STUDY OF GAMMA IRRADIATED OIL PAINTING SAMPLES BY FTIR AND FT-RAMAN SPECTROSCOPY

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Gamma irradiation treatment is an efficient means of mass decontamination of art objects such as oil paintings. The investigation of possible physical and chemical changes induced by gamma irradiation in the materials used in oil painting increases the confidence of conservators/ restorers in this still exotic decontamination method. The aim of the present work is to evaluate by different spectroscopic techniques changes induced by gamma irradiation in oil painting samples prepared with pigments of historical importance. In this respect we have used four series of samples: untreated, γ-irradiated, thermally treated, thermally treated and γ-irradiated. Characterization of molecular structure was performed by FTIR and FT-Raman spectroscopy.

Keywords: pigments, Gamma irradiation, FTIR and FT-Raman spectroscopy

INTRODUCTION

Infrared spectroscopy is wide spread amongst within the museum art conservation laboratories, mainly because of the scientific contribution to the organic material characterization in art and archaeometry (Derrick *et al*., 1999). FTIR and FT-Raman spectroscopy may be used to characterize genuine and fake artifacts, to obtain information for art restorers and museum conservation scientists, to quantify effects of environmental degradation on exposed artwork and to identify pigments (Edwards, 2009; Saverwyns, 2010; Kaminska *et al.*, 2006). The use of Raman spectroscopy and microscopy is a developing trend in art objects analysis due to the non-distructive investigation and sensibility (Vandenabeele *et al.*, 2008; Kriznar *et al.*, 2011). In order to increase the confidence in irradiation technologies applied for restoring of biologically contaminated artworks, artificial ageing experiments are necessary to estimate the impact of the irradiation process on the organic and inorganic materials (Rizzo, 2002; Feller, 1994).

In Romania, the IRASM facility commisioning (2001) opened the access for cultural heritage objects decontamination by gamma irradiation (http://www.irasm.ro). Our group developed a FTIR, FT-Raman and reflectance spectroscopy study before and after the radiation treatment of the powder pigments/painted wood panels (Negut *et al.*, 2007; Negut *et al.*, 2010; Negut *et al.*, 2012; Manea *et al.*, 2012; Ponta, 2008).

The purpose of the present work is to evaluate by FTIR and FT-raman spectroscopy the gamma irradiation and thermally treated induced changes in the supramolecular structure of the painting layer of the oil painting samples.

MATERIALS AND METHODS

Materials

Experimental models (four series of samples) consisted of pieces of canvas covered by pigments in mixture with oil, there are:

a) untreated;

b) γ-irradiatied in a SVST Co-60/B irradiator, average dose of 20.4 kGy, dose rate of 0.6 kGy/h (γ);

c) thermally treated at 70˚C for 48 h (t);

d) thermally treated at 70˚C for 48 h and γ-irradiated: average dose of 20.4 kGy (dose rate of 0.6 kGy/h (t+γ).

Pigments manufactured by Kremer Pigmente were chosen as they are typically used in Romanian devotional painting (Fig. 1):

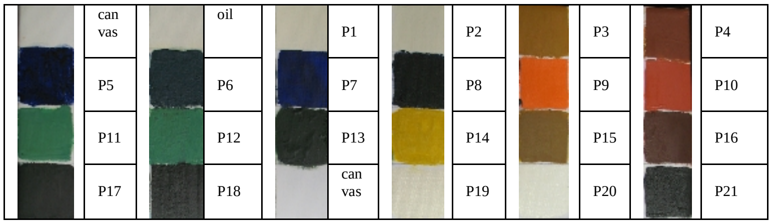

Figure 1. Experimetal model: flake white historical (P1), marble dust (P2), yellow ochre (P3), red ochre (P4), smalt (P5), azurite natural (P6/P13), ultramarine blue (P7), Prussian blue (P8), minium (P9), cinnabar (P10), malachite natural (P11), green earth (P13), cobalt yellow (P14), raw sienna (P15), burnt sienna (P16), bone black (P17), furnace black (P18/P21), titanium white (P19/P20)

Methods

Oil painting samples were irradiated in air at a temperature of 25˚C, by using the National Institute for Physics Nuclear Engineering Co-60 IRASM irradiator facility at a constant dose rate of 0.6 kGy/h. Absorbed doses were evaluated by means of an ethanol-chlorobenzene dosimetry system with oscillometric read-out method, and expressed as absorbed dose in water (ISO/ASTM 51538:2002).

The non-destructive and non-contact vibrational spectroscopy techniques are the ones accepted by the conservators and curators communities. Samples structure characterization was performed with a FT-IR/Raman Bruker Vertex 70 instrument equipped with two mobile probes: a MIR fibre, with a LN2 cooled detector and a RAMPROBE fibre with a LN2 cooled Ge detector, Nd:YAG laser of 1064 nm and 1-500 mW. FT-IR spectra were recorded between 650 and 4500 cm^{-1} with 1000 scans (~ 7.5 min) and FT-Raman were recorded between 50 and 3500 cm^{-1} 500 scans (~ 15 min). Resolution in all cases was 4 cm^{-1}.

RESULTS AND DISCUSSION

Structural changes were monitored by vibrational (FTIR with MIR probe and FT-Raman) spectroscopy on every type of pigment. FTIR and FT-Raman spectra were recorded for pigments' characterization and to monitor the changes induced by the treatments.

FTIR Analysis

FTIR spectra were very sensitive to the organic content of the oil paint. Table 1 gives FTIR bands' position (cm^{-1}) and assignment of oil unirradiated.

Table 1. FTIR bands' position (cm^{-1}) and assignment of oil unirradiated

No.	FTIR bands' position (cm^{-1}) / intensity	Assignment
1	877 / w	$-CH_3$, $-CH_2-$
2	1019 / w	$-CH_2-$, $>CH_2=CH_2<$
3	1109 / w	$-CH_3$, $-CH_2-$
4	1222 / m	C-O-
5	1468 / s	$-CH_3$, $-CH_2-$
6	1589 / m	$>C=C<$
7	1745 / m	-C=O
8	2860 / w	$-CH_3$, $-CH_2-$
9	2927 / m	$-CH_3$, $-CH_2-$
10	2963 / m	$-CH_3$, $-CH_2-$

m-medium, s-strong, w-weak

Fig. 1 gives the FTIR spectra of oil unirradiated, irradiated, thermally treated, irradiated and thermally treated.

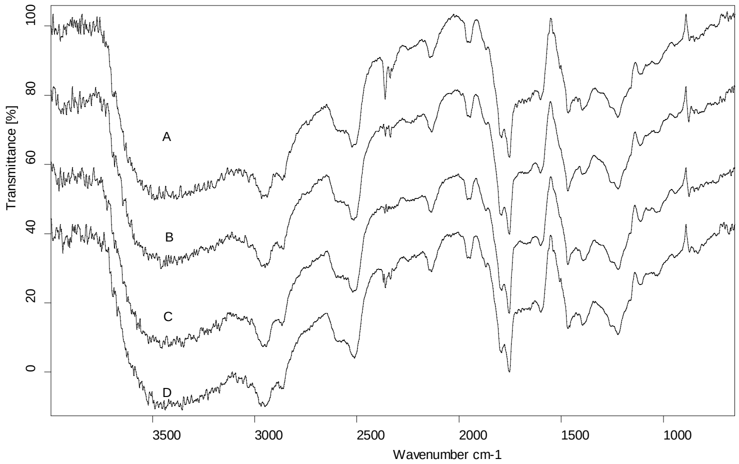

Figure 1. FTIR spectra of oil unirradiated (A), γ-irradiated (B), thermally treated (C), thermally treated and γ-irradiated (D)

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In general, very small band variations are observable in the FTIR spectra of oil (very small variations of oxidation peaks intensity were observed at 1420 cm^{-1} and 1507 cm^{-1} in spectra of oil).

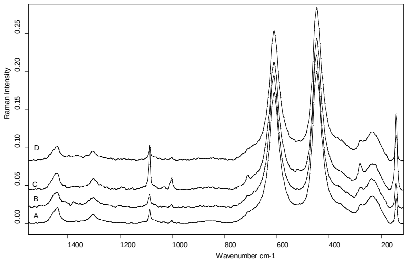
FT-Raman Analysis

FT-Raman spectra offered better information on the pigment.

Fig. 2 gives the FT-Raman spectra of some pigments of oil painting samples.

For every type of pigment four samples (unirradiated, irradiated, thermally treated, irradiated and thermally treated) were analyzed and pigments peaks were assigned as follows: titanium white 610s, 448s, 234m, 143w; flake white historical 1439w, 1365w, 1305w, 1087m, 1050vs, 1002w, 633w, 420w, 281w, 143m; marble dust 1438w, 1303w, 1087vs, 1002w, 713w, 634w, 447w, 281m, 144s; azurite natural 1578s, 1455s, 1431s, 1302s, 1095s, 935w, 836w, 762w, 539m, 399s, 292w, 248m, 197w; ultramarine blue 1613m, 1443m, 1297m, 1185w, 1086s, 1002m, 713w, 632w, 548vs, 438m, 362sh, 279m, 145vs; Prussian blue 2150s, 2120m, 2092m, 537m, 274m; minium 549s, 474br, 456w, 391s, 314m, 228m, 151m, 120vs; cinnabar 344m, 285w, 254vs; red ochre 1607m, 1441m, 1288m, 1087m, 615w, 465w, 408w, 292m, 240m, 225w, 145m; cobalt yellow 1398m, 1327vs, 1257w, 837m, 821s, 304s, 276m, 180m, 111w; yellow ochre 1086m, 1002w, 633w, 462w, 405w, 279w, 146m; raw sienna 1086w, 147w (s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad).

Pigments smalt, malachite natural, green earth, raw sienna, burnt sienna, bone black, furnace black were not detectable by Raman spectroscopy using 1064 nm excitation (Castro *et al.*, 2005; Burgio and Clark, 2001).



titanium white

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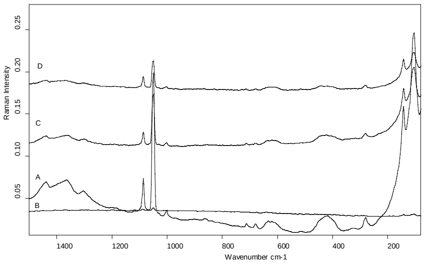

flake white

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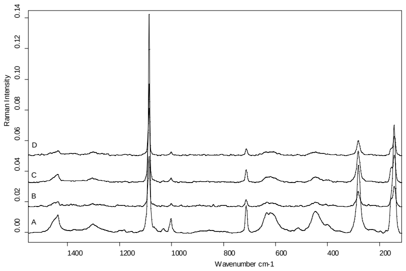

marble dust

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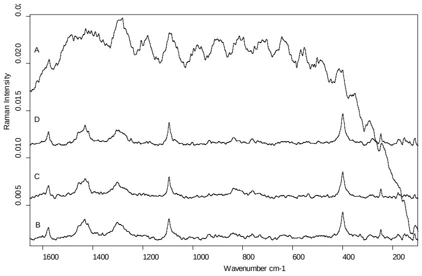

azurite

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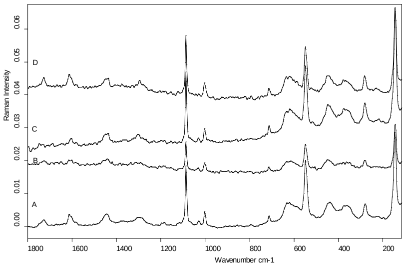

ultramarine

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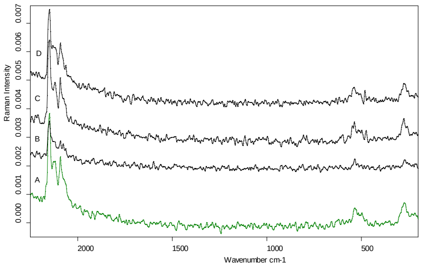

Prussian blue

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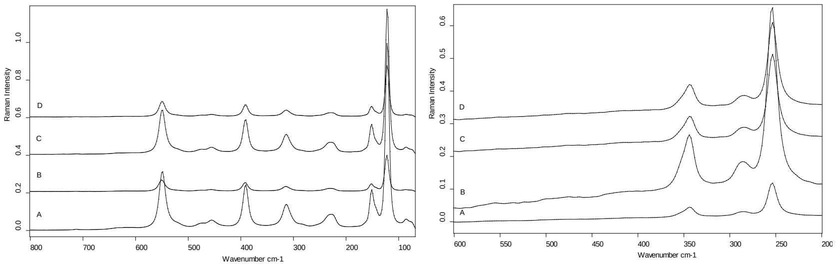
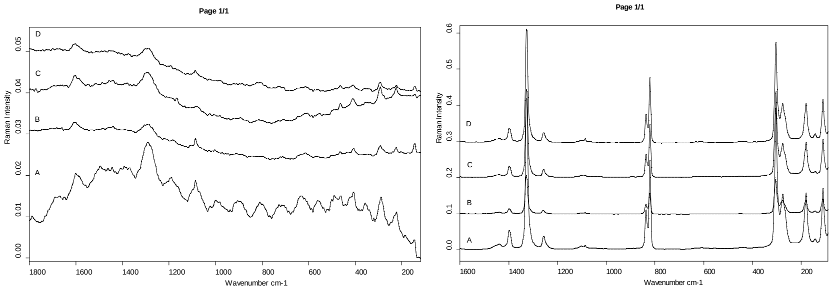
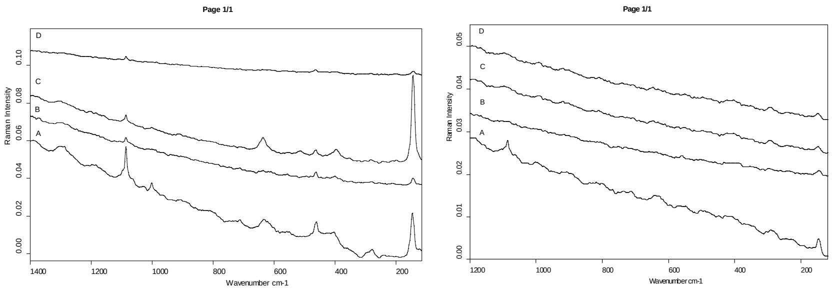


minium cinnabar



red ochre cobalt yellow



yellow ochre raw sienna

Figure 2. FT-Raman spectra of pigments: unirradiated (A), irradiated (B), thermally treated (C), irradiated and thermally treated (D)

CONCLUSIONS

FTIR and FT-Raman spectra of pigments do not present significant changes regardless of applied treatment.

The negligible structural changes recommend the use of gamma irradiation in the disinfection of oil paintings.

Acknowledgements

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