# Non-destructive methods of analysis to characterize an easel painting by Victor Meirelles

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# Non-destructive methods of analysis to characterize an easel painting by Victor Meirelles

**J Schenatto**[1,a], **P H O V Campos**[2,a] **and M A Rizzutto**[3,a]

[a]Department of Nuclear Physics, Physics Institute, São Paulo's University, São Paulo/SP, BR

E-mail: [1]schenatto@usp.br, [2]pedrofields@gmail.com and [3]rizzuto@usp.br

**Abstract.** The use of analytical, non-destructive, non-invasive, and portable techniques applied to the Cultural Heritage research represents a great collaboration between different sciences. With these methods, artwork can have its original pigments identified, as well as be checked for other pigments used in interventions. These techniques allow to identify the artist's creative process without having to move the artwork to the laboratory. This study's main advantage is assisting art historians, restorers and conservators, and correlating time-period artworks. The painting "Dr José Maria Chaves" (1873) by Victor Meirelles, from MASP's collection, was the subject of this study by using imaging (VIS, RAK, UVL, and IRR) and spectroscopies (ED-XRF and Raman) methods. Through these it was possible to identify a few "pentiments" performed by the artist, many interventions, and different layers of varnish. Besides that, it was suggested the pigments used by the artist, highlighting the base preparation with Lead White and the uncommon use of Naples Yellow. This results help to increment the database about the Brazilian artist and his historical period, providing a better understanding of creative techniques, palletes, interventions, and strengthing the database for future works.

## 1. Introduction

The collaboration between different sciences, such as physics, chemistry, art history, restoration and conservation, allows studying the cultural heritage with analytical techniques. It provides information about its elementary and chemical composition, its state of conservation, previous interventions that may have happened, and the artist's creative process. This cooperation has taken place in the last millennia [1] and has been developed on a great scale in the last three decades, helping the museums and private collectors to develop strategies to better conserve and restore the artwork, verify its authenticity and improve the knowledge about the object and its artist's history. [2]

This kind of research deals with valuable and delicate artwork, thus they must not be moved or, if necessary, be moved as little as possible from their original place to be analyzed. Also due to the importance of the art pieces, removing a small sample is not always possible. Therefore the analysis is performed with methods of study that are portable, non-destructive and non-invasive, allowing the researchers to study an artwork by moving the laboratory into the museum.

The main objective of this study is to characterize easel paintings of Brazilian artists better, determine their pallet, creative processes, the artwork's conservation condition, and identify interventions/restorations that may have occurred. In particular, we will discuss the characterization of the painting "Dr. José Maria Chaves" (1873) by Victor Meirelles (figure 1) that belongs to the MASP's collection, through espectroscopic and imaging methods.

Figure 1: Visible photography of the painting "Dr. José Maria Chaves" by Victor Meirelles with a ColorChecker chart. The painting's dimensions are 221 *cm* x 136 *cm* x 3 *cm*, and it belongs to the MASP's collection. Photo by Pedro Campos/IFUSP.

Victor Meirelles (1832-1903) was one of the most brilliant graduates of the Imperial Academy and one of the first national masters to receive recognition abroad. He was one of the favourite painters of the emperor D. Pedro II, being in line with his proposal to renew the image of Brazil. He became an esteemed professor at the Imperial Academy of Fine Arts, and played an important role in the formation of several painters during his thirty years of teaching. There are a few studies with analytical techniques about Victor Meirelles' paintings [3][4] and this paper proposes to contribute to the knowledge about his work.
The spectroscopic methods, such as Energy Dispersion X-ray Fluorescence (ED-XRF) and Raman, permit to identify the chemical and molecular composition from selected points of analysis, respectively, acting as complementary methods to define the pigments used by the artist. The imaging methods, such as photography with Visible Light (VIS), Raking Light (RAK), UV-induced visible luminescence (UVL), and Infrared Reflectography (IRR), provide additional information about brushstrokes, underlying drafts and painting, and possible modifications done by the artist during the artwork creation. In the analysis with visible light, a ColorChecker chart is used to RGB color correct and to obtain a reliable visible image to document the object.

## 2. Methods
The analysis techniques used to characterize the painting fall into two categories, spectroscopic and imaging methods. The artwork studied was "Dr José Maria Chaves" (1873), an oil painting by Victor Meirelles, belonging to the São Paulo's Art Museum (MASP) collection, with the identification code MASP.00270 and dimensions of 221 *cm* x 136 *cm* x 3 *cm*.

### *2.1. Spectroscopic methods*
The portable, non-invasive and non-destructive spectroscopic methods are practical ways to identify the chemical and molecular composition in the artwork with an *in situ* analysis.
Through the Energy Dispersion X-ray Fluorescence (ED-XRF), it is possible to identify the chemical elements present in the analyzed object due to the interaction of an X-ray beam with the material. The irradiated atoms absorb the X-ray energy, causing the expulsion of its innermost layers' electrons. When the vacancy opened in those layers is occuppied, characteristic photons are emitted. These photons are identified and accounted by the detector, giving the atom's fingerprint. The portable ED-XRF system consists of an AmpTek® Mini-X X-ray tube with a silver (Ag) transmission target and a 2 $mm$ beam exit collimator and the AmpTek® detector fast XR-100 SDD detector (25 $mm^2$ x 500 $\mu m$ x 0.5 $mil$) with a thin beryllium window of 12.5 $\mu m$, with an energy resolution of 125 eV FWHM @ 5.9 keV (55Fe). The parameters are set to a voltage of 30 $kV$, an electric current of 5 $\mu A$, and an acquisition time of 100 $s$. The equipment is positioned around 1 $cm$ close to the artwork's surface at each of the 54 selected points across the painting.

The Raman Spectroscopy is based on the inelastic scattering of a monochromatic radiation beam by the material's molecules. Every molecule has its own vibrational and rotational energy levels. When a photon with more energy irradiates the molecule, the photon may interact with the material and be elastic or inelastic scattered. In the first case, a photon with identical energy is emitted by the molecule, characterizing the Rayleigh Scattering. In the last case, a photon with slightly different energy (more or less) than the original photon is emitted, consisting of the Raman Scattering. The energy difference between the original and the emitted photon corresponds to the shift energy between the vibrational and/or rotational levels. Those photons are accounted by the detector, giving the characteristic spectra of each molecule. The Raman Spectroscopy system is composed of a laser, lens to focus it on the point of interest, a detector, and standard electronics. The portable equipment is an EZRamanDual-G, operating with lasers at 785 $nm$ and 532 $nm$. The chosen wavelengh was 785 $nm$ with $20 - 30$ $mW$ and the selected points were the same from the ED-XRF technique analysis.

### *2.2. Imaging methods*

The imaging techniques are important tools for documentation, registration and study of the artwork. Through this methods it's possible to determine the color pallet used, the conservation state and the artist's creative process.

With Visible Light (VIS) the color pallet and stylistic details of the painting were registered using the high quality digital camera Nikon D90 and two halogen lamps. This allows reproducing a trustworthy picture of the artwork with the help of and ColorChecker chart, which has RGB's reference values.

The Raking Light (RAK) method consists of shining tangential white light into the painting, highlighting brushstrokes, volumes, reliefs, roughness, etc. The equipment used to photograph was the same Nikon camera with a setup of led track-light. Due to its size, the painting was divided and photographed into quadrants.

The UV-induced visible luminescence (UVL) is a technique that registers the visible fluorescence caused by the incidence of ultraviolet light in the painting, reacting differently with each material. The shades of fluorescence are not always easy to interpret, but they can help identify restored and intervened regions, and differ varnishes and similar pigments in visible light. The equipment used was the same photographic camera with a UV filter's lens and two UV lamps. After some exposition, the different materials emitted their characteristic fluorescensce and the picture of the whole piece and some important details was taken.

Infrared Reflectography (IRR) is a technique that allows seeing what is underneath the pictorial surface, identify subjacent drawings, and differ pigments that look similar in visible light, as well to highlight some intervened areas. It happens due to a combination of the absorption, reflection, and transmission of the infrared radiation when it interacts with the painting, translated as an image with shades of gray by the detector. In particular, the drafts underneath the painting are seen due to the high reflectance of the carbon material. The image is obtained by the digital camera OSIRIS from Opus Instruments, with an InGaAs line sensor, and using two halogen lamps. To have a good distinction of details, the painting was divided and photographed in quadrants.

## 3. Results and Discussion

The VIS photography and the RAK method it became evident regions with brushstrokes volume, reliefs, roughness, and deformations (figure 2). Still, most of the painting doesn't present volume, characterizing a smooth surface, which may be a characteristic of the artist's process.

The UVL technique allowed to identify regions with lost of polychromy and evidenced restorations, such as in the medals, around the model's head and thumb, in his cap, and around his eyes. These and other restorations could be found due to the fluorescence contrast, appearing

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(a) (b)

Figure 2: The RAK image highlighted (a) brushstrokes volumes, (b) deformation, and roughness in the painting "Dr. José Maria Chaves" by Victor Meirelles from MASP's collection. Photos by Pedro Campos/IFUSP.

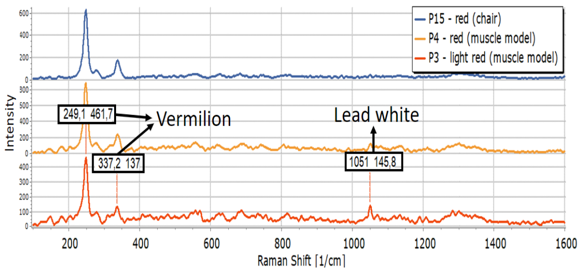
Figure 3: The UVL image shows regions with restoration. For example, the model's head contour, around his thumb, below and in the center of the medal, highlighted in the figure. It was revealed the presence of different varnishes, identified by their green and blue fluorescence. Moreover, there are regions in the painting where varnishes appear clearly, as can be seen on the inferior left side of the image. Painting "Dr. José Maria Chaves" by Victor Meirelles from MASP's collection. Photos by Pedro Campos/IFUSP.

(a) (b) (c) (d) (e) (f)

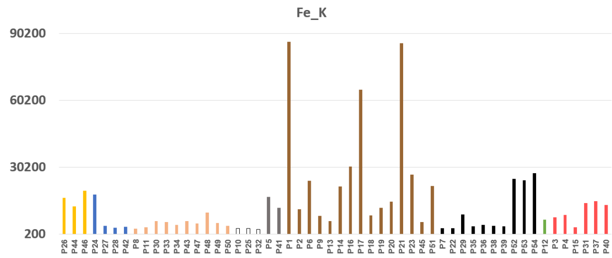
Figure 4: Corrections made by the artist at (a) the model's finger, (b) his cape, and (c) a paper sheet painted after the table underneath. The black pigment in the background around the model's (a) cap and (d) head suggests a modification in its contours. (f) The grey contrast in the IRR images shows that the pigments used in the model's shoes and in between them could be different (maybe a restoration pigment used), although it appears as the same color when seen with VIS. Painting "Dr. José Maria Chaves" by Victor Meirelles from MASP's collection. Photos by M.Rizzutto/Pedro Campos/IFUSP.

darker than their surroundings. Also, the UVL image of the painting presented varnishes with different fluorescence, identified by their blue and green colors. Some of these layers of varnish presented dripping, suggesting different interventions. These elements can be seen in figure 3.
The IRR method showed that before painting the final image the artist sectioned the canvas to reproduce the scenery proportionally to the real scale (some horizontal and vertical lines can be seen in figure 4). Besides that, design corrections can be found at the model's fingers holding his cap, a slight change at his cape and at his arm, and a paper sheet added to the painting after the table underneath was finished. It's suggested that the model's cap and head contour were modified, having its black pigments integrated into the background (figures 4(a) and 4(d)). Finally, the grey contrast of the IRR image indicates that the pigments used to paint the shoes and the shadow between them could be different (maybe due to the use of a restoration pigment).

However it appears to be the same color through the VIS method (figures 4(e) and 4(f)).
Due to the layers of varnish, the Raman signal obtained was very low and most of the data were noise, making it very difficult to interpret. A good signal identified was the bands of the red pigment Vermilion ($HgS$) at some red points selected across the painting. Figure 5(a) presents the Raman spectra of 3 selected red points (P3, P4 and P15) where it's identified the Vermilion bands. Figure 5(b) present a bar graph of photon counting of iron (Fe) K-lines spectra, resulting from the ED-XRF application. It's possible to correlate the presence of high amounts of Fe with other pigments, including in the red points with low counting on mercury (Hg).
With the ED-XRF data obtained, it was constructed table 1, indicating which pigments the artist may have used based on the chemical presence and historical knowledge about the production and use of pigments. It's highlighted that the presence of lead (Pb) at all 54 measuring points suggests that the artist prepared a Lead White base before painting (figure 6(a)). This technique was commonly applied during his artistic period and it was concluded that Victor Meirelles had this habit in other researches.[3][4] Also, it was identified the use of Naples Yellow pigment in his work, characterized by the presence of antimony (Sb) in the yellowish regions (figure 6(b)). This pigment suffered many modifications along the 19th century and became more uncommon while pigments with other compositions were manufactured to replace the original Naples Yellow. [5]




(a)

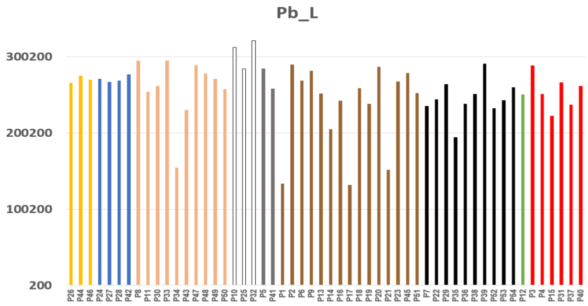



(b)

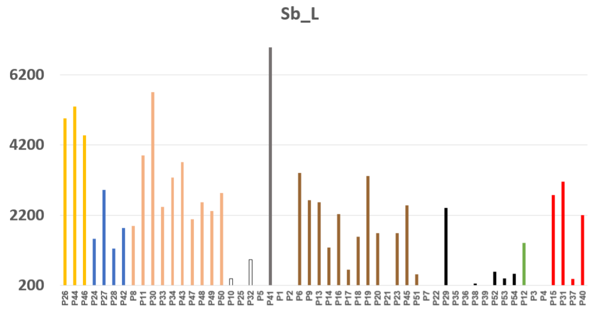
Figure 5: (a) Raman spectras of the red points P3, P4 and P15, present well defined peak of the pigment Vermilion. (b) The resulting bar graph with K-lines photon counting from $Fe$ obtained trough ED-XRF analysis shows the high amount of $Fe$ in various pigments across the painting.

Table 1: Suggestion of the pigments that may have been used by Victor Meirelles in the painting "Dr. José Maria Chaves" from MASP's collection.

| Color | Common name | Chemical Composition | Identity in XRF | Period of use |
|---|---|---|---|---|
| White | Lead white | $2PbCO_3.Pb(OH)_2$ | $Pb$ | Antiquity - 20th century |
| | Zinc white | $ZnO$ | $Zn$ | 19th century - Present |
| Yellow | Cadmium yellow | $CdS$ | $Cd,\ S$ | 19th century - Present |
| | Naples yellow | $Pb(SbO_3)_2, Pb_3(SbO_4)_2$ | $Pb,\ Sb$ | 16th century - Present |
| | Yellow ochre/Limonite | $Fe_2O_3.nH_2O,\ clay,\ silica$ | $Fe$ | Pre historic/20th century - Present |
| Red | Mars red | $Fe_2O_3$ | $Fe$ | 18th century - Present |
| | Red ochre/Red earth | $Fe_2O_3,\ clay,\ silica$ | $Fe$ | Pre historic - Present |
| | Vermilion/Cinnabar | $HgS$ | $Hg,\ S$ | Antiquity/8th century - Present |
| Blue | Prussian blue | $Fe_4(Fe[CN]_6)_3$ | $Fe$ | 18th century - Present |
| Green | Chromium oxide | $Cr_2O_3$ | $Cr$ | 19th century - Present |
| | Viridian/Guignet's green | $Cr_2O_3.2H_2O$ | $Cr$ | 19th century - Present |
| Black | Carbon black | $C$ | – | Antiquity - Present |
| | Ivory black/Bone black | $C,\ Ca_3(PO_4)_2$ | $Ca,\ P$ | Antiquity - Present |
| | Iron black/Mars black | $Fe_3O_4$ | $Fe$ | Antiquity/18th century - Present |
| Orange/ Brown | Manganese oxide | $MnO,\ Mn_2O_3$ | $Mn$ | Pre historic - Present |
| | Burnt siena | $Fe_2O_3.nH_2O, Al_2O_3$ | $Fe$ | Antiquity - Present |
| | Mars orange | $Fe_2O_3$ | $Fe$ | 18th century - Present |
| | Ochre/Goethite | $Fe_2O_3.nH_2O,\ clay$ | $Fe$ | Pre historic - Present |




(a)




(b)

Figure 6: Bar graphs presenting the photon counting of ED-XRF L-lines spectra from (a) lead (Pb) and (b) antimony (Sb) in the painting "Dr. José Maria Chaves" by Victor Meirelles from MASP's collection.

## 4. Conclusion

Portable and non-destructive methods of analysis combined with an interest in comprehending the Cultural Heritage's story allows us to explore the ramification of interdisciplinary studies. Through the application of imaging and spectroscopic techniques it's possible to determine the visible and invisible characteristics of the artwork, like the artist's creative process, their choices of pigments, interventions that the object suffered, etc. These studies contributes to the professionals who work with Cultural Heritage, suppling information that helps in restoration and preservation. The application of imaging techniques to the study of the painting "Dr José Maria Chaves"(1873), by Victor Meirelles from MASP's collection, showed creative techniques, like the sectioning of the canvas before painting, corrections made by the artist, and occured interventions. With the spectroscopic methods it was suggested the artist's palette and identified the use of Lead White as base preparation underneath the painting. This is reinforced by previous studies that suggested this practice was customary in his works. Finally, the use of an uncommon Naples Yellow pigment was discovered. To better characterize Victor Meirelles's period and style, new researches about his work and other contemporary painters can be done, improving our knowledge about the Brazilian artists.

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