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Materials and techniques of twentieth century Argentinean murals

Patrizia Moretti[a*], Damasia Gallegos[c], Fernando Marte[c], Bruno Brunetti[a,b], Antonio Sgamellotti[a,b], Costanza Miliani[a,b]

[a] *Istituto CNR di Scienze e Tecnologie Molecolari, CNR-ISTM, Via Elce di Sotto 8, 06123 Perugia, Italy*
[b] *Centro di Eccellenza SMAArt, Via Elce di Sotto 8, 06123 Perugia, Italy*
[c] *Instituto de Investigaciones sobre el Patrimonio Cultural (IIPC), Universidad Nacional de San Martín, Benito Quinquela Martín 1784, 1296 Buenos Aires, Argentina*

Abstract

In 1946 TAM (*Taller de Arte Mural*) a group of famous Argentine artists namely Castagnino, Spilimbergo, Urruchúa and Colmeiro, realized the decoration of four lunettes placed above the entrances of the *Galerías Pacífico* in Buenos Aires. Twenty-four samples coming from these lunettes have been analyzed by means the infrared transmission micro-spectroscopy to determine the composition of the preparation layer (mainly composed by gypsum) and the nature of binder (a drying oil), while the investigation of Raman micro-spectroscopy has allowed to identify the inorganic pigments and the synthetic organic dyes present.

Keywords: wall painting; modern pigments; synthetic dyes; Raman; FTIR

1. Introduction

This work is part of a collaborative research project among scientists and curators on a corpus of Argentinean mural paintings dated back to mid of the twentieth century, a distinctive historical moment that was characterized by a high technological innovation due to the fact that new synthetic paint materials were put on the market. The scientific characterization of materials and techniques of twentieth century Argentinean murals, carried out in this study, is aimed to answer doubts and questions arising during the recovery process of these emblematic paintings half of 20th century.

* Corresponding author. Tel.: +39-075-5855569; fax: +39-075-5855569.
E-mail address: m.patry@alice.it.

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David Alfaro Siqueiros, exiled from his native Mexico, arrived to the Río de la Plata at the beginning of the 1930s. With his *avant-garde* concepts on art and his revolutionary ideas, the conservative Argentina of that time was not an encouraging place to produce the remarkable and monumental murals he was used to do. For this reason, he developed his art in a private and almost hidden place like the cellar of villa *Los Granados*. The property belonged to Natalio Botana, owner of the successful newspaper *Crítica* and protector of Siqueiros since his arrival in Argentina [1].

Despite the intimate and confined nature of the basement, the vaulted structure of the space was, paradoxically, a perfect attraction for the Mexican painter. Influenced by Italian Futurism, and including the ideas of movement developed by the filmmaker Sergei Eisenstein, Siqueiros found on this architectural topography, the ideal support to paint the mural *Ejercicio Plástico* [1].

Together, with Lino Enea Spilimbergo, the young Juan Carlos Castagnino, Antonio Berni, and the Uruguayan playwright Enrique Lázaro, Siqueiros brought together and led the *Equipo Poligráfico*. This team carried out that magnificent visual illusion of figures that surround and involve the spectator.

Ejercicio Plástico was a turning point towards a new conception for mural painting. In this way, the mural was an innovation, not only in its painting technique and the tools, but also in its composition. Composed almost totally by swimming women, that look and explore in a display of foreshortening and wriggle silhouettes. This mural, without political or social content, was for Siqueiros an unusual and isolated event.

During his stay in Los Angeles, Siqueiros had begun looking for new materials and forms of execution. In the three murals painted in that city, he already used the airbrush to paint on the wall and he was also very interested in working with a team, in this specific case a group of students. These were important antecedents of his innovations [2].

The challenge of new supports, generally cement, required to give up the traditional fresco techniques. Also, the need to cover large areas in short periods of time imposed new painting methods. Mechanical tools replacing the brush and industrial paints were the chosen materials. Finally, after a hard work of sketches using multiple perspectives and aided by the projection of images, at the end of 1933, *Ejercicio Plástico*, has been completed [2].

In 1944, some artists from that team like Castagnino, Berni, Spilimbergo, formed together with Demetrio Urruchúa and Manuel Colmeiro, the *Taller de Arte Mural* (TAM). Two years later, the enormous dome of *Galerías Pacífico* was the propitious scenario for carrying out a significant set of murals. This colossal task was the first and only work of TAM team. However, although influenced by *Ejercicio Plástico*, these larger murals constituted the second phase of the mural art in Argentina. In this case, the painters worked in a more traditional manner, with traditional tools, helped with models and using flexible rules divided space into geometric shape [3]. Each artist painted a different theme in the assigned extension, with a single range of tones that served to maintain the unity of the whole area. By that period, TAM concern was the development of mural painting in Argentina and the experience at *Galerías Pacífico,* a prominent place in the city of Buenos Aires, anticipated a successful future. Nevertheless, the lack of support from the political sector, in the Argentina of the 1940s, that should had promoted this kind of cultural programs ended with the dissolution of the group [4].

In the 1990s *Galerías Pacífico* became a mall and the four mural paintings that covered the lunettes of the access were extracted and subsequently forgotten in a store. For more than fifteen years, the lunettes were abandoned and the damage suffered altered the appearance of them. Besides, an accidental fire that took place and destroyed the central part of *Otoño* image, painted by Castagnino. The losses exceed 50 per cent of the surface, distorting not only the correct reading of this work, but of the whole group, consisting of the four seasons of the year represented in each lunette.

This article is intended to show the results obtained from the material characterization of a specific group of murals painted by Lino Enea Spilimbergo (*Primavera*), Manuel Colmeiro (*Verano*), Juan Carlos Castagnino (*Otoño*) and Demetrio Urruchúa (*Invierno*). The research addresses then, the examination of materials and techniques of these Argentinean relevant artworks as a fundamental part of the mural history in Argentina and its relationship with Mexican muralism.

2. Materials and methods

2.1. Samples

The analyzed samples coming from the four lunettes are twenty-four. These samples have been named according to each corresponding author:

- seven samples coming from three areas of sampling (Fig. 1) in *Otoño* by Castagnino (Cast_1, Cast_2, Cast_6, Cast_7, Cast_8, Cast_9 and Cast_10);
- seven samples coming from three areas of sampling (Fig. 2) in *Primavera* by Spilimbergo (Spil_1, Spil_4, Spil_5, Spil_6, Spil_8, Spil_9 and Spil_14);
- five samples coming from three areas of sampling (Fig. 3) in *Verano* by Colmeiro (Col_1, Col_2, Col_3, Col_4 and Col_7);
- five samples coming from two areas of sampling (Fig. 4) in *Invierno* by Urruchúa (Urr_1, Urr_2, Urr_5, Urr_8 and Urr_12).

Some samples, available in more than a fragment, have been prepared as cross-section, using a pretreatment with cyclododecane (CDD) [5]. For the preparation of these cross-sections an epoxy resin (weight ratio resin-catalyst equal to 100:45) able to harden in contact with air in 24-36 hours has been used. CDD having the property to sublimate at room temperature, has been used in order to form a barrier against the intrusion of the resin inside the sample.

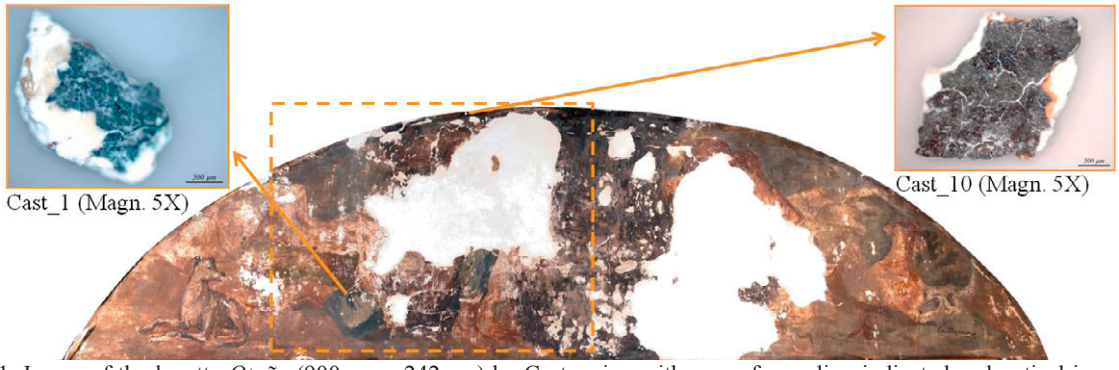

Fig. 1. Image of the lunette *Otoño* (900 cm x 242 cm) by Castagnino with area of sampling indicated and optical images of two samples.

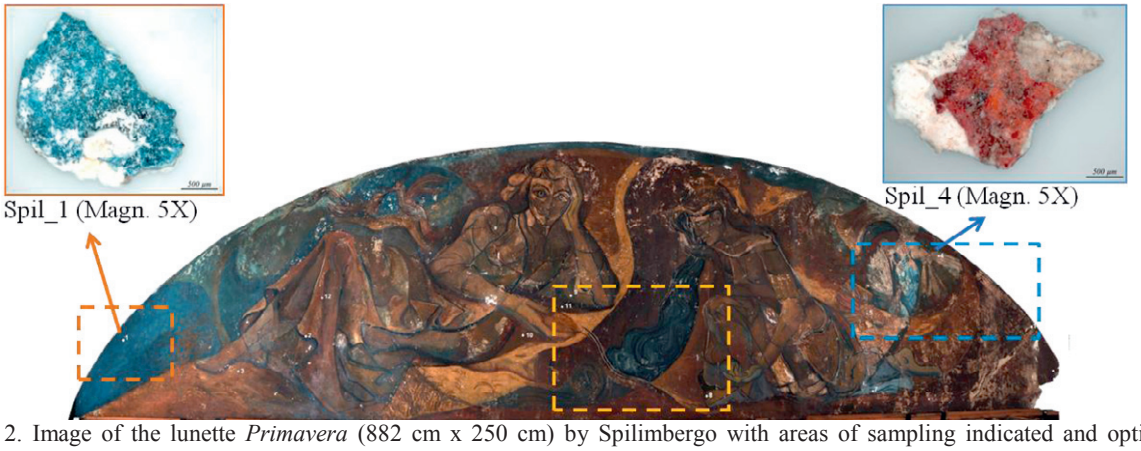

Fig. 2. Image of the lunette *Primavera* (882 cm x 250 cm) by Spilimbergo with areas of sampling indicated and optical images of two samples.

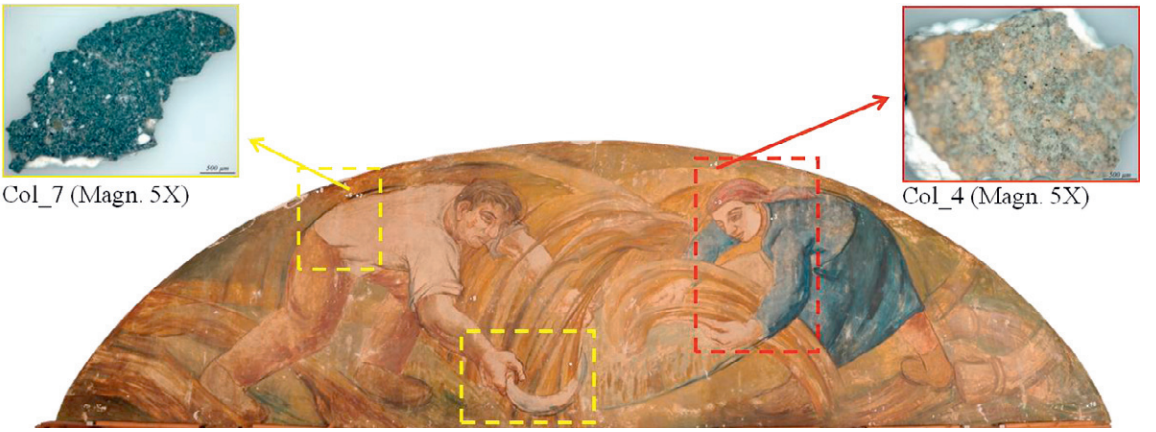

Fig. 3. Image of the lunette *Verano* (900 cm x 242 cm) by Colmeiro with areas of sampling indicated and optical images of two samples.

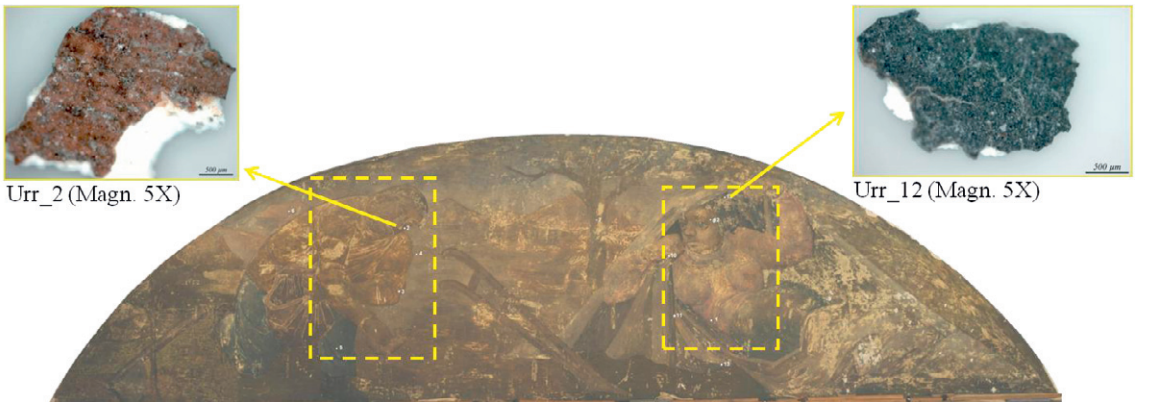

Fig. 4. Image of the lunette *Invierno* (900 cm x 242 cm) by Urruchúa with areas of sampling indicated and optical images of two samples.

2.2. Instrumentation

2.2.1. Optical microscope

All the loose samples and the cross-sections, were observed using a Leica DMRX Optical Microscope, to perform a first morphological characterization. Optical images were captured by a Digital Camera Leica DC 300 in reflection mode using polarized visible light and at several different magnifications (5x, 10x and 40x).

2.2.2. Micro-FTIR spectroscopy

Micro-destructive FTIR analyses were carried out by a Jasco FTIR 4100 spectrophotometer, equipped with a nitrogen cooled mercury cadmium telluride (MCT) detector and a Jasco IMV 4000 optical microscope. The measurements were performed in transmission mode using a diamond cell with a Cassegrain 16x objective, in the range 600 - 4000 cm^{-1}, with a spectral resolution of 4 cm^{-1} and adding 1200 scans. These measurements have been carried out on minute portions selectively taken from preparation and paint layer of each sample and pressed between two diamond cells to obtain a thin thickness transparent at the infrared radiation. The single-beam spectrum was always rationed to the single-beam spectrum of the background (diamond cell).

2.2.3. Micro-Raman spectroscopy

Micro-Raman measurements were performed with a laboratory NRS-3100 spectrophotometer equipped with: Ar^+ laser source with wavelengths of excitation equal at 488 or 514 nm, a diode laser emitting at 785 nm, a triple grating (800 l/mm, 1200 l/mm and 1800 l/mm), an optical microscope provided with four objectives (5x, 20x, 50x and 100x) and a charge-couple device (CCD) detector cooled to -50°C with a Peltier cooling system. For these measurements have been utilized the 488 nm emission and the 1200 l/mm grating to obtain a spectral resolution of 2 cm^{-1}. The areas of interest on the surface of all samples and on the cross-sections of some of them have been focused with the objective 100x, while the spectra were recorded in the range 200 - 2000 cm^{-1} by adopting different values of the exposure time, from 2 to 10 s, the number of accumulations, from 5 to 20 and the laser power, ranging from 0.3 to a maximum of 2.7 mW.

3. Results and discussion

The twenty-four samples coming from the four lunettes placed above the entrances of the *Galerías Pacífico* in Buenos Aires, have been analyzed by spectroscopic techniques with the principal aim to provide a complete characterization of the original materials of both the preparation and the paint layer, ultimately to identify the painting technique used by the artists. In particular, the infrared transmission measurements have provided useful information in determining the composition of the preparation layer and the nature of the binder, while the obtained results by Raman analyses have allowed to identify both inorganic pigments and synthetic organic dyes.

3.1. Preparation layer

For the analysis of the composition of the preparation layer a selective sampling from the back of each sample has been carried out. The infrared analyses of these fragments have allowed to find the presence of gypsum in the preparation layer of all four the lunettes. Moreover, the gypsum has been identified also in all spectra acquired for the paint layer of the examined samples. In these spectra (Fig. 5 a), in fact, the signals generated by O-H stretching (3547 and 3407 cm^{-1}) and bending (1684 and 1620 cm^{-1}) and the absorptions relative at the S-O stretching (1151 and 1122 cm^{-1}) and bending (669 and 600 cm^{-1}), can be observed. Only in the samples coming from the lunette painted by Castagnino (*Otoño*) have been identified also the hemihydrate and anhydrous forms of the calcium sulphate (Fig. 5 b), respectively bassanite ($CaSO_4 \cdot 1/2H_2O$) and anhydrite ($CaSO_4$). In the case of bassanite it can be noted a shift of the hydroxyl groups towards more high frequencies (3614 and 3560 cm^{-1}), while in the spectrum of anhydrite these signals do not appear [6]. The presence of bassanite and anhydrite in the samples coming from this painting can be correlated to the fire suffered by the lunette that could have caused the dehydration of the original gypsum. In addition in the spectra recorded for the analysis of the plaster in the lunette by Castagnino (Fig. 5 a, b) are observed also the typical absorption bands of the calcium carbonate at 2510 cm^{-1} (combination band $\nu_1 + \nu_3$ of CO_3^{2-}), 1794 cm^{-1} (combination band $\nu_1 + \nu_4$ of CO_3^{2-}), 1446 cm^{-1} (ν_3 of CO_3^{2-}), 876 cm^{-1} (ν_2 of CO_3^{2-}) and at 712 cm^{-1} (ν_4 of CO_3^{2-}) [7]. The calcium carbonate, therefore, can be considered an integral part of the preparation layer only in the lunette by Castagnino, as in the other paintings this material has been identified exclusively in the paint layer.

3.2. Nature of the binder

The investigations for the characterization of the binder used by the Argentine painters have been performed by means of infrared analysis of the paint layer of each sample. In the majority of the spectra acquired (Fig. 6 a) can be observed strong signals at 2925 cm^{-1} (ν_{as}) and at 2854 cm^{-1} (ν_s) of the C-H methylene and the band at approximately 1738 cm^{-1} assigned to the -C=O ester carbonyl [8]. The position and shape of these signals strongly suggested the presence of a drying oil in all examined samples, except for two samples coming from the lunette by Spilimbergo in which an acrylic binder was identified. In the spectra recorded for these samples (Fig. 6

b), in fact, can be noted a different shape of the signals of the C-H and a series of structured bands between 1500 and 1300 cm^{-1} that are well correlated with an acrylic binder. Probably this type of binder was employed in a subsequent intervention of restoration as the first experimentations of acrylics date back at the fifties [9], about a decade after the realize of the four lunettes.

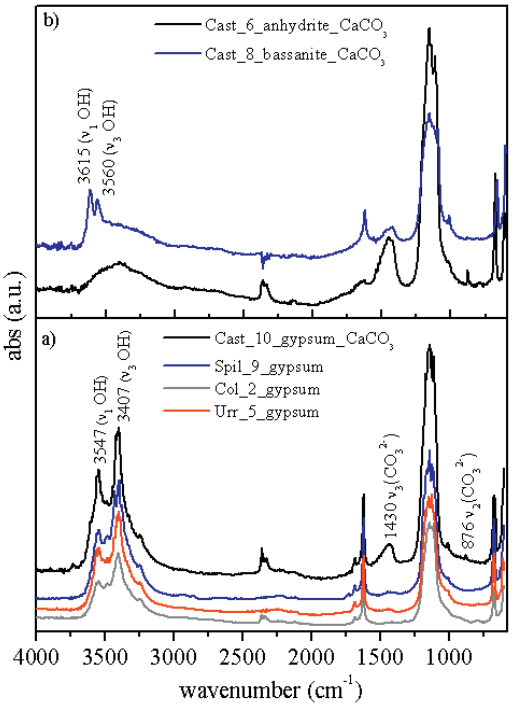

Fig. 5. Micro-FTIR spectra of the preparation layer of some samples: a) gypsum and calcium carbonate (only in the sample of Castagnino); b) bassanite, anhydrite and calcium carbonate.

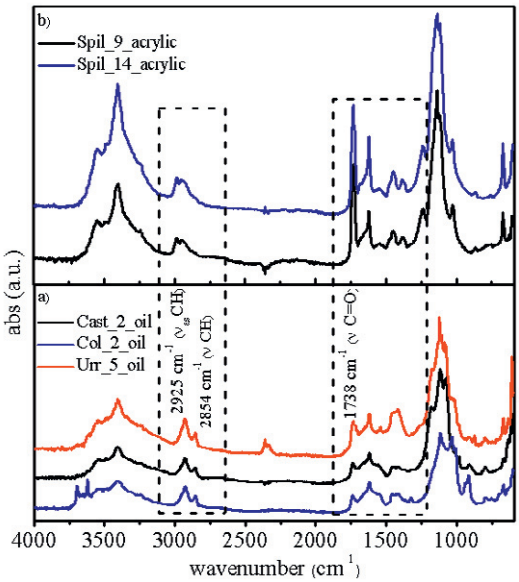

Fig. 6. Micro-FTIR spectra of the paint layer of some samples: a) drying oil; b) acrylic binder.

3.3. Pigments

The results obtained by Raman analyses have allowed both inorganic pigments and synthetic organic dyes to be identified. The measurements have been carried out on the surface of all samples and on the cross-sections of some of them. The analysis in cross-sections, in particular, have enabled to verify and to analyze overlapping layers of color present in some fragments. Below are the Raman data related to the identified pigments separated for chromia.

3.3.1. Red pigments

Three different red pigments have been identified: a inorganic pigment, hematite, and two synthetic organic dyes monoazo, namely PR 49:1 and PR 166 (Fig. 7 a). In particular, the hematite (Fe_2O_3) was found in the samples Cast_2, Urr_2, in the cross-section of the sample Spil_14 and in a small crystal of the sample Col_3. In these spectra, in fact, can be observed the signals at 222 cm^{-1} (ν_s), 292 cm^{-1} (ν_s) and at 396 cm^{-1} (ν_s) related to the bond Fe-O [10]. In the sample Spil_14 these signals appear along with those of the barium sulfate, while in the case of the sample Urr_2 can be noted also the strong bands attributed to phthalocyanine blue. For the samples Spil_4, Col_2 and Urr_1, instead, have been identified the characteristic signals of the monoazo pigment PR 49:1 at 480 cm^{-1}, 722 cm^{-1} (s), 995 cm^{-1}, 1097 cm^{-1} (m), 1211 cm^{-1} (vs), 1346 cm^{-1} (s), 1413 cm^{-1} (vs), 1484 cm^{-1} (vs), 1554 cm^{-1} (m) and at 1605 cm^{-1} (m) [11]. Finally, in the Raman spectrum recorded for the sample Spil_5 the weak bands at 1282 cm^{-1}, 1365 cm^{-1} and at 1485 cm^{-1} suggest the presence of an other monoazo pigment [12], the PR 166.

3.3.2. Yellow pigments

The identified yellow pigments are: two inorganic pigments, as goethite (FeOOH) and zinc yellow ($ZnCrO_4$), and two monoazo organic pigments, namely PY 3 and PY 74 (Fig. 7 b). In the Raman spectra acquired for some brown crystals in the samples Spil_9, Col_1 and Col_7 can be observed the characteristic signals of the goethite at 296 cm^{-1} (δ_s of Fe-OH) and at 393 cm^{-1} (ν_s of the bond Fe-O-Fe/-OH) [10]. In the case of the sample Spil_9, these signals appear along with those of the phthalocyanine blue. The zinc yellow characterized by Raman signals at 870 cm^{-1} (s), 890 cm^{-1} (m) and at 938 cm^{-1} (m) [13], instead, was found in three samples: Col_1, Col_4 and Col_7. Probably in this latter the zinc yellow was added to the phthalocyanine blue to form the green color of the sample. Also in the samples of green color Spil_1 and Spil_6 the identified yellow pigment, the PY 3, was added to the unknown blue pigment. The dye PY 3 presents strong Raman bands at 410 cm^{-1} (m), 700 cm^{-1}, 744 cm^{-1} (m), 1137 cm^{-1} (vs), 1191 cm^{-1} (m), 1228 cm^{-1} (s), 1334 cm^{-1} (vs), 1388 cm^{-1} (s), 1492 cm^{-1} (vs) and at 1611 cm^{-1} (vs) [12]. In the spectrum recorded for the sample Spil_8 in addition at the signals of the rutile there are also those at 803 cm^{-1} (m), 1166 cm^{-1} (m), 1265 cm^{-1} (s), 1333 cm^{-1} (vs), 1407 cm^{-1} (m), 1507 cm^{-1} (m) and at 1594 cm^{-1} (s) [12] related to monoazo pigment PY 74.

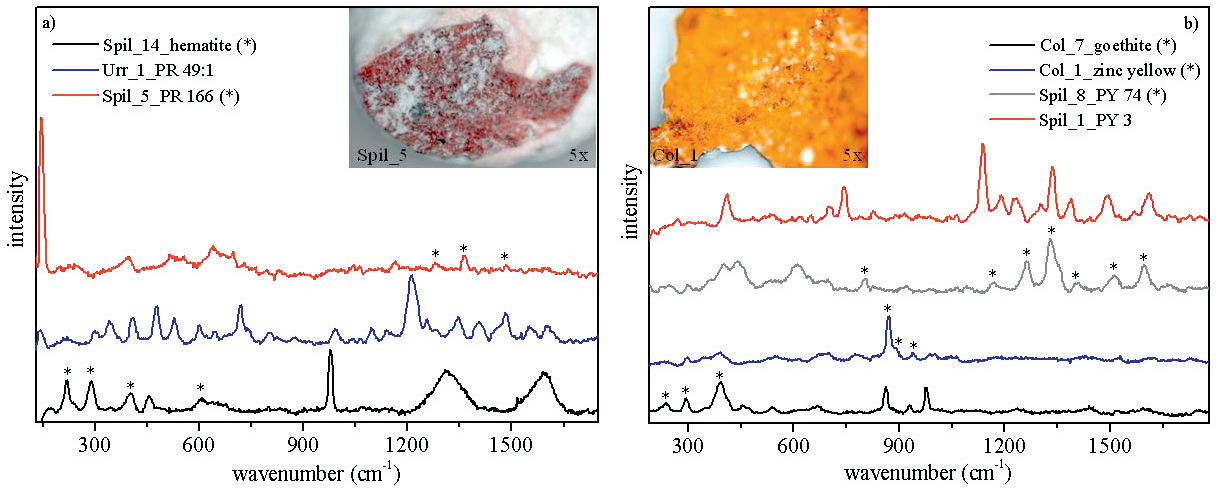

Fig. 7. Micro-Raman spectra: a) red pigments identified in some samples (inset: microphoto of the sample Spil_5, 5x magnification); b) yellow pigments identified in some samples (inset: microphoto of the sample Col_1, 5x magnification).

3.3.3. Blue pigments

In many of the analyzed samples (Cast_1, Cast_9, Cast_10, Spil_4, Spil_9, Spil_14, Col_7, Urr_1, Urr_2 and Urr_5) the phthalocyanine blue ($C_{32}H_{16}N_8Cu$) has been identified (Fig. 8 a). This synthetic organic dye is characterized by the Raman signals at 1525 cm^{-1} (vs), 1449 cm^{-1} (s), 1335 cm^{-1} (vs), 680 cm^{-1} (ms) and at 592 cm^{-1} (ms) [12]. In the samples coming from the painting by Spilimbergo the phthalocyanine blue was found by means of the Raman analysis in cross-section, in a layer below at the surface, while in the samples Urr_1 and Urr_2 this blue pigment was determined on some dark crystals dispersed in other pigments. In addition in the lunette by Castagnino was found also the ultramarine blue ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$). In the micro-Raman spectra of the samples Cast_9 and Cast_10 can be observed the bands at 255 cm^{-1} (ν_2), 542 cm^{-1} (ν_1), 1083 cm^{-1} (2 ν_1) and at 1630 cm^{-1} (3 ν_1), generated by the S_3^- radical anion of the ultramarine [14]. The presence of this pigment, moreover, was confirmed by the kaolin [$Al_2Si_2O_5(OH)_4$], identified in the infrared spectra recorded for these samples. Often, in fact, the kaolin can be found in the ultramarine artificial blue as residual of the synthesis process [15].

3.3.4. White and black pigments

The white pigment identified in the majority of the analyzed samples (Cast_2, Cast_9, Cast_10, Spil_1, Spil_4, Spil_9, Spil_14, Col_2, Col_3, Col_4, Col_7, Urr_1, Urr_2, Urr_5 and Urr_8) is the barium sulfate with its characteristic Raman signals at 460 cm^{-1}, 617 cm^{-1} and at 986 cm^{-1} [13]. In addition in two samples coming from the lunette by Spilimbergo was found the titanium dioxide, in both of its crystalline forms, named anatase and rutile. In particular, the typical bands of the anatase at 145 cm^{-1} (vs), 395 cm^{-1} (w), 512 cm^{-1} (w) and at 632 cm^{-1} (m) [13] have been identified in the samples Spil_9 and Spil_5, while the rutile was recognized only in the sample Spil_8 (Fig. 8 b). Finally the only black pigment identified in a only sample (Cast_6) is the carbon black (Fig. 8 b), characterized by the strong Raman signals at 1346 cm^{-1} and at 1597 cm^{-1} [16]. Probably the nature of this black pigment is vegetable, as in the infrared spectrum acquired for the paint layer of the sample Cast_6 do not appear the signal at 2010 cm^{-1} specific for the presence of the bone black [17].

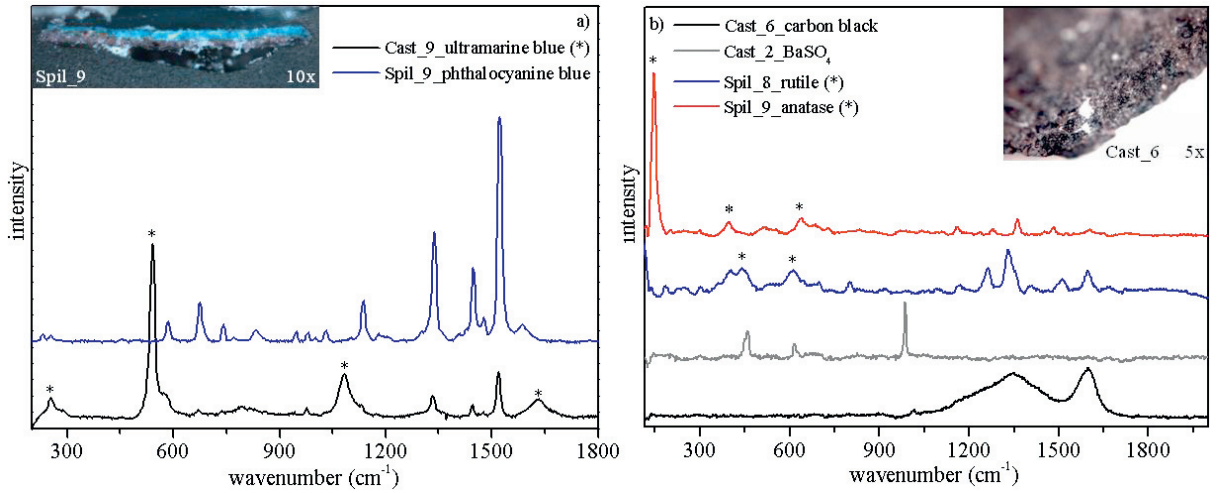

Fig. 8. Micro-Raman spectra: a) blue pigments identified some samples (inset: microphoto of the cross-section Spil_9, 10x magnification); b) white pigments identified in samples and the only black pigment found in the sample Cast_6 (inset: microphoto of the sample Cast_6, 5x magnification).

4. Conclusion

The experimentation carried out in this study has allowed to obtain results useful for the characterization of the polychromatic materials of the four lunettes placed above the entrances of the *Galerías Pacífico* of Buenos Aires. The investigation micro-FTIR in transmission using a diamond cell, performed on fragments taken from the preparation and paint layers, has provided important information about the composition of the preparation layer and the nature of the binder. In particular, the preparation layer has resulted to be mainly composed by gypsum that has been found in all samples examined. This material has been found in the fragments taken from the preparation layer and in that pictorial, while the calcium carbonate can be considered an integral part of the plaster only in the lunette by Castagnino. In the other paintings, in fact, the calcium carbonate has been identified exclusively in the paint layer. In addition in some samples of the lunette by Castagnino have been found the hemihydrate, bassanite, and anhydrous, anhydrite, forms of the calcium sulfate. The samples characterized by the presence of bassanite and anhydrite coming from the most altered part by the fire, therefore these materials could be the result of a process of dehydration of the original gypsum. For this reason it is necessary taking into consideration the possibility to develop a process of re-hydration in phase of restoration.

As for the nature of the binder, in the majority of the analyzed samples the presence of a drying oil was suggested by the strong signals of the C-H methylene and the -C=O ester carbonyl present in the infrared spectra acquired for the paint layer. Only in two samples coming from the lunette by Spilimbergo an acrylic binder has been identified, probably this binder was used in subsequent retouches to which the artwork was subjected. The use of acrylics, in fact, is documented since the fifties [9]. Actually, Berni said that by the end of 1970s he "restored" the murals; he was advice by specialists from one of the largest paint factories that even prepared the paint he used during the restoration [3].

The micro-Raman analyses, instead, have proved useful to identify the pigments used by these Argentine painters. The results have been obtain by means of a series of measurements performed on the surface of all samples and on the cross-sections of some of them. The identified pigments are both inorganic pigments (hematite, goethite, zinc yellow, ultramarine blue, titanium dioxide, barium sulphate and carbon black) and

synthetic organic dyes (phthalocyanine blue, PR 49:1, PR 166, PY 3 and PY 74), the use of which was developed since half of the nineteenth century [18].

The decoration of the *Galerías Pacífico* is emblem of the muralist tradition in Argentina and its realization was surely influenced by the arrival in the country of a great innovator like the Mexican muralist Siqueiros.

The researches approached in this work represent, therefore, a first step towards the characterization of the materials and the investigation of new painting techniques that have marked the Latin-American artistic scenario of the twentieth century.

Acknowledgements

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