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RAMAN IDENTIFICATION OF PIGMENTS IN THE WORK OF THE CHILEAN CONTEMPORARY VISUAL ARTIST IGNACIO GUMUCIO

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ABSTRACT

The main pigments in the painting by the Chilean artist Ignacio Gumucio were identified by using micro-Raman spectroscopy. Three works by the artist, two paintings with wooden stand and a wall painting were analyzed. Pigments were vibrationally identified from cross-section samples of the contemporary paints on wood *Río* and *Saludo* and the wall painting *Mental*. The blue color Raman bands corresponds to cooper phthalocyanine. In the green areas, the Raman signals were ascribed to the azopigment acetoacetic arylide and copper phthalocyanine; the green color is then the result of a combination of the yellow and blue pigments. Raman bands in the pink areas were assigned to the azopigment β-naphthol. The dark green color in the Saludo paint is due to a chlorinated copper phthalocyanine pigment. Other materials in the artworks were also identified: rutile (TiO_2) in Saludo in white areas and calcite ($CaCO_3$) in Mental and Río. On this basis and taking into account the identification of the state of conservation a protocol for the preservation of the artworks Río and Saludo can be assessed.

Keywords: Contemporary visual art; Ignacio Gumucio; Mental wall paint; Río and Saludo paints; micro-Raman spectroscopy; conservation and restoration.

INTRODUCTION

A better understanding of our civilization, and an improvement of the restoration and conservation methods, necessarily considers the knowledge of the materials involved in artistic and cultural heritage. Nowadays, the study of artworks is performed through several scientific techniques between them the spectroscopic analyses which are the most frequently used [1,2]. Raman spectrometry is one of the most powerful due to its characteristics. The unique properties of this technique involve non-destructive nature, no sample preparation, reliability, specificity and sensitivity [3-5]. Raman spectrometers have become the instrument of choice when analyzing archaeological artifacts and pigments on art works [6]. It is also amenable to *in situ* analysis, based in the development of fiber optics technology [7-9]. Most of the Raman spectrometers are today coupled with a microscope thus making possible to observe the sample and scan the spectrum from a small area down to one micrometer [10,11]. The use of micro-Raman spectrometers gives information on the microstructure of analyzed samples also improving the spatial resolution. Nevertheless, its meaningful disadvantage still lies in the formation of undesirable fluorescence, which is an accompanying phenomenon of measurements of diverse materials and which is very difficult to forecast. The main applications of Raman in heritage studies concern the identification of pigments and dyes on various support materialities [12-14]. Pigments together with binders and fillers give important information about artists, artistic schools or technological evolution. The development of contemporary painting involves the use of industrial materials, experimentation with different supports, and incorporation of new concepts and techniques. An example of this painting is the Chilean visual artist Ignacio Gumucio [15], who performs a work that oscillates between instinct and its pictorial projection to the wall, through an exhaustive series of formal experiments [16]. This paper reports on the micro-Raman spectroscopic investigation of colors used in three paints of Ignacio Gumucio. The choice of this artist is based on the following fundamental aspects. He is an artist recognized and respected by the Chilean academic circle of art. Moreover, the painter is inserted into the tradition of the School of Art of the University of Chile, which has maintained a historical-critical link with painting and has continued the work of Juan Francisco Gonzalez, whose modern and experimental character projected to artists like Pablo Burchard, Adolfo Couve and Gonzalo Diaz. Gumucio relates to this pictorial tradition. Finally, the artist represents a formal complexity since uses poor quality materials, which are a problem for future conservation. Thus, the work of Gumucio proposes a critical turning point, linking the contemporary pictorial tradition and experimentation, challenging conventional strategies in the paint restoration. A wall painting *Mental* and two paintings with wooden stand *Río* and *Saludo* of Gumucio, were analyzed. As far as we know, this is the first time in Chile that this noteworthy kind of paints has been investigated by means of micro-Raman spectroscopy. The *Mental* wall paint (2012) is located at the Yono Gallery, Providencia, Santiago, covered by several layers of painting; *Río* (2006) and *Saludo* (2011) works, in the studio of the artist, were painted on playwood and agglomerate wooden supports, respectively; both supports easily degraded.

EXPERIMENTAL

Materials and Methods

Paints description, samples and instrument

Mental

The temporary wall paint was performed on four walls [15]. Details of the wall painting displaying archetypal figures of the Chilean landscape such as river, willow and waterfall are shown in Fig. 1a. The piece was synthetically represented in a non-realistic form. A wall of concrete was the support for the *Mental* paint. This material is obtained by mixing cement, sand and water in specified proportions. The cement is a mixture of lime, clays and other calcined and pulverized materials. The artist also uses spackling paste covering, and an acrylic resin as pictorial layer.

Río

In this painting of 40x40 cm, it is possible to distinguish landscapes organized from a non-naturalistic viewpoint. The mixed technique paint was elaborated on plywood. This material consists in few wooden planks millimeters thick, hitting on each other, usually alternating fiber direction until a desired thickness. The most common disadvantages are due to moisture, which are reflected in the occurrence of cracks in the sense of the fiber, as well as of general material deformations. Detail of the paint is given in Fig. 2b.

Saludo

The artist uses the same visual operation that in *Río*, that is a superposition of some elements from different pre-manufactured supports. The painting (32,3x60 cm) was elaborated on agglomerate wood consisting in wood flakes bonded at low pressure. In general, this material is a low stable support being easily deteriorated by the moisture and displaying a feeble mechanical behavior; humidity and interactions with other kind of woods induce irreversible structural deformation. The paint is shown in Fig. 3.

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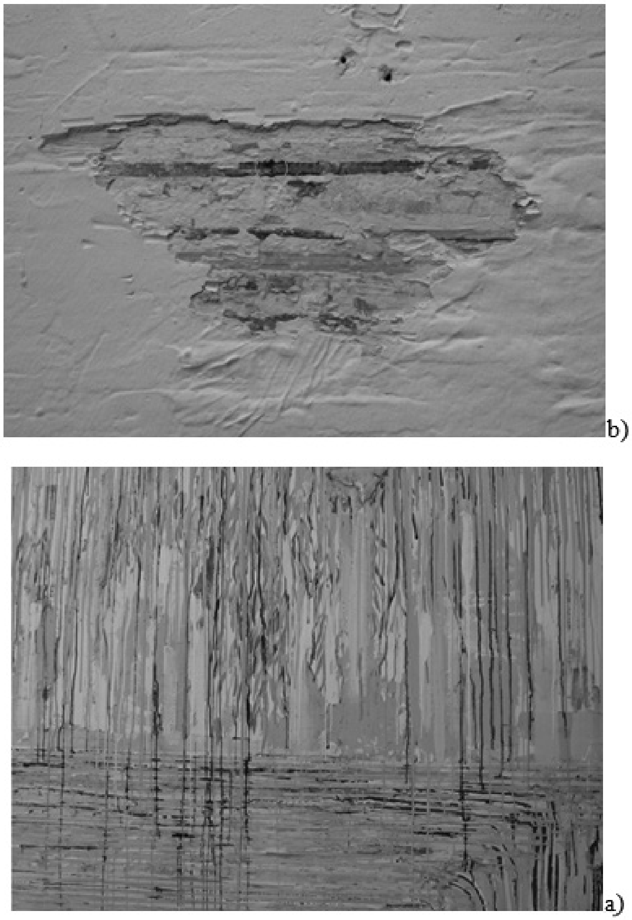

Figure. 1. a) Detail of the *Mental* wall paint. b) Red circles indicate places where the samples were extracted.

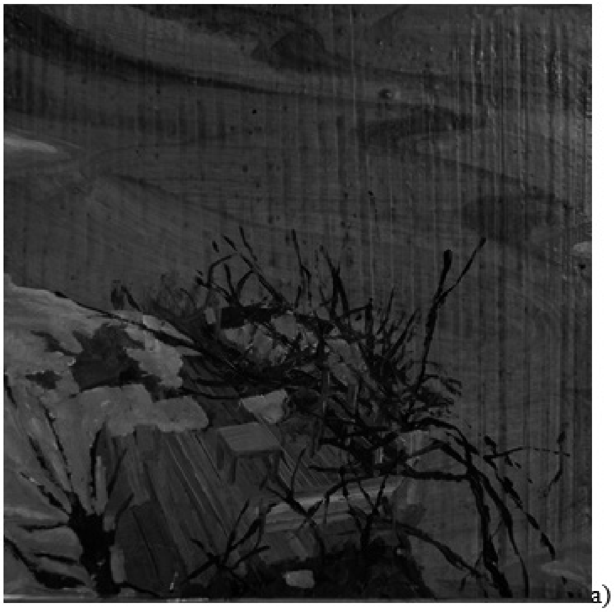

Figure. 2. a) *Río* paint. b) Red circle indicates the place where the sample was extracted.

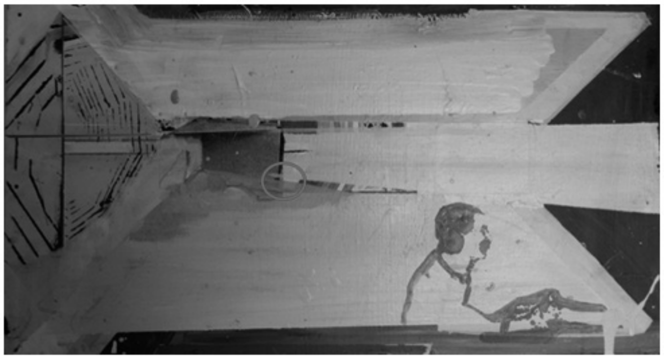

Figure. 3. *Saludo* paint. Red circle indicates the place where the sample was extracted.

Sample collection

Samples of dimensions 0.5-1 mm^2, collected in January 2014, were extracted from the three selected paintings following internationally accepted procedures [17]. Samples were selected according to the main colors displayed in the artworks. Figs. 1-3 display the spots where the samples were collected. In the case of samples *Río* and *Saludo*, the paint layer was analyzed separately from the wood and the supporting material. A similar procedure was used to study samples from the wall.

To prepare the cross-sections, samples were embedded in an acrylic resin and polished using micromesh polishing cloths up to 12000. The Raman spectral scanning was performed for the cross-sections directly deposited on a slide.

Instrument

Raman spectroscopy

The Raman measurements were performed using a Renishaw micro-Raman RM 1000 spectrometer, equipped with laser lines 514, 633 and 785 nm. The apparatus is coupled to a Leica microscope and a CCD camera cooled electrically. The Raman signal was calibrated to the 520 cm^{-1} line of silicon through a 50x objective. The laser power on the sample was 0.14 mW. Acquisition time was set between 10 and 20 s per accumulation; the average of accumulations was 10 with spectral resolution of 4 cm^{-1}. The spectra were recorded between 200 and 1800 cm^{-1}. Spectral recording conditions and the choice of the laser line were selected in order to avoid degradation (photobleaching or photodecomposition) of the sample; the 785 nm line was used. The main identified species are described in Figs. 4-6 and in Table 1.

Table 1. Artwork, color and pigments.

Artwork	Colors	Pigments
Mental	Cream and blue tonalities	β-naphthol Copper phthalocyanine Calcite
Río	Green and yellow	Copper phthalocyanine Acetoacetic arylide Hansa yellow
Saludo	Green and white tonalities	Copper phthalocyanine Acetoacetic arylide Rutile

RESULTS AND DISCUSSION

A. Raman spectra

The artwork, color and pigments found in the samples are displayed in Table 1. The Raman spectra were analyzed in the 200-1800 cm^{-1} region. The bands assignment of the samples is based on general Raman data [18-20], for dyes [19-25] and pigments [21-26]. The spectra are shown as obtained and are illustrated along with the discussion.

B. Raman spectrum of pigments

The inorganic compound calcite, $CaCO_3$, was identified in several samples of the pink and sky-blue areas of the wall painting *Mental*; in fact, bands at 1090, 713 and 278 cm^{-1} are ascribed to calcite [26], probably used as filler material, see Fig. 4d. Rutile, TiO_2, was identified [23] in various white areas of the *Saludo* paint displaying bands at 607, 442 and 258 cm^{-1} see Fig. 6a. The set of vibrations of rutile it is also visible in the dark-green area at 609, 442 and 260 cm^{-1}. No organic binders were identified in the artworks. No bands ascribed to the acrylic resin used to prepare the cross-sections were identified in the Raman spectra of pigments.

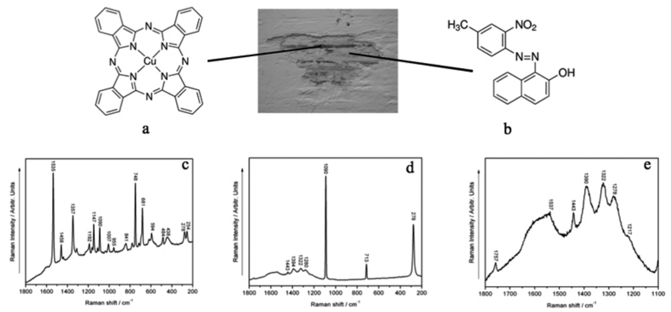

Figure. 4. *Mental* paint detail. a) Cu(II) phthalocyanine and b) β-naphthol model structures, and Raman spectra of the c) blue and d) pink colored areas. e) Detail of the Raman spectrum of the pink colored area in the 1800-1100 cm^{-1} spectral region.

The wall paint *Mental*. The intense blue color in a cross-section segment of the sample is due to copper phthalocyanine (CuPc), see Figs. 4a and 4c. In fact, the spectral profile is in perfect coincidence with the Raman spectrum published by Scherrer et al. [19] reference C.I. 74160:4. Calcite was identified in a low tonality pink area along with another azopigment, β-naphthol (1-(4-methyl-2-nitrophenylazo)-2-naphthol), see Figs. 4b, 4d and 4e. This azopigment displays bands at 1537, 1443, 1390, 1322 and 1278 cm^{-1} that are in good agreement with those observed in the published reference Raman spectra [22-23], for β-naphthol commercially named PR 3 or Hansa Scarlet RNC. The sky-blue tonality area is also dominated by the calcite bands, displaying additional very weak bands at 1535, 748 and 681 cm^{-1} attributable to CuPc, which probably is the responsible of the observed tonality.

The paint *Río*. Several colored cross-section segments of the sample display different green tonalities, see Fig. 5. The Raman spectrum analysis of the most intense green area suggests the coexistence of at least two different pigments: the blue CuPc and the yellow monoazopigment acetoacetic arylide, see Figs. 5a and 5b. In fact, the intense bands at 1620, 1501, 1312, 1250, 1144 and 960 cm^{-1} along with the general spectral profile, Fig. 5c, is highly consistent with the Raman data reported [19] for acetoacetic arylide C.I. 11741 and the Hansa yellow reported by Burgio and Clark [21], reported as the pigment PY65 by Vandenabeele et al. [22]. Other bands in the spectrum mainly those at 1546, 742 and 687 cm^{-1} are consistent with the presence of CuPc. The bands assignment is displayed in Table 2 and it is based on published Raman data [18-26]. According to the molecular structure of CuPc and acetoacetic arylide, various functional chemical groups can be distinguishing. On this basis, it is possible to differentiate the corresponding Raman signals. This is the case for instance for the amide I and amide III vibrational modes (1650-1675 cm^{-1} and 1230-1280 cm^{-1}, respectively), the CH_3 deformation modes in the spectral range 1340-1400 cm^{-1}, NO_2 deformation modes (620-650 cm^{-1}) and the aromatic-chlorine stretching, between 300 and 400 cm^{-1} of acetoacetic arylide. In the case of CuPc some vibrations such as those involving the isoindolic moiety around 1312 and 776 cm^{-1}, the metal nitrogen stretching mode at 276 cm^{-1} and macrocycle ring deformation at 393 cm^{-1} can be differentiate. Several other bands arise from vibrations involving similar structural moieties such as the aromatic rings. Other bands were identified as belonging to the filler $CaCO_3$. Thus, the green color area in the *Rio* paint sample resulted from a combination of the yellow and blue pigments. It has been observed that the wavenumbers of the green color spectra in Fig. 5c, are not exactly the same of the references [19,21,22]; this is interpreted in terms that there is probably a rather feeble chemical interaction between both chemicals.

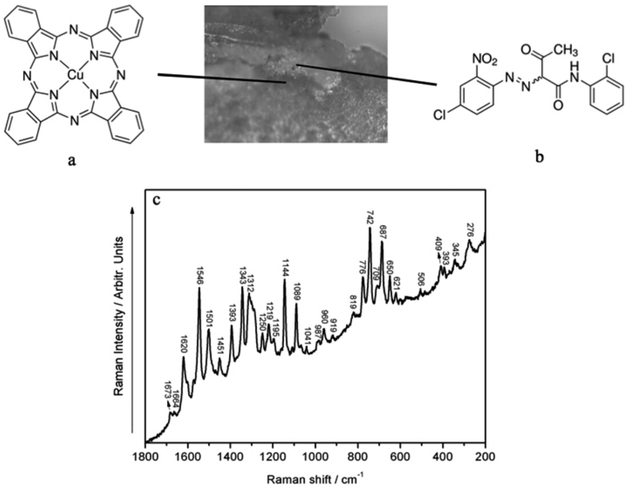

Figure. 5. *Río* paint cross-section. a) Cu(II) phthalocyanine and b) acetoacetic arylide model structures, and c) Raman spectrum of the green colored areas.

The paint *Saludo*. White fragment of the cross-section in this paint correspond mainly to rutile, see Fig. 6a; the polymorph anatase displays bands at 641, 517, 400 and 196 cm^{-1}. Green areas are dominated by a green CuPc, see Fig. 6b. Bands of the green pigment are intense, which is probably the reason of the dark green color fragments. The present spectrum is highly coincident with that reported by Chaplin et al.[27] and Poon et al.[28] for a green chlorinated copper phtalocyanine. Chaplin et al.[27] concluded that in the case of the screen alone, in a large painted leather screen and two illuminated title pages in 17th century books of ordinances of the Worshipful Company Barbers, London, that a restoration in the 1980s was carried out with different pigments – haematite, green Cu phthalocyanine, rutile, and a mixture of azurite, malachite and barium sulfate. Neither bands ascribed to chromium green $Cr_2O_3x2H_2O$, normally active at 611, 552 and 348 cm^{-1}, nor bands of the green chlorinated copper phthalocyanine C.I. 74250 reported by Scherrer et al. [19] were detected, thus discarding those compounds in the *Saludo* paint.

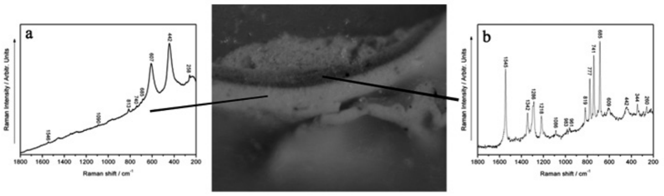

Figure. 6. *Saludo* paint cross-section. Raman spectra of the a) white and b) dark-green colored areas.

Table 2. Raman wavenumbers (cm^{-1}) and bands assignment of the spectrum in Fig. 5c for the green colored areas.

Wavenumbers and relative intensity	Most probable bands assignment
1673 vw*	Amide I, νCO** a.a.***
1664 vw	Amide I, νCO a.a.
1620 m	νCCφ, CuPc, a.a.
1546 s	νCCφ, νCN CuPc
1501 ms	νCCφ, CuPc, a.a.
1451 w	νCCφ, CuPc, a.a.
1393 m	δCH$_3$, νNO$_2$ a.a.
1343 s	δCH$_3$ a.a, νCN CuPc
1312 bms	νCNNC a.a, isoindole def.
1250 w	δCH, νCN a.a. Amide III
1219 m	νCN
1195 vw	δCHφ, νCC
1144 s	δCH a.a.
1089 ms	δCH, ν_sCO$_3$
1041 vw	ρCH$_3$ a.a, δCH
960 w	ρCH$_3$, δCH a.a.
919 vw	ρCH
819 vw	ρCH
776 m	ρCH, isoindole breath
742 s	CuPc. δCNC, δNCC
709 sh	δ_sCO$_3$
687 ms	ρCH, δCNC CuPc
650 m	δNO$_2$ a.a.
621 w	δNO$_2$ a.a.
506 vw	δNCO a.a.
409 w	macro. def. CuPc, $\nu\varphi$Cl a.a.
393 w	macro. def. CuPc.
345 w	macro. def. CuPc, $\nu\varphi$Cl a.a.
276 bm	νCuN, T(Ca CO$_3$)

* Bands intensity description: w, weak; vw, very weak; b, broad; mw, medium weak; s, strong; m, medium.

**Symbols: ν, stretching; ν_s, symmetric stretching; φ, aromatic ring; δ, deformation; δ_s, symmetric deformation; ρ, out-of-plane deformation; T, external vibration of the CO$_3$ group involving translatory oscillations of the group.

***Abbreviations: a.a, acetoacetic arylide; CuPc, Cu(II) phthalocyanine; breath, breathing mode; macro. def., macrocycle deformation; Cl, chlorine.

CONCLUSIONS

Three works of the artist Ignacio Gumucio, a wall painting *Mental* and two paintings with wooden stand *Río* and *Saludo*, were analyzed by using micro Raman spectroscopy. The blue, dark green and pink areas in the painting were identified as due to CuPc, acetoacetic arylide/CuPc, chlorinated CuPc and β-naphthol, respectively. Other materials in the artworks were also identified, the pigment rutile (TiO$_2$) in white areas and the filler calcite (CaCO$_3$). On this basis and taking into account the identification of the main pigments a protocol for the preservation of the artworks *Río* and *Saludo* could be proposed. In the case of the wall paint *Mental* a photographic record and or video describing the creative process of the artist and on the time that the artwork was exhibited are available on request. Solutions and strategies of a conservation protocol are multidisciplinary allowing entering to the specificity of the debate generated by new issues in the production of contemporary art. In the present case, the Raman analysis allowed to identify and characterize the materials used by Gumucio, thus being a contribution to conservation procedures, considering that many artists are not concerned with the composition of the materials used. The present work remains open to other scientific analyzes that complement and enable further study in other artworks in Chile allowing to develop complete conservation protocols.

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