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## Contemporary artists' spinel pigments: Non-invasive characterization by means of electronic spectroscopy

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### ABSTRACT

The identification of artistic materials represents a fundamental step in supporting the conservation of cultural heritage objects. The importance of their appropriate characterization is particularly relevant in modern-contemporary art, since they could be affected by the occurrence of rapid changes in chemical formulation over time. This paper focuses on an investigation of a series of contemporary blue-green commercial acrylic paints constituted of spinel pigments, using non-invasive spectroscopic techniques. The spectroscopic and color measurements obtained make it possible to characterize the acrylic paints under investigation and to compare the results obtained with those reported in the literature and in spectral databases. To be more precise, the proposed UV–vis–NIR reflectance spectroscopic technique was sensitive enough to characterize the acrylic paints according to their *d-d* ligand field and the charge transfer (CT) electronic transitions involved in the spinel structures. In addition, an overview of this class of inorganic pigments is also given.

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### 1. Introduction

Nowadays, the paint materials also used by contemporary artists are evolving mostly thanks to the introduction of several new products on the global market. In addition, paint manufacturers can basically modify the formulations over time, in a search to find a better balance between stability properties and production costs without notifying their customers and/or artists. As reported in previous works [1–6], finding out about these changes in formulation can support documentation for the history of materials and the conservation of artworks in the contemporary art field.

Organic, metal-organic, and inorganic compounds constitute the basis of paint materials. Over the past two centuries, in an attempt to respond to commercial and performance demands, some of the traditional artists' materials have been replaced by new formulations. Toxicity, instability to environmental factors, and high production costs represent the prevalent reasons for these replacements [7]. Within this context, the traditional cerulean blue (CoSnO<sub>3</sub>, cobalt stannate) has been replaced by a new family of inorganic compounds constituted of synthetic spinels of cobalt [8,9]. This particular category of materials, which are industrially defined as *complex inorganic colored pigments* (CICPs), has already been examined for industrial purposes by testing

its heat and chemical stability, UV opacity, hiding power, and infrared (IR) reflectivity [10,11]. To the best of our knowledge, this work represents the first study in the field of contemporary art conservation to be specifically focused on the spectroscopic properties of a set of acrylic paints constituted of synthetic cobalt spinels. To be more precise, paints from Winsor & Newton's Artists' Acrylic and Liquitex's Heavy Body Acrylic series were considered.

This study was performed mainly by using a non-invasive reflectance spectroscopic technique in the ultraviolet (UV), visible (vis) and near infrared (NIR) ranges in order to explore the potential of this particular technique in characterizing the said pigments at the chemical level. Promising results were obtained by using a bench spectrophotometer, and suggest extending this non-destructive technique with a different configuration set-up to *in situ* analyses by means of Fiber Optic Reflectance Spectroscopy (FORS) devices. In addition, XRF and XRD analyses supported the spectroscopic results in the investigation of commercial artists' materials studied, thus providing further compositional information.

### 2. Spinel Pigments

Spinel constitute a large class of inorganic compounds that are found as minerals and some of which are valued as gems [12]. Their general formula is AB<sub>2</sub>O<sub>4</sub>, where A and B are bivalent and trivalent cations, respectively. In the so-called "normal" spinels, cations A and B are situated in tetrahedral and octahedral sites, respectively, while the situation is reversed in "inverse" spinels. If the inversion of spinels is

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incomplete, the structure will be referred to as “partly inverse” (mixed or random) [13–17]. Wide variations in composition can be encountered in spinels, owing to the possibility that solid solutions can form in which  $Mg^{2+}$  is replaced by  $Zn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ , and  $Al^{3+}$  by  $Cr^{3+}$  and  $Fe^{3+}$ . When artificial spinels are prepared, their structure depends on the synthesis procedure and the formation conditions (temperature and pressure). Many parameters, such as the ionic oxidation state and the ionic radius, can modify the distribution of cations among the lattice sites. Moreover, inversion rates depend on chemical composition and the method of preparation [15,18].

Synthetic spinels are employed as semiconductors, catalysts, and magnetic materials. As regards pigments, the first synthetic spinel is cobalt blue or Thénard's blue, named after the French chemist who first prepared the pigment, at the beginning of the nineteenth century [19]. Cobalt blue is a typical spinel of formula  $CoAl_2O_4$ , with  $Co^{2+}$  in tetrahedral sites and  $Al^{3+}$  in octahedral ones. Nowadays, many other spinel-type pigments have been produced, and are characterized by excellent optical properties and physico-chemical stability. Thanks to these particular features, synthetic spinels are widely used in the manufacture of industrial pigments [13]. In addition to their use for coloring ceramics owing to their high temperature stability, at present spinel pigments are also commonly marketed as painting materials because they are stable in modern binders such as acrylic and alkyd resins [20].

Spinel occurs in a range of colors, which are directly related to the nature and coordination geometry of chromophore ions within the spinel lattice. Moreover, the possibility of widely varying the composition of the solid solution also provides the possibility of obtaining different shades simply by altering the percentage of the various ions [21].

In the present paper we have focused on synthetic spinels of Co(II), which are some of the most important inorganic compounds used as blue and green pigments. In particular, cobalt aluminate blue spinel  $CoAl_2O_4$  (commercially available as PB28) and cobalt chromite green spinel  $CoCr_2O_4$  (commercially available as PG26) were extensively studied. The former is characterized by a bright reddish-blue hue, while the latter is distinguished by a typical military green shade.

The presence in different amounts of zinc, aluminum and chromium creates a new typology of spinels, ones which have an intermediate shade somewhere between blue and green [7]: e.g. cobalt chromite blue-green spinels  $Co(Al,Cr)_2O_4$  (commercially available as PB36) and cobalt chromium zinc aluminate spinels  $Co,Zn(Al,Cr)_2O_4$  (commercially available as PB36:1). Both pigments, which have hues ranging roughly between blue and cyan, are known as cerulean blue [22,23]. To be more precise, the cobalt chromite PB36 blue-green spinel has been available since the 1960s [24]. The color manufacturers have replaced the traditional cerulean blue cobalt stannate-based pigment (commercially available as PB35) with PB36 in the field of contemporary art, owing to the high production cost and instability in acrylic paints of the PB35 pigment [8]. In this work, PB36 acrylic cerulean blue was also investigated because of its ascertained use in contemporary art.

### 3. Materials and Methods

Three commercial acrylic paint samples were purchased from Winsor & Newton and Liquitex (Table 1). All the samples, which are based on synthetic spinel pigments of Co(II), were prepared directly from the tube color on labelled glass slides, using a metallic spatula, to obtain

opaque coatings. The samples were dried in the laboratory at room temperature (approximately 22–24 °C and 45–55% RH) for ten days prior to their analysis.

#### 3.1. X-ray Fluorescence (XRF)

XRF measurements were performed with a Bruker Handheld XRF instrument, mod. Tracer III-SD equipped with an Rh anode and an energy dispersive SDD (Silicon drift detector) operating at 40 KeV, 12  $\mu$ A. X-ray fluorescence analysis was carried out under vacuum conditions in order to identify or verify the sample's elemental content for elements with lower atomic numbers. The instrument head was placed in contact with the measurement area (4 mm  $\times$  7 mm), and the XRF spectra were acquired in 100 s. The ARTAX, Version 7.4.0.0, by Bruker Nano GmbH (Germany) was used to process the data acquired.

#### 3.2. X-ray Diffraction (XRD)

The composition of the acrylic paint samples was investigated using a PANalytical X'Pert PRO X-ray diffractometer under the following operative conditions: a Cu anticathode ( $\lambda = 1.54 \text{ \AA}$ ), with a current intensity of 30 mA and voltage 40 kV, explored the  $2\theta$  range between 3° and 70°; the step size was 0.02°, and the time to step, 50 s. The instrument was equipped with an X'Celerator multirevelatory and High Score data acquisition and interpretation software. The ICDD reference database (2010), Powder Diffraction File Inorganic and Organic Data Book, edited by Dr. Soorya Kabekkodu (International Centre for Diffraction Data, Newtown Square, PA USA), was used to interpret the XRD patterns. The data were processed with Software HighScore, Version 3.0d (3.0.4), by PANalytical B.V. (The Netherlands).

#### 3.3. UV–vis–NIR Reflectance Spectroscopy

UV–vis–NIR reflectance spectra were recorded using a Perkin-Elmer Spectrophotometer, model Lambda 1050, equipped with a Perkin-Elmer Integrating Sphere ( $\varnothing$  60 mm) in the 200–2500 nm range. 0°/d measurement geometry with the specular component excluded was used. Calibration of the spectrophotometer was carried out using a 99% Labsphere Spectralon diffuse reflectance standard (LABSPHERE, INC. North Sutton, NH, US). Software PerkinElmer UV WinLab 6.0.3 (Perkin Elmer, Global Headquarters: Waltham, MA, US) was used to process the data.

#### 3.4. Color Measurements

A Konica Minolta (Minolta Co. Ltd., Japan) CM-700d spectro-colorimeter was used to measure the visible reflectance spectrum of the samples. The spectro-colorimeter was equipped with an integrating sphere ( $\varnothing$  40 mm), and had a d/8° measurement geometry. It worked on the spectral range from 400 to 700 nm using a 10 nm acquisition step. The light source and detector were a pulsed xenon lamp with UV cut filter and a silicon photodiode array, respectively. The instrument was calibrated with a white (100% reflective) and black (0% reference) balance, in accordance with the Konica Minolta calibration procedure. The white standard was provided by the manufacture (Konica Minolta, Tokyo, Japan). The measurements were acquired without the reflected

**Table 1**  
Color name, code and formulation studied in this work.

Color name	Index color	Firm/product	Pigment name	Declared pigment chemical formula
Cobalt blue	PB28	Liquitex Heavy Body Acrylic	Cobalt aluminate blue spinel	$CoAl_2O_4$
Cerulean blue	PB36	Liquitex Heavy Body Acrylic	Cobalt chromite blue-green spinel	$Co(Al,Cr)_2O_4$
Cobalt green deep	PG26	Winsor & Newton Artists' Acrylic	Cobalt chromite green spinel	$CoCr_2O_4$

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