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Multi-technical analysis as a tool to investigate structural species in the "replica" of First Mass in Brazil painting by Sebastião Vieira Fernandes

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ABSTRACT

Constituent materials of the painting "*Primeira Missa no Brasil*" by Sebastião Vieira Fernandes, which belongs to the Historical Museum of Santa Catarina, were analyzed by using imaging through UV-induced visible luminescence, FTIR, μ-FTIR, EDX and GC-MS with the aim of characterizing the materials and correlating them with Victor Meirelles' pigment elemental analysis reported in the literature. The images obtained under ultraviolet light showed alterations in the painting's aging process and instances of possible repainting confirmed by μ-FTIR, where characteristic bands of barium sulfate were identified. EDS analyses showed that there is a correlation between the elemental composition of pigments used by Meirelles and Fernandes, especially for lead, associated with lead white and proven by FTIR, used for giving a light tone to the paint, and found in all the analyzed samples. The GC-MS results revealed the presence of the mixture of linseed and animal oil as the main binding components with the predominance of palmitic, stearic, oleic, and linolenic acids.

1. Introduction

In recent years, there have been a growing number of studies using scientific tools for preservation of movable and immovable cultural heritage due to the preoccupation with safeguarding assets that transcend market borders and represent historical and cultural characteristics, reflecting the identity of a society. In the light of this situation, several paintings by renowned artists from Santa Catarina, portraying the history of Brazil, are worth highlighting. For example, the "*Primeira Missa no Brasil*" (First Mass in Brazil) by Victor Meirelles, painted in 1860, is one of Brazil's most popular works [1], while it is also one of the symbolic works of the national identity building process, establishing a history for Brazil based on the purpose of creating a continuity between an idealized colonial past and an independent empire [2].

In this context, another artist from Santa Catarina, Sebastião Vieira Fernandes, also stands out. He began his artistic training in *Desterro*, now called Florianópolis, where he attended nighttime art classes taught by Manoel Francisco de Oliveira (Maneca Margarida). Subsequently, he went to the city of Rio de Janeiro, enrolled in the *Liceu de Artes e Ofícios* (School of Arts and Crafts) and later in the *Academia de Belas-Artes* (Academy of Fine Arts) where he was a student of Vitor Meirelles and Zeferino da Costa [3]. As a disciple and contemporary of Meirelles, Sebastião faithfully reproduced his master's painting in 1929, "*Primeira Missa no Brasil*" (First Mass in Brazil), at the request of Lauro Müller, the first Republican Governor of Santa Catarina after the proclamation of the Republic. Given the fact that the latter offered the artist a derisory amount for his completed work, Sebastião retained possession of the painting [4]. After his death, his sister then donated the painting to the *Palácio do Governo de Santa Catarina* (Government Palace of Santa Catarina)

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[5], now called the *Museu Histórico de Santa Catarina* (History Museum of Santa Catarina).

The perfection in the detail of the replicated work is noteworthy, and many have questioned the extent to which Meirelles influenced his disciple in the production of this replica, particularly from the point of view of the materials in use. At this stage, scientific concepts and instrumental analysis methods were applied to answer questions about the materials used by Sebastião in the production of this work, and those results were compared with the materials found in the original work by Meirelles [6] in order to prove the existence of similar techniques and materials between the artists in the production of the replica painting.

Spectroscopic and separation methods are successfully utilized in this type of investigation [7], particularly infrared spectroscopy – FTIR and micro infrared spectroscopy μ-FTIR in conjunction with energy dispersive X-ray spectroscopy – EDS for the characterization of binders and pigments respectively [8–12] and chromatographic methods, especially gas chromatography/mass spectrometer detector – GC-MS to prove the structure of the binder used [13–15]. In this research work, these techniques were chosen because of their success in the resolution of these types of analysis [16–20]. It is worth mentioning the collaboration between the Materials Laboratory of the *Fundação Catarinense de Cultura* – FCC, a pioneer in Santa Catarina in the area of research in the field of chemistry applied to the preservation of cultural heritage, and the Capillary Electrophoresis Laboratory at UFSC, both of which contribute to the dissemination of this state of the art knowledge in Brazil.

Therefore, the main objective of this research paper is to map and identify the materials used by Sebastião Fernandes, a disciple and contemporary of Victor Meirelles, in the replication of the canvas painting "*Primeira Missa no Brasil*", in order to pinpoint the artist' palette and study the relations between the materials used in the replica and in Meirelles' original work, so that it may be possible to answer questions on Meirelles' influence on the execution of the replica painting.

2. Material and methods

2.1. Sample collection

Micro fragments of pictorial layer were collected by the conservator-restorer in the History Museum of Santa Catarina with the aid of an OPITIVISOR DA5 magnifier visor and a scalpel with new blades, sterilized with ethyl alcohol and dried in an oven at 80 °C for 3 h. Each collection point was carefully studied so that the sample collected represented a set of materials used by the artist. Fig. 1 shows a photograph of the painting "*Primeira Missa no Brasil*" by Sebastião Vieira Fernandes, identifying points from which each of the samples was taken. The choice of points for the collection of the samples was first based on UV-induced visible luminescence assays in order to identify possible areas of intervention, and then based on the analysis of Meirelles's canvas [6].

2.2. Scientific imaging documentation

Scientific imaging documentation was carried out using a Nikon câmera, model D5000 with Nikon lens AF-S DX NIKKOR 18–55 mm f/3.5–5.6 G with the following configuration: ISO 100; focal length 46 mm corresponding to 69 mm in the 35 mm film due to the court factor; exposure time 1 s with manual white balance. For color correction, Camera Raw in Adobe Photoshop CS6 was employed using 18% gray card Qpcard 101, under fluorescent light. For UV-induced visible luminescence the magnifying glass coupled with a Ramsor 300 nm ultraviolet lamp was used. The images in presence of UV light were performed with the balance to set the camera as "*shadow*", and exposure times ranged from 10 to 20 s.

2.3. Infrared spectroscopy – FTIR

Infrared spectra from each sample were obtained using a JASCO FTIR-4100 spectrometer, with 4 cm^{-1} resolution, in attenuated total reflectance mode – ATR with direct sampling under the ZnSe crystal; all spectra were collected with 64 scans.

2.4. Micro FT-IR spectroscopy – μ-FTIR

The μ-FTIR values were measured on a Varian F7000e spectrometer coupled with a Varian UMA 600 FT-IR microscopy. The samples were dispersed on a glass slide and the spots selected have the dimension area of 100 μm × 100 μm. The spectra were collect in the reflectance mode using a 15× reflecting objective and a nitrogen cooled MCT detector. The spectra are an average of 64 scans with 4 cm^{-1} resolution.

2.5. Energy dispersive X-ray spectroscopy – EDS

The semi-quantitative elemental analyses studies for each sample were performed using an energy dispersive spectrometer coupled to a JEOL JSM-6390V scanning electron microscope with acc. voltage: 15.0 kV, magnification range 1000×, and NanoTrace detector, in the Electronic Microscopy Central Laboratory – LCME in the Federal University of Santa Catarina (UFSC).

2.6. Gas chromatography with mass spectrometer detector – GC-MS

The analyses of fatty acids by GC-MS were carried out in an Agilent 7829 series chromatographic system, equipped with a 7683 automatic injector sampler with electronic pressure control and interfaced with an Agilent 5975 mass detector. Operating temperatures of the detector: transfer line, 280 °C; ion source, 230 °C; interface, 280 °C; quadrupole, 170 °C. Scan detection in the mass range from 50 to 900, with a scanning time of 20 ms. Electron impact ionization at 75 eV. Chromatograph operating conditions: injector, 250 °C; column, 120 °C (initial temperature, 5 min); followed by a gradient of 10 °C min^{-1} to a final temperature of 300 °C min^{-1} (10 min); total flow, 1.0 mL/min; pressure, 9.4 psi; mean linear velocity, 41.2 cm s^{-1}; 1 μL of sample injected in splitless mode. A HP-5 fused silica capillary column (30.0 m × 0.25 mm × 0.25 μm thick film) was used.

Samples underwent a derivatization process according to the literature [21,22] with some adaptations: 100 μL of the sample was added to a tube with a screw-on cap. 2.0 mL of a 0.5 mol L^{-1} de NaOH/Methanol solution was added and the sample was then kept in a boiling water bath for 20 min. After, 2.5 mL of the esterifying solution was added, 0.6 mol L^{-1} NH4Cl + 0.9 mol L^{-1} de H_2SO_4 in methanol, and this solution was kept in a boiling water bath for 5 min 2 mL of the saturated NaCl solution was then added. Finally, 2.5 mL of Hexane was added and the sample was stirred for 30 s. After decantation, an aliquot from the organic phase was collected for analysis.

3. Results and discussion

3.1. UV-induced visible luminescence images

The imaging process coupled to a radiation source is widely used in conservation science to identify materials and repainting, assess the state of conservation, and also to identify pathologies