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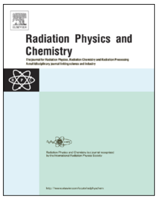

X-ray fluorescence and imaging analyses of paintings by the Brazilian artist Oscar Pereira Da Silva

P.H.O.V. Campos [a], E.A.M. Kajiya [a], M.A. Rizzutto [a,*], A.C. Neiva [b], H.P.F. Pinto [b], P.A.D. Almeida [a]

[a] *Instituto de Física da Universidade de São Paulo, Rua do Matão, Travessa R, 187, São Paulo, SP 05508-090, Brazil*
[b] *Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Química, Av. Prof. Luciano Gualberto, Travessa 3, 380, São Paulo, SP 05508-010, Brazil*

HIGHLIGHTS

- Performed Energy-Dispersive X-Ray Fluorescence spectroscopy and image analysis to characterize easel paintings
- The analyses allow the identification of the pigments elements
- Intensity ratio between the emitted characteristic rays is affected by the absorption of the outgoing rays.
- Image analysis allow some identification as hidden underlying lines,

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ABSTRACT

Non-destructive analyses, such as EDXRF (Energy-Dispersive X-Ray Fluorescence) spectroscopy, and imaging were used to characterize easel paintings. The analyzed objects are from the collection of the Pinacoteca do Estado de São Paulo. EDXRF results allowed us to identify the chemical elements present in the pigments, showing the use of many Fe-based pigments, modern pigments, such as cobalt blue and cadmium yellow, as well as white pigments containing lead and zinc used by the artist in different layers. Imaging analysis was useful to identify the state of conservation, the localization of old and new restorations and also to detect and unveil the underlying drawings revealing the artist's creative processes.

1. Introduction

EDXRF (Energy-Dispersive X-Ray Fluorescence) spectroscopy and photography analyses with infrared reflectography (IR), visible light, tangential lighting and visible light with ultraviolet (UV) illumination, which are non-destructive analyses, were used to characterize Oscar Pereira da Silva's easel paintings from the collection of the Pinacoteca do Estado de São Paulo (Pinacoteca, 2011) with the aim of identifying the artist's techniques and starting a database of this painter. This paper presents the results obtained through the analyses of two paintings, "Hora de Música" ("Music Time"), henceforward referred to as "HM", oil on canvas (1901), and "Auto-Retrato" ("Self-Portrait"), henceforward referred to as "AR", oil on panel (1936). The EDXRF technique was used to identify the pigments and several techniques of imaging were applied to obtain information on the multiple layers of the paintings. Imaging techniques included: (a) grazing visible light, which provides information on topography, craquelure in the polychrome, etc.; (b) ultraviolet (UV) light, which gives information on the surface of the painting, such as coatings, retouching, nature of the pigments, etc; and (c) infrared reflectography (IR), which reveals the underdrawing preparation.

Oscar Pereira da Silva is a very important academic Brazilian painter. Born in 1867, he was one of the last Brazilian painters sent to France to study with Gérôme, who leaded the École des Beaux-Arts for decades (Focillon, 1928), and above all with Léon Bonnat, the famous portraitist, who, although also considered academic, was a friend of Manet, Degas and other impressionist painters (Celebonovic, 1974), and whose paintings had some influence from the color work of his Spanish masters. Like Gérôme (Lafont-Couturier, 1998) and Bonnat, Silva was criticized over the years for promoting the so-called "eclectic" academicism, but Brazilian curators and public have always valorized his works. Both biographic and style data about Silva are well described by Tarasantchi (2006) and Formico (2012), but no studies about the pigments of his palette are found in the literature, in contrast with

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[*] Corresponding author. Tel.: +55 11 30916939; fax: +55 11 3031 2742.
E-mail address: rizzutto@if.usp.br (M.A. Rizzutto).

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other important Brazilian XIX-Century artists, whose palettes were studied by Calza et al. (2010).

2. Methods

The image inspection analyses with fluorescence of ultraviolet (UV) radiation, visible light, near-infrared reflectography (NIR) and tangential lighting are non-destructive optical techniques in which the image is obtained with a digital camera with a CCD sensor. For UV measurements, four UV Granlight 40 W lamps were used in a dark environment. UV, visible light and NIR imaging were obtained with a high resolution digital camera that operates from 380 to 1000 nm, thus covering the upper part of the UV region, the visible region and the lower part of the IR region. Appropriate filters were used in order to select the desired range. UV fluorescence, for instance, is clearly observed in the visible region. For IR imaging, on the other hand, it is interesting to avoid UV and visible light. Particularly, the resulting IR image is a combination of observed phenomena of reflection, absorption and transmission of the surface layer, revealing the hidden features as the sketching tracings made by the artist before painting. Combinations of pigments excited by ultraviolet radiation give rise to fluorescence of different colors such as yellow, violet, lilac, pink, green, etc. The fluorescence can also be observed as in the case of pigments that contain sulfide, strontium, barium and zinc, which produce greenish/yellow shades and more intense violet (darker) tones, which are characteristic of the restored regions (Stuart, 2007).

A semi-portable EDXRF spectrometer with an X-ray tube with W anode and a Si-drift Ketek X-ray detector was temporally installed and used in the museum. The mounted devices allowed the equipment to perform horizontal and vertical movements in front of the paintings, which were maintained in their normal positions. Both incident and detection angles to the painting surface were 45°. Given this constraint, the geometry was planned so that the air gap between the painting and the detector was as small as possible to minimize absorption by the atmosphere. To avoid any damage to the painting, the minimum distance between the lateral border of the detector nose and the painting surface was planned as 1 mm. Thus, as the detector nose diameter is 14 mm and the angle was established as 45°, the distance from the center of the detector window to the painting surface was approximately 8 mm. Before vertical and horizontal movements of the equipment, it was moved 10 mm backward, to avoid contact with the painting. In the region to be analyzed, the correct working distance and position of the equipment was defined with the help of laser pointers and a webcam assembled close to the detector. The incident X-ray beam was collimated to a diameter of 1.5 mm. The tube was operated at 55 kV and 0.7 mA, leading to input rates below 5000 counts/s. The areas of the peaks in the EDXRF spectra were obtained with PyMCA software (Solé et al., 2007).

Although in some cases EDXRF results can be used for quantitative mass fraction determination, in this research the results were used qualitatively, based mainly on the areas of the peaks, for three main reasons: (a) the pictorial layer is heterogeneous; (b) some important light elements present in the pigments, like O, N, H and C, are not detected; (c) different pigments are mixed in variable proportions, so that quantitative results, even if possible, would not be useful.

3. Results and discussion

3.1. Imaging

The use of grazing light highlighted all the roughness of the surface and deformation of the support as well as craquelure, thus revealing, so to say, “the mode of the artist's painting”. Imaging technique with infrared reflectography, on the other hand, was used to detect and unveil the underlying drawings, in order to reveal the artist's creative processes and some *pentimenti*. The infrared analysis in HM painting revealed that, before painting, the artist has drawn a grid on this particular canvas as shown in Fig. 1. This feature was also observed in AR, suggesting that this technique is a characteristic of the author's preparation process. The UV radiation allowed us to obtain information on the pictorial surface layer, such as the localization of dirty regions, fungi and cracks in the polychrome and retouched areas, which are sometimes difficult to be distinguished from the original areas by naked eye. The UV analysis easily identifies the restored area due to the different violet tones. These results, together with the visible light images, oriented the choice of the points to be analyzed by EDXRF in the paintings. Twenty three points were chosen in each painting and are represented in Fig. 2. They were chosen according to the color, obeying, when possible, the following criteria: (a) for colors which were used frequently in the painting (typically clothes, walls, skin, furniture, shadows), three to five analyzing points were chosen, as far as possible from other colors; (b) for colors used only in specific and small regions, other similar places were analyzed (typically the white in the eyes or the red in the lips); and (c) regions identified by imaging techniques as restored were avoided.

3.2. Elements and pigments

All the 46 spectra obtained with XRF in the paintings showed the presence of very strong Pb–L and Zn–K peaks, which accounts for 79% and 19%, respectively, of the peaks average area of all the spectra. They may be mainly ascribed to white pigments, which are present both in the preparation underlayer and in the external layer, usually mixed with other pigments. Other elements are very clearly observed as shown in Fig. 3. The most important of them, in terms of area, are Fe, Hg, Cd, Ba, Ca, Cu, Sr, Co and As as shown in Tables 1 and 2. Table 1 lists, for each important element (or group of elements), some specific spectra where their peaks are strong, correlating this information with possibilities of pigments. Table 2, on the other hand, classifies the analyzed regions in seven groups according to their predominant color and presents qualitatively the average areas of the peaks observed in each group.

Some general remarks can be made about Tables 1 and 2: (a) Zn is very strong in every group of both paintings; (b) Pb is also very strong in many regions, but there are clear differences among

Fig. 1. Infrared photography showing the sketched tracings made by the artist before painting.

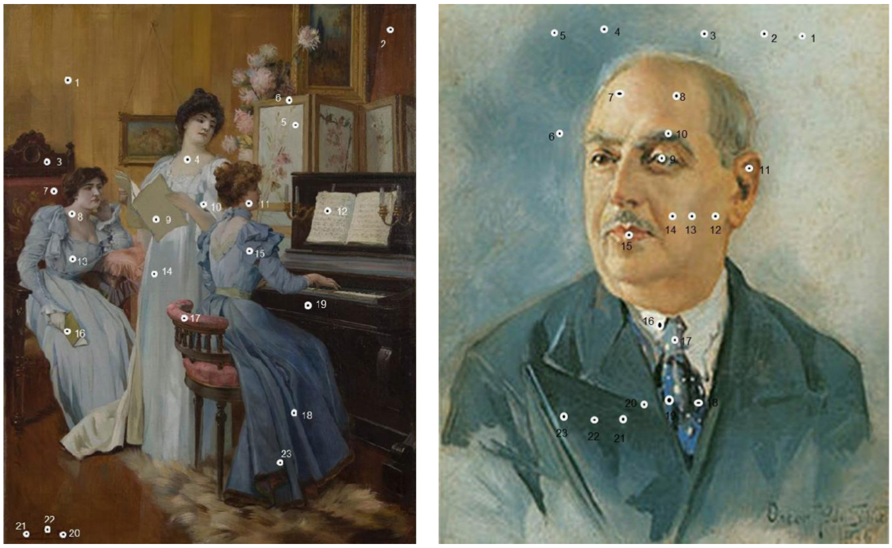

Fig. 2. Visible light photography with the points analyzed by EDXRF measurements—“Hora de Música” (HM) on the left, “Auto-Retrato” (AR) on the right.

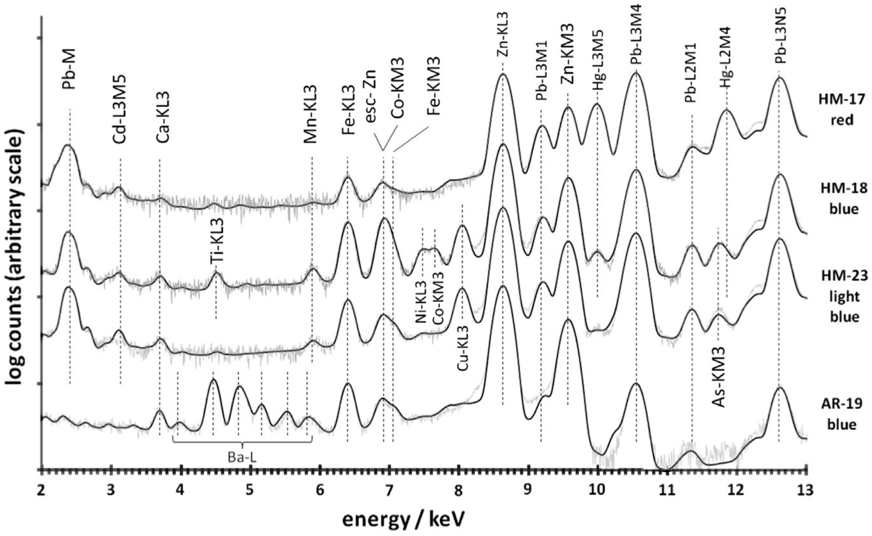

Fig. 3. Examples of peaks fitted in the spectra. Black: fitting. Gray: experimental.

regions and especially between the two paintings; in AR the amount of Pb is much smaller than in HM, especially in the blue and brown regions; (c) Fe is present in many different regions of the paintings and it is difficult to ascribe it to single pigments because it may be present in blue, brown, red, gray and black ones, so for each region different possibilities arise. In the black and gray regions, Fe can be ascribed to some black iron oxide in agreement with Calza et al. (2010). For other colors, Fe may be present in pigments such as Prussian Blue, red ocher and brown ocher, as also observed by Calza et al. (2010), and in burnt sienna, which was frequently used by the French academicians; (d) as Cd can be present in a number of different pigments, some of them with Ba, some with Ba and Hg, and some without Ba, it was convenient to distinguish spectra according to these three situations as shown in Table 1. Additionally, although Cd pigments with Hg, Se and Cr are frequently used, but not in these particular paintings, a remark was made remembering that only small peaks of these elements were present in the corresponding high-Cd/low-Ba spectrum; (e) similarly, it was important to distinguish spectra with high Ba from the ones with low Cd, which can be ascribed to Cd-free white, purple, blue and orange pigments; (f) all spectra with high Cu also presented high As, and vice-versa, and they can be ascribed to Scheele's green. These elements were observed only in HM; (g) some few spectra in HM present high Co, which can be ascribed to Thenard Blue, when Sn is not present, or to Cerulean Blue, when Sn is present; (h) some few spectra in HM present high Sr, which can be ascribed to Lemmon Yellow or to white SrS; (i) Ca, which can be ascribed, for instance, to Ivory Black and to $CaCO_3$, is strong in most AR spectra, and absent or very weak in every HM spectrum; and (j) high Hg, which should be ascribed to Vermillion (as no corresponding Cd is found), is observed only in HM, while AR red colors are mainly associated with Fe pigments, such as red ocher, thus indicating an important change in the artist's palette.

One should comment that the suggested pigments in Table 1 do not necessarily match with the predominant color of the analyzed region. Sometimes, this is because the same spectrum may be listed in two or more fields of Table 1, and so it includes more pigments than those suggested in each field. One should also remember that Fe is very strong in several spectra and, therefore, it is possible that the corresponding Fe pigments—which may have several colors (Hradil et al., 2003)—have a strong influence on the color result.

Table 1
Some possible pigments corresponding to strong peaks of elements.

Element	Spectra with strong peaks of each element in HM	Spectra with strong peaks of each element in AR	Possible pigments
Zn	All (except at the white HM-10)	All (but, in blue, less strong than in HM)	ZnO (white zinc) [a]
Pb	All	All (but less strong than in HM, especially in blue and brown)	$2PbCO_3 \cdot Pb(OH)_2$ (white lead) [b]
Fe	HM-1,2,3,6,9 (brown) HM-19,20,21,22 (black) HM-7 (red) HM-16 (green)	AR-9,10 (brown) AR-11,12,13,14 (carnation) AR-8 (red)	Black: mars black (PBk-9), Magnetite, black Fe spinels Yellow, red and brown Fe oxides Hooker green, $C_3OH_{18}FeN_3O_6 \cdot Na$ Raw umber (brown)
Cd–Ba (low Hg, Se)	HM-1,6 (brown) HM-7 (red)	AR-9 (brown) AR13,14 (carnation) AR-8,15 (red) AR-7 (yellow)	Yellow $CdSBaSO_4$ (PY-35:1) Yellow $CdSZnBaSO_4$ (PY-37:1)
Cd–Ba–Hg	HM-3 (brown)		Red $CdS \cdot xHgS \cdot BaSO_4$ Orange $CdS \cdot xHgS \cdot yBaSO_4$
Cd(low Ba, Hg, Se, Cr)	HM-20,21,22 (black over brown) HM-2 (brown)		Yellow CdS (PY-37)
Ba (low Cd)	HM-8 (carnation) (+Cu, As, Sr, S)	AR-5 (blue)(+Sr) AR-18 (blue)(+Mn, Sr, Sn)	White $BaSO_4$ [c] HM-8: Han purple, $BaCuSi_2O_6$ AR-18: blue $BaMnO_4BaSO_4$
Ca		All	Ivory black, $C.xCaPO_4$ $CaCO_3$ (preparation layer)
Cu–As	HM-13,18, 23 (blue) HM-8 (carnation)		Scheele's green, $CuHAsO_3$ Paris green, $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$
Hg (low Cd)	HM-7, 17 (red) HM-3 (brown) HM-18 (blue) HM-11 (carnation)		Vermillion, red, HgS
Co (no Sn/Cr)	HM-14 (blue)(no Sn/Cr)		HM-14: Thenard blue, $CoAl_2O_4$
Co–Sn	HM-13 (blue)(+Sn)		Cerulean BLue, $CoO.n(SnO_2)$
Sr	HM-13 (blue) HM-8 (carnation)		Lemon yellow $SrCrO_4$ White SrS

[a] Zn may also be in color pigments, as: green $CoO \cdot ZnO$/orange $4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O$/yellow CdSZn/yellow $CdSZnBaSO_4$.

[b] Pb may also be in color pigments, as: orange PbCrO4+PbO/yellow $Pb_3(SbO_4)_2$/yellow $PbCrO_4$/Naples yellow $Pb(SbO_3)_2/Pb_3(Sb_3O_4)_2$.

[c] Other Ba pigments without Cd: orange $BaCrO_4$/Han blue, $BaCuSi_4O_{10}$.

3.3. *Pb in the external and in the preparation underlayer*

The elements Pb, Zn and Ca can be in both the external layer and the preparation underlayer. When they are in the underlayer, their spectra are affected by absorption by the external layer, in two ways. First, the excitation ratio between the families L1, L2 and L3 (or M1, M2, M3, M4 and M5) is affected by the profile change of the incident beam. Second, the resulting intensity ratio among the emitted characteristic rays is affected by the absorption of the outgoing rays.

These effects can be simulated by defining layers in a Fundamental Parameters software, but the painting is too heterogeneous for obtaining reasonable results. Another approach is to let L1, L2 and L3 families be fitted independently and compare their values with those of a single layer sample. This approach is usually not adequate because overlapped peaks of other elements can be under or overestimated. In the case of Pb in the present study, this problem is not significant, because Pb peaks were much stronger than those of other elements, with the exception of Zn. A third approach for Pb is to compare the ratio Pb–M/Pb–L. For low Pb contents, this method in not adequate, because the uncertainty of Pb–M areas may be very high, but for the strong Pb peaks of this study it is adequate. Fig. 4 shows Pb–M vs. Pb–L and counts for all the 46 spectra obtained in the paintings. The spectra can be separated into three groups, corresponding, respectively, to Pb–M/Pb–L ratios fitted to 0.0034, 0.0170 and 0.0445. The first should correspond to the presence of Pb essentially in the underlayer, the third to its presence essentially in the external layer, and the second to a mixed distribution.

One may observe that the first group consisted mainly of spectra obtained in HM (70%), while the third group consisted mainly of spectra obtained in AR (83%). Coherently, the average Pb–M/Pb–L ratio for HM is 0.014, while for AR it is 0.030. Thus, we may suppose that the use of lead white in the underlayer was more intensive in HM, while in AR it was used mainly in the external layer.

4. Conclusions

Surface examination methods with different wavelengths of light helped to analyze and characterize two easel paintings of the nineteenth century. The photograph with visible light coupled with the tangential image provided information about the deformations present in support, cracks, etc., resulting in a precise diagnosis of the conservation status of the work. Images with

Table 2
Average areas (in ranges) of important peaks classified by painting and predominant color.

Color and painting		n⁺	Zn–K	Pb–L	Fe–K	Hg–L	Cd–K	Ba–L	Ca–K	Cu–K	Sr–K	Co–K	As–K	Mn–K	Sn–K	Cr–K	Se–K	Ni–K	Br–K
Blue	**HM**	**5**	**XXXXX**	**XXXXX**	***	**	*	*		***	**	***	***				*	*	
	AR	**9**	**XXXXXXX**	**X**	***		*	***	**	*	*			*	*				
White	**HM**	**3**	**XXXXXXX**	**XXXXX**	**		*			**		*					*	*	
	AR	**1**	**XXXXXXX**	**XXXXX**	*				***						*		*		
Brown	**HM**	**5**	**XXXXXXX**	**XXX**	****	**	**	*	*		*			*		*			
	AR	**2**	**XXXXXXX**	**X**	**X**		**	**	**		*			**	*	*			
Carnation	**HM**	**3**	**XXXXX**	**XXXXX**	**	***	*	***		**	**		**						
	AR	**4**	**XXXXXXX**	**XXX**	****		**	**	***		*			*	*	*			
Black/gray	**HM**	**4**	**XXXXXXX**	**XXX**	**X**		****	*	*	*	*	*		**		*			
	AR	**4**	**XXXXXXX**	**XXX**	***		*	*	***						*				
Red	**HM**	**2**	**XXXXX**	**XXXXX**	***	**XXX**	**	*	*	*	*								
	AR	**2**	**XXXXXXX**	**XXX**	****		**	**	***	*	*			*	*	*	**		*
Green	**HM**	**1**	**XXXXXXX**	**XXXXX**	****	**	*	**			*	**		*		**			

Counts	**Code**	**Counts**	**Code**	**Counts**	**Code**
above 1,000,000	**XXXXXXX**	31,622–100,000	**X**	1000–3162	**
316,227–1,000,000	**XXXXX**	10,000–31,622	****	316–1000	*
100,000–316,227	**XXX**	3162–10,000	****		

n⁺—number of spectra in the group.

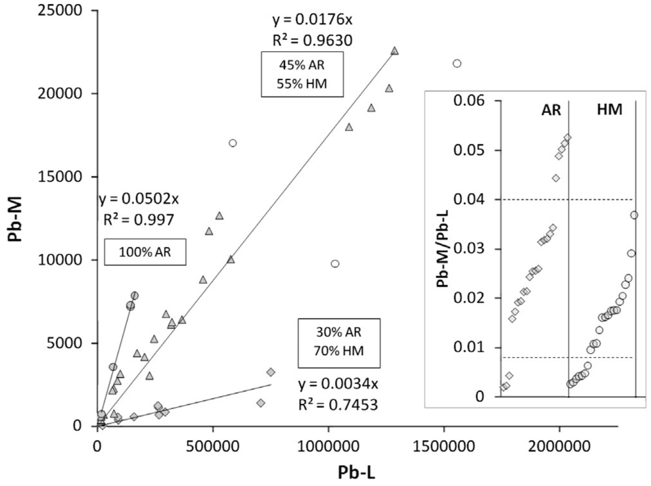

Fig. 4. Pb–M vs. Pb–L areas in all the paintings spectra. Three groups of spectra were selected for linear fitting, according to their Pb–M/Pb–L ratio: below 0.008 (rhombus), between 0.008 and 0.04 (triangle), and above 0.04 (filled circle). Some spectra not considered for the fittings are identified with unfilled circles. Inset: Pb–M/Pb–L ratio of all spectra for both paintings (horizontal axis: arbitrary sequence of the spectra, ordered by increasing Pb–M/Pb–L ratio).

ultraviolet (UV) radiation allowed the observation of the phenomena of fluorescence of the pigments as well as the differentiation of interventions of restoration in the original paintings, helping us to identify the original pigments to be analyzed with EDXRF. The studies carried out with infrared reflectography revealed hidden peculiarities as the underlying grid lines made by the artist as in the typical technique preparation process.

Although Zn and Pb peaks correspond to 78% of the average K or L-areas, peaks of several other elements could be clearly identified and fitted, and very clear differences among regions and between the two paintings could be depicted. For Zn, there are no clear differences between the two paintings. For Pb, a smaller amount in AR than in HM was observed especially in the blue and brown regions. Iron shows strong peaks and is present in many different regions of the paintings. Therefore, it should not be ascribed to a single pigment, but rather to the black, yellow, red and brown Fe-oxides, as well as to multielemental compounds as Hookers Green and Prussian Blue. This is in accordance with the tradition of the French academicians, who used many iron-based pigments, as Yellow Ocher, Mars Yellow, Light Red, Burnt Sienna, and Prussian Blue, described, for instance, by Hradil et al. (2003). Hg pigments peaks were found only in HM, and should be mainly attributed to Vermillion, also used by the French academicians. In AR, most red and carnation regions, as well as brown and blue regions, presented high Fe, Cd and Ba peaks, thus suggesting the use of iron oxide pigments and Cd–Ba pigments. Ba-free Cd pigments, and Cd-free Ba pigments, however, should have also been used in other regions of the paintings. Pigments with Cu–As were observed in HM painting, while, in contrast, Cu and As peaks are weak in AR.

It was also concluded that the distribution of Pb between the external layer and the preparation underlayer is very different in the two paintings. In HM, Pb–M/Pb–L area ratio is lower in most regions than in AR, thus suggesting that in the beginning of the century (HM), the author used more lead white in the preparation layer than in the thirties (AR). One should emphasize that the French academicians used to prepare an underpainting (*ébauche*), well-described by Elliot (2007), which was used as a draft of the structure of the work, and which sometimes was partially shown in the finished work. Taubes (1953) describes the palette of this underpainting as consisting of lead white, ocher, umber, Prussian Blue, and Venetian red.

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References

Calza, C., et al., 2010. Characterization of Brazilian artist's palette from the XIX century using EDXRF portable system. Appl. Radiat. Isot. 68, 866–870.
Celebonovic, A., 1974. The Heyday of Salon Painting: Masterpieces of Bourgeois Realism. Thames & Hudson Ltd, UK.
Elliot, V., 2007. Traditional Oil Painting: Advanced Techniques and Concepts from the Renaissance to the Present. Watson Guptill Publications, New York.
Focillon, H., 1928. La peinture au XIXe et XXe siècles Du realisme à nous jours. H. Laurens, Paris.

Formico, M.R., 2012. A Escrava Romana de Oscar Pereira da Silva: Sobre a Circulação e Transformação de Modelos Europeus na Arte Acadêmica do Século XIX no. Universidade Estadual de Campinas, Brazil. (M.S. thesis).

Hradil, D., et al., 2003. Clay and iron oxide pigments in the history of painting. Appl. Clay Sci, 22, 223–236.

Lafont-Couturier, H. 1998. Gérôme. Herscher, Paris.

Pinacoteca, 〈http://www.pinacoteca.org.br/pinacoteca/〉, (accessed in: september, 2011.).

Tarasantchi, R.S., 2006. Oscar Pereira da Silva. Empresa das Artes, São Paulo, Brazil.

Taubes, F., 1953. The Mastery of Oil Painting. Bramhall House, New York.

Solé, V.A., et al., 2007. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. Spectrochim. Acta Part B 62, 63–68.

Stuart, B., 2007. Analytical Techniques in Materials Conservation. John Wiley & Sons Ltd, England.