Journal of Archaeological Science: Reports xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

A review of infrared spectroscopy in microarchaeology: Methods, applications, and recent trends

Gilliane F. Monnier

Department of Anthropology, University of Minnesota, United States

A B S T R A C T

Infrared (IR) spectroscopy has emerged as one of the most powerful analytical tools available to archaeologists. It has been used to document site formation processes and understand the preservation of organic remains within sites; to investigate pyrotechnology including control of fire, heat treatment of stone, and plaster manufacture; to assess the preservation of charcoal and bone prior to dating or isotope analyses; and, to identify unknown substances inside containers or on artifact surfaces such as stone tools. Most importantly, IR spectroscopy has become an essential tool in the field of microarchaeology, the analysis of the portion of the archaeological record which cannot be seen with the naked eye, yet which contains a wealth of data to address the research areas listed above. IR spectroscopy, long a workhorse of analytical chemistry, is particularly suited to archaeology because it is applicable to many kinds of materials - organic as well as inorganic - and can therefore be used to address a wide range of questions. Sample preparation is rapid and, since minute quantities of a substance are necessary, the technique is 'microdestructive'. It can also be performed on-site, yielding results in real time that help guide excavation and sampling strategies. The purpose of this review is to detail the basic principles and instrumentation of IR spectroscopy as it has been applied in microarchaeology and related fields of research. The discussion centers on major archaeological applications to date, methodological issues, and recent trends. A special focus is placed on new reflectance techniques.

Outline of the Review

E-mail address: monni003@umn.edu.

https://doi.org/10.1016/j.jasrep.2017.12.029
Received 9 April 2017; Received in revised form 5 November 2017; Accepted 13 December 2017

1. Introduction

In the twenty-five or so years since infrared (IR) spectroscopy first began to be applied to the microarchaeological record, a number of important methods to solve archaeological problems using this technique have been developed. Today, these constitute a well-established methodology for excavating and analyzing the microscopic component of archaeological deposits, in which IR spectroscopy and micromorphology play key roles (Weiner, 2010; Goldberg and Berna, 2010; Mallol and Mentzer, 2015).

The emergence of IR spectroscopy as an invaluable analytical technique in archaeology can be attributed to three main factors: first, it can be used to characterize the composition and structure of a wide range of substances: organic and inorganic molecules, compounds, and mixtures. Second, it is relatively inexpensive, easy to use, and requires minute quantities of a substance. It is, therefore, 'microdestructive' or even non-destructive when using non-contact instrumentation. Increasingly, innovations in instrumentation mean that infrared measurements can now be conducted on many different kinds of samples, ranging from bulk sediment samples and micromorphological thin sections, to artifacts, faunal materials, and micro-residues on stone tools. Third, because FTIR instruments are portable (vis. Vandenabeele and Donais, 2016), they can be brought on-site, where they enable the integration of microarchaeology, the study of the portion of the archaeological record that cannot be seen with the naked eye (Weiner, 2010:1), with macroscopic archaeological excavation. This means not only that the myriad unknown substances found while excavating can be identified in real time, but that fundamental research questions involving site formation processes and the remains of human activity can begin to be addressed while on-site, and excavation and sample collection strategies (for further laboratory analyses) adjusted accordingly.

This review sets out to explain the basic principles behind IR spectroscopy, to describe the instruments currently available, including new reflectance-based instruments, and to summarize major archaeological applications of IR spectroscopy using both traditional techniques and the newer reflectance-based techniques. Its aim is to provide an overview of the types of information which can be obtained via IR analyses, to discuss methodological issues, and to present future techniques which may come into archaeology via cultural heritage science. It is intended as a complement to Weiner's *Microarchaeology* (2010; especially chapter 12, *Infrared Spectroscopy in Archaeology*), which describes the role of IR spectroscopy within this new field, provides extensive descriptions of materials amenable to IR spectroscopic analysis, and details the types of archaeological information that can be recovered from them. This review presents the development of these methods and summarizes important advances in this field since the publication of this work. The target audience is archaeologists new to infrared spectroscopy, who are interested in applying IR spectroscopic techniques in their research on archaeological materials and sediments.

2. Principles of infrared spectroscopy

The infrared (IR) region of the electromagnetic spectrum is composed of radiation whose wavelengths range from 700 nm to 1 mm. These wavelengths are longer than those associated with visible light (Fig. 1). The frequency of a radiation wave is inversely proportional to its wavelength, as shown by the equation $\upsilon = c/\lambda$ where υ = the frequency of light, c = the speed of light, and λ = the wavelength of light. Accordingly, the frequency of infrared radiation is less than that of visible light. Furthermore, according to the equation $E = h\,\upsilon$, where E = the energy of light, h = Planck"s constant, and υ = the frequency of light, the energy of light is proportional to its frequency. Therefore, the energy of infrared light is less than that of visible light, as well, and infrared 'light' is felt as radiant heat (Hesse et al., 2008:33; Pavia et al., 2001:13).

Radiation striking a material can affect it at the molecular level. High-energy radiation such as X-rays, for instance, causes energy transitions within atoms that are strong enough to break molecular bonds, and is used in measurement techniques such as X-ray fluorescence. Low-energy radiation, such as microwaves, can only cause nuclear or electron spin transitions within molecules, and is exploited in nuclear magnetic resonance and electron spin resonance techniques (Pavia et al., 2001:13). Infrared radiation contains sufficient energy to bring about molecular vibrations or rotations in most molecules having covalent bonds. This property enables infrared spectroscopy to act as a 'fingerprinting' technique for identifying molecules.

IR spectroscopy is based upon the principle that atom locations in molecules fluctuate continuously as they vibrate and rotate about their bonds. Vibrations come in two major types: stretching vibrations, characterized by a change in the interatomic distance between two atoms along the axis of the bond, and bending vibrations, in which the angle between two bonds changes. Bending vibrations are divided into rocking, scissoring, wagging, and twisting motions. Each vibrational motion has its own frequency, which is based upon the type of motion, the masses of the atoms, and the strength of the bonds. These frequencies correspond to the infrared region of the electromagnetic spectrum. When a source of infrared radiation is directed at a substance (which can be a gas, liquid, or solid), the molecules in it undergo a net change in dipole moment and absorb photons whose energies correspond to the difference between two of the molecule's quantized vibrational energy levels (note: bonds that do not have an electrical dipole that is changing at the same frequency as the incoming radiation do not absorb energy). These energy absorptions can be measured using IR spectrometers, generating an IR spectrum for the substance. Normal

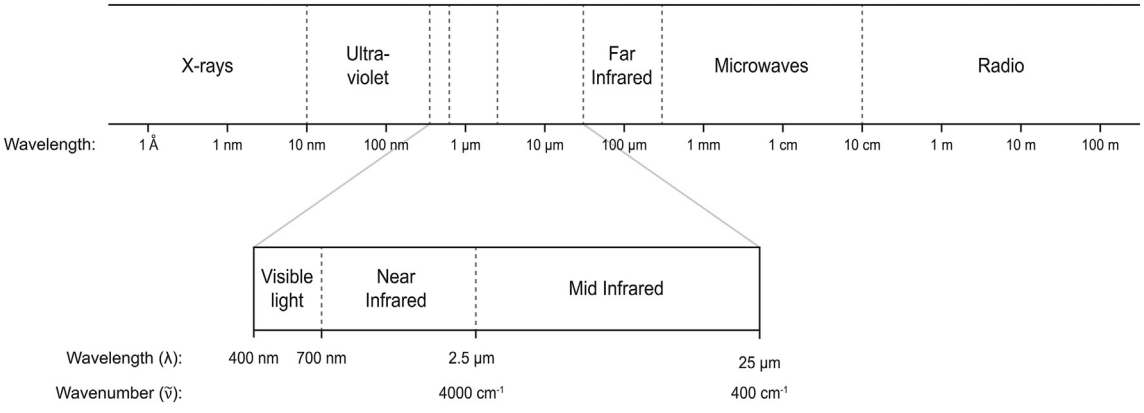

Fig. 1. Electromagnetic spectrum showing regions of interest.