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Infrared reflectance spectroscopy as an analytical technique for the study of residues on stone tools: potential and challenges

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ABSTRACT

FTIR (Fourier transform infrared) spectroscopy is a non-destructive analytical method that has been used successfully to analyse both inorganic and organic archaeological material. Using a microscope attachment has the additional benefit of analysing very small spots (diameter 100 μm) directly on an artefact without sample preparation or destruction. It is therefore a suitable method to study residues on prehistoric stone tools. However, using a microscope without an ATR (attenuated total reflection) microscope objective, results in a combination of reflection and transmission/absorbance FTIR spectra, which is not always as easy to interpret as directly measured transmission/absorbance spectra. In order to improve the interpretation of spectra recorded on archaeological samples, the method was tested with replicated Middle Stone Age stone points used during hunting and butchery experiments on parts of a blue wildebeest (*Connochaetes taurinus*) published in 2004 (Lombard et al., 2004). In this case, the residues on the tools were known and post-depositional contamination was eliminated. Additional samples of the organic materials, and the minerals from which the tools were made were also available. Therefore, we could assess the viability of FTIR reflectance spectra for distinguishing between bone, fat and protein residues.

1. Introduction

Detecting, identifying and interpreting micro-residues on Middle Stone Age or Middle Palaeolithic stone tools is never an easy or straight-forward exercise. Non-destructive micro-residue analysis on archaeological stone tools is mostly done using high-power, reflected light microscopes (e.g., Hardy and Moncel, 2011; Langejans, 2012; Lombard, 2011). Blind test results attest to the general reliability of the identification of micro-residue types left on stone tools as a result of their use and/or hafting using reflected light microscopy (Hardy and Garufi, 1998; Lombard and Wadley, 2007; Monnier et al., 2012; Wadley et al., 2004). To increase the dependability of interpretations, concomitant support for the identification of such residues should be sought. For example, the repetitive clustering of attendant residues, such as the combination of fat, blood, bone, and animal tissue on a tool portion provides a far more secure interpretation of an animal residue type than any single residue (Wadley and Lombard, 2007). This approach is particularly relevant to archaeological contexts where some residues may be partially degraded and where the potential of ancient, post-depositional or post-excavation contaminants is high (Langejans, 2011).

In some cases the removal and destruction of ancient residues on stone tools for specific morphological or biochemical analysis are warranted. Yet, it is our contention that – depending on the quality and certainty of results, age of the material, sample size and research question – non-destructive analyses remain one of the most responsible, contextual and informative approaches. Destructive processes are often focused on extracting only certain residue types, for example starch grains (e.g., Li et al., 2013), or animal proteins (e.g., Högberg et al., 2009), paying little attention to other residues, and destroying or disturbing their *in situ* context on the tool (although the work of Högberg et al. (2009) is exemplary in its integration of usewear and residue analysis). Also, despite the increased sensitivity of biochemical techniques, useful results from ancient material are seldom guaranteed. This is so because: a) the biochemistry of the micro-remains might have changed over time as a result of diagenesis, fossilization or soil chemistry, b) there is

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too little left for successful analysis, or c) the micro-residues are too 'messy' or contaminated (from use or from post-depositional/curational conditions) to provide conclusive biochemical results.

Thus far, the best biochemical results for very old material (for example 60.5 ± 1.9 ka from Diepkloof) are obtained when macroscopic residues (relatively large quantities) are available for destructive analysis, and when there is a specific question at hand, for example, identifying the ingredients in adhesives (e.g., Cârciumara et al., 2012; Charrié-Duhaut et al., 2013). Yet, we know of few 'trouble-free' biochemical results relating to very old stone tools with animal residues such as bone, fat, animal tissue or collagen. With this initial paper we investigate the potential of detecting animal residues on stone tools in a non-destructive way, applying FTIR (Fourier transform infrared) spectroscopy to replicated stone points used for hunting and carcass processing, and we highlight potential archaeological applications, methodological improvements needed, and some difficulties associated with the technique.

FTIR spectroscopy has been used to analyse both inorganic and organic archaeological material (Cârciumara et al., 2012; Cotte et al., 2005; Mizzoni and Cesaro, 2007; Thompson et al., 2013; Yaroshevich et al., 2013). A benefit of this technique is that inorganic and organic phases can be analyzed simultaneously and a microscope attachment has the additional advantage of analyzing very small areas directly on an artefact without sample preparation or destruction. Infrared spectroscopy is also not hindered by fluorescence in the same way as Raman spectroscopy during the recording of spectra associated with organic materials (Prinsloo et al., 2013). Therefore, depending on biochemical preservation, FTIR spectroscopy is an ideal method to study micro-residues on prehistoric tools.

Preferably, an attenuated total reflection (ATR) microscope objective should be used to measure spectra directly in transmission or absorbance mode, but we have found that it is very difficult to record spectra on the uneven surfaces of the stone tools. It is even more difficult if the spot of interest is on the edge of a tool. Breakages can occur on the tool edge due to uneven pressure applied by the ATR objective on rough surfaces. However, using a microscope in reflectance mode results in a combination of reflection and transmission/absorbance FTIR spectra, which is not always as easy to interpret as directly measured transmission/absorbance spectra.

Recently it has been shown that FTIR specular reflectance spectra can be used to distinguish between minerals and for imaging material properties of bone specimens (Acerbo et al., 2012; Nicholson et al., 2012; Ostrooumov, 2009). In the identification of gemstones the technique is gaining ground, and has been in use for quite some time for remote sensing of minerals (e.g., Hainschwang and Notari, 2008; Clark, 1999). In the field of heritage studies, where non-invasive techniques are imperative, FTIR reflectance spectroscopy was also found to be useful in the study of pigments and binders in spite of the difficulties in interpreting reflectance spectra (Buti et al., 2013; Lojewski et al., 2011; Miliani et al., 2012; Rosi et al., 2011; Unger et al., 2013).

Using experimental material, we attempt to establish whether reflection-based FTIR micro-spectroscopy can be used to study use-related animal residues adhering to stone tools. In contrast to genuine archaeological samples, the residues on the tools are known and reference material is readily available. Furthermore, post-depositional contamination is absent as the samples are only 10 years old and have been stored in sterile conditions. Therefore, we are able to assess the viability of FTIR reflectance spectra for distinguishing between bone, fat and protein residues.

2. Materials and methods

2.1. Stone tool points

Six stone points, resembling those from the southern African Middle Stone Age and used during hunting and carcass processing experiments on parts of a blue wildebeest (*Connochaetes taurinus*) carcass (Lombard et al., 2004) were selected to test the ability of FTIR microscopy to identify animal residues that adhered to the points as a result of their use. A summary of the points selected for this study is provided in Table 1. Points 108 and 109 were used in thrusting experiments, 214, 217 and 219 in throwing experiments and Point 311 in a scraping experiment. In Fig. 1 from left to right an example of a replicated spearhead used during the hunting experiments, a hafted spear stabbed into the shoulder of a blue wildebeest carcass and a short-handled replicated point used for scraping a portion of the carcass are shown.

2.2. Contact materials

During the hunting and butchery experiments, samples were collected from animal parts that came into contact with the stone points. These residues were stored on microscope slides for future use. We recorded transmission and reflectance infrared spectra of these materials as control samples for comparative purposes, and to observe and record potential differences between transmission and reflectance spectra.

2.3. Experimental detail

Infrared reflectance spectra were recorded using a Hyperion microscope attached to a Vertex 70v (Bruker Optics) spectrometer. The samples were placed directly under the 10× microscope objective and a spot selected for analysis. The spectra were then recorded using a 15× IR objective after optimising the focus to obtain the maximum signal. For small samples the aperture was decreased and background spectra were recorded under the same conditions. The recording time varied according to the quality of spectra obtained and ranged between 500 and 1000 scans and spectral resolution was 4 cm^{-1}.

Infrared transmission/absorbance spectra of the powdered minerals from which the points were made were recorded using a diamond Golden Gate ATR cell (Bruker), which fits in the macro sample compartment of a Vertex 70v (Bruker Optics) spectrometer. The sample compartment was evacuated during acquisitions and the contact area between the sample and the diamond ATR crystal is 2 mm in diameter. Spectra were recorded with 32 acquisitions at 4 cm^{-1} resolution over a spectral range of 4000–600 cm^{-1}.

Table 1
Summary of samples used in this study.

Point no.	Minerals used	Haft material	Binding material	Action	Contact materials
108	Medium-grained quartzite	Commercial dowel	Sinew	Thrusting	Muscle, bone
109	Medium-grained mudstone	*Combretum erythrophyllum*	Sinew, leather thong	Thrusting	Muscle, bone
207	Fine-grained quartzite	Commercial dowel	Fibrous plant twine	Throwing	Muscle, bone
214	Fine-grained chert	*Tapiphyllum parvifolium*	Bark	Throwing	Muscle, bone
219	Fine-grained hornfels	Commercial dowel	Leather thong	Throwing	Muscle, fat, bone
311	Fine-grained hornfels	*Canthium inerme*	Leather thong	Scraping	Bone