1 Introduction

Infrared spectroscopy is a branch of molecular spectroscopy that investigates the interaction of infrared radiation with matter, be it gas, liquid, or solid. When irradiated with infrared light, molecules in a substance vibrate and/or rotate in different ways depending on the nature of the atoms, the strength, length, and symmetry of their bonds with other atoms, and the overall spatial arrangement. Each vibration translates into an absorption at a specific wavelength in the infrared region of the electromagnetic radiation, resulting in a spectrum that exhibits absorption bands characteristic of specific molecules. Therefore, infrared spectroscopy is able to identify organic and inorganic compounds, including in heterogeneous mixtures, as is the case for the sediments that are found at archaeological sites (Weiner 2010).

Infrared light was discovered in 1800, when Sir William Herschel proved that there is a form of light able to carry heat that propagates at frequencies lower than those of the visible spectrum (Herschel 1800). This discovery became relevant to the field of materials science in the 1930s, when the first infrared spectrometers were developed based on the demand for analytical work in the synthetic rubber industry (Derrick *et al.* 1999). These instruments were of the dispersive type, based on a monochromator that requires long acquisition times in order to obtain an infrared spectrum. In the 1950s, a major technological breakthrough in infrared spectroscopy was the introduction of the Michelson interferometer, a device that produces an interferogram in a much shorter span of time, which is then converted into an infrared spectrum by applying a Fourier transform – hence the acronym FTIR, which stands for Fourier transform infrared spectroscopy. By the 1970s, the combination of FTIR spectrometers with a dedicated computer significantly reduced spectrum acquisition times and thus made these instruments more commercially viable, and applications in materials science, biomineralization, medicine, heritage conservation, and archaeometry gained momentum (van der Marel & Beutelspacher 1976; Schrader 1995; Derrick *et al.* 1999).

The systematic application of FTIR spectroscopy to the study of archaeological sediments was pioneered in the 1980s by Steve Weiner, who used this method to study bone preservation and the integrity of the archaeological record at prehistoric cave sites in Israel. Furthermore, he demonstrated that infrared spectrometers can be successfully operated on site, a major advantage in terms of real-time information for the adjustment of excavation and sampling strategies (Weiner & Goldberg 1990). In the following years, FTIR spectroscopy became one of the most important methods in the field of microarchaeology, which is the investigation of the invisible archaeological record (Weiner 2010), and saw the development of major applications in the study of diagenetic processes at archaeological sites, prehistoric and ancient pyrotechnology, and the molecular integrity of materials used in paleoenvironmental reconstructions and absolute dating (Monnier 2018).

While some manuals about FTIR spectroscopy of artworks and archaeological materials have been published in the past three decades (e.g., Derrick *et al.* 1999; Boyatzis 2022), as well as review articles of applications of FTIR in archaeology and other disciplines (e.g., Kirkbride 2009; Gaffney *et al.* 2012; Margaris 2014; Berna 2017; Shoval 2017; Monnier 2018; Toffolo & Berna 2018), to date the only guide to the interpretation of spectra of the main components found in archaeological sediments is that of Weiner (2010: 275–316). This Element aims at providing up-to-date information on the most recent developments in FTIR spectroscopy of archaeological sediments, including the grinding curve method and advances in the study of diagenesis and pyrotechnology. This is done based on the interpretation of the spectra of the most important components of archaeological sediments, which are displayed in both transmission and attenuated total reflectance (ATR) modes.

2 Theoretical and Methodological Framework

This section illustrates the basic concepts of infrared spectroscopy that form the base for the interpretation of spectra, and provides an overview of the instrument setup, sample collection guidelines, and the acquisition of spectra in different modes, including microspectroscopy. Finally, it provides the means of extracting archaeological information from the analysis of spectra.

2.1 Fundamentals of Infrared Spectroscopy

The existence of infrared radiation was demonstrated by Herschel (1800), who discovered it in a clever experiment. While investigating the amount of heat carried by the different components of sunlight, he decided to measure the temperature of colors in the visible light spectrum by passing sunlight through a prism and placing thermometers on a table where the different colors were cast. For each color, he took control measurements of temperatures in the shade. In the process, he also took a measurement beyond the red end of the visible spectrum, and found that the temperature was one degree higher compared to red light. Based on this observation, he concluded that there must be a type of invisible light able to carry heat, which was later named infrared, from the Latin word *infra*, which means “below.” Research works that followed found that infrared light is a type of electromagnetic radiation characterized by wavelengths between microwaves and the visible spectrum (e.g., Schrader 1995).

Depending on the wavelength, different types of interactions between electromagnetic radiation and matter may be probed, and their study is called molecular (or atomic) spectroscopy. Since infrared radiation produces vibrational transitions, it is part of the vibrational spectroscopy branch of molecular spectroscopy (together with Raman spectroscopy). The infrared spectrum is further subdivided into the near-infrared (NIR) range, ~0.7–2.5 µm or 14,000–4,000 cm^{-1}; the mid-infrared (MIR) range, ~2.5–25 µm or 4,000–400 cm^{-1}; and the far-infrared (FIR) range, ~25–1,000 µm or 400–10 cm^{-1}, where the cm^{-1} unit measures the wavenumber, which is the reciprocal of the wavelength. The MIR range is better suited for the study of the fundamental molecular vibrations in a wide range of compounds, both organic and inorganic. The FIR range allows to better detect rotational transitions and some compounds with transition metals, for instance the oxides. This is because the mass of the atoms in the molecular bond that produces the vibration is inversely correlated to the wavenumber, that is, larger chemical species tend to absorb at lower wavenumbers. The NIR range highlights overtones and combined vibrational modes. For these reasons, the MIR is the preferred range to probe the composition of archaeological sediments and materials, where silicates, carbonates, and phosphates are the major mineral classes (van der Marel & Beutelspacher 1976). Therefore, the explanations and examples provided herein are all based on the MIR range.

Molecular vibrations in matter are triggered when the frequency of the incident radiation matches the vibrational frequency of functional groups in molecules, generating a change in the molecular dipole moment. The degree of change in the dipole moment of the molecule, particle size, wavelength, differences in the refractive index of the sample and dispersion medium, and the direction of the vibration with respect to the electric vector of the incident light determine the intensity of the vibration (van der Marel & Beutelspacher 1976). Functional groups are groups of atoms that are responsible for the characteristic chemical reactions of a molecule, for instance, the carbonate moiety (CO_3^{2-}) in calcium carbonate or the phosphate moiety (PO_4^{3-}) in hydroxyapatite. Vibrations can be of different types, called vibrational modes. These are represented by Greek letters depending on the type of molecule and its symmetry species, and include stretching modes (ν) and several deformation modes: bending or scissoring (δ), rocking (ρ), wagging (ω), and twisting (τ) (Herzberg 1945). In the case of minerals, most vibrations are labeled with ν (Farmer 1974). Vibrations increase the temperature of the material by dissipating as heat. Infrared light is absorbed by different molecules only at specific wavelengths or regions in the spectrum, which results in an infrared spectrum characterized by reduced intensities in the portions where molecules absorb, which are called absorption bands. The ratio of the intensity of the incident light and that of the light transmitted by the sample is called transmittance (*T*), which is the unit measure of the intensity of absorption and is displayed as a function of wavenumber, varying between 0 and 1. Often, transmittance is multiplied by 100 and shown in %*T* units. The %*T* unit was commonly used in infrared spectra until recently, although today transmission spectra are displayed in absorbance (*A*), which is the negative logarithm of the transmittance, and thus a unitless quantity. Similar to %*T*, when samples are probed using reflected light (see Section 2.4.2), the unit measure is reflectance (%*R*). In the ATR mode, absorbance is used, but the scale is different compared with the transmission mode due to the different path of the infrared beam through a crystal (Farmer 1974; van der Marel & Beutelspacher 1976; Schrader 1995; Diem 2015; Kaur *et al.* 2021).

Given that different molecules and groups of molecules absorb in specific portions of the infrared spectrum, the position and shape of their absorption bands can be used to determine the nature of the material being analyzed. Therefore, infrared spectroscopy is mainly used as a qualitative method of analysis to determine the composition of a sample. Quantification of phases in single-compound materials and in mixtures is possible, although rather laborious, to the point that X-ray diffraction (XRD) offers a more accurate and rapid option in the case of crystalline phases, including complex mixtures. One way to quantify phases using infrared spectroscopy is to calculate the absorptivity of each band (e.g., Vagenas *et al.* 2003). Alternatively, calibration standards such as single compounds or mixtures of two compounds in known amounts can be prepared and measured to determine changes in band intensity or area caused by changing proportions (e.g., Loftus *et al.* 2015).

2.2 Instrument Setup

Infrared spectrometers include a broad band “black body” light source (generally a hot filament) that generates the infrared beam. Mirrors direct the beam to the interferometer, where the light intensity is divided into two components by a beamsplitter, one that is transmitted and one that is reflected. The transmitted component is redirected to the beamsplitter by a fixed mirror, whereas the reflected component is reflected by a movable mirror (moving back and forth), through which it reaches the beamsplitter again where it is recombined with the other component. Here, half of the light intensity is directed back to the source and half is directed to the sample by a mirror, and from the sample it reaches the detector, usually through another mirror. Detectors are mainly thermal (pyroelectric) of the DTGS (deuterated triglycine sulfate) type. At this stage, there are two light beams propagating to the detector, one generated

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by the fixed mirror and one generated by the movable mirror. These beams undergo destructive and constructive interference depending on the difference in their paths, which is determined by the position of the movable mirror at any given time. The intensity pattern in the infrared beam produced by the movable mirror, called interferogram, is the signal recorded by the detector (Figure 1). The path difference between the two components of the beam needs to be measured accurately, and for this reason, a reference He-Ne laser beam travels through the interferometer and a separate detector measures the laser intensity variation produced by the interferometer. When the movable mirror moves half the laser wavelength, which in He-Ne lasers is stable and accurately known, the spectrometer software reads the signal from the DTGS detector and records it as a point in the interferogram. The high accuracy of the laser wavelength reference translates into excellent alignment of the repetitive scans of the interferometer and the high accuracy of the wavenumbers. The software then performs a Fourier transform on the interferogram to obtain an infrared spectrum. See Diem (2015) for a detailed description of infrared spectrometers and their theoretical background.

Commercial infrared spectrometers are produced by several brands and come as benchtop (i.e., not movable) or “portable” (movable) instruments. The portable version can be safely transported by car and by plane (cabin only to avoid damage) and used at archaeological excavations, including at cave sites and under conditions of high humidity. Depending on the type of detector,

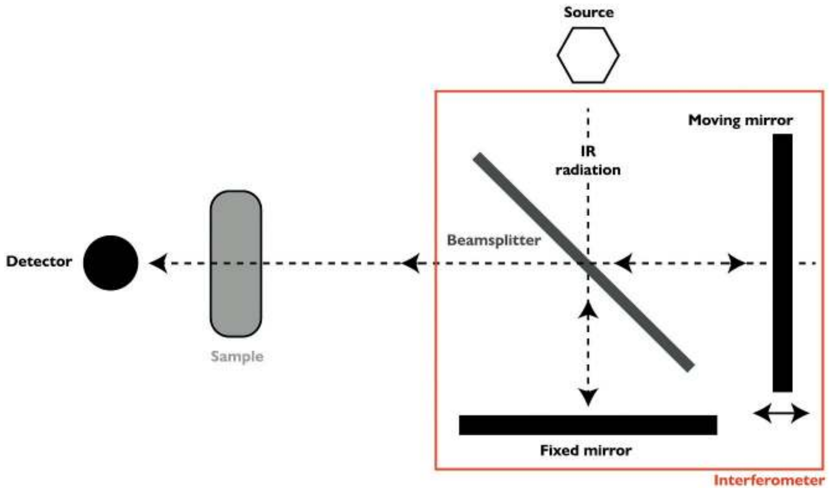

Figure 1 Schematic representation of the main components of an infrared spectrometer.

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infrared spectrometers may cover only the MIR range, or they may reach into the NIR and FIR. All spectrometers require dry-air atmosphere to preserve the internal optics from oxidation, avoid deterioration of the potassium bromide (KBr) windows that link the instrument to the sample chamber, and limit noise in the spectra caused by humidity and CO_2. To that end, instruments include a replaceable desiccant (which can be dried in an oven if wet) and also the option to purge the instrument with a dry-air or nitrogen system. In addition, instruments should always be kept on to prevent the accumulation of humidity. Besides the desiccant, infrared spectrometers require little maintenance, such as the verification of the beam alignment by means of a polystyrene standard and the replacement of the light source and KBr windows every ~10 years. Generally, infrared spectrometers are designed in a way that allows to change the sample compartment based on the acquisition mode and the nature of the sample (gas, liquid, or solid), which in turn requires a specific gear for sample preparation (see Section 2.4). Different brands produce their own software to operate the spectrometer and elaborate spectra, for example, to create macros for the swift calculation of band intensity and area ratios.

2.3 Sample Collection

Fourier transform infrared spectroscopy of archaeological sediments starts in the field. The sampling strategy should be devised according to the question(s) driving the research design, and keeping in mind the limitations posed by logistics and available resources. Clearly, an on-site laboratory including an infrared spectrometer allows more rapid and substantial analyses, since spectra are collected in a matter of minutes and samples do not require shipment to the home laboratory (e.g., Weiner 2010; Finkelstein *et al.* 2012). In the absence of such a setup, systematic sampling of all sediments and features might be more convenient if the site is located in a remote area and a second visit is not planned, or in the case of a salvage excavation. On the contrary, targeted sampling is certainly more cost-effective for recurrent fieldwork seasons.

Ideally, samples should be collected from standing sections at the edge of a trench or in witness baulks, if the site is excavated by large squares. This approach allows distinguishing different sedimentary features and layers, whose thickness cannot be assessed by looking at a horizontal surface, which in the end might lead to the mixing of sediments. Often, however, this is not possible at sites excavated by large open areas, where the lateral variability of horizontal surfaces needs to be taken into consideration. Obviously, in this case, samples should be collected from a horizontal surface as soon as it is uncovered and by avoiding trampling. Complex features such as cooking installations, kilns, burials, storage pits, and so on, given their inherent variability, cannot be reduced to general guidelines and should be the object of dedicated sampling strategies in line with the goals of the research.

Sediments should be collected with metal tools, such as trowels and spoons, which allow better control on sediment removal (especially when it is compacted) and prevent contamination in the case of organic materials for radiocarbon dating. These tools are impractical when it comes to thin laminae of powdery substances (e.g., phytoliths, wood ash, organics), which should be collected using small spatulas or tweezers, as in the case of fragile chunks. Sediments can be placed in any type of container, although the choice should be dictated by logistics, storing capacity, and the type of laboratory analysis. Several scientists prefer liquid scintillation vials made of polyethylene because they are small enough for swift storing and shipping and yet they contain enough sediment (20 ml) to allow multiple types of analysis. Bigger vials may be used if large quantities of sediments are required. Zip-lock plastic bags are another viable option, although they tend to break and do not last many years in storage. Glass vials could be used as well; however, besides being significantly more expensive than polyethylene, they increase the overall weight of the samples, which translates into increased shipping costs. In addition, they are more prone to breakage during transport. Nevertheless, glass vials should be considered for samples that are subject to contamination from carbon, such as charcoal for radiocarbon dating. The latter is often stored in aluminum foil folded up in an envelope, which is convenient during fieldwork but may eventually oxidize and break with time and continuous handling. Larger items embedded in sediments, that is, rocks, ceramics, and faunal material, should be collected by hand with the necessary precautions in view of specific laboratory analyses (e.g., DNA, residue analysis, radiocarbon dating), and stored accordingly. Regardless of the storage medium, all containers should be labeled following the numbering system relevant to the fieldwork project and in a manner that prevents fading of the ink. Labels written with an indelible marker on masking tape wrapped around vials seem to be durable; plastic-lined stickers add protection from liquids. Eventually, after several fieldwork seasons, these efforts will lead to the establishment of a sediment library that documents the stratigraphic sequence of the site.

2.4 Acquisition Modes and Sample Preparation

Samples may be analyzed using three acquisition modes: transmission, reflectance, and photoacoustic. In transmission, the sample is suspended in a pellet made from a medium that does not absorb infrared radiation in the MIR, such as

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KBr or potassium chloride (KCl). The infrared beam travels through the pellet, and the portion that is not absorbed reaches the detector, from which it is converted into a spectrum showing the absorption bands of the molecules in the sample. In reflectance, the infrared beam impinges on the sample, and the detector collects the reflected component. This can be achieved in different ways, called total reflectance, ATR, and diffuse reflectance (DRIFT). In total reflectance, the instrument collects the entire reflected component of the infrared beam. In ATR, the instrument collects the component of the infrared beam that is reflected as an evanescent wave through a crystal in contact with the sample. In DRIFT, the instrument collects the component of the infrared beam reflected by a powdered sample mixed with KBr placed in a cup holder. In photoacoustic spectroscopy (PAS), the sample absorbs modulated infrared light and produces thermal waves that in turn generate acoustic waves through a carrier gas inside an enclosed cell, which are detected by a microphone or a cantilever.

These acquisition modes require specific sample preparation procedures, which are described in Sections 2.4.1 and 2.4.2. Given the limited archaeological applications of DRIFT and PAS in MIR spectroscopy (e.g., Angelini & Bellintani 2005; Stevenson *et al.* 2013), these methods are not discussed any further. All reference spectra of standard materials included here are provided in transmission and ATR modes.

2.4.1 Transmission

To obtain transmission infrared spectra, it is first necessary to suspend the sample in a pellet made of KBr (Stimson & O’Donnell 1952). The gear for pellet preparation includes FTIR-grade KBr, a mortar and pestle made of agate or porcelain, a pellet die, a metal spatula with cup holder to transfer sample from the vial to the mortar, a similar spatula to transfer KBr from its container to the mortar, weighing paper to transfer the sample–KBr mixture from the mortar to the pellet die, paper wipes for cleaning, a pellet press (handheld or benchtop), and a ceramic lamp with infrared reflector bulb (at least 250 W) to keep KBr and sample dry (Figure 2). Coarse-grained KBr tends to be less hygroscopic because of the smaller amount of surface area exposed to air. It is advisable to place all the tools near the heat lamp to keep them dry. Pellet preparation is shown in Video 1.

A small amount of sample, typically 5 mg or less, is transferred to the mortar using the spatula to avoid inadvertently sorting grains, and ground to a fine powder using the pestle. The particle size of this powder is not fixed, although a rule of thumb is to stop grinding when grit is no longer felt between

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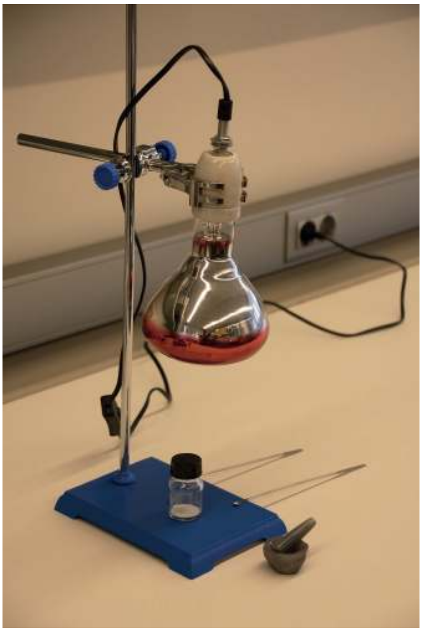
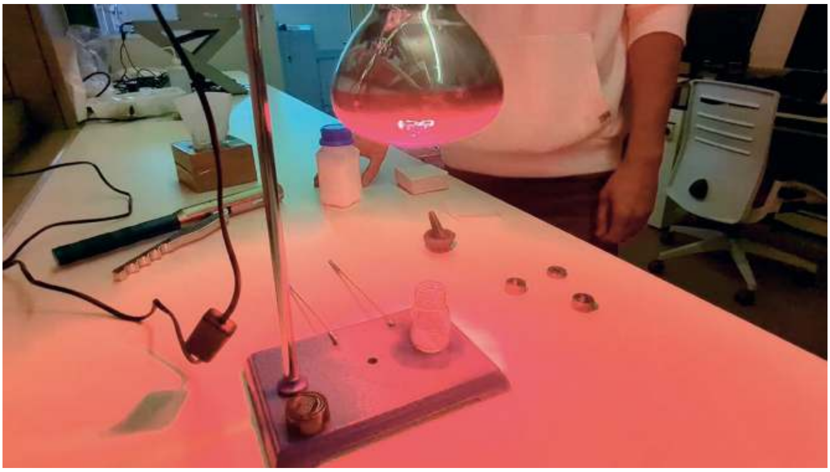


Figure 2 Heat lamp and reflector bulb with KBr vial, agate mortar and pestle, and spatulas.



Video 1 Sample preparation for transmission mode. Video files available at www.cambridge/toffolo

the mortar and the pestle. This operation is not only meant to facilitate sample suspension in KBr but also to homogenize the many components in the sample, thus making it representative of a certain sediment layer, feature, or material. In addition, reducing particle size allows decreasing the loss of radiation caused by the reflection of the infrared beam onto large particles. Loose sediments can be easily crushed provided that large pebbles are removed prior to grinding (also to avoid overrepresentation of components that might be minor ones or that can be analyzed separately), whereas larger fragments such as rocks, plasters, ceramics, teeth, and bones require greater effort, especially when the latter contain collagen. After grinding, all excess material is removed with a wipe to avoid overloading of the infrared spectrum, which results in “broken” bands for high absorbance values (Figure 3). After that, a few mg of KBr are added to the mortar and ground with the sample using the pestle. The amount of KBr varies depending on the diameter and thickness of the pellet die. For pellets with a diameter of 7 mm, ~20–40 mg of KBr are sufficient depending on the thickness of the die. Larger diameters require greater quantities of KBr to prevent pellet failure upon pressing. The mixture is then transferred to the pellet die using weighing paper, and pressed. Benchtop presses include a gauge that helps quantifying the amount of pressure necessary to obtain a pellet. Usually, 2 tons suffice for 7-mm pellets. Some hand presses allow a rough, indirect measure of the exerted pressure based on the degree of tightening of the screw that holds the die set in place when pressed with the piston. This method requires some practice to become accustomed to it and avoid breakage of the press, but it is slightly faster than a benchtop press. The resulting pellet should appear transparent with the suspended sample clearly visible. If the pellet is not well pressed, or too thick, it may be opaque, and this translates into a sloping spectrum baseline

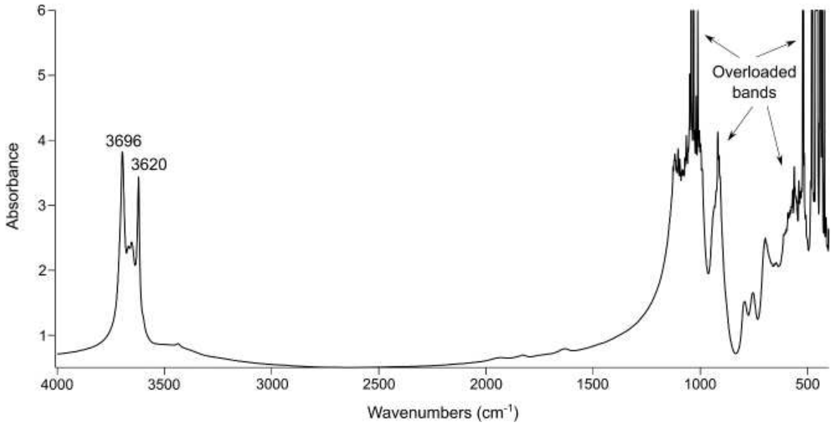


Figure 3 Overloaded spectrum of kaolinite. Note the high absorbance value that translates into “broken” bands under 1,200 cm^{-1}.