

THERMOGRAVIMETRIC ANALYSIS OF FRESH AND ARCHEOLOGICAL WATERLOGGED WOODS

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ABSTRACT

The thermogravimetric analysis of waterlogged archeological samples of woods and of samples of fresh woods, of the same nature, yielded quantitative information on some components (water, ashes, cellulose, lignin) and qualitative data concerning some decomposition processes which occurred in the wood. Obtained data are compared with those from traditional chemical methods.

INTRODUCTION

A thermogravimetric study was performed in order to characterize and analyse archeological woods obtained from a relict of a Roman ship of the 1st century A.D. found at Ladispoli. These ancient woods were previously identified, by microscopic analysis, as waterlogged ones from coniferous and broadleaf trees.

The same analysis was also performed on fresh samples of duramen from coniferous and broadleaf species. The aims of this research were twofold: (1) the comparison between thermoanalytical data and results obtained by traditional chemical methods, or from the literature and (2) useful observations and evaluations on some procedures, generally applied to the analysis of fresh and archeological wood samples, and encouraged by the satisfying results obtained by Wiedemann who applied thermal analysis to the study of ancient Egyptian tree stumps [1].

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EXPERIMENTAL

The waterlogged archeological samples belonging to the Roman relict from Ladispoli [2], were drawn by hand carrotage and stored dipped in water. The microscopic analysis of these samples [3,4] allowed us to classify them as woods originating from coniferous and broadleaf trees.

As it was not possible to identify in more detail the tree species in these samples, a comparison with fresh woods was performed with samples from four different tree species which the archeological woods had the greatest probability of belonging to. The samples of fresh woods were composed of small cubes of duramen of red fir (coniferous), larch (coniferous), elm (broadleaf) or beech (broadleaf). The sawdust of these samples [3,5], on which analysis was performed, was obtained by grinding, dehydration in a hot air stream and sieving, so that particles of a predetermined granular size could be obtained. Reference standard cellulose was supplied by Merck-Darmstadt; reference lignin was Klason lignin prepared by us [3].

Analysis of cellulose and lignin was performed by standard chemical methods for wood (TAPPI * methods). For lignin, hydrolysis of the polysaccharic matter, by a strong acid (H_2SO_4), was used. The insoluble lignin (Klason) was then gravimetrically determined [6], while the soluble part was determined spectrophotometrically [7]. To determine cellulose, the separation of the polysaccharic fraction of wood was performed by removing the lignin using an oxidizing agent, such as sodium chlorite in a weakly acid medium [8], then by gravimetrically determining the cellulose. The hydrolyzed polysaccharide was determined by spectrophotometry [8,9].

The ash and moisture content was obtained gravimetrically by dehydrating the sample in an oven at $105^\circ C$ [8] and by ashing it in a muffle at $530^\circ C$ for two hours [3], respectively.

TG and DTG curves of all samples examined were obtained with a Mettler TG 50 thermobalance, coupled with a Mettler TC10-TA processor system and a print swiss matrix. The heating rate used was $10^\circ C \text{ min}^{-1}$; the atmosphere was an air stream at a flow rate of 100 ml min^{-1} .

RESULTS

Thermogravimetric determinations were performed and repeated in dynamic air (100 ml min^{-1}) between 20 and $900^\circ C$ (heating rate $10^\circ C \text{ min}^{-1}$) for the archeological, waterlogged samples and the coniferous and broadleaf woods (stored dipped in water till the analysis) (Figs. 1 and 2). This procedure was repeated after having rapidly heated the samples to $140^\circ C$,

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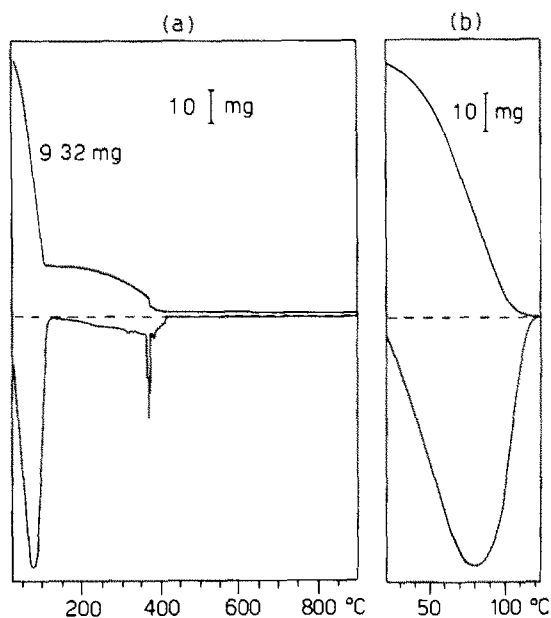


Fig. 1. TG and DTG curves for analysis of waterlogged, archeological woods of coniferous nature. (a) Full TG and DTG curves in the temperature range 20–900 °C; (b) TG and DTG curves relative to saturation water loss only. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{ C min}^{-1}$.

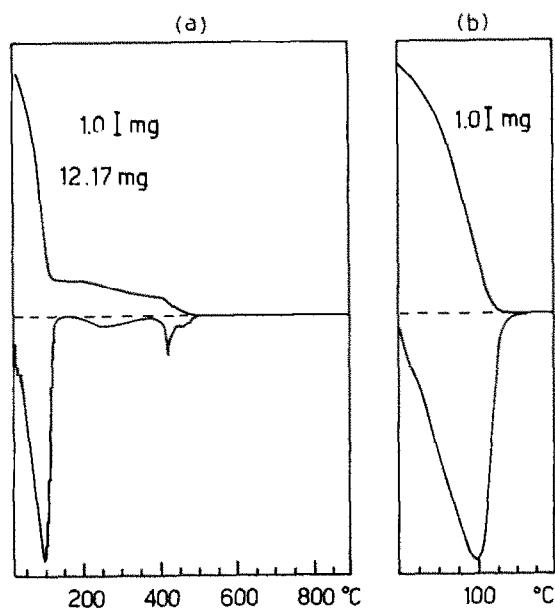


Fig. 2. TG and DTG curves for analysis of waterlogged, archeological woods of broadleaf nature. (a) Full TG and DTG curves in the temperature range 20–900 °C; (b) TG and DTG curves relative to saturation water loss only. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{ C min}^{-1}$.

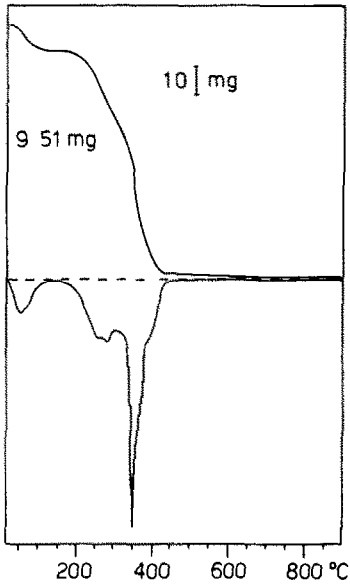


Fig. 3. TG and DTG curves for analysis of waterlogged, archeological woods of coniferous nature, previously rapidly heated at 140°C , to remove most of the saturation water. In air stream ($100\text{ cm}^3\text{ min}^{-1}$) and heating rate $10^{\circ}\text{C min}^{-1}$.

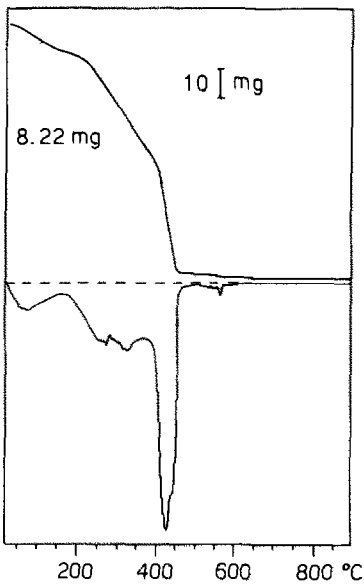


Fig. 4. TG and DTG curves for analysis of waterlogged, archeological woods of broadleaf nature; previously rapidly heated at 140°C , to remove most of the saturation water. In air stream ($100\text{ cm}^3\text{ min}^{-1}$) and heating rate $10^{\circ}\text{C min}^{-1}$.

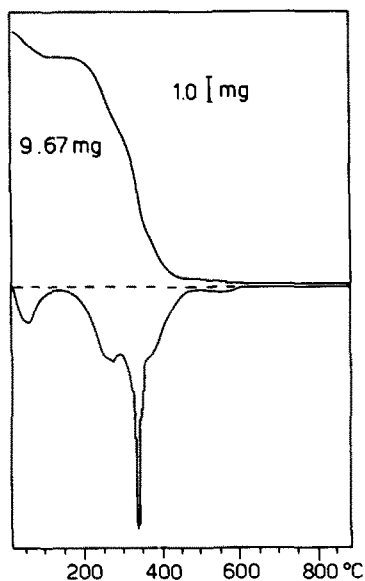


Fig. 5. TG and DTG curves for analysis of sawdust of archeological wood of coniferous nature. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

in order to remove most of the saturation water (Figs. 3 and 4). Finally, the sawdust samples, obtained from the same woods by the homogenization, drying and sieving procedure, were analysed in the same manner (Figs. 5

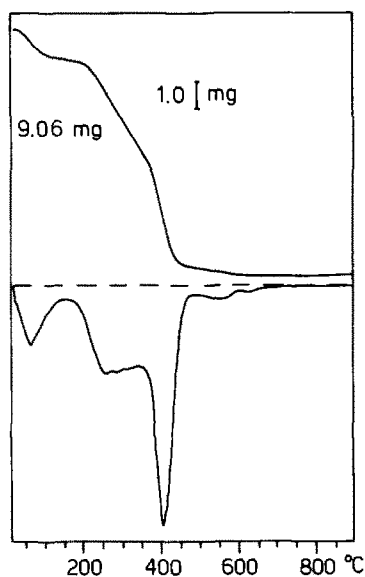


Fig. 6. TG and DTG curves for analysis of sawdust of archeological wood of broadleaf nature. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

TABLE 1

Thermal analysis of waterlogged, archeological woods. TG in air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) of samples previously rapidly dried at 140°C . The percentages loss by weight, at the different steps and of the residues, refer to the sum of the weight of dry sample and of the moisture, while the saturation water percentage content is referred to the total weight of the sample fully saturated with water. Also, the percentage of TG residues, between 500 and 700°C , are reported. pdt = procedural decomposition temperature

	Satura- tion water (%)	pdt	Mois- ture (%)	pdt	1st step loss (%)	pdt	2nd step loss (%)
Archeological coniferous (red fir or larch)			9.7	23 58 132	15.3	140 250 270	11.5
	81.0	21 80 138					
Archeological broadleaf (elm or beech)			9.4	24 75 140	16.0	159 273 283	18.1
	84.4	22 99 149					

pdt	3rd step loss (%)	pdt	4th step loss (%)	pdt	Residue (%)		
					500°C	600°C	700°C
270	56.1	305	3.9	451	6.3	5.7	5.6
283		350		530			
305		451		650			
283	48.0	365	1.6	503	7.9	6.5	6.2
320		427		565			
365		503		650			

and 6). These treatments were carried out using reference methods for the systematic analysis of wood laid down by TAPPI [5]. In Table 1 the thermal data corresponding to the thermogravimetric steps and the percentage relative weight losses of the archeological samples, previously dried at 140°C , are reported; the corresponding TG and DTG curves are shown in Figs. 3 and 4. The thermal data for the sawdust of the samples are

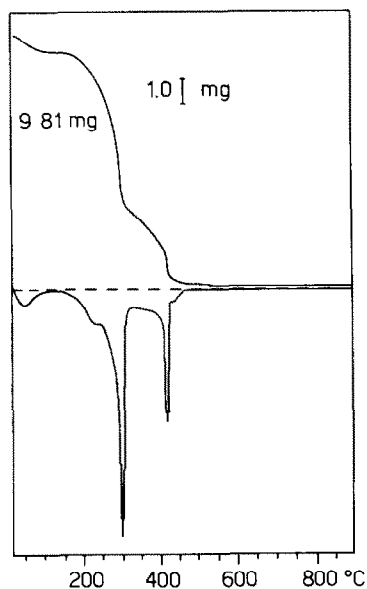


Fig. 7. TG and DTG curves for analysis of duramen of fresh wood of red fir (coniferous). In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

practically identical, within the variability range of the method. The thermal data for the archeological samples still fully soaked (TG and DTG curves in Figs. 1 and 2) do not differ significantly, except those for of saturation

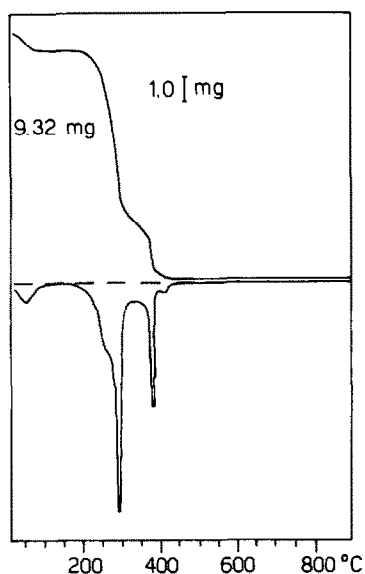


Fig. 8. TG and DTG curves for analysis of duramen of fresh wood of elm (broadleaf). In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

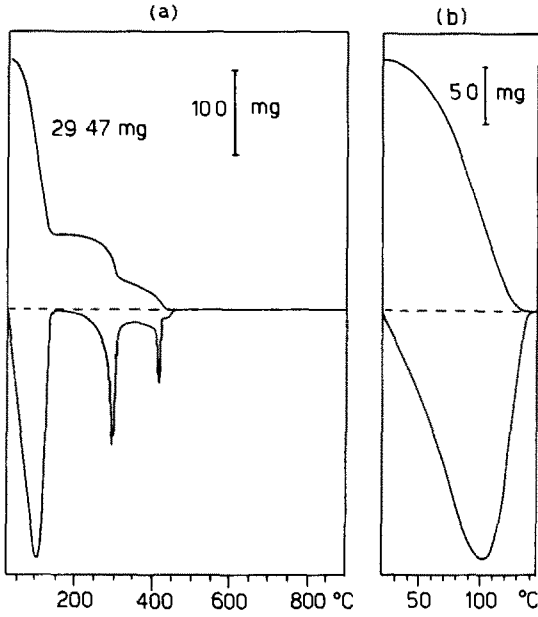


Fig. 9. TG and DTG curves for analysis of duramen of fresh wood of red fir (coniferous), previously fully soaked in water. (a) Full TG and DTG curves in the range 20–900 °C; (b) TG and DTG curves relative to saturation water loss only. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$); heating rate $10^\circ \text{C min}^{-1}$.

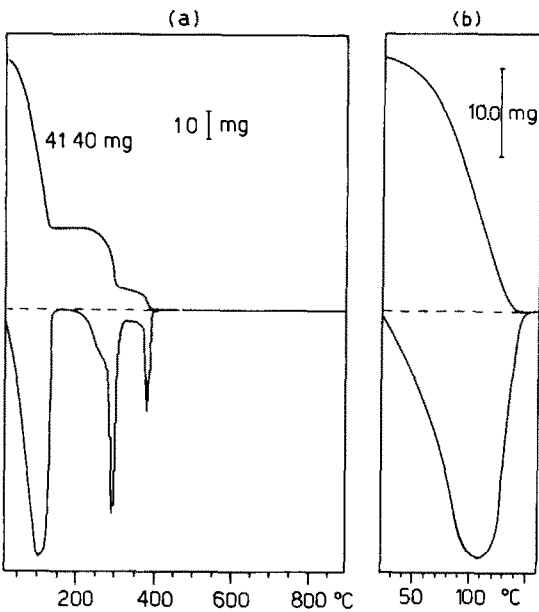


Fig. 10. TG and DTG curves for analysis of duramen of fresh wood of elm (broadleaf), previously fully soaked in water. (a) Full TG and DTG curves in the range 20–900 °C; (b) TG and DTG curves relative to saturation water loss only. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

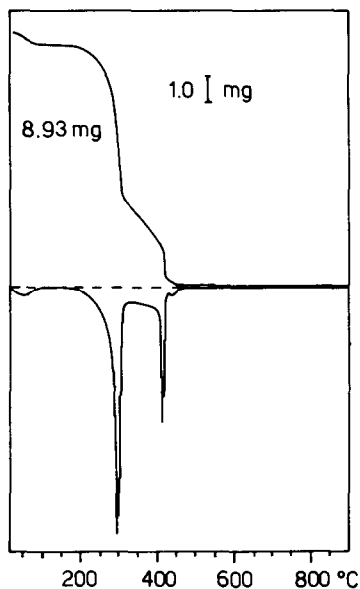


Fig. 11. TG and DTG curves for analysis of duramen of fresh wood of red fir (coniferous), previously fully soaked in water and then dried by rapidly heating at 140°C , to remove the most of the saturation water. In air stream ($100\text{ cm}^3\text{ min}^{-1}$) and heating rate $10^{\circ}\text{C min}^{-1}$.

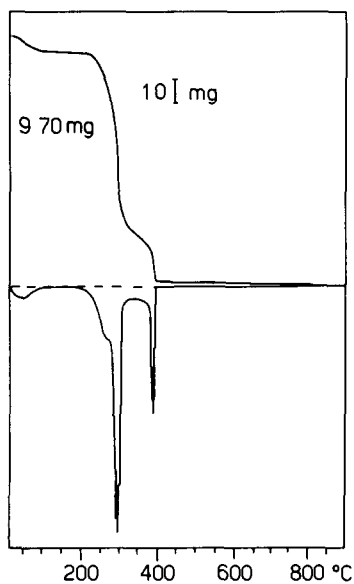


Fig. 12. TG and DTG curves for analysis of duramen of fresh wood of elm (broadleaf), previously fully soaked in water and then dried by rapidly heating at 140°C , to remove the most of the saturation water. In air stream ($100\text{ cm}^3\text{ min}^{-1}$) and heating rate $10^{\circ}\text{C min}^{-1}$.

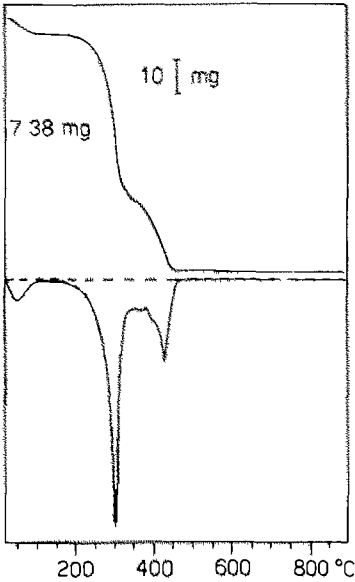


Fig. 13. TG and DTG curves for analysis of sawdust of fresh wood of red fir (coniferous). In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{ C min}^{-1}$.

water. The thermal data of this last process, for completeness, are reported in Table 1, where the values of the thermogravimetric residues (ashes) obtained at 500, 600 and 700° C , are also tabulated.

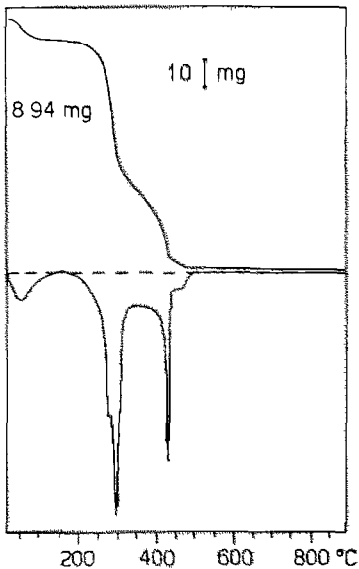


Fig. 14. TG and DTG curves for analysis of duramen of fresh wood for larch (coniferous). In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{ C min}^{-1}$.

TABLE 2

Thermal analysis of duramen of fresh woods. TG in air stream ($100 \text{ cm}^3 \text{ min}^{-1}$). The percentage weight loss by weight, at the different steps and of the residues, refer to the sum of the weight of the dry sample and of the moisture, while the saturation water percentage content is referred to the total weight of the sample fully saturated with water. Also, the percentages of TG residues, between 500 and 700 °C, are reported. pdt = procedural decomposition temperature

	Satura- tion water (%)	pdt	Mois- ture (%)	pdt	1st step loss (%)	pdt	2nd step loss (%)	pdt	Residue (%)	
									500 °C	600 °C 700 °C
Fresh coniferous (red fir or larch)			6.1	25	70.2	151	22.0	333	0.9	0.7
				54		304		420		
	69.3	21 100 145		117		333		481		
Fresh broadleaf (elm or beech)			7.4	22	68.7	173	22.8	337	0.5	0.4
				53		293		380		
	66.8	21 101 147		107		337		433		

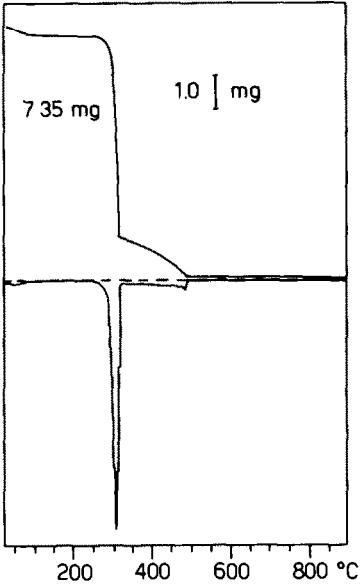


Fig. 15. TG and DTG curves for analysis of reference standard cellulose, analytical grade. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

Thermogravimetric analyses of the samples of fresh red fir (coniferous) and of fresh elm (broadleaf), both before (Figs. 7 and 8) and after full immersion in water (Figs. 9 and 10), then fully soaked in water, and dried by

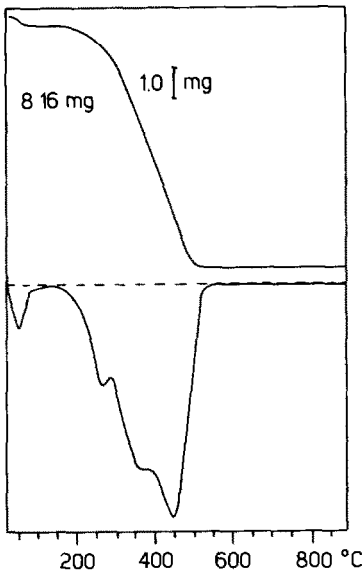


Fig. 16. TG and DTG curves for analysis of Klason lignin. In air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate $10^\circ \text{C min}^{-1}$.

rapidly heating at 140 °C (Figs. 11 and 12) were also carried out using the forementioned procedure.

In Fig. 13, the TG and DTG curves are shown for a sample of sawdust of fresh red fir; in Fig. 14, the thermogravimetric curve of the duramen of fresh larch (coniferous) is shown. Data relative to the thermogravimetric steps and the corresponding weight losses of fresh coniferous and of broadleaf tree samples (curves in Figs. 7 and 8) are summarized in Table 2. This table also contains the data for water losses and residues (ashes) at 500, 600 and 700 °C.

The thermal data (TG and DTG) of the different decomposition steps, with the exception of the saturation water-loss step, do not differ significantly for the duramen of fresh wood either before or after full immersion in water, soaked and then dried at 140 °C. This was also true for the sawdust samples.

Finally, in Figs. 15 and 16, TG and DTG curves of a cellulose standard, of analytical grade, and obtained under the same experimental conditions, and of lignin, insulated from the wood by acid attack (Klason lignin) [6], are shown.

DISCUSSION

The thermogravimetric curves of the archeological, waterlogged woods (Figs. 1(a) and 2(a)), or of the fresh woods, after full immersion in water (Figs. 9(a) and 10(a)), show that more than 50% of these samples is made up of saturation water. The analysis of the dehydration step, in an expanded scale (Figs. 1(b), 2(b), 9(b) and 10(b)), allows us to evaluate rapidly and precisely the saturation water content. It is very easy, through the thermograms, to obtain the value of the liquid/solid matter ratio in the archeological samples and to compare it with the corresponding ratio for the fresh, saturated samples.

As it affects the accuracy, the possible decomposition of the wood before the end of the dehydration process needs investigation. It is observed that, on the basis of the thermal data (Tables 1 and 2), obtained by TG curves, the beginning of the first decomposition step is well enough separated from the final temperature of the dehydration process. Also, a recent thermogravimetric study we performed on different vegetable matrices [10] has shown a strict correlation between the percentage water contents, determined by TG and by more sophisticated techniques (such as the NMR relative relaxation time method).

The analysis of the successive step results becomes much more detailed, especially for archeological woods, if performed on samples previously dried at about 140 °C (Figs. 3 and 4). This pretreatment does not cause any change to the solid part of the sample. This is demonstrated by the

comparison of the thermograms of fresh woods (Figs. 7 and 8) and of the same dried woods after soaking in water (Figs. 11 and 12): these are practically identical (ignoring very small differences in the loss of moisture). Also, within the precision range of the method, the curves of fresh woods, either before soaking or as sawdust, are also identical (see TG curves of Figs. 7 and 13). As for the archeological woods, the microscopical analysis was not able to distinguish between two different kinds of coniferous trees [3,4]. This was also the case, using thermoanalysis, for fresh woods, as shown by the comparison, for instance, between Figs. 7 (red fir), 14 (larch) and 8 (elm). However, if the TG and DTG curves of archeological woods are compared, after drying at 140 °C (Figs. 3 and 4), with those of the fresh wood samples (Figs. 7 and 8), or those of the freshly soaked woods and then dried again at 140 °C, (Figs. 11 and 12), some marked differences are observed. While the TG and DTG curves of fresh woods present two decomposition processes at 300 and 400 °C, the archeological woods show one marked step, at 350–450 °C, a series of little steps, not well resolved, but at least two, between 200 and 350 °C and finally a step, generally very small, corresponding to the oxidation of carbon residues, between 450 and 650 °C.

The thermogram of the cellulose standard (Fig. 15), showing a large decomposition step at 300 °C, allows us to identify the step, at the same temperature, in the decomposition of the fresh wood samples. In these samples, the other decomposition step, observed in the thermograms at about 400 °C, can be reasonably attributed to the thermal decomposition of lignin. It should be noted that a standard, analytical grade of lignin, cannot be easily obtained, because of its hetero-polymeric nature (most likely a mixture of macro-molecules with different polymerization degrees) [11]. Moreover, the commercially available samples of lignin differ from each other according to the preparation method. Thus, it is possible to distinguish a Klason lignin [6], from an enzymatic lignin [8,12]. Also, these kinds of prepared lignin, if compared with natural lignin, contains some cellulose impurities. The thermogravimetric curves (Fig. 16) show the thermal decomposition of a sample of Klason lignin [3,13], and, from the above, its behaviour can only be considered as a qualitative reference, with respect to natural lignin. It is possible to observe that the greatest rate of the decomposition process, occurs around 400 °C, agreeing well with the results from other researchers [14] on the thermal degradation of sulphuric acid lignin: it is therefore reasonable to assign the step occurring at this temperature in the thermograms of fresh woods to the decomposition of natural lignin. DTG curves are, in this case, particularly useful as their peaks, at about 400 °C, can be used to define the interval of the degradation process of lignin, compared to that due to oxidation of carbon residues, which, even though occurring at about the same temperature, is characterized by a lower trend and end result, especially for archeological woods, at temperatures higher

than that at which lignin degradation occurs. On the other hand, qualitatively, the ratio of the two steps, relative to the decomposition of cellulose and lignin, agrees well with literature data [8,13,15] on the relative amount of these two compounds in the duramen of the examined fresh woods: it is well known that the cellulose content is markedly higher than that of lignin. Also, the two steps assigned to decomposition of lignin and cellulose, taking into account the different experimental conditions, are in good agreement with results by Wiedemann and Bayer [1]. The examination of the thermograms of the archeological samples confirms the evidence of the chemical analysis performed with traditional methods [3], that is the advanced decomposition of the cellulosic component and, consequently, the marked increase of the percentage content, if compared with fresh samples of the lignin, even if probably partially degraded. The main decomposition step of lignin, between 350 and 450 °C, is still clearly evident in all the thermograms of the archeological residues, while those of cellulose are scarcely able to be identified. On analysing the thermograms of the fresh and archeological woods, it can be observed that, for the former a residue of ashes, practically constant in the range 500–570 °C, was obtained, however, for the archeological woods, ashes without carbon residue can only be obtained at temperatures higher than 650 °C. Thus, the unreliability of traditional methods,

TABLE 3

Comparison between the values of moisture, ash, cellulose, lignin and saturation water content in waterlogged archeological woods obtained by thermogravimetry and TAPPI methods. The saturation water percentage content refer to the total weight of the sample fully soaked, while, the other component percentages, refer to dry samples. The reported values are the mean of at least three determinations

Nature of the sample	Analyzed species	Values obtained by TAPPI methods ^a (a)	S.D. (%)	Values obtained by TG method (b)	S.D. (%)	(b - a/b)%
Archeological coniferous (red fir or larch)	Saturation water (%)	89	–	81.0	0.5	–9.9
	Moisture (%)	8.8	0.5	9.7	4	+9.3
	Ash (%)	6.3 (at 530 °C)	0.8	6.2 (at 700 °C)	0.8	–1.6
	Cellulose (%)	19.0	2.3	18.3	8	–3.8
	Lignin (%)	73.5	5.1	73.4	3.5	–0.1
Archeological broadleaf (elm or beech)	Saturation water (%)	73	–	84.7	0.5	+13.8
	Moisture (%)	10.5	0.5	12.2	4	+13.6
	Ash (%)	9.5 (at 530 °C)	0.8	7.7 (at 700 °C)	0.8	–23.4
	Cellulose (%)	16.0	2.3	19.0	8	+15.8
	Lignin (%)	72.6	5.1	70.1	3.5	–3.6

^a TAPPI = Technical Association of the Pulp and Paper Industry.

TABLE 4

Comparison between the values of moisture, ash, cellulose, lignin and saturation water content in duramen of fresh woods obtained by thermogravimetry, TAPPI methods and with the values reported in literature. The saturation water percentage content refer to the total weight of the sample fully soaked, while the other component percentages refer to dry samples. The reported values are the mean of at least three determinations

Nature of the sample	Analysed species	Values reported in literature (a)	Reference	Values obtained by TAPPI method (b)	S.D. (%)	Values obtained by TG method (c)	S.D. (%)	(c-a/c)%	(c-b/c)%
Archeological coniferous (red fir or larch)	Saturation water (%)	-	-	-	-	69.3	0.5	-	-
	Moisture (%)	-	-	8.4	0.5	7.0	4	-	-20.0
	Ash (%)	0.21(at 530-575 °C)	13	0.22(at 530 °C)	0.5	0.26(at 700 °C)	0.8	+19.2	+15.4
	Cellulose (%)	70	13	60.0	2.0	68.4	3	-2.3	+12.3
	Lignin (%)	29	13	34.4	5.0	30.1	3	+3.7	-14.3
Archeological broad-leaf (elm or beech)	Saturation water (%)	-	-	-	-	66.8	0.5	-	-
	Moisture (%)	-	-	10.6	0.5	8.0	4	-	-32.5
	Ash (%)	0.91(at 530-575 °C)	18	0.54(at 530 °C)	0.5	0.50(at 700 °C)	0.8	-82.0	-8.0
	Cellulose (%)	74	19	71.0	2.0	74.2	3	+0.3	+4.3
	Lignin (%)	24	19	21.7	5.0	24.6	3	+2.4	+11.8

based on ashing in a muffle at temperatures around 530–575 °C [3,16], was highlighted, when the ash content value was evaluated. On the basis of the experimental results, starting from the thermograms of fresh and archeological woods, data concerning saturation water, moisture, ash content, percentage cellulose and percentage lignin can be obtained. They can also be compared (Tables 3 and 4) with results, for the same samples, from the most common reference methods, such as “TAPPI” (Technical Association of Pulp and Paper Industry) and with literature data. The results from thermogravimetry (Tables 3 and 4) represent the mean of the percentage weight losses of repeated determinations relative to the different steps and identified as indicated above. In the case of the archeological samples the lignin and cellulose percentages were obtained by tentatively attributing the weight loss of the first step to the cellulose percentage content and that of the second and third steps (see Table 2) to the percentage lignin content.

CONCLUSIONS

From a methodological point of view, the application of thermogravimetry to the study of fresh and archeological woods did not cause any problems, or require any pretreatment; for instance, TG and DTG curves of wood samples, either cut into small cubes or powdered as sawdust, do not show any difference of temperature, only a broadening and flattening of the peaks being observed. As it concerns the study of waterlogged archeological samples and of those fresh, fully soaked ones, the percentage of saturation water and therefore the liquid/solid ratio can be suitably obtained directly from the samples just extracted from the liquid in which they were stored: the TG study of the solid part of these samples is easier and more detailed if performed on samples previously dried at about 140 °C. The thermoanalytical study allowed us to:

- (a) Obtain data on the saturation water content by a simple and fast method. This is particularly useful for archeological samples, for which the liquid/solid ratio is a meaningful index of the damage to the inner structure of the wood and of the decomposition processes occurring in these samples.
- (b) Establish with great precision the ash content. The thermogravimetric curves highlight the poor reliability of the traditional methods and demonstrated, especially for archeological samples, that the thermogravimetric residue, at about 650–700 °C, yields a much more reliable value for the ash content. This is in agreement with our previous observations on different matrices [10,17]. It is opportune to note that knowledge of these analytical data is often necessary, both for fresh samples, for research on botany and vegetable physiology, and for archeological samples, when, in some cases, a marked modification of the original ash content occurs because of their contact with soils or sludges rich in clay and colloidal metal hydroxides.

(c) Obtain a sort of thermal “finger print”, and thus able to address and validate the information from other kinds of analysis (for instance by microscopy), with an aim to ascertaining the nature of the species from which the archeological wood comes from: in our case, for instance, TG and DTG finger prints of the waterlogged archeological samples allowed us to state whether they were of a coniferous or broadleaf nature.

(d) Rapidly estimate the cellulose and lignin content of fresh wood samples, by the weight-loss data, relative to the two thermogravimetric steps at 300 and 400 °C, observed in the thermograms of the examined samples. The results of the comparison of TG data, with literature [13,18,19] and TAPPI data, for the content of these substances, are surely meaningful on this point (see Table 4).

(e) Yield and confirm qualitative information, on the processes occurring in the archeological woods: for instance the decomposition of the cellulose [20] or the confirmation of the persistence of lignin. From the quantitative point of view, the thermogravimetric evaluation of the lignin and of the cellulose contained in these samples is quite difficult and the data on this subject (Table 3), obtained as described above, must be considered as only a research effort on the interpretation of the experimental data, rather than as rigorous results of new methodological proposals. On the other hand, for the examined archeological samples, and also for the values from TAPPI method (Table 3), the results must be considered with caution, since these methods were developed to be applied to fresh woods, not for determinations on waterlogged, archeological samples.

ACKNOWLEDGEMENT

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