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Non-invasive identification of metal-oxalate complexes on polychrome artwork surfaces by reflection mid-infrared spectroscopy



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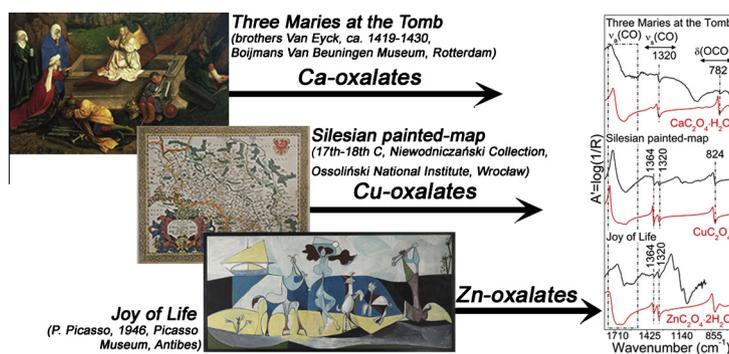
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HIGHLIGHTS

- The spectra of twelve metal-oxalate complexes were studied by using reflection IR spectroscopy.
- The spectral distortions were evaluated by applying the KK transform.
- Different type of oxalates were discriminated non-invasively on 13 polychrome artworks.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work a reflection mid-infrared spectroscopy study of twelve metal-oxalate complexes, of interest in art conservation science as alteration compounds, was performed. Spectra of the reference materials highlighted the presence of derivative-like and/or inverted features for the fundamental vibrational modes as result of the main contribution from the surface component of the reflected light. In order to provide insights in the interpretation of these spectral distortions, reflection spectra were compared with conventional transmission ones. The Kramers–Kronig (KK) algorithm, employed to correct for the surface reflection distortions, worked properly only for the derivative-like bands. Therefore, to pay attention to the use of this algorithm when interpreting the reflection spectra is recommended. The outcome of this investigation was exploited to discriminate among different oxalates on thirteen polychrome artworks analyzed *in situ* by reflection mid-infrared spectroscopy. The visualization of the $\nu_s(\text{CO})$ modes ($1400\text{--}1200\text{ cm}^{-1}$) and low wavenumber bands (below 900 cm^{-1}) in the raw reflection profiles allowed Ca, Cu and Zn oxalates to be identified. Further information about the speciation of different hydration forms of calcium oxalates were obtained by using the KK transform. The work proves reflection mid-infrared spectroscopy to be a reliable and sensitive spectro-analytical method for identifying and mapping different metal-oxalate alteration compounds on the surface of artworks, thus providing conservation scientists with a non-invasive tool to obtain information on the state of conservation and causes of alteration of artworks.

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Introduction

Oxalate patinas are frequently observed on artworks but their mechanism of formation is not yet completely understood.

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Calcium-based oxalate patinas are the most commonly found, generally associated to outdoor carbonate-based objects, such as marble and alabaster sculptures [1–3]. Here the origin of oxalic acid has been ascribed to the metabolic activity of fungi and/or bacteria, as well as to the oxidative process of organic materials applied with aesthetic/conservation purposes on the artwork's surface [1,2].

On polychrome artworks, such as decorate stoneware objects, paintings and manuscripts, the presence of alteration patinas of calcium oxalates [4–7] but also of other metals, such as Cu [8–12], Zn [13–15], Pb [16] and Cd [17,18], has been proved (by employing both conventional as well as synchrotron radiation (SR)-based facilities). Indeed, Zoppi et al. [19] report that a series of pigments, such as malachite [CuCO₃·Cu(OH)₂], azurite [2CuCO₃·Cu(OH)₂], lead white [2PbCO₃·Pb(OH)₂] and calcite (CaCO₃), show a high reactivity toward oxalic acid with the formation of the corresponding metal-oxalate complex. On the other hand, it is also reported that synthetic pigments of the end of 19th century, such as cadmium sulfide [20], can contain the corresponding metal-oxalate as an additive component.

The understanding of the causes of formation of oxalate patinas, the development of cleaning methods for their effective and safe removal as well as the implementation of preventive conservation strategies, would greatly benefit from an analytical tool able to identify the various metal-oxalate in a non-invasive way. In fact, a non-invasive approach could allow for mapping the presence of alteration compounds on the entire artwork surface, before and after the cleaning and also over time.

Regarding non-invasive methods, Fourier transform infrared (FTIR) spectroscopy in reflection mode proved to be very effective for the *in situ* investigation of the artworks surfaces, revealing both the pigments and binders composition [21]. This technique is also extremely sensitive toward the identification of surface contaminants [4,5,22], and thus appropriate for oxalate patinas that are generally present as superficial thin layers; several studies employing high lateral resolution SR-based methods report these patinas typically show a thickness of *ca.* 10–50 μm [12,17,18]. Next to the evident advantages of the non-invasive reflection FTIR spectroscopy, difficulties are generally encountered in the interpretation of the vibrational profiles, since distortions appear with respect to the spectra acquired in the conventional transmission mode.

When the infrared light interacts with the surface of an opaque material, surface and/or volume reflection can take place [23–25]. The former phenomenon (called also specular reflection) is ruled by the Fresnel's equation, while the latter one (called also diffuse reflection) is described by the Kubelka–Munk's equation (a detailed discussion of both equations is reported elsewhere) [23,25]. The surface reflection gives rise to distortions that in the reflection FTIR spectrum appear as derivative-like spectral features and/or inverted bands, following the so-called *reststrahlen* effect [23–26]. Infrared volume reflection spectra show differences in terms of relative band intensities when compared to the corresponding absorption spectra [23,24]. The relative contribution of volume and surface reflection components of the light is not only related to the optical properties of the investigated material but also to the morphology of its surface. The specular reflection is the predominant phenomenon when surfaces optically flat are investigated, while greater amount of the diffuse light is obtained from the analysis of rougher surfaces.

The distortions arising from the surface and volume reflection can be corrected by using the Kramers–Kronig (KK) operation and the Kubelka–Munk (KM) correction, respectively. Both the methods give reliable results if applied to spectra containing only the pure specular or diffuse component of the reflected light. In the case of reflection spectra recorded from artworks, the complex

morphology and heterogeneity of the surface is such that these two components can co-exist in variable and unknown proportions, thus making the use of the KK and KM algorithms limited [23].

Whilst some studies demonstrated that the KK correction works properly on the derivative bands related to organic materials (with absorption index $k < 1$) [27], it is reported that this algorithm does not yield satisfactory results for the *reststrahlen* bands of inorganic compounds, such as carbonates, sulfates and silicates (with $k > 1$) [28–30]. For this latter class of materials positive outcome arises from the possibility to employ the combination and/or overtone bands as markers for their identification in artworks [23,29,31]. However, this is not always possible, such as it is for example the case of metal-oxalate complexes. The fundamental vibrational modes of these compounds generally appear as derivative-like and/or inverted bands in the reflection FTIR spectra and neither combination or overtone bands are observable [4,6–8,13,22].

Based on the available vibrational data of several metal-oxalate complexes [32–40], the present work is aimed to extend knowledge by studying the reflection FTIR vibrational profiles and the corresponding spectral distortions due to the surface reflection of twelve metal oxalate-based complexes that can be reasonably revealed on alteration patinas of polychrome artworks.

Advantages and drawbacks resulting from the KK transform are discussed by comparing the specular reflection profiles obtained from the flat surface of oxalate-based pellets with respect to the corresponding conventional transmission FTIR data. The information thus acquired from the reference powders is employed for a detailed discussion of reflection mid-FTIR data collected from thirteen polychrome artworks, that have been investigated during a series of national and transnational access of the mobile laboratory (MOLAB) [21].

Materials and methods

Metal-oxalate reference materials

Measurements were carried out on the following commercial powders: CaC₂O₄·H₂O (Acros Organics), PbC₂O₄, Fe₂(C₂O₄)₃·6H₂O, MgC₂O₄·2H₂O, CuC₂O₄ (Alfa-Aesar), FeC₂O₄·2H₂O (VWR Prolabo), ZnC₂O₄·2H₂O (Sigma–Aldrich), Na₂C₂O₄ (Carlo Erba) and Cr₂(C₂O₄)₃ (City Chemical LLC).

The synthesis of CaC₂O₄·3H₂O was performed according to Grases et al. [41], while CaC₂O₄·2H₂O was prepared by slowly mixing in a stoichiometric amount 0.1 M aqueous solutions of Na₂C₂O₄ (Carlo Erba) and CaCl₂ (Merck) at 0.4 °C. The resulting precipitate was filtered by a vacuum pump and dried under N₂ flux for *ca.* 6–7 h.

CdC₂O₄·3H₂O was obtained by employing a stoichiometric amount of 0.1 M aqueous solutions of Na₂C₂O₄ and CdCl₂ (both Carlo Erba). The reaction was led at room temperature and after filtration by a vacuum pump, the resulting material was dried for 48 h at 40 °C.

X-ray diffraction (XRD) measurements (not reported) were performed in order to check the composition of the in-house synthesized powders. For CaC₂O₄·3H₂O, next to the predominant trihydrate phase, smaller amounts of both the monohydrate and the dihydrate forms were identified. Less than 5 wt% of the monohydrate phase was also detected in CaC₂O₄·2H₂O.

Artworks

Non-invasive *in situ* reflection mid-FTIR investigations have been carried out on thirteen museum artworks (cf. Table 1 and

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