

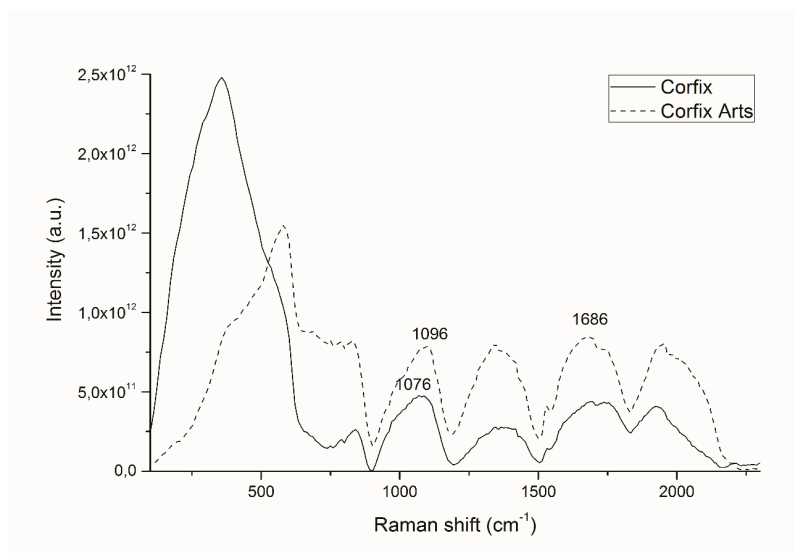


Fig. 3. Raman spectra of phthalo blue (BPc) Corfix and Corfix Arts (BRA)

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 (α 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].

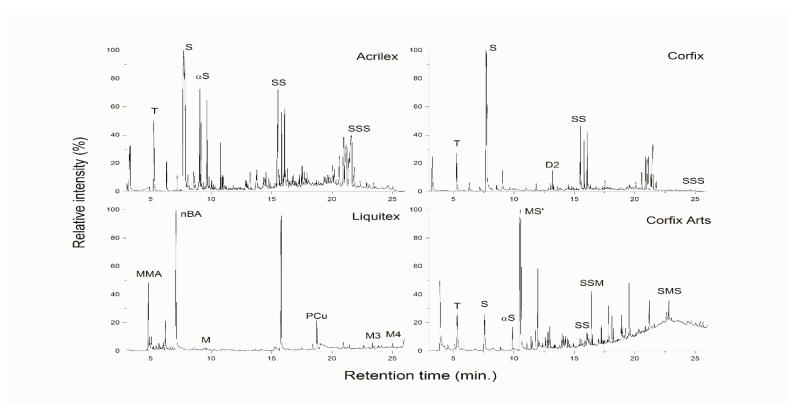


Fig. 4. Py-GC/MS spectra of phthalo blue (BPc) paints:
Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)

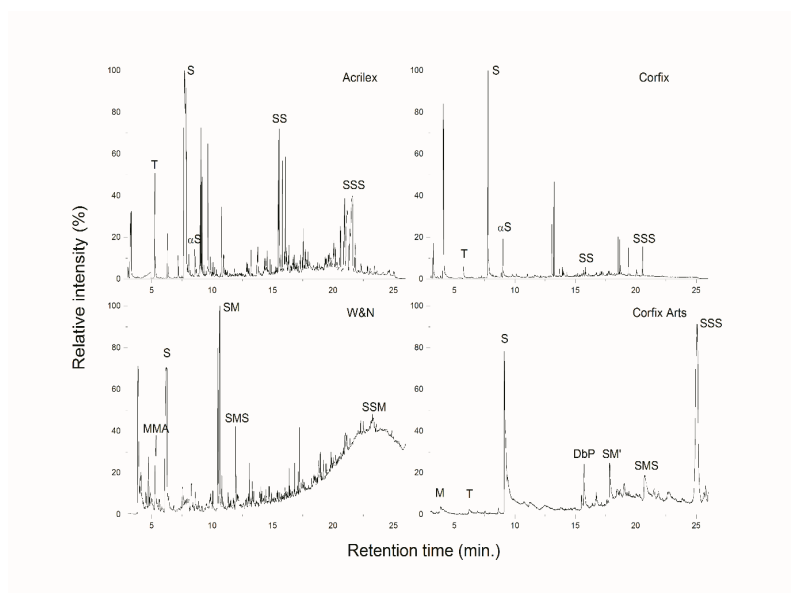


Fig. 5. Py-GC/MS spectra of Prussian blue (BPr) paints: Acrylic, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

Pigments and extenders

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

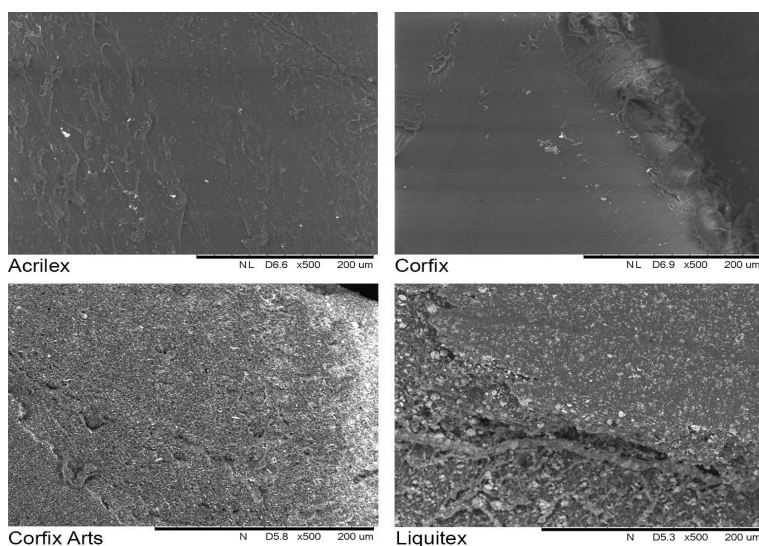


Fig. 6. Micrographs (200µm) of phthalo blue (BPc) paints: Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)

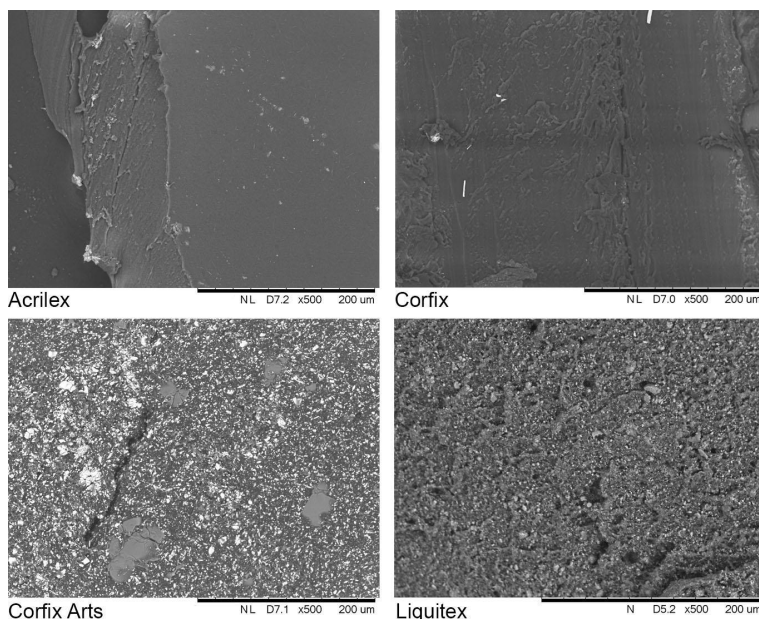


Fig. 7. Micrographs (200µm) of Prussian blue (BPr) paints: Acrilex, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

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 ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) as filler, except for sample Bpr Acrilex, which contains talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$). FTIR analyses indicate the presence of these fillers with peaks at 1039cm^{-1} ($\nu\text{Si-O}$), $3750\text{-}3500\text{cm}^{-1}$ ($\nu\text{O-H}$) and $789\text{-}754\text{cm}^{-1}$ ($\nu\text{Al-Si-O}$).

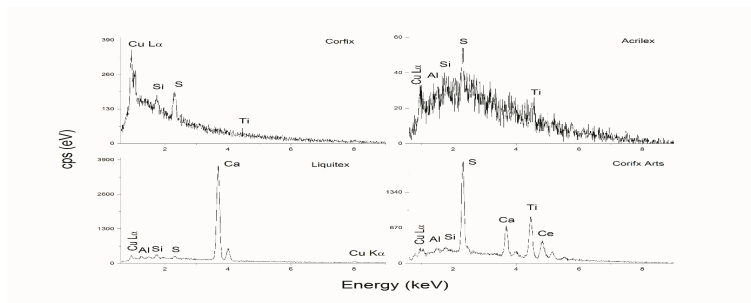


Fig. 8. EDS spectra of phthalo blue (BPc) paints: Acrilex Corfix, Corfix Arts (BRA) and Liquitex (USA)

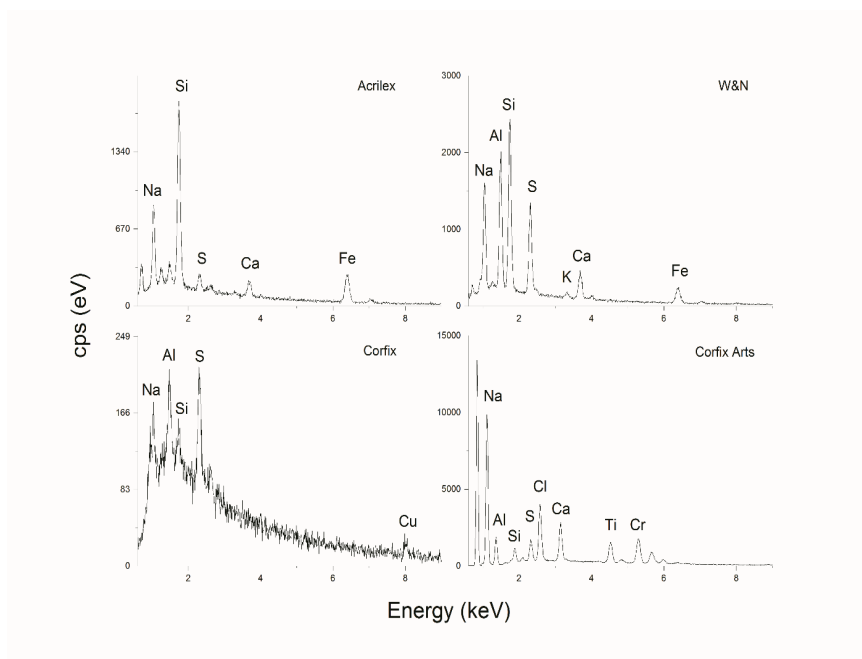


Fig. 9. EDS spectra of Prussian blue (BPr) paints: Acrilex Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

Corfix Arts samples of both BPc and BPr paint present 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 TiO₂ 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

The authors are grateful to the CNPq National Council of Scientific and Technologic Development for supporting this project, to the Center for Lasers and Applications' Multiuser Facility at IPEN-CNEN/SP and to Anton Paar Brasil for the use of the Raman spectrometer. We also thank Teodora Camargo and Tatiana Russo from the *Núcleo de Conservação e Restauro* in *Pinacoteca do Estado de São Paulo* for the invaluable advices.

REFERENCES

- [1] T.J.S. Learner, **Analysis of Modern Paints**, The Getty Conservation Institute, 2004, p. 236
- [2] N. L. Engel, S. Zumbühl, *An evaluation of selected retouching media for acrylic emulsion paint*, **Journal of the American Institute of Conservation**, **54**, 2015, pp. 224-237.
- [3] E. Jablonski, T.J.S. Learner, J. Hayes, M. Golden, *Conservation concerns for acrylic emulsion paints*, **Studies in Conservation**, **48**, 2003, pp. 3-12.
- [4] G. Giovani, L.A.C. Souza, Y. Froner, A. Rosado, *The use of industrial paint on wood by Lygia Clark*, **Studies in Conservation**, **61:2**, 2016, pp. 291-293.

- [5] J.H.R. Barbosa, *O uso de materiais pictóricos industriais pelos artistas nas décadas de 1950 e 1960*, **PhD Thesis**, Universidade Federal de Minas Gerais, 2017 p. 312.
- [6] C.E. Rogge, B.A. Eppley, *Behind the Bocour label: Identification of pigments and binders in historic Bocour oil and acrylic paints*, **Journal of the American Institute of Conservation**, **56**, 2017, pp. 15-42.
- [7] A. Mejía-González, S. Zetina, M. Espinosa-Pesqueira, N. Esturau-Escofet, *Characterization of commercial artists' acrylic paints and the influence of UV light on ageing*, **International Journal of Polymer Analysis and Characterization**, **22**, 2017, pp. 473-482.
- [8] M. Christiansen, E. Baadsgaard, J. Sanyova, K. Simonsen, *The artists' material of P.S. Krøyer: An analytical study of the artist's paintings and tube colours by Raman, SEM-EDS and HPLC*, **Heritage Science**, **5**, 2017, pp. 39-50.
- [9] N. Khandekar, E. Nagy, J. Miller, P. Gottschaller, C. Mancusi-Ungaro, *The re-restoration of Donald Judd's 'Untitled, 1965'*, **Modern Paints Uncovered** (Editors: T.J.S. Learner, P. Smithen, J.W. Krueger, M.R. Schilling), First edition, Getty Publications, Los Angeles, 2007, pp. 157-164.
- [10] S. Lomax, S. Fisher, *An investigation of the removability of naturally aged synthetic picture varnishes*, **Journal of the American Institute of Conservation**, **29**, 1990, pp. 181-191.
- [11] M.T. Doménech-Carbó, M.F. Silva, E. Aura-Castro, A. Doménech-Carbó, L. Fuster-López, J.V. Gimeno-Adelantado, S.U. Kröner, M.L. Martínez-Bazán, X. Más-Barberá, M.F. Mecklenburg, L. Osete-Cortina, D.J. Yusá-Marco, *Multitechnique approach to evaluate cleaning treatments for acrylic and polyvinyl acetate paints*, in: **New insights into the cleaning of paintings** (editors: M.F. Mecklenburg, A.E. Charola, R.J. Koestler), Smithsonian Institution Scholarly Press, 2013, pp. 125-134.
- [12] S. Tsuge, H. Othani, C. Watanabe, **Pyrolysis - GC/MS Data Book of Synthetic Polymers**, First edition, Elsevier, 2011, p. 420.
- [13] J. Hayes, M. Golden, G.D. Smith, *From formulation to finished product: Causes and potential cures for conservation concerns in acrylic emulsion paints*, **Modern Paints Uncovered** (Editors: T.J.S. Learner, P. Smithen, J.W. Krueger, M.R. Schilling), First edition, The Getty Conservation Institute, Los Angeles, 2007, pp. 58-65.
- [14] V.R. Sastri, *Applications*, **Modern Aspects of Rare Earths and Their Complexes** (Editors: V.R. Sastri, J.C. Bünzli, V. Ramachandra Rao, G.V.S. Rayudu, J.R. Perumareddi), First edition, Elsevier, 2003, pp. 893-981.