

# **The use of acids and alkalis in cleaning archaeological wood**

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## **Summary:**

Due to the complex composition of all types of wood, acids and alkalis affect the two major wood components, because they may either breakdown the cellulose or the lignin. So far it has not been possible to prevent the use of either acids or alkalis during cleaning of archaeological wood. Diluted acetic acid and ammonium hydroxide are the two most common reagents used for this purpose in most of the archaeological sights. The negative effect of these reagents on the chemical composition of archaeological wood is usually neglected. Using FTIR spectroscopy, the break down of the molecular bonds in both lignin and cellulose of wood treated with the two most commonly used reagents, is studied.

**Keywords: chemical cleaning; archaeological wood; FTIR**

## **Introduction:**

It is a known fact that newly seasoned wood can be used in factories and industries where the use of either acid or alkali is inevitable, because wood can withstand reasonably high concentrations of either. The effect of either acids or alkalis depends on their type, concentration, pH-value, the length of exposure and temperature. In general, softwoods are more resistant to both acids and alkalis than hardwoods, but in all cases attack by either will first lead to color changes in the wood (Unger, et al., 2001). Therefore for woodworking and finishing purposes acids or alkalis can be used to change the colour of the end product.

The deteriorating effect on wood is not really notable or put into consideration in the case of new wood, which may easily be replaced any time, but in the case of archaeological wood the effect of either acid or alkali can be destructive. Thick layers of dirt and foreign matter on archaeological wood may be removed mechanically, but fine layers of dirt need chemical intervention, therefore acids and alkalis are often used in cleaning archaeological wood *in situ*.

The major wood components that are easily affected by chemicals are:

- 1) Cellulose and Hemicellulose
- 2) Lignin
- 3) Extraneous materials (4-10%)

The chemical composition of archaeological wood may vary a lot. In some cases the carbohydrate percentage may be as low as 10% (in newly cut wood it ranges between 65-75%), in other cases the lignin content may jump up to over 40% or be as low as 5% (in newly cut wood it ranges between 18-25%). There is no standard for archaeological wood components and every wooden object has to be dealt with separately (Sjöström, 1992). But it is worthy to note that extended exposure to acids leads to hydrolysis of the polysaccharides, starting on the wood surface. Alkalis will first cause wood swelling, followed later by decomposition of hemicelluloses and lignin. According to previous studies hardwoods such as oak and beech are less resistant to acids and alkalis than softwoods such as pine and fir. The corrosion resistance of modern oak had been measured by Müller (1993). He noted that oak was completely stable to 2% acetic acid (mass loss  $<0.1 \text{ mg/m}^2\text{-h}$ ) but was barely stable to 2% ammonium hydroxide (mass loss  $3.0\text{-}10 \text{ mg/m}^2\text{-h}$ ).

### **Materials and Methods:**

Ancient deteriorated samples that had been replaced by new wood during restoration were taken from the Mashrabieh of Bazarah and were used for studying the effect of acetic acid, which is a simple organic acid, and ammonium hydroxide, a relatively weak alkali, commonly used for cleaning wood in Egypt at the present time. The wood taken from a 400 year old Mashrabieh was classified as a hardwood, *Quercus sp.* (oak) that had been exposed for centuries to weathering effects and pollutants.

In the context of conservation acids are used as a component in cleaning solutions, e.g. pH buffers, chelating agents and resin and bile soaps. Ammonium hydroxide may sometimes be added to remove surface dirt or greasy accretions from varnished paintings (pH of 8.5-9), because the volatility of ammonia ensures that it will not leave a residue and its alkalinity brings thin films of oil and grease into solution (Rivers, et al., 2003).

Three wood samples were immersed in either 1% acetic acid or 1% ammonium hydroxide separately for one hour. Samples were then removed and left to dry out in normal room temperature and humidity conditions.

Samples were then divided into three groups, each group consisting of 3 samples; i.e. archaeological sample before immersion in reagent and archaeological sample after immersion in one of the two reagents. The first group was studied by FTIR spectroscopy (JASCO FTIR plus 460) to document the changes that happened in the chemical bonds of both wood cellulose and lignin during its use over the centuries. The second group was aged using UV radiation (Spectroline UV A lamp, wave length 365 nm) for 100 hours in total, with alternating conditions of light and darkness, similar to natural conditions. Samples were placed at a distance of 15 cm from the light source in normal room temperature which was around 15-20°C during the last week of November 2006. The third group was aged by heating for 100 hours at 105°C ± 3°C. Samples from the second and third group were also studied by FTIR spectroscopy and results were compared. The reason for ageing the samples was that any archaeological object is either displayed or stored after treatment and that is when the effect of different materials starts to become evident.

## **Results:**

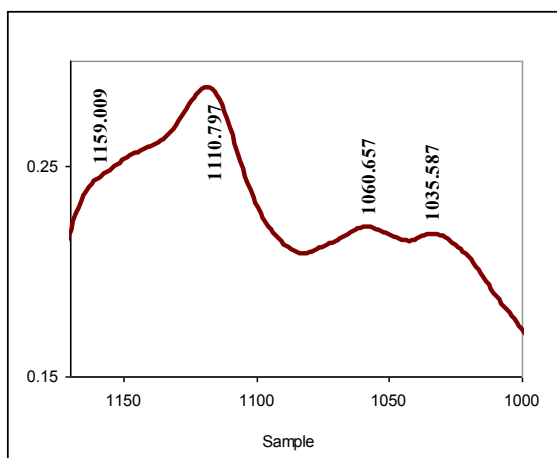
### **Effect of heat and U.V ageing on archaeological wood**

Using FTIR spectroscopy it was noticed that the most prominent bands of both cellulose and lignin in the archaeological sample were present (fig.1&2). Heat ageing accelerated hydrolysis, oxidation, dehydration and free radicals cleavage. Carbon atoms occupying various positions in the glucopyranose ring gradually transformed by oxidation into various carbonyl groups, so intensities of C-O bands decreased and that of carbonyl groups increased. Oxidation was detected as fairly broad and overlapping bands. As a result of heat ageing, both water stretching and bending modes were removed. Similar results were obtained by Lojewska, *et al.* (2005 a & b) who noted that at elevated temperature water desorbed and did not redesorb again. Tjeerdsma, *et al.* (1998 a & 1999) noted that water, acetic and formic acids liberated from hemicelluloses during heating of wood causing carbohydrates cleavage, and a reduction of degree of polymerization of the

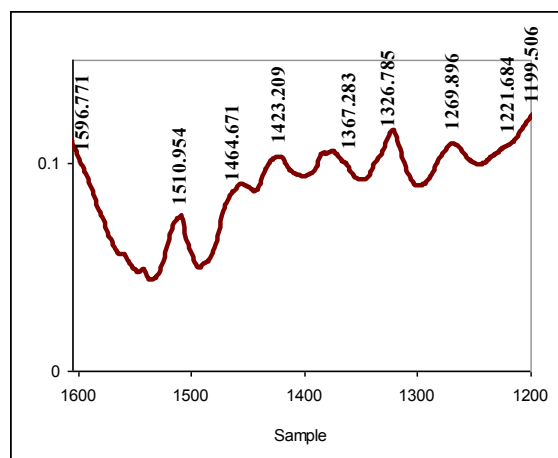
carbohydrates. The band at  $1158\text{ cm}^{-1}$  became prominent as a result of the cleavage of the terminal ring i.e.  $\text{C}_5\text{-OH}$  was formed.

U.V ageing showed a slight variation compared to heat ageing. Lignin adsorbs UV energy and free radicals that are formed are stabilized in the lignin molecule. The free radicals can migrate deep into the lignin structure but mainly degrade the surface layers of lignin (Rowell, 2006). These photo induced free radicals are very active, decaying rapidly at ambient temperature, and are capable of reacting with oxygen molecules. Leary and Zou (1994) mentioned that UV causes an oxidation of the phenoxy radicals in lignin giving quinons, which appeared in the  $1600\text{ cm}^{-1}$  region. Photo-cleavage of lignin (the photo labile component of wood) generates carbonyl-containing compounds (Anderson, *et al.*, 1991; Horn, *et al.*, 1994 and Pandey, 2005).

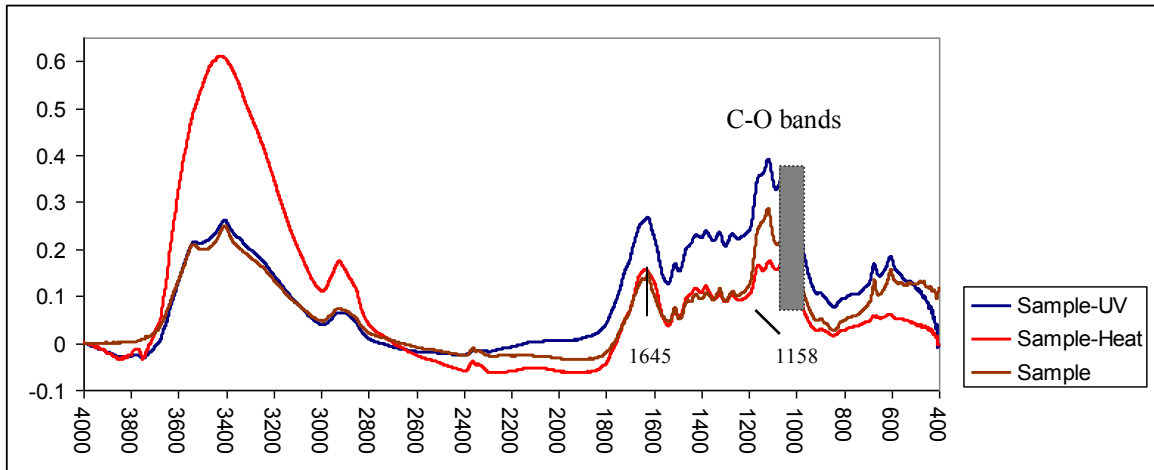
It was noticed that most cellulose and lignin bands decreased as a result of heat and U.V ageing (fig. 3); i.e. the intensities of various bands observed in the O-H bending and C-H deformation zone (between  $1400$  to  $1200\text{ cm}^{-1}$ ) and in associated ring vibrations zone (below  $1200\text{ cm}^{-1}$ ) decreased. That could be explained, because according to Hon and Feist (1993), wood contains small amounts of stable free radicals that are generated on the wood surface when exposed to UV light.



**Fig. 1: FTIR spectra of archaeological sample showing the most prominent carbohydrate bands of cellulose**



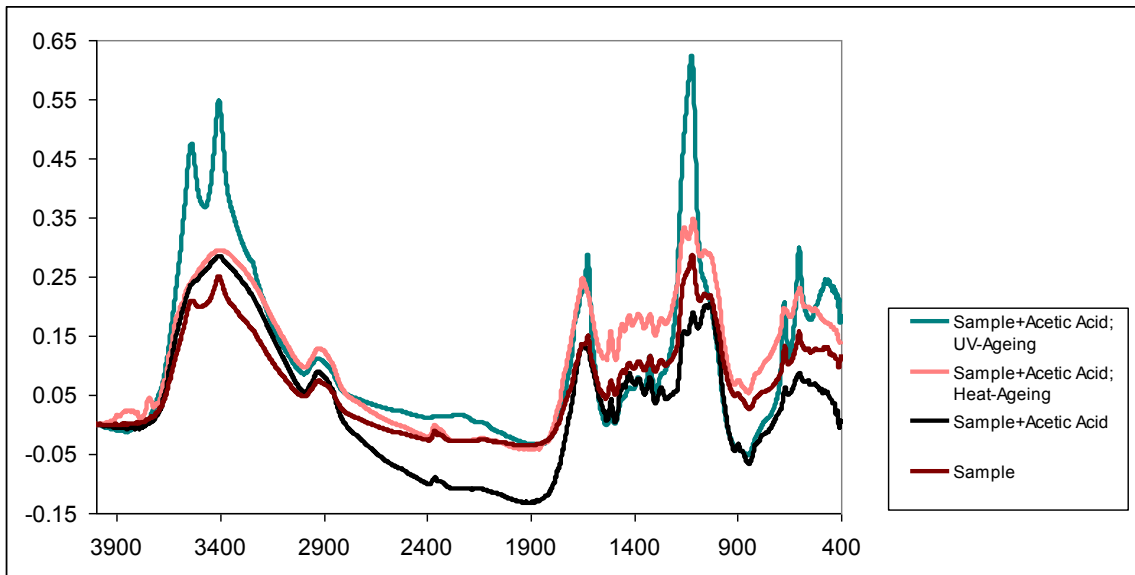
**Fig. 2: FTIR spectra of archaeological sample showing the major lignin bands**



**Fig. 3; FTIR spectra of heat and UV ageing of archaeological wood sample showing several changes and the formation of a new band due to ring cleavage**

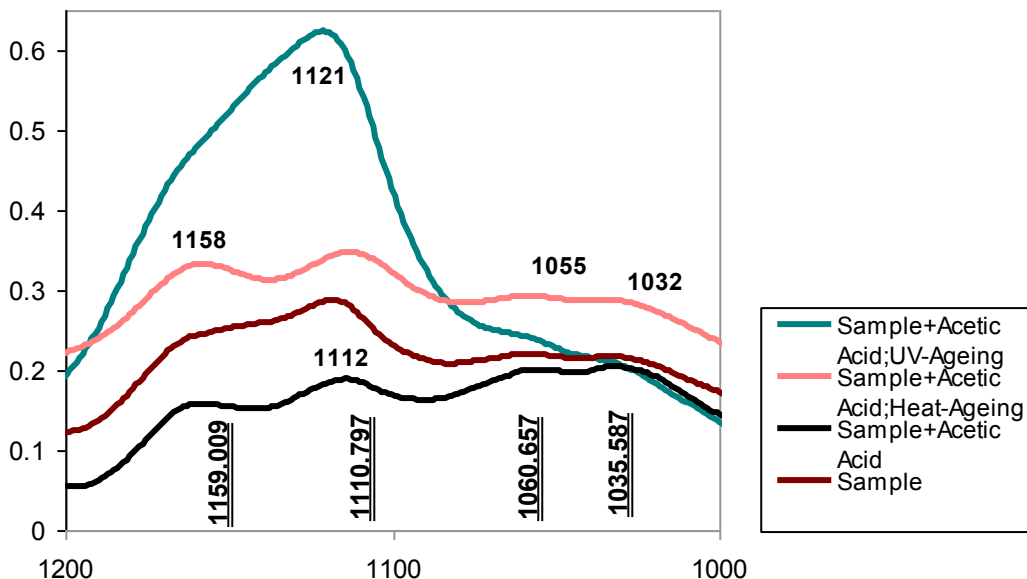
### Effect of acetic acid on archaeological wood

Wood itself is weakly acidic, but it may be discoloured by exposure to acids. Acids alone increase the reactivity of hydrolysis and oxidation of cellulose. After immersion of the archaeological sample in 1% acetic acid followed by both heat and U.V. ageing the following changes were noted, as seen in fig.4-8 and summarized in table 1.



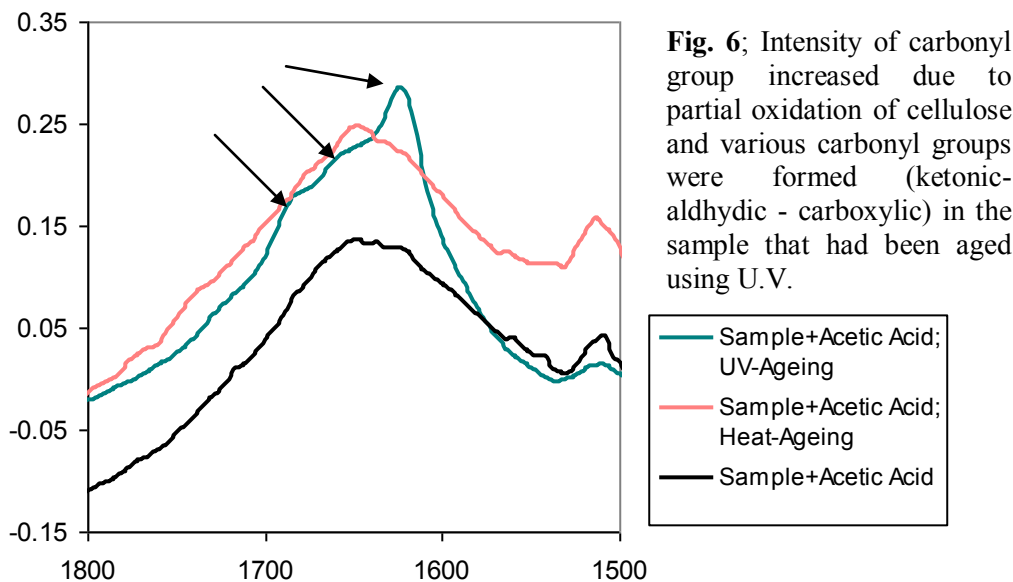
**Fig. 4; FTIR spectra of the sample before and after immersion in 1% acetic acid, and after heat and UV ageing.**

### C-O stretching zone



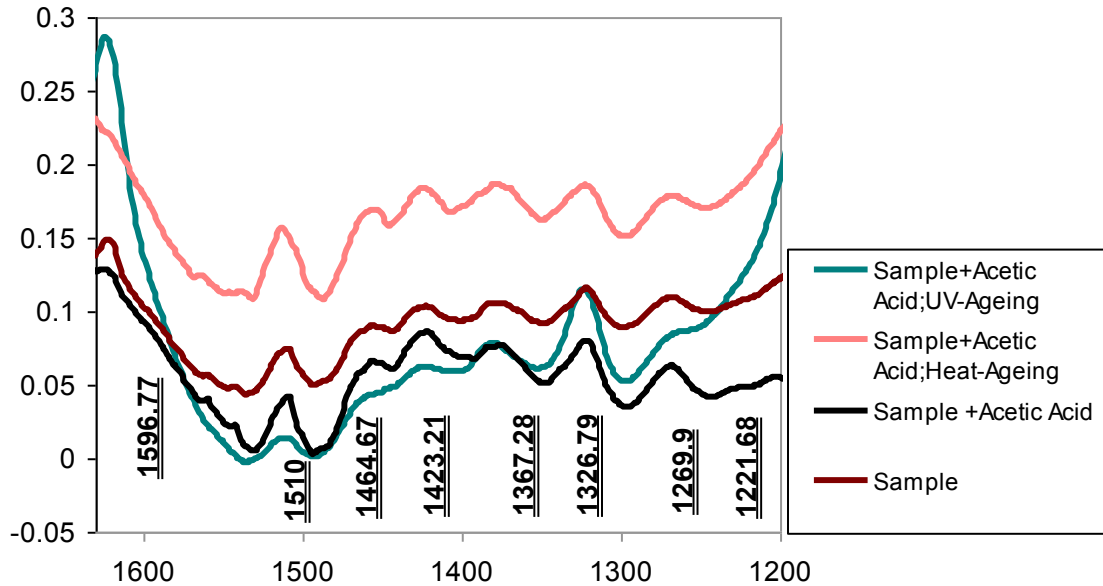
**Fig. 5;** Acid decreased the intensity of C-O band at 1112  $\text{cm}^{-1}$ . The band at 1158  $\text{cm}^{-1}$  became prominent after immersion in acetic acid and after heat ageing, which may be a result of hydrolysis of  $\text{C}_1\text{-O-C}_5$  bond of terminal glucopyranose ring and new C-O was produced. Due to heat ageing, bands disappeared at 1055 & 1032  $\text{cm}^{-1}$  as a result of an oxidation process. Only one band appeared due to U.V ageing at 1121  $\text{cm}^{-1}$  and the rest of the cellulose bands coalesced and decreased.

### C=O stretching zone



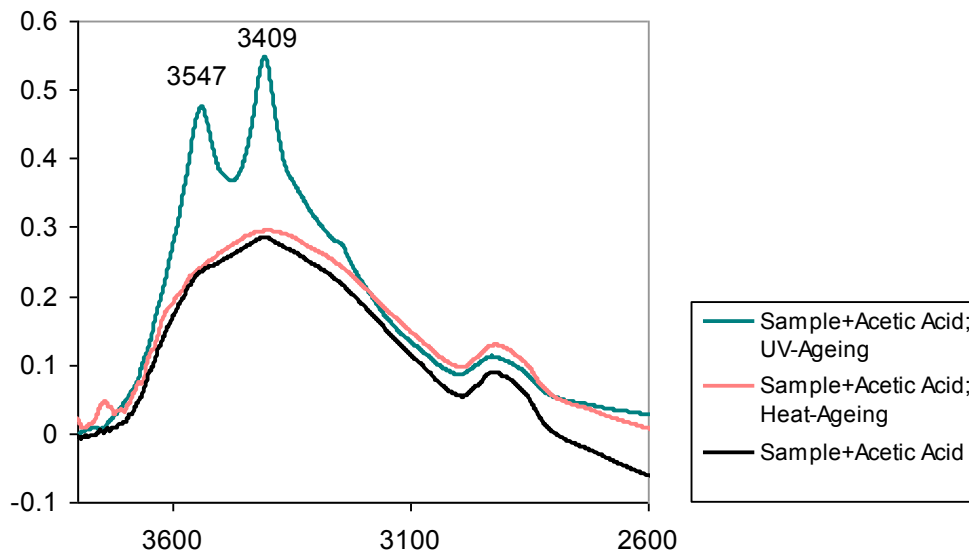
**Fig. 6;** Intensity of carbonyl group increased due to partial oxidation of cellulose and various carbonyl groups were formed (ketonic-aldhdyic - carboxylic) in the sample that had been aged using U.V.

### OH bending and CH deformation zone



**Fig.7;** The intensity of various bands observed in the OH bending and CH deformation zone (between 1400  $\text{cm}^{-1}$  -1200  $\text{cm}^{-1}$ ) decreased after immersion of the sample in acetic acid. Heat ageing caused a slight increase in all lignin bands, whereas broadening of the bands and coalescence was observed in most of the lignin bands after UV ageing. A slight increase of the bands was noted at 1326  $\text{cm}^{-1}$ . A prominent band at about 1600  $\text{cm}^{-1}$ , which probably represents skeletal vibrations of fused-ring aromatic structures developed after heat and UV ageing or quinone structures resulting from photo degradation of lignin.

### O-H stretching zone



**Fig. 8;** Very broad bonded O-H stretching band due to the formation of acid – wood complex in the sample that had been immersed in acetic acid before and after heat-ageing. After UV ageing (in humid condition) two bands due to water stretching modes appeared as water molecules replaced acid in the complex.

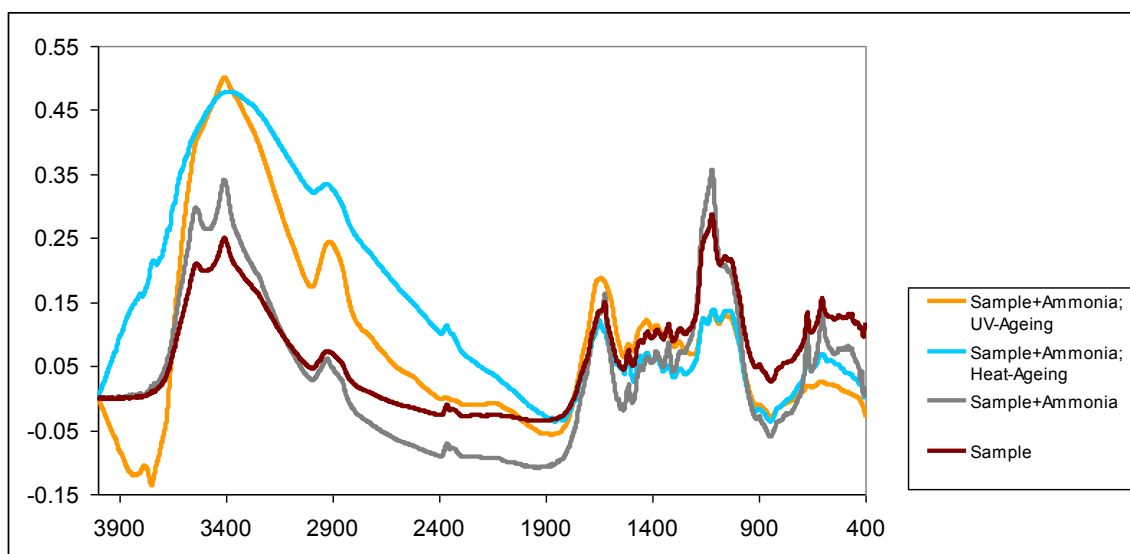
**Table 1:** summarizes the main changes that occurred after treating the sample with acetic acids (percentage of absorption of alkoxy and phenoxy bonds (C-O zone) in the wood)

	Phenoxy band (lignin) 1267 cm <sup>-1</sup>	Alkoxy bands (cellulose)			
		New additional band 1158 cm <sup>-1</sup>	1118 cm <sup>-1</sup>	1058 cm <sup>-1</sup>	1033 cm <sup>-1</sup>
Sample	100	0.00	100	100	100
Sample + Acetic Acid	36.19	19.2	50	61.8	63.39
Sample + Acetic Acid; Heat-Ageing	139.9	52.9	121.97	128.68	0.00
Sample + Acetic Acid; UV-Ageing	0.00	0.00	151.56	0.00	0.00

### Effect of ammonium hydroxide

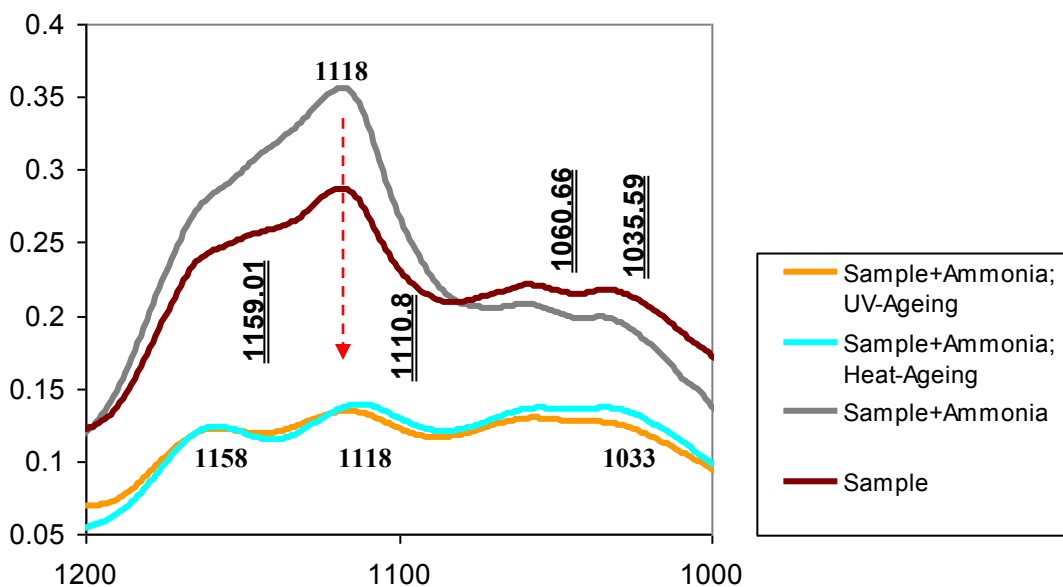
Alkaline solutions may cause alkaline hydrolysis of oils and fats. Waxes and resins, which contain ester bonds, may also be saponified. Problems may occur if an ammonium hydroxide solution with an excessively high pH is used to clean alkaline sensitive surfaces or materials (Rivers, *et al.*, 2003). It was evident during our study that 1% NH<sub>4</sub>OH solution accelerated lignin degradation (fig. 9-13 and table 2).

The intensities of all lignin bands decreased, and with heat and U.V. ageing further changes were noticed.



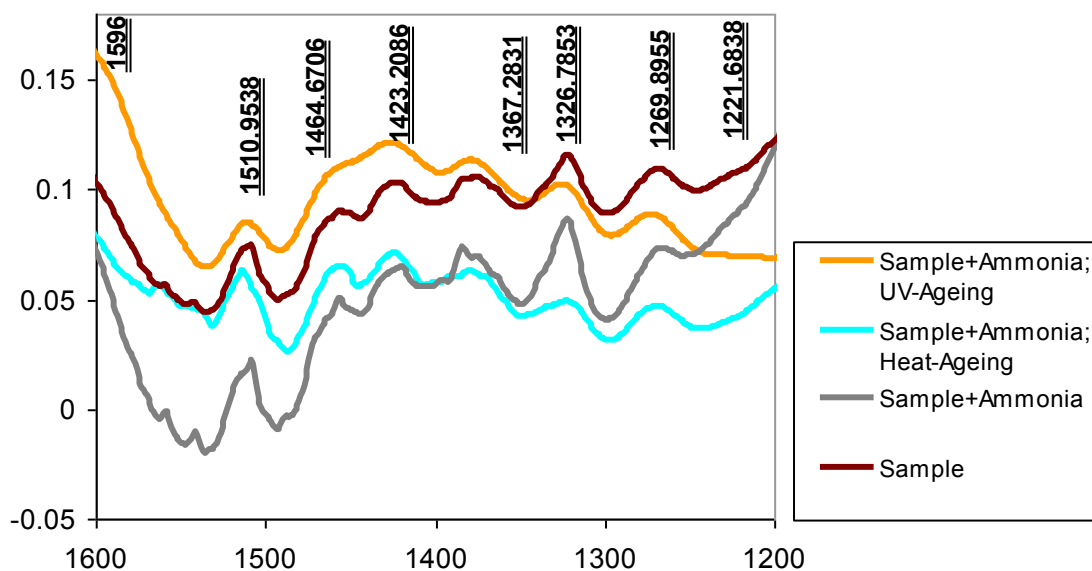
**Fig. 9;** FTIR spectra of the sample before and after immersion in 1% acetic acid, and after heat and UV ageing.





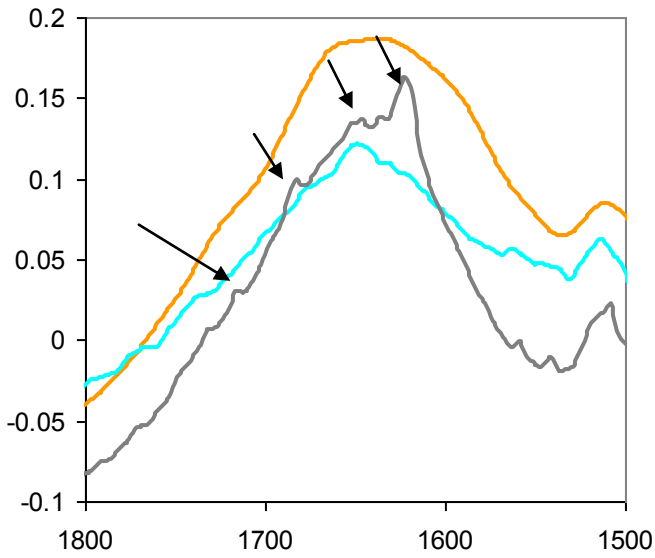
**Fig. 10;** One C-O band appeared and increased at  $1118\text{ cm}^{-1}$  in case of ammonia treatments. After heat and U.V ageing the C-O band at  $1033\text{ cm}^{-1}$  disappeared and the C-O band at  $1118\text{ cm}^{-1}$  decreased, the two remaining cellulose bands coalesced. The band at  $1158\text{ cm}^{-1}$  became prominent in both cases of ageing.

#### OH bending and CH deformation zone

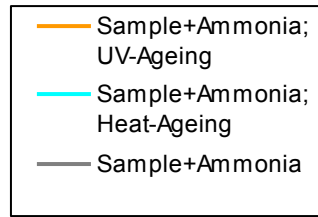


**Fig. 11;** The intensity of various bands observed in the OH bending and CH deformation zone (between  $1400\text{ cm}^{-1}$ - $1200\text{ cm}^{-1}$ ) changed after immersion of the sample in ammonium hydroxide and all lignin bands decreased, but a slight increase of the bands was noted at  $1326\text{ cm}^{-1}$ . Heat ageing caused a slight decrease in all lignin bands, whereas broadening of the bands and coalescence was observed in most of the lignin bands after UV ageing. A prominent band at about  $1600\text{ cm}^{-1}$ , which probably represents skeletal vibrations of fused-ring aromatic structures or quinone structure, developed after UV ageing, but decreased after heat ageing.

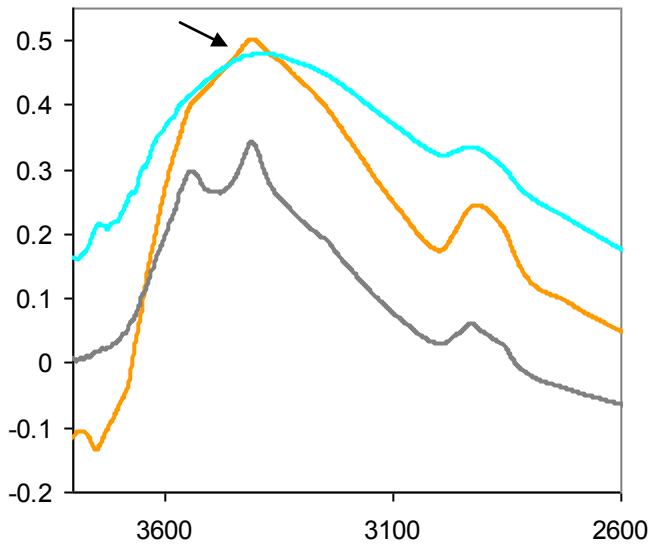
C=O stretching zone



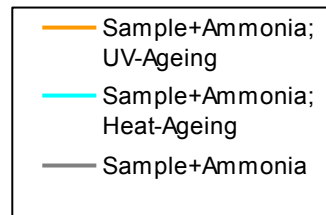
**Fig. 12;** Multiple carbonyl bands were formed as a result of lignin and cellulose degradation in the sample that had been immersed in ammonia. Various C-O groups were oxidized to C=O groups.



O-H stretching zone



**Fig. 13 ;**Very broad O-H stretching band of carboxylic group was detected in both cases of ageing.



**Table 2:** summarizes the percentage of absorption of alkoxy and phenoxy bonds (C-O zone) in the wood that was treated with 1% ammonium hydroxide.

	Phenoxy band (lignin) 1267 cm <sup>-1</sup>	Alkoxy bands (cellulose)			
		New additional band 1158 cm <sup>-1</sup>	1118 cm <sup>-1</sup>	1058 cm <sup>-1</sup>	1033 cm <sup>-1</sup>
Sample	100	0.00	100	100	100
Sample + Ammonium Hydroxide	36.56	0.00	85.2	0.00	0.00
Sample + Ammonium Hydroxide; Heat-Ageing	28.73	15.39	37.89	0.00	44.03
Sample + Ammonium Hydroxide ; UV-Ageing	45.89	0.00	37.89	43.15	0.00

### Discussion:

The two major wood components are cellulose and lignin. The percentages of both lignin and cellulose of different wood species has been studied and recorded in references, but in the case of archaeological wood the percentages of these two major components may vary a lot due to the different deteriorating factors. The chemical structure and degree of polymerization may change drastically from one case to the other, and it is difficult to predict the percentages of different wood components in ancient wood.

For conservation purposes chemical cleaning is often applied, using different reagents. In some cases the chosen concentrations are very low; in other cases the concentrations used could be too high and unsuitable. Usually conservators depend on data mentioned in wood chemistry references or conservation handbooks, when choosing type and concentration of chemicals. The idea of referring to wood chemistry is not wrong, but the fact that these references usually use modern wood as their standards means that the effects of chemicals had been studied on non degraded wood. According to Feller (1994) a common practice is to test specially prepared samples rather than naturally aged materials. The problem with recently prepared samples is often increase in strength before it begins to decline with age, and that is the main reason why we chose an archaeological sample for the evaluation of the effect of both acid and alkali on

archaeological wood. Heat and UV-ageing were applied before and after wood treatment, so as to check the future effects of decaying factors after treating wood samples, because even in a museum showcase, decay continues and cannot be totally prevented or stopped. Previous studies (Edney, *et al.*, 1986) showed that ultraviolet radiation and heat, in the presence of moisture, promoted the sequential reactions to various compounds, many of which were acidic.

Rutherford, *et al.* (2005) noted that ‘the 1-hour heating at 250°C had caused a substantial diminution of the cellulose bands in the FTIR spectra relative to the lignin bands; however, the carbohydrate spectral bands were better resolved, and most likely their results indicated decomposition of the hemicellulose in the wood. Heating at 250°C for 8 hours caused further diminution of the FTIR carbohydrate bands of the wood samples and broadening of the bands. The heating for eight hours apparently had caused decomposition of cellulose in addition to hemicellulose’.

According to Hon & Feist (1993) ‘certain phenoxy radicals from lignin and alkoxy radicals from cellulose, as well as carbon radicals generated from both cellulose and lignin degraded when new wood was irradiated with UV. Phenoxy radicals are stable at 25°C, but carbon and alkoxy radicals decay rapidly’. In archaeological samples the results may again vary.

By comparing results obtained from the archaeological sample that was heat and UV-aged with results obtained by Rutherford, *et al.* (2005) and Hon & Feist (1993), and the effects of both heat and UV ageing, it is worthy to note that results are only partially similar, but that could be attributed to two facts;

- a) they used modern samples
- b) methods and time of artificial ageing were different

According to Horvath (2006) a strong base is required for penetrating the cellulose crystallites in modern wood to produce ionization of the cellulosic hydroxyls, but cellulose can be directly dissolved in concentrated acids (e.g. phosphoric acid and trifluoroacetic acid). In that case the dissolution leads to a hydrolytic cleavage of the cellulose chains and the cellulose molecules are transformed to derivatives such as esters.

Archaeological wood weakens with age, and the chemical bonds could either become weaker or by time new bonds are formed. That may be the reason why

archaeological wood showed chemical changes after its treatment with very low concentrations of acids or alkalis, even before ageing. The effect of 1% acetic acid or 1% ammonium hydroxide was clearly evident in either the formation of new bands or the increase or decrease of cellulose or lignin bands.

In the case of the Bazarah wood samples several changes were evident after acid treatment;

- the intensity of the alkoxy bands at 1033, 1058 and 1118  $\text{cm}^{-1}$  decreased (ca. 50-60% in comparison to the archaeological sample). This change could be due to oxidation of these bonds and partial dissolution of cellulose or partial hydrolysis of terminal pyranose ring eliminating glucose units. This was referred to by Sjöström (1992) as acidic hydrolysis of glycosidic bonds (acidic cleavage).

- an increase of intensity in the alkoxy bands was clearly noted in the sample that was treated with acetic acid and aged with heat, but the band at 1033  $\text{cm}^{-1}$  disappeared, probably this may be due to the hydrolysis of the glycosidic bond that was followed by the generation of new hydroxyl groups.

- A new additional alkoxy band was detected at 1158  $\text{cm}^{-1}$  probably due to opening of the terminal rings and formation of a new C-OH group. This new band was detected in only two of the samples; i.e. the sample treated with acetic acid and the sample that was treated with acetic acid and aged with heat. The archaeological sample and the sample that was treated with acetic acid and aged with UV did not have this new band.

- the alkoxy bands in the sample that was treated with acetic acid and aged with UV, seems to have coalesced in the 1118  $\text{cm}^{-1}$  band, which had a relatively high intensity, and all other alkoxy bands disappeared.

- Due to partial hydrolysis of phenoxy bonds, the C-O intensity decreased to 36% in the sample treated with acetic acid. After heat-ageing of the treated sample, an increase of C-O bands was noted, and was probably due to the combination of C-O of the carboxylic groups that resulted from repeated oxidation of carbonyl groups and the C-O-H groups present in the wood. The ether linkages in lignin were transformed into OH. After UV-ageing the phenoxy peaks were not detected, and that was due to the formation of phenoxy free radicals (Leary, 1994). Another probability could be that the acid itself accelerated the photo degradation.

- the intensity of the band at  $1509\text{ cm}^{-1}$  decreased due to the accelerated reactions of the acid, which lead to the degradation of lignin.
- by comparing the effect of UV on the acid treated sample, it was notable that UV had a stronger effect on lignin than on cellulose, and one of the prominent lignin bands at  $1509\text{ cm}^{-1}$  showed a substantial diminution, whereas the total sum of the intensities of the alkoxy bands in the same sample showed almost no decrease in comparison to the sample after acid treatment.
- the band detected in the archaeological sample at  $1646\text{ cm}^{-1}$  is due to the combination of a hydration band and a carbonyl band resulting from naturally oxidized hydroxyl group. After treating the wood with acetic acid a decrease in this band was detected due to the formation of a wood-acid complex (replacement of water with acid). Whereas in the case of heat ageing the intensity of this band increased. This could be explained as follows; heat broke the hydrogen bonding and due to the high reactivity of the hydroxyl groups they were easily oxidized to carbonyl groups. In addition to that heat and acid accelerated the oxidation process of the terminal rings after their opening at  $C_1$  and  $C_5$ . This assumption could be easily confirmed by the changes that occurred in the OH peak at ca.  $3400\text{ cm}^{-1}$ . In the archaeological sample asymmetric and symmetric stretching modes of water molecules were clearly seen. After acid hydrolysis this was replaced with a typical broad bonded OH stretching band. After heat ageing a rise of intensity was noticeable, which is probably due to the oxidation of the hydroxyl groups forming a permanent complex? In the case of UV ageing asymmetric and symmetric stretching modes of water molecules with a rise in intensity were detected, due to the reaction with moisture (from room humidity)
- another explanation for the presence of the carbonyl band could be due to the breaking down of the Lignin-Carbohydrate complex, which is according to Sjöström (1992) either ester or ether type and even glycosidic bonds.

After treating the Bazarah sample with ammonium hydroxide further results were obtained;

- the alkoxy bands decreased in all cases after treating the wood with ammonium hydroxide and after ageing (heat or UV). Most of the bands disappeared completely or

coalesced in one or two bands. A very small new band was detected at  $1158\text{ cm}^{-1}$  after heat ageing of the sample treated with ammonium hydroxide. Possible explanations would be as follows:

a) the alkali oxidized the C-OH;

b) endwise mechanism hydrolysis of terminal  $\beta$ , 1-O-4 glycosidic bond as mentioned by Sjöström (1992) or

c)  $\beta$  – alkoxy elimination (peeling reaction in which OH of C<sub>3</sub> disappears)

- the decrease of phenoxy bands exceeded 55% in all treated samples (non-aged and aged), due to partial dissolution. That is clearly seen when comparing the intensity that decreased in the bands at  $1268$  and  $1509\text{ cm}^{-1}$  after alkali treatment and heat ageing. UV-ageing hardly caused any change of intensities in the same bands after alkali treatment. Complete dissolution did not occur, and a definite explanation may be difficult, but according to a discovery made in the research laboratories of the Library of Congress (2006), cellulose itself, as it ages, generates several acids, which in turn are probably neutralized by the alkali, and therefore the effect of the alkali is minimized.

- Slight changes were detected in the carbonyl band at ca.  $1600$ , where a minute increase of intensity was noted. The hydroxyl group at  $3400$  coalesced after heat-ageing formed one broad band. In the case of UV- ageing the band was less broad, and coalescence was less than in the case of heat-ageing.

### **Conclusion:**

Many difficulties may arise when choosing a suitable method and material to clean archaeological wood, mechanical cleaning may sometimes be insufficient and conservators may choose chemicals for removing foreign matter. The main problem, though is that the effect of an acid or an alkali cannot be easily removed from wood, and continuous washing with water for the removal of reagents may cause a raise in wood moisture content, which would be the source of future microbial decay. Acids and alkalis seriously affect the chemical composition of wood, and the choice of acids and alkalis should therefore be limited during the cleaning process of archaeological wood.

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