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Effects of ionizing radiation on artistic paints and pigments used in the restoration of works of art

Antonietto*, H.P.; Oliveira, M.J.A.; Araujo, M.S.; Otubo, L.; Mello Castanho, S.R.; Vasquez, P.A.S.

IPEN-CENEN/SP, Instituto de Pesquisas Energéticas e Nucleares – Centro de Tecnologia das Radiações. Av. Prof. Lineu Prestes, 2242. CEP 05508-000. São Paulo, SP, Brazil

Correspondence: * hantonietto@usp.br

Abstract: Ionizing radiation is an alternative in combating the deterioration of cultural heritage as it is effective in eliminating biological infestations, from the presence of insects to contamination by fungi and bacteria. The process took place through the emission of gamma radiation (^{60}Co). The objects of study refer to 3 samples of canvas that received layers of paints and pigments, both intended for the practice of restoring works of art and that were exposed to cumulative doses of 3 to 15 kGy. Instrumental analyzes included X-ray Fluorescence Spectroscopy – XRF, Colorimetry, Scanning Electron Microscopy - SEM and Fourier Transform Infrared Spectroscopy - FTIR. The results of the analyzes showed that the samples remained without significant changes.

Keywords: gamma ionization, cultural heritage, pigments for restoration, painting restoration.

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Efeitos da radiação ionizante em tintas e pigmentos artísticos utilizados na restauração de obras de arte

Resumo: A radiação ionizante é uma alternativa no combate à deterioração do patrimônio cultural pois se mostra eficaz na eliminação de infestações biológicas desde a presença de insetos até a contaminação por fungos e bactérias. O processo se deu por meio da emissão de radiação gama (^{60}Co). Os objetos de estudo referem-se a 3 amostras de telas que receberam camadas de tintas e pigmentos, ambos destinados à prática do restauro de obras de arte e que foram expostas a doses cumulativas de 3 a 15 kGy. As análises instrumentais incluíram Espectroscopia de fluorescência de raios X – XRF, Colorimetria, Microscopia Eletrônica de Varredura - MEV e Espectroscopia do Infravermelho com Transformada de Fourier – FTIR. Os resultados das análises apontaram que as amostras permaneceram sem alterações significativas.

P**alavras-chave:** ionização gama, patrimônio histórico, pigmentos para restauração, restauração de pinturas.

1. INTRODUCTION

The National Historical and Artistic Heritage Institute – IPHAN – manages Brazilian cultural heritage according to the characteristics of each group of assets: material heritage, intangible heritage, archaeological heritage and world heritage and plays a fundamental role in identifying, classifying and safeguarding the various aspects of the country's cultural heritage [1].

Given the evident importance of society's cultural heritage, the notion of preserving the set of assets related to this heritage is explained by the desire to keep alive the memory and identity of a nation. Among the sets of goods that constitute material cultural heritage are works of visual arts in their multiplicity of materials such as paper, wood, textiles, rocks, metals, leather, glass, plaster, acrylics, with or without paint finishes [1].

Preserve and conserve in addition to preventing damage that may arise means reducing, controlling and eliminating as well deterioration factors that affect works of art of historical and aesthetic values. Deterioration agents are present in collections and may have physical, chemical or biological origin. Traditional control methods do not guarantee the complete elimination of agents and still have disadvantages such as contamination by toxic substances, carcinogenic risks, flammability, residual effects, environmental pollution and changes in material properties. Some of these techniques include fumigation, heat treatment, the use of solvents, anoxia, and dry cleaning [2].

Another effective possibility in combating the deterioration of cultural heritage is the use of ionizing radiation, which is efficient in removing biological contamination, which includes insects, and the presence of fungi and bacteria. Ionizing radiation has been used in industrial processes, consisting in the emission of electromagnetic waves, such as gamma rays (Cobalt-60 and Cesium 137), X-rays, and acceleration of electrons (EB), which interact with matter, causing energy transfer and breakdown of some chemical bonds and the formation of free radicals that reach the molecules and cause their oxidation [3]

The ionizing irradiation method aims to achieve the parameters of conservation and restoration ethics before both the owner and society, in order to promote the stabilization of the object in its meaning without structural changes that might modify its historical and aesthetic perception. Cultural heritage conservation activities usually include instrumental analysis, preventive care, documentation, stabilization treatment, restoration and any procedure that contributes to the appreciation and understanding of the cultural asset [4].

The works covered by this article refer to easel paintings. As in any other category of work to be restored, image records must be taken, historical research on the property must be carried out, the state of conservation must be determined, the constituent materials must be analyzed, and an intervention plan must be defined [5].

There are some researches that discuss the impacts of gamma radiation on paintings made with historical pigments and artistic paints [6, 7, 8]. However, there are no studies related to specific paints for painting restoration such as Maimeri. This gap in the researches on restoration paints motivated the analyzes carried out on paints and pigments used in the practice of chromatic reintegration in works of art, presented in this work.

2. MATERIALS AND METHODS

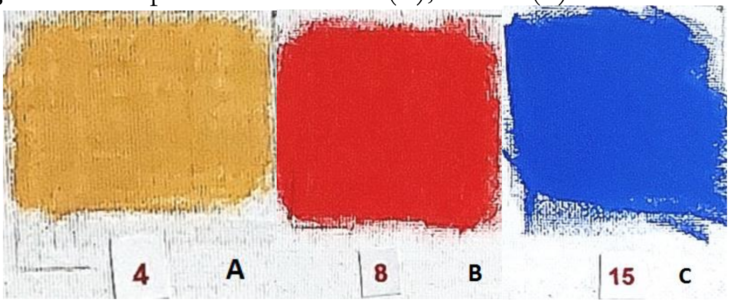
2.1. Preparation and selection of material

Three samples were produced (Table 1) including paints for the restoration of works of art and pure pigments prepared with Paraloid B72 resin. They were applied to a canvas covered with a compound of calcium carbonate ($CaCO_3$) and titanium white (TiO_2), forming a base with high covering power and suitable for receiving layers of paint. Each color was applied to an area of approximately 4x3 cm. For instrumental analysis, fractions of approximately 1cm^2 were removed. The set (Figure 1) was created with Maimeri paints (Italy), formulated with natural resin obtained from the Pistacia bush Lentiscus. It originated the Mastic Varnish, by using the pure pigments Kremer (Germany) and Mahler (Brazil) which were added to the Paraloid B72 resin diluted with Xylene solvent at a proportion of 2.5%.

Table 1 - List of paint and pigments used in the research.

SAMPLE	PIGMENT	FORMULA	TRADMARK	ORIGIN
COR4	Yellow Ochre	Fe2O3 -x H2O	Maimeri	Italy
COR8	Red Cadmium	CdS -x CdSe	Mahler	Brazil
COR15	Ultramarine Blue	Na8(S2)(Al6Si6O24)	Kremer	Germany

Figure 1 – samples named COR4 (A), COR8 (B) and COR15 (C)



The selection of paints and pigments mentioned aims to allude to some of the most common options for color reintegration, although they do not reflect all brands available in the paint market.

2.2. Ionizing radiation

Processing by ionizing radiation took place at the CTR-IPEN Radiation Technology Center facilities. The Multipurpose Irradiator contains 64 sealed 60Co sources for emission of gamma rays. When not in operation, the sources remain submerged seven meters deep in a water tank inside the irradiator. The screen was packaged and introduced into the Multipurpose Irradiator and was exposed to the emission of gamma radiation with cumulative 3, 5, 10 and 15 kGy with a dose rate of 5 kGy.h-1. The appropriate doses to eliminate insects are 0.5 to 2 kGy and for microorganisms 10 kGy [9]. The objective of the experiment was to determine the limits to which material can be exposed for disinfestation without causing important changes upon its physical-chemical properties.

2.3. X-ray Fluorescence Spectroscopy – XRF

Analysis were carried out with an Energy Dispersive X-ray Fluorescence Spectrometer from the Shimadzu brand, model EDX-720, which enable qualitative and semi-quantitative analysis of the material, at CECTM/IPEN.

2.4. Colorimetry

Analyzes were carried out by using PCE-CSM 8 spectrophotometer with SQC8 color management system, 0º/45º measurement geometry, wavelength range from 400 to 700 nm, from the CETER/IPEN Radiation Technology Center facilities.

2.5. Scanning Electron Microscopy – SEM

The micrographs for morphological analysis of the surface of the samples were obtained by Scanning Electron Microscopy, by using the Hitachi Tabletop TM3000 electron microscope from the Center for Materials Science, and Technology CECTM/IPEN as well.

2.6. Fourier Transform Infrared Spectroscopy – FTIR

The samples were analyzed before and after the process using ionizing radiation at 10 kGy to evaluate changes or formation of organic chemical groups. These analyzes were carried out in the Center for Materials Science and Technology CECTM/IPEN facilities.

3. RESULTS AND DISCUSSIONS

The elemental composition of samples with inorganic pigments was determined by the X-ray fluorescence technique. X-ray fluorescence equipment works by exposing the sample to high-energy X-rays, observing the characteristic fluorescence emitted by the atoms in the sample, and analyzing these signals to determine its elemental composition. The analysis showed the important presence of Ca and Ti in all samples, which can possibly be explained by the composition of the preparation base applied to the screen, which is normally composed of these elements. The concentrations of such elements in each color were noted in Table 2, as an example of COR8 in the table refers to Cadmium Red with a high concentration of S, Cd and Se and proven in its formula CdS-xCdSe.

Table 2 – XRF analysis results for COR4, COR8, COR15.

	COR4 %	COR8 %	COR15 %
Fe	7.583	0.111	0.570
Ti	4.538	1.388	22.480
Si	3.258		21.481
Ca	32.771		24.498
Al			16.474
Zr		0.094	0.060
Zn	37.049		
Cu		0.101	
Cr	0.215		
S	14.439	21.834	7.564
Sr	0.147		
K			1.592
Cd		61.067	
Se		15.405	
Co			0.215
Na			5.064

Spectrophotometer measured the light reflected from the samples at each wavelength or in specific bands. The spectral data were calculated to determine the color coordinates of the sample in the L*a*b* color space and presented the information in numerical terms and calculated the Delta E (ΔE), which indicates the magnitude of the total color difference [10].

Colorimetry to measure color changes before and after each session, as color is an important factor to evaluate the effects of radiation. Considering the reference values in Table 3, the results obtained with colorimetry showed that all irradiated samples remained below Hardeberg (1999) level 3, as illustrated in Figures 2.

Figure 2 - DeltaE referring to the COR4, COR8 and COR15 samples with doses of 3, 5, 10 and 15 kGy.

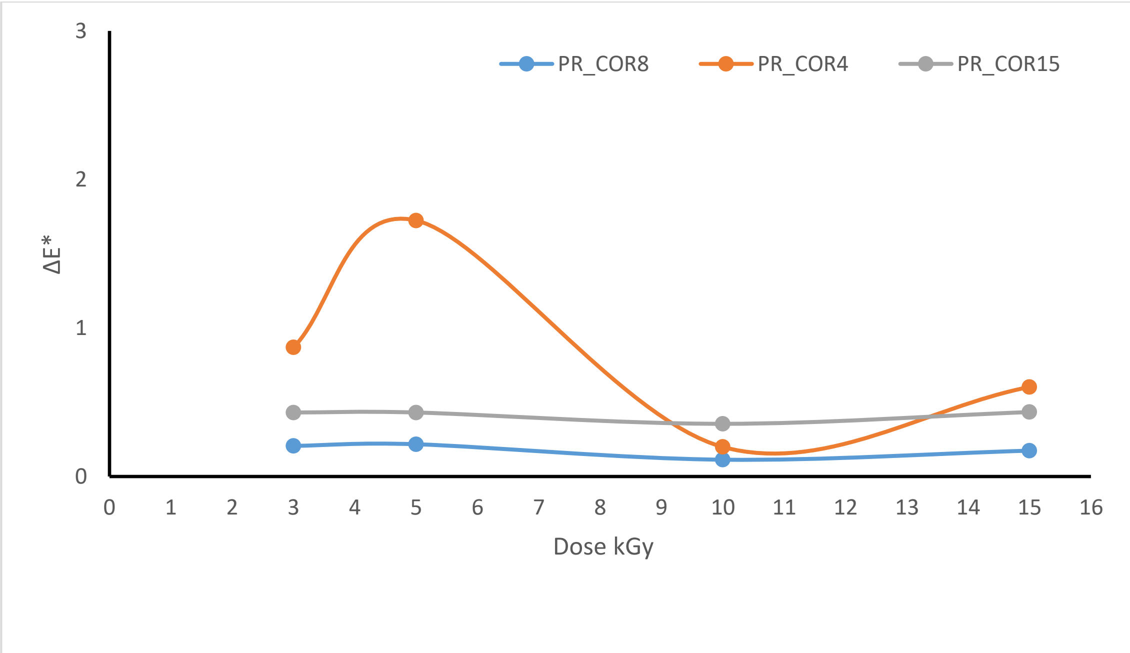


Table 3 - Rules of thumb for the practical interpretation of ΔE^*_{ab} measuring the color difference by Hardeberg, 1999.

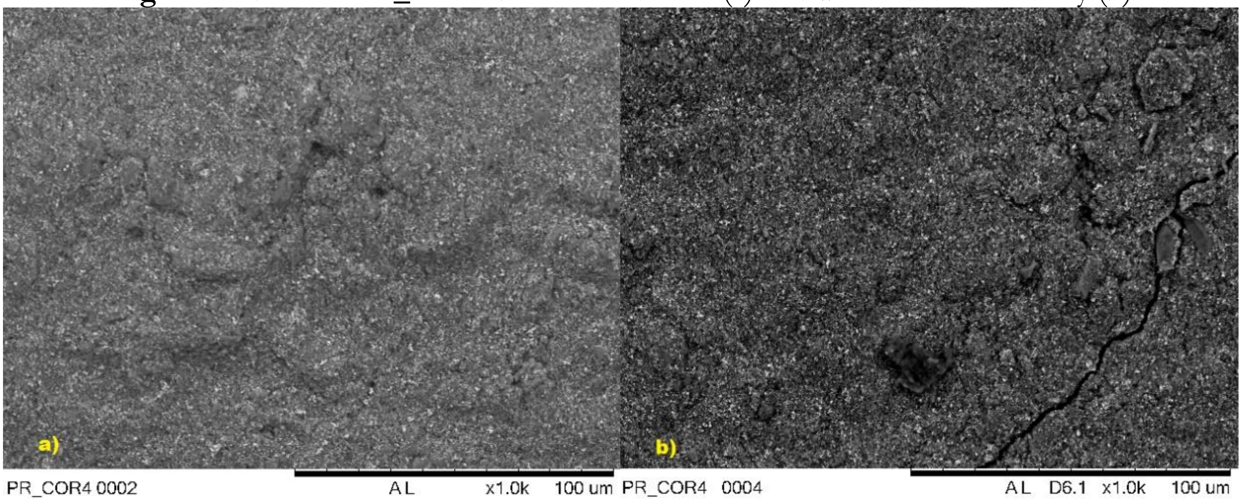
ΔE^*_{ab}	Effect
< 3	Hardly perceptible
$3 < 6$	Perceptible, but acceptable
> 6	Not acceptable

The data prove that changes occurred after gamma ionization, but the analyzed colors showed variations lower than ΔEab 3. However, it is important to note that the chemical purity of pigments and paints may differ between manufacturers [12]. Pigments or paints can exhibit different behaviors depending on its additives or preparation methods [13].

Scanning Electron Microscopy HITACHI TM3000 uses a beam of electrons to act on the sample and works by applying an electric field to extract electrons from a tungsten filament. These electrons are accelerated and focused to form the beam that will act on the samples. The equipment is provided with detectors sensitive to the signals produced that include secondary electrons and backscattered electrons. The intensity and distribution of these signals were used to form the image of the sample. The referred image often provides details at microscopic scales, allowing morphological analysis of the sample [14].

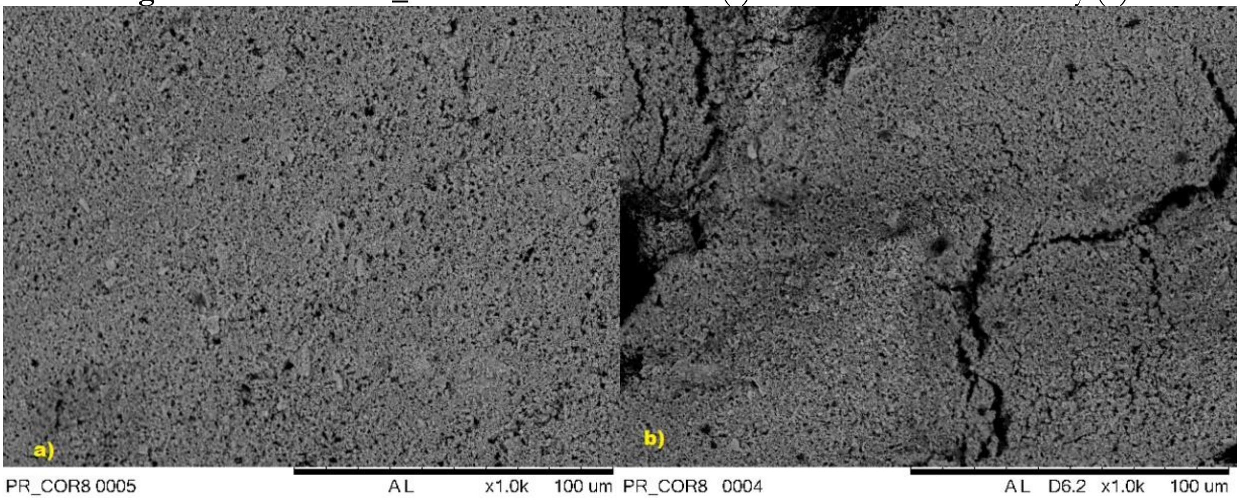
The samples were analyzed with electron microscopy before and after irradiation with 10 kGy and compared (Figures 3 to 5). The sample PR_COR4 (Figure 3) refers to industrialized restoration paint from the Maimeri brand, color Yellow Pale Ocher (PY43).

Figure 3 - SEM of PR_COR4 before irradiation (a) and with a dose of 10 kGy (b)



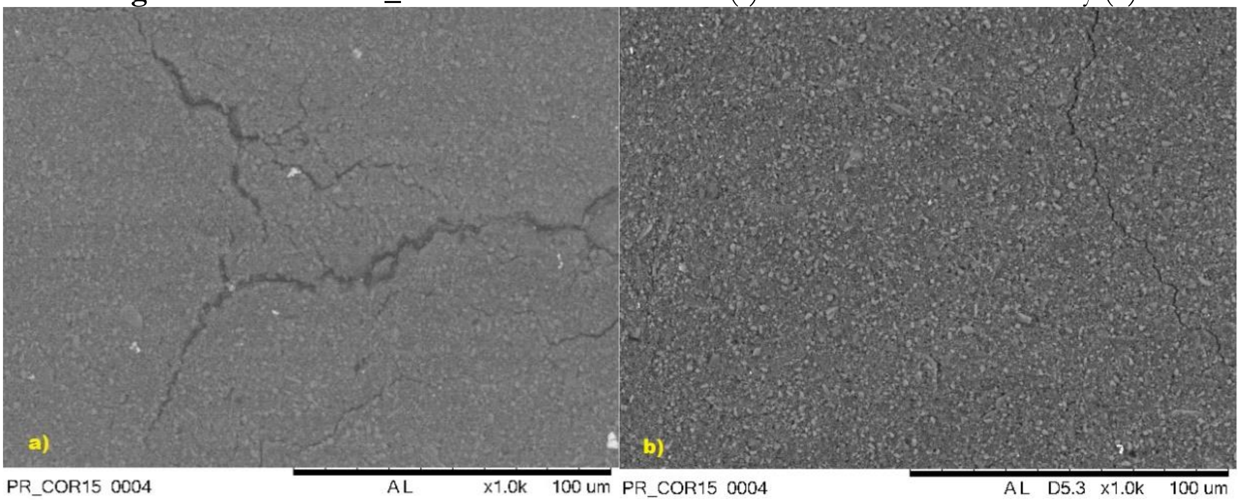
The sample PR_COR8 (Figure 4) refers to the powder pigment with Paraloid B72 resin from Mahler, color Cadmium Red (PR108).

Figure 4 - SEM of PR_COR8 before irradiation (a) and with a dose of 10 kGy (b)



Sample PR_COR15 (figure 5) refers to powder pigment with Paraloid B72 resin from Kremer, color Ultramarine Blue (PB29).

Figure 5 - SEM of PR_COR15 before irradiation (a) and with a dose of 10 kGy (b)



From the analysis of the images, it was possible to notice that the paint for restoration (Figure 3) has different particle size characteristics than the powder pigments (Figures 4 and 5). These were prepared with Paraloid B72 resin dissolved in Xylene solvent while the paints are industrialized products, which makes it difficult to identify all their components. The surface of the irradiated samples (b) remained similar to the non-irradiated ones (a) suggesting that the gamma ionozation did not severely modify the physical structures of the samples in line with the results obtained by colorimetry.

Fourier Transform Infrared Spectroscopy – FTIR: the analytical technique of IR spectroscopy with Fourier Transform is widely used for characterization of pigments, identification of paints, binders, possible degradation products associated with different types of paints [15, 16, 17].

The FTIR spectrometer emits a beam of infrared radiation that is directed towards the sample that absorbs part of the incident infrared radiation. The amount of radiation absorbed varies according to the types of chemical bonds present in the sample. Each type of chemical bond has characteristic vibration frequencies, which correspond to different infrared energies. The resulting infrared spectrum is a graph that shows the intensity of infrared radiation as a function of wavenumber - frequency - or wavelength as shown in Figures 6 to 8. Each peak in the spectrum corresponds to a specific molecular vibration of the sample, allowing the identification of the chemical bonds present. The samples were observed in the middle spectral region – MIR, which covers the frequency range between 4000 cm^{-1} to 500 cm^{-1} [18].

Figure 6 - Ftir COR4 spectrum black band 0kGy and pink band 10kGy

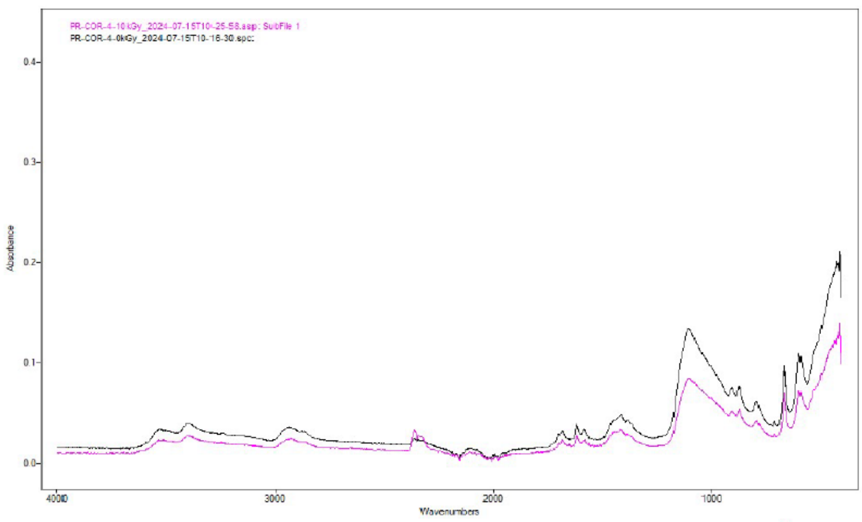


Figure 7 - Ftir COR8 spectrum blue band 0kGy and green band 10kGy

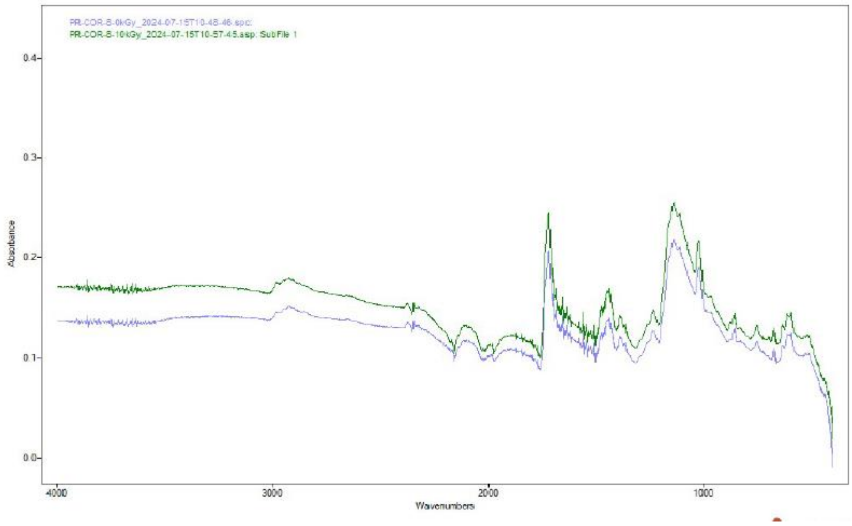
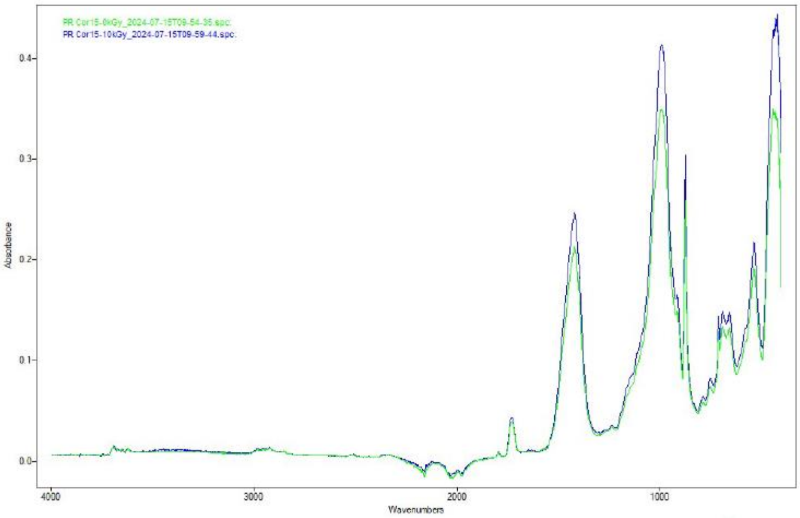


Figure 8: Ftir COR15 spectrum green band 0kGy and blue band 10kGy



In figure 6 the spectrum of COR4 Yellow Ochre, Fe_2O_3 -x H_2O Maimeri, revealed absorption bands in the region between 1000 cm^{-1} and 1200 cm^{-1}, in the region of 1450 cm^{-1} and between 900 cm^{-1} to 700 cm^{-1} attributed to CO which can be associated with the carbonate present in the base formulation ($CaCO_3$). Between 1650 cm^{-1} and 1750 cm^{-1} carbonyl peak C=O; close to 3000 cm^{-1} CH peak; these bands can also be associated with Mastic resin [18].

In figure 7, the spectrum of COR8 Cadmium Red, CdS-xCdSe Mahler, showed CO stretching bands in the region from 500 cm^{-1} to 900 cm^{-1}; in the region of 1660 cm^{-1} to 1740 cm^{-1} stretching range C=O carbonyl; in the region from 3000 cm^{-1} to 2800 cm^{-1} CH bands; in the region of 2000 cm^{-1} associated with the triple carbon bond, which bands suggest they are associated with Paraloid B72 resin [18].

In figure 8 the spectrum of COR15 Ultramarine Blue Na_8 (S_2) $(Al_6\,Si_6\,O_{24})$ Kremer, overlapping stretching bands from 50-950 cm^{-1} for Si-O-Si [18], between 1000 and 650 cm^{-1} with multiple C-C connections; Carbonyl at 1750 cm^{-1}.

In all three cases, the characteristic peaks of each sample remained similar when it is read before and after irradiation, with a dose of 10kGy, indicating that there were no relevant changes with the use of gamma ionization.

4. CONCLUSIONS

According to the results obtained so far, it is possible to consider that processing by ionizing radiation with gamma rays is an alternative for disinfestation of pests and microbiological contaminants, as it did not significantly alter the color of the analyzed samples, remembering that they represent a small sample given the variety of colors, brands of paints and pigments for painting restoration offered on the market. Reading the data obtained by spectrophotometry was of particular relevance in this work since the stability and permanence of color within the pieces were verified. The research is in line with the expectations of professionals in the field of conservation-restoration of cultural heritage in choosing materials that do not alter the physical and aesthetic properties of the works. The continuation of research is essential so that conservation-restoration professionals may have access to available and appropriate methods for each situation, considering the variety of materials that make up easel paintings and taking into account that the production and commercialization of specific paints for chromatic reintegration tends to grow.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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