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Towards the identification of plant and animal binders on Australian stone knives

Alisa J. Blee[a], Keryn Walshe[b], Allan Pring[b], Jamie S. Quinton[a], Claire E. Lenehan[a,*]

[a] School of Chemical and Physical Sciences, Flinders University, Adelaide, South Australia, Australia
[b] Science Centre, South Australian Museum, Adelaide, Australia

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ABSTRACT

There is limited information regarding the nature of plant and animal residues used as adhesives, fixatives and pigments found on Australian Aboriginal artefacts. This paper reports the use of FTIR in combination with the chemometric tools principal component analysis (PCA) and hierarchical clustering (HC) for the analysis and identification of Australian plant and animal fixatives on Australian stone artefacts. Ten different plant and animal residues were able to be discriminated from each other at a species level by combining FTIR spectroscopy with the chemometric data analysis methods, principal component analysis (PCA) and hierarchical clustering (HC). Application of this method to residues from three broken stone knives from the collections of the South Australian Museum indicated that two of the handles of knives were likely to have contained beeswax as the fixative whilst *Spinifex* resin was the probable binder on the third.

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1. Introduction

The use of plant resins as adhesives, fixatives and pigments has been well documented in traditional indigenous Australian culture [1]. For example, the roots of *Drosera whittakeri* (scented sundew plant) were crushed to make a plant-based pigment for decoration whilst the juice of the *Dendrobium affine* (bracket orchid) was used in the tropics as a fixative for ochre on bark paintings and human torso drawings. Clarke has reported the use of a variety of plant resins for the manufacture of stone tools. The *Xanthorrhoea* species (grasstree), the *Callitris* species (Australian cypress pine) and the *Spinifex* species (porcupine grass) were the commonly used for the attachment of knife blades to their wooden handles [1], with the choice of species often dependent on the locality and accessibility. Resins from other species including *Acacia pycnantha*, *Acacia decurrens* and *Acacia dealbata* (golden wattle, black wattle and silver wattle, respectively), *Grevillea striata* (beefwood), *Acacia cambagei* (gidgee), *Gardenia megasperma* (bush gardenia), *Myoporum platycarpum* (sugarwood) and *Erythrophleum chlorostachys* (northern ironwood) have also been reported as adhesives for stone tools and weaponry [1]. Each plant resin is botanically and geographically specific to the environment in which a particular group of people are living and are collected in isolation of other resins [2].

The analysis of such residues from archaeological materials is not a trivial task. They are often complex mixtures that may have undergone various degradation processes over time [3,4]. In addition, the unique nature of historical objects dictates that sampling is required to be non-destructive or micro-destructive, further reducing the suite of analytical techniques available to the analyst [3,4]. In general, destructive chemical analysis techniques including gas chromatography mass spectrometry (GCMS) and high performance liquid chromatography (HPLC) along with DNA analysis have been reported for the analysis of archaeological residues [5–11]. Characterisation and identification of ancient organic residues generally relies on destructive chemical analysis and subsequent matching of 'fingerprint' spectral and chromatographic data with those of contemporary natural substances. Alternatively, analysis may be achieved with Fourier transform infrared spectroscopy (FTIR) [3]. The majority of previous studies have focussed on the characterisation of protein and lipid residues of animal origin such as dairy products, animal fats and beeswax and are concentrated on residues found on European artefacts [12,13]. Surprisingly, given the stark contrast between Australian and European landscapes, there has been little research into determining the types of fixatives found on Australian Aboriginal artefacts [14,15]. A survey of the open literature identified only two studies on the analysis of Australian binding media. Parr established that the morphology of starch grains present within resins from a variety of *Xanthorrhoea* species were suitable for discrimination between species [15]. In her work on the identification of traditional binders used on Australian Aboriginal painted objects, Gatenby reported the use of a series of commercially available colorimetric test kits for the classification of binders into protein, lipid and carbohydrate sub-groups [14]. She also presented some very preliminary studies into the use of FTIR for binder analysis and identified carbonyl, amine and

* Corresponding author. Tel.: +61 8 82012191; fax: +61 8 82012905.
E-mail address: claire.lenehan@flinders.edu.au (C.E. Lenehan).

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Table 1
Specimens used in this study (from the South Australian Museum collection).

Sample	(SAM) number	Species	Locality
Native beeswax	A13945	Not recorded	Not recorded
Native honey	A14838	Black species of *Trigonia*	Mac Donald Downs, Central Australia
Acacia gum	A2182	Not recorded	Cooper Creek (Nqurliwajaka), South Australia
Beefwood gum	A1893	*Grevilla* species	Not recorded
Ironwood gum	A17755	Not recorded	Mt Zeil, Central Australia
Spinifex gum	A17752	Not recorded	West of Mt Liebig, South Australia
Yacca gum	Number not allocated	*Xanthorrhoea tateana*	Kangaroo Island, South Australia
Yacca gum	A66781	*X. tateana*	Muston, Kangaroo Island, South Australia
Yacca gum	A66782	*Xanthorrhoea semiplana*	2 miles west of Clarendon, South Australia
Broken Aboriginal knife A	Number not allocated	Unknown	Arnhem Land, Northern Territory
Broken Aboriginal knife B	Number not allocated	Unknown	Arnhem Land, Northern Territory
Broken Aboriginal knife C	Number not allocated	Unknown	Not recorded

hydroxyl moieties from lipid, protein and carbohydrate binding materials, respectively.

The use of chemometric methods, such as principal component analysis (PCA) and hierarchical clustering (HC), to extract additional information from experimental data is well established in analytical chemistry, archaeometry and conservation [6,16–19]. Such methods have been employed to differentiate between material compositions [4,18], assist in the dating of archaeological objects [20] and in provenance studies [21,22]. This 'proof of concept' study employed both PCA and HC chemometric techniques for the analysis of FTIR data from a series of known Australian plant and animal residues along with fixatives from three stone knives from the collections of the South Australian Museum. Due to a lack of available equipment for truly non-destructive sampling, the FTIR spectra in this study were obtained with a traditional benchtop instrument using potassium bromide pellets.

2. Experimental

2.1. Model samples

Specimens of native beeswax, native honey, acacia gum, beefwood gum, ironwood gum, *spinifex* gum and yacca gum were obtained from the collections of the South Australian Museum as described in Table 1. Rendered emu oil was purchased from Talyala Emu Farm (Murray Bridge, South Australia). Goanna oil was extracted from the tail of a sand goanna (*Varanus gouldii*) by simmering a section of the tail in deionised water. Upon cooling the oil and water separated into two layers and the oil layer was collected and stored in a dessicator. No further treatment of this sample was undertaken. Orchid juice was obtained by grinding the stems of the rock lily orchid (*Thelychiton speciosus*, also known as *Dendrobium speciosum*) with a mortar and pestle. The ground mass was then pressed and the juice collected and dried for approximately 24 h in an oven at 100 °C. The model samples (with the exception of goanna oil, emu oil, and orchid juice) were aged in non-laboratory conditions for around a century. These specimens are of similar age to the three stone knives examined (see Table 1), which were collected from the Aboriginal community as a part of an ethnographic study.

2.2. Sample preparation

Forty-six samples of the various resins (see Table 2 for the number and type of each) were prepared by grinding approximately 1 mg of sample with 180 mg of potassium bromide (IR grade, Scharlau Chemie, Stennick Scientific, Australia) in a mortar and pestle for 3–5 min. The resultant mixture was then transferred to a hydraulic die press and a pressure of 10 tons was applied for 7 min whilst under vacuum. A disc of pure potassium bromide was prepared and used as to collect the background spectra.

The liquid samples (goanna oil and emu oil) were directly pipetted onto sodium chloride plates for analysis and analysed as neat samples.

Solid samples (~1 mg) taken from three stone knives from the South Australian Museum (described in Table 1) were prepared as described above.

2.3. IR spectroscopy

IR spectra were recorded using a Nicolet Nexus 870 (Thermo Scientific, Sydney, Australia) FTIR Spectrometer. Mid-infrared spectra were acquired over the range 4000–500 cm^{-1} using a resolution of 4 cm^{-1}, a gain of 1.0, an aperture of 100 and a velocity of 0.6329 $cm\,s^{-1}$ with 32 scans per spectrum. Data was baseline corrected using the Autobaseline tool in the Ez-Omnic instrument control program (Thermo Scientific).

2.4. Data pre-processing

Replicate spectra of subsamples from the different resins and the unknowns were scaled between 0 and 1 according to the function described in Eq. (1). In each case the maximum and minimum were the maximum and minimum transmittance values for that particular spectra. The observed value was the transmittance of the same spectra at any one wavelength.

$$\text{Normalised value} = \frac{(\text{observed transmittance} - \text{minimum transmittance})}{(\text{maximum transmittance} - \text{minimum transmittance})} \quad (1)$$

The algorithm normalised the spectra such that the most intense band in the spectrum was set as having a response of one and the least intense band having a response of zero. This step is commonly used when preparing spectra for a qualitative identification library, and retains information of peak position and relative intensities but removes scaling factors that may have resulted due to the use of differing sample concentrations between samples [23].

In order to reduce the number of data points used for chemometric analysis, the minimum transmittance for the

Table 2
A summary of the samples used for multivariate analysis.

Sample	Number of samples
Emu oil	4
Goanna oil	4
Spinnifex	3
Native beeswax	4
Native honey	3
Acacia gum	4
Beefwood gum	4
Orchid juice	4
Ironwood gum	4
Yacca gum (*X. tateana*)	8
Yacca gum (*X. semiplana*)	4

Table 3
Characteristic absorption peaks in IR spectra. Ticks indicate the peaks that were observed in the spectra of each sample type.

Wavenumber (cm^{-1})	Functional group	Acacia	Ironwood	Beefwood	Orchid juice	Yacca	Yacca 66781	Yacca 66782	Emu oil	Goanna oil	Spinifex	Beeswax	Native honey
3380–3450 (broad)	O–H ν	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓
3470 (sharp)	N–H ν								✓				
3000–3200	C–H ν (sp^2 hybridised)					✓	✓	✓					
2850–3000	C–H ν (sp^3 hybridised)				✓	✓		✓	✓	✓	✓	✓	✓
1700–1800	C=O ν		✓		✓				✓	✓	✓	✓	✓
1650	N–H δ or C=C ν								✓	✓			
1615 and 1425	COO ν	✓	✓	✓	✓	✓	✓	✓				✓	✓
1600 and 1475	C=C ν in ring					✓	✓	✓					
1360–1380	CH_3 bending	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
1475–1490	CH_2 rocking	✓	✓	✓	✓				✓		✓	✓	✓
1160–1170	C–O ν and O–H bending interactions				✓	✓	✓	✓				✓	✓

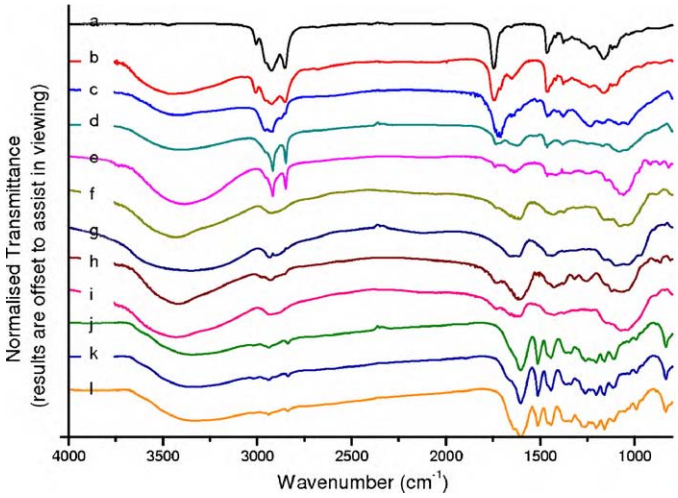

Fig. 1. Typical FTIR spectra. a, emu oil; b, goanna oil; c, spinifex; d, native beeswax; e, native honey; f, acacia gum; g, beefwood gum; h, orchid juice; i, ironwood gum; j, yacca gum (*Xanthorrhoea tateana*); k, yacca gum (*X. tateana*); and l, yacca gum (*Xanthorrhoea semiplana*).

normalised data in the regions 3500–3000 cm^{-1}, 3000–2800 cm^{-1}, 1750–1650 cm^{-1}, 1650–1600 cm^{-1}, 1600–1500 cm^{-1}, 1500–1400 cm^{-1}, 1400–1300 cm^{-1}, 1300–1250 cm^{-1}, 1250–1100 cm^{-1}, 1100–1050 cm^{-1}, 1050–1000 cm^{-1}, 1000–950 cm^{-1}, 950–900 cm^{-1}, 900–850 cm^{-1}, 850–800 cm^{-1} and at the peak 1112 cm^{-1} were obtained using a Macro written within MS Excel and subjected to chemometric analysis. These regions were chosen in order to highlight the maximum differences between spectra.

Chemometric analysis was achieved using Minitab 15 (Minitab Inc.) statistical analysis software, using a covariance matrix. Hierarchical cluster analysis was achieved using Euclidean distance and single linkage, with the group number set at either 10 or 11.

3. Results and discussion

3.1. Infrared spectra

Typical infrared spectra of the samples listed in Table 1 are depicted in Figs. 1 and 2. Visual inspection of the IR spectra revealed that the 12 samples can be categorised into three main groups, namely those of 'oils', 'plant origin' and 'bee residues'. Whilst many of the binding media possess similar functional groups (see Table 3

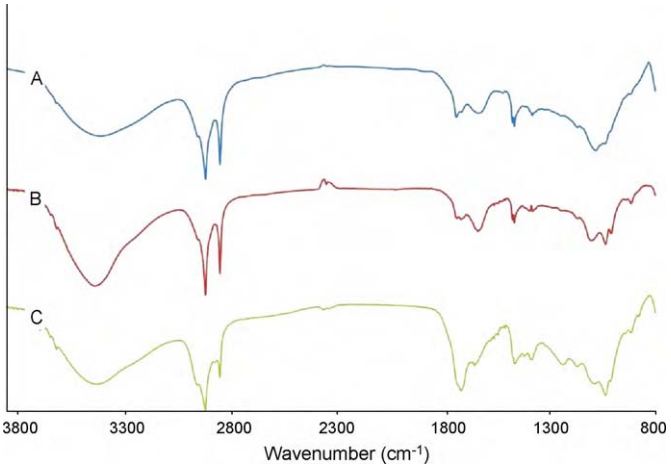

Fig. 2. Typical FTIR spectra of the fixatives from the stone knives (A–C).

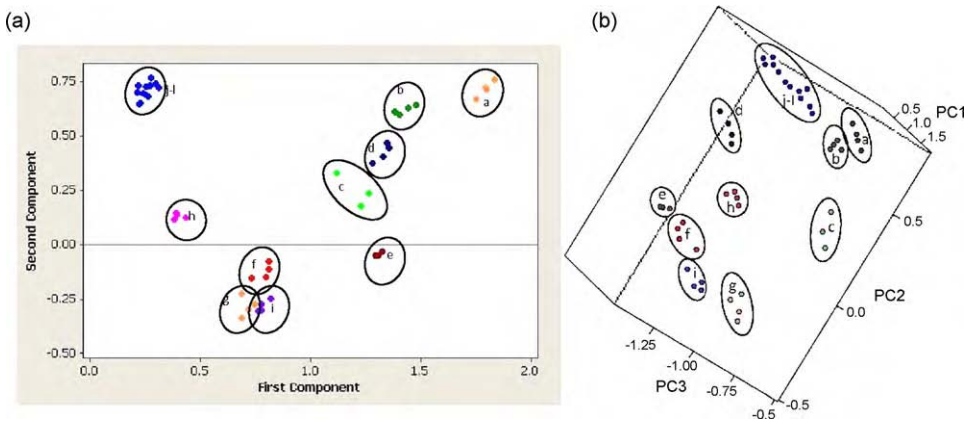

Fig. 3. PCA plots showing clustering of similar sample types. (a) Two-dimensional plot of PC1 versus PC2 and (b) the better discrimination achieved using a three-dimensional scores plot of PC1 versus PC2 versus PC3. Clustered groups are labelled a–l according to their sample type. a, emu oil; b, goanna oil; c, spinifex; d, native beeswax; e, native honey; f, acacia gum; g, beefwood gum; h, orchid juice; i, ironwood gum; j, yacca gum (*X. tateana*); k, yacca gum (*X. tateana*); and l, yacca gum (*X. semiplana*).

for a tentative assignment of peaks) and overall shapes, there are both subtle and obvious differences that can be used to discriminate between samples. Tentative assignment of the peaks was done using IR correlation charts, and, in the case of orchid juice, comparison to previously reported literature [14].

The most distinctive medium examined was emu oil (Fig. 1a) as it was the only sample to exhibit a sharp, weak peak at 3471 cm^{-1}. This vibration is characteristic of a secondary amide. The IR spectra of goanna oil (Fig. 1b) and *spinifex* (Fig. 1c) had many similarities, however close inspection revealed sufficient differences in the location and relative intensities of peaks for visual discrimination. Goanna oil could be clearly differentiated from *spinifex* as it had a peak at 3007 cm^{-1} (C–H stretching) that was absent from the *spinifex* spectrum. Furthermore, *spinifex* had peaks in the region 1082–1030 cm^{-1} (attributed to in plane C–H bending) that were not present in the goanna oil spectrum.

Beeswax and native honey (Fig. 1d and e, respectively) resulted in very similar spectra, however close examination revealed several differences between the two samples. The native honey possessed more intense O–H stretching bands at ~3400 cm^{-1} than beeswax. Conversely, beeswax yielded stronger C=O and COO absorption bands at ~1741 cm^{-1} and 1625 cm^{-1} than those of native honey. Furthermore native honey exhibited 3 peaks in the fingerprint region (916, 866 and 818 cm^{-1}) that were not present in the beeswax.

Acacia gum resin (Fig. 1f), beefwood gum resin (Fig. 1g), orchid juice (Fig. 1h) and ironwood resin (Fig. 1i) yielded very similar spectra. One feature that changed in each of these four samples was the relative difference in intensity between the peaks at ~1615 cm^{-1} and ~1426 cm^{-1}, which both relate to a COO– stretching functionality. There was also an acute difference between the number and intensity of the C–H stretching bands for these samples in the region between 2980 cm^{-1} and 2840 cm^{-1}. Though the yacca species is also of plant origin, visually its infrared spectra (Fig. 1j–l), were quite different to the other plant materials analysed. The spectra for each of the three yacca samples show C–C ring stretching and ring bending vibrations that was not observed in the other plant materials analysed.

3.2. Chemometric analysis

Rather than simply distributing the samples into categories based on the visual appearance of the IR spectra, we employed the multivariate statistical techniques of principal component analysis (PCA) and hierarchical cluster analysis to emphasize the structure in the data.

3.3. Preliminary work

PCA studies the relationship between samples by investigating similarities and differences between a particular set of variables (extracted from the experimental data and put into a matrix) by looking at the variance across the entire data set [24]. PCA was applied to a data matrix of 46 known samples (described in Table 2). Initial experiments which probed all of the data (each of the 46 samples with all 1670 variables, which were normalised transmittance values at different wavelengths) were unsuccessful, with the score plot of PC1 versus PC2 exhibiting overlapping clusters (ironwood, acacia, beefwood, orchid juice). These were not readily distinguishable by incorporating PC3 as the third dimension. On examination of the IR spectra (Figs. 1 and 2), it can be clearly seen that the region between 2800 cm^{-1} and 1800 cm^{-1} resulted in minimal transmittance beyond the baseline signal. As such, transmittance values in this region were removed from the data set prior to a second attempt at PCA. Once again this was unsuccessful, with acacia, beefwood and ironwood clustering strongly together. As a result, we divided the data into a further 15 subsections (transmittance across the wavelength ranges described in Section 2) and interrogated them individually. These subsections were extracted from the original data set using a Macro written in MS Excel. Individually none of the sections were sufficient to differentiate all of the different sample types using PCA, as the samples types were still but overlapping to some degree on the PC1 versus PC2 scores plot. Combining several of the subsections was also unsuccessful.

On careful scrutiny of the IR spectra obtained for each of the samples it was noticed that often the peaks occurred in a similar position, however the relative heights were often different. As such it was decided to pre-treat the data to extract the minimum transmittance signal from each of the spectral regions described in Section 2. This data was subjected to PCA and three components (PC1, PC2 and PC3) were identified as significant, describing 89% of the variation in the original data. When describing the original data by the first two principal components (PC1 versus PC2) all sample types clustered into their respective groupings with the exception of a slight overlap between acacia, beefwood and ironwood (Fig. 3a). However, the three-dimensional scores plot of PC1 (50%) versus PC2 (29%) and PC3 (10%), for the known samples (shown in Fig. 3b), clearly shows that each known sample can be discriminated, with acacia, ironwood and beefwood being the most similar.

Similarly to PCA, hierarchical clustering (HC) also looks at variance within a data set, however rather than looking at variance across a data set, it looks at the variance between sample pairs. This information is displayed in a two-dimensional plot of 'simi-

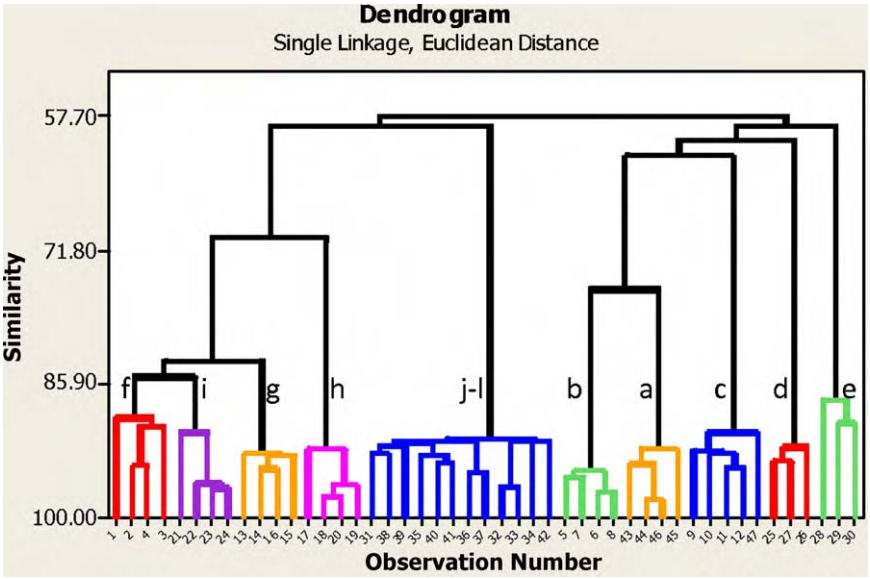

Fig. 4. Hierarchical Clustering Dendrogram showing clustering of similar sample types. Branches are labelled a–l according to the clustered group. a, emu oil; b, goanna oil; c, spinifex; d, native beeswax; e, native honey; f, acacia gum; g, beefwood gum; h, orchid juice; i, ironwood gum; j, yacca gum (*X. tateana*); k, yacca gum (*X. tateana*); and l, yacca gum (*X. semiplana*).

larity', a relative measure of a distance between samples, against samples. This distance between samples is calculated from each of the samples coordinates. A plot illustrating these distances for a set of data is known as a dendrogram. The HC analysis performed in this research used a method of single linking with Euclidean distances. This method works by linking samples based on the distance between the 'nearest neighbours' [24].

The results of hierarchical cluster analysis on the extracted data set described in the experimental are depicted in the dendrogram shown in Fig. 4. As can be seen, each of the 12 residues was clearly differentiated into their species of origin, with beefwood, acacia and ironwood resins being the most similar of the samples analysed. Given that the hierarchical cluster analysis resulted in simpler visual identification of subcategories within the data set, it was decided to use this method of chemometrics for subsequent application to samples of unknown origin.

3.4. Application to "blind" samples

In order to validate the hierarchical cluster analysis methodology prior to identification of unknown samples a blind study was undertaken. Colleagues independently prepared a series of 10 samples obtained randomly from the binding material collection, and collected their FTIR spectra. The data was saved and submitted for chemometric analysis. Results of this study are presented in Table 4. Of the 10 samples, eight were clustered into the correct species using the chemometric approach described above. The two that were incorrectly classified were beefwood resins, and were both clustered with ironwood. As shown in Fig. 1, beefwood and ironwood resins exhibit very similar FTIR spectra; therefore it was not unexpected that they may be incorrectly classified. Furthermore, the beefwood plant is often confused with the *Acacia stenophylla* plant, which is believed to belong to the same genus as the ironwood plant (*Acacia estrophiolata*), suggesting that the two samples analysed could be closely related depending on evolution or the original samples mislabelled in the Museum collection. In addition, it was accepted that the resins analysed may be quite heterogeneous which may cause differences in the analysis results. Although incorrect results came back from the blind study, these incorrect results were consistent with one sample in one region of the dendrogram. Thus when applied to the unknown knives it is reasonable to conclude that if samples from a unknown knife or artefact cluster with samples in the region not associated with beefwood they are likely to similar to the other materials in the method.

Table 4
Samples used in a blind study to test the suitability of the hierarchical clustering technique.

Unknown	Sample	Identified as	Correctly assigned?
A1	Ironwood	Ironwood	Yes
A2	Spinifex	Spinifex	Yes
A0	Beeswax	Beeswax	Yes
C1	Beefwood	Ironwood	No
C2	Beefwood	Ironwood	No
D1	Spinifex	Spinifex	Yes
D2	Ironwood	Ironwood	Yes
L	Beefwood	Beefwood	Yes
Yuendumu cake resin	Spinifex	Spinifex	Yes

3.5. Application to stone knife artefacts

Samples of the fixative resins from three Aboriginal stone knives of the South Australian Museum were analysed by FTIR and the resultant data subsequently subjected to hierarchical cluster analysis as described above. These knives were selected from the collection due to their poorer conservation status, making them ideal candidates for undertaking low level destructive analysis. The adhered resin was in all cases flaking off and the blades had been damaged over time. The knives are typical of the long silcrete blades used for a variety of purposes from central to northern Australia.

Knives A and B, both collected from Arnhem Land, Northern Territory, clustered very strongly with beeswax (knife A with 73% similarity, knife B with 91% similarity). Beeswax is often associated with artefacts from the north of Australia and Arnhem land [25,26], thus indicating that these particular knives are likely to have been made in the local area or not traded any great distance. Knife C, on the other hand, was of unknown locality and contains a resin that is most similar to that of *Spinifex* (77% similarity). This indicates either an arid or tropical Australian origin, as *Spinifex* is native to this area, but without further data and curatorial information it is not possible to comment on its possible trade history.

Whilst it is plausible that a mixed resin may be present, it is generally accepted that Australian Aboriginals did not mix plant resins prior to use [2]. Resins were usually collected in isolation of other resins, as each requires a unique set of collecting, preparing and curating steps. For example, *Spinifex* resin was kept in a solid mass from which pieces could be broken off and melted down again for use. These properties of the *Spinifex* resin are highly valued and would have been compromised if other resins were mixed with it [2]. Furthermore, microscopic evaluation of the stone knives did not reveal any indication of a layered composite structure of different binder applications. Future work will focus on the further development of this classification tool, including the incorporation of non-destructive sample interrogation using fibre optics for other resins.

4. Conclusions

Identification of binder residues provides valuable information towards the successful provenance (for unearthing the history) of artefacts. In this research we have demonstrated methods for identifying 10 different complex Australian plant and animal fixatives on Australian stone artefacts. Despite having very similar infrared signatures, these fixatives could be discriminated when multivariate (principal component and hierarchical clustering) methods were used in conjunction with chemical analysis. Application of this methodology to residues from three broken stone knives from the collections of the South Australian Museum indicated that two of knife handles were likely to have contained beeswax as the fixative (and thus likely to have originated from northern Australia or Arnhem land) whilst *Spinifex* resin was the probable binder on the third (indicating an arid or tropical Australian origin, but more data is required to provenance this artefact).

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