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Fourier transform infrared spectroscopic analysis of organic archaeological materials: background paper

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Fourier transform infrared (FTIR) spectroscopy is ideally suited to the cultural heritage sector due to the ability to apply it minimally or non-destructively with limited sample preparation, fast analysis times (spectra can be obtained in a matter of minutes), relatively low cost, and relative ease of use. FTIR has been applied to answer a range of archaeological research questions through analysis of both organic and inorganic materials. Examples include determining the firing temperatures of archaeological clays or identifying types of textile.

Organic archaeological materials (*e.g.* wood, bone, leather, and textiles) carry enormous cultural significance because although rare, they represent a significant record of the human past (Fig. 1). However, they are also highly vulnerable to degradation or irreversible physical transformation caused by environmental changes (either *in situ*, or post excavation/during conservation). Changes in the chemical composition of organic materials caused by chemical or biological degradation lead to altered IR spectra; the high resolution and sensitivity afforded by FTIR analysis can therefore help us understand the mechanisms of decay.[1] This understanding allows the evaluation of any continued decay of objects and is critical for the accurate characterisation of aged materials.

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Understanding organic archaeological materials

The vulnerability of organic archaeological materials to decay means that they present complex challenges in terms of preservation and conservation. Understanding the processes involved in their decay is critical to managing these challenges. Determining the state of preservation of an organic object helps inform appropriate conservation and storage procedures and allows the monitoring of further decay. Deterioration processes may include oxidative decay (which may result in a higher abundance of oxidised functional groups) or hydrolysis (resulting in the breakdown of polymers). Additionally, certain components might be broken down more quickly than others, changing the relative composition of the material. Understanding how decay processes transform the chemical composition of the materials therefore also allows the accurate identification and characterisation of aged and decayed samples.

Using FTIR to characterise decayed organic materials

Spectroscopic analytical techniques produce a spectrum that is specific to the chemical composition of the analysed material, allowing its identification. In IR spectroscopy, infrared light is absorbed at different wavelengths depending on the vibrational activity of specific groups of atoms (functional groups) within the material.[1] A spectrum is therefore determined by both the types of functional group present, and the relative abundance of each; a spectrum is therefore unique to the chemical composition of a material.

IR instruments with Fourier transform processing (FTIR) are the most commonly used in heritage applications, as the improved signal-to-noise ratio allows the analysis of subtle changes in spectra as well as increased speed of analysis.[1] This means that changes in the chemistry and composition of organic archaeological materials caused by decay can be determined through assessment of the characteristic absorption peaks. By assigning peaks to individual components of a material, its relative composition can be measured semi-quantitatively through comparison of the relative heights or areas of these peaks. Peak assignment is typically done with the aid of in-house or commercially available databases.[2] Changes in the position or shape of the peaks can also be related to specific changes driven by decay. Comparison with modern reference samples gives an indication of the extent to which the material has degraded. Decay levels in different samples can also be compared, allowing an assessment of differences in preservation between, for example, samples that have been stored under different conditions or undergoing different conservation methods.

Fig. 1 Organic materials excavated at the Bronze Age site of Must Farm (East Anglia) displayed exceptional levels of preservation. Left: an expanse of timbers, part of the collapsed settlement; right, top: yarn wound around dowels; right, bottom: a complete axe haft. Images from Knight *et al.*, 2019, reproduced under a creative commons license.[4]

Practical considerations in the use of FTIR

FTIR spectrometers consist of an IR source, which is directed through (transmission mode) or at (reflectance mode) a sample, before a detector is used to determine the wavelengths of light that have been absorbed by the sample. In transmission mode, traditionally samples would be mixed into a KBr matrix, requiring a relatively large amount of sample. Attenuated total reflectance (ATR) units are increasingly the preferred type of instrument within heritage science laboratories as these permit the direct analysis of unprepared materials within a matter of minutes. If the size of the sample allows, ATR can be carried out non-destructively, although depending on the material the application of pressure may cause damage (Fig. 2). As water tends to produce broad FTIR peaks which obscure some other signals, sensitivity is higher if samples are dry. Although no further preparation is required, good contact does need to be made between the sample and the crystal window (Fig. 2), meaning that for harder samples (*e.g.* bone) powdering may be required.

A range of bench top FTIR instruments are available. These are increasingly small and transportable, and can operate outside dedicated labs, enabling in-field use and the rapid gathering of data. Whilst many are connected to a desktop or laptop computer in order to operate the instrument and gather spectra, some can be controlled *via* a built-in computer.

FTIR is an attractive method of analysis for several reasons including its speed, low cost, and limited sample preparation requirements. It can be used in a minimally destructive manner by taking only very small amounts of sample (several milligrams for ATR), or completely non-destructively if the nature of the sample allows. FTIR analyses only a very tiny fraction of an object, which may not be representative of the bulk, particularly in cases where heterogeneous decay has occurred. However, the speed of analysis allows this to be circumvented by collecting multiple measurements. Whilst FTIR instruments are relatively straightforward in terms of operation, data interpretation still demands expert knowledge, in particular requiring the correct assignment of spectral peaks to maximise the value of the data. Methods of data analysis may also vary between studies, for example in terms of how data is manipulated prior to interpretation, meaning that comparison between studies is not necessarily straightforward. Furthermore, FTIR data does not offer the detailed structural characterisation that analysis by, for example, nuclear magnetic resonance (NMR) or analytical pyrolysis would allow (see AMC Technical Brief 85).[3]

Chemometric methods (such as partial least squares modelling or principal component analysis (see AMC Technical Brief 100))[3] are increasingly applied to FTIR data. These methods have the potential to improve the sensitivity of detection of changes in different materials, as several variations in the spectra can be accounted for simultaneously.

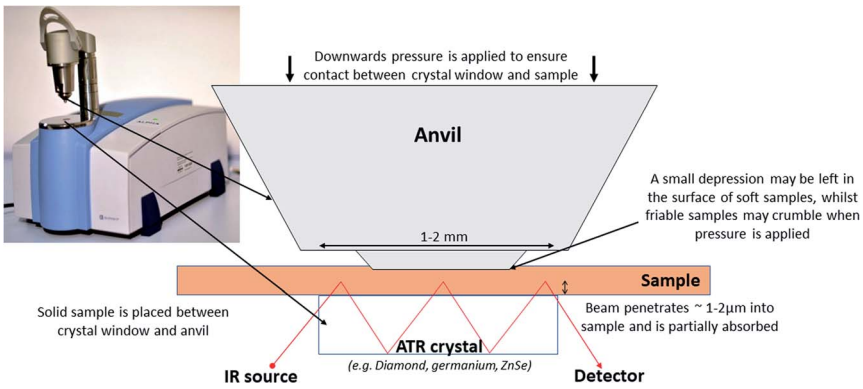

Fig. 2 Schematic showing the operation of a typical FTIR-ATR instrument, illustrating how damage to a sample could be caused by the application of pressure.

Case studies

Assessing decay in waterlogged archaeological wood

Waterlogged wooden archaeological objects are rare but diverse, ranging from shipwrecks and prehistoric trackways to small objects such as cups and bowls (Fig. 1). Waterlogged wood can present significant management and conservation challenges due to its inhomogeneity and extreme vulnerability to decay. Assessing preservation in waterlogged wood is vital in informing its conservation as the amount of cellulose lost often influences the choice of consolidating agent.

Wood is composed of three major biopolymers: cellulose, hemicelluloses, and lignin. These are closely bound within the wood structure alongside

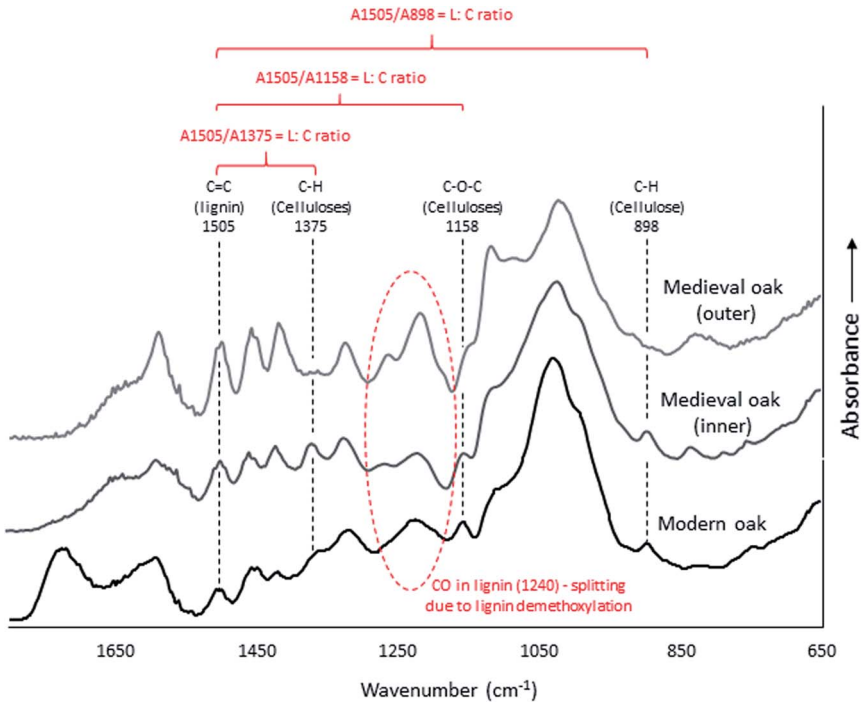

Fig. 3 FTIR spectra of modern oak compared to the inner (better preserved) and outer (more deteriorated) sections of an oak timber excavated from the medieval site of Wooton Creek (Isle of Wight). Diagnostic peaks relating to cellulose and lignin are indicated. The peak at 1505 cm^{-1} relates to the highly stable phenolic skeleton of lignin and is therefore often used to calculate a L : C ratio by comparing it to peaks related to celluloses. Peak shapes can also indicate decay, for example the peak at 1240 cm^{-1} (circled) splits with increasing decay as methoxy groups are lost from lignin [Author's own data; samples provided by Rosie Lansley, Isle of Wight Council].

small amounts of non-structural components (*e.g.* tannins, resins and oils). In an FTIR spectrum of wood, certain peaks can be solely attributed to one of these components. Others contain contributions from more than one polymer and must be interpreted with caution. The relative heights or areas of these identified peaks are typically used to derive a lignin : cellulose (L : C) ratio (Fig. 3). Due to the greater vulnerability of cellulose to biological decay, this ratio is assumed to increase with increasing wood deterioration.

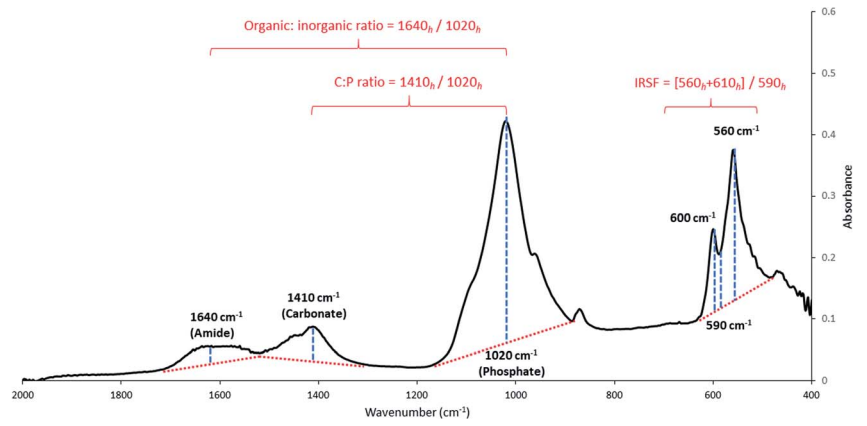

Fig. 4 FTIR spectrum of a degraded bone sample from the Glastonbury Lake Village archaeological site. Four key peaks are typically used to assess bone preservation. The infrared splitting factor (IRSF) provides a measure of bone mineral crystallinity.

Other indicators of decay such as the oxidation of C=O groups, cellulose hydrolysis, and demethylation of lignin can be identified by changes in the position or shape of the peaks related to these functional groups (Fig. 3).

Rapid screening of biomolecular preservation in archaeological bone

Archaeological bone is more robust to decay than other organic materials, as an inorganic component (hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$) lends protection to the organic component (primarily type I collagen, a triple helix of amino acids). Consequently, bone is relatively common in archaeological sites and the study of both human and animal bones can provide a wealth of information, for example regarding farming or butchery practices. The successful extraction of ancient DNA or collagen from bone can greatly enhance this information, for example enabling migration or dietary isotope studies. However, the success of these biomolecular techniques depends on the overall state of preservation of the sample; as biomolecular techniques are expensive and time intensive, FTIR can be used as a rapid screening tool to assess the likelihood of their success.

FTIR analysis of bone yields information on both the organic and inorganic components (Fig. 4). Hydroxyapatite content is represented by peaks at 1410 cm^{-1} relating to the carbonate component and at 1020 cm^{-1} relating to phosphate. Hydroxyapatite deterioration is indicated by an increase in carbonate content, determined by comparing both peaks. Comparison with the amide stretch at 1640 cm^{-1}, attributed to collagen, provides a measure of the organic : inorganic ratio.

Hydroxyapatite is thought to increase in crystallinity with increasing deterioration. This can be assessed by analysis of the doublet at 560 and 610 cm^{-1} which becomes increasingly split with increasing crystallinity (known as the infrared splitting factor (IRSF); illustrated in Fig. 4).

Identification of archaeological fibres

Archaeological textiles are rare, being found primarily in environments where

reduced levels of oxygen prevent decay, such as waterlogged sites (*e.g.* Must Farm, Fig. 1). Archaeological textiles range from rope and basketry to clothing and tapestries, and are composed of processed polymeric fibres from either plants or animals. Identifying the composition of these fibres can be critical for their appropriate treatment and provides valuable archaeological information. Conventionally, textiles are identified microscopically. However, this requires a great deal of experience and in some cases degradation of the fibres may have altered their appearance irreparably.

FTIR can alternatively be used to identify textiles based on their chemical composition. This allows the analysis of even decayed samples and may yield additional information such as the identification of dyes and treatment processes. There are marked differences between the spectra from plant-based fibres which are primarily cellulose, and animal-based fibres which are mainly protein. It is therefore relatively easy to distinguish between the two, even when chemical or biological deterioration has occurred. Through more careful examination of the ratios between characteristic peaks, it may also be possible to distinguish between different cellulose-based fibres (*e.g.* cotton which contains no lignin, and jute which contains around 11% lignin will have quite different spectra). Statistical analysis such as principal component analysis (PCA) may further help distinguish between fibre types when differences in spectra are subtle. Although animal-based fibres have different relative amino acid compositions, FTIR is unlikely to be able to distinguish between types (for example wool *vs.* silk). Methods such as pyrolysis gas chromatography mass spectrometry (py-GC/MS) or amino acid analysis by high performance liquid chromatography (HPLC) may be more suitable.

Ref. 5–8 provide further information on the use of FTIR in the analysis of archeological materials.

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This Technical Brief was prepared for the Analytical Methods Committee (AMC), with contributions from members of the AMC Heritage Science Expert Working Group, and approved by the AMC on 25th January 2021.

Further reading

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