



Infrared spectroscopic characterization of residues on archaeological pottery through different spectra acquisition modes



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ABSTRACT

Fourier transform infrared spectroscopy (FT-IR) is a versatile analytical method, very useful in many fields. Although a crucial step in producing good spectra is the use of the appropriate technique, the acquisition mode is sometimes not accurately selected and the results are partial or lacking.

In recent years, FT-IR analysis has been proposed as a screening method for characterization of archaeological potteries and identification of the residues on these artifacts before turning to destructive, more expensive, and time-consuming techniques.

In this study, a set of pottery shards, classified as fragments of amphorae, was subjected to FT-IR analyses. The results obtained from different sampling procedures and different spectra acquisition modes, were examined and compared.

The as-received ceramic fragments were subjected to micro attenuated total reflectance (μ -ATR) analyses. Investigations in diffuse reflectance (DRIFT) mode were performed on samples collected by abrading the surfaces of the shards with abrasive paper. Samples scraped from either the surfaces of the pottery fragments or the interior of the ceramic body, were analyzed in transmission mode as a powder in KBr pellets or after extraction with acetone.

The sampling by abrasion of the surface with an abrasive disk, and consequently the analyses in DRIFT mode, were successful only in identifying the inorganic compounds coming from the pottery and/or the environment, while materials related to the content of the jar were not detected. Also the analyses in transmission mode provided information mainly about inorganic materials, which, even where in a limited amount, masked the signals of organic compounds. Just an extraction with a solvent made it possible a more detailed, but still partial, characterization of these organic substances. On the contrary, the content of the jar was easily detected using the μ -ATR mode, even in areas where no residue was observed.

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1. Introduction

Fourier transform infrared spectroscopy (FT-IR) has become a very popular analytical technique, for many years now. This method is fast, relatively cheap, and easy to use, and because of these advantages, it is applied to the study of a wide range of materials in many fields.

A crucial step in producing good FT-IR spectra is the use of the appropriate technique for presenting the sample to the spectrometer [1]. The selection of the suitable analysis method should be based on the type, form and amount of sample to be analyzed. The physical state of the sample, its preparation, and the analysis method have an effect on the resulting spectrum, modifying the

absorption pattern. In fact, the above mentioned factors influence the peak position, as well as the band shape and intensity. Nevertheless, the spectra acquisition mode is sometimes not accurately selected and, as a result, the information that can be gleaned from the spectra are partial or lacking.

In recent years, FT-IR spectroscopy has been proposed as a quick and cheap method to screen archaeological samples before subjecting them to more expensive and time-consuming methods (e.g., gas chromatography–mass spectroscopy) [2–6]. Most of the studies concerning such research topics proved the effectiveness of FT-IR analyses for the detection of organic residues in archaeological materials, as well as for investigations of the fabrication conditions [7–11] and for provenance studies [12–14].

Since ancient time, ceramic artifacts have been largely employed for storing materials, as well as for preparing or cooking food. As a result, traces of the materials which were in

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contact with the vessels can be found as surface deposits or as adsorbed residues into the porous structure [15]. The characterization of these residues is very helpful to provide information on cultural, technological, and commercial activities of ancient societies. Chromatographic techniques are frequently employed in identifying the organic residues [15–21]. However, these methodologies are destructive, while non-destructive or micro-destructive diagnostic techniques would be preferred, and procedures for sample preparation, usually taking a long time, are required.

Published papers dealing with characterization of archaeological potteries and identification of the residues in ceramic vessels, frequently discuss the application of FT-IR spectroscopy in transmittance mode [7,8,19,22–25]. Analyses performed in diffuse reflectance (DRIFT) [5,26,27] or in attenuated total reflectance (ATR) mode (sometimes coupled with a microscope, that is, the μ -ATR mode) [6,9,28] are also used in these studies. However, despite the fact that the results depend on the sample, on its collection and preparation, as well as on the analysis methods, the different acquisition modes have been frequently used with no distinction. Consequently, the characterization of the materials under study has been not comprehensive and the FT-IR technique has been undervalued and underused.

Starting from these issues, the present research was aimed at investigating residues on archaeological ceramic samples by means of FT-IR spectroscopy. A set of pottery shards, classified as fragments of amphorae, was subjected to analyses carried out in μ -ATR mode, in DRIFT mode and in transmittance mode. The results obtained from different sampling procedures and different spectra acquisition modes were examined and compared.

2. Materials and methods

2.1. Archaeological samples

The investigated samples were collected from a set of pottery shards discovered in the archaeological site of Hierapolis (modern Pamukkale, Turkey) [29]. Archeologists classified these ceramic objects as fragments of amphorae manufactured and used in the early-Byzantine period (V–VI century A.D.) [30,31]. The unearthed shards were only unsoiled with a soft brush, while washing with either water or any other cleaning agent, was avoided.

The examined fragments have different shapes and dimensions (not exceeding $5 \times 5 \text{ cm}^2$), with an average thickness of 0.5 cm. Their concave side (hereinafter called internal side) always was the interior surface of the jar.

Shards with residues distinguishable to the naked-eye onto the internal side, were chosen. The observed residues were blackish and/or brownish in color and exhibited a quite good adhesion to the shards, but they never fully coated the pottery surface.

An example of the pottery shards under investigation is shown in Fig. 1.

2.2. Sequence of the analyses

A preliminary visual inspection of the pottery surfaces was performed through a binocular stereomicroscope (Zeiss, mod. Stemi SV11) at magnifications of up to $100\times$. This examination was aimed at distinguishing the residues from the pottery material, in order to optimize the sampling.

The as-received ceramic fragments were firstly subjected to the μ -ATR analyses. The shape and the limited dimension of the shards examined in this study allowed a direct analysis. In this case, sampling or preparation procedures are not required, hence the specimen is not damaged at all and it can be used later for other

kinds of analysis. Consequently, several characterization tests can be carried out on the same sample.

In the next step, DRIFT analyses were performed on samples collected by abrading the surfaces of the shards with abrasive paper, as detailed in Section 2.4.2. In this manner, small amounts of sample can be taken from the surfaces with insignificant damage. Furthermore, the tools for sampling are portable and can be easily used without transferring in the laboratory the items under investigation.

Subsequently, FT-IR analyses in transmission mode were carried out on samples scraped from the surfaces of the pottery fragments. This methodology made it possible to collect, and then analyze, materials from different parts of the archaeological fragment, with no limitation due to the original shape, dimensions or form of the sample. In fact, the presence of residues from the jar's content was checked also inside the ceramic body. Moreover, FT-IR analyses in transmission mode were performed after extraction with acetone to identify the organic residues without interferences from the ceramic material.

Finally, small flakes of the residues on the internal surfaces of the shards were analyzed in μ -ATR mode. This method allows selective examination of the residue, particularly when other sampling procedures are difficult to perform or the archaeological artifacts cannot be moved into the laboratory.

The analyses were carried out in the reported order, so that the destructive or micro-destructive samplings were performed last, because the removal of the residues from the surfaces could make ineffective the investigations performed directly on the shards (i.e., the μ -ATR analyses).

2.3. FT-IR instrumentation

A FT-IR ThermoNicolet Nexus spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector, was used to record the FT-IR spectra in transmission mode. A 13 mm KBr die (Model 129, Thermo Spectra-Tech) and a hydraulic press (Mod 660, Silfradent) were employed to shape the pellets for the analyses. Following the manufacturer's suggestion, 6000 kg load was applied for approximately 1 min.

A Smart Diffuse Reflectance accessory (ThermoNicolet) was inserted in the spectrometer to perform the DRIFT analyses. This module included a slide with a slot that can hold the sampling disk. A kit consisting of handle and plate (which keep the adhesive-backed silicon-carbide paper used to abrade the surface) was employed in the sampling.

The ThermoNicolet Continuum IR microscope coupled with the spectrometer was used to acquire the FT-IR spectra. This was equipped with a mercury-cadmium-telluride (MCT) detector, which was cooled with liquid nitrogen. A $15\times$ Refflachromat objective with a slide-on ATR attachment (Thermo Spectra-Tech), using a Si crystal (refractive index = 3.4; incident angle = 45° ; contact area = $50 \times 50 \mu\text{m}$), was employed to collect the μ -ATR spectra. To ensure reproducibility and uniformity, the contact between the ATR crystal and the sample surface was automated and computer controlled. After each analysis, the crystal was cleaned with a soft cloth soaked in acetone.

The employed instrumentations were not purged with dry and CO_2 -free air, therefore the contribute of absorption bands of both CO_2 (appearing in the spectrum as a doublet around 2340 cm^{-1}) and water vapor (resulting in sharp and very close peaks over 3700 cm^{-1}) are observed in the reported spectra, although a background spectrum was acquired before each analysis and automatically subtracted (by software) from the sample spectrum.

All the FT-IR data were processed with the OMNIC 8.1 software (Thermo Fisher Scientific Inc.).

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