^{-1}) tends to become more pronounced, and sometimes an —OH stretching band (3600–3200 cm^{-1}) may appear, both a result of ester degradation.

GC-MS is by far the most common analytical technique for wax characterisation in heritage objects.² The unknown composition and mixed nature of heritage wax samples may make it difficult to select the most appropriate experimental conditions and obtain a complete profile of the material but several studies have addressed this challenge. Distinguishing between different types of waxes in a GC-MS total or reconstructed ion chromatogram relies on the evaluation of the retention peaks in the chromatogram, corresponding to variations in the components of the wax (Fig. 3).

X-ray diffractometry (XRD) has been used to assess the change in crystallinity in various mixtures with changes in

environmental conditions, or with ageing. It is this method that has provided clues to the changing physical

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References

1 L. Shearer, An evaluation of Fourier transform infrared spectroscopy for

the characterization of organic compounds in art and archaeology, PhD thesis, University College London, 1989.

2 M. Regert, Direct Mass Spectrometry to Characterise Wax and Lipid Materials, in *Organic Mass Spectrometry in Art and Archaeology*, ed. M. P. Colombini and F. Modugno, John Wiley & Sons, Sussex, UK, 2009, pp. 97-129.

3 J. Langlois, G. Mary, H. Bluzat, A. Cascio, N. Balcar, Y. Vandenberghe and M. Cotte, Analysis and conservation of modern modeling materials found in

Auguste Rodin's sculptures, *Studies in Conservation*, 2017, 62(5), 247-265, DOI: 10.1080/00393630.2015.1131029.

4 Analytical Methods Committee AMCTB No. 98, X-ray micro computed tomography in cultural heritage, *Anal. Methods*, 2020, 12, 4496-4500, DOI: 10.1039/D0AY90112A.

5 D. Gramtorp, K. Boffeldt, J. Glastrup, *3D4(M.)34*