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FROM PIGMENTS TO PAINTS: STUDYING ORIGINAL MATERIALS FROM THE ATELIER OF THE ARTIST MARIANO FORTUNY Y MADRAZO

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Abstract

We present the first study related to the painting materials used by Mariano Fortuny y Madrazo (Granada 1871 - Venice 1949). This eclectic artist, whose activities ranged from photography to painting, produced his own tempera colours Tempere Fortuny. His atelier in Palazzo Pesaro degli Orfei in Venice still conserves several kinds of painting materials employed in different stages of paint manufacture: from raw colourant materials (e.g. pigments and dyes) to a ready-to-use paint tube containing a complex mixture of pigment, binder ad additives. Micro samples collected from 29 "raw" materials and 2 handcrafted coloured paint mixtures were characterised by XRF, FT-IR and PyGCMS analysis. Through this multi-analytical approach, both inorganic and organic fractions were detected. According to the obtained results, Mariano Fortuny used both traditional and innovative materials- commercial products which were available at his time and sold for artistic practice and paint manufacture. This study allowed to understand the procedures followed by Fortuny in the production of his own colours, in particular highlighting the technical expedients the artist used in binding medium processing. These pieces of information prove Fortuny's deep proficiency in paint manufacture and explain why his own Tempere were appreciated by his contemporaries.

Keywords*: Mariano Fortuny y Madrazo; XX century tempera; Paint manufacture; FT-IR; PyGCMS; Rapeseed oil; Lead soaps*

Introduction

In 1899 Mariano Fortuny y Madrazo (Granada 1871 - Venice 1949) established his own atelier in Palazzo Pesaro degli Orfei in Venice. Here he pursued several artistic activities - e.g. textile printing and design, photography, scenic design, engraving and painting [1, 2] - and produced his own *Tempere Fortuny*, tempera colours in paint tubes whose recipe has been kept secret until nowadays and very well appreciated by his contemporaries [3]. In 1975 Palazzo Pesaro degli Orfei became the siege of Fortuny Museum [4]. It still conserves many original materials and tools used by Mariano in his artistic activities, thus constituting an extraordinary collection. Thanks to the collaboration between the Conservation Science research group of Ca' Foscari University and Fondazione Musei Civici of Venice, it was possible to study this relevant collection and acquire precious information about the experimentations carried out by

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Mariano, which were presented in 2015 with prof. Simona Rinaldi at the Conference "**The Study of the Painter's Atelier in the Nineteenth and Twentieth Centuries"** in Pisa [5].

The great variety of materials included in the collection demonstrates the plurality of Mariano's artistic activities and techniques. Indeed, it is possible to list materials used for photographic purposes, inks and varnishes for etching and engraving, waxy materials used for modelling and also several products devoted to painting purposes (Fig. 1).

Fig. 1. Some of the original materials for artistic purposes conserved in Palazzo Pesaro degli Orfei, in Venice. © F. C. Izzo, C. Zanin 2016

A preliminary examination of the collection pointed out that Fortuny y Madrazo used to employ ready-to-use commercial products from the most popular manufacturers operating in Europe in the first decades of Nineteenth Century - e.g. Carlo Erba S. A. (Milan), Lefranc (Paris), Schöenfeld (Düsseldorf), Rowney (London) and Roberson et Co (London) - but we could find also raw materials - e.g. pigments, natural resins, oils, natural gums, glues - used by Mariano in manufacturing his own handcrafted painting formulations.

The interest evoked by this extraordinary collection, which was never been studied before, drove us to develop a multidisciplinary research.

The main aim of this research was to recognise painting materials and techniques used by Mariano Fortuny y Madrazo in his painting activity and colour production. It was possible to collect several micro samples from substances constituting the collection and to characterise them by means of different analytical techniques. The importance of a comprehensive and detailed knowledge of materials and techniques used by an artist is crucial in defining best strategies for preservation and conservation of the artworks he made.

This paper is particularly focused on the results obtained by a multi-analytical research performed on painting materials representative of different stages of paint manufacture: from raw colourant materials (e.g. pigments and dyes) to a ready-to-use paint tube containing a complex mixture of pigment, binder ad additives. Studying unprocessed and processed materials allowed us to understand the technical procedures followed by Mariano in the production of his own colours. Indeed analytical results highlighted which kind of technical expedient Mariano used in paint manufacture in order to obtain with best siccative features in paints.

Experimental

Sample description

Pigments and dyes

To characterise the composition of pigments and dyes used by Mariano Fortuny and to investigate their purity we firstly analysed 29 samples collected from raw colourant materials conserved in Fortuny Museum, whose names and description are reported in Tables 1-4.

Most of raw colourant pigments and dyes considered are in a fine powdery form. However, some of the collected samples (namely R20, R46, R65, R69, R70 and R71) show bigger grain size, indicating that they were purchased to be ground in the atelier.

Only few colourant materials show commercial labels indicating comprehensive information regarding their commercial origin and composition. Samples R22 and R60 were collected from paper wraps labelled respectively as *Biacca* (Lead White) and *Bianco di Volterra* (commercial variety of gypsum) purchased from *Ditta Luigi Calcaterra*, a colour supplier operating in Milan and specialised in selling foreign painting products [6]. Samples R23 and R26 were taken from paper wraps by *Ditta Pellegrini*, ~~a~~ art materials supplier still operating in Milan. R23 is labelled as *Terra Verde* (Green Earth), while R26 is described as *Terra di Siena Bruciata* (Burnt Sienna). Sample R52 is representative of a vivid orange powder, probably of synthetic origin, collected from a glass vial labelled as *Jaune Orange* (Orange Yellow) purchased from Moirinat, a Parisian colour supplier [7]. Sample R21 has been collected from a wooden box containing *Laque de Gaude* (Yellow Lake from vegetable source) purchased from the well-known French manufacturer Lefranc.

The majority of these analysed materials presented handwritten labels which generally provide indication about the colour hue but not about colours composition (Fig. 2), e.g. sample R29 is reported as *Rosso che non si conosce il nome* (Red colour whose name is not known), R56 as *Bianco che non si conosce il nome* (White colour whose name is not known) and R65 as *Blu in pezzi che non se ne conosce il nome* (Blue colour in grains whose name is not known). These labels have been probably filled in after Mariano's death by his wife Henriette Nigrin or by some of his assistants.

Fig. 2. Paper wrap which sample R56 has been collected from. © F. C. Izzo, C. Zanin 2016. Its handwritten label reports: *" Color bianco che non si conosce il nome"* (White color whose name is unknown). Many of raw colorant materials analyzed present similar labels, indicating their hue but not their origin, name or composition. These labels have been probably filled in after Mariano's death by some of his assistants.

Moreover, some of the pigments conserved in Fortuny Museum were inherited by Mariano from his mother relatives, members of the influent Spanish dynasty known as Madrazos (Fig. 3). Indeed, sample R3, R4 and R5, (representative of different blue powders conserved in glass vases) once belonged to Federico de Madrazo y Kunz (1815-1894), Mariano grandfather, who was a relevant painter and art *connoisseur* himself and who had been appointed as Prado Museum Director in 1860. By the other hand, sample R47 was collected from a little ceramic vase presenting a not completely legible label in which it seems to be cited *Josè de Madrazo y Agudo* (1771-1859), Federico's father. Josè was a talented painter too and the Director of Prado Museum since 1838.

It is to notice that the bequeath of pigments from father to son can demonstrate the high quality and value that Madrazos attributed to painting materials and can also suggest the practice of teaching painting techniques through generations.

Fig. 3. Blue pigments once belonging to Federico de Madrazo y Kuntz, Mariano Fortuny y Madrazo's grandfather. © F. C. Izzo, C. Zanin 2016 . From left to right we can read: " Cobalt celeste / E. Morin / - Paris -"; "Ultramar / LAPISLAZULI / Prov. F. de Madrazo"; "Cenizas de Ultramar / sacadas de LAPISLAZULI / Prov. F. de Madrazo"; "Ultramar ligero sacado / de LAPISLAZULI / que traje de España / prov. F. de Madrazo".

Paint mixtures

One of the most relevant features of painting materials collection conserved in Fortuny Museum is the presence of substances representative of different stages of paint manufacture, as mentioned before.

Beside raw colourant materials, some little ceramic pots used by Mariano for mixing colourant powder, binders and additives are conserved in Fortuny Museum (Fig. 4, on the left).

Sample R67 was collected from one of them. It consists of a paint mixture having a red colouration and being still tacky.

Further indications about Fortuny y Madrazo paint manufacture practice are deductible by the analysis of a sample collected from a paint tube (Fig. 4, on the right). The paint tube has a handwritten label reporting *R. Pozzuoli H*, probably related to a Pozzuoli Red, an earth pigment. The absence of commercial marks on the tube and the handwritten label seem to suggest that the tube had been filled by Mariano himself with a paint of his own formulation. The chance to analyse samples collected from a paint tube is of fundamental importance in order to understand Mariano paint manufacture practice.

Fig. 4. On the left: ceramic pot used by Mariano in manufacture painting admixtures. © F. C. Izzo, C. Zanin 2016. On the right: paint tube probably filled by Mariano Fortuny himself. The handwritten label reports: "R. Pozzuoli / H".

Methods

To gain information about organic and inorganic compounds in Fortuny's materials, a multi-analytical approach was followed.

Elemental analysis was performed through X-ray fluorescence (XRF) using a Minipal Philips XRF spectrometer equipped with Rh-tube. XRF measurements were carried out by fixing the tube voltage at 50kV and 15kV exploring a field of analysis from 1 to 40keV. The collected spectra were elaborated with Minipals software.

Fourier-Transformed Infrared spectroscopy (FTIR) analyses have been performed with a Thermo Nicolet Nexus 670 FT-IR spectrophotometer equipped with a Smart Orbit Single

Reflection Diamond ATR accessory, from 4000 to 400cm^{-1} for 64 scans with 4cm^{-1} resolution. The collected spectra were elaborated with Omnic 9.0 and Origin 9.0 software.

Interpretation of FTIR-ATR and XRF results has been based on comparison with data collected in reference databases and/or with data obtained by the analysis of reference samples with known composition.

To further identify organic binders and additives in the paint formulations, the micro-samples were transesterified using a solution of 2.5% (trifluoromethyl phenyl) trimethyl ammonium hydroxide in methanol, overnight reaction, as described in [8, 9]. The pyrolysis- gas chromatography-mass (Py-GC/MS) analyses were performed using a Focus ISQ Thermo Quest spectrometer equipped with a Supelco Column Equity®-5, Capillary GC Column L × I.D. 30m, 0.25mm, df 0.50µm interfaced with MD-800 Mass Spectrometer. Samples were pyrolysed in One-shot Pyrolysis ode at 550°C. The inlet temperature was 300°C, the MS interface was at 270°C. The temperature program was set from 80°C to 300°C with a ramp of 10°C/min, held at 300°C for 2 minutes. The MS was run in Full Scan mode (m/z 40-600), 1.9 scans/sec. The solvent delay was set at 4.5 min. The transfer line was at 240°C and the source temperature was 220°C. Electron Ionisation energy was 70eV. Quantitative GC-MS analysis was performed using nonadecanoic acid as the internal standard. The data were elaborated with Xcalibur 1.4 software.

The interpretation of compounds detected by Py-GC/MS has been performed analysing molecular profiles recorded, identifying peculiar markers and taking in account quantitative ratios of specific molecular fragments.

Generally, the molar ratio of palmitic over stearic (P/S) is conventionally considered to identify the vegetable source of siccative oil employed in paint manufacture. Typically, in the case of linseed oil, the P/S ratio is approximately 1.7, whereas for walnut oil and poppy-seed oil values of 2.6 and >3 are respectively [10]. Nevertheless, when dealing with modern materials, this parameter could not always be reliable. Indeed the presence of semi and/or non-siccative oils or the addition of metal stearates as dispersing agents in modern paint formulations can influence the P/S ratio, as indicated by previous results obtained by the authors on 20th century artists oil paints [9-11].

To detect possible thermal treatments used in processing oil media, the molar ratio of azelaic over suberic acid (A/Sub) is taken into account, as described in [12, 13]. A crude oil not thermally processed shows A/Sub ratio values higher than 6, whereas values ranging from 2 to 3 indicate that the oil has been subjected to heating (boiled oil).

Results and Discussions

Pigments and dyes

White pigments

Table 1 lists the results obtained by XRF and FTIR analysis performed on selected white pigments. It is to notice that the majority of white powders analysed show a traditional composition, consisting of gypsum, chalk and lead white. In particular, XRF analyses performed on samples R16 (unlabeled) and R22, cited as *Bianco di Volterra* (Volterra White) showed signals suggesting the presence of Calcium and Sulphur. Moreover, FT-IR analyses denoted vibrations related to -OH groups (3547, 3405, 1685 and 1622cm^{-1}) and sulphates (-SO_4^{2-} stretching between 1250 and 1020cm^{-1} and -SO_4^{2-} bending at 670 and 600cm^{-1}). Thus it is possible to suppose that R16 and R22 samples are mainly composed of gypsum. XRF results identify in samples R55, R68 and R69 the presence of Calcium (with a weaker Sulphur signal in the R68 sample, probably due to impurities). The comparison with infrared spectroscopy results - showing typical -CO_3^{2-} stretching vibration at 1430cm^{-1} and -CO_3^{2-} bending vibrations between 920 and 600cm^{-1} - allow to identify the samples composition as Calcium Carbonate ($CaCO_3$) [14, 15].

R60 has been collected from a commercial paper wrap indicating its content as *Biacca* (White Lead), $2PbCO_3 \cdot Pb(OH)_2$. Thanks to XRF and FT-IR analyses it was possible to confirm the reliability of commercial label: XRF spectrum of R55 sample showed calcium and lead signals, while FT-IR spectrum shows -OH stretching vibrations at 3534 and 3424cm^{-1} and signals at 1420, 1045, 838 and 682 cm^{-1}, related to the presence of lead carbonate [16].

Fortuny y Madrazo may have used gypsum, chalk and lead white either as pigments or as fillers in colour production, for the manufacture of priming layers or, in the case of gypsum, as modelling materials for sculpturing.

In Fortuny's atelier not only traditional whites are conserved. Sample R56 is described in the handwritten label as *Coloure bianco che non si conosce il nome* (White colour whose name is not known) and shows an uncommon composition. The infrared spectrum of R56 shows common features with reference FT-IR spectrum of wollastonite, $CaSiO_3$, basically employed in ceramic manufacture. Starting from the second half of 20th century, wollastonite has been introduced in the paint manufacture as filler [17]. Considering that Fortuny y Madrazo died in 1949, the use of $CaSiO_3$ in paint formulation could demonstrate that he was in touch with the novelties introduced in colour manufacture.

Even if written sources suggest that Mariano was used to employing extensively modern white pigments like Titanium White and Zinc White [18], we could not find them among pigments conserved in Fortuny Museum.

Table 1. White pigments in Fortuny Museum painting materials collection: description, analytical results and interpretation.

Sample	Description/Label content	XRF results	FT-IR absorptions (cm^{-1})	Interpretation
R16	White powder in paper wrap, unlabeled	Ca, S	3547, 3405, 1685 and 1622 (-OH) 1151, 672 and 597 ($-SO_4^{2-}$)	Calcium Sulfate $CaSO_4$
R22	White powder in paper wrap, its commercial label reports: *Bianco di Volterra* (Volterra White); supplier: Ditta Luigi Calcaterra, Milan	Ca, S, Fe	3547, 3405, 1684 and 1621 (-OH) 1132, 667 and 601 ($-SO_4^{2-}$)	Calcium Sulfate $CaSO_4$
R55	White powder in paper wrap; its handwritten label reports: *Bianco che non si conosce il nome* (White whose name is not known)	Ca	1796, 1436, 874 and 713 ($-CO_3^{2-}$)	Chalk ($CaCO_3$).
R56	White powder in paper wrap; its handwritten label reports: *Color bianco che non si conosce il nome* (White color whose name is not known)	Ca, Si, Fe, Al, K, Ti, S, Mn	1059, 1016, 967, 936 and 903 (Si-O-Si) 1150, 681 and 645 ($-SO_4^{2-}$) < 550 (oxides)	Calcium silicate ($CaSiO_3$) with sulfates and other impurities
R60	White powder in paper wrap, its commercial label reports:*Biacca* (Lead white); supplier: Ditta Luigi Calcaterra, Milan	Pb, Ca	3534 and 3424 (-OH) 1420, 1045, 838 and 682 ($-CO_3^{2-}$)	Lead White ($2PbCO_3 \cdot Pb(OH)_2$)
R68	White powder in grains, its handwritten label reports: *Calce Webster* (Webster Chalk)	Ca, S	1794, 1452, 875 and 713 (CO_3^{2-}) < 550 (oxides)	Chalk ($CaCO_3$) with oxides and other impurities
R69	White pigment in grains, unlabeled	Ca	1794, 1429, 875 and 713 (CO_3^{2-})	Chalk ($CaCO_3$)

Blue pigments

Many blue pigments are conserved in the atelier. As reported in Table 2, we can find traditional pigments, e. g. ultramarine blue, but also more recent synthetic pigments, e.g. cobalt aluminate.

Sample R3, R4 and R5 were collected from blue pigments once belonged to Federico de Madrazo y Kuntz, Mariano's grandfather. The high value and quality of these pigments seem to be analytically confirmed. Regarding sample R3, labelled as *Cobalt Celeste* (Cobalt Light Blue), the presence of Al, Zn, Co and minor amounts of S, Ca and Fe was found by XRF

analysis. Moreover, FT-IR spectroscopy shows main absorptions at >820cm^{-1}, indicating that the sample mainly contains oxides. Thus it is possible to hypothesise that sample R3 consists of a mixture of cobalt aluminate ($CoAl_2O_4$), also referred as Thènard Blue, and Zinc White (ZnO) [19]. Considering that Thènard Blue and Zinc White had been introduced only in the first half Nineteenth century [20, 21], we can point out that this modern painting materials had been taking in great account by Federico de Madrazo, who decided to donate them to his grandson Mariano.

Moreover, the analysis performed on sample R4 and R5, labelled as *Ultramar Lapis lazuli* (Ultramarine) and *Ultramar ligero sacado de Lapis lazuli* (Light Ultramarine extracted from Lapis lazuli) respectively, seems to confirm the high quality of these precious pigments. As a matter of fact, besides Si, Al, Na, K and Mg related to silicate compounds, XRF analysis denoted the presence of calcium, sulfur and iron. It is known that impurities of calcite ($CaCO_3$) and pyrite (FeS) are common in lapislazuli veins [22] and that their presence can be use in distinguishing authentic ultramarine pigments from the synthetic imitation, actually patented as painting pigment in 1828 by *J.B. Guimet* [23].

Table 2. Blue pigments in Fortuny Museum painting materials collection: description, analytical results and interpretation.

Sample	Description/Label content	XRF results	FT-IR absorptions (cm^{-1})	Interpretation
R3	Blue powder in glass vase, once belonged to Federico de Madrazo y Kuntz. Its handwritten label reports *Cobalt Celeste / E. Morin / -Paris-*	Al, Zn, Co, S, Ca, Fe	815, 691 and 550 (oxide) < 550 (oxide)	Admixture of Cobalt Blue ($CoAl_2O_4$) and Zinc White (ZnO)
R4	Blue powder in glass bottle, once belonged to Federico de Madrazo y Kuntz. Its handwritten label reports *Ultramar lapislazuli prov de F. de Madrazo*	Si, Al, Ca, S, Na, K, Fe, Ti	1000, 700 and 658 (Si-O-Si) < 550 (oxide)	Natural Ultramarine pigment $[(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2]$
R5	Blue powder in glass bottle, once belonged to Federico de Madrazo y Kuntz. Its handwritten label reports *Ultramar ligero sacado de lapislazuli que traje de la España prov. de F. de Madrazo*	Si, Al, Ca, K, Mg, S, Ti, Fe	991 Si-O-Si) < 550 (oxide)	Natural Ultramarine pigment $[(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2]$
R11	Grey shaded blue powder in glass vase, unlabeled	Si, Ca, K, Al, Mg, Na, Ti, S, Fe, Cu	997 (Si-O-Si) < 550 (ossidi)	Admixture of Natural Ultramarine pigment $[(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2]$, silicate compound and copper-based pigment
R17	Blue powder in paper wrap, unlabeled	Ba, S, Sr, Fe	1177, 1120, 1081, 982, 633 and 608 ($-SO_4^{2-}$) 2088 (-CN)	Admixture of Prussian Blue ($Fe_4[Fe(CN)_6]_3$) and Barium Sulfate ($BaSO_4$).
R18	Blue powder in paper wrap, unlabeled	Al, Co, Ca, Fe	811, 689 and 555 (oxide)	Cobalt Blue ($CoAl_2O_3$)
R54	Blue powder in paper wrap, its handwritten label reports *Beau Bleu Meissen*	Si, Al, S, Ca, Fe, Ti	3695 and 3620 (-OH) 1032 and 1010 (Si-O-Si) < 550 (oxide)	Silicate-based compound
R54 bis	Blue powder in paper wrap, unlabeled	Si, Ca, Al, K, S, Ti, Fe, Cu	1080, 1000, 866 and 464 (Si-O-Si) 464 (oxide)	Ultramarine blue with copper impurities
R58	Blue powder in paper wrap, its handwritten label reports *Celeste che non si conosce il nome*	Si, Ca, S, Cu, Al, Fe, K, Ti, Ba	3552, 3404, 1693, 621, 670, and 596 ($CaSO_4$) 1075 (Si-O-Si) 2103 (-CN) < 550 (oxide)	Admixture of Prussian Blue ($Fe_4[Fe(CN)_6]_3$), calcium sulfate, silicate compound and oxides
R65	Blue powder in paper grains, its handwritten label reports *Blu in pezzi che non se ne conosce il nome*	Ba, Ca, S, Fe, Sr, K	3546, 3404, 1685, 1621 and 669 ($CaSO_4$) 1170- 1080, 983, 638 and 606 ($BaSO_4$) 2090 (-CN)	Admixture of Prussian Blue ($Fe_4[Fe(CN)_6]_3$), barium sulfate and calcium sulfate

Cyanide typical stretching vibrations at almost 2090cm^{-1}, detected in infrared spectra of samples R17, R58 and R65 suggest that they are containing Prussian Blue ($Fe_4[Fe(CN)_6]_3$). However, they show different additional IR signals, suggesting the presence of other inorganic substances mixed together. In particular, sample R17 (unlabelled) seems to contain also barium sulphate ($BaSO_4$), as suggested by -SO_4^{2-} vibrations at 1177, 1120, 1081, 982, 633 and 608cm^{-1} in the infrared spectrum, and confirmed by the presence of barium, sulfur and minor amounts of strontium and iron in the XRF spectrum.

By the other hand, XRF analysis performed on sample R58 (labelled as "Unknown light Blue") shows the presence of Si, Ca, S, Cu, Al, K, and a minor amount of Ti and Ba. Moreover, signals related to the vibration of sulphates, silicates and oxides groups detected via FT-IR spectroscopy, seems to suggest that sample R58 is representative of a light blue pigment obtained adding to Prussian blue, white clay and gypsum. On his side, R65 seems to contain a mixture of Prussian blue, gypsum and barium sulphate. Additions of inorganic white materials to Prussian blue pigments can be due to the willing of obtaining lighter hues [24, 25]. Actually, it has to be recalled that pure Prussian blue shows a very deep blue colour. Unfortunately, it's not possible to know if Mariano bought these colours already mixed or if he lightened blue hues adding white powders by his own.

Red pigments and dyes

The results on samples R20, R26, R57 and R70 are consistent with the presence of iron oxide-based pigments (Table 3). FT-IR spectra reported in figure 5, along with elemental analysis results, allowed to distinguish specific compositional features of iron oxides.

In particular samples R70 and R26 (the latter labelled as Burnt Sienna) consist in red natural earth pigments (absorption bands ascribable to silicates, aluminosilicates, and oxides) extended with gypsum. The presence of the latter is suggested by XRF signals attributable to sulfur and calcium, and by infrared absorption related to -SO_4^{2-} group.

Sample R57 is characterised by a relatively high arsenic content, as suggested by XRF results. This finding may be consistent with a natural origin of Hematite mineral, probably excavate from a vein particularly rich in this element [26].

In the case of sample R20, no signals ascribable to silicate or alumino-silicate compounds were identified. XRF results show the presence of iron, calcium, sulfur and barium and FT-IR spectrum shows the signals attributable to oxides and calcium and barium sulphates. Therefore analytical results suggest that sample R20 consists in an iron oxide pigment has a synthetic origin [20], mixed with Gypsum and Barite.

Not only iron oxide pigments can be listed among red colourant materials collected in Fortuny Museum. Sample R47 is constituted by an orange powder labelled as Chinese Vermillion. This pigment probably once belonged to Josè de Madrazo y Agudo, Mariano's great-grandfather. XRF spectrum of sample R47 seems to confirm the reliability of sample label, denoting the presence of mercury and sulfur, present as HgS (vermilion or cinnabar) and highlights the high purity of this precious pigment, showing no extenders, fillers or adulterants [27].

Analysis performed on sample R29 identified it as a red lake. The shift of sulphate band in FT-IR spectrum to 1090cm^{-1} and presence of calcium and a high amount of phosphorous highlighted by XRF analysis suggest that the precipitating agent used during lake manufacture is constituted by calcium phosphate. Interestingly, *Kirby et al.* [28] observed the use of lakes containing phosphate compounds in artworks attributed to Pierre Andrieu (1821 - 1892) and Gustave Moreau (1826 - 1898). Both of them mastered Renè Piot (1866 - 1934), a painter himself and Fortuny y Madrazo's close friend.

Finally, sample R52, showing a bright orange colour, is probably constituted by an organic dye with a synthetic origin and containing Sulphur. The presence of a synthetic organic

dye demonstrates once again Fortuny's tendency to experiment both traditional and innovative materials in painting practice.

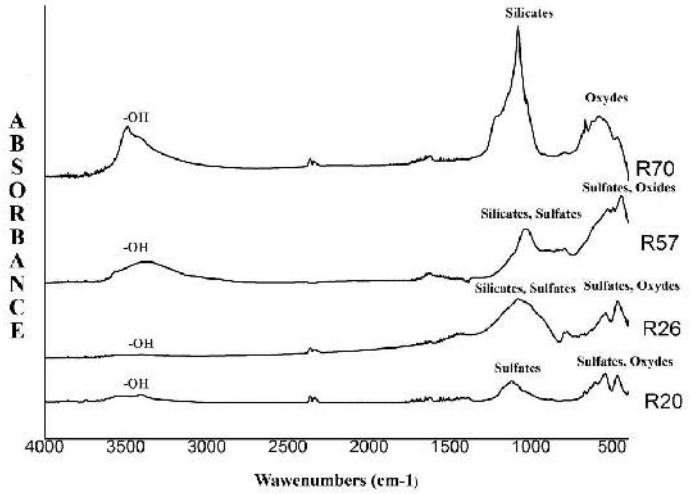

Fig. 5. FT-IR spectra of red iron pigments conserved in Fortuny Museum.

Table 3. Red pigments and dyes in Fortuny Museum painting materials collection: description, analytical results and interpretation.

Sample	Description/Label content	XRF results	FT-IR absorptions (cm^{-1})	Interpretation
R20	Red grains in paper wrap	Fe, Ba, Ca, S	3547, 3404 and 1620 (-OH) 1118, 1031, 982, 667, 606 and 544 ($-SO_4^{2-}$) < 550 (oxide)	Admixture of iron oxide pigment (Fe_2O_3), calcium sulfate and barium sulfate
R26	Red powder in paper wrap, its handwriten label reports *Terra di Siena Bruciata - Ditta Pellegrini*	Fe, Si, Ca, Al, K, Ti, S, Mn	1080, 1010 and 640 ($-SO_4^{2-}$) < 550 (ossidi)	Admixture of iron oxide pigment (Fe_2O_3), calcium sulfate, silicate and aluminosilicate
R29	Red powder in paper wrap, its handwriten label reports *Rosso che non si conosce il nome*	P, Al, Ca, Fe	3650-3000 (-OH) 1090 ($-SO_4^{2-}$, PO_4^{3-}) 1638, 1467, 1286, 1268, 838 and 719	Red lake with calcium phosphate as precipitating agent and calcium sulfate as extender
R47	Vivid orange powder in ceramic vase once belonged to Josè de Madrazo y Agudo. Its handwritten label, not completely legible reports *Vermillon de Chine*	Hg, S	No significant infrared absorption detected	Vermillion (HgS)
R52	Bright orange powder in glass vial, its commercial label reports *Jaune Orange / Toiles et couleurs fines 7Articles de dessin (Moirinat / Faubourg Saint Honorè Paris*	S	1620, 1597, 1553,1509, 1452, 1255, 1226, 1209, 1122, 1035, 836, 757 and 645	Organic pigment, synthetic
R57	Red powder in paper wrap, unlabeled	Fe, As, Si, Ca	3562 and 3406 (-OH) 1033 and 802 (Si-O-Si) < 550 (oxide)	Admixture of iron oxide pigment (Fe_2O_3) and silicate compounds
R70	Red grains, unlabeled	Fe, Al, Pb e/o S, K, Si, Ca, Ti, Zn	3488 (-OH) 1080, 1022 and 660 ($-SO_4^{2-}$) 1138 (Si-O-Si) < 550 (oxide)	Admixture of iron oxide pigment (Fe_2O_3), silicate compounds and calcium sulfate.

Other pigments and dyes

Table 4 lists results obtained by XRF and FTIR analysis performed on samples R21, R46, R71, R23 and R14, showing different colours.

The data obtained from sample R21, labelled as *Laque de Gaude* and purchased by Lefranc, show that it actually consists of a yellow lake. Moreover, XRF and FT-IR analysis allowed understanding that as like as R29, sample R21 contains a phosphorus compound as mordant and gypsum as an extender. FT-IR spectrum of sample R46, labelled as *Ocre Amarillo* (Yellow Ochre), shows effectively typical feature of ochre, with hydroxide bands at 3697, 3651 and 3621cm^{-1}, Si-O-Si vibrations at 1101, 983, 911 and 796cm^{-1} and oxide band at < 550cm^{-1}. XRF results indicate the presence of Fe, Si, Al and K, consistent with silicate and aluminosilicate compounds, whereas small amounts of titanium and calcium can be due to natural impurities [29]. Sample R71, unlabelled, has been identified as a lead-based pigment, probably Massicot (PbO), extended with calcium sulphate.

FT-IR spectrum of sample R23, labelled as *Terra Verde* (Green Earth) shows many features in common with natural earth pigments, revealing absorption bands ascribable to hydroxide groups, silicate and oxides [30]. This result is confirmed by XRF analysis which identifying the presence of Fe, Si, K, Al and Ca.

Finally, the absence of relevant signals in XRF and FT-IR spectra of sample R14 seems to suggest that this black powder probably consists in carbon black.

Table 4. Other pigments and dyes in Fortuny Museum painting materials collection: description, analytical results and interpretation.

Sample	Description/Label content	XRF results	FT-IR absorptions (cm^{-1})	Interpretation
R21	Yellow powder in wooden box. It commercial label reports *Laque de Gaude/Couleurs et vernis pour la carrosserie / LF*	P, Al, Ca, K, Pb e/o S, Fe, Zn, Cu	3650-3000 (-OH) 1098 (-SO_4^{2-}, PO_4^{3-})	Yellow lake with calcium phosphate as precipitating agent and calcium sulfate as extender
R46	Yellow grains in glass vase. Its handwritten label reports *Ocre Amarillo molido in agua*	Fe, Si, Al, K, Ti, Ca	3697, 3651 and 3621 (-OH) 1101, 983, 911 and 796 (Si-O-Si) < 550 (oxide)	Yellow Ochre
R71	Yellow pigment in grains, unlabeled	Pb e/o S,Ca,Fe,Zn, Si, Ni	3547, 3408, 1684 and 1622 (-OH) 1141, 1115 667 and 594 (-SO_4^{2-})	Admixture of Massicot (PbO), calcium sulfate and other impurities.
R23	Green powder in powder. Its handwritten label reports *Terra verde/Ditta Pellegrini*	Fe, Si, K, Al, Ca	3602, 3557 and 3528 (-OH) 1114, 1075, 976, 958 and 799 (Si-O-Si) < 550 (oxide)	Green earth
R14	Black powder, unlabeled	Ca, Fe	No significant infrared absorption detected	Carbon-based pigment

Paint formulations

Table 5 reports the results obtained by XRF, FT-IR and Py-GC/MS on samples R67 and R62.

As already mentioned, sample R67 was collected from the little ceramic pot shown on figure 4, on the left. It consists of a handcrafted red coloured paint mixture. XRF analysis revealed the presence of Fe, K, Al, S and minor amounts of Si, Ca and Ti: it is likely that the colourant material conferring the red colouration to the mixture has many features in common with iron oxide red pigments found as raw materials in Fortuny Museum collection. Regarding

the binding medium, FT-IR analysis results (Fig. 6, below) suggests that the organic component of the mixture is constituted by a siccative oil, as demonstrated by the presence of C-H bonds stretching vibration at 2924 and 2853cm^{-1}, C-H bending vibration at 1460, 1408 and 1371cm^{-1}, carbonyl peak at 1733cm^{-1}, carboxylic absorption at 1708cm^{-1} and C-O bond vibrations at 1206, 1151 and 1075cm^{-1}. The detection of carboxylic absorption at 1708cm^{-1} could be related to the oil ageing processes, resulting in the hydrolysis of the glycerol esters [31-33].

Table 5. Summary of analytical results from samples R67 and r62: description, analytical results and interpretation.

Sample	Description/ Label content	XRF results	FT-IR results	Py-GC/MS results	Interpretation
R67	Unlabeled colored paint mixture collected from a paramo pot	Fe K Al S Si Ca Ti.	3485 cm^{-1} (OH) 2924, 2853, 1460, 1408, 1371 cm^{-1} (CH$_2$ and CH$_3$); 1733 cm^{-1} (C=O); 1708 cm^{-1} (COO$^-$) 1236, 1151, 1075 cm^{-1} (C-O) 1024, 930 cm^{-1} (Si-O-Si); > 700 cm^{-1} oxides	Glycerol derivatives. nonanoic a., pelargonic a., capric a. (short chain saturated fatty acids) miristic a., palmitic a., stearic a., arachidic a., behenic a., lignoceric a. (long chain saturated fatty acids) azelaic a., pimelic a., suberic a., azelaic a., sebacic a. (dicarboxylic acids) oleic a., linoleic a., linolenic a. (long chain unsaturated fatty acids) erucic a. (rapeseed oil marker)	Pigments: red earth iron oxide containing Binding medium: heat cured siccative oil Additives: rapeseed oil
R62	Reddish paint mixture collected from a paint tube. Inscription: label reports R. Pozzuoli H.	Fe, Fe, Al, K, Ca, Ni	3850 cm^{-1} (OH) 3010, 2923, 2853, 1457, 1377 cm^{-1} (CH$_2$ and CH$_3$); 1733 cm^{-1} (C=O) 1709 cm^{-1} (COO$^-$) 1525, 1405 cm^{-1} (lead carboxylates); 1230, 1163, 1051 cm^{-1} (C-O) <700 cm^{-1} oxides	Glycerol derivatives. nonanoic a., pelargonic a., capric a. (short chain saturated fatty acids) miristic a., palmitic a., stearic a., arachidic a., behenic a., lignoceric a. (long chain saturated fatty acids) azelaic a., pimelic a., suberic a., azelaic a., sebacic a. (dicarboxylic acids) oleic a., linoleic a., linolenic a. (long chain unsaturated fatty acids) erucic a. (rapeseed oil marker)	Pigments: red earth iron oxide containing Binding medium: heat cured siccative oil Additives: rapeseed oil and litharge

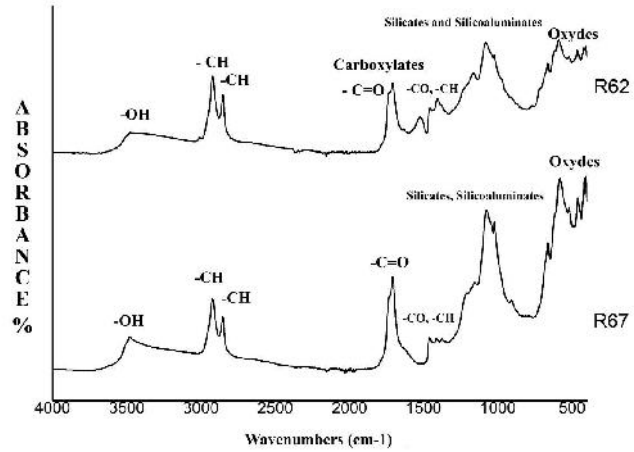

Fig.6. FT-IR spectrum of sample R67, collected from a ceramic pot used by Mariano in paint manufacture (below) and FT-IR spectrum of sample R62, collected from a paint tube probably filled by Mariano himself

Figure 7 reports the total ion current (TIC) chromatogram obtained after derivatisation and Py-GC/MS analysis on sample R67 (see Table 6 for peak assignments). It shows peaks effectively attributable to lipidic binding media. In particular it is possible to recognize: glycerol derivatives; short-chain saturated fatty acid (succinic acid, pelargonic acid, capric acid), long-chain saturated fatty acid (miristic ac., palmitic ac., stearic ac., behenic ac., lignoceric ac.); di-carboxylic acids (adipic, pimelic, suberic, azelaic, sebacic) and long-chained unsaturated fatty acids (oleic, linoleic, linolenic).

Amongst the characteristic drying oil compounds, two uncommon fatty acids were detected by Py-GC/MS analysis: erucic (13-docosenoic) and gondoic (11-eicosenoic) acids (and traces of their oxidation products 13, 14-dihydroxydocosanoic and 11, 12-dihydroxyeicosanoic acids, respectively).

These unsaturated fatty acids are considered to be bio-markers as they are present only in oils obtained from the seeds of *Brassicaceae*, such as rapeseed oil. Rapeseed oil is slow-drying oil which could be added to the lipidic binding medium in order to increase drying time of the paint mixture or to enhance the paint spreading and workability, thanks to its high content of oleic acid and the consequentially high degree of unsaturation. Rapeseed oil was also added as an adulterant of more expensive vegetable oils traditionally used in painting practice e.g. linseed oil, walnut oil and poppy seed oil [9, 34, 35].

It is not clear if Mariano Fortuny added erucic acid by himself, if he was aware of the rapeseed oil presence, or if this slow-drying oil has been added by the oil manufacturer.

Although the pyrolysis profile shows a high content of unsaturation (oleic acid and erucic acid, for instance), azelaic acid (peak 4) is one of the main peaks, thus suggesting the presence of a siccative oil.

The P/S ratio is 1.2, value which traditionally is intended for linseed oil [9, 10]. Nevertheless, as stated before, the fact that the paint mixture included also rapeseed oil did not allow us to identify the vegetable source of the siccative oil only based on its P/S ratio [10-13, 35].

On the other hand, interesting is the A/Sub ratio, which turned out to be 1.6: it is possible to suggest that the oil used in the paint formulation had been subjected to a heating pre-treatment. It is known that the preparation of drying oil using heat (to obtain, for instance, boiled oils) was very common in the Nineteenth century, when the use of quick-drying binding media was much appreciated among painters as reported in painting techniques manuals and treatises [36]. These processing treatments, indeed, were employed to promote partial pre-polymerization of lipid medium and thus fastening its drying time.

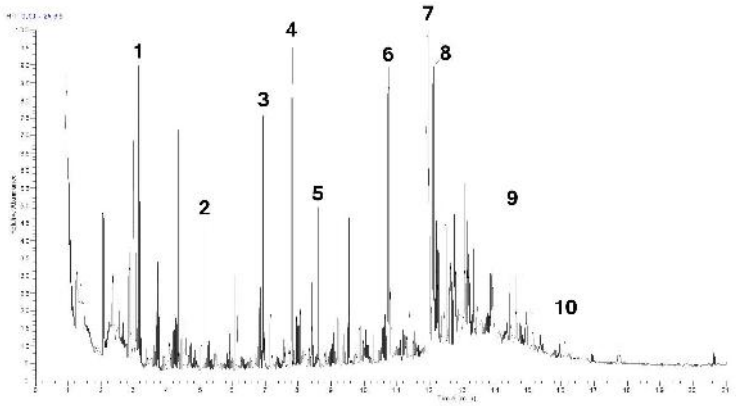

Fig. 7. Py-GCMS chromatogram of the sample R67. Peak assignments are reported in Table 6.

Table 6. Compounds identified in the pyrogram reported in Figure 7.

Peak Number	Retention time (min)	Identified Compound
1	3.14	Glycerol derivative
2	5.09	Pelargonic acid. methyl ester
3	6.95	Suberic acid. dimethyl ester
4	7.83	Azelaic acid. dimethyl ester
5	8.61	Sebacic acid. dimethyl ester
6	10.76	Palmitic acid. methyl ester
7	11.96	Oleic acid. methyl ester
8	12.13	Stearic acid. methyl ester
9	14.47	Erucic acid methyl ester
10	16.13	Behenic acid. methyl ester

Among painting materials included in Fortuny Museum collection, it is possible to find several bottles which handwritten labels seems to indicate that Fortuny used to employ processed oils (Fig. 8).

Fig. 8. Among painting materials included in Fortuny Museum collection, it is possible to find several bottles with handwritten labels indicating that Fortuny was used to employ processed oils. For example, we can read a label reporting "Olio cotto. 19 - 4 - 45" (Heated oil. 19-4-45) and another one reporting "Olio papavero. Arrivato il 24 - 4 - 1935 - lasciato in macchina fino l'1- 8 -1935" (Poppy oil. Arrived in 24-4-1935 - left in the machine until 1-8-1935).

As reported above sample R62 was collected from the content of a paint tube labelled as *R. Pozzuoli*. Multi-analytical results collected indicates that the paint tube contains a paint mixture similar but not identical to sample R67. Regarding the organic fraction, Py-GC/MS analysis, which results are reported in figure 9 (see Table 7 for peak assignments) suggests that the binding medium included in the paint consists once again of a mixture of heating-cured siccative oil and rapeseed oil. The P/S ratio is 1.3, while the A/Sub ratio turned out to be 1.5.

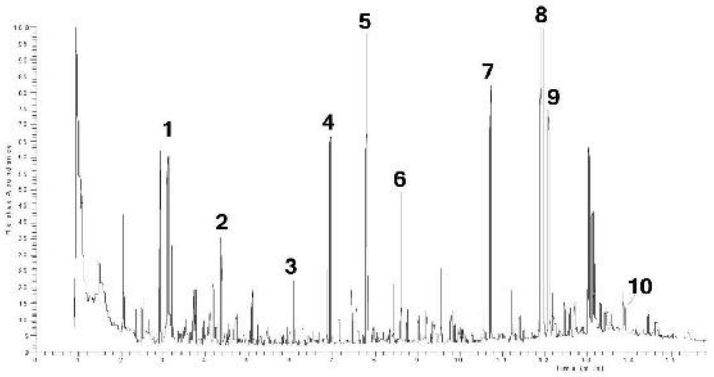

Fig. 9. Py-GCMS chromatogram of the sample R62. Peak assignments are reported in Table 7.

Table 7. Compounds identified in the pyrogram reported in Figure 9.

Peak Number	Retention time (min)	Identified Compound
1	3.09	Glycerol derivative
2	5.09	Pelargonic acid. methyl ester
3	6.07	Pimelic acid. dimethyl ester
4	6.94	Suberic acid. dimethyl ester
5	7.81	Azelaic acid. dimethyl ester
6	8.61	Sebacic acid. dimethyl ester
7	10.72	Palmitic acid. methyl ester
8	11.93	Oleic acid. methyl ester
9	12.08	Stearic acid. methyl ester
10	13.89	Erucic acid, methyl ester

However, XRF spectrometry identified - besides signals suggesting that the paint formulation includes once again iron oxide-based pigment - the presence of a relevant signal ascribable to Lead, not detected in sample R67. Moreover, FT-IR spectrum of sample R62 shows additional absorption bands in comparison with sample R67 (Fig. 6). These additional absorption bands are centred at almost 1525 and 1404cm^{-1} and, according to [31], they can be attributed to the presence of lead carboxylates. It is possible to hypothesise that lead carboxylates have been formed by reaction between the fatty acids present in the binding medium and the Lead included in the paint inorganic fraction, probably as lead oxide [37]. Lead-based compounds and particularly litharge (PbO) were often employed in drying oil processing because of their capability to activate metal-catalyzed red-ox reactions responsible for accelerating the drying process. Litharge was also added in drying oil processing to pursue a special clarification [38]. It is not to be excluded that Mariano Fortuny intentionally added litharge to the paint formulation in order to obtain a binding medium even more quick-drying than the heat-treated siccative oil.

Conclusions

The results obtained by this multi-analytical research performed for the first time on the painting materials conserved in Fortuny Museum demonstrate that Mariano Fortuny y Madrazo used both traditional and innovative materials available at his time for painting practice. Moreover, it was possible to suggest that Fortuny may have adopted some technical expedients in order to modify binding medium drying time. These findings seem to prove Fortuny's deep proficiency in paint manufacture and binding medium processing.

Regarding the reliability of commercial labels for raw colourant materials, analytical results pointed out that commercial name of samples R22 (Bianco di Volterra from Luigi Calcaterra), R60 (Biacca from Luigi Calcaterra), R23 (Terra Verde from Pellegrini) are indeed matching with their composition. On the contrary label of samples R21 (Laque de Gaude from Lefranc) and R26 (Terra di Siena Bruciata from Pellegrini) do not mention calcium sulphate, actually detected as an additive in the pigment formulation.

10 of 29 raw pigments and dyes presented the addition of inorganic white materials, mainly Gypsum $CaSO_4 \cdot 2H_2O$ (R58, R26, R29, R70, R21, R71), Barite $BaSO_4$ (R17) and admixture of both (R65 and R20) and ZnO (R3). The addition of these inorganic compounds to colourant materials could be related to the willing of modifying their visual characteristic (e.g. lightening deep hue), but also to adulterate pigment/dye formulations mixing cheap colours and thus reduce manufacture costs [34].

Finally, the multi-analytical results allowed revealing the complexity of substances used by the eclectic artist in his painting practice. It is mandatory to take in account this complexity when dealing with preservation treatments of his artworks (e.g. the use of lead-based siccatives might provoke dangerous and disfiguring lead metal soaps).

This research reinforces previous conclusions which stated that early 20^{th} century painters and paint producers used varying forms of the traditional lipidic binding media, which need to be accurately studied to avoid counterproductive generalizations about drying and curing of oil-based artworks.

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