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ABSTRACT

Resin use by Australian Aborigines has been documented in ethnographic accounts across the continent and is also evident from archaeological and anthropological artefacts. This research assesses the use of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and gas chromatography coupled mass spectrometry (GC/MS) for the identification of native plant resins on museum artefacts. A collection of thirteen museum artefacts were analysed using light microscopy and characterised using both ATR-FTIR and GC/MS. The resins were identified to the plant genus and one to the species level, as spinifex (*Triodia* spp. R.Br.), ironwood (*Erythrophleum chlorostachys* (F.Muell.) Baill.) and grass tree (*Xanthorrhoea* spp. Sm.) by comparison to a reference collection of modern exudates from 34 Australian plant species. The two analytical methods used, produced a significant agreement in results but one has practical advantages. On eight of the artefacts, ATR-FTIR was able to be performed on the residue in situ, without removal, presenting a non-destructive analytical method for the identification of resins which is applicable to rare and delicate artefacts from museum collections. Permission to remove the residue off the artefact is not always granted or feasible, so ATR-FTIR has a significant advantage over GC/MS and other methods which require chemical treatment or even destruction of the archaeological sample. Both of the methods examined are demonstrated to accurately infer the botanical origin of archaeological and anthropological resins, providing insight on the use, preparation and trading of resins, with the consequent
contribution to an understanding of the development and use of hafted tools and other aspects of cultural development.

KEYWORDS: Archaeological residues, Archaeological chemistry, Plant resin, *Triodia*, *Xanthorrhoea*, *Erythrophleum*, ATR-FTIR, GC/MS, Aboriginal artefacts, Spectrophotometry, Australia
1.0 INTRODUCTION

Plant resins have been used as an important binding media by past societies all over the world, while in modern culture, plant resins are used almost exclusively in art and various manufacturing industries (Brody et al., 2002; Findeisen et al., 2007; Lambert et al., 1999; Lambert et al., 2005; Verbeken et al., 2003). In Australia, plant resins have been used by the Australian Aborigines for thousands of years as a binding media, primarily as an adhesive for hafting lithic material to create tools (Cribb and Cribb, 1982; Flood, 1995). The most commonly documented sources of plant resins used by Australian Aborigines include spinifex (Triodia spp. R.Br.), ironwood (Erythrophleum chlorostachys (F.Muell.) Baill.), sugarwood (Myoporum platycarpum R.Br.), cyprus (Callitris spp. Vent.) and grass tree (Xanthorrhoea spp. Sm.) (Boot, 1993; Cane, 1987; Kamminga, 1988; Latz et al., 1996; Maiden, 1975). Resins contain primarily terpenoid compounds with little or no carbohydrates and are insoluble in water, unlike gums which are water soluble and predominantly comprised of carbohydrates (Langenheim, 2003). These features mean that resins perform better as binding media and adhesives. However gums were readily available and frequently collected for use as a food source so may have been used as a binding media in situations where strength or longevity were not important. Plant resins were selected, collected, prepared and processed by Australian Aborigines in a variety of ways according to the plant species, technical knowledge and culture. Resin was generally heated until soft and pliable and could be used on its own or mixed with other materials (Cribb and Cribb, 1982; Kamminga, 1982). For example, mixing resin with beeswax, fine sand, plant fibres and ash, modifies its physical characteristics, allowing it to be used for a wide variety of adhesive functions (Cribb and Cribb, 1982; Kamminga, 1982).
Archaeological and anthropological artefacts and their residues provide rare glimpses of the past but their organic elements degrade easily and are often poorly preserved. Concerns about the removal of resin and destruction of the sample are two significant factors that have limited the application of many scientific techniques to archaeological and anthropological artefacts. Museum curators prefer non-destructive and non-invasive (minimally destructive) techniques, which places restrictions on access to rare artefacts. Permission to remove the residue from the artefact or to destroy the artefact is not always granted or feasible. Unfortunately, many of the techniques available to study plant resins do require the removal and destruction of material and cannot be carried out *in situ*. The importance of finding accurate analytical methods that preserve the artefact is critical.

For research on Australian Aborigines, archaeological resins can provide an important component in our understanding of their culture, including the trade and manufacture of composite tools. Resins were used as cements or fixatives in the manufacturing of numerous types of traditional items and hafted artefacts which are of particular interest in this study. Australian Aborigines manufactured a great variety of artefacts ranging from weapons and utensils to jewellery and ceremonial items. They include Bondi points, Kimberly points, backed blades, burrens, ground edge axes, leiliras, tulas, armlets, anklets, necklaces, message sticks and ceremonial sticks (Flood, 1995; Kamminga, 1977; McCarthy, 1976; Tindale, 1965). Many of these artefacts used resins to bind the different components together (e.g. stone and wood). Boot (1993) presents evidence of plant resins being used on two different artefact forms, unmodified flakes and backed blades, as an example of the varied use of resins by Aborigines in the Graman district (New South Wales). Trace amounts of resin found on the unused margins of stone tools indicate that these artefacts were hafted but the shaft has disintegrated due to taphonomy (Boot,
Blee et al. (2010) characterised the binding material used on a selection of lithic blades interpreted as stone knives. Resin has also been identified on working surfaces of various artefacts including flakes and grinding implements (Boot, 1993). Examination of trace residues can be used to infer the botanical source and possibly the process by which a resin resource is procured, prepared and applied. It can also indicate how the tool has been manufactured or used, potentially elucidating tool typology. When this analysis is applied to museum artefacts, it may also verify the catalogue information. When combined with trace elemental analysis of lithics, it may be possible to determine the geographical extent of resource collection, trade and exchange networks with greater confidence.

1.1 Techniques for the Characterisation of Resins

There are a number of physical and chemical methods that have been used to characterise plant resins. Chromatography, spectroscopy (mass spectroscopy and nuclear magnetic resonance) and capillary electrophoresis have been used in the destructive analysis of resins from museum objects (Blee et al., 2010; Bradshaw, 2013; Findeisen et al., 2007; Helwig et al., 2014; Lambert et al., 1999; Lambert et al., 2007; Lambert et al., 2005; Larson et al., 1991; Martinez-Richa et al., 2000; Silva et al., 2002). Paper chromatography is a simple method for the analysis and identification of resins and has been used to characterise Australian Xanthorrhoea spp. Sm. resin (Duewell, 1997) and to identify archaeological resins as Xanthorrhoea spp. Sm. (Boot, 1993). Other forms of chromatography (Matuszewska and John, 2004; Mills and White, 1977) have been used, however gas chromatography coupled mass spectrometry (GC/MS) has been the principal chromatographic technique applied to the determination of the biological source of
resins (Andreotti et al., 2006; Bradshaw, 2013; Cartoni et al., 2004; De la Cruz-Canizares et al., 2005; Helwig et al., 2014; Modugno et al., 2006a; Modugno et al., 2006b; Niimura and Miyakoshi, 2003; Pitthard et al., 2006a; Pitthard et al., 2006b; Scalarone et al., 2005; Shillito et al., 2009). In contrast to the destructive techniques, light microscopy, Raman spectroscopy and infrared spectroscopy have great potential as non-invasive means of determining the nature, and in some cases the identity, of plant resins from archaeological collections (Helwig et al., 2014; Mizzoni and Cesaro, 2007; Shillito et al., 2009). Light microscopy has been employed to characterise and identify resins on Australian artefacts including the analysis of incorporated starch grains and cellulose within the resin (Akerman et al., 2002; Boot, 1993; Cooper and Nugent, 2009; Fullagar et al., 2006; Fullagar et al., 2009; Parr, 2002; Robertson, 2009). Microscopic characterisation and the distribution pattern of resin on an artefact that is compatible with its postulated use, is considered to confirm the presence of a resinous residue; however to identify the plant origin of the resin requires the application of biochemical analyses. Raman spectroscopy and modifications of Fourier Transform Raman spectroscopy have been used to analyse glazes (Sendova et al., 2007), copal and amber (Brody et al., 2001) and archaeological resins (Blee et al., 2010; Brody et al., 2002; de Faria et al., 2004; Edwards et al., 2007; Shillito et al., 2009) and also in the forensic analysis of heritage, artwork and archaeological artefacts (Edwards and Munshi, 2005). Infrared (IR) spectroscopy is a valuable method for the detection and characterisation of resins as it produces chemical profiles in the form of a spectrum for each resin, produced by the chemical bonds that are present in the substance being analysed. The generated spectrum allows the resin to be characterised by chemical type (diterpenoid, triterpenoid etc.) and in some instances it can be compared to known reference samples for more specific identification. Fourier transform infrared spectroscopy (FTIR) has been used for the
identification of natural resins in both historic furniture finishes (Cartoni et al., 2003; Derrick, 1989; Guiliano et al., 2007; Langenheim and Beck, 1965; Mizzoni and Cesaro, 2007) and archaeological residues (Blee et al., 2010; Bruni and Guglielmi, 2013; Helwig et al., 2014; Nunziante Cesaro and Lemorini, 2012; Prinsloo et al., 2014; Shillito et al., 2009). These studies include characterising binding material used on stone knives with the identification of material from *Triodia* sp. R.Br. (Blee et al., 2010), commonly known as spinifex grass.

1.2 Techniques Used in this Study

A comparison is made between applied chromatography and spectroscopy, specifically light microscopy in conjunction with diamond crystal attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and Gas Chromatography coupled Mass Spectrometry (GC/MS). The first technique is a non-destructive surface reflectance method that produces a high resolution spectrum in a very short scan time. This allows the integration of a large number of scans, effectively averaging any “noise” and yielding spectra with a very high signal-to-noise ratio which produces a very clear profile. The second technique, GC/MS, is destructive but can be performed in a way that is minimally invasive, using solvents to dissolve only the surface of the residue and remove minute amounts.

To be a valid method for this purpose, the technique must be able to work effectively with modified resin because ethnographic sources have documented that Australian Aborigines heated resin during preparation and mixed it with other material. Both ATR-FTIR and GC/MS are appropriate for use on museum samples and have different advantages. GC/MS is established as a method to identify compounds present in a mixture. By contrast, ATR-FTIR has generally
been applied to the identification of chemical bonds in pure substances. If it is applicable to resin
residues on the surface of artefacts, it offers a rapid technique with no sample preparation that
can be used in a non-destructive in situ (without removal) manner as demonstrated with great
potential in the study of ambers and copals (Guiliano et al., 2007).

2.0 METHODS

2.1 Modern Reference Samples

A modern reference collection (n=34) of plant exudates was assembled and analysed by
the two methods (ATR-FTIR and GC/MS) to generate a reference library of spectra. There was
no microscopy performed on the modern reference collection. These modern plant exudates
including resins and gums were collected from 34 species representing 16 genera of Australian
native plants (Table 1). The samples were collected from identified plants at the Brisbane and
Sydney Botanical Gardens.

2.2 Artefact Samples

Thirteen artefacts were provided for analysis, by the Anthropology Museum at the
University of Queensland (Table 2). They include seven processed resin clumps, five resin sticks
(Figure 1) and one hunting spear. Seven of these artefacts had been donated to the Anthropology
Museum at the University of Queensland, with two of unknown provenance and the others from
various locations in Australia including Western Australia, South Australia, Northern Territory
and Queensland (Table 2). The resin on these seven were recorded to the taxonomic level of
genus in the museum catalogues (Spinifex grass, grass tree and ironwood resin) but the accuracy of these records was uncertain. One of the resin sticks (artefact 28683) has Abrus seeds embedded in the resin (Figure 1) which is commonly found on fire sticks.

2.3 Microscopy

All the museum artefacts were examined and sketched prior to microscopic analysis under an Olympus BX51 microscope. For the hunting spear a systematic grid approach was used to examine and locate the resin residue under bright field - low magnification - incident light microscopy but this was not required for the other artefacts. Under the microscope resin exhibits a reflective, lustrous surface and polished appearance. Increasing magnification and polarised light microscopy were used to characterise the resin clumps and resin sticks. The physical characteristics like colour, transparency, homogeneity and the presence of any inclusions were examined and recorded.

2.4 ATR-FTIR Spectroscopy

All 34 of the modern reference collection and the 13 museum artefacts were analysed using ATR-FTIR with eight of the artefacts analysed in situ. Spectra were obtained using a Perkin Elmer Spectrum 2000 spectrometer equipped with a diamond crystal DuraSampIR II accessory. The Spectrum IR software package was used for the collection of data, acquired between 4000 cm\(^{-1}\) and 550 cm\(^{-1}\) and set at a spectral resolution of 8 cm\(^{-1}\). The modern resin samples were tested by placing a resin chip onto the diamond crystal window for analysis. The analysis of the modern reference samples was performed using triplicate samples of each resin
and an ATR-FTIR spectrum generated in triplicate for each sample. Eight of the museum artefacts were analysed in situ by placing a flat exposed resin coated surface of the artefact in contact with and completely covering the diamond crystal window of the ATR platform. The remainder of the resins from the artefacts were analysed in the same way as the modern reference samples, by taking a small resin particle (approximately 0.5-2.0 mg) off the artefact and placing it onto the diamond crystal window for analysis. The resin residue on the hunting spear was found to be strongly bound to the lithic surface.

2.5 Gas Chromatography coupled Mass Spectrometry (GC/MS)

All of the reference collection and some of the museum artefacts were analysed using GC/MS. This method is considered to be destructive but can be performed in a minimally invasive way. It requires the application of minute amounts of solvent to the artefact’s surface to dissolve the residue and extract less than 2 mg of the trace residues. Permission for this analytical method was denied for some of the artefacts (Table 3). A small amount of resin (approximately 0.4-1.5 mg) was dissolved from the artefact surface and 500 µL of 100% ethanol added to the sample in a sterile 2 ml autosampler vial and mixed by vortexing before heating at 70°C for 8 hours. Once dissolved, the ethanol solutions were centrifuged and transferred to another sterile 2 ml autosampler vial, freeze dried under a vacuum (Labconco Freezone 12) for 8 hours or until dry. The samples were then derivatised with 0.15 ml of BSTFA, 1% trimethylchlorosilane (Sigma-Aldrich) and 0.35 ml of cold acetonitrile (Sigma-Aldrich). The vials were purged with nitrogen, sealed by a crimped cap, and then heated to 120°C for 30 minutes on a Baxter Scientific Multi-Block. A final dilution of 0.5 ml of acetonitrile was then injected into the sealed vials which were then lightly mixed and immediately analysed.
A Varian model 450 gas chromatograph was coupled with a Varian model 300-MS quadrupole GC/MS mass spectrometer equipped with Factor Four capillary column (VF-5 ms, 30 m x 0.25 mm ID, DF=0.25 µm). Helium was used as the carrier gas at a flow rate of 1.0 ml/min. Samples were introduced via splitless mode in an autosampler with the injection port at a temperature of 270°C. The column temperature was initially held at 50°C for 2 minutes then increased from 50°C to 155°C at a rate of 8°C/min and then from 155°C to 275°C at a rate of 40°C/min and held at 275°C for 9 minutes. The ionisation energy was 70 eV and the ion source was set at 200°C under electron ionisation (EI) conditions. The scan range was from 40 to 500 m/z. The GC/MS interface temperature was set at 266°C. Output files were analysed using Varian MS workstation version 6 and the NIST98 Mass Spectral Database.

3.0 RESULTS

3.1 Modern Reference Collection

The ATR-FTIR and GC/MS spectra obtained for each of the 34 modern exudate reference samples exhibit discriminating spectral profiles or fingerprints for individual plant species, each with characteristics that are unique and distinctive within the collection (Supplementary Material). The ATR-FTIR spectral profiles generated are consistent with those modern reference samples in the study by Blee et al (2010). The spectral characterisation of each reference exudate was then compared to the results from analysis of all thirteen museum artefacts.

3.2.1 ATR-FTIR Characterisation of *Erythrophleum chlorostachys* (F.Muell.) Baill.
The characterisation of the spectrum for *E. chlorostachys* (F.Muell.) Baill. exhibits a weak but broad hydroxyl peak in the 3100-3400 cm\(^{-1}\) region (Figure 2). There are weak peaks present in the alkyl region 2850-3000 cm\(^{-1}\), due to the methyl and methylene stretches within the compounds. Multiple weak carbonyl peaks are present in the region of 1600–1750 cm\(^{-1}\), these multiple peaks are due to differences in the chemical structures adjacent to these carbonyl units. There are peaks between 1430-1490 cm\(^{-1}\) corresponding to the methyl and methylene bending. The remaining peaks are located in the fingerprint region of the spectra containing various CH\(_2\) rocking and C-C stretching vibrations.

3.2.2 ATR-FTIR Characterisation of *Triodia* sp. R.Br.

The *Triodia* sp. R.Br. spectrum exhibits peaks in the alkyl region 2850-3000 cm\(^{-1}\) (Figure 3). These alkyl peaks are similar in intensity, shape and position to those found in *E. chlorostachys* (F.Muell.) Baill.. The combination of no broad hydroxyl peak in the 3100-3400 cm\(^{-1}\) region and the presence of the alkyl peaks in the 2850-3000 cm\(^{-1}\) region is similar to other resins in the reference collection particularly the terpenoids. However there is a strong carbonyl peak with a shoulder peak present at 1690–1750 cm\(^{-1}\) and a unique sharp double peak located at 1000-1050 cm\(^{-1}\) of the spectra. There are also strong peaks specifically at 2921-2926 cm\(^{-1}\), 1700-1705 cm\(^{-1}\), 1450-1455 cm\(^{-1}\), 1380-1385 cm\(^{-1}\), 1225-1230 cm\(^{-1}\) and 1029-1032 cm\(^{-1}\). This combination of peaks denotes the characterisation of *Triodia* sp. R.Br.

3.2.3 ATR-FTIR Characterisation of *Xanthorrhoea* spp. Sm.
The reference spectrum for each species of *Xanthorrhoea* exhibited slight variations. However, the intense broad hydroxyl peak in the 3100-3400 cm\(^{-1}\) region (Figure 4), due to the O-H bond stretching, distinguishes this genus from *Triodia* sp. R.Br. (Figure 3) and *E. chlorostachys* (F.Muell.) Baill. (Figure 2) in this study. This peak is however, present in other gums and resins within the modern reference collection (for example *Agathis*, *Angophora*, *Araucaria*, *Brachychiton*, *Corymbia* and *Eucalyptus*). *Xanthorrhoea* also has spectral peaks in the alkyl region 2850-3000 cm\(^{-1}\) and the intensity of these varies depending on the species. These peaks are due to the methyl and methylene functional groups of the molecules in the resin mixture and are can be found at various intensities in some of the other reference samples. A particularly strong peak in this region is 2932-2941 cm\(^{-1}\).

Carbonyl peaks are present in the region of 1690–1750 cm\(^{-1}\) and these are found in all of the reference resins but are at different intensities and with slightly different positions due to the neighbouring chemical structures adjacent to these carbonyl structures. There are distinctive peaks at 1735 cm\(^{-1}\) in *Xanthorrhoea johnsonii* A.T.Lee and 1634 cm\(^{-1}\) in *Xanthorrhoea macronema* F.Muell. ex Benth. as well as at 1844 cm\(^{-1}\) in *Xanthorrhoea australis* R.Br. while *Xanthorrhoea resinosa* Pers. has a number of distinctive peaks at 2925 cm\(^{-1}\), 2853 cm\(^{-1}\), 1620 cm\(^{-1}\) and 1435 cm\(^{-1}\). Many of these characteristic peaks are in the region below 1800 cm\(^{-1}\) and they are due to C-H, C-O and C-C bond bending and stretching vibrations. They may provide sufficient distinctions to characterise an unknown sample of *Xanthorrhoea* to the species level if there is a comprehensive reference collection.

3.3.1 GC/MS Characterisation of *Erythrophleum chlorostachys* (F.Muell.) Baill.
The chromatographs for *E. chlorostachys* (F.Muell.) Baill. show the bulk of the peaks between 17 and 23 minutes retention time (Figure 5). The majority of these peaks are fatty acids, sterols and plant waxes and include tetradecanoic acid, hexadecanoic acid, octadecanoic acid, 9,10-epoxy-18-hydoxy-octadecanoic acid, anthracene and oxanilic acid. The exudate from *E. chlorostachys* (F.Muell.) Baill. is a gum or resin-gum not a terpenoid resin and does not have any of the typical resin acids.

3.3.2 GC/MS Characterisation of *Triodia* sp. R.Br.

The chromatographs for *Triodia* sp. R.Br. (Figure 6) show a smaller number of compounds present. This resin has not previously been characterised but this research indicates the presence of aromatic hydrocarbons like anthracene and fatty acids including hexadecanoic acid and octadecanoic acid.

3.3.3 GC/MS Characterisation of *Xanthorrhoea* spp. Sm.

The chromatograph for the various *Xanthorrhoea* spp. Sm. (Figure 7) show a variety of compounds that are found in all species in varying quantity. These compounds include anthracene, cinnamic acid, flavones, sterols, hexadecanoic acid and octadecanoic acid. *Xanthorrhoea* produce a phenolic resin sometimes referred to as an acaroid resin. These resins do not have terpenoids and are dominated by phenolic and aromatic hydrocarbons. All these chromatographs had anthracene and cinnamic acid in appreciable quantities which for all the resins in native Australian plants, is a combination unique to this genus.
3.4.1 GC/MS Analysis of Museum Artefacts

Permission was obtained for five of the artefacts to be sampled for analysis by GC/MS at locations previously identified by using microscopy. Chromatographs were generated for the extracted residues on all five of the artefacts and they were compared to the reference collection. The residues from Artefacts 17031 (Figure 6) and 20172 were consistent with *Triodia* sp. R.Br., with abundant quantities of anthracene, hexadecanoic acid and octadecanoic acid. The extracts from Artefact 22947 (Figure 5) were consistent with *E. chlorostachys* (F.Muell.) Baill. having the compounds decanoic acids, anthracene and oxanilic acid present in greatest quantity. Residue extracts from Artefact 1428 (Figure 8) resembled the *Xanthorrhoea* species with abundant quantities of cinnamic acid and fatty acids while the residue from Artefact 1625 (Figure 9) had distinctive peaks consistent with *X. resinosa* Pers.

3.4.2 ATR-FTIR Analysis of Artefacts

The ATR-FTIR spectra of artefacts 22947 and 404 exhibited the greatest similarity with the reference sample of *E. chlorostachys* (F.Muell.) Baill. (Figure 2). The spectra shared all of the peaks within a 5 cm⁻¹ band width and all had characteristic peaks at 1828 cm⁻¹, 1734 cm⁻¹ and 1458 cm⁻¹, peaks not found in combination in any other reference sample.

The ATR-FTIR spectrum of artefacts 3193, 17031, 18193, 20172, 25282 and 28683 are consistent with *Triodia* sp. R.Br. (Figure 3). They all share the absence of the broad hydroxyl
peak in the 3100-3400 cm$^{-1}$ region and the presence of strong peaks at 2921-2926 cm$^{-1}$, 1700-1705 cm$^{-1}$, 1450-1455 cm$^{-1}$, 1380-1385 cm$^{-1}$, 1225-1230 cm$^{-1}$ and 1029-1032 cm$^{-1}$.

The ATR-FTIR spectra of artefacts 1428, 1623, 1624, 1625 are 25281 are consistent with *Xanthorrhoea* spp. Sm. (Figure 4). The spectrum of the artefacts 1428 and 25281 are very similar and most consistent with the *X. johnsonii* A.T.Lee reference sample, with the distinctive peak at 1735 cm$^{-1}$. Artefact 1623 and 1624 are most consistent with each other but do not specifically match any of the *Xanthorrhoea* species in the reference collection. Artefact 1625 is most consistent with *X. resinosa* Pers. with distinctive peaks at 2925 cm$^{-1}$, 2853 cm$^{-1}$, 1620 cm$^{-1}$ and 1435 cm$^{-1}$.

4.0 DISCUSSION

Resin from museum artefacts were successfully correlated with spectral profiles of the modern reference samples for *Xanthorrhoea* spp. Sm., *E. chlorostachys* (F.Muell.) Baill. and *Triodia* sp. R.Br. resin using both ATR-FTIR and GC/MS methods. Both ATR-FTIR spectral profiles (Figure 2-4) and GC/MS chromatographs (Figure 5-9) gave analytical profiles of sufficient complexity, reproducibility and individuality that comparison to a comprehensive database allows identification of resin material to at least the genus and sometimes to the species level. The two methods showed a high degree of agreement. Both test methods classified one of the processed resin clumps (artefact 22947) to the species level as *E. chlorostachys* (F.Muell.) Baill. which is supported by the museum records that catalogue this artefact as being ironwood (*E. chlorostachys* (F.Muell.) Baill.) sap (exudate). The previously unidentified resin used in hafting the hunting spear (artefact 404) also produced an ATR-FTIR spectrum consistent with
ironwood (*E. chlorostachys* (F.Muell.) Baill.). This suggests a regional exploitation of ironwood resin, since both 22947 and 404 were collected from two locations only 310 km apart (at Port Keats, Northern Territory and Kalumbra Mission, Western Australia).

A second group of resins on artefacts 3193, 17031, 18193, 20172, 25282 and 28683 is most consistent with *Triodia* sp. R.Br. (spinifex) from the reference collection, according to both the ATR-FTIR spectra (Figure 3) and the GC/MS chromatographs (Figure 6). There are many species of *Triodia* and while the reference collection contains only one modern sample, this plant genus presents spectra that are readily distinguished from the other 34 species in that collection.

The identification of the resin on these six artefacts is consistent with the four available museum catalogue records for artefacts 3193, 17031, 18193 and 20172 which refer to spinifex resin. Resin from *Triodia* or spinifex is known to be exploited throughout Australia as demonstrated by the geographically wide spread of these artefacts from Queensland, Western Australia and South Australia.

For the third group of results, it was again demonstrated that both methods identified artefacts 1428 and 1625 as *Xanthorrhoea* resin and ATR-FTIR alone identified artefacts 1623, 1624 and 25281 as *Xanthorrhoea* which agreed with the two available museum catalogue records (for 1428 and 25281). Artefact 1625 was consistent with one of the species, *X. resinosa* Pers., from the reference collection but the identification of the other five samples at the species level was not conclusive because of the following observations. The ATR-FTIR of the residue on artefacts 1428 and 25281 indicated *X. johnsonii* A.T.Lee but the GC/MS of artefact 1428 (the only one of these two analysed by GC/MS) did not match *X. johnsonii* A.T.Lee. This difference in results could be due to the additives used in the preparation of the resin and would require further analysis. The residues from Artefacts 1623 and 1624 had similar spectra but these did not
unequivocally match with any of the five *Xanthorrhoea* species in the reference collection (*X. australis* R.Br., *X. fulva* (A.T.Lee) D.J.Bedford, *X. johnsonii* A.T.Lee, *X. macronema* F.Muell. ex Benth. and *X. resinosa* Pers.). There are many *Xanthorrhoea* species and some are geographically specific. Two potentially relevant Queensland species (*Xanthorrhoea glauca* D.J.Bedford and *Xanthorrhoea latifolia* (A.T.Lee) D.J.Bedford), are not in the reference collection. Although ATF-FTIR spectra for artefacts 1623 and 1624 are very similar, they are different from artefact 1625 even though all three are from the same location (Coomooboolaroo Station, Queensland); this is of interest as it may suggest exploitation of more than one species of *Xanthorrhoea* sp. Sm. or differences in the additives used in processing each sample by the same people. The spectra generated from the residue of artefacts 1428 and 25281 are also similar and categorised as *Xanthorrhoea* but do not match the spectrum of a single species in the reference collection; so it is suggested they are both from the same unidentified species of *Xanthorrhoea*.

Both methods gave the same result for artefact 1625, which was consistent with *X. resinosa* Pers.. The geographical range for that species is not known to extend to the region of Queensland where this artefact was collected (Coomooboolaroo Station). There may be a number of explanations for this difference: 1) it may be another local *Xanthorrhoea* sp. Sm. that is not in the reference collection, 2) the museum records of origin for this artefact may be in error or 3) this artefact was traded from another location.

All methods have limitations and both these methods require a geographically relevant reference collection. Identifying a resin to the species level rather than just the genus presents greater challenges due to environmental influences on the chemical composition of the resin. The relative intensity of ATR-FTIR spectral peaks that are diagnostic for the plant species may vary slightly in different soils, different individuals of the same species and also in samples of the
same species from different geographic locations. Accurate identification is reliant on a comprehensive reference collection which includes the relevant temporal and spatial samples, appropriate to the context of the project. In anthropological, historical or aged samples compounds in the resins could also be modified through exposure to oxygen, light, temperature, pressure and humidity. This chemical modification would be even greater in archaeological samples exposed to the environment and buried in the ground.

As an example, it was noted that the reference samples of *X. fulva* (A.T.Lee) D.J.Bedford and *X. australis* R.Br. are very similar. This may indicate that ATR-FTIR is not reliable enough to identify *Xanthorrhoea* to species or it may reflect a close botanical association of these two species of the grass tree. Further investigation of all of the *Xanthorrhoea* species is required.

GC/MS is classed as minimally destructive since it only requires the application of small amounts of solvent to small areas of an artefacts surface. However, for delicate items it may be impossible to guarantee there is no risk of discolouration or even some damage to the fabric of the item. For some museum curators this may still be an unacceptable risk. ATR-FTIR on the other hand only requires minimal contact with the artefact and nothing is removed. Nevertheless there are at least three practical limitations of ATR-FTIR: (a) Size: the resin on the artefact must be able to be placed within a 3cm space in the ATR attachment of the FTIR equipment; (b) Pressure: care must be taken when the artefact is clamped onto the ATR platform since a small amount of pressure must be applied to the residue and the artefact, which could crack or damage the residue surface or even the artefact itself; and (c) Flat Surface: the surface of the resin must be laid flat so as to cover the diamond crystal window and so avoid contamination of the spectra with peaks caused by atmospheric gases and water. This can be challenging for large artefacts and in cases where the suspected resin is not exposed on a concave surface or an edge of the
arterfact. However, the peaks in the spectrum produced by atmospheric gases and water can be identified and excluded (small peaks between 3600-4000 cm$^{-1}$ for water and a peak or negative peak between 2100 cm$^{-1}$ and 2200 cm$^{-1}$ for carbon dioxide). A variation on the method, called micro-ATR-FTIR uses a coupled microscope to overcome these challenges but it does require a larger surface area and therefore the method suffers from a loss of intensity.

CONCLUSIONS

Diamond crystal ATR-FTIR in conjunction with light microscopy was successfully used on the surface of artefacts to non-destructively analyse the resin residues in situ. The reference collection of modern resins provided a consistent characterisation for all thirteen resin samples. From the resin residues on thirteen artefacts analysed from a museum collection, Xanthorrhoea sp. Sm. (grass tree), Triodia sp. R.Br. (spinifex) and E. chlorostachys (F.Muell.) Baill. (ironwood) plant resins were identified by ATR-FTIR. The results were consistent with museum archive records which were available for 7 of the 13 artefacts. Similarly GC/MS was used to characterise five of the resins from the artefacts. These results were also consistent with the reference collection and with the ATR-FTIR method. The reference collection resins were sufficiently diverse to provide distinctions between genus and in some cases to species.

ATR-FTIR and GC/MS have both been validated as reliable methods, with advantages for the non-destructive identification of resins from archaeological and anthropological collections. This provides a choice of methods to prudently examine artefacts including rare and delicate items from museum collections. Either method can be used as part of an integrated study with ethnographic records and other molecular techniques to provide a comprehensive
understanding of the botanical source of the resin, plant exploitation practices, use of natural
materials, development of technologies and their impact on cultural practices. Application of
either method will allow identification of the distribution of artefacts with which a particular
plant resin has been associated, whether that distribution corresponds to one Aboriginal group or
allied groups, the significance of resins as trade items and whether the trade in resin correlates to
known trade networks. Further identification of artifact resins will indirectly provide information
regarding past inhabitants and their adaptation to surroundings, the technology used to process
plant material for artefact manufacturing, modes of technology transfer and the botanical
knowledge of Aboriginal groups.

ACKNOWLEDGEMENTS

I would like to thank Gail Robertson, Sue Nugent and Barbara Rowlands of the Archaeological Sciences Laboratory (School of Social Science) and George Blazaks and David Rosolin of the Analytical Chemistry Laboratory (School of Molecular and Microbial Sciences) at the University of Queensland for their help and support during this research. Thanks to the Jane Willcock at the Anthropology Museum at the University of Queensland for access to the Australian anthropological artefacts that were analysed for this project. I would like to thank Brian Cooney for permission to collect the modern reference samples from the Brisbane Botanical Gardens and Louisa Murray for permission to collect samples from the Royal Botanical Gardens, Sydney. Finally I would like to thank Kim Vernon for comments on the manuscript, Brian Vernon for assisting in some of the editing and the anonymous reviewers of this manuscript.
REFERENCES


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Figure 1. A selection of the resin sticks. Note artefact 28683, resin with embedded Abrus seeds.
Table 1. Plant reference samples used in this study

<table>
<thead>
<tr>
<th>Botanical classification</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Acacia mearnsii</em> de Wild.</td>
<td>Black Wattle</td>
</tr>
<tr>
<td><em>Agathis atropurpurea</em> B. Hyland</td>
<td>Black Kauri Pine</td>
</tr>
<tr>
<td><em>Agathis robusta</em> (C. Moore) F.M. Bailey</td>
<td>Queensland Kauri Pine</td>
</tr>
<tr>
<td><em>Angophora costata</em> (Gaertn.) Britten</td>
<td>Apple Gum</td>
</tr>
<tr>
<td><em>Angophora floribunda</em> Domin</td>
<td>Rough Barked Apple Gum</td>
</tr>
<tr>
<td><em>Angophora leiocarpa</em> K.R. Thiele &amp; Ladiges</td>
<td>Smooth Barked Apple Gum</td>
</tr>
<tr>
<td><em>Araucaria bidwillii</em> Hook</td>
<td>Bunya Pine</td>
</tr>
<tr>
<td><em>Araucaria cunninghamii</em> A. Cunn.</td>
<td>Hoop Pine</td>
</tr>
<tr>
<td><em>Araucaria heterophylla</em> Franco</td>
<td>Norfolk Island Pine</td>
</tr>
<tr>
<td><em>Brachychiton populneus</em> R. Br.</td>
<td>Karrajong</td>
</tr>
<tr>
<td><em>Callitris columellaris</em> F. Muell.</td>
<td>Coastal Cypress Pine</td>
</tr>
<tr>
<td><em>Callitris endlicheri</em> F. M. Bailey</td>
<td>Black Cypress Pine</td>
</tr>
<tr>
<td><em>Callitris intratropic</em> Benth.</td>
<td>White Cypress Pine</td>
</tr>
<tr>
<td><em>Corymbia citriodora</em> (Hook.) K. D. Hill &amp; L. A. S. Johnson</td>
<td>Spotted Gum</td>
</tr>
<tr>
<td><em>Corymbia gummifera</em> (Gaertn.) K. D. Hill &amp; L. A. S. Johnson</td>
<td>Red Bloodwood</td>
</tr>
<tr>
<td><em>Corymbia henryii</em> (S. T. Blake) K. D. Hill &amp; L. A. S. Johnson</td>
<td>Large Leaved Spotted Gum</td>
</tr>
<tr>
<td><em>Erythrophleum chlorostachys</em> (F. Muell.) Baill</td>
<td>Ironwood</td>
</tr>
<tr>
<td><em>Eucalyptus coolabah</em> Blakely &amp; Jacobs</td>
<td>Coolabah</td>
</tr>
<tr>
<td><em>Eucalyptus microcorys</em> F. Muell.</td>
<td>Tallowwood</td>
</tr>
<tr>
<td><em>Eucalyptus saligna</em> Sm.</td>
<td>Blue Gum</td>
</tr>
<tr>
<td><em>Eucalyptus siderophloia</em> Benth.</td>
<td>Grey Ironbark</td>
</tr>
<tr>
<td><em>Eucalyptus sideroxylon</em> A. Cunn.</td>
<td>Red Ironbark</td>
</tr>
<tr>
<td><em>Ficus</em> sp. L.</td>
<td>Native Fig</td>
</tr>
<tr>
<td><em>Grevillea striata</em> R. Br.</td>
<td>Beechwood</td>
</tr>
<tr>
<td><em>Polyscias murrayi</em> (F. Muell.) Harms</td>
<td>Pencilwood</td>
</tr>
<tr>
<td><em>Triodia</em> sp. R. Br.</td>
<td>Spinifex Grass</td>
</tr>
<tr>
<td><em>Wollemia nobilis</em> W. G. Jones, K. D. Hill &amp; J. M. Allen</td>
<td>Wollemi Pine</td>
</tr>
<tr>
<td><em>Xanthorrhoea australis</em> R. Br.</td>
<td>Austral Grass Tree</td>
</tr>
<tr>
<td><em>Xanthorrhoea fulva</em> (A. T. Lee) D. J. Bedford</td>
<td>Swamp Grass Tree</td>
</tr>
<tr>
<td><em>Xanthorrhoea johnsonii</em> A. T. Lee</td>
<td>Forest Grass Tree</td>
</tr>
<tr>
<td><em>Xanthorrhoea macronema</em> F. Muell.</td>
<td>Bottlebrush Grass Tree</td>
</tr>
<tr>
<td><em>Xanthorrhoea resinosa</em> Pers.</td>
<td>Spear Grass Tree</td>
</tr>
</tbody>
</table>

Species names are listed with the name of the person who classified the plant with reclassifications also listed in brackets for clear identification of botanical specimens.
Table 2. The artefacts analysed from the Anthropology Museum at the University of Queensland.

<table>
<thead>
<tr>
<th>Artefact Number</th>
<th>Artefact Location (Australia)</th>
<th>Catalogue resin identification</th>
<th>Artefact type</th>
</tr>
</thead>
<tbody>
<tr>
<td>404</td>
<td>Kalumburu Mission, Western Australia</td>
<td>Unidentified Resin</td>
<td>Hunting Spear</td>
</tr>
<tr>
<td>1428</td>
<td>Bald Hill, Queensland</td>
<td><em>Xanthorrhoea</em> Resin</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>1623</td>
<td>Coomooboolaroo Station, Queensland</td>
<td>Unidentified</td>
<td>Resin Stick</td>
</tr>
<tr>
<td>1624</td>
<td>Coomooboolaroo Station, Queensland</td>
<td>Unidentified</td>
<td>Resin Stick</td>
</tr>
<tr>
<td>1625</td>
<td>Coomooboolaroo Station, Queensland</td>
<td>Unidentified</td>
<td>Resin stick</td>
</tr>
<tr>
<td>3193</td>
<td>Ernabella, South Australia</td>
<td>Spinifex Resin</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>17031</td>
<td>Sturt Creek Station, Western Australia</td>
<td>Spinifex Resin</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>18193</td>
<td>Unknown</td>
<td>Spinifex Resin</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>20172</td>
<td>Luma, Western Australia</td>
<td>Spinifex Resin</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>22947</td>
<td>Port Keats, Northern Territory</td>
<td>Ironwood Sap</td>
<td>Resin Stick</td>
</tr>
<tr>
<td>25281</td>
<td>Aurukun, Queensland</td>
<td><em>Xanthorrhoea</em> Resin</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>25282</td>
<td>Aurukun, Queensland</td>
<td>Unidentified</td>
<td>Processed Resin</td>
</tr>
<tr>
<td>28683</td>
<td>Unknown</td>
<td>Unidentified</td>
<td>Resin stick with Abrus seeds$^a$</td>
</tr>
</tbody>
</table>

$^a$ – this artefact resembles a fire stick.
Table 3. The artefacts analysed from the Anthropology Museum at the University of Queensland.

<table>
<thead>
<tr>
<th>Artefact Number</th>
<th>GCMS</th>
<th>FTIR</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>404</td>
<td>NDA</td>
<td>√</td>
<td><em>Erythrophleum chlorostachys</em></td>
</tr>
<tr>
<td>1428</td>
<td>√</td>
<td>√</td>
<td><em>Xanthorrhoea</em> spp.</td>
</tr>
<tr>
<td>1623</td>
<td>NDA</td>
<td>√</td>
<td><em>Xanthorrhoea</em> spp.</td>
</tr>
<tr>
<td>1624</td>
<td>NDA</td>
<td>√</td>
<td><em>Xanthorrhoea</em> spp.</td>
</tr>
<tr>
<td>1625</td>
<td>√</td>
<td>√</td>
<td><em>Xanthorrhoea resinosa</em></td>
</tr>
<tr>
<td>3193</td>
<td>NDA</td>
<td>√</td>
<td><em>Triodia</em> spp.</td>
</tr>
<tr>
<td>17031</td>
<td>√</td>
<td>√</td>
<td><em>Triodia</em> spp.</td>
</tr>
<tr>
<td>18193</td>
<td>NDA</td>
<td>√</td>
<td><em>Triodia</em> spp.</td>
</tr>
<tr>
<td>20172</td>
<td>√</td>
<td>√</td>
<td><em>Triodia</em> spp.</td>
</tr>
<tr>
<td>22947</td>
<td>√</td>
<td>√</td>
<td><em>Erythrophleum chlorostachys</em></td>
</tr>
<tr>
<td>25281</td>
<td>NDA</td>
<td>√</td>
<td><em>Xanthorrhoea</em> spp.</td>
</tr>
<tr>
<td>25282</td>
<td>NDA</td>
<td>√</td>
<td><em>Triodia</em> spp.</td>
</tr>
<tr>
<td>28683</td>
<td>NDA</td>
<td>√</td>
<td><em>Triodia</em> spp.</td>
</tr>
</tbody>
</table>

NDA – non-destructively analysed only, permission not given for destructive analysis.
**Figure 2.** The ATR-FTIR spectra of the museum artefact resins which are consistent with the spectrum of *Erythrophleum chlorostachys*.
Figure 3. The ATR-FTIR spectra of the museum artefact resins which are consistent with the spectrum of *Triodia* *spp.*
Figure 4. The ATR-FTIR spectra of the museum artefact resins which are consistent with the spectrum of *Xanthorrhoea spp.*
Figure 5. The gas chromatograph comparing Artefact 22947 (top panel) with *Erythrophleum chlorostachys* (bottom panel).
Figure 6. The gas chromatograph comparing Artefact 17031 (top panel) with *Triodia* sp. (bottom panel).
Figure 7. The gas chromatograph comparing Artefact 1428 (top panel) with *Xanthorrhoea macronema* (second panel), *Xanthorrhoea australis* (third panel), *Xanthorrhoea fulva* (fourth panel) and *Xanthorrhoea johnsonii* (bottom panel).
Figure 8. The gas chromatograph comparing Artefact 1428 (top panel) with *Xanthorrhoea johnsonii* (bottom panel).
Figure 9. The gas chromatograph comparing Artefact 1625 (top panel) with *Xanthorrhoea resinoso*a (bottom panel).
Highlights

- Australian Native Plant Resins from Museum artefacts were identified.
- Identification was performed using microscopy, FTIR and GC/MS.
- The microscopy and FTIR can be performed in a non-destructive manner.
- Assessment of ATR-FTIR was performed and compared to GC/MS.