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Original article

Time resolved laser induced fluorescence for characterization of binders in contemporary artworks

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ABSTRACT

Contemporary artworks are often realized with multi-component mixtures with unknown compositions, which may be subjected to an unforeseeable degradation. A detailed characterization of these materials provides relevant information both to plan proper restoration strategies and to prevent damages. In particular, binders identification represents one of the major problems in the conservation of the contemporary works of art. In this paper, five binders routinely employed in contemporary paintings, i.e. acrylic resins, ethylene vinyl acetate, dammar varnish and linseed oil, were studied by Time Resolved Laser Induced Fluorescence Spectroscopy (TR-LIF). Experimental results confirm the TR-LIF analysis capability to isolate specific contributions from the investigated constituents. The spectral features of ten commercial paints containing the above mentioned binders were analyzed as well. In this latter case, additional diagnostic techniques, such as X-Ray Fluorescence Spectroscopy and Fiber Optics Reflectance Spectroscopy, were demonstrated to provide useful complementary information to integrate TR-LIF results.

1. Introduction and research aims

The development of modern chemical industry, during the XVIII century, allowed the production of many synthetic resins since 1920s [1]. Due to their versatility, many of these new easy-to-use products were employed as binding materials by contemporary artists [2]. In particular, synthetic resins mixed with ancient and newest pigments allowed painters to express themselves, their ideas and inwardness, differently from the traditional tempera and oil [3].

Acrylic and vinyl polymers represent the most common binders used since the 1940s [4]. However, contemporary artists were often unaware of the chemical and physical properties of these new materials, and their role in the degradation process of painted surfaces. Nevertheless, many of them decided to experiment such products in their artworks and mixing them together in order to achieve their expressive goals. Indeed, one of the major problems about the conservation of contemporary works of art is the use of multi-component mixtures, whose stability and durability are not well assessed to date [5]. The identification of contemporary binders is thus mandatory in order to plan appropriate conservation and restoration strategies. This would also allow the identification of contemporary over-paintings and/or restorations in ancient artworks as well. However, due to the complex nature of these multi-component mixtures, their detailed characterization is not straightforward by conventional non-destructive diagnostic techniques. As an example, X-Ray Fluorescence (XRF) spectroscopy, routinely employed for pigment characterization [6,7], cannot be used to detect light elements, typically contained in polymeric binders and synthetic dyes. Other techniques, such as gas chromatography (GC) [8] and mass spectroscopy (MS) [9] are well suited to analyze binders, but they are micro-destructive techniques, thus not always applicable in the field of Cultural Heritage. Raman spectroscopy is also widely used for the characterization of artwork materials, with a variety of databases available for ancient and contemporary pigments [10–13]. Such a technique provides the molecular "fingerprint" of a large number of compounds [14]. However, some materials do not show a characteristic spectrum. In addition, an intense fluorescence emission is often observed, making it difficult or even impossible to appreciate weak Raman signals [15]. Fourier Transform Infrared Spectroscopy (FTIR) can be considered a method for a non-invasive characterization of synthetic binders as well, even though the difficulties encountered in the interpretation of the resulting spectral features limit the use of such a technique [4].

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Spectroscopic methods using ultraviolet laser sources, such as Laser Induced Fluorescence (LIF), were recently proposed as complementary techniques, aimed at solving the above issues and significantly improving our capacity to study the chemical compositions of artworks [16,17]. The main advantages of LIF are high sensitivity, non-invasiveness and prompt response [16,18,19]. However, fluorescence spectra obtained by standard LIF spectroscopy are often consisting of relatively wide bands. This makes it difficult to isolate the contributions arising from single constituents. Even more so when a mixture of different compounds is investigated. This issue can be overcome by using Time Resolved LIF (TR-LIF), which allows discriminating the emissions from different compounds by analyzing the time evolution of their fluorescence spectra [20,21].

The aim of the present work is to investigate the potentiality of the TR-LIF technique for the characterization of painting materials. In particular, five binders routinely employed in contemporary art, such as acrylic resins, ethylene vinyl acetate, linseed oil and dammar varnish, were studied by TR-LIF. The above listed binders were mixed with three common pigments used in contemporary artworks, blue phthalocyanine, Zinc white and Titanium white [22], in order to characterize the spectral contributions from the resulting compounds. Ten commercial paints, nominally containing the previously analyzed binders and pigments, were investigated as well by TR-LIF to compare the obtained results with the ones by the laboratory samples. Finally, X-ray Fluorescence (XRF) and Fiber Optics Reflectance Spectroscopy (FORS) analysis were also used to achieve complementary information.

2. Materials and methods

2.1. Materials and sample preparation

All of the samples investigated in the present work are listed in Table 1, divided in four different categories: (i) binders, (ii) powders, (iii) binders + powders, (iv) commercial paints.

Table 1/binders: five reference samples were prepared by applying the pure binder on a black cardboard. The selected support was chosen due to its low fluorescence emission, which permits fluorescence measurements with negligible contribution arising from the support itself [23]. A detailed description of the investigated commercial binders is reported in the following:

- PRIMAL B-60A: an ethylacrilate-co-methacrylate made by Rhom and Has and commercialized in water dispersion by CPR (Rome, Italy), mainly used as a pictorial binder since the 1940s [24];
- Acrytal C12: acrylic resin in water dispersion made by Iridon and commercialized by Vertecchi, (Rome, Italy);
- Vinil Pritt: a binder based on to ethylene vinyl acetate (EVA) commercialized by Henkel Italia (Milan, Italy), used as a pictorial binder since its introduction since 1950s [25];
- Linseed Oil: Refined linen seed extract commercialized by Maimeri (Milan, Italy), one of the most used binders since ancient times [26];
- Dammar Varnish: natural dammar resin with turpentine commercialized by Maimeri (Milan, Italy), using as a binders since the XII century [27].

Table 1/powders: three pigments were chosen and purchased by the Sigma Aldrich, namely titanium dioxide (TiO_2) (99.99%), copper phtalocyanine (PB15-β form) (90%), zinc oxide (ZnO) (99.99%). Three samples were prepared by pressing the pigment powders onto an aluminum holder, allowing to evaluate their spectral features with no contribution from the binder. The aluminum support was chosen due to its negligible fluorescence emission. Similar aluminum supports could not be used for binders and paints due to poor adhesion issues.

Table 1
Summary of the investigated samples.

Sample/supplier	Sample description
Binders	
PRIMAL B-60A/Rhom and Hass	Water dispersion of acrylic polymer
Acrytal C12/Iridron	Water dispersion of acrylic polymer
Vinil Pritt (EVA)/Henkel	Ethylene-vinyl acetate (EVA)
Linseed Oil/Maimeri	Refined linen seed extract
Dammar/Maimeri	Dammar varnish in turpentine
Powders	
TiO_2 powder/Sigma Aldrich	Powder of titanium dioxide (PW6)
PB15 powder/Sigma Aldrich	Powder of copper phthalocyanine (PB15 β-form)
ZnO powder/Sigma Aldrich	Powder of zinc oxide (PW4)
Powders + Binders	
TiO_2 + PRIMAL B-60A	Powder of titanium white (PW6) mixed with the PRIMAL B-60
TiO_2 + Acrytal C12	Powder of titanium white (PW6) mixed with the Acrytal C12
TiO_2 + Vinil Pritt	Powder of titanium white (PW6) mixed with the Vinil Pritt
TiO_2 + Linseed oil	Powder of titanium white (PW6) mixed with the linseed oil
TiO_2 + Dammar	Powder of titanium white (PW6) mixed with the Dammar varnish
PB15 + PRIMAL B-60A	Powder of phthalocyanine (PB15) mixed with the PRIMAL B-60
PB15 + Acrytal C12	Powder of phthalocyanine (PB15) mixed with the Acrytal C12
PB15 + Vinil Pritt	Powder of phthalocyanine (PB15) mixed with the Vinil Pritt
PB15 + Linseed Oil	Powder of phthalocyanine (PB15) mixed with the linseed oil
PB15 + Dammar	Powder of phthalocyanine (PB15) mixed with the Dammar varnish
ZnO + PRIMAL B-60A	Powder of zinc white (PW4) mixed with the PRIMAL B-60
ZnO + Acrytal C12	Powder of zinc white (PW4) mixed with the Acrytal C12
ZnO + Vinil Pritt	Powder of zinc white (PW4) mixed with the Vinil Pritt
ZnO + Linseed oil	Powder of Zinc white (PW4) mixed with the linseed oil
ZnO + Dammar	Powder of Zinc white (PW4) mixed with the Dammar varnish
Commercial paints	
Titanium White Polycolor 018/Maimeri	Fine Vinyl Colours (PW6)
Titanium White Polycolor 018/Maimeri	Fine Art Acrylic Colour (PW6)
Titanium White Van Gogh 118/Royal Talens	Oil Colour: Linseed Oil (PW6, PW4)
Titanium White Polycolor 018/Maimeri	Fine Art Acrylic Colour (PW6)
Phthalo Blue Polycolor 378/Maimeri	Fine Acrylic Colours (PB15:1,PW6)
Phthalo Blue Polycolor 378/Maimeri	Fine Vinyl Colours (PB15:1,PW6)
Cerulean Blue Phthalo Van Gogh 535/Royal Talens	Oil Colour (PB15, PW6)
Primary Blue Polycolor 400/Maimeri	Fine Acrylic Colours (PB15:3,PW6,PG7)
Phthalo Blue Artisti 378/Maimeri	Traditional Oil Colours (PB15:3)
Prussian Blue (PHTHALO)/Royal Talents	Designer Temperafarbe

Table 1/binders + powders: fifteen more samples were realized on a black cardboard by mixing each binder with every analyzed pigment powder.

Table 1/commercial paints: finally, ten samples were prepared with common commercial acrylic, vinyl and oil paints containing blue phthalocyanine, zinc white and titanium white.

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