Infrared Absorption Spectroscopy (IR, FTIR, DRIFT, ATR)

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Infrared (IR) absorption spectroscopy is the study of the interaction of infrared radiation with matter. When irradiated, functional groups (clusters of atoms or bonds within molecules, e.g. $[CO_3]^{2-}$) in solid, liquid, and gaseous materials vibrate or rotate in specific modes that depend on the nature of atoms, interatomic chemical bonds and dynamic group properties. Each vibration mode corresponds to the absorption of a particular frequency in the infrared region $(14{,}000–20\,cm^{-1})$, which results in a spectrum characteristic of a specific functional group (Diem 2015). Therefore, IR absorption spectroscopy can be used to identify different compounds in organic and inorganic substances, including materials of archaeological importance (Artioli 2010).

Infrared radiation was discovered in 1800 by Sir William Herschel, but its application to materials science did not expand until the 1930s, when the first commercial IR spectrometers were developed for the synthetic rubber industry. These instruments included an infrared radiation source, a sample chamber, a monochromator based on an optical grating or prism, and a detection system (Derrick, Stulik, and Landry 1999). A major technological breakthrough was the replacement of the monochromator with a Michelson interferometer in the 1960s. This device produces an interferogram that is converted into an infrared spectrum using the Fourier transform, thus improving the resolution of measurements and reducing noise and detection limits. This method, called Fourier transform infrared spectroscopy (FTIR), quickly became the standard in IR studies. By the 1970s, FTIR spectrometers were combined with a dedicated computer, which dramatically increased the rapidity of measurements (Derrick et al. 1999).

FTIR measurements are mostly performed in transmission mode by calculating the absorbed component of the incident beam as a function of frequency. The beam passes through a few tens of micrograms of powdered sample suspended in a potassium bromide (KBr) pellet or dispersed in an oil film in between potassium chloride (KCl) windows. Both mediums do not absorb IR radiation. The non-absorbed component of the incident beam is collected by a detector. The frequency absorptions of the functional groups in the sample are obtained against a background of air to subtract the contributions from water vapor and carbon dioxide (CO_2). Sample preparation and measurement typically take less than five minutes. The identification of the different phases that appear in the infrared spectrum is done by comparison with reference spectra of standard materials (e.g., Chukanov 2014; the online library of the Kimmel Center for Archaeological Science, http://www.weizmann.ac.il/kimmel-arch/ infrared-spectra-library). As the intensity of the IR absorptions has a precision ranging between 10–20%, FTIR spectroscopy is a method preferentially used to determine the presence of different chemical phases above the detection limit. Semi-quantification can be achieved by preparing standard mixtures for calibration. If the sample is crystalline, X-ray diffraction is preferred for quantification.

Another important acquisition mode of IR spectra is based on the reflection of the incident beam. In diffuse reflectance Fourier transform spectroscopy (DRIFT), about 2 mg of powdered sample mixed with KBr is placed in a cup-holder and leveled off to obtain a flat surface, which is then irradiated with infrared light. The beam penetrates the surface by a few micrometers and is partially absorbed and reflected by the functional groups in the sample. The diffusely reflected component of the beam is finally directed to a detector. The background spectrum is collected on a pure KBr powder. In attenuated total

reflectance (ATR), the incident IR beam passes through a crystal of high refractive index (e.g., diamond, silicon, germanium, or zinc selenide) that is in contact with the surface of a powdered sample. The beam reflects within the inner surface of the crystal and generates an evanescent wave that penetrates into the sample by a few micrometers. The reflected component is then collected by a detector. The background spectrum is generally collected on air. DRIFT and ATR devices usually consist of sample chambers that can be conveniently attached to a regular FTIR spectrometer by replacing the transmission chamber.

Transmission and reflectance measurements can be performed also on extremely small samples by combining a spectrometer with an optical microscope, where the nosepiece includes optical objectives and IR condensers. Reflectance measurements are generally carried out in total reflectance mode, where the beam does not penetrate the surface, or in ATR mode following the procedure described above. In total reflectance, the background spectrum is collected on a gold plate. The IR microscope setup is particularly useful in the characterization of minute particles (approximately 50–300 µm), and thus it is suitable for the structural analysis of valuable works of art, as well as in forensic investigation (Derrick et al. 1999). FTIR microscopy can also be used in the analysis of archaeological sediments in thin-section (e.g., Berna et al. 2012). Therefore, it is possible to integrate chemical, mineralogical and spatial information regarding the different components that occur in sediments. The use of automated stages allows chemical mapping of relatively large areas.

Due to the small sample size required for analysis, FTIR spectroscopy has been applied to archaeological materials since the 1950s, and significantly contributed to the development of the fields of archaeometry and conservation science. More specifically, FTIR spectrometry has proved useful in the characterization of materials such as amber, parchment, textile, bone, mollusk shell, plaster and mortar, faience, varnishes, dyes, pigments, and organic compounds used in paintings (Derrick et al. 1999; Artioli 2010). For instance, DRIFT analysis has been successfully employed in the provenancing of amber artifacts by matching their infrared spectra with the spectra of geological samples from a reference database (Angelini

and Bellintani 2005). In addition, FTIR spectrometry is routinely used as a screening method to check the purity of charcoal, collagen, and cellulose for radiocarbon dating (Weiner 2010).

With the advent of portable spectrometers in the 1980s, FTIR spectroscopy became a rapid and convenient method for on-site analysis at archaeological excavations (Weiner and Goldberg 1990). This approach to fieldwork presents major advantages, including the possibility of obtaining real-time information regarding the archaeological record that can be used to modify the excavation strategy as needed, and the ability to trace the boundaries of features that are invisible to the naked eye. In addition, samples are collected only from specific archaeological contexts relevant to the research questions at stake and immediately analyzed, instead of blind-sampling the entire site for post-excavation laboratory work (Weiner 2010).

Since FTIR spectroscopy is sensitive to the molecular bond interaction level, this method is especially suited for the identification of both crystalline and amorphous/disordered inorganic materials, as well as organic materials. Disordered and organic materials are particularly common in sediments at archaeological sites, and include opaline phytoliths, bone collagen, charcoal, lignin, cellulose, and humic acids. Using FTIR spectroscopy it is also possible to assess the degree of atomic order of crystalline phases exposed to fire, which changes their interatomic chemical bonds, and thus identify pyrogenic calcite, heat-altered clay minerals, and burnt bone (Berna et al. 2007; Regev et al. 2010; Weiner 2010). Another important aspect is the state of preservation of the archaeological record, which depends on the nature of the sedimentary matrix and on environmental conditions at a specific site. Diagenesis may alter the chemical properties of sediments and artifacts and thus lead to misleading interpretations of formation processes and human occupation. FTIR spectroscopy can track the formation of authigenic diagenetic minerals such as phosphates, nitrates, and sulfates, which form under specific environmental settings (Karkanas et al. 2000). In general, the results of FTIR analysis are best interpreted when integrated with the information obtained through other methods that address

the microscopic record, such as micromorphology (see MICROMORPHOLOGY) of sediments, phytolith analysis (see PHYTOLITH ANALYSIS), X-ray fluorescence (see X-RAY FLUORESCENCE SPECTROMETRY (XRF)), X-ray diffraction, Raman spectroscopy (see RAMAN SPECTROSCOPY), and more. This approach allows a better understanding of the archaeological record as a whole (see also MICROARCHAEOLOGY).

FTIR spectrometry is therefore a valuable method for the chemical characterization of archaeological artifacts and sediments, and can significantly contribute to addressing problems related to the preservation of the archaeological record, site formation processes, post-depositional alterations, stratigraphic correlations, absolute chronology, pyrotechnology, and more in general to past human activities. Currently, FTIR spectroscopy is being used to explore in more detail the different degrees of atomic disorder of mineral species altered or produced by fire and diagenesis, such as calcite (plaster and mortars), aragonite (wood ash), quartz (stone tools), clay minerals (combustion features), carbonate hydroxylapatite (bone and enamel), and other phosphates (authigenic). This requires the characterization of small samples within their original depositional context or structural configuration, and thus FTIR microscopy on thin-sections is a preferred method of analysis (Berna 2017). However, the large amount of point data collected from a thin-section poses the question of imaging and mapping of extensive surfaces into sizeable output, and the need for dedicated statistical means of interpretation of large datasets of infrared spectra. It can be predicted that in the near future the mapping of relatively large surfaces will be routinely applied to works of art that cannot be altered with sampling, such as paintings and frescoes, by using portable reflectance devices that operate in the near- and mid-IR spectral range ($14,000–400\ cm^{-1}$). This approach will be extended also to standing sections of sediment at archaeological sites.

SEE ALSO: Archaeological Fieldwork; Archaeometry; Archaeomineralogy; Chemistry in Archaeology; Diagenesis of Bone; Formation Processes; Geoarchaeology; Human Skeletal Geochemistry; Infrared Reflectance Spectroscopy; Microarchaeology; Micromorphology; Mortuary Analysis; Raman Spectroscopy; Raman Spectroscopy and Material Analysis; Raman Spectroscopy in Conservation; Soil Chemistry in Archaeology; Taphonomy

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