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Capabilities and limitations of handheld Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for the analysis of colourants and binders in 20th-century reverse paintings on glass

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ABSTRACT

A non-invasive method has been carried out to show the capabilities and limitations of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for identifying of colourants and binders in modern reverse glass paintings. For this purpose, the reverse glass paintings "Zwei Frauen am Tisch" (1920–22), "Bäume" (1946) (both by Heinrich Campendonk), "Lofoten" (1933) (Edith Campendonk-van Leckwyck) and "Ohne Titel" (1954) (Marianne Uhlenhuth), were measured. In contrast to other techniques (e.g. panel and mural painting), the paint layers are applied in reverse succession. In multi-layered paint systems, the front paint layer may no longer be accessible. The work points out the different spectral appearance of a given substance (gypsum, basic lead white) in reverse glass paintings. However, inverted bands, band overlapping and derivative-shaped spectral features can be interpreted by comparing the spectra from the paintings with spectra from pure powders and pigment/linseed oil mock-ups. Moreover, the work focuses on this method's capabilities in identifying synthetic organic pigments (SOP). Reference spectra of three common SOP (PG7, PY1, PR83) were obtained from powders and historical colour charts. We identified PR83 and PY1 in two reverse glass paintings, using the measured reference spectra. The recorded DRIFTS spectra of pure linseed oil, gum Arabic, mastic, polyvinyl acetate resin and bees wax can be used to classify the binding media of the measured paintings.

1. Introduction

The technique of painting on the reverse side of glass was rediscovered by artists in the early 20th century and gained great popularity, especially in Germany. The artist group "Der Blaue Reiter" (the Blue Rider) around Wassily Kandinsky and Franz Marc got in touch with this technique in the summers of 1908 and 1909. Heinrich Campendonk (1889–1957) joined the group in 1911 and conducted his first reverse paintings on glass [1]. He created >70 paintings with this technique during his career. Campendonk met the Belgian artist Edith van Leckwyck (1899–1987) in 1929, and married her in 1935. Painting on the reverse side of glass became popular among artists in Germany during the first half of the 20th century, and many known and unknown artists tried this technique. The Bavarian artist Marianne Uhlenhuth created a single reverse glass painting in 1954. However, no further information is available about her, using this technique.

In contrast to other paint techniques (e.g. panel and mural painting), the paint layers are applied in reverse succession starting with the foremost paint layer and ending with the primer (backmost layer). The paintings are viewed in reflected light, thus revealing an impressive gloss, luminosity and depth of colour. The glass plate behaves like a varnish for the front layers. Therefore, compared with other techniques, the viewing side (front) is better protected against climate-induced damages. Due to the lack of early references for recommendations of certain materials, there are no strict rules about which materials should preferably be used for reverse glass paintings. Until the 19th century, paints were produced by the artists themselves by mixing pigment powders with binders, additives and siccatives. In most cases, they used drying oil (linseed or nut spike oil), proteins (e.g. egg, casein), resins (e.g. dammar) and gums (e.g. gum Arabic). However, mixtures of several binding media (e.g. protein & oil) were also common. In the 20th century, paint tubes were highly recommended for reverse glass paintings, because of their good quality and low price [2,3]. In his publication, Stahl mentions about 40 common colourants for oil colours that can be used in reverse glass paintings [4]. However, there are no pigment recommendations specifically for reverse glass paintings [3].

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Another characteristic technique for reverse glass paintings is etching a dried paint layer, a metal foil or a gold leaf and then overpainting the etched structure with another colour [3,5,6]. Metal foils (e.g. tin, aluminium), coloured paper or cartons are common protective layers.

Reverse glass paintings comprise a non-porous glass substrate and multi-layered paint system; hence, delamination and flaking of the paint layer are the most common conservation problems [7]. However, fractures of the glass panel can also be observed. Scientific investigation of the material provides important information for appropriate conservation concepts. Moreover, thorough research on reverse glass paintings will lead to a better understanding of the artistic technique. A comparison of the materials used in reverse glass paintings and in easel paintings in classic modern art reveal certain differences.

Recently, several studies of medieval reverse glass paintings using minimal-invasive methods were published [7–10]. After several extraction steps, samples were analysed using gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS) and amino acid analysis (AAA), allowing the identification of binding media used in the artworks [10].

Moreover, Hahn et al. reported on non-destructive analyses of colourants of reverse glass paintings from the 14th to the 16th century using in-situ techniques like digital microscopy, visible reflectance spectroscopy (VIS), and X-ray fluorescence analysis (XRF) [11]. Using a mobile reflectance IR device, Miliani et al. found bassanite ($CaSO_4 \cdot 0{,}5H_2O$) in an Italian reverse glass painting from the 17th century [12].

Only the study by Baumer et al. deals with a reverse glass painting from the classical modern period (1905–1955) [10]. The study presents an overview of the binding media analysed using minimal-invasive analytical techniques. In particular, the results obtained for Franz Marc's – "Landschaft mit Tieren und Regenbogen" (1911) reveal the complexity of this kind of painting. The painting is a collage of reverse painting on glass, paper, and metal foil and was executed with gouache distemper (animal glue, egg, polysaccharide gum) as binding media [10].

The literature on the chemical analysis of modern reverse glass paintings using non-destructive techniques is limited. To the best of our knowledge, this is the first work that presents the study of modern reverse glass paintings using non-destructive techniques.

For several years, portable reflectance Fourier Transform Infrared Spectroscopy (FTIR) has been a convenient tool for the non-destructive analysis of cultural heritage objects. Powerful and robust spectrometers became available at lower cost. Thorough in-situ reflection, IR analyses of various cultural heritage objects, like easel paintings [13], canvas painting [14], panel paintings [15,16], mural paintings [17], wall paintings [18,19], illuminated manuscripts [20,21], painted metal sculptures [22], stringed musical instruments [23,24] and built heritage materials [25–27] have been conducted, showing the high potential of this technique.

Generally, when light irradiates a sample material, it can be directly reflected from the surface, or it penetrates the material and can then be absorbed, refracted, reflected or scattered before reaching the surface again. In the case of DRIFT, the total amount of reflected light that passes the detector consists not only of diffuse reflected light (volume reflection), but also of surface-reflected light (specular reflection), as they cannot be optically separated.

Specular reflection causes two main distortions in diffuse reflection spectra: derivative-like features [12,28] and inverted bands (*reststrahlen* bands) [12,29,30]. The specular reflection contribution can be corrected with the Kramers-Kronig (KK) algorithm [13,31–33]. It can correct the relation between the refractive index and the absorption coefficient when the surface reflection is dominant, but it gives inconclusive results when both specular and diffuse-reflected components are present [25,34].

Diffuse reflection originates from an absorption process, as IR light refracts through each particle and is scattered by the combined process of reflection, refraction and diffraction [28]. Compared with transmission spectra, undistorted diffuse-reflection spectra yield no significant band shifting (as occurs in the ATR technique); however, some differences in relative band intensities can be observed [35,36,51]. Moreover, diffuse reflection leads to an enhancement of weak absorption bands because the light can travel a longer distance in a material with small absorption coefficient by repeated refractions [12]. Diffuse reflection lacks an exact theoretical explanation, but the Kubelka-Munk theory tends to be the most practical [37].

For reflection FTIR measurements of artworks, both diffuse reflection and specular reflection are present, and their proportion cannot be predicted. The amount of diffuse-reflected light strongly depends also on the sample surface, i.e. optically flat surfaces (with particles larger than the IR wavelength) will increase the amount of specular reflection, whereas rougher surfaces (with particle dimensions similar to the IR wavelength) will generate mostly diffuse-reflected light [12].

In the literature, three modifications of portable reflection FTIR spectrometers are generally reported: reflectance FTIR spectroscopy without fibre optics [16,21,22,24,33,42,43] (also called "external" reflectance FTIR); Infrared Fibre Optic Reflectance spectroscopy (IR-FORS) [12,38–42,47,48,52–54] and handheld Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) [14,18,19,25,44,45].

The external reflectance FTIR is able to measure in a range of 7500–375 cm^{-1} and preferably collects specular reflected light [15]. For this reason, most external-reflection FTIR studies have used the KK transform to get absorption-like spectra. Zaffino et al. claim that the quality of the specular reflection IR spectrum depends on the sample surface. A highly reflective surface will yield a better spectrum, which can be easily corrected by the KK transform [21]. However, when diffuse reflection is more active (i.e. the surface is rougher), the KK correction cannot be applied with this setup [22,43]. The optical layout for reflection measurements is 22°/22° with a working distance of 15 mm [22,24]. The width of the measured area is ~6 mm [21]. The optical path is vertical. Thus, paintings can be measured only when they are hanging on the wall. The device (~7 kg) can be placed on a tripod for this purpose [16].

The IR-FORS setup works in 0°/0° geometry (angle of incidence and angle of collection are perpendicular to the sample surface) [12]. It has been successfully applied for both the mid-infrared (MIR) range (7000–900 and 4000–900 cm^{-1}) and the near-IR range (12,500–4000 cm^{-1}) [40,52]. The spectra show strong contributions of both diffuse- and specular-reflected IR light, depending on the surface roughness of the sample [12]. Thus, KK corrections are often not feasible [12]. However, Monico et al. showed that applying the KK correction only to certain areas of the spectrum may give positive results [33]. The chalcogenide glass fibres are orientated perpendicularly to the sample surface by a mechanical arm. The device (~35 kg) shows a working distance of ~5 mm and a sampling spot of ~5 mm width [12]. Due to the Se—H stretching absorption of the fibres, the 2200–2050 cm^{-1} region is not accessible with this set up [38].

The handheld-DRIFTS device (3.2 kg) works in the MIR range (4000–650 cm^{-1}). It emits IR radiation at 0° (i.e. perpendicular to the sample) and collects the reflected light inside an imaginary cone of 45° around the emission beam. This configuration supports the collection of diffuse-reflected light [25]. However, it needs to be emphasized that both specular- and diffuse-reflected IR light are collected and their ratio depends on the surface roughness of the sample. The device measures contact-free close to the sample surface (working distance ≤1 mm) with a sampling spot of ~10 mm width. It can be used handheld or on a tripod.

We want to study the advantages, capabilities and limitations of the handheld DRIFTS device for the analysis of modern reverse glass paintings. The over-arching objectives of this study are (1) to examine the different spectral appearances of a given substance; (2) to review critically the interpretation of distorted bands and the applicability of correction algorithms; and (3) to study the limitations of the device for identifying pigments and classifying binders in modern reverse glass paintings. To attain these objectives, a detailed study of reference materials, mock-ups properly prepared and careful examination of each