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THERMOGRAVIMETRIC ANALYSIS OF ANCIENT AND FRESH WOODS

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ABSTRACT

Thermogravimetric analysis was applied to the analysis of fresh and ancient woods belonging to portals of old churches. Also, other different archeological wood samples were analysed by TG. Quantitative data and qualitative information concerning age and damage, also supported by elemental analysis and micrographs, were obtained for all these samples.

INTRODUCTION

The analysis of the main constituents of wood matrices and the characterisation of the degradation state of handmade wood pieces of artistic value are problems not easily solved with traditional chemical methods [1], because these require very long experimental times and yield results of doubtful accuracy, especially if applied to finds that are severely damaged because of poor storage conditions. Modern instrumental methods of analysis yield faster and useful alternatives, among which thermal analysis can be used with good results [2,3].

In previous work we performed research on the qualitative and quantitative aspects of the thermal analysis of woods of the 1st century A.D. [4,5]. While running this study, we concluded that much research is still necessary in this field with problems of primary importance. In this paper results of the most recent research, i.e. TG curves and micrographs, performed by us on finds of wood from portals of ancient churches are compared with the corresponding experimental data for fresh woods and for some archeological, waterlogged, or fossil woods.

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EXPERIMENTAL

Fresh wood samples of spruce (*Picea abies*, also called by us red fir in a previous paper [4]), fir and larch were supplied by the Biologia Vegetale department of Rome University "La Sapienza". Ancient woods were small samples of spruce, fir and larch, belonging to portals of churches near Verona (Italy), dating from the 13th to 18th centuries [1]. An archeological waterlogged sample of wood, of coniferous origin, was from a Roman shipwreck of the 1st century A.D., described in previous papers [4,6], and two samples were fossil woods from central Italy, Villafranchian age, about two millions years old.

The microscopic analysis of ancient and archeological samples [1,7] allowed us to classify them as coniferous woods (spruce, fir, larch), but it was not possible to identify in more detail the older tree species.

TG and DTG analyses of all samples were carried out with a Mettler TG 50 thermobalance, coupled with a Mettler TC 10-TA processor system and a Swiss matrix printer. The heating rate used was $10\,^{\circ}C\ min^{-1}$; the atmosphere was an air stream, at a flow rate of 100 $cm^3\ min^{-1}$. Elemental analysis data were obtained with a Perkin–Elmer elemental analyser model 240C. Microscopic analysis and micrographs were obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) carried out with Siemens ETEC SEM and Philips EM 400 TEM microscopes.

RESULTS

TG and DTG curves, between 20 °C and 900 °C, of the three different species of fresh woods, the same species recovered by microscopic analysis of the ancient woods, are shown in Figs. 1–3 and the thermal data, corresponding to the thermogravimetric steps and to the percentage relative weight losses, are reported in Table 1. In Table 2 are summarised thermal data and weight losses of TG and DTG curves, shown in Figs. 4–8, for ancient wood samples, dating from 13th to 18th centuries A.D. Finally, In Figs. 9–11 and in Table 3, TG and DTG curves, thermal data and weight losses for two fossil wood samples and to another waterlogged wood sample, analysed as sawdust and obtained from the same wood by the homogenization, drying and sieving procedure previously described [4,8], are shown. Tables 1–3 also contain data for the ashes from TG residues at 700 °C.

As described previously [4], TG and DTG curves of fresh woods (Figs. 1–3) after the moisture loss step in the range between room temperature and 150 °C present two main steps, at about 300 °C and 400–450 °C, previously identified [2,4], corresponding to respectively cellulose and lignin oxidative decomposition processes.

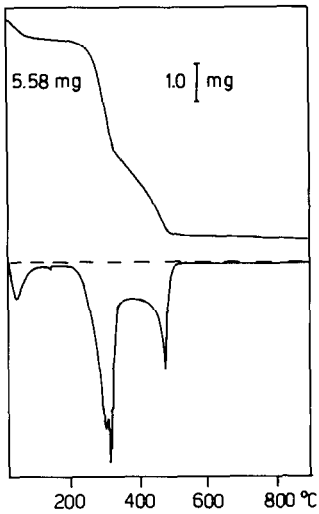

Fig. 1. TG and DTG curves for analysis of fresh wood of larch. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

Curves for ancient woods (Figs. 4–8) still present a moisture loss (first step), and the step at about 300 °C, corresponding to the cellulose decomposition. The lignin decomposition process sometimes occurs in only one step (Figs. 5 and 7), or in a main step, at about 400–450 °C, with a small unresolved step near them (Figs. 4 and 8), or sometimes (Fig. 6) by two

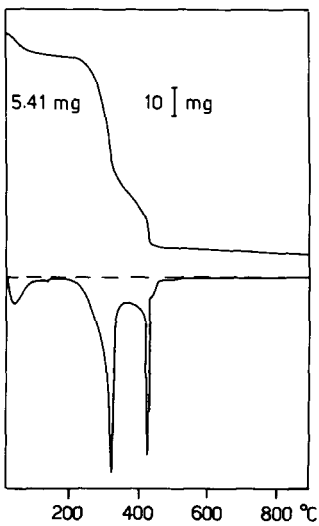

Fig. 2. TG and DTG curves for analysis of fresh wood of spruce. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

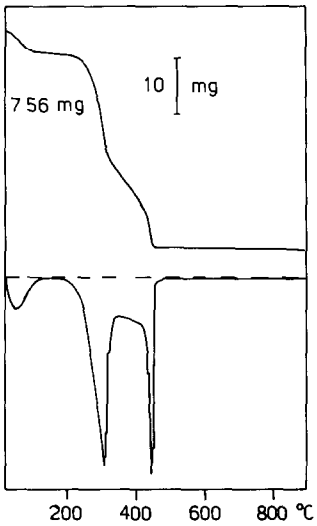

Fig. 3. TG and DTG curves for analysis of fresh wood of fir. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

separate steps: one still at about 450 °C, another at a lower temperature (about 370 °C). At higher temperatures a very small weight loss, due to the oxidation of carbon traces, can be generally observed. In the case of sawdust of archeological waterlogged wood (Fig. 11) TG and DTG curves show one marked step at about 375 °C and at least two small steps, not well resolved, between 160 °C and 320 °C. TG and DTG curves of two examined fossil wood samples (Figs. 9 and 10) show different behaviour: one (Fig. 9)

TABLE 1

Thermal analysis of fresh woods

Sample	Moisture loss (%)	pdt	First step loss (%)	pdt	Second step loss (%)	pdt	Residue at 700 °C (%)
Fresh	9.82	23	64.7	160	29.4	380	0.3
larch		45		310		470	
		155		380		505	
Fresh	10.3	23	60.9	160	28.4	370	0.7
spruce		50		320		425	
		150		350		500	
Fresh	10.5	23	57.8	150	32.1	370	0.2
fir		55		305		445	
		150		370		485	

TG in air stream (100 cm^3 min^{-1}) and percentage weight loss at different steps. Percentages (by weight) of TG residues, at 700 °C, are also reported. pdt = procedural decomposition temperature.

TABLE 2

Thermal analysis of ancient woods

Sample	Moisture loss (%)	pdt	First step loss (%)	pdt	Second step loss (%)	pdt	Residue at 700 °C (%)
Larch	6.7	23	60.1	150	29.7	365	0.8
(18th century (A.D.)		50		320		400	
		140		365		550	
Larch	7.0	23	59.7	150	31.2	360	0.6
(13th century A.D.)		40		320		450	
		140		360		500	
Spruce	8.6	23	57.2	150	19.3	340	1.8
(17th century A.D.)		50		300		370	
		140		340		420	
					10.8	420	
						450	
						500	
Spruce	8.4	23	56.8	150	31.5	360	1.7
(15th century A.D.)		50		320		385	
		140		360		500	
Fir	8.9	23	57.1	140	33.6	360	0.7
(17th century A.D.)		50		300		410	
		130		360		500	

TG in air stream (100 cm^3 min^{-1}) and percentage weight loss at different steps. The percentages (by weight) of TG residues, at 700 °C, are also reported. pdt, procedural decomposition temperature.

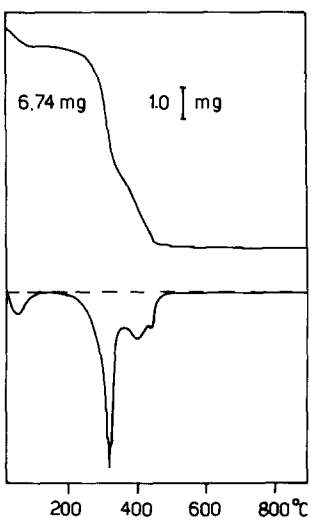

Fig. 4. TG and DTG curves for analysis of ancient wood (18th century A.D.) of larch. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

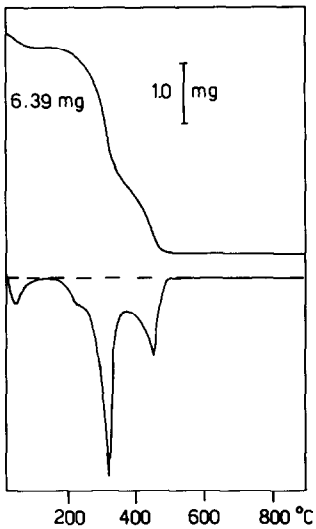

Fig. 5. TG and DTG curves for analysis of ancient wood (13th century A.D.) of larch. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

presents two typical decomposition steps at about 300 °C and 400 °C, corresponding to cellulose and lignin degradation process, even though the "cellulose step" is small compared with the corresponding "cellulose step" in the fresh woods; TG of the other fossil sample (Fig. 10) shows a behaviour very similar to that of waterlogged woods (Fig. 11; see also Figs. 3–5 of ref. 4).

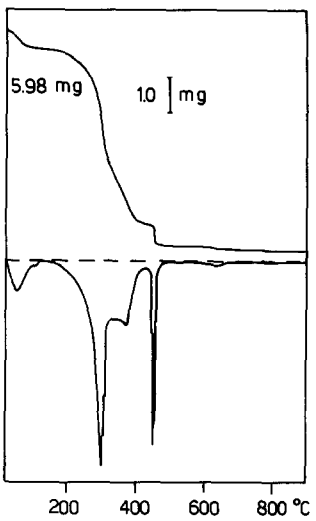

Fig. 6. TG and DTG curves for analysis of ancient wood (17th century A.D.) of spruce. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

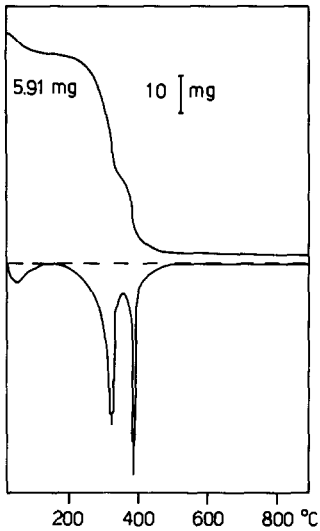

Fig. 7. TG and DTG curves for analysis of ancient wood (15th century A.D.) of spruce. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

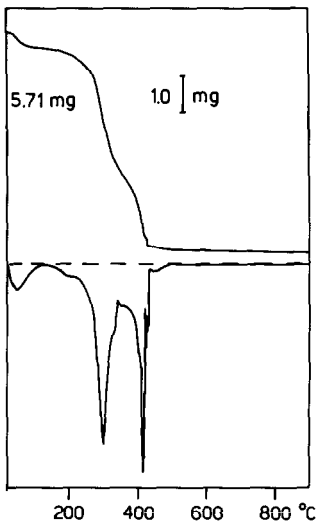

Fig. 8. TG and DTG curves for analysis of ancient wood (17th century A.D.) of fir. In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

DISCUSSION

As shown in previous papers [4,5], data from the TG curves of fresh woods, reported in Table 1, allow the moisture, cellulose, lignin contents and ash values of these samples to be obtained.

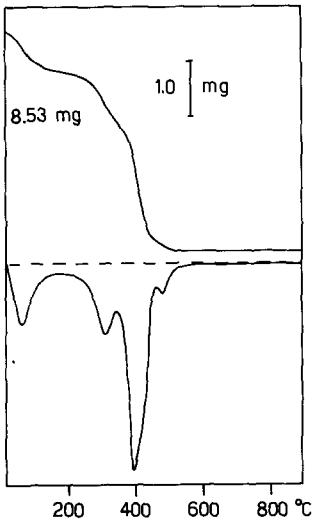

Fig. 9. TG and DTG curves for analysis of fossil wood (sample A). In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

In Table 4, the values obtained by TG are compared for the three different kinds of fresh woods examined with some values reported in the literature [9,10] for the same tree species. It is possible to observe that the agreement for the lignin, cellulose and ash values is generally satisfying; nevertheless, literature values by different authors vary within quite a large range, as shown in Table 4.

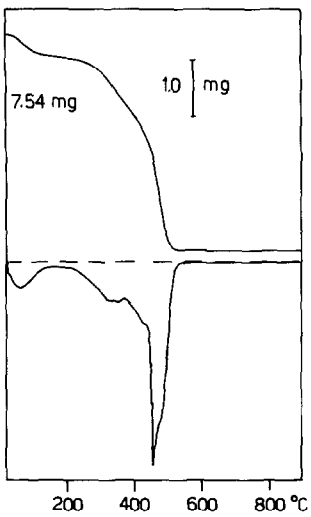

Fig. 10. TG and DTG curves for analysis of fossil wood (sample B). In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

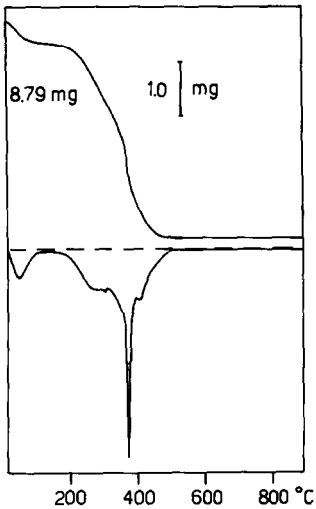

Fig. 11. TG and DTG curves for analysis of sawdust of waterlogged wood (1st century A.D.). In air stream (100 cm^3 min^{-1}) and heating rate 10 °C min^{-1}.

For the waterlogged wood samples, it is possible also in this case to determine the content of the main components with the criteria explained above [4,5]. In the case of the fossil woods, further research is needed on a more consistent number of samples. Nevertheless, on the basis of the two samples examined so far, it seems that for certain fossil woods (Fig. 9) the determination can be performed by applying the same criteria used for the

TABLE 3

Thermal analysis of archeological (fossil or waterlogged) woods

Sample	Moisture loss (%)	pdt	First step	pdt	Second step	pdt	Third step	pdt	Residue at 700 °C (%)
Fossil wood (sample A)	14.5	23 60 170	20.7	180 310 345	–	–	56.7	345 400 540	6.3
Fossil wood (sample B)	9.9	23 60 170	12.5	180 – 335	7.7	335 350 370	66.4	370 460 530	2.4
Archeological waterlogged wood	9.5	23 50 140	17.2	155 – 290	7.1	290 300 315	58.9	315 375 500	7.3

TG in air stream (100 cm^3 min^{-1}) and percentage weight loss at different steps. The percentages (by weight) of TG residues, at 700 °C, are also reported. pdt, procedural decomposition temperature.

TABLE 4

Comparison between the values of cellulose, lignin and ash content (as per cent by weight) in fresh woods obtained by thermogravimetry with the values reported in the literature

Nature of the sample	Cellulose (%)				Lignin (%)				Ashes (%)		
	Literature (a)	Reference	TG (SD = 2%) (b)	$(b-a)/b$ (%)	Literature (c)	Reference	TG (SD = 3%) (d)	$(d-c)/d$ (%)	Literature	Reference	TG (SD = 0.5%)
Fresh larch	70 (63–70) [a]	9	64.7	−8.2	29 (25–29) [a]	9	29.4	+1.4	0.2 (0.2–0.3) [a]	9	0.3
Fresh spruce	64 (59–67) [a]	10	60.9	−5.1	28.3 (28–29) [a]	10	28.4	+0.4	0.8 (0.8–1) [a]	10	0.7
Fresh fir	57.1 (58–64) [a]	10	57.8	+1.2	29.4 (27–29) [a]	10	32.1	+8.4	0.4 (0.2–0.7) [a]	10	0.2

TG values are the mean of at least three determinations.

[a] Range of several values reported in the literature by different authors [9–14].

TABLE 5

Lignin and cellulose contents (as per cent by weight) by TG analysis of fresh and ancient woods.

Sample	Lignin content (%)	Cellulose content (%)
Fresh larch	29.4	64.7
Larch (18th century A.D.)	29.7	60.1
Larch (13th century A.D.)	31.2	59.7
Fresh spruce	28.4	60.9
Spruce (17th century A.D.)	30.1	57.2
Spruce (15th century A.D.)	31.5	56.8
Fresh fir	32.1	57.8
Fir (17th century A.D.)	33.6	57.1

Samples are in decreasing chronological order for each species.

fresh woods while for others (Fig. 10) it seems more opportune to use the criteria adopted in the TG analysis of the samples of sawdust of waterlogged archeological woods. Lastly, in the case of ancient wood samples (Figs. 4–8), the determinations of the main components can be performed analogously to the analysis of fresh woods, obviously by summing the losses during two steps when the lignin degradation occurs in two separate processes (Fig. 6).

The data for the lignin and cellulose contents of these samples, listed in decreasing chronological order, are reported in Table 5, where the percentages of these components relative to fresh woods are also shown. In Table 6 the percentages of carbon, hydrogen, nitrogen and oxygen obtained by elemental analysis of some samples of larch and both fresh and ancient woods belonging to portals of churches, dating from the 13th to the 18th centuries are listed, again in chronological order for the different species. It can be observed that, for each species, the percentage carbon content increases with the age of the sample while that of oxygen decreases. This trend cannot be clearly quantified, but a correlation is surely present. This observation is already known in the literature for the fossil woods [15]: this was interpreted as resulting from an increase of the percentage lignin content, caused mainly by the decrease in cellulose due to fungal and

TABLE 6

Elemental analysis data for samples of fresh and ancient larch wood

	C (%)	H (%)	N (%)	O (%)
Fresh larch	49.6	6.0	–	44.4
Larch (18th century A.D.)	50.0	6.0	0.3	43.7
Larch (13th century A.D.)	51.3	6.5	0.5	41.6

Samples are in the decreasing chronological order.

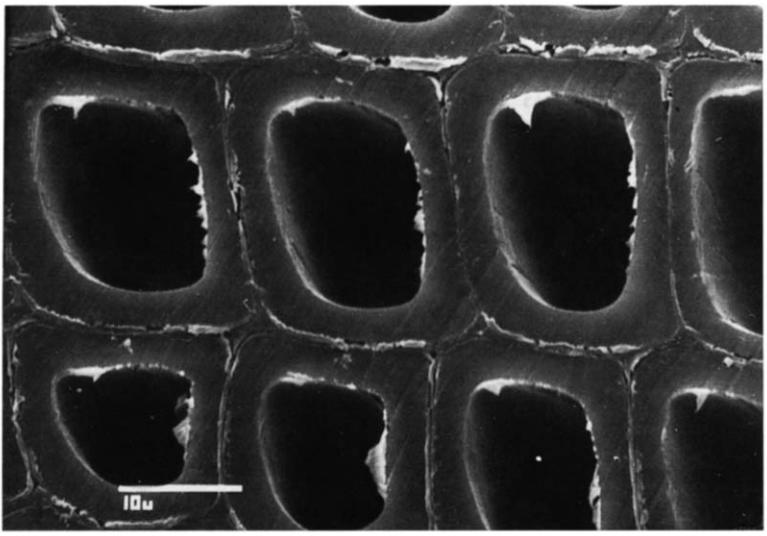

Fig. 12. SEM micrograph of fresh coniferous wood.

bacterial activity [16]. In our case this hypothesis found experimental support if the lignin and cellulose contents for fresh and ancient woods (Table 5) are considered. Of course, in this case also the trend can only be evaluated qualitatively, but it is meaningful and well evident. For nitrogen too a trend similar to that of carbon can be observed (Table 6), probably resulting from organic nitrogen due to saprophytic bacterial activity through the ages.

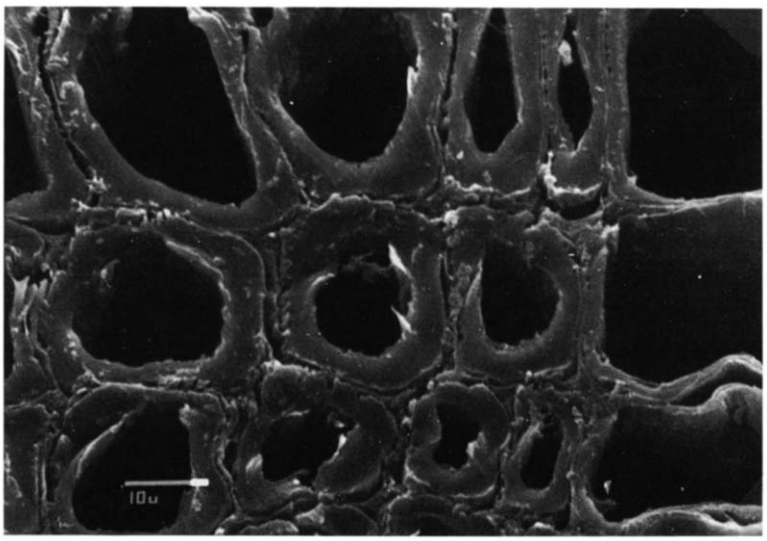

Fig. 13. SEM micrograph of ancient coniferous wood (17th century A.D.).

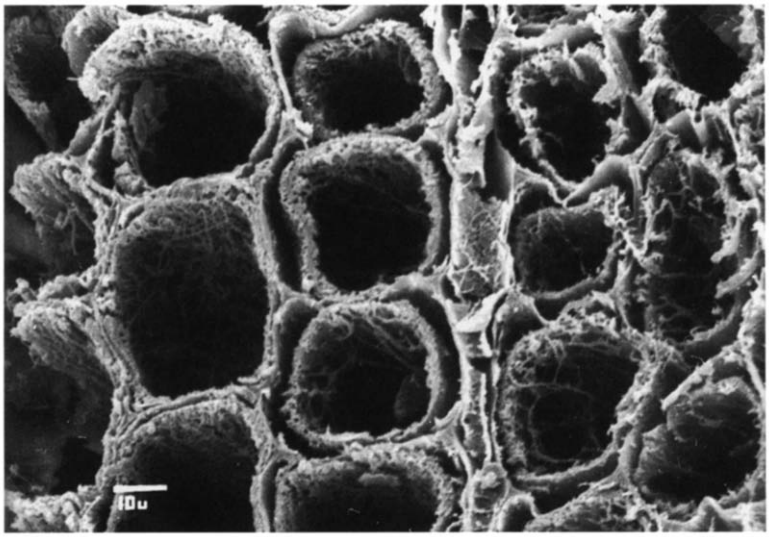

Fig. 14. SEM micrograph of archeological waterlogged coniferous wood (1st century A.D.).

For the waterlogged and fossil woods, the data of Table 3 indicate very clearly a marked damage in the cellulose; however, lignin too seems to be modified as shown by the behaviour and the maximum temperature shift of the corresponding DTG step, such as that well evidenced in Fig. 11. It is

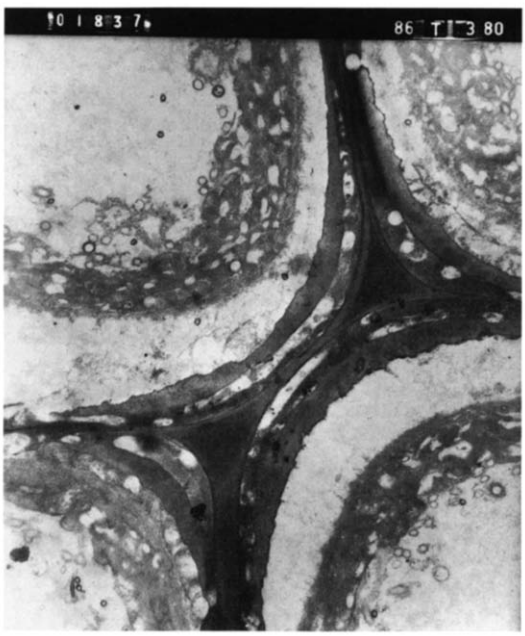

Fig. 15. TEM micrograph of the cell wall of archeological waterlogged coniferous wood (1st century A.D.).

clear that in these cases the damage, structural and chemical, is due more to the particular environmental conditions where the find remained for such a long time than to the age. Structural damage of the archeological and ancient wood samples is clearly confirmed by comparing the micrographs of Figs. 12–14. These show SEM micrographs of three samples of coniferous wood, one fresh (Fig. 12), one from the 17th century (Fig. 13), and the last from the 1st century A.D. (Fig. 14), stored in sea water. It can be observed that the oldest samples show a larger number of breaks of the cell structure (Fig. 13) than the fresh sample (Fig. 12); also, an increase of the cohesion loss among the zones of the cell walls is observed.

In the case of the waterlogged sample (Fig. 14), the outermost part of the cell wall, oriented toward the lumen of the tracheae, is very degraded and the ordered cellulose structure is substituted by an aggregation of spongy-looking degradation products.

These products absorb the electron beam of SEM and TEM microscopy very well. The degradation products, collected in ring-shaped figures, appear to be separated from the cellule's wall. In some cases they are completely separated from the rest of the cellular wall, and in some cases only partly; nevertheless, only very seldom are they well preserved or are already degraded parts still sufficiently compact.

Figure 15 gives a TEM picture of the cell wall of the same sample and demonstrates the difference between degraded and well-preserved zones.

CONCLUSIONS

The application of thermogravimetric analysis to this study

(1) has determined the content of the main components (lignin, cellulose, moisture) and the ashes of the different kinds of fresh woods,
(2) has also determined the content of these components for samples of ancient woods and estimated the same data for archeological water-logged and fossil woods,
(3) has confirmed a qualitative correlation between the lignin and cellulose contents and the age of the wood sample, and
(4) has pointed out the great damage produced in wood samples by the environmental conditions, in full agreement with the results from the micrographs of these samples.

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REFERENCES

1 R. Tomellini, Thesis in Chemistry, Rome University, La Sapienza, 1986.
2 H.G. Wiedemann and G. Bayer, Thermochim. Acta, 100 (1986) 283.
3 G.E. Domburg and V.N. Sergeeva, J. Therm. Anal., 1 (1969) 53.
4 M. Tomassetti, L. Campanella, R. Tomellini and C. Meucci, Thermochim. Acta, 117 (1987) 297.
5 L. Campanella, M. Tomassetti and S. D'Urbano, in Proc. Int. Symp. on the Conservation of Monuments in the Mediterranean Basin, Bari, June 7–10, 1989.
6 C. Meucci, Archeological ICR Report on a Roman Wreck Found at Ladispoli (Roma), 1984.
7 TAPPI T8 sm-61 (Technical Association of Pulp and Paper Industry, Standard Administration, 1 Dunwoods Park, Atlanta, GA 30341).
8 TAPPI T257 OS-76 (Technical Association of Pulp and Paper Industry, Standard Administration, 1 Dunwoods Park, Atlanta, GA 30341).
9 H.F.L. Wenzl, The Chemical Technology of Woods, Academic Press, New York, 1970.
10 E.H. Agglund, Holzchemie, Verlagsgesellschaft MBH, Leipzig, 1928.
11 B.L. Browning, Methods of Wood Chemistry, Interscience, New York, 1967.
12 E. Gianni, L'industria della carta, Vol. 1, V. Hoepli, Milano, 1961.
13 C. Wehmer, Die Pflanzenstoffe, Verlag Gustav Fischer, Jena, 1931.
14 F.F.P. Kollman and W.A. Côtè, Principles of Wood Science and Technology, Vol. I, Solid Wood, Springer, Berlin, 1968.
15 D. Fengel, D. Grosser and V. Wegener, Anatomische und chemische Untersuchungen an zwei fossilen Nadelholzern, Abt. B, Paleontographica, Stuttgart, 1973.
16 T. Higushi, Biosynthesis and Biodegradation of Wood Components, Academic Press, New York, 1979.