Infra-red (Reflectance) Spectroscopy of Ceramics from Tell Halawa, Syria

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Abstract: Many scientific studies characterizing archaeological ceramics rely upon techniques that are becoming obsolete. Infra-red microspectroscopy (IR), long in use by the materials science community, is here applied to archaeological ceramics. This fast, non-destructive technique provides constraints on the mineralogic make-up of samples. Examining a group of ceramics from Tell Halawa, Syria, from the early Bronze Age (before c. 2800 BC) we note variability in firing technology.

Key words: Infra-red spectroscopy, archaeological ceramics, Tell Halawa, Syria, firing technology

Introduction: Determination of Firing Conditions: Previous Studies

While there are a number of methods that can be used to characterize ancient firing environments, few have become standard practice. The technique for examining the colour (using the Munsell colour system) of ancient ceramic materials to propose firing temperature has been used for a number of years (Matson, 1971). Many excavations as a matter of course categorize all diagnostic shards using this technique. Ideally, test-briquettes are made from local clay and fired in controlled conditions. These samples are then graded according to colour, and compared with archaeological samples. This method requires the investigator to analyze separately variations in value, chroma, and hue, as each aspect records a facet of source materials and firing environment. This method has a number of serious drawbacks:

A. Because assessment of colour differs between individuals, one person must be entrusted with recording colour, which can be a time-consuming task, prone to error.

B. In cases where re-firing experiments are performed, there are several important variables. Clay preparation can reduce the larger fraction of particles, remove organic matter, altering the colour of the clay.

C. Without petrographic or chemical tests one cannot be certain that particular wares were not imported. There is the possibility that a fraction of the sample group will be from a distinct clay source that will not match the parameters of the local clay.

D. This complicated visual method of investigation has never gained universal acceptance, and the reproducibility of the results is doubtful. Methods of recording colour not using the Munsell system are also used, particularly in many European countries (Orton et al., 1993).

In contrast, IR offers several advantages over this technique:

A. The majority of samples require essentially no preparation.

B. Analysis time for the majority of samples is several minutes.

C. Information about the firing environment, as well as the raw materials, is presented. Spectra may be quickly matched with similar spectra, making a rapid assessment of many samples possible.

Calcite is particularly reflective, and can serve as a useful diagnostic mineral to estimate maximum firing temperature. There is also an increasing demand for non-destructive methods of analysis. Museum curators are becoming less enthusiastic about releasing shards for destructive tests, while complete vessels have almost never been sampled. Infra-red spectroscopy when used in reflectance mode is totally non-destructive, and if a sample of powder is required, it can often be obtained from a broken surface of a sample. With further work to define the parameters of the method, this technique can be applied to a wide range of materials from a number of sources.

Previous Archaeological Studies

IR has been used to determine the nature of resinous deposits adhering to pottery (Sandermann, 1965; Sauter, 1967). The technique was also used to characterize deposits on the inside of a jar from Godin Tepe, Iran, dating to the mid-fourth millennium B.C. The presence of tartaric acid in the samples demonstrates that this vessel was used to store wine (Badler, 1996). Amber is the archaeological material that is most closely associated with IR, and it is here that an archaeological methodology is effectively used.

Early chemical investigations into the amber trade confirmed assumptions - based largely upon textual sources - that amber was traded from the Baltic region. Due to the time required to prepare amber for wet chemical analysis, this method was used to analyze a small number of samples. Using new information from IR spectroscopy (Beck, 1986; Beck and Shennan, 1991; Beck et. al., 1964), it was found that the amber trade was much more complicated. It also demonstrated that IR spectroscopy could be successfully applied to archaeological materials. There are also some isolated applications of the technique to firing history. Maniatis et al. (1982) characterized the hydration state of low fired terra-cotta statuettes from Greece, and Blasius et al. (1983) examined Roman tile fragments using IR. Duraiswamy et al. (1992) used the technique to examine Indian clays from an archaeological site.

The Technique

Infrared spectroscopy has been extensively utilized to characterize modern industrial ceramic materials, as well as a broad range of inorganic, organic, and mineralogic specimens. It is also gaining ground among conservation scientists (Derrick et al. 1999). A large number of reviews of the applications and theoretical aspects of infrared spectroscopy exist (eg McMillan and Hofmeister, 1988 Mitra, 1989; Williams, 1995; McMillan et al., 1996), and we provide only an abbreviated description of the technique here. The usefulness of infrared spectroscopy in characterizing archaeological ceramics lies primarily in its ability to yield a 'fingerprint' spectral pattern that can be readily associated with the mineralogic constituents of samples. Essentially every mineral of importance to ceramics has had its infrared spectra characterized (eg Farmer, 1974, Salisbury et al., 1991), and these spectra fall into different groupings depending on the type of bonding within the different minerals of the sample. For example, carbonates are readily distinguishable from framework silicates (such as quartz and feldspars) which in turn are easily distinguished from chain silicates (amphiboles and pyroxenes). The overall mineralogic make-up of samples can be used to provide constraints on the firing temperature of the ceramics, an effect noted by Maggetti (1982).

The simplest underlying principle of infrared spectroscopy has long been used in the archeological sciences, that is, characterizing the colour of a sample as a classification tool. Infrared spectroscopy involves characterizing the colour of samples in the wavelength range of 1-200 microns, or equivalently 10000-50 cm^{-1} in units of frequency. For ceramic characterization, we focus primarily on the frequency range between 500-2000 cm^{-1} (20 to 5 microns), as this spectral region proves to be the most diagnostic of different ceramic types. This range of infrared light is at comparable energies to those of interatomic vibrations of solids, liquids, and gasses. The energies of these vibrations are determined by the strengths of bonds within a sample, and the masses of the atoms. Stronger bonds produce higher frequency vibrational bands, as do less massive atoms. The local symmetry surrounding the atoms (particularly in crystal structures) also plays a major role in determining which types of vibrations are infrared-active within a crystal. For example, calcite ($CaCO_3$) has eight symmetry-allowed infrared-active vibrations (Williams, 1995), with three of these lying above 600 cm^{-1} (typically, spectra of mixed phase materials such as ceramics are not notably diagnostic below 600 cm^{-1}). Of these three, two (near 1400 cm^{-1} and 880 cm^{-1}) are strong and completely diagnostic of the presence of calcite within the sample.

We found that reasonably high quality and completely reproducible data can be produced from flat regions of shards (or shards oriented so that their curvature is small in the region being sampled) in areas as small as 50 microns in diameter. It is of considerable importance that the characteristic grain sizes in the bulk (inclusion-free portions) of archeological ceramics are generally smaller than the wavelength of the incident infrared light. Large grains of material can bias the observed reflectance spectra, and we occasionally observe such effects when, for example, reflectance spectra are taken near macroscopic inclusions. In many instances, we found that light scraping of the surface were necessary to remove dirt or surface alteration products from the sample. In the majority of cases the uppermost 100 - 500 microns were removed. Because of the spatial selectivity of the infrared reflectance technique, such scraped areas could be confined to spots less than 1 mm^2 in area.

The increased utility of IR can largely be traced to technologic advancements in over the last two decades. Archaeological ceramic samples are not particularly reflective in the infrared (only about 1% that of a metallic mirror). Accordingly, to conduct spatially selective measurements, in which reflected light is collected from areas with lateral dimensions as small as 50 microns, requires that infrared light be extremely efficiently collected and detected. We utilize a Fourier Transform Infrared (FTIR) Spectrometer coupled with an infrared microscope to conduct all of our measurements. The infrared microscope is equipped with Cassegrain all-reflecting optics (reflecting optics are required for IR microscopes, as conventional lenses absorb infrared light). Specifically, we utilize a Bruker Industries IFS-66v evacuated FTIR spectrometer, equipped with a KBr beamsplitter and glowbar source to conduct all of our measurements. The reflectance measurements are conducted on an infrared microscope attachment (also Bruker Industries) equipped with a liquid-nitrogen cooled intermediate range mercury cadmium telluride (MCT) detector. All spectra were run with 4 cm^{-1} resolution, with typical collection times of approximately 1-3 minutes for each reflectance spectrum. The spectra were referenced against a front-silvered aluminum mirror (which has a flat spectral response across the frequency range of interest) to remove instrument response from the spectra. In most cases, multiple spectra were collected from each sherd to both ensure reproducibility and to verify that the

spectra were not aliased by a shallow sub-surface inclusion.

IR Applied to Archaeological Ceramics

The detailed mineralogy of ceramic samples is intimately connected to both their firing temperatures and the composition of the original source materials of the clay. As a simple example, pure kaolinite ($Al_2Si_2O_5(OH)_4$), a major component of many ceramics, undergoes a sequence of mineralogic transformations as it is treated at progressively higher temperatures. Specifically, kaolinite dehydrates near 550EC to an anhydrous phase with a chemical composition of $Al_2Si_2O_7$ (metakaolin). This phase alters to a mixture of SiO_2 (initially amorphous, but which can ultimately crystallize to quartz or cristobalite) and a structurally complex and defect-rich spinel phase with a stoichiometry such as $Al_{21.33}O_{32}$ at 950-1000EC (Carty and Senapti, 1998). This spinel phase reacts in turn to form mullite ($Al_6Si_2O_{13}$) near 1075EC. The critical point raised by the transformation sequence undergone by this simple clay is that even though a sample containing a kaolinite-rich starting material undergoes no changes in its chemistry (other than the loss of water near 550EC) during firing, the resultant mineralogy of the sample shifts markedly as a function of the temperature to which the sample has been exposed. Thus, kaolinite starting materials converge at high temperatures to SiO_2-bearing assemblages with aluminum-bearing accessory phases, and this progression can be monitored (and firing temperature bounded) through mineralogic characterization. Clearly, when more chemically complex clays such as smectites and illites are present, the range of minerals that can result during firing is markedly expanded (Kingery, 1976). Mineralogic characterization can not only yield bounds on the firing temperature of a ceramic sample, but also the starting materials mixed into clays (as well as constraining the identities of the clays).

Determination of the presence of calcite within ceramics is not straightforward using a number of analytic techniques. For example, bulk chemical analyses of ceramic samples do not typically record the contents of elements such as carbon and hydrogen, so the presence or absence of calcite cannot be readily derived from such measurements. Furthermore, as with the mineralogic changes undergone by kaolinite as a function of temperature, the presence of calcite also provides a first-order bound on the temperature of firing: calcite breaks down to lime (CaO) and carbon dioxide at a temperature of 894EC, which is thus a firm upper bound on the temperature of firing of calcite-bearing ceramics (eg. Southard and Royster 1936). The firmness of this upper bound is accentuated by the effect that free SiO_2 can have on lowering of the decarbonation temperature of calcite: the reaction of $CaCO_3 + SiO_2 \rightarrow CaSiO_3$-wollastonite + CO_2 is well known to proceed at lower temperatures than the simple decarbonation of calcite alone (Wyllie and Huang, 1976).

Samples

Tell Halawa, in northern Syria about 100 km east of Aleppo, is a multi period site. There are many graves and in general the ceramic sequence is well stratified, yielding remains that are characteristic of the region (Orthmann, 1981;1989). While details of the site will not be covered here, the ceramics fit into an ongoing research programme into Mesopotamian ceramic technology (Eiland in press a and b). Archaeological ceramics from Tell Brak has received detailed consideration using IR as well (Eiland and Williams 2000). Here we present several samples - housed at the Institut für Mineralogie, Frankfurt - all taken from Layer 3, early Bronze IV period (before c. 2800 BC) from Tell Halawa. Colour is noted but as this is such a small sample no Munsell numbers will be used.

HL 13 Thin dark grey 'Euphrates ware' shard. Very hard texture. This would have been a 'luxury' vessel.
HL 8 Thick grey (typically Mesopotamian) fabric. Coarse and friable ceramic body.
HL 7 Red fabric similar texture to HLW 8 barring colour.
HL 3 Buff fabric with large number of calcite inclusions visible by eye. Thick fabric is visually much like HLW 8 and HL 7, barring colour.

Interestingly, chemical analysis (X-ray fluorescence) showed little difference between the Euphrates ware and the common ware (HL 13 and 8 respectively), though there is a clear difference by eye. This is particularly the case for bulk elements, here rounded to the nearest percent, and is also the case for trace elements (not considered here). Silica, roughly representing sand, and aluminium, roughly the feldspar-clay fraction, are essentially identical in the two samples, as is iron. Calcite would be expected to vary both according to initial mixture as well as firing temperature.

	SiO_2	Al_2O_3	Fe_2O_3	CaO
HLW 13	49	12	8	14
HLW 8	49	12	8	15

While this may suggest that these two samples were made with similar raw materials (at the same locality) using similar techniques, the IR spectra present a different picture. (Fig. 1) The roughness (or lack thereof) in the region of the spectra from 1300-1400 cm^{-1} shows variations in the particle sizes of the various samples. HL 13 has little carbonate, and the major peaks at 1250 cm^{-1} and 1080 cm^{-1} are quartz, which is about the only phase clearly shown in the spectrum, implying that the sample is crystallized.

HL 3 and HL 8 show clear evidence of carbonate, with the amount in HL3 being much greater (the peak at 860 cm^{-1} is diagnostic, and a portion of the 1200 1400 cm^{-1} slope is also due to carbonate). HL 8 may have a small amount as well, with a weak 860 cm^{-1} feature and a smaller feature (than HL 3 and HL 8) near 1380 cm^{-1}. Otherwise, the silicate fraction of the bottom three spectra are similar, with a major peak at 1050 cm^{-1} for all three. This feature is probably feldspar related. The most parsimonious interpretation is that firing temperature increases from top to bottom. Alternatively, it could be that HL 3 had a large amount of carbonate, and was fired to about the same temperature as HL 7. We suggest that HL 8 has been fired to a slightly higher temperature. From the differences in the spectra, it appears much of the initial carbonate has been broken down. The latter observation has been supported by thin section studies that show the carbonate as voids of a characteristic shape with a

reaction rim with the ceramic matrix. All these observations are in keeping with what may be deduced from the ceramic assemblage logically. While a 'fineware' vessel may have been fired to a temperature where it was vitrified and could hold water, more common vessels were fired in a range of environments. Most likely, as long as the vessel was 'baked' into a ceramic, it was deemed acceptable, as it is doubtful that thousands of everyday wares would have warranted careful attention during firing.

While the latter observation may cast doubt upon the necessity of recording the colour of potsherds, it cannot be doubted that given a wide temporal range, changes in firing technology - from oxidising to reducing atmosphere - can be detected. At the same time it should be realized that there can be considerable variation in ceramics from a single segment of archaeological time.

Further Research

Perhaps the most limiting aspect of the technique is that methods of presentation have largely been limited to 'squiggly lines', which do not lend themselves to numerical presentation. The interpretation of the spectra depend upon the relationships with other mineral phases, and frequently the presence of a mineral is indicated by more than one peak in different spectral regions. The result is that few spectra can be effectively presented. The majority - particularly at archaeological conferences - will not be able to easily assimilate the differences (though gross morphology of the spectra will be obvious). Several suggestions for presentation were made during the conference, and the authors would welcome others.

Particularly regarding the well stratified sequence of ceramics from Tell Halawa, there exists the opportunity to contrast the Munsell method with an independent test. While much more work needs to be done, it is clear that while major differences in firing temperatures are reflected in colour, there are a number of cases where this criteria alone can be misleading. While a difference in colour can indicate a change from one sample to another, different IR spectra can yield a temperature range. With the gradual reduction in cost, and weight, of IR equipment, it should be possible to take a small apparatus into the field. After a range of thousands of shards had been examined there would both be an extensive database, and the opportunity to retain material of interest for further research after a large scale programme of analysis.

Perhaps the applications that lie further in the future are of even greater interest. It is clear that infrared equipped satellites are increasingly being used to characterize earth materials. For many areas of the Near East, with a minimum of plant cover to obscure signal, it should be possible to correlate the IR signal obtained from a satellite with spectra obtained from archaeological ceramics. The major question is if it is possible, even if the region offers mineralogic diversity, to spatially discern what may be slight differences in outcrops. Bearing in mind that raw clays can be heterogeneous and that one can expect changes in mineralogy after firing, any correlation would assume several factors. At the same time, given a wide enough range, it may be possible to propose, at least in a tentative way, if a chemically anomalous sample is from a nearby region, or from a distant source.

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Figures

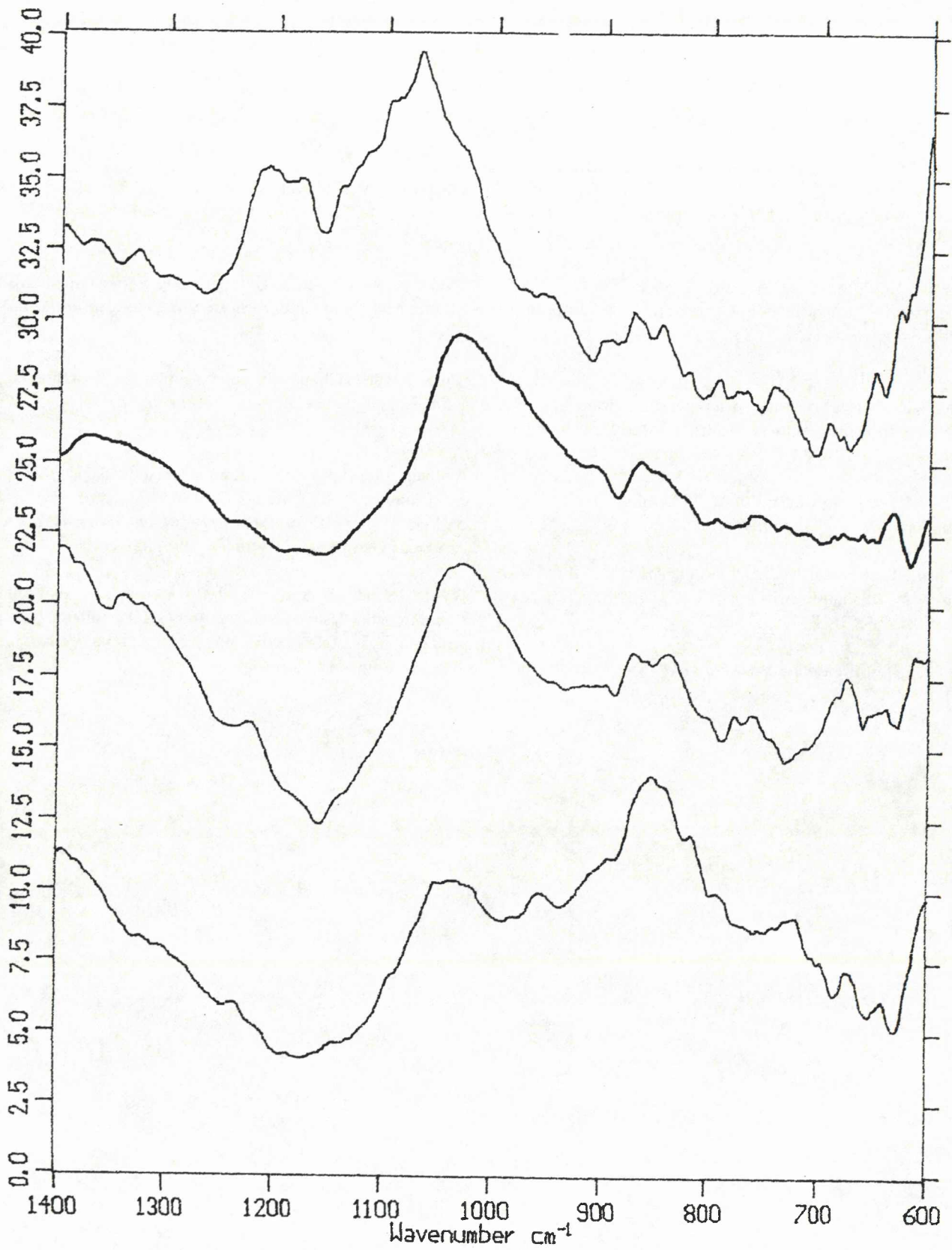*Figure 1.*