FTIR Investigation of Paraloid B72 as Consolidant for Old Wooden Artefacts

Principle and Methods

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Consolidation of old frail wood by impregnation with polymers is a key step in wooden cultural heritage conservation. Paraloid B72 is an acrylic polymer widely used for this purpose. FTIR spectroscopy, though microdestructive, was found to be a versatile method able to reveal the presence / penetration of Paraloid B72 into the wood structure. A semiquantitative method of investigation was developed with the aim of correlating FTIR data with gravimetric analysis. Relative consolidant retention indexes were calculated based on the integrated areas of relevant absorption bands and compared with gravimetric data of consolidant retention, resulting a fairly good correlation. The method developed on laboratory treated samples made of new sound wood (poplar Populus tremula) was further applied on three case studies, representing heavily degraded wooden artefacts from cultural heritage.

Keywords: Paraloid B72, wood consolidation, FTIR, cultural heritage

Wood is a natural material strongly linked to human culture and civilisation [1]. Therefore, wooden artefacts of very different types from furniture, domestic traditional ustensils and tools, to icons, iconostasis, polychrome wooden statues, up to old wooden houses and churches, represent a very significant part of cultutal heritage at both national and international level. Conservation of cultural heritage is a moral duty enforced by internationally recognised laws, rules and principles of action for good practice. A scientific approach in all the phases of the conservation process is compulsory [2] .

Consolidation of old frail wood, which has lost internal cohesion and mechanical strength due to biodegradation and biodeterioration phenomena, combined with the action of non-biotic factors, such as variable atmospheric humidity, UV radiation, ambiental uncontrolled temperature and atmospheric pollutants, is a key step in the conservation of old wooden objects. Keeping the authenticity of the old objects would not be possible without adequate preservation and consolidation treatments of severely degraded and frail wooden areas/elements [3-10].

Thermoplastic polymers as solutions in adequate solvents are most frequently employed for consolidation of frail wood and other materials in conservation. Paraloid B72, an acrylic polymer with medium degree of polymerisation, is such a polymer, extremly important for wood conservation [5-8, 10]. The efficiency of a consolidation process depends on the amount of solid polymer fixed into the structure of the treated substrate, the depth of penetration and uniformity of distribution. These are influenced by the characteristics of the treating solution (concentration of polymer, viscosity, polarity and volatility of solvent), the properties and conservation state of the treated material and the actual treating procedure [6, 10-15] .

Paraloid B72 is also employed for the consolidation of wooden surface finishing layers such as gilding, painting, lacquers [16].

Evaluation of the efficiency of a consolidation process is related therefore to the investigation of polymer presence and distribution into the treated wood/material. Non-destructive structural investigation methods, such as X-ray radiography and synchrotron imaging techniques are preferred [10, 17], but as these are not ready available, other molecular analysis methods, such as infrared spectroscopy are often employed [17-27]. Infrared spectroscopy is well known as a valuable, versatile method for characterising and identifying organic compounds, including natural or synthetic polymers, based on their chemical structural features, revealed as characteristic absorption bands in the range of 4000-400cm^{-1}, out of each the range 1500-400cm^{-1} is the „fingerprint" region [28]. Fourier-transform infrared spectroscopy (FTIR) has become a recognised scientific tool for conservation [29], and modern PC assisted spectrometers with attenuated total reflectance (ATR) or diffuse reflectance (DRIFT) accessories made this investigation more rapid, cost-effective and precise.

Previously published research of the authors demonstrated the usefullness of FTIR spectroscopy to reveal the presence / penetration of different consolidants, including Paraloid B72, into the wood structure, based on their most characteristic absorption bands which can be differentiated from wood components absorptions [7, 30]. The present paper aimed at further developping this method as a semiquantitative investigation and to corelate it with gravimetric analysis. Relative consolidant retention indexes were calculated based on the integrated areas of relevant absorption bands and compared with gravimetric data of consolidant retention. The method developed on laboratory samples made of new sound poplar wood (*Populus tremula*) was applied on three case studies, representing heavily degraded wooden artefacts from cultural heritage.

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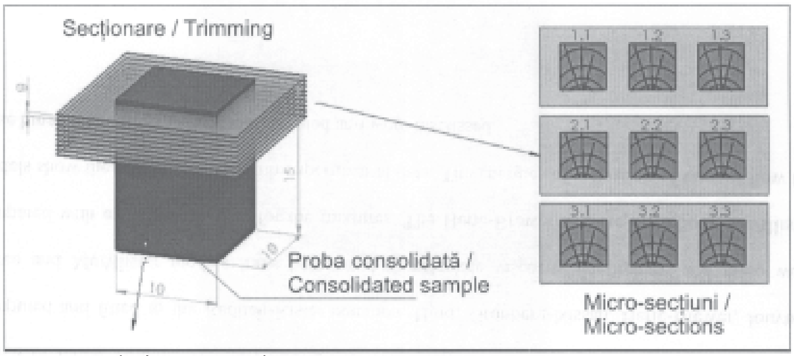


Fig. 1. Laboratory test samples from new sound poplar wood (*Populus tremula*) and their microtome sectioning for obtaining 3 series of transversal thin microsections for FTIR investigation [from ref 24]

Table 1
SUMMARY OF LABORATORY SAMPLES OF NEW, SOUND POPLAR WOOD (*POPULUS TREMULA*) INVESTIGATED BY FTIR AS MICROSECTIONS

Type of sample	**Code**	**Consolidant solution**	**Treating procedure**	**WPG [%]**	Microsections codes
Untreated control	Control	-	-	0.00	
Treated	C2-IT30'	C2: Paraloid B72, 5%	Total immersion, 30min/20°C	0.74	41C2-Lx.y x=1-3; y=1-4
Treated	C4-IT24	C4: Paraloid B72, 10%	Total immersion, 24h/20°C	5.34	42C4-x x=1-4
Treated	C4-vac3		Vacuum impregnation, V3	9.27	C4-V3-x x=1-4
Treated	C4-vac4		Vacuum impregnation, V4	11.03	C4-V4-x x=1-4
Treated	C4-ZnO-1	C4 with 1% nano ZnO	Total immersion, 24h/20°C	6.15	C4-ZnO-1-x x=1-4
Treated	C4-ZnO-2.5	C4 with 2.5% nano ZnO		7.09	C4-ZnO-2.5-x x=1-4
Treated	C4-ZnO-5	C4 with 5% nano ZnO		6.97	C4-ZnO-5-x x=1-4

Notes: Paraloid B72 from CTS - Romania was employed. The solvent used for the preparation of consolidant solutions was a mixture of acetone – ethanol (pro analysis) in proportion of 1:1 (v:v); Nano-ZnO as dispersion in ethanol from Sigma&Aldrich was used. V3 and V4 are the codes of two vacuum impregnation schedules, both containing an actual vacuum phase of 30 min at 0,4 atm, following an initial immersion phase at normal pressure 1.0 atm; the total duration of schedule V3 was 85 min, while for V4 was longer 155 min.

Experimental part

Materials and methods

The experimental research reported in this paper was carried out on laboratory samples of sound wood (*Populus tremula*) impregnated with solutions of Paraloid B72 by different procedures and on relevant samples from three degraded wooden artefacts requesting wood consolidation in their conservation schedule.

New, sound wood laboratory samples

Small samples (15 x 10 x 10 mm) of new, sound poplar wood *(Populus tremula)* were treated by total immersion or vacuum impregnation with different solutions of Paraloid B72, conditioned to constant weight to determine weight percent gain (WPG, [%]) and further cut with a microtome to obtain series of thin (40μm) transversal microsections (3-4 lamellas L1-L4 with 3-4 successive microsections) as presented in figure 1.

The first microsectiov was obtained after an initial trimming of about 100μm, so that each microsection represents a different penetration depth on the longitudinal direction, which can be easily calculated. A summary of the types of samples investigated in this research, with codes and information on the respective composition of the consolidant solution, treatment procedure and solid consolidant retention, expressed as WPG [%], is presented in table 1. Details on the wood samples preparation, consolidation products and treating procedures, WPG calculation and the further cutting of treated and control samples for investigations are available in previous publications [6-9, 30].

Old, degraded wood samples from artefacts

Three old wooden artefacts were selected as case studies within this research. These were: the upper ornament of a bishop's throne (case A), a fragment of a gilded sculptured frame (case B) and a „Lira" element of a piano (case C). The objects coded A and B belong to "Adormirea Maicii Domnului (Assumption of the Virgin)" Orthodox Church from Săcele Turcheş-Braşov, an historical monument of B category, built in 1781-1783.

The Bishop's throne ornament (case A) was made of lime wood, finely carved with floral ornaments. It was in a quite poor stage of conservation due to severe fragilisation of the wooden material as result of insects attack. Some marginal and back side parts were detached or broken and lost due to the material weakness, intensive use or inappropriate storage.

The gilded frame (case B) was made of two wood species: spruce on the backside and lime on the upper side, which is carved with stylised acanthus leaf motif. The two wooden elements are jointed together by an interesting mitred half lap joint. Almost 50% of the frame was missing. The wood was extremely fragile, up to almost complete disintegration into dust in some areas. Because of alternating wet and dry conditions and insects holes, the integrity and adherence of the gesso ground layer was affected, so that the gilding layer was lost on some areas or had the tendency to flake off from the substrate very easily. Accordingly, consolidation was necessary for both the substrate and the gilding layer.

The "Lira" piano element (case C) was made of lime solid wood veneered on both faces and edges with walnut veneer. A fine, central triple-lined marquetry decoration gives personality to this artefact. Again, insects attack caused fragilisation of lime wood and one of the three tenons was broken and missing.

Some images of these old artefacts and details illustrating the severe degradation of the wooden material, which has become soft, spongy and frail, with areas of

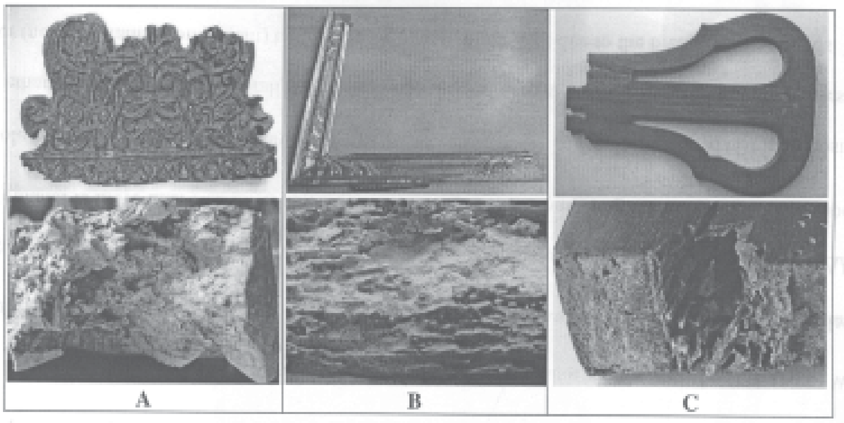


Fig.2. General view (top) and details illustrating heavily degraded, frail wooden material (bottom) of the three artefacts considered as case studies: A – Bishop's throne ornament; B – fragment of a gilded frame; C – "Lira" piano element

disintegration to dust or evident tendency to disintegrate, qualifying them as good candidates for consolidation case studies, are presented in figure 2.

Before consolidation, small samples were extracted for FTIR investigation, from different frail areas, usually in the proximity of deteriorated areas, such as ruptures or cracks.

Solutions of Paraloid B72 in acetone-ethanol (C2, C4 and C4-ZnO-2.5) were employed for consolidation of the artefacts, following a previous curative biological treatment with a solution of 0.2g/L deltamethrine in ethyl alcohol. The consolidation solutions were applied in successive phases, by injecting into the insects galleries until saturation, each application phase being followed by a conditioning phase. For a deeper penetration into the substrate, C2 was used in the first treatments, then C4, while C4-ZnO2.5, with increased resistance to UV ageing [9], was employed for the last treatment.

FTIR investigations

A Perkin Elmer spectrometer BX2 equipped with ATR system was used to record the FTIR spectra of untreated control and treated wood microsections, as well as the spectra of solid Paraloid B72 as reference. A single spectrum of a central area (representing an integration of a sample surface with a diameter of 1.8 mm) was registered for each microsection as the result of 4 scans. The spectra were registered in reflectance mode in the range of 4000-600 cm^{-1} at a resolution of $4cm^{-1}$.

An Alpha Bruker FTIR spectrometer with ATR unit was employed for the investigation of the old, degraded wooden samples extracted from artefacts, prior and after consolidation. The samples were analysed as thin flakes or crushed powders. A minimum 2 spectra were recorded for each artefact/sample and an average spectra was calculated. The spectra were registered in absorption mode in the range of 4000-400 cm^{-1} at a resolution of $4cm^{-1}$, each spectra being the result of 24 scans. The recorded spectra were base line corrected and smoothed before normalisation.

The software of the FTIR equipment was employed to further evaluate the corrected heights and integrated areas of some characteristic bands for untreated and treated wood. These values were used to reveal the presence of Paraloid B72 in the treated wood and to estimate semiquantitatively its relative concentration, based on the calculation of an index of consolidant retention, IR, as proposed by Chadefaux *et al* [31] and further adapted for consolidated wood by Timar *et al* [30]. The ratio A1730/A3340 between the areas of the peaks at ~1730 cm^{-1} (assigned to unconjugated carbonyl groups) and ~3300-3400 cm^{-1} (assigned to hydroxyl groups in wood) was found to be the most suitable for this purpose.

Results and discussions

FTIR investigation of the new, sound wood samples

Some examples of FTIR spectra recorded for series of microsections of new, sound poplar wood treated with Paraloid B72, in comparison with the spectra of untreated poplar as control (average spectra of a series of microsections) and the spectra of Paraloid B72 reference are presented in figures 3 and 4.

The presence of Paraloid B72 in the treated samples is revealed by the increased intensity of the absorption band at around 1730 cm^{-1}, assigned to unconjugated carbonyl groups. The carbonyl group is an important characteristic feature of Paraloid B72, a mixture of poly-ethyl-methacrylate and poly-methyl-acrylate, while the amount of unconjugated carbonyl groups in the wood structure is limited, being present seldomly in the structure of some noncellulosic polyoses as ester of free acidic groups [5,

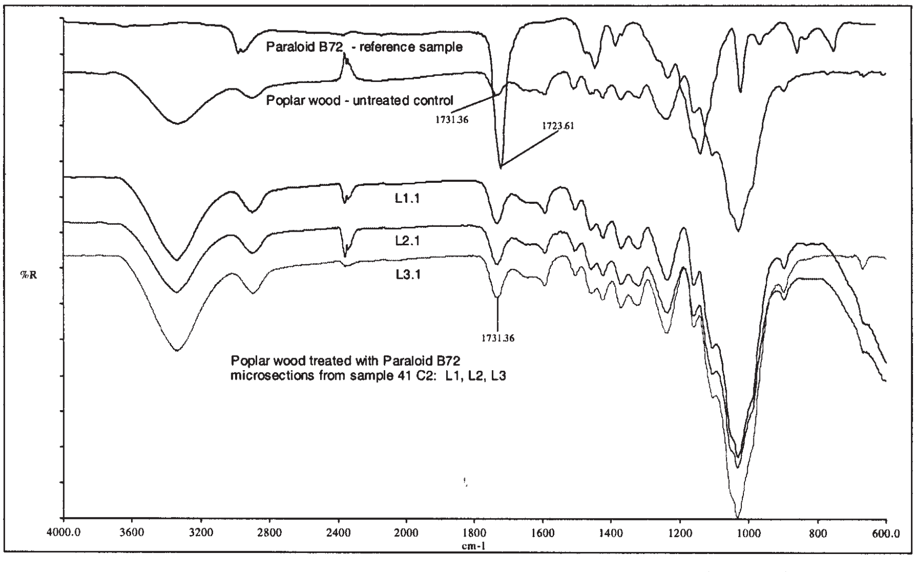


Fig. 3. Comparative FTIR spectra of paraloid B72, untreated control wood and wood impregnated with Paraloid B72 – solution C2 (3 microsections)

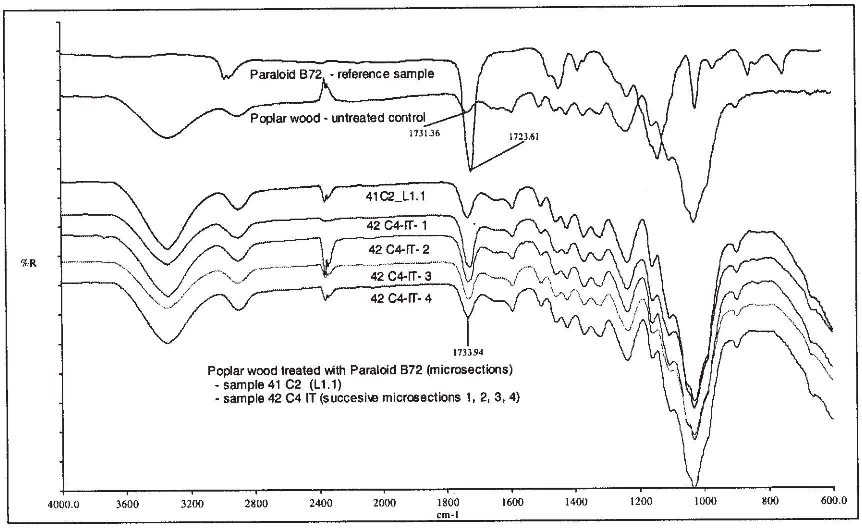


Fig. 4. Comparative FTIR spectra of Paraloid B72, untreated control wood and wood impregnated with Paraloid B72 – solution C2 (1 microsection), solution C4 (4 microsections)

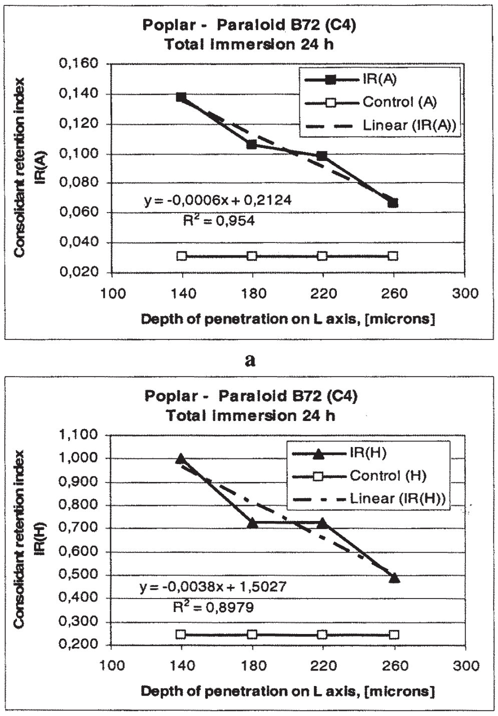
29, 32-36]. Therefore, as previously reported by Timar et al [30], this band can reveal with satisfactory confidence the presence of Paraloid B72 in wood.

Furthermore, the ratios A1730/A3340, H1730/H3340, of the corrected areas or heights of the respective absorption bands, defined as consolidant retention indexes, IR(A), IR(H), allowing a semiquantitative appreciation of the presence and relative amount of Paraloid B72 in the treated wood [30] were calculated and compared. In all the cases the calculated IR indexes values for the laboratory treated samples were higher than the mean value for the control untreated sample. For exemplification, there are presented in table 2 the calculated values from the FTIR spectra plotted in figures 3 and 4.

These values clearly demonstrate the presence of Paraloid B72 in the unvestigated areas of treated wood and indicate that the degree of impregnation with consolidant varied more or less between the investigated samples as a function of the concentration of the treating solution and the treating procedure. Higher IR values were calculated for the samples treated by immersion for 24h in the solution C4 (microsections coded 42C4-1-4 in fig. 4) than for those immersed only 30 min in the solution C2 (microsections coded 41C2-L1.1-L3.1 in fig.3, fig.4). Furthermore, when the IR indexes obtained for a series of microsections were plotted against the corresponding calculated depth of penetration on the longitudinal direction, penetration profiles as those depicted in figures 5 and 6 were obtained.

The profiles in figure 5, obtained from IR(A) and respectively IR(H) calculated values are very similar, showing that the two series of values, though different in terms of absolute value, are equivalent as information on the relative concentration of consolidant in wood. Therefore, only the consolidant retention indexes calculated from the integrated areas of the significant absorption bands IR(A) will be further used in this paper.

The penetration profiles in figure 5 indicate that the relative concentration of Paraloid in wood decreases progressivelly, from the surface towards inside and that only a penetration depth of about 300-330μm on the longitudinal direction could be expected under the respective treating conditions (sound wood, 24h immersion in solution of 10% concentration). It is obvious that the penetration will be different in old, degraded wood, generally higher absorptions and deeper penetrations being



b

Fig. 5. Profile of Paraloid B72 penetration into wood on the longitudinal direction, as resulted from retention indexes based on absorption bands areas (a) and absorption bands heights (b)

Type of sample	Code	Absorption band 1 ~3340 cm⁻¹, -OH		Absorption band 2 ~ 1730 cm⁻¹, carbonyl		IR(A)	IR(H)
		A1	H1	A2	H2	A2/A1	H2/H1
Wood	Control	2553.9	7.8	78.84	1.9	***0.031***	***0.243***
Paraloid B72	Reference	-	-	825.4	19.59	-	-
C2-IT30'	41C2-L1.1	3032.2	10.52	201.77	4.93	**0.067**	**0.469**
	41C2-L2.1	2584.5	8.84	186.13	4.49	**0.072**	**0.507**
	41C2-L3.1	3612.6	11.8	207.68	4.85	**0.057**	**0.411**
C4-IT24	42C4-1	2552.9	7.59	309.57	7.59	**0.137**	**1.000**
	42C4-2	2560.6	9.15	270.99	6.65	**0.106**	**0.727**
	42C4-3	2112.8	6.99	207.65	5.08	**0.098**	**0.727**
	42C4-4	2795.7	9.17	185.23	4.48	**0.065**	**0.489**

Table 2
EXAMPLE OF CALCULATION OF THE CONSOLIDANT RETENTION INDEXEX IR(A) AND IR(H) CORRESPONDING TO THE SPECTRA IN FIGURE 3 AND FIGURE 4

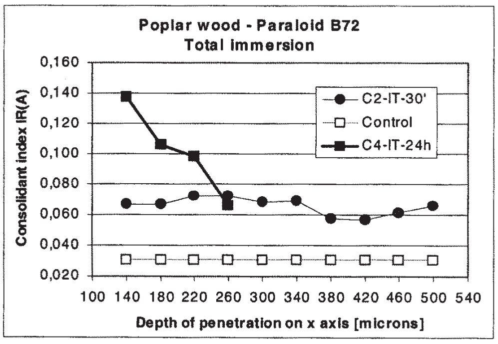


Fig.6. Profile of Paraloid B72 penetration into wood on the longitudinal direction for Paraloid solutions with different concentrations (5%, 10%)

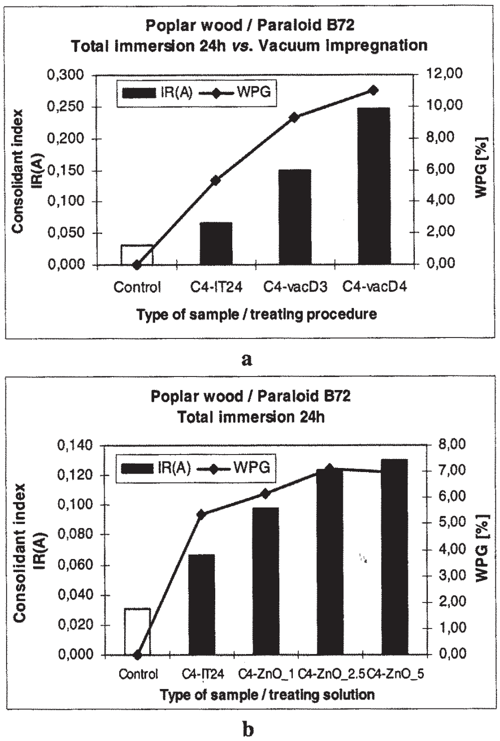


Fig.7. Calculated FTIR indexes of consolidant retention IR(A) in relation to the actual gravimetric consolidant retention WPG [%], revealing: a - influence of the treating procedure; b – influence of composition of consolidant solution- effect of nano-ZnO

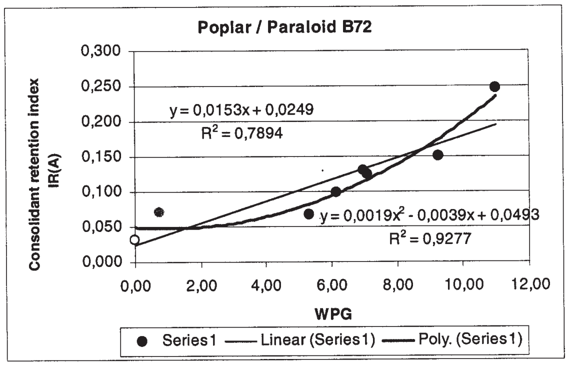


Fig. 8. Mathematical correlation between consolidant retention indexes IR(A) obtained by FTIR and the actual gravimetric values of consolidant retention expressed as WPG [%]

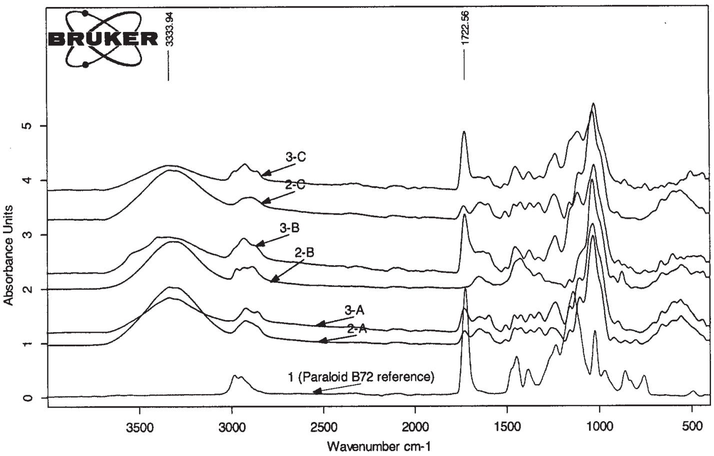


Fig. 9 FTIR investigation of consolidant penetration into old, degraded wood for the three case studies A, B, C: 1- reference spectra for paraloid B72, 2 – spectra of degraded wood before consolidation; 3- spectra of consolidated wood

obtained for degraded wood, due to the extra-porosity brought about by degradation [7, 12, 15].

The penetration profile depends very much on the concentration of the treating solution, as illustrated in figure 6. The treatment with a more diluted solution (5% compared to 10%) ensures a deeper penetration, though the retention of consolidant is evidently lower. This is in accordance to previously published results [12, 13]. As penetration depth is critical in the practice of conservation, diluted solutions and repeated treatments are preferred.

A further step in developing and checking the applicability of this FTIR semiquantitative investigation method was to correlate the FTIR consolidant retention indexes IR(A), calculated for the same depth of penetration of about 260μm corresponding to microsection 4, with the actual quantitative values of consolidant retention in wood, expressed as weight percent gain, WPG [%], determined by gravimetric analysis [7, 13].

The graphs in figure 7 show a fairly good correspondence, increased IR(A) values corresponding to higher WPG values. Thus, the influence of the treating procedure (i.e vacuum impregnation vs. immersion at atmospheric pressure) or of composition of the treating solution (i.e. effect of nano-ZnO as additive [9, 13, 14] on the consolidant retention expressed as WPG, is satisfactorily revealed by the calculated IR(A) indexes.

If all the experimental data IR(A) versus WPG, irrespective of the concentration /composition of the impregnation solution or treating procedure were plotted (fig. 9), then a polynomial mathematical regression equation of order 2 could be obtained with relevant significance ($R^2 = 0.92770$). All these findings demonstrate the validity and usefullness of the proposed method [36 - 40].

The developed method was found to be useful for investigating the efficiency of the consolidation procedure for old, frail wood, as results from the FTIR spectra in figure 9. For all the three artefacts, the noticeable difference between the spectra of the extracted samples before and after consolidation, demonstrated the penetration of Paraloid B72 in the treated wood.

Furthermore, the calculated IR(A) indexex before and after consolidation and their relative increase are useful for controlling the process efficiency. These are plotted in figure 10 for the three case studies. According to these values the best consolidation was achieved for the „Lira" piano element (case study C), followed by the gilded frame (B), the smallest amount of Paraloid being evidentiated in the case of the Bishop's throne ornament (A).

However, one should bear in mind that the amount and penetration of consolidant could be different in different areas of the investigated artefacts, as a function of initial conservation state and actual treatment, and more samples should have been extracted and investigated for a more precise result, which would have been

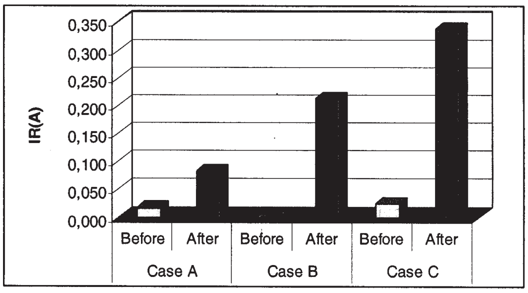


Fig.10. The efficiency of the consolidation procedure for the three case studies (A, B, C) as revealed by the increase of IR(A) values following treatment with Paraloid B72

unacceptable. A non-destructive investigation of the consolidated artefacts, such as X-ray radiography or density profile would be useful to corroborate the results.

Conclusions

FTIR investigation was used to reveal the presence and penetration of Paraloid B72, an acrylic polymer frequently used in wooden cultural heritage conservation, into the wood structure. An useful, versatile, semiquantitative analysis method was developed and applied.

Method development was based on FTIR investigation of microsections of laboratory treated small samples made of new sound wood (poplar *Populus tremula*). These were relevant for the influence of concentration and composition of Paraloid B72 based consolidation solutions and of the treating procedure on the penetration and retention of solid consolidant into the wood. Relative consolidant retention indexes were calculated based on the integrated areas of relevant absorption bands and compared with gravimetric data of consolidant retention, resulting a fairly good correlation. This was expressed mathematically by a polynomial equation of order 2.

The developed method was found useful for investigating the efficiency of the consolidation procedure for old, frail wood in three real case studies. The calculated indexes of consolidant retention before and after consolidation and their relative increase help monitoring the process efficiency. However, corroboration of these data with other non-destructive investigation methods would be benefficial and will be considered in further research.

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