Macrozoobenthos Communities Found In The Waters Of Mariah Bandar Springs

Masdiana Sinambela[1*], Martina Asiati Napitupulu[2], Tonggo Sinaga[3]

[1,2,3] Biology Department, Mathematics And Natural Sciences Fakulty, Universitas Negeri Medan, Medan Indonesia
*Corresponding Author:
Email: masdiana@unimed.ac.id

Abstract.

Macrozoobenthos found in the waters of Mariah Bandar Springs, Pematang Bandar District, Simalungun Regency, along with physical and chemical parameters, where biological samples, namely macrozoobenthos, were taken using a quadrant and physical and chemical parameters of the water were taken using a dark colored sample bottle and then analyzed at the BTKL The waters that originate from the Mariah Bandar spring have very clear and shallow water, so that the bottom of the waters (substrate) can be seen directly, which consists of sandy rocks. The macrozoobenthos community in the waters of Mariah Bandar spring consists of four classes, namely Clitellata, Gastropod, Bivalvia, Insecta, and eight families, namely Lumbricidae, Thiaridae, Cyrenidae, Chironomidae, Gomphidae, Paludicola, Coenagrionidae, Libellulidae. The temperature at each observation station ranges from 22^0C – 35^0C, brightness ranges from 4 – 4.5 m from the surface, dissolved oxygen (DO) ranges from 6.84-8.25 mg/l, pH ranges from 7.36-8.85 , BOD ranged from 1.01-3.42 mg/l. In general, the physical and chemical parameters measured still support the life of freshwater organisms, unless the pH is classified as acid.

Keywords: *Macrozoobenthos, community, springs, factors and abiotic.*

I. 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 0.25µm 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^{-1} rate and final temperature of 350°C (2 min). The MS split was 1:150 and the m/z was scanned from 40 to 600µm in electron impact ionization mode (EI+, 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^{-1} and for 100 scans with a resolution of 1cm^{-1}, 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^{-1} range with resolution of 12cm^{-1} 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 3087-3018 cm^{-1} for aromatic C-H stretching (ν), 1428cm^{-1} for ring breathing and 1612cm^{-1} for C=C stretching. Raman spectra for Corfix and Corfix Arts paints are presented in figure 3. Characteristic peaks 1076cm^{-1} for aromatic ring stretching and

1686cm^{-1} for aromatic νC-H are observed. The presence of MA in Corfix Arts sample is indicated by infrared peaks 1742cm^{-1} (νC=O), 1229cm^{-1} (νC-O) and 1427cm^{-1} (νCH_3) and Raman peaks 1096cm^{-1} (νC-O-C) and 1686cm^{-1} (νC=O).

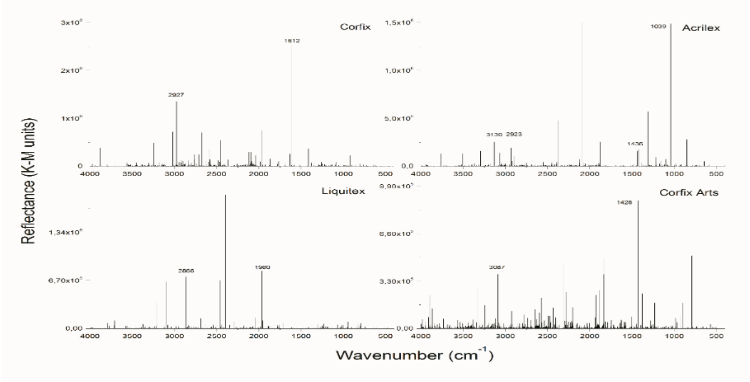

Fig 1. FTIR spectra of phthalo blue (BPc) paints: Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)

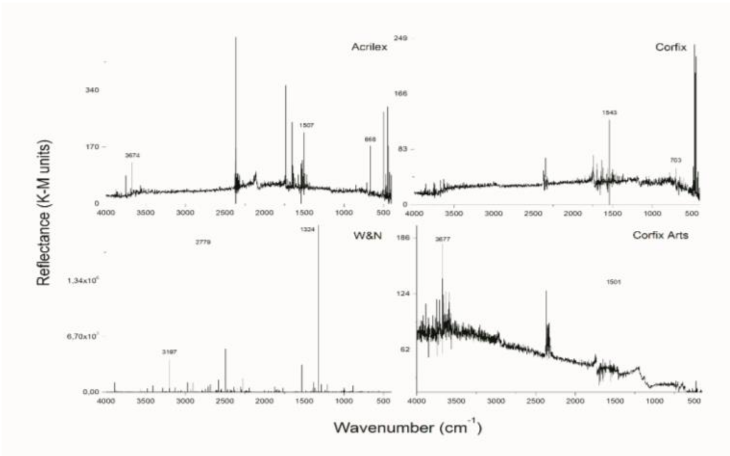

Fig 2. FTIR spectra of Prussian blue (BPr) paints: Acrilex, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

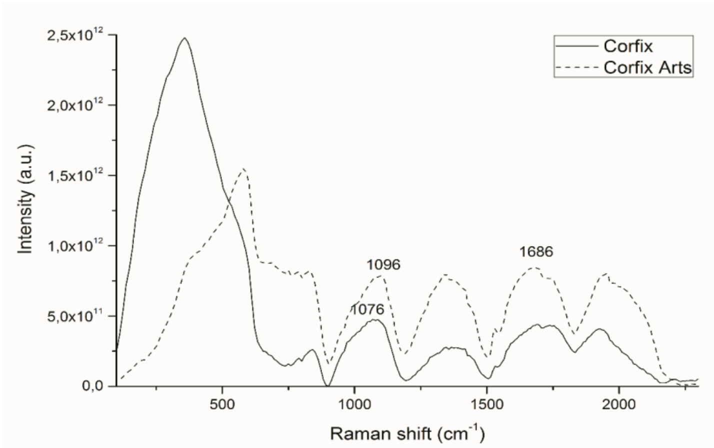

Fig 3. Raman spectra of phthalo blue (BPc) Corfix and Corfix Arts (BRA)

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 (αS), 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].

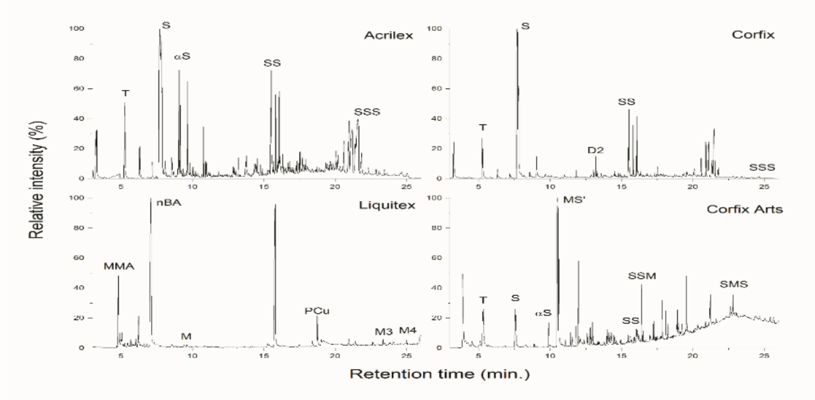

Fig 4. Py-GC/MS spectra of phthalo blue (BPc) paints: Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)

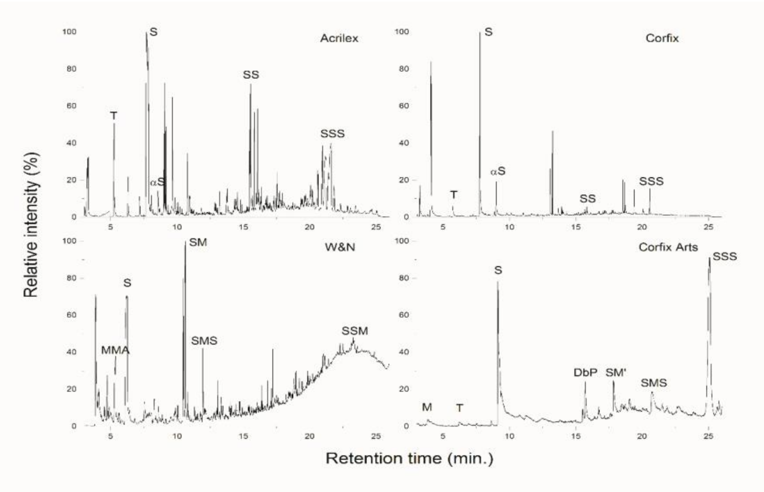

Fig 5. Py-GC/MS spectra of Prussian blue (BPr) paints: Acrilex, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

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.

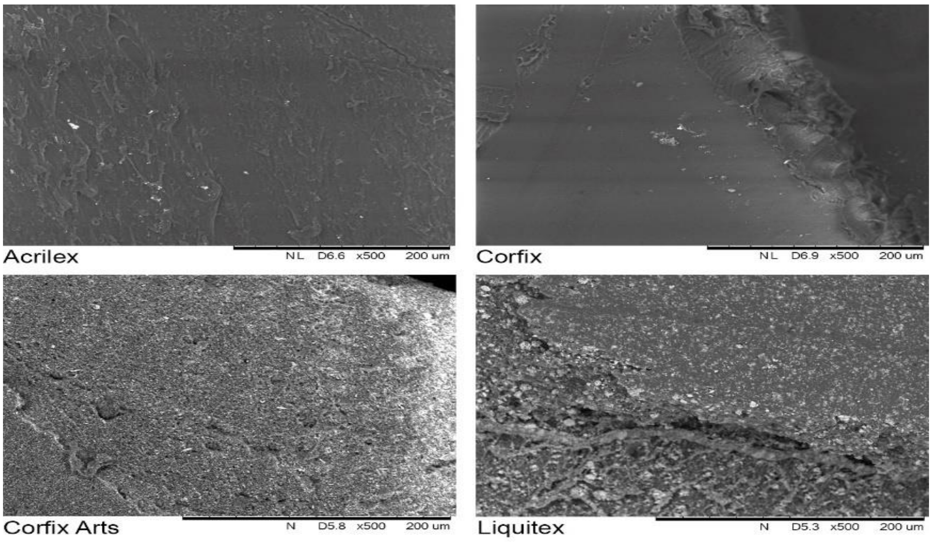

Fig 6. Micrographs (200µm) of phthalo blue (BPc) paints: Acrilex, Corfix, Corfix Arts (BRA) and Liquitex (USA)

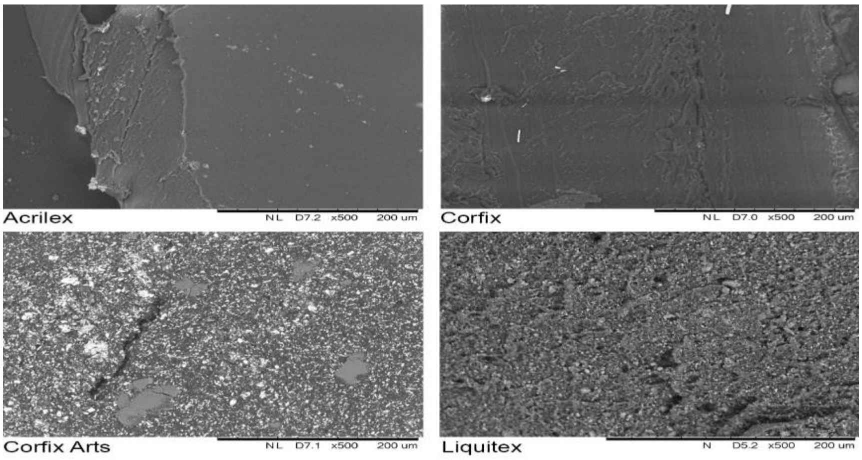

Fig 7. Micrographs (200µm) of Prussian blue (BPr) paints:
Acrilex, Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

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 ($Al_2Si_2O_5(OH)_4$) 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} (νSi-O), 3750-3500cm^{-1} (νO-H) and 789-754cm^{-1} (νAl-Si-O).

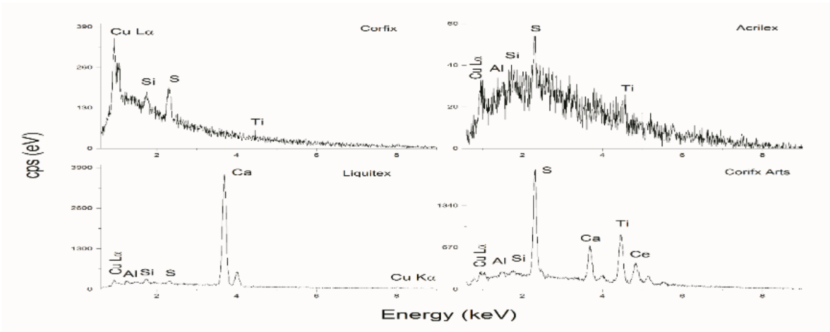

Fig 8. EDS spectra of phthalo blue (BPc) paints: Acrilex
Corfix, Corfix Arts (BRA) and Liquitex (USA)

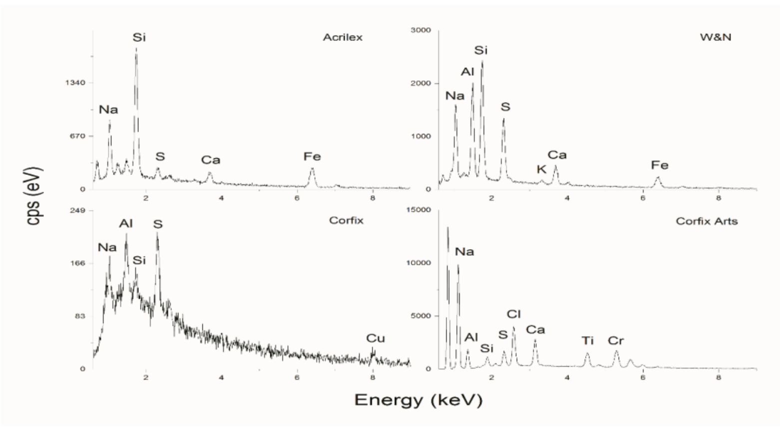

Fig 9. EDS spectra of Prussian blue (BPr) paints: Acrilex
Corfix, Corfix Arts (BRA) and Winsor & Newton (GBR)

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 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

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 Characterizatoin***, ***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),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.