Investigation and Characterization of Artistic Techniques in Works of Modern and Contemporary Art

The scientific study of pigments and materials used by painters in their works is clearly important for the knowledge of the different artistic techniques, for planning the appropriate interventions of cleaning and restoration of the paintings. Moreover, identification of industrial varnishes and pigments in artistic works often helps the art historian and the conservator to date the considered paintings or, at least, to define post quem chronology.
The present research and study, conducted on titanium white and its applications in the field of historical works of art, is focused on two important but different artists and related paintings of the modern era as Sargent's "Caffè Orientale sulla Riva degli Schiavoni", oil on canvas, 1882, and Picasso's "Cubist Figure", oil on canvas, 1909. The analysis has been carried out using modern diagnostic technology: stereomicroscope and SEM/EDAX

Stefania Bruni, Giuseppe Maino, Carmela Vaccaro, Lisa Volpe

Introduction

The study of color is a very complex research field since color is not to be considered only as a natural phenomenon, but a "complex cultural construction that avoids generalizations and presents difficult problems, [...] the color is primarily a social fact" [1]. This concept is particularly reflected by the color, subject matter of this study: The white pigment based on titanium.
The titanium white is a pigment consisting of titanium dioxide, calcium sulfate and barium sulfate. In nature, titanium exists in various forms (brookite, rutile and anatase) and was discovered in 1791 thanks to rev. W. Gregor, who identified it in ilmenite rocks. Further research – which took place in subsequent years and aimed at finding a pigment with more pros and non-toxic property with respect to the white pigment used until the beginning of XX century (lead white, etc.) – led the chemist H. Rose, in 1821, to discover the compound of titanium dioxide. Officially, the production of this pigment on an industrial scale began from 1916-1918. Although titanium traces can be found in pigments and ink manufacturing prior to 1900, the frequent use of this pigment, in particular the artificial one, will start from 1908. The spread in Europe of titanium artificial white, in particular, will develop from 1910 onwards, when the European Community banned the use of white lead, considered toxic. Several studies have demonstrated the presence of industrial titanium white pigment in

Stefania Bruni
ENEA, Unità Tecnica Ingegneria Sismica
Giuseppe Maino
Unità Tecnica Metodi per la Sicurezza dei Reattori e del Ciclo del Combustibile
Carmela Vaccaro, Lisa Volpe
Università di Ferrara

paintings dated around 1908, thus corresponding to the artists' period of experimentation in leading centers, such as Paris, with these new industrial products.
The present research and study, conducted on titanium white and its applications in the field of art-historical works, is focused on two important but different artists and their related paintings of the modern era as Sargent's *"Caffè Orientale sulla Riva degli Schiavoni"*, oil on canvas, 1882, and Picasso's *"Cubist Figure"*, oil on canvas, 1909. Other paintings, namely "Pond" (oil on plywood, 1885 approx.) by a follower of Claude Monet, *"Scholar with the picture book"* (oil on canvas, 1905 ca.) by Amedeo Modigliani, did not show any presence of titanium white as expected, since Modigliani's work belongs to the first Italian period of the artist, whereas the other oil is attributed to a follower.
These two former works have been analyzed using modern diagnostic technology, stereomicroscope, SEM/EDAX, etc. for a better understanding of painting techniques, pigments and materials used by the two artists, with particular attention to the white pigment of titanium, thus deriving information about its possible date and state of preservation, the support too, and a possible future restoration and/or maintenance.

Results

Samples are observed by using a stereomicroscope OPTIKA SZ6745TR (total magnification 90x), equipped with a webcam MOTICAM 2005 5.0 Mp, and the diagnostic tests were performed on Sargent's and Picasso's paintings, by using a scanning electron microscope (SEM) and electronic microanalysis EDAX (Fig. 1), at the Laboratory of Electron Microscopy UTSISM ENEA-Bologna.

Analysis of Sargent's Painting

The study, aimed primarily at identifying the pigments used, focused on the analysis of some samples taken in different areas of the painting, corresponding to regions of light color or white color (Fig. 2) before starting restoration.
The relevant study allowed us to identify different pigments of industrial origin. In particular, the

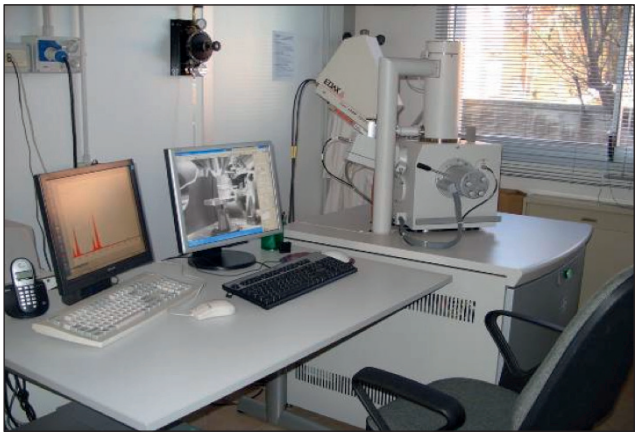


FIGURE 1 Laboratory SEM/EDXRS
Source: ENEA

FIGURE 2 John Singer Sargent - Caffè Orientale sulla Riva degli Schiavoni - oil on canvas, 1980/1882 (Private collection): sampling points
Source: ENEA

electronic microanalysis of the samples has proved that the pigment is a light-colored titanium white. The chemical microanalysis, in fact, has revealed the presence of elements characteristic of this pigment, like titanium, barium, sulfur, calcium and oxygen, as shown in the following spectrum (Fig. 4) and the corresponding table.
In the observed form, titanium is a white pigment consisting of titanium dioxide, calcium sulfate and barium sulfate and, being extracted from the mineral

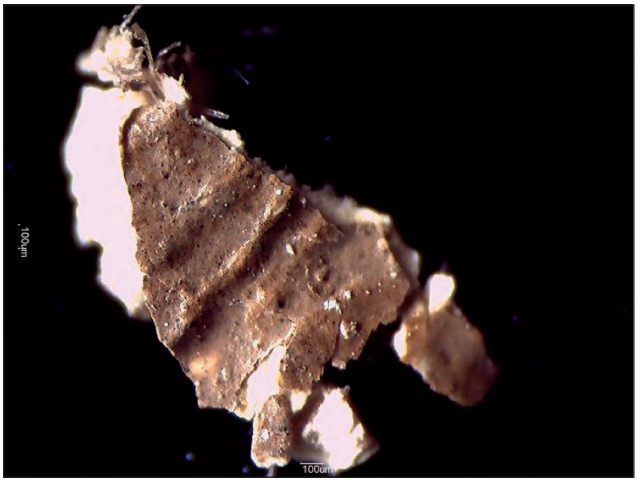
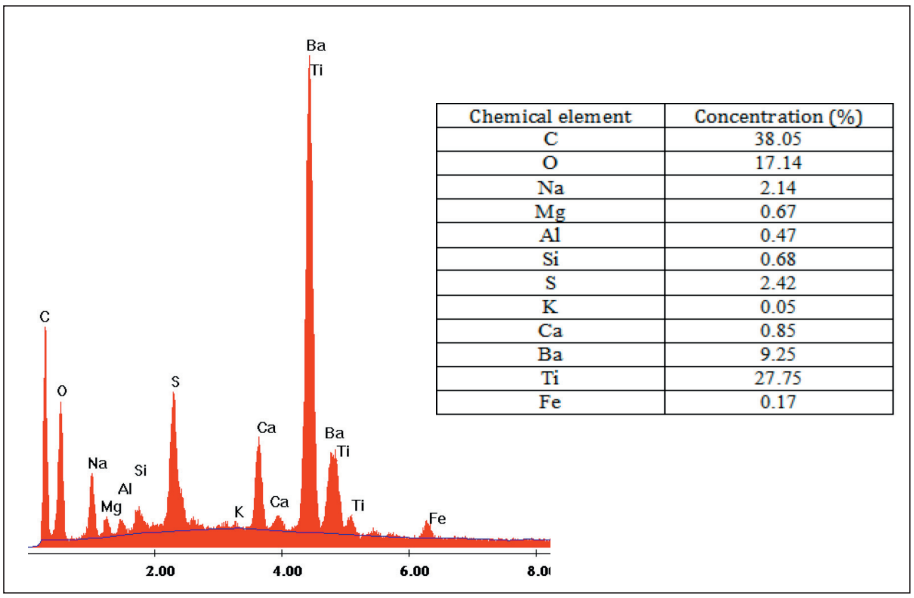


FIGURE 3 Stereomicroscope analysis of a Sargent's sample
Source: Università di Ferrara, Dip. di Scienze della Terra

ilmenite, an iron and titanium oxide (FeTiO3), it may also present iron, silicon, aluminum, magnesium, sodium and potassium in lesser concentration.
From the morphological point of view, the pigment is characterized by small rounded crystals with homogeneous particle size, due to the process of industrial production of the pigment itself. Moreover, analysis of the samples allowed to notice some areas with slightly darker images, characterized by rounded particles larger than those found in areas of pure titanium white.
The latter, in fact, shows particles of infinitesimal size, homogeneous among them and representing – from microanalysis investigation – pure titanium white pigment, unlike those found in a darker region, shown in the former figure, which are the largest form of agglomerations and arise from a mixture of different colored pigments. This may arise because, to get different tones, the white pigment was mixed with other pigments of organic origin or with a medium.
In conclusion, the electronic microanalysis in all analyzed Sargent's samples has identified the pigment as a light-colored titanium white, highlighting the presence of characteristic elements, such as titanium, sulfur, calcium and oxygen (Fig. 6).
It is worth remarking that a related watercolor painting (1880-1982, watercolor on paper, 24.8 x 34.3 cm, private collection) was displayed on the occasion of the exhibition, *Gondola Days: Isabella Stewart Gardner and the Palazzo Barbaro Circle*, Isabella Stewart Gardner Museum, Boston, April 21 - August 15, 2004. Due to the similarities with this work, that of Fig. 2, subject matter



Chemical element	Concentration (%)
C	38.05
O	17.14
Na	2.14
Mg	0.67
Al	0.47
Si	0.68
S	2.42
K	0.05
Ca	0.85
Ba	9.25
Ti	27.75
Fe	0.17

FIGURE 4 SEM/EDXRS analysis of Sargent's sample: White Titanium Oxide
Source: ENEA

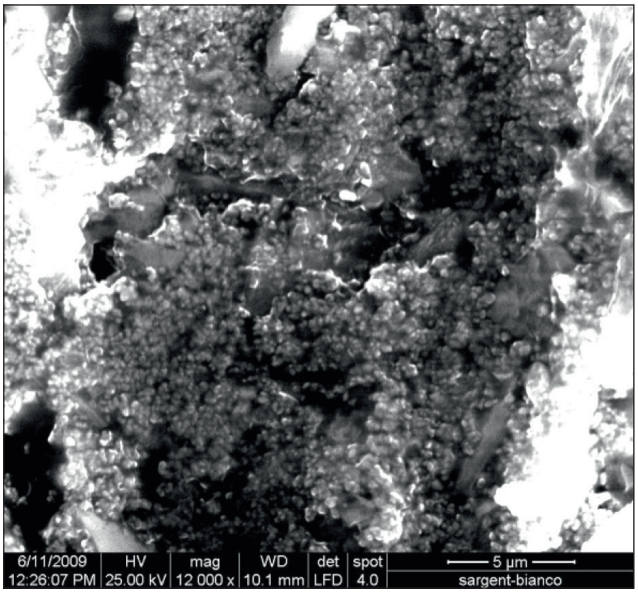


FIGURE 5 SEM analysis of a Sargent's sample
Source: ENEA

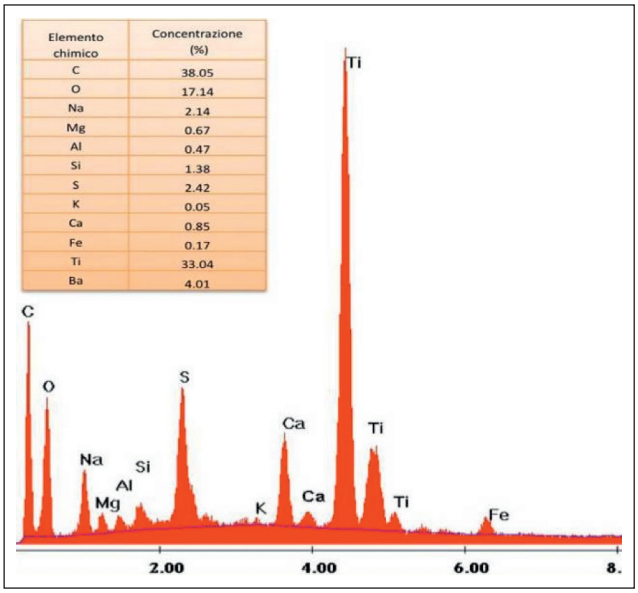


FIGURE 6 SEM/EDXRS Sargent's sample: Titanium White
Source: ENEA

of the present study, was then dated to 1880, but the current findings about the presence of titanium white allow us to propose another dating, close to 1913, when Sargent travelled again to Italy and Venice.

Analysis of Picasso's Painting

In order to extend our investigation to the introduction of artificial titanium white in paintings at the beginning of the XX century, we performed other SEM observations and the relevant microanalysis on a few tiny samples taken from a painting attributed to Picasso (*Cubist figure,* oil on canvas, fig. 7) and dated around 1909. As a matter of fact, the painting appears to be signed and to have a date of '9' near the word 'Picasso'.
The analysis by SEM/EDAX showed the characteristic appearance of titanium white granules, confirmed by microanalysis. In this case, however, one may notice that, in the samples of Picasso's painting the pigment granules are not of perfectly spherical shape, and the microanalysis shows a different chemical composition than that found in the samples of Sargent's work discussed in the previous section; in fact, elements such as sulfur, aluminum, sodium, silicon and calcium are missing. It would seem, therefore, that in Picasso titanium white can be natural and not artificial, as found in the samples of Sargent's painting.

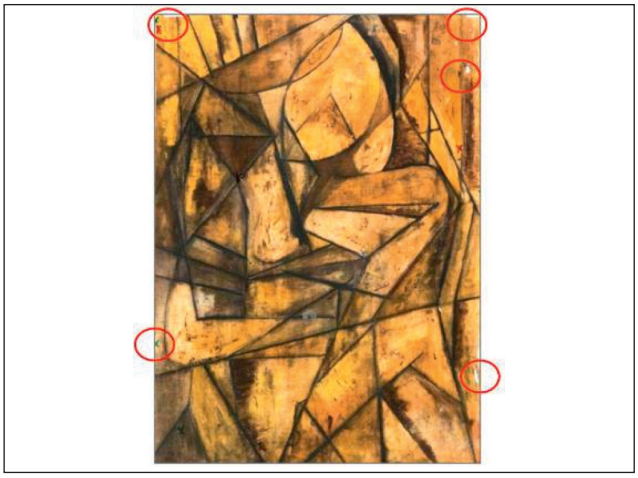
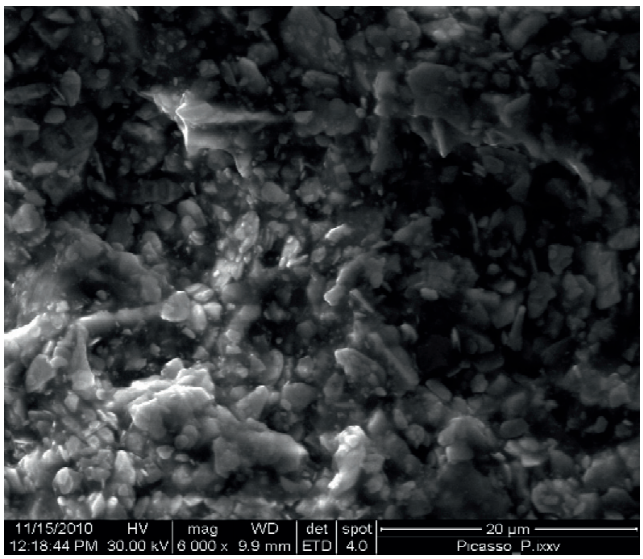


FIGURE 7 Sampling points on "Cubist figure" by P. Picasso (Private collection)
Source: ENEA



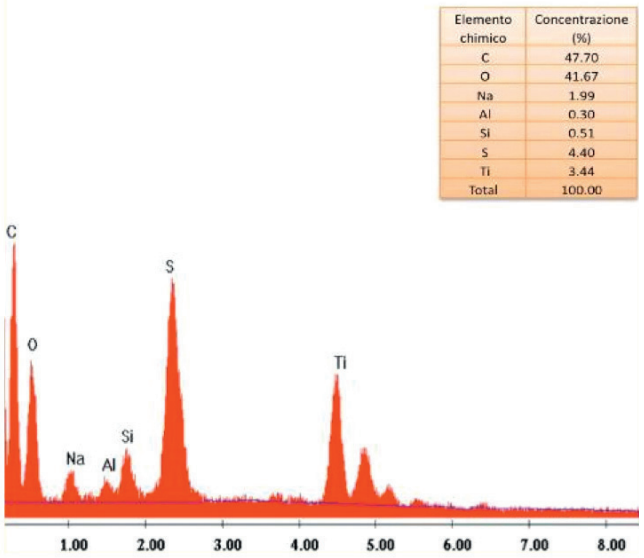


FIGURE 8 SEM/EDAX investigation of Picasso's sample with titanium white
Source: ENEA

Finally, the stereo microscope analysis of Picasso's samples showed that, as for the pigment, the coating is 70 µm thick and it was applied directly onto the canvas, since it is not indeed present in the preparatory layer (Fig. 9).

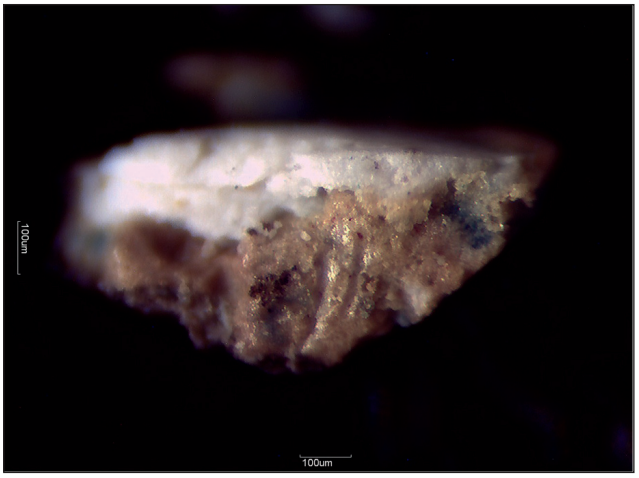


FIGURE 9 Picasso's sample analysis under the stereomicroscope (90X)
Source: Università di Ferrara, Dip. di Scienze della Terra

Further analyses were performed at the University of Melbourne. Before the SEM microanalysis, a non-destructive investigation was carried out by means of X-ray fluorescence (XRF) with a portable equipment, a Keymaster Bruker portable XXRF Tracer III-V. Results show the presence of elements usually found in pigments such as ochre, barium white, verdigris, lead white and strontium yellow. Also chromium and zinc were found, the latter on the verso of the painting, whereas lead is on the recto. All these data have been then confirmed by the microscopic analyses of the Australian group as well as by our studies.
Important information is provided by the Commonwealth Scientific and Industrial Research Organization (CSIRO; Clayton, Victoria, Australia), the Australia's national science agency, where a Raman spectroscopy analysis was conducted in April, 2010. The Raman spectra indicated the rutile form of titanium, as explained in the relevant Preliminary Report.
Rutile is the most common form of titanium and the Hunter process allows the production of high-quality titanium from it. The Hunter process dates to 1910 and, therefore, the presence of titanium white in this painting is not contradictory with a dating around 1909.

In conclusion, the materials used and the techniques adopted are compatible with an attribution to the Cubist period of Picasso; however, any definite authentication assessment must rely on the provenance and an art-historical study of this work.

Conclusions

The methods of investigation applied to the two works by Sargent and Picasso have revealed two different types of pigment, artificial vs. natural, obtained from different production processes, comparing two well-known painters of different generations and artistic currents, as J.S. Sargent and P. Picasso.

References

[1] L. Appolonia, S. Volpin, *"Le analisi di laboratorio applicate ai Beni artistici policromi"*, Il Prato (2002).

[2] M. Pastoureau, *"Bleu: Histoire d'une couleur"*, Du Seuil (2002), cons. ed. "Blu. Storia di un colore", Saggi Ponte alle Grazie (2008).

[3] M. Laver, *"Titanium Dioxide Whites"* in "Artists' Pigments. A Handbook of Their History and Characteristics", 3, Elisabeth West Fitzhugh, ed., National Gallery of Art, Washington D.C. and Oxford University Press (1997), 295-355.

[4] R. Mayer, *"The Artist's Handbook of Materials & Techniques"*, 5th edition revised and expanded by Steven Sheehan, London (1991), 116.

[5] N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall, *"Pigment Compendium, A Dictionary of Historical Pigments"* (2004), 364-366.

[6] *"Pigment Compendium, A Dictionary and Optical Microscopy of Historic Pigments"* (2008).

[7] L. De Rossi, *"John Singer Sargent, Caffè Orientale sulla Riva degli Schiavoni a Venezia"*, in Arte | Documento 23, Edizioni della Laguna (2008), 236-239.