



Raman spectroscopy of archaeological and ancient resins: Problems with database construction for applications in conservation and historical provenancing

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ABSTRACT

The adoption of Raman spectroscopy as a screening technique for the presence of organic resins on diverse substrates is now being advocated for the first pass non-destructive examination of potential sites for limited sampling using other analytical techniques. The characterisation of ancient resins in art work and specimens recovered from archaeological excavations is critically dependent upon the analytical capability of Raman spectroscopy using different wavelengths of excitation from the visible to the near infrared and the interpretation of the data illustrates the advantages and limitations of the technique. Resin specimens from art works and artefacts span a period of about 7000 years of recorded history and the influence of factors such as the environmental degradation, burial deposition, reaction with associated substrates and mineral pigments on the observed Raman spectra have been assessed. The key molecular Raman spectral features that are definitive for the discrimination between contemporary resins are considered in respect of these factors and thereby illustrative of the difficulties posed for the creation of a Raman spectral database of ancient resins, in contrast with the extensive and definitive literature equivalents that are available for their mineral pigment and organic dye analogues.

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1. Introduction

Resins have been used by different cultures for many thousands of years for a variety of purposes centred on their adhesive, protective and decorative properties and many of these are still being used today; for example, fossilised amber and copal resins are very desirable items of jewellery and the more modern botanical tree resins such as *Pinus* and *Cedrus* resins are used as sealants and varnishes [1]. The conservation strategy for materials such as resins, gums and waxes which are prone to degradation requires the provision of information about what has survived and what has been lost [2–6]. Classically, mass spectrometric analytical techniques have been utilised for the analysis of ancient resins from archaeological relics and art works, but this involves the consumption of specimen, which often is available in only limited quantities. The Raman spectroscopic analysis of resins has been demonstrated to provide a suitable first-pass method for their identification on ancient art works and artefacts and this has been shown to be especially useful in cases to locate areas where only limited sampling was permitted without involving the detachment of the specimen from the artefact or art work. Despite the often stated advantage

of Raman spectroscopy in its analytical application to art and archaeological specimens in that it is possible to acquire molecular information about both their inorganic and organic components simultaneously, hitherto a major problem in the achievement of definitive spectra has been the presence of fluorescence emission that swamps the Raman spectra, particularly in the case of materials that have been subjected to environmental degradation. The advent of long wavelength laser excitations for Raman spectroscopy, particularly those at 1064 nm using Fourier-transform and at 785 nm using charge coupled detection techniques, has provided an impetus for the recording of Raman spectra that were hitherto inaccessible to study because of fluorescence emission at visible wavelengths of excitation [7,8]. Despite the inherently weaker Raman effect in the near infrared region due to the inverse dependence of the molecular scattering intensity on the fourth power of the wavelength of excitation, the minimisation of the fluorescence emission background that can swamp the weaker Raman bands dictates that the longer wavelength laser excitation is advocated particularly for organic specimens that contain low energy electronic states or which may contain fluorescent impurities; archaeological resins provide a typical example of this type of specimen. Hence, in spite of the fact that the Raman spectral excitation at 1064 nm is some 350X weaker intrinsically than the same spectrum excited in the ultraviolet at 250 nm, all other instrument response parameters being equal [8], the best chance of observing

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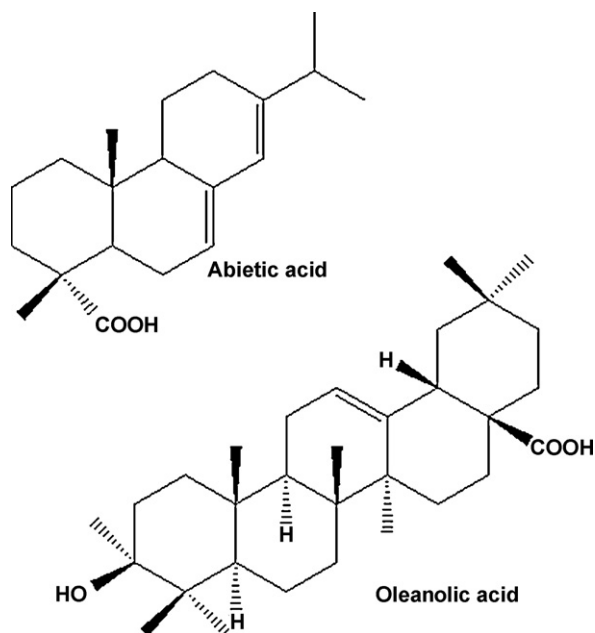


Fig. 1. Molecular structures of a diterpenoid (abietic acid) and a triterpenoid (oleanolic acid).

the Raman spectra of archaeological resins would be anticipated to be provided by long wavelength excitation at 1064 nm as, even at 785 nm, residual fluorescence emission can be problematic.

From previous studies of resins and gums relevant to art history and archaeological science, a limited database has now been established which can be used to verify the presence of certain resins on artefacts obtained from archaeological excavations [9–14]. In addition, the presence of spectral features indicative of specimen degradation, either from the processing technology adopted in an ancient culture or from the influence on the specimen of the depositional environment from which it has been excavated, can be of use to conservators and art historians. In some cases, even with 1064 nm excitation, the resin specimens studied exhibited a troublesome fluorescence emission background, which resulted in a diminished spectral quality that can be deleterious for the correct

classification of the resin. Raman spectroscopic studies of organic materials in artworks [15–17], although not strictly archaeological, have also addressed the effects of degradation of waxes, gums, resins and proteinaceous binders in storage environments. However, it would be expected that resins will have been subjected to a longer exposure and contact with a wider range of depositional environments that could well result in an expectation of poorer quality analytical information being provided [18].

Tree resins are composed of diterpenoids (C_{20} alicyclic structures) and triterpenoids (C_{30} alicyclic structures), which are generally not found together in any one resin [19] and the properties of a triterpenoid resin such as those derived from the *Pistacia* genus are very different from diterpenoids derived from the *Pinus* genus, for example, frankincense and pine resins, respectively.

In previous studies reported from our laboratories [9–14], we have demonstrated the viability of FT-Raman spectroscopy for the discrimination between modern standard diterpenoid and triterpenoid resins, including several species from the *Pistacia*, *Pinus*, *Cedrus*, *Boswellia*, *Commiphora* and *Agathis* genera. Typical molecular structures of a diterpenoid (abietic acid) and triterpenoid (oleanolic acid) resin component are shown in Fig. 1. A Raman spectroscopic protocol for the discrimination between diterpenoids and triterpenoids on the basis of key Raman spectroscopic marker signatures has been provided in the literature [9] and this is a good

starting point for the derivation of sources for a selection of ancient resins. Examples of the sourcing protocols will be provided for resin specimens of previously unknown composition excavated from a number of documented archaeological sites dating from some 7000 years of recorded human history and prehistory. All resin specimens were analysed without any prior chemical or mechanical treatment or sample preparation being undertaken to properly assess the information that can be provided from the adoption of Raman spectroscopy as a first-pass non-destructive analytical screening technique, which will be relevant in the selection of sites for the further application of limited destructive sampling techniques such as GCMS.

2. Experimental

2.1. Resin specimens

Sample: resin adhering to the inner surface fragment of Canaanite jar sherd, Tell-el Amarna, XVIIIth Dynasty, ca. 1350 BC.

Sample 562: several small and larger pieces, 5–25 mg, from Gurob, XVIII–XIXth Dynasty, ca. 1250 BC.

Sample 3024: one medium size resin bead, 10 mg, from Hawara, Graeco-Roman period, ca. 100 BC to 300 AD;

Samples 5090, 5091: two medium-sized pieces of resin, 10–15 mg, pre-dynastic, from Tomb H29; El Mahasna, ca. 3200 BC.

Sample: “resin” eye-bead from cat mummy, 120 mg, Beni Hasan, XVIIIth Dynasty, ca. 1350 BC.

Resin agglomerations on ethnic cultural skin footwear which needed identification prior to conservation of the substrate.

Resin specimens were in archival storage at the Manchester Museum, following their cataloguing from the original excavations carried out by Sir William Flinders Petrie in the late 19th Century, in the Museum of Ethnography, Sao Paulo, Brazil, in the Royal Botanic Gardens, Kew, UK, and in the Victoria and Albert Museum, London; analyses had not been carried out on these specimens hitherto. Any specimen numbers refer to catalogue entries in the appropriate Museum archive.

2.2. Raman spectroscopy

FT-Raman spectra were excited using a Bruker IFS66 instrument with FRA106 Raman module attachment and a Nd^{3+}/YAG laser operating at 1064 nm with a nominal power of 100 mW at the specimen. Resin spectra were collected from up to 4000 single scans accumulated over the wavenumber range 100–3750 cm^{-1} at a spectral resolution of 4 cm^{-1} and with a spectral footprint of 100 microns. Resin specimens were mounted directly in an aluminium cup secured against a spring-loaded locator; several regions on the surface of each specimen were examined for sample inhomogeneity and to check band wavenumber positions, which for sharp bands were accurate to better than $\pm 1 cm^{-1}$. To maintain the requirement of specimen integrity and nondestructive sampling, the samples were not fractured or cleaved. However in some cases the project called for an assessment of any change manifest between the surface and the interior of the resin and this could readily be accomplished—in particular, for the excavated archaeological resin artefact [20].

3. Results and discussion

3.1. Amarna potsherd resin

The Canaanite jar sherd, excavated in the capital city of the XVI–IIth Dynasty pharaoh Akhenaten (Amenophis IV) at Tell-el-Amarna by Sir William Flinders Petrie in the early 1890s, is important

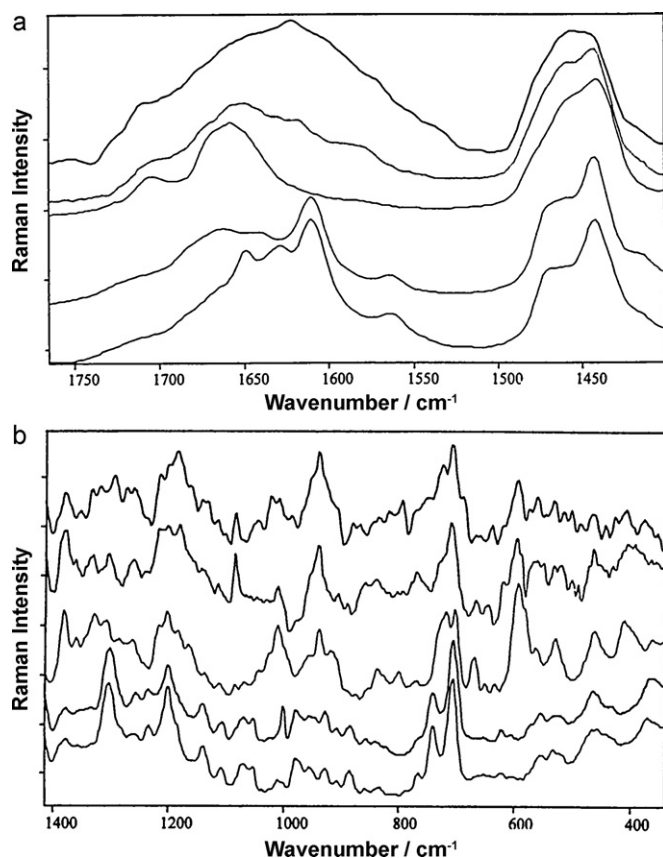


Fig. 2. FT-Raman spectral stackplot of, from top, Amarna archaeological resin, *Pistacia terebinthus*, *Pistacia lentiscus*, *Cedrus libani* and *Pinus halepensis*; wavenumber region (a) 1750–1400 cm^{-1} , (b) 1400–350 cm^{-1} .

because of the limited period of occupation of the site founded by Akhenaten in 1361–1350 BC. Canaanite amphorae manufactured in Syria and Palestine were used to transport resins, oils and honey in the Mediterranean region; the resin fragment studied here possessed a possible residue of resin on its inner surface, which gave the Raman spectrum shown in Fig. 2a and b over the wavenumber regions 1750–1400 cm^{-1} and 1400–350 cm^{-1} , respectively, along with several resin standard specimens of *Pistacia*, *Cedrus* and *Pinus* recorded for comparison. It can be seen that the spectra of the resin standards are all visually similar to that of the unknown resin on the potsherd fragment surface. In the Raman spectrum of the Amarna resin, a very broad, strong feature centred at 1621 cm^{-1} and a medium-strong band at 1456 cm^{-1} with a shoulder at 1446 cm^{-1} are the main signals (Fig. 2a) which show a closely similar spectrum to that of a modern specimen of *Pistacia terebinthus* resin, even allowing for the possible degradation expected to have occurred in the archaeological resin specimen over some 3500 years. The band profile of the 1621 cm^{-1} feature in the Amarna resin assignable to C=C stretching vibrations of the component terpenoid alicyclic rings is observed to be significantly broader than that of the standard *Pistacia* resin, unlike that of the band centred at 1450 cm^{-1} in both specimens.

Fig. 3 gives a stack-plot, from the top, of standard diterpenoid (frankincense) and triterpenoid (*Pistacia terebinthus*) resins and the Amarna resin for comparison over a wavenumber region that is critical for the discrimination between terpenoids; the bands at 1303, 970, 740, 370 and 305 cm^{-1} characteristic of diterpenoid resins [9] are absent from the spectrum of the Amarna resin, indicating that this specimen is probably therefore derived from a triterpenoid source. In confirmation of this conclusion, bands at 1380, 939, 597, 532 and 408 cm^{-1} characteristic of a *Pistacia terebinthus* resin can

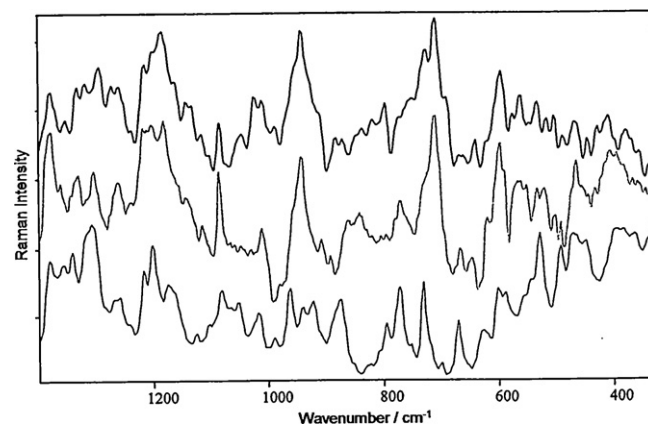


Fig. 3. FT-Raman spectral stackplot of, from the top, a triterpenoid resin standard (*Pistacia terebinthus*), Amarna resin, a diterpenoid resin standard (frankincense); wavenumber region 350–1400 cm^{-1} .

all be identified in the Amarna sample. We can therefore conclude that the source of the Amarna resin is closely similar to that of the triterpenoid *Pistacia terebinthus* resin despite the presence of the additional but rather featureless 1621 cm^{-1} band in the archaeological specimen.

As the historical implications of this result obtained from non-destructive Raman spectroscopy were important, it was permitted subsequently to undertake the destructive GCMS analysis of the Amarna resin, from which the presence of moronic acid, oleanolic acid, isomasticadienic and masticadienic acids were identified, which confirmed the Raman spectroscopic assignment of this resin specimen to a *Pistacia* genus triterpenoid.

3.2. Gurob, Hawara and El Mahasna resins

All specimens were excavated by Petrie in the 1890s. Gurob, Tell Medinet Ghurab, is an XVIII–XIXth Dynasty pharaonic (1450–1220 BC) site in the Fayoum delta founded by Tuthmosis III. Its importance is that this was the first excavation of an Egyptian town site (1888–1890 season). Hawara, also in the Fayoum delta region, is a later Graeco-Roman necropolis (100 BC to 300 AD) which was excavated in 1887/88. El Mahasna is a pre-dynastic burial site dating from before 3200 BC; the resin specimens from Tomb H29 therefore represent the oldest analysed in the present work and indeed to date in the Raman spectroscopic literature.

The spectra obtained from these three sites reflect a timespan of 3500 years of ancient civilisation and trade. The brown-black Hawara resin (Fig. 4A), although being the most recent of the three specimens, in fact exhibits the most severe signs of degradation and the FT-Raman spectrum shows only diffuse and broad features. Hence, with the absence of reasonably clear signatures in the Raman spectrum indicative of an organic compound(s) no sensible characterisation of this resin is possible from the spectral analysis. In contrast, the pre-dynastic El Mahasna resin, which is some 3500 years older, gives a Raman spectrum (Fig. 4B) with clear features at 2932, 1709, 1608, 1453, 1442, 1380, 1357, 1304 and 977 cm^{-1} . Whereas several of these, such as those at 1709, 1453 and 1442 cm^{-1} are assignable to a triterpenoid resin, others, such as that at 977 cm^{-1} are characteristic of a diterpenoid resin [9].

The two Gurob resin specimens, one red-brown and the other amber-coloured, have Raman spectra (Fig. 4C and D) that are very similar to each other which show the presence of assignable Raman spectral signatures; the FT-Raman spectral stackplot in Fig. 5 shows the wavenumber region 1400–300 cm^{-1} for the Gurob amber resin specimen and several standards, namely *Pinus halepensis* (A), frankincense (B), *Pistacia terebinthus* (C) and the Gurob resin (D).

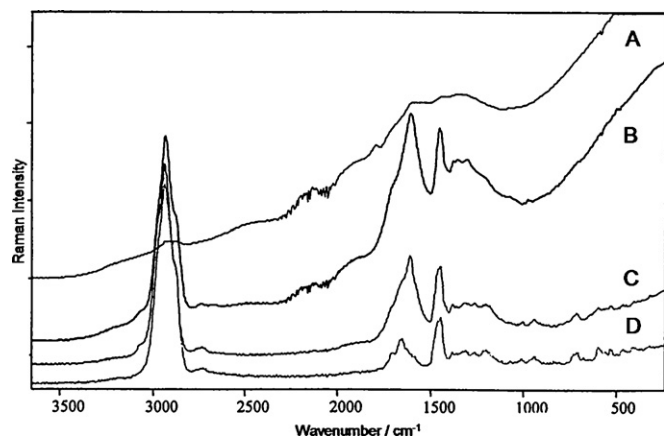


Fig. 4. FT-Raman spectrum of (A) a highly degraded archaeological resin from Hawara, Egypt, (B) a resin specimen from El Mahasna, (C) and (D) red-brown and amber coloured resins from Gurob; despite the rather broad features at 2930, 1613, 1456 and ~ 1270 cm^{-1} visible on a spectral background for the latter three resins, resin (D) can be compared with standards in Fig. 5.

Although the band at 1608 cm^{-1} is distinctly broader in the spectrum of the red-brown resin specimen, which is possibly indicative of more significant degradation having occurred [9,20], the presence of several weaker intensity bands between 1400 and 300 cm^{-1} can assist in the identification of the source of this resin. The comparison of the spectra of the amber coloured Gurob resin with the Raman spectra of frankincense, *Pinus halepensis* and *Pistacia terebinthus* standards over the 1800 – 1400 cm^{-1} wavenumber region shows a clear match of our unknown archaeological resin specimen with the standard *Pistacia terebinthus* specimen. The amber coloured resin has bands at 1707 , 1655 , 1620 , 1583 cm^{-1} which exactly match the wavenumbers and relative intensities of the bands for *Pistacia terebinthus* in this region. In contrast, the diterpenoid resin frankincense, which also has a band at 1621 cm^{-1} , does not have component features [9,11] at 1707 and 1655 cm^{-1} . Examination of the wavenumber region between 1400 and 300 cm^{-1} (Fig. 5) therefore provides confirmation of the attribution of the amber Gurob resin to a *Pistacia* resin species; although bands at 1382 , 1202 , 1182 , 939 , 597 , 530 and 411 cm^{-1} all occur in both spectra but, significantly, the frankincense bands at 962 , 875 and 492 cm^{-1} are absent from the Gurob resin spectrum. Hence, the Gurob resin can be assigned to a triterpenoid resin closely similar to our standard sample of the *Pistacia* genus [9].

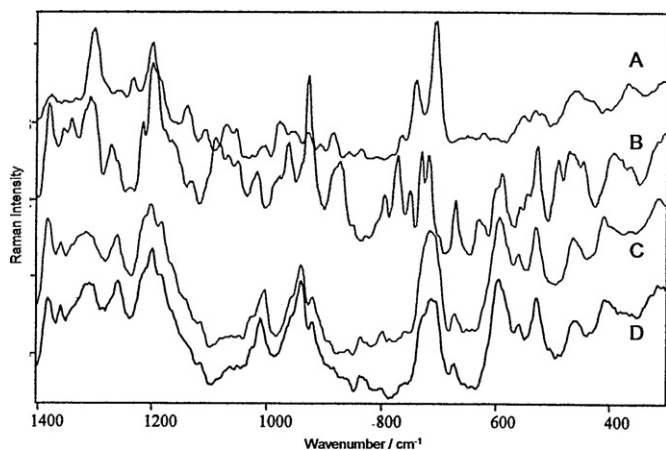


Fig. 5. FT-Raman spectral stackplot of (A) *Pinus halepensis* resin, (B) Frankincense resin, (C) *Pistacia terebinthus* resin, (D) Gurob resin, amber coloured; wavenumber region 300 – 1400 cm^{-1} .

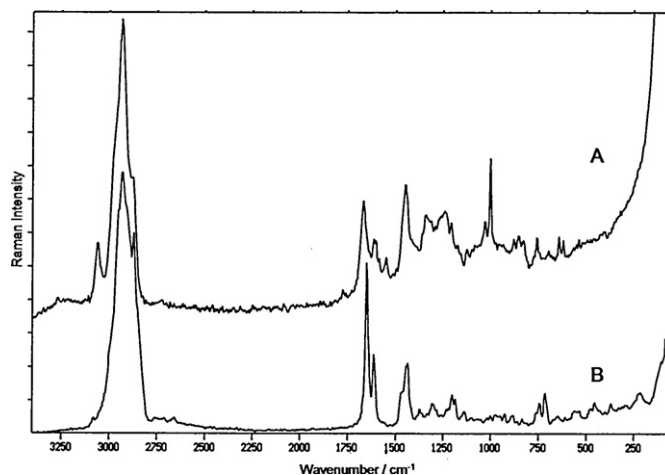


Fig. 6. FT-Raman spectra of (a) ancient cat mummy eye-bead resin and (b) amber resin; wavenumber region 50 – 3300 cm^{-1} .

3.3. Eye-bead, cat mummy

An XVIIIth dynasty mummified cat, *Felix libyanus*, from the necropolis at Beni Hassan near Der Rifeh, Egypt, dating from about 1350 BC was unwrapped in the Manchester Museum and a small bead was discovered in an eye-socket; this was a highly unusual discovery and the specimen was judged to be historically too valuable to sacrifice for normal analysis. Some possibilities were that the bead was glass or amber resin; in fact, as the Raman spectrum in Fig. 6A shows, the spectral signatures of a keratotic specimen are indicated with bands due to the amide I (CONH) stretching mode at 1660 cm^{-1} , NH bending at 1450 cm^{-1} and CH bending at 1250 cm^{-1} . A strong sharp Raman band at 1003 cm^{-1} is characteristic of phenylalanine. The Raman spectrum of an amber resin [21,22] is also shown in Fig. 6B, from which it can be concluded that the eye-bead is clearly not assignable to an amber resin, nor, of course to glass, which generally has broad features characteristic of Si–O bonds in the region between 400 and 1100 cm^{-1} . The Raman spectrum of the cat mummy eye-bead (A) is very similar indeed to that of a cat's claw (B), and the comparison spectra are shown stackplotted in Fig. 7a and b, for the wavenumber regions 2700 – 3100 and 400 – 1800 cm^{-1} , respectively; although the spectra in the CH stretching region (Fig. 7A) are very closely similar to each other, a notable difference between these two spectra in Fig. 7B is the absence in the eye-bead spectrum of the broad asymmetric band centred at 510 cm^{-1} in the spectrum of the cat's claw which is assignable to the CSSC cross-links in the keratin [23,24]. Previous studies [25,26] have shown that this feature is the first to disappear in the Raman spectrum upon degradation of keratotic specimens—this is reinforced by the appearance in the eye-bead spectrum of increased Raman intensity in the CSH stretching modes at 610 and 640 cm^{-1} . An example of a degraded keratotic specimen is shown in Fig. 8, in which the broadening of the amide bands and the absence of the SS stretching modes near 500 cm^{-1} are significant clues. It is therefore reasonable to suggest that the cat mummy eye-bead is a keratotic material that has been thermally processed to some degree to assist in its shaping and construction; what cannot be decided here, of course, is the purpose of the cat's eye-bead and whether it was designed as a false eye during the animal's lifetime or was a product of a hitherto unrecognised funerary practice [27].

In several specific cases some really novel and surprising conclusions have been forthcoming from the application of Raman spectroscopic analyses to ancient resins; in one very recent example to illustrate this, a small amount of a yellow material removed

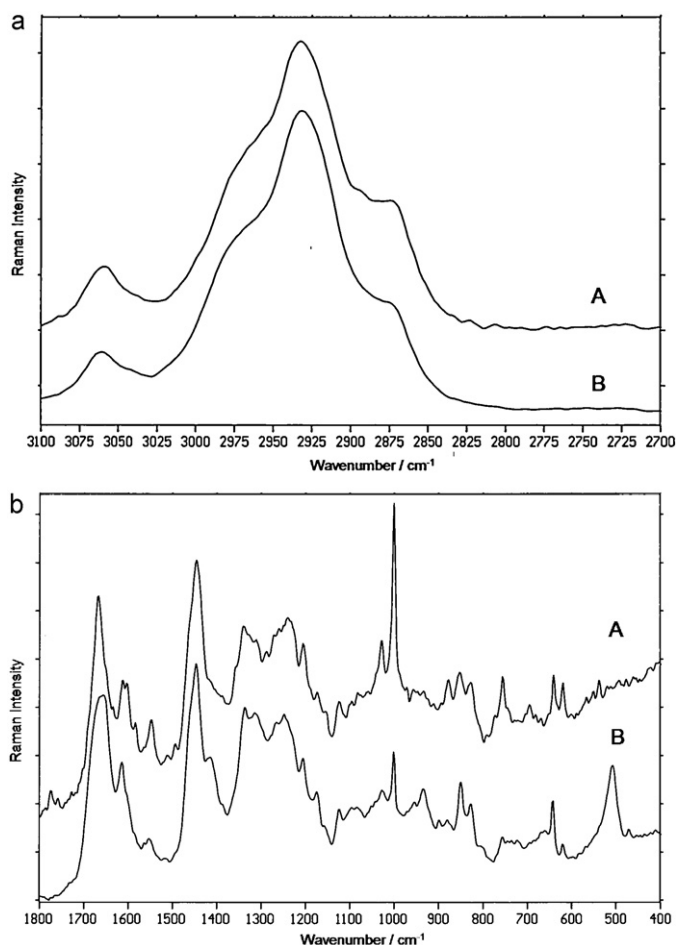


Fig. 7. FT-Raman spectra of (A) ancient cat mummy eye-bead resin and (B) modern cat's claw; wavenumber regions: (a) 2700–3100 and (b) 400–1800 cm^{-1} .

from a leather boot used in an Inuit culture was subjected to Raman spectroscopic study and proved to be a pine resin and not an animal wax as previously believed. However, in the particular Arctic source location of this boot, there are no pine trees; the custom in this culture of using pine needles as an insulating device, although suspected hitherto, now demands further investigation [28].

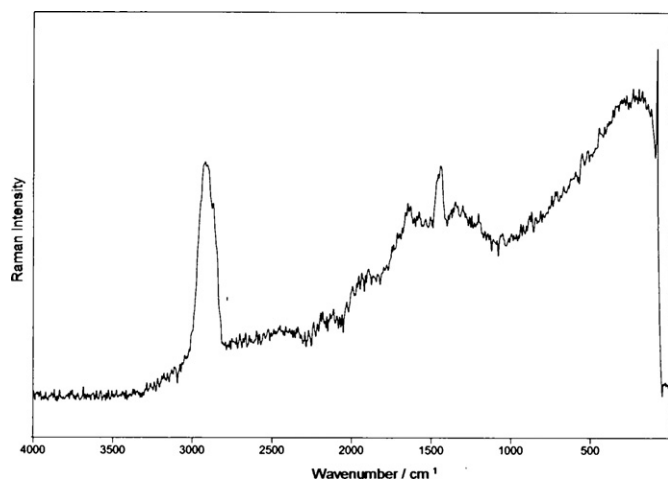


Fig. 8. FT-Raman spectrum of a degraded keratotic specimen, ca. 1000 years old, from a cold desert environment, wavenumber region 100–4000 cm^{-1} ; the absence of the SS feature and the broadening of the amide signatures, along with the spectral emission background and high noise levels in the spectrum should be noted.

Another surprise attribution from Raman spectroscopic studies of ancient resins revealed itself in the spectra of a *tembeta*, a T-shaped lip plug that was used as a hierarchical motif and symbol in Amazonian tribal cultures. The spectra from the red–brown resin plug showed clear spectroscopic evidence [29] of it being a local hardwood resin of the *Haematoxylum* species and therefore differentiated this particular specimen as being rather unique from others made of wood and bone, but what interested the conservators most about this specimen was the composition of a red powdery material on its outer surface; was this evidence of an applied pigment in its manufacture perhaps? It transpired that the powder coating on the outer surface of the *tembeta* was in fact a degraded form of the constituent resin and was present probably from the interaction of the resin artefact with its interment in the burial environment.

4. Conclusions

Raman spectroscopy using long wavelength excitation has proved successful in the recording of spectra from archaeological resins of some age excavated from a variety of sites and depositional environments. The information provided from the non-destructive analysis of organic specimens without preparative chemical or mechanical treatment is in many cases novel and not accessible by other means. Degradation of the resin specimen can be identified in the spectral signatures and, in the case of the mummified cat, points additionally to a possible ancient technological application related to its thermal history that was hitherto unsuspected in this culture [27].

Clearly, only the provision of a much wider and more comprehensive database of standards would facilitate the more exact description and classification of archaeological resins and care needs to be exercised in this respect. For example, we have found that *Pistacia terebinthus*, *Dipterocarpus alatus* and dammar resins have very similar Raman spectra, since all are triterpenoids. On the other hand, previous Raman spectroscopic studies of archival *dragon's blood* resins from several botanical and geographical sources have yielded spectral signatures which have enabled the discrimination to be effected between visually identical resin specimens. Another potential and inescapable problem is related to the degradation suffered by the archaeological resin specimens that have been buried for considerable periods of time. Finally, the development of miniaturised, portable Raman instruments for field applications will have direct relevance for the first-pass non-destructive screening studies of artworks, archaeological artefacts and materials excavated from depositional environments [30]; with such data, the selection of materials for further laboratory study can be accomplished and informed on-site conservation of selected specimens can be rapidly undertaken.

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