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Applicability of a Diffuse Reflectance Infrared Fourier Transform handheld spectrometer to perform in situ analyses on Cultural Heritage materials

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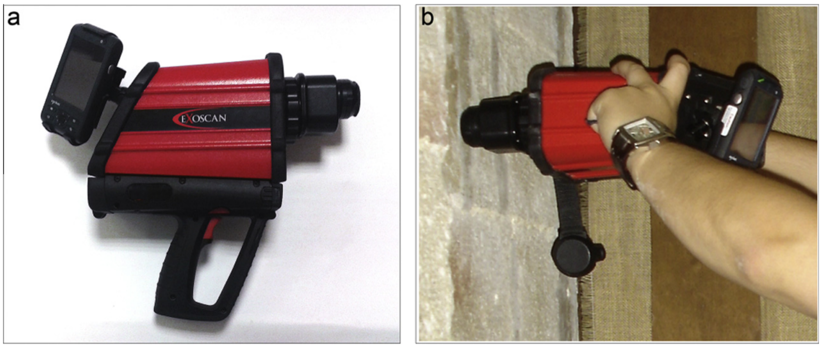
HIGHLIGHTS

- Applicability of a Diffuse Reflectance Infrared Fourier Transform handheld device.
- Reststrahlen distortions in the diffuse reflectance spectra obtained in situ.
- This work proposes a few guidelines to acquire good spectra and resolve them easily.
- DRIFT handheld device a real alternative to the Raman spectroscopy.

GRAPHICAL ABSTRACT

This paper studies the applicability of a different optical configuration implemented on a diffuse reflectance handheld device to perform in situ analyses of several samples belonging to Cultural Heritage and also tries to solve the problems that may arise during the interpretation of the spectra, such as, how to prepare the standards, where to measure the standards, how to correct the distortions or in which cases it is possible to correct the distortions. Finally this work proposes a few guidelines to acquire good spectra and resolve them easily.



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ABSTRACT

This work studies the applicability of a Diffuse Reflectance Infrared Fourier Transform handheld device to perform in situ analyses on Cultural Heritage assets. This portable diffuse reflectance spectrometer has been used to characterise and diagnose the conservation state of (a) building materials of the Guevara Palace (15th century, Segura, Basque Country, Spain) and (b) different 19th century wallpapers manufactured by the Santa Isabel factory (Vitoria-Gasteiz, Basque Country, Spain) and by the well known Dufour and Leroy manufacturers (Paris, France), all of them belonging to the Torre de los Varona Castle (Villanañe, Basque Country, Spain). In all cases, in situ measurements were carried out and also a few samples were collected and measured in the laboratory by diffuse reflectance spectroscopy (DRIFT) in order to validate the information obtained by the handheld instrument. In the analyses performed in situ, distortions in the diffuse reflectance spectra can be observed due to the presence of specular reflection, showing the inverted bands caused by the Reststrahlen effect, in particular on those IR bands with the highest absorption coefficients. This paper concludes that the results obtained in situ by a diffuse reflectance handheld device are comparable to those obtained with laboratory diffuse reflectance spectroscopy equipment and proposes a few guidelines to acquire good spectra in the field, minimising the influence caused by the specular reflection.

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1. Introduction

Some years ago, the collection of a small number of samples was the critical step to perform analyses in the field of Cultural Heritage. But, with the development of the portable devices, these analyses can be performed in situ with successful results, because one analysis means a spectroscopic shot and not one collected sample that must be analysed later on in the laboratory. That is, 100 in situ non-destructive analyses can be equivalent to 100 samples taken. The use of portable spectroscopic techniques is growing over traditional methods and, from some years [1] till now [2], many works can be found in the literature that were carried out in situ using several portable spectroscopic devices. Among them, Raman spectroscopy portable devices have experienced a great development and it has become one of the most used techniques [3–5]. Unfortunately, the samples analysed in Cultural Heritage could contain cromophore compounds which can produce a great fluoresce making the analysis very difficult in many cases [6].

These fluorescence problems that could overlap the signal of the analysed compounds could be avoided by using Fourier Transform Infrared spectroscopy (FTIR). This is a very versatile technique, moreover; it can be used in transmittance [7,8], reflectance FTIR [9], Attenuated Total Reflection (ATR) [10], diamond anvil [11] and Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy alone [12] or combined with Far Infrared Spectroscopy [13]. According to the literature, different kinds of analyses have been carried out in several materials, such as pigments [13–15], binders [16,17], varnishes [18], parchment documents [19], cross sections of paintings [20] as well as coatings for marbles [21] and limestones [22]. Therefore, considering the wide range of available modes and materials analysed, a new optical configuration of a diffuse reflectance FTIR handheld device could be a great tool for molecular analysis in situ in Cultural Heritage.

In the literature several works can be found analysing materials in situ with non-invasive infrared reflectance equipments and most of them have been made with Fibre Optic Reflectance Spectroscopy (FORS) [22,23]. This technique has been applied to a variety of samples achieving very good results. In a recent work, benefits and limitations of non-invasive Fibre Optic Reflectance Spectroscopy in Cultural Heritage have been discussed [24]. Most of these limitations come from the geometry of the fibre optic device that works at 0° in – 0° out (incident radiation is sent perpendicular to the sample and total reflection is collected at the same angle), a problem that has been well solved for the laboratory devices [12] where practically all the distortions of the specular reflections are not observed in the spectra due to the different angles of the incident radiation and collected reflection.

This paper studies the applicability of a different optical configuration implemented on a diffuse reflectance handheld device to perform in situ analyses of several samples belonging to Cultural Heritage and also tries to solve the problems that may arise during the interpretation of the spectra, such as, how to prepare the standards, where to measure the standards, how to correct the distortions or in which cases it is possible to correct the distortions. Finally this work proposes a few guidelines to acquire good spectra and resolve them easily.

2. Theatrical aspects of the reflectance

When any radiation is emitted against a sample, this radiation could be absorbed, transmitted, directly reflected (specular reflection), internally reflected, or diffused in all directions (diffuse reflection). Diffuse and specular reflectance allows us to perform analyses in solid materials without sampling or sample preparation. Nevertheless, the spectra obtained by diffuse, specular or total reflectance may result difficult to interpret as their quality heavily depends on the characteristics of the sample surface. The results will be determined by the properties of the sample such as, particle dimensions, homogeneity, refractive index, concentration, absorption index and so on. In the measurements performed in situ by reflectance spectroscopy the biggest drawback is that diffuse component cannot be optically separated from specular one and this interaction is the main source of distortions [25].

According to the Fresnel equation, the specular reflectance depends on the refractive index (n) and absorption index (k) of the material:

$$R_s = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{1}$$

Being n about 1.5 and k less than 0.04 for typical infrared absorption bands, i.e. the condition $k \ll (n-1)$ is fulfilled [26]. In the case of surface reflection, two types of spectral distortion can happen, first, when the sample has $k < 1$ the spectra is characterised by a derivative-like features and this happens with most organic molecules including polymers. The second type of distortion can appear when the sample contains a compound with a $k \gg 1$ [26,27]. In these cases, inverted or Reststrahlen bands appear with strong oscillators and this happens with most inorganic salts containing oxyanions such as carbonates, sulphates and/or silicates [24], but also for oxalates [28]. The term Reststrahlen was proposed one century ago by H. Rubens, after observing that the repeated reflection of an infrared beam on the surface of the sample has the consequence of suppressing the radiation at all wavelengths except for certain spectral intervals [29]. In the Reststrahlen area the reflectance is up to 80% or even more, while the maximum reflectance in the infrared bands of dielectric materials are usually <10%. This contrast increases with the number of reflections and explains the observation made by Rubens and the term Reststrahlen (residual rays) was used to describe this spectral selection [29].

Diffuse reflection is originated from an absorption process but in different way to the internal attenuated total reflection (ATR) or specular reflection spectroscopy. Diffuse reflection spectroscopy lacks an exact theoretical description, being the Kubelka–Munk model the most widely accepted description [30].

$$KM = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k}{s} = \frac{2.303ac}{s} \tag{2}$$

KM is the value of Kubelka–Munk units, R_∞ is the diffuse reflectance coefficient of an infinitely thick sample, s is the scattering coefficient of the sample, k is the absorption coefficient, a is the molar absorptivity and c is the analyte concentration. The diffuse reflectance spectra are very similar to those obtained in transmittance mode but some differences in the relative intensities of IR bands can be seen. Diffuse reflectance spectroscopy makes the width of the sample appear larger. In the sample many reflections take place and, as a consequence, overtones (integral multiples of the fundamental absorption frequencies) and combination bands (addition and subtraction of the fundamental absorption frequencies) increase their signals, giving more clear information about the nature of the compound under study.

In situ reflection spectroscopy has already been used in various recently published works and these measurements have shown many of the distortions discussed above, making the interpretation of the spectra very complicated. In the literature, there have been attempts to minimise these distortions with correction algorithms and the results have been different depending on the characteristics of the samples. When the sample has a large specular component the relation of the refractive index and the absorption coefficient could be corrected using the Kramers–Kronig (K–K) correction algorithm [31–34]. However, if both the specular and