THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^{0}. 1 – 2008, ISSN 1453 – 083X

THE CONSERVABILITY OF OLD WOOD AT THE CONTACT WITH METALLIC STRUCTURAL COMPONENTS FROM ARTIFACTS

Ion SANDU[1], Viorica VASILACHE[2], Mikiko HAYASHI[3], Narcisa VRÂNCEANU[1], Adelina CIOCAN[1], Andrei-Victor SANDU[2]

[1] „Al.I.Cuza" University of Iasi, ARHEOINVEST Platform,
Laboratory of Scientific Investigation and Cultural Heritage Conservation
[2] Romanian Inventors Forum, RDI Department
[3] Ochanomizu University Tokyo
e-mail: ion.sandu@mail.dntis.ro

ABSTRACT

The paper presents the impact of metallic pieces being in contact with wood, as structural elements, used in obtaining artifacts. The paper studies, based on old samples, the reciprocal effect obtained at the wood-metal interface, the diffusion and segregation area of metallic cations in wood and the protective role of some wood volatile components on metal.

KEYWORDS: metallic cations, corrosion products; wood-metal interface, diffusion and segregation processes, protection layers.

1. Introduction

It is known that wood into an artifact is affected in time, together with the exogenous factors and a series of endogen agents and factors, related to the natural defects, quality of materials and the fabrication technology of the artifact.

Some known research work has distinguished the influence of metals on the reciprocal conservability [1]. For instance, the iron close to oak wood is conserved by the tannin from it and the wood on the other side by the Fe (II) and Fe(III) ions, even under conditions of the presence of the mushroom *Merullius Lacrymans*, which creates a tough regime for the wood degradation.

In this context, in our laboratory there are going on some studies about the influence upon some different essence of old wood bases, the preparation layer based on gyps and chalk powder and the iron nails utilized at the assembling or for hanging up.

The present work studies have been done with an electronic microscopy and a micro FT-IR for the effects of the nails and other structural elements made out of iron upon the bases of lime, poplar, fir and oak.

2. Experimental part

In these studies there were used some old wood samples from lime, poplar, fir and oak which have been influenced by the iron nails used in assamblation or for display.

The affected interfaces and zones have been analyzed by SEM-EDX and μ-FT-IR

The investigation was performed by means of a SEM VEGA II LSH scanning electronic microscope manufactured by TESCAN for the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by ROENTEC Germany. The microscope, entirely computer operated, contains an electron gun with tungsten filament that may achieve a 3nm resolution at 30KV, with a magnifying power between 13 and 1,000,000 X in the resolution mode, a gun potential between 200 V and 30 kV, a scanning speed between 200 ns and 10 ms per pixel. The working pressure is lower than 1x10-2 Pa. Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analysis in industry, research and education, which performs quantitative measurements without using specific calibration standards. It has an active area of 10 mm^2, and it can analyze all items heavier than carbon, smooth or rough samples, thin coatings or particles, with a resolution below 1.33 eV (MnKα, 1000 cps). Quantax QX2 uses a 3rd generation Xflash detector, which does not require liquid nitrogen cooling and is about 10 times faster than the traditional Si(Li) detectors. IR absorption measurements have been performed with a FT-IR spectrometer, coupled with a Hyperion microscope, both from Bruker Optics, Germany. FT-IR spectrometer is a TENSOR 27, which is an advanced flexible bentchtop instrument suitable for routine applications as well as laboratory research. TENSOR 27 is designed for measurements mainly in the mid – infrared region.

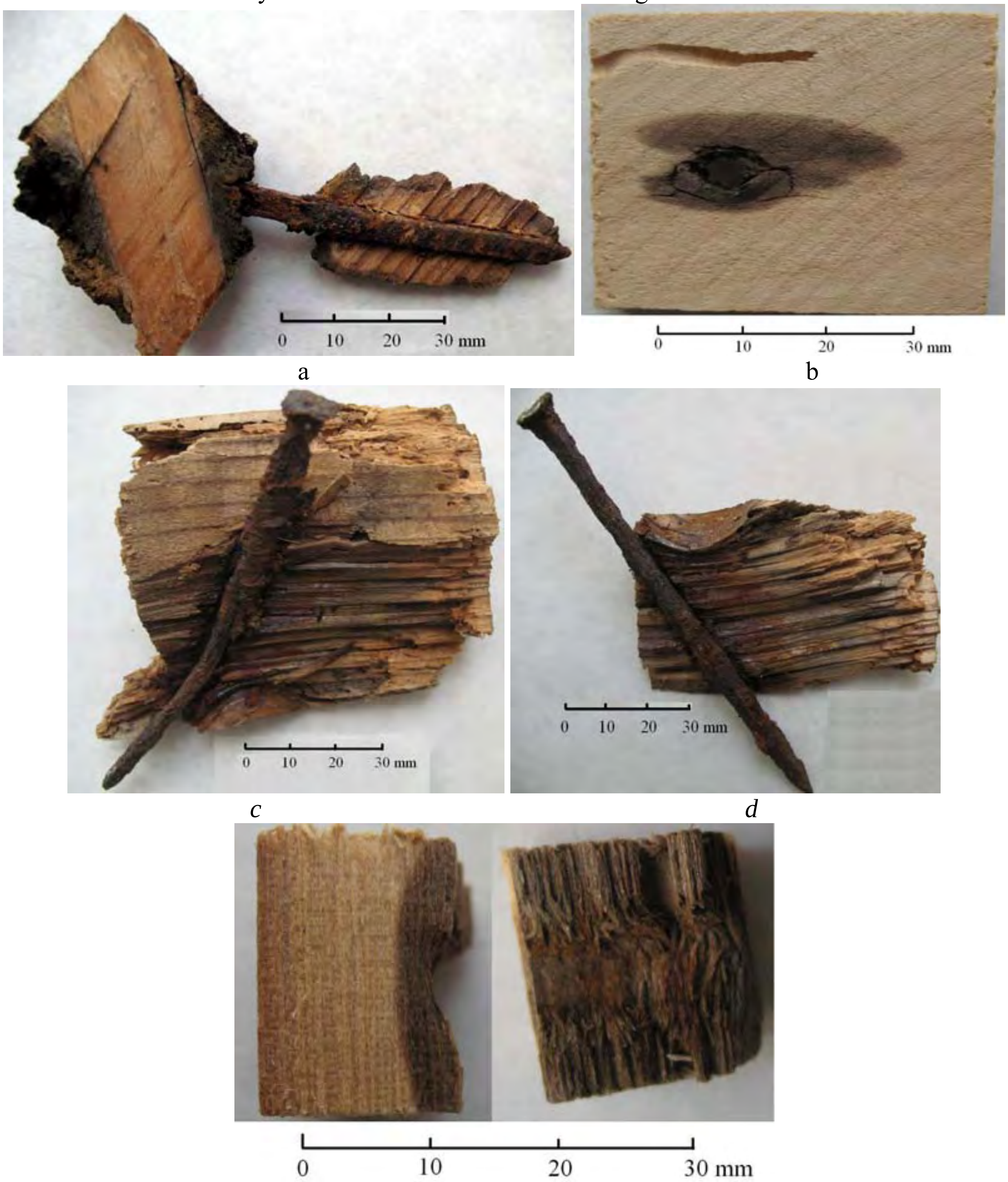


Fig.1. *Samples of old wood: a – oak (1820 A.D.); b – poplar (XVIII Century); c – fir (1860 A.D.); d – fir (1830 A.D.); e – poplar (XVII Century).*

The standard detector is a DLaTGS detector, which covers a spectral range from 12000 to 370cm^{-1} and operates at room temperature. The resolution is normally 4cm^{-1} but it can go up to more than 1cm^{-1} (apodized). The wave number accuracy is more than 0.01cm^{-1} at 2000cm^{-1}.TENSOR is equipped with a He-Ne laser which emits red light with a wavelength of 633nm, and an output power of 1mW. TENSOR has also a high stability ROCKSOLID alignment of the interferometer. The high throughput design ensures the highest possible signal – to – noise – ratio. TENSOR is completely software controlled, by OPUS software. The HYPERION microscope is an accessory that can be coupled to almost any Bruker FT-IR spectrometer. The software provided is an OPUS/VIDEO software for video interactive data acquisition. It can work both in transmission and reflectance modes. The detector is a MCT cooled with liquid nitrogen (-196^{0}C). The spectral range is 600-7500cm^{-1} and the measured area is optimized for a diameter of 250μm with a possibility of reaching a minimum diameter of 20μm. It is provided with a 15X objective.

3. Results and discussions

Fig. 2 presents the SEM microphotography with the two positions of the vector chosen by the analysis of the variation of the main components from the old oak wood (1820 A.D.) – metal interaction area.

From the EDX spectrum, one can point out the continuous and uniform variation of the penetration effect of the Fe oxidihydroxide (II, III) on the two directions in the preservation area of the old oak wood. Table 1 presents the average composition for the surface of the preserved area of the old oak wood by impregnation with the Fe oxidihydroxides.

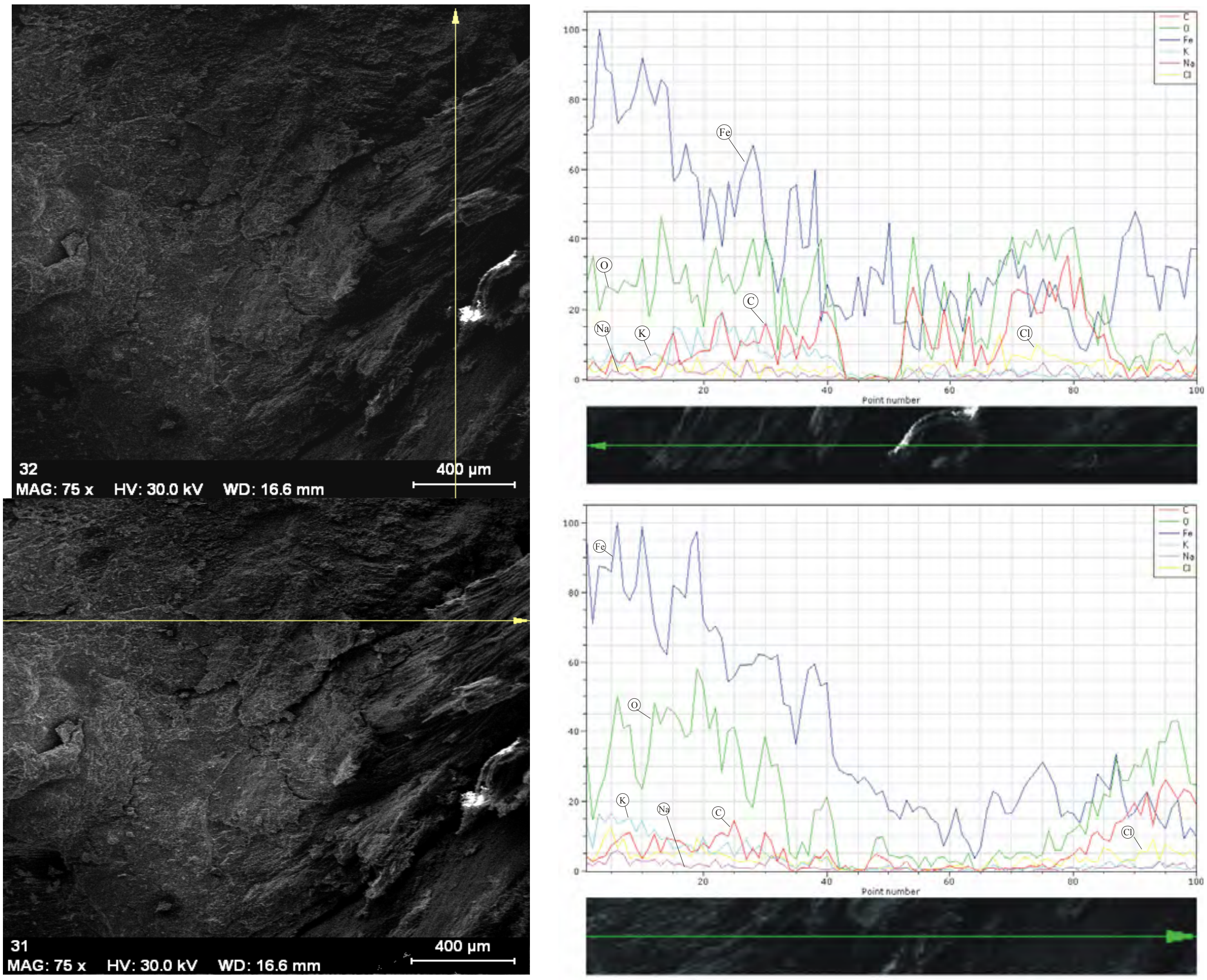


***Fig. 2.** SEM Image with EDX spectra of distribution along a line on the sample from old oak wood with iron*

***Table 1.** Composition on diffused structure surface: old oak wood-iron*

Element	Weight	Atomic	Error
	[%]		
Iron	48,50823	21,5885	1,315599
Carbon	3,876974	8,0227	1,491539
Potassium	2,508171	1,594433	0,121529
Chlorine	0,301288	0,211222	0,046833
Sodium	2,160776	2,33605	0,238743
Oxygen	42,64456	66,24709	5,868803
	100	100	

One can notice a very high concentration of the Fe ions (II, III). In spite of the fact that in the structure we can find the chloride anion (the main corrosion agent of iron and the most active one, a real catalyst) due to the inhibitor components from the oak wood, the iron nail has been pretty well preserved. Table 2 presents the composition of the alloy from which the nail has been manufactured (OL37). In figures 3, 4 and 5 there are shown SEM images and EDX spectra of the distribution along a line on the sample from other old wood samples with iron: fir (1860 A.D.), poplar (XVII and XVIII century).

***Table 2.** Composition of the iron nail*

Element	Weight	Atomic	Error
	[%]		
Iron	95,849774	87,917083	2,664899
Carbon	0,353141	1,417842	0,558082
Silicon	0,247112	0,424298	0,059891
Phosphorus	0,186209	0,289913	0,051035
Sulfur	0,124372	0,187042	0,043107
Oxygen	3,239392	9,763822	0,884542
	100	100	

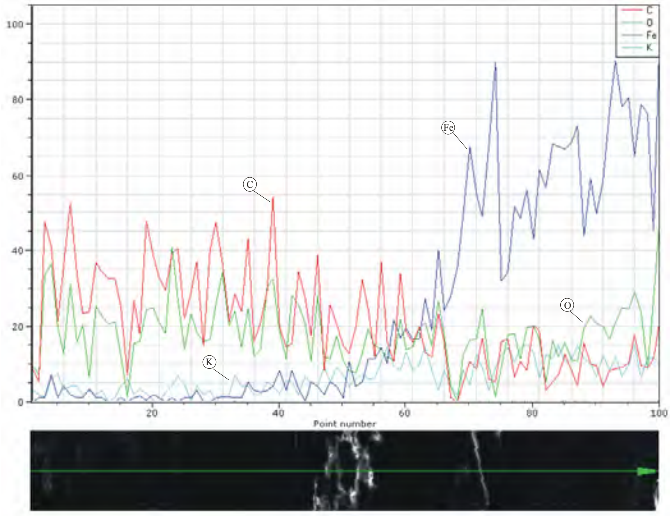


***Fig.3.** SEM Images and EDX spectra of the distribution along a line on the sample from old fir wood (1860 A.D).*

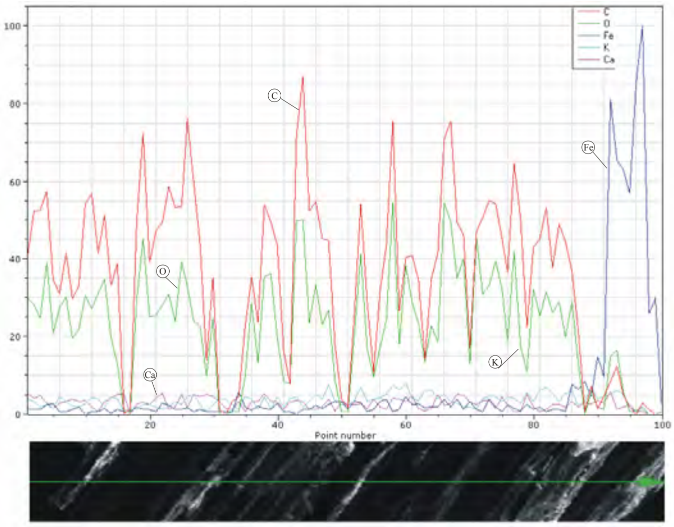


***Fig.4**. SEM Images and EDX spectra of the distribution along a line on the sample from old poplar wood (XVII century).*

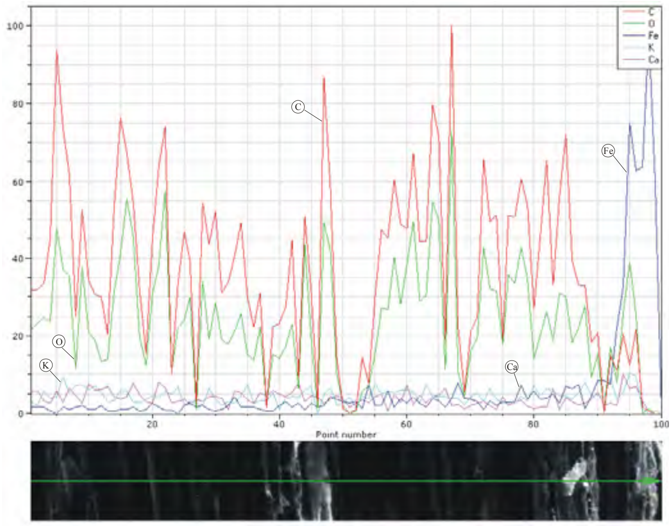
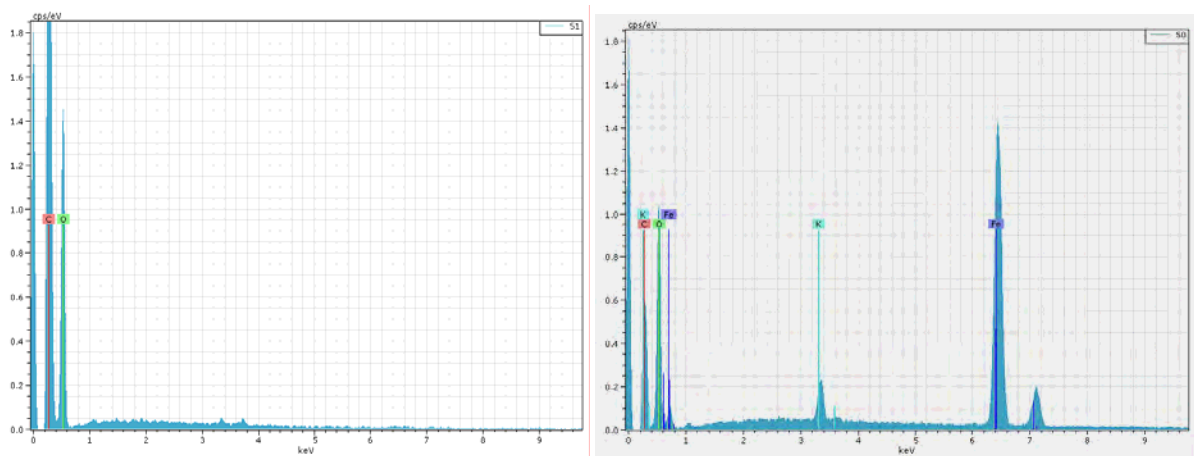


***Fig.5**. SEM Images and EDX spectra of the distribution along a line on the sample from old poplar wood (XVIII century).*

From these figures one can observe the capacity of penetration in time of the iron ions, which is different depending on the wood species, which interacts in a different way with the metal. If in the case of oak it is observed a reciprocal conservability wood-metal, due to the complex system of the coordination compound tanin - Fe (II, III) on the contrary in the case of fir and poplar it doesn’t observe the same phenomenon due to the acidity of the wood increases with time.

In figures 6, 7 and 8 are shown the EDX spectra and the chemical composition.

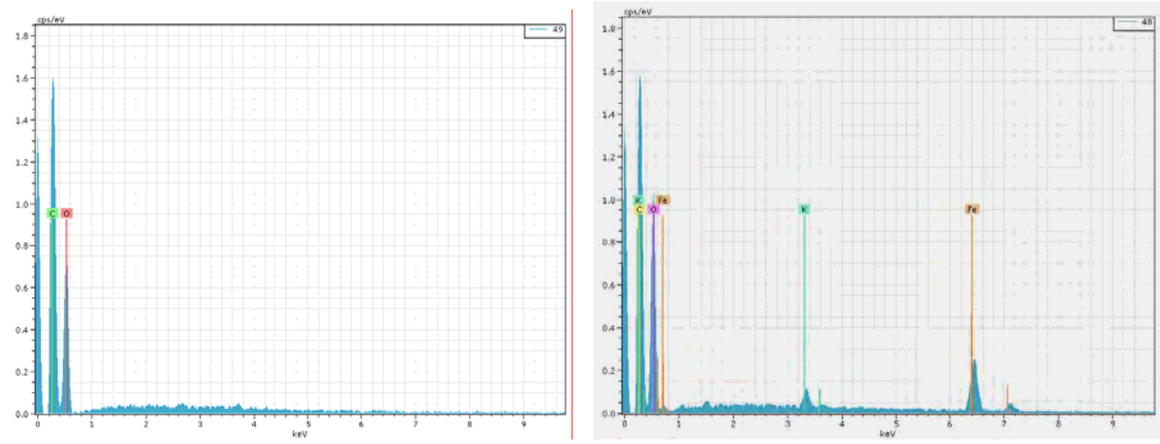


a **b**

Area of pure wood			
Element	**Weight**	**Atomic**	**Error**
	[%]		
Carbon	20,89	26,02	6,68
Oxygen	79,11	73,98	26,13
Total	100,00	100,00	

Area of the wood penetrated by iron ions			
Element	**Weight**	**Atomic**	**Error**
	[%]		
Carbon	10,22	17,80	1,92
Oxygen	51,80	67,67	6,91
Iron	35,94	13,44	0,85
Potassium	2,04	1,09	0,09
Total	100,00	100,00	

***Fig. 6**. EDX spectra and the chemical composition for the old fir wood (1860 A.D.): a – area of pure wood; b- area of the wood penetrated by iron ions.*

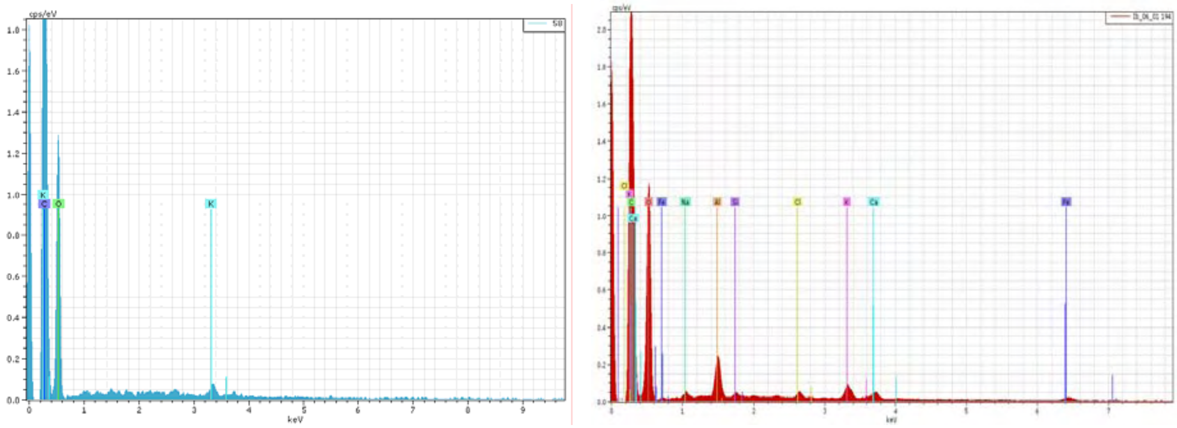


a b

Area of pure wood			
Element	Weight %	Atomic %	Error %
	[%]		
Carbon	20,47	25,53	6,60
Oxygen	79,53	74,47	26,52
Total	100,00	100,00	

Area of the wood penetrated by iron ions			
Element	Weight %	Atomic %	Error %
	[%]		
Carbon	17,60	23,18	7,29
Oxygen	75,67	74,80	25,05
Iron	5,81	1,65	0,21
Potassium	0,92	0,37	0,07
Total	100,00	100,00	

***Fig. 7**. EDX spectra and the chemical composition for the old poplar wood (XVII century): a – area of pure wood; b- area of the wood penetrated by iron ions.*



a b

Area of pure wood			
Element	Weight	Atomic	Error
	[%]		
Carbon	19,84	24,99	7,08
Oxygen	78,83	74,49	26,20
Potassium	1,33	0,52	0,10
Total	100,00	100,00	

Area of the wood penetrated by iron ions			
Element	Weight	Atomic	Error
	[%]		
Carbon	20,08	25,42	7,85
Oxygen	77,64	73,78	25,37
Iron	0,81	0,22	0,06
Potassium	1,26	0,49	0,07
Chlorine	0,21	0,09	0,04
Total	100,00	100,00	

***Fig. 8**. EDX spectra and the chemical composition for the old poplar wood (XVIII century) a – area of pure wood; b- area of the wood penetrated by iron ions*

In the figure 9 there are presented μFT-IR spectra obtained with a poplar old wood sample which had an iron nail in it. The spectra were background corrected using a gold mirror which doesn't absorb IR radiation. The spectra were averaged over 64 scans for more precise results. It can be observed from the spectra of the four areas: not contaminated by iron ions; the area in contact with iron nail; the area in contaminated/decontaminated limit; the contaminated central area, that there are slight differences between the group vibrations from 2950 – 2900 cm^{-1}, 2150-2000cm^{-1}, 1750-1600cm^{-1} and bigger differences in the domain of 900-600cm^{-1} which represents the contribution of iron ions in the penetration area.

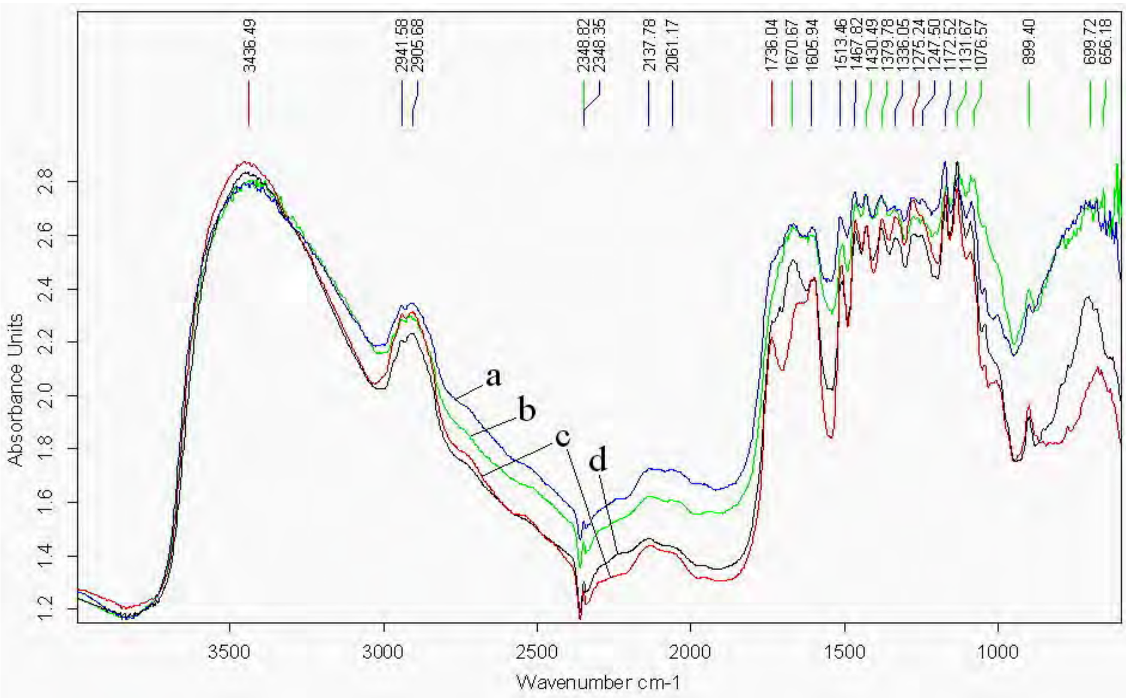


***Fig. 9**. μ-FT-IR spectrum for poplar old wood (XVIII Century):*
a – not contaminated by iron ions; b – the area in contact with iron nail;
c – the area in contaminated/necontaminated limit; d – the contaminated central area

4. Conclusions

In this paper the SEM-EDX and μ-FT-IR techniques have shown the way of interaction between iron and wood used in artefacts depending on time, with the impact upon the reciprocal conservability.

If the oak wood, due to tanin which forms with the iron ions coordination compounds, increases the capacity of dispersion and penetration and offers a reciprocal conservability, in the case of fir and poplar wood, the volatile compounds through degradation become compounds which decrease pH leading to the acceleration of the corrosion processes, and the compounds hard soluble from the wood-metal interface play the role of a membrane difficult to be penetrated by the iron ions in case of poplar wood and very porous for fir wood, Fe ions penetrating easily the wood along their fibers.

References

[1]. Sandu I., Hayashi M., Quaranta, M., Bejinariu C., Stanciu C., Sandu I.C.A., Vasilache V., 2007, *The study of metal – old wood interactions under the influence of pedological factors*, Advanced Technologies and Materials UGALMAT 2007, „Dunărea de Jos" University of Galaţi, p. 350-355

[2]. Sandu I., Hayashi M., Sandu I.C.A., Vasilache V., Stanciu C., Sandu A.V., 2007, „*Implication of the sem-edx technique in the study of old wood*", Advanced Technologies and Materials UGALMAT „Dunărea de Jos" University of Galaţi, p. 345-349

[3]. Sierra-Alvarez R., **Process Biochemistry, 42**, 5, 2007, p. 798-804

[4]. Rakotonirainy M.S., Caillat L., Heraud C., Memet J.B., Tran Q.K., 2005, Journal of Cultural Heritage, 8, 2, 2007, p. 160-169;

[5]. Li X.S., Englezos P., Journal of Colloid and Interface Science, 281, 2, p. 267-274;

[6]. Dominkovics Z., Danyadi L., Pukanszky B., 2007, Composites Part A: Applied Science and Manufacturing**, 38**, 8, 2007, p. 1893-1901;

[7]. Bjordal C.G., Nilsson T., Petterson R., Journal of Archaeological Science, 34, 7, p. 1169-1177;

[8]. Selwyn L.S., Rennie-Bisuillion D.A., 1993, Studies in Conservation, 38, p. 180-197.