

# Monitoring Of Macroinvertebrates Along Streams of Bilah River, Labuhanbatu Regency, North Sumatra Indonesia

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## Abstract.

*The present study reports the first comprehensive study on the freshwater macroinvertebrates and its habitat preferences in Bilah River, the largest river in the Northern Sumatra. The riverside is characterized by the presence of anthropogenic and industrial activities which may alter the macroinvertebrate assemblage and biodiversity. Five months of investigation on 10 sampling stations from December 2016 to October 2017 was conducted based on the river flow in Bilah River. Principal component analysis indicated a decrease in trophic status from upstream to downstream of the river. A total of 27 taxa were recorded, with the most abundant group were members of Odonata, Gastropoda, and Decapoda. The highest density of macroinvertebrate was observed from station 1 (160 ind m<sup>-2</sup>), while the lowest density was observed from station 9 (38.64 ind m<sup>-2</sup>). Based on species distribution and similarity, two groups of habitats may be distinctively recognized based on the Bray-curtis similarity coefficient. Group 1 consisted of station 1, 2, 3 and 4 while group 2 consisted of station 5, 6, 7, 8, 9, and 10. Based on the diversity indices as ecological parameters, the habitat condition in Bilah River is categorized from low to moderately polluted. Spatial patterns in both environmental conditions affecting the macroinvertebrate assemblage was observed using canonical correspondence analysis (CCA) revealed the preferences from each macroinvertebrate species towards environmental conditions.*

**Keywords:** Bivalvia, bray-curtis, canonical correspondence analysis, density, gastropoda.

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## 1. INTRODUCTION

The social revolution caused by the popularization of synthetic polymer-based products have also influenced the arts. Since 1930, acrylic emulsion and alkyd paints have been progressively incorporated into the artist's palette [1]. Somewhat, acrylics were protagonists of Abstract and Contemporary Art. The use of these, as opposed to oil, also meant a break from tradition for many artists.

For the past twenty years, studies have been conducted on how to properly conserve acrylic painted canvases [2, 3], as they are more prone to attract dirt and require specific cleaning processes, different from oil paintings.

Brazilian contemporary artists, such as Maurício Nogueira Lima, Hermelindo Fiaminghi, Geraldo de Barros, Mira Schendel and Lygia Clark [4], have used acrylic paints extensively. According to art historians and artists' testimonies, Brazilian painters favored national-made paint over high-price imported products during the most prolific period of their career. Materials retrieved from artists' studios, such as Ivan Serpa, Maurício Nogueira Lima and Tomie Ohtake, confirm their preference for Brazilian paints [5]. This long-lasting cost problem is illustrated in the 1954 *colorless strike* led by artists Djanira da Motta e Silva, Iberê Camargo and Milton DaCosta. More than 600 artists engaged in this movement, painting solely in black and white to protest high import taxes for artist paint, which although being oil paints were still very costly. Heretofore, imported (USA, GBR, ITA, NLD) paints are almost ten times more expensive than Brazilian paints.

Studies have been conducted on acrylic paints manufactured in the USA [6], Mexico [7] and Denmark [8], but not in countries with sparse tradition in artist paint making. Chemical characterization is vital information for conservators, given the case of Donald Judd's Hi-Fi Purple, where the artist himself adverted the wrong use of purple paint to restore his artwork [9] and in cleaning processes, as pointed out by Lomax *et al.* [10] and Doménech-Carbó *et. al.* [11].

This paper presents the characterization of acrylic blue paints manufactured by two Brazilian companies, Acrilex and Corfix. Results were compared with two reputed imported brands available in Brazil, Liquitex and Winsor & Newton. Analyses were carried out by pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and scanning electron microscopy coupled with energy dispersive x-ray fluorescence spectrometry (SEM-EDS) techniques.

## II. METHODS

The analytical techniques selected to conduct this investigation are based on the suitability for characterizing art materials. Therefore, the instrument parameters must meet conservation standards regarding sampling, where minimum or no samples should be taken from artworks. Py-GC/MS offers broad insight on chemical composition, as the sample components are fully identified based on their molecular mass after being separated by chromatography. A rapid differentiation of medium acrylic polymer is provided by FTIR technique, based on the identification of organic functions of the monomer main chain. Raman spectroscopy was also employed as a complimentary technique to FTIR. The aforementioned techniques do not provide conclusive information on inorganic pigments or fillers. For that reason, SEM-EDS was used to evaluate pigment and filler presence on each sample. Microscopy not only indicates the distribution of pigments but also their particle size, while EDS provides qualitative elemental analysis.

### *Py-GC/MS*

The instrument used was a PY-3030D microfurnace pyrolyzer (Frontier Lab) mounted over a Shimadzu Co. GCMS-QP5000 equipped with SGE BPX5 column 5% phenyl polysilphenylene-siloxane (30m x 0.25 $\mu$ m x 0.25mm). Pyrolysis was performed at 610°C for 0.20min with Py-GC interface at 300°C and GC-MS interface at 280°C. The GC oven temperature was 40°C (held for 2min.) with a 10°C·min<sup>-1</sup> rate and final temperature of 350°C (2 min). The MS split was 1:150 and the m/z was scanned from 40 to 600 $\mu$ m in electron impact ionization mode (EI<sup>+</sup>, 70eV). Spectra were compared to NIST library standards and the works of Tsuge *et al.* [12] and Tom Learner [1].

#### *FTIR*

Infrared spectra were collected on a Varian 660IR model coupled with a VeeMax II reflectance accessory (Pike Technologies), from 4000 to 400cm<sup>-1</sup> and for 100 scans with a resolution of 1cm<sup>-1</sup>, reflectance angle at 51°. Kubelka-Munk (K-M) function was used.

#### *Raman*

The spectrometer used was a Cora Family 5500 (Anton Parr) equipped with 785nm excitation laser, covering the 100 to 2300cm<sup>-1</sup> range with resolution of 12cm<sup>-1</sup> and laser power of 450mW. Vibrational spectra, FTIR and Raman, were compared with IRUG (Infrared and Raman Users Group) database.

#### *SEM-EDS*

Microscopical analyses were performed on a TM3000 (Hitachi Co.) scanning electron microscope coupled with a Quantax70 energy dispersive X-ray fluorescence spectrometer (Bruker Nano GmbH). Images and elemental analyses were obtained at 15kV and working distance 5.1mm.

### **III. RESULT AND DISCUSSION**

Acrylic paints are a complex formulation that includes numerous ingredients. The final product must meet commercial (shelf life, material costs, environmental and health safety) and artistic (durability, color and film stability, drying rate) demands. Therefore, the paint tube might contain the acrylic binder, pigment or dye, wetting and dispersing agents, thickeners, biocides and defoamers [13].

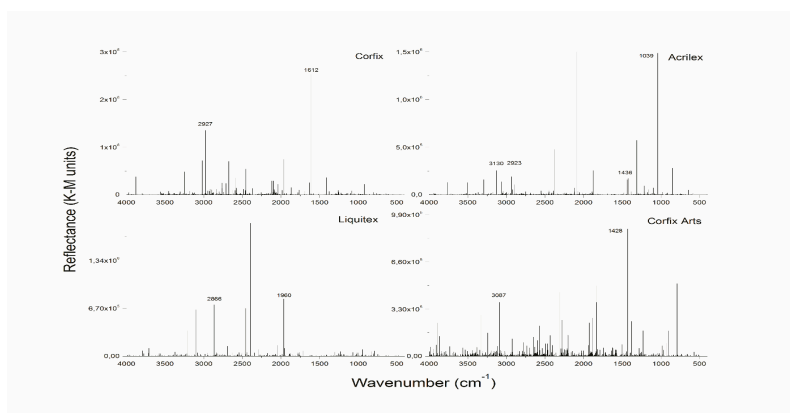
FTIR and Raman spectroscopies were used to identify binding media, SEM-EDS was used to identify inorganic pigments and fillers, Py-GC/MS was used to identify minor binders and plasticizers. Results are presented in Table 1.

#### ***Binding media***

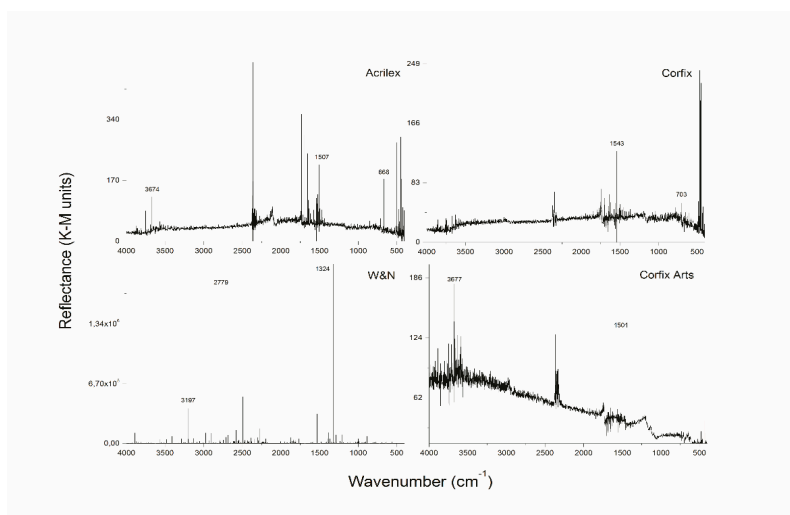
Brazilian paints present styrene (S) as the major component. Differently, the binding media of imported paints, namely from USA and Great Britain, is a copolymer of metyhl methacrylate (MMA). Nevertheless, the newly released *professional grade* Brazilian paint (Corfix Arts) presents poly(styrene-co-methacrylate), P(S/MA), as binding media.

The use of MMA as binding media yields a paint film which is stable, resistant to hydrolysis and transparent to UV. In general, substitution of methacrylate copolymers for polystyrene is due to cost issues [2].

Monomers of each paint sample are identified by infrared and Raman spectroscopies. Figures 1 and 2 show, respectively, FTIR spectra of phthalo blue (BPc) and Prussian blue (BPr) samples. Styrene presence is characterized by infrared peaks at  $3087\text{--}3018\text{ cm}^{-1}$  for aromatic C-H stretching ( $\nu$ ),  $1428\text{ cm}^{-1}$  for ring breathing and  $1612\text{ cm}^{-1}$  for C=C stretching. Raman spectra for Corfix and Corfix Arts paints are presented in figure 3. Characteristic peaks  $1076\text{ cm}^{-1}$  for aromatic ring stretching and  $1686\text{ cm}^{-1}$  for aromatic  $\nu\text{C-H}$  are observed. The presence of MA in Corfix Arts sample is indicated by infrared peaks  $1742\text{ cm}^{-1}$  ( $\nu\text{C=O}$ ),  $1229\text{ cm}^{-1}$  ( $\nu\text{C-O}$ ) and  $1427\text{ cm}^{-1}$  ( $\nu\text{CH}_3$ ) and Raman peaks  $1096\text{ cm}^{-1}$  ( $\nu\text{C-O-C}$ ) and  $1686\text{ cm}^{-1}$  ( $\nu\text{C=O}$ ).

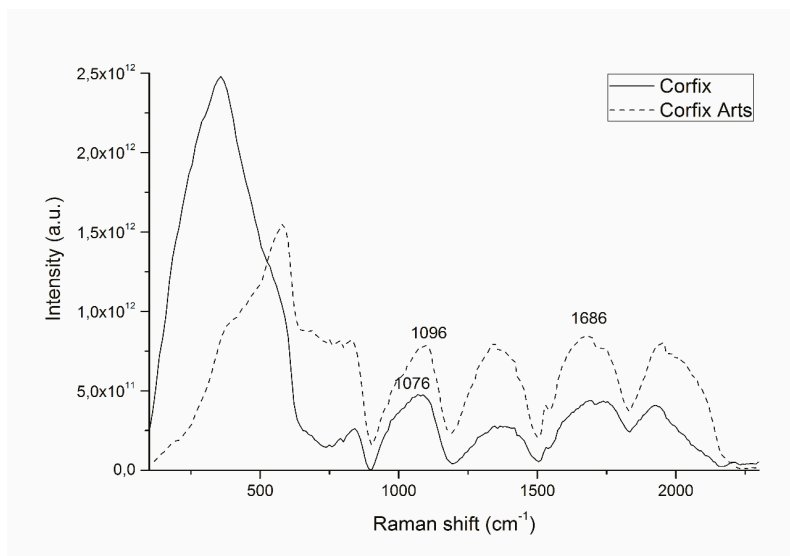


**Fig. 1.** FTIR spectra of phthalo blue (BPc) paints: Acrylic, Corfix, Corfix Arts (BRA) and Liquitex (USA)



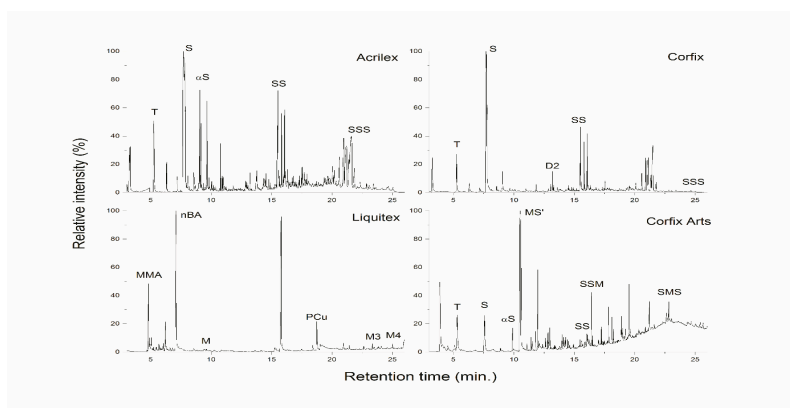
**Fig. 2.** FTIR spectra of Prussian blue (BPr) paints: Acrylic, Corfix, W&N, Corfix Arts

Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

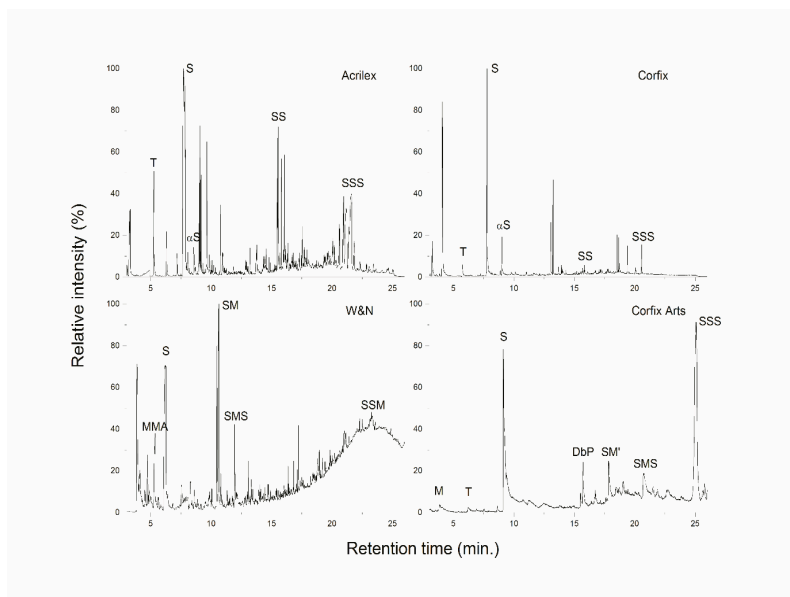


**Fig. 3.** Raman spectra of phthalo blue (BPc) Corfix and Corfix Arts (BRA)

The binding media present in phthalo acrylic paints are confirmed by Py-GC/MS technique. Figures 4 and 5 present the chromatogram of phthalo blue (BPc) and Prussian blue (BPr) samples. Peaks for PS are indicated by presence of styrene (S), alpha-methylstyrene ( $\alpha$ S), styrene dimer (SS and D2) and trimer (SSS). Peaks for P(S/MA) are confirmed by methacrylate (M), styrene (S), a hybrid dimer (SM') and trimer (SSM and SMS). Chromatogram of P(S/MMA) differs mainly for the MMA monomer identification at 5 min in Winsor & Newton BPr sample. Characteristic peaks of P(nBA/MMA) sample are described elsewhere [1].



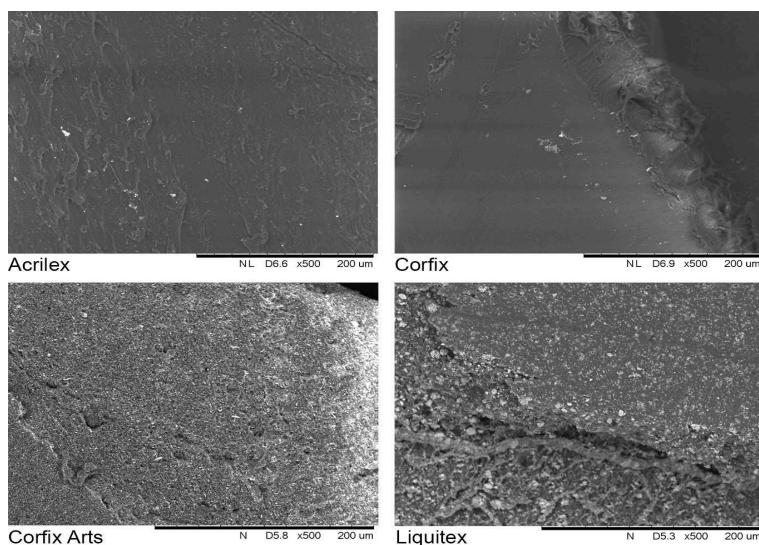
**Fig. 4.** Py-GC/MS spectra of phthalo blue (BPc) paints: Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)



**Fig. 5.** Py-GC/MS spectra of Prussian blue (BPr) paints: Acrilex, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

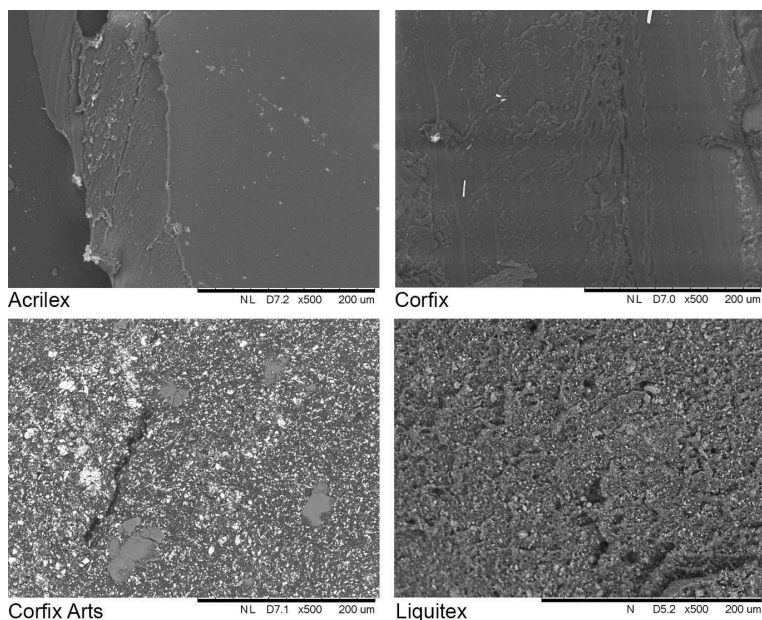
### *Pigments and extenders*

Figures 6 and 7 present SEM images (micrographs) of BPc and BPr samples, respectively. Results indicate that Corfix Arts is the only to resemble the composition of imported materials. Images of samples Acrilex and Corfix, for both paints, BPc and BPr, present lower ratio of particles either pigments or extenders.



**Fig. 6.** Micrographs (200μm) of phthalate blue (BPc) paints:

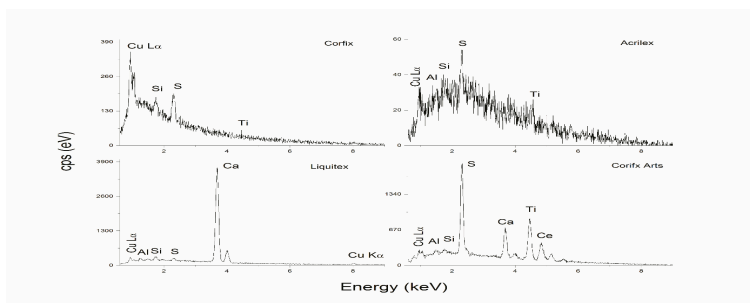
## Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)



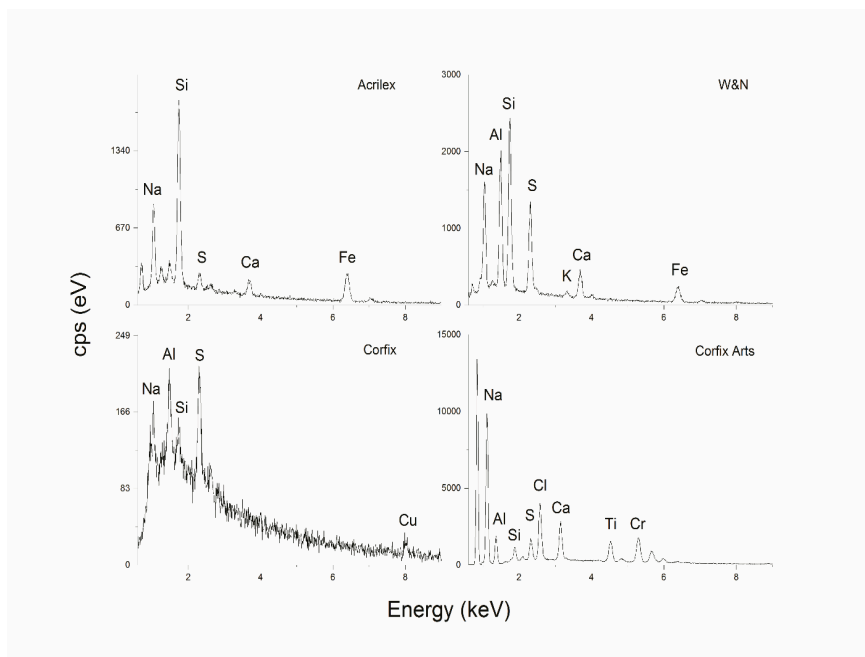
**Fig. 7.** Micrographs (200µm) of Prussian blue (BPr) paints: Acrilex, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

Phthalocyanine blue ( $C_{32}H_{16}CuN_8$ ) is indicated by EDS (Table 1) by presence of copper in all four BPC samples. Prussian blue ( $C_{18}Fe_7N_{18}$ ) is detected in BPr samples Acrilex, Corfix Arts and Winsor & Newton. Sample Corfix of Prussian blue is composed of copper. Phthalocyanine blue pigment is also detected by Py-GC/MS in Liquitex sample (Fig. 4).

EDS elemental analysis (Table 1, Figs. 8 and 9) indicate that all samples present kaolinite ( $Al_2Si_2O_5(OH)_4$ ) as filler, except for sample Bpr Acrilex, which contains talc ( $Mg_3Si_4O_{10}(OH)_2$ ). FTIR analyses indicate the presence of these fillers with peaks at  $1039cm^{-1}$  ( $\nu Si-O$ ),  $3750-3500cm^{-1}$  ( $\nu O-H$ ) and  $789-754cm^{-1}$  ( $\nu Al-Si-O$ ).



**Fig. 8.** EDS spectra of phthalocyanine blue (BPC) paints: Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)



**Fig. 9.** EDS spectra of Prussian blue (BPr) paints: Acrilex Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

Corfix Arts samples of both BPc and BPr paint present  $\text{TiO}_2$  and cerium (Ce). Titanium dioxide is often used to moderate hue and saturation. Rare earth metals, especially Ce, are known to enhance paint properties such as light fastness, chemical resistance and drying time [14].

#### IV. CONCLUSION

Chemical composition of artist paints commercialized in Brazil varies greatly. Therefore, a multi-component characterization requires multi-technique analyses. Advantages of each technique (FTIR, Raman, Py-GC/MS and SEM-EDS) were pointed out to present a broader knowledge of the paints used by Brazilian contemporary artists.

FTIR and Raman are, complimentary, able to rapidly identify the main binders, while Py-GC/MS provides further information of copolymers, even in minor concentration levels. SEM-EDS successfully identifies pigments and extenders.

Brazilian paints of *student* grade are composed of PS binding media and low pigment ratio, whereas the *professional* grade paint is composed of P(S/MA) binding media, higher pigment ratio and extenders such as  $\text{TiO}_2$  and Ce.

Conservation concerns over the ageing processes of these paints will be addressed in future studies.

In conclusion, this initial study provides conservators, artists and conservation scientists information on the composition of artist paints manufactured in Brazil.

## V. ACKNOWLEDGMENTS

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