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# THERMOANALYSIS OF ANCIENT, FRESH AND WATERLOGGED WOODS

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TG, DTG and DSC curves are presented and analytical results, obtained by thermogravimetry and DSC calorimetry, of ancient, fresh and waterlogged wood samples, are discussed. The criteria by which the percent content of lignin, cellulose, water and ashes (residue after heating at 700°) were obtained by thermogravimetry, are outlined. Finally DSC curves are reported and the degradation which happen in some wood samples evidenced, especially in the case of waterlogged wood.

## Introduction

The application of the thermal analysis are continuously increasing both in the field of the restoration and in the study of archeological founds of different nature (inorganic, as ceramics [1], plasters [2], bronzes [3], or organic, as papyrus, tissues, silks, pigments [3, 4]). The application of thermal analysis to woods has been recently developed [5, 6], especially due to H. G. Wiedemann who studied some egyptian ancient woods [3].

We performed investigations over a period of some years [7] in cooperation with some researchers of the 'Istituto Centrale del Restauro, Roma' (C. Meucci, S. D'Urbano). The aim of this work has been focused on the development of thermoanalytical methods, applied to particular wood samples, especially also to waterlogged samples of the 1st century A.D., belonging to the residues of a Roman ship wreck. More recently we extended the study to wood samples of different epoches such as some fresh woods, especially of coniferous nature and some ancient ones, of historical interest, belonging to portals of ancient churches, aging from 13th and 18th centuries [8]. In this paper we summarize the criteria which enable to perform the

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quantitative analysis of the different samples by TG. DSC curves, of some of these samples, are also shown and discussed.

## Experimental

The study was performed by a Mettler thermobalance TG 50 and a Mettler DSC 20, coupled with a processor system TC 10–TA and a printer Swiss Matrix. The aim was to get, on the basis of the TG and DSC curves, both qualitative informations and quantitative ones. All the TG curves were recorded in an air stream (100 $cm^3 \cdot min^{-1}$); heating rate was 10 $deg \cdot min^{-1}$ and the selected temperature interval ranged from 20° and 900°. However, the DSC measurement were performed with a heating rate of 5 $deg \cdot min^{-1}$ and the temperature was limited to the interval of 23 and 600°. The main characteristics of the examined wood samples were previously described [7, 8.].

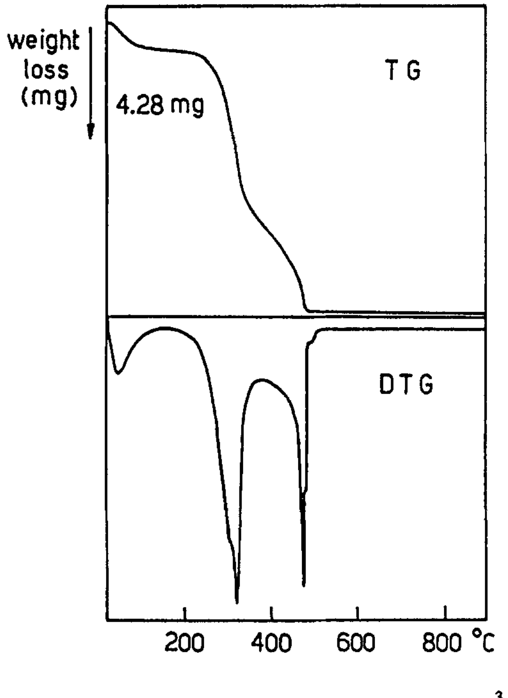


**Fig. 1** TG and DTG curves of fresh wood of larch. In air stream (100 $cm^3 \cdot min^{-1}$); heating rate 10 $deg \cdot min^{-1}$

## Results

TG curves of duramen of fresh wood show a behaviour presented in Fig. 1. The TG curves and the corresponding derivatives reveal three steps: the first, between room temperature and 150°, which corresponds to the loss of all the moisture of the sample, generally of the order of 10% by weight; the second step, between 160° and 370°, is corresponding to a large mass loss, about 60% of the total weight; between 370 and 500°, we can observe the third step, during which a mass loss occurs of the order of 30% of the total weight. Lastly, at about 700°, a residual of only ashes is obtained, about 0.2–0.5% of the total weight, surely free of any carbon content. According to investigations by Wiedemann [3] and confirmed by us experimentally, with TG curves of lignin and cellulose standards [7], the 2nd and 3rd of these TG steps, are corresponding to the oxidizing thermal degradation of cellulose and lignin of the wood sample. Thermogravimetry enables a rapid and accurate moisture, cellulose, lignin contents and % ashes residues determination in the fresh wood samples. The samples of ancient woods, as those ones from doors of the churches of different epoches, from 13th and 18th centuries, show ther-

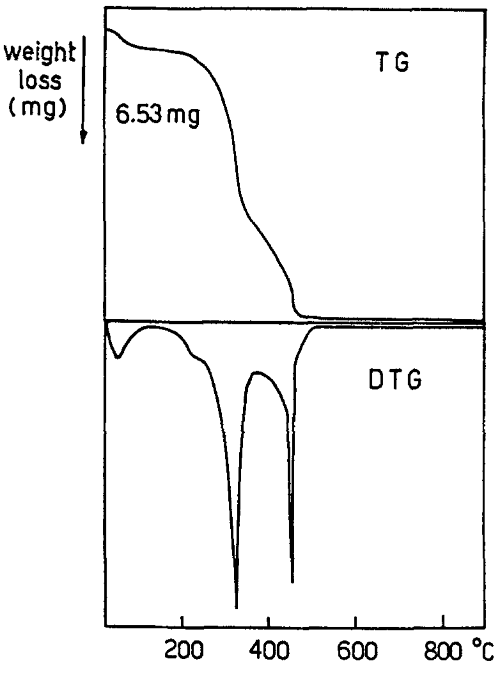


**Fig. 2** TG and DTG curves of ancient wood of larch (XIII A.D.). In air stream ($100\ cm^3 \cdot min^{-1}$); heating rate $10\ deg \cdot min^{-1}$

mogravimetric curves, generally with a behaviour not too much different from those ones of fresh woods. Nevertheless, the thermal oxidizing step of the lignin, appears, for certain samples, more articulated and shifted to different temperatures. Furthermore the ash content is relatively higher (of about 0.5–1.5% by weight). An example is shown in Fig. 2. TG analysis of ancient wood samples reveal the same quantitative informations which can be obtained for the fresh woods.

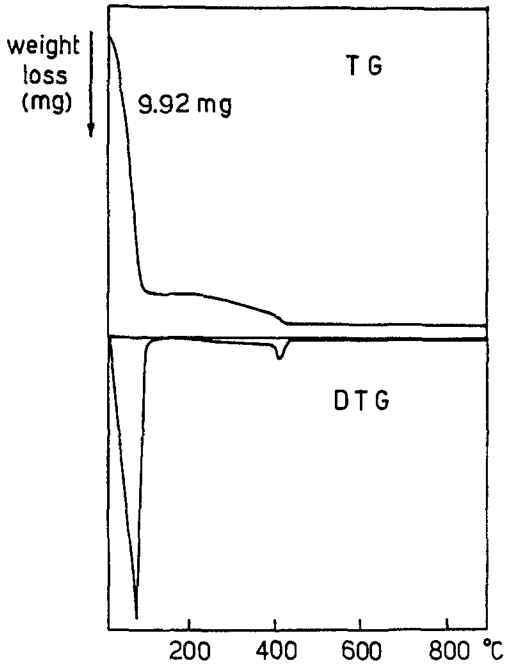


Fig. 3 TG and DTG curves of waterlogged wood of coniferous (I A.D.). In air stream (100 $cm^3 \cdot min^{-1}$); heating rate 10° $deg \cdot min^{-1}$

In the case of waterlogged wood samples of the 1st century A.D., the full immersion in water for long periods, even for centuries, has favoured some funginal and bacterial attacks, rather than slow chemical degradation processes of the cellulose as well as the lignin. A drastic molecular degradation of the cellulose and of the lignin is a consequence of the aging. The TG curves of waterlogged wood samples are shown in Figs 3 and 4. The first one related to a sample still soaked of water, the second one, to the same sample, after drying, reduction to sawdust and after fractionation of particle size by sieving [2, 7, 9].

In this case TG analysis, as outlined in previous papers [2, 7, 8], allows to determine very well the soaking water from the weight loss (about 80–85%)

which happen in the first great step of the TG curve of the waterlogged wood sample between room temperature and about 150° (Fig. 3) and to estimate, by sufficient accuracy, the cellulose and lignin contents from the weight loss observed in the TG curve of dried sawdust (Fig. 4), respectively between 150° and about 300° and this latter temperature up to about 500°. Finally the % ashes is determined from the value of TG residue at 700°.

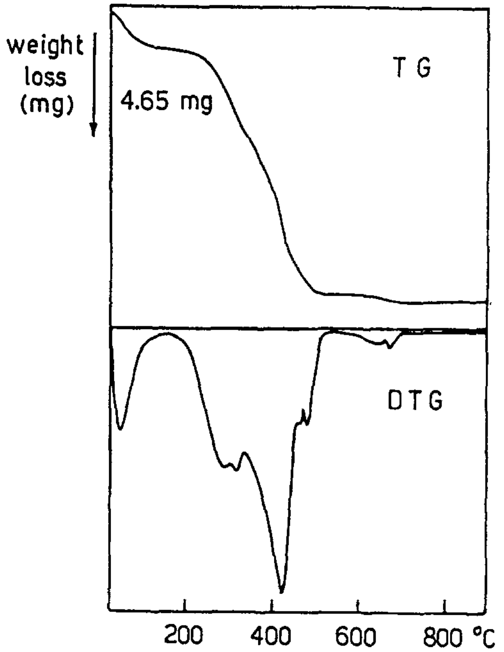


**Fig. 4** TG and DTG curves of dried sawdust of waterlogged wood of coniferous (I A.D.). In air stream (100 $cm^3 \cdot min^{-1}$); heating rate 10 $deg \cdot min^{-1}$

The comparison of the values obtained by TG and values from classical chemical methods of analysis ('TAPPI': Technical Association of the Pulp and Paper Industry [7, 9], performed on a certain number of samples (Table 1), confirmed our assumption.

In Figs 5–7, DSC curves, between 23 and 600° are presented of fresh coniferous woods, or of the same ancient wood of thirteenth century and for the dried sawdust of a waterlogged coniferous wood of the first century A.D. In all the DSC curves, a first endothermic peak, is observed, due to the water evaporation, between 23 and about 130°, then in the case of the fresh wood and in the ancient one, an exothermic peak, at about 320° can be measured, due to the cellulose combustion. Finally, for both two latter kinds of wood

**Table 1** Comparison of percent w/w content of cellulose lignin and of the ashes of archeological waterlogged woods, obtained by TG analysis and by 'TAPPI' methods. Values refer to the dried samples

| Wood sample no. | Kind of tree | % cellulose by TG (RSD = 5–8%) | % cellulose by 'TAPPI'* (RSD = 2.5%) | % cellulose Δ % | % lignin by TG (RSD = 3.5%) | % lignin by 'TAPPI'* (RSD = 5%) | % lignin Δ % | % of ashes by TG (RSD = 1%) | % of ashes by 'TAPPI'* (RSD = 1%) | % of ashes Δ % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Coniferous (Spruce, or larch) | 18.2 | 18.0 | − 1.1 | 72.5 | 76.5 | +5.5 | 7.3 | 5.6 | −23.3 |
| 2 | " | 22.2 | 19.0 | −14.4 | 70.0 | 73.5 | +5.0 | 8.0 | 6.3 | −21.3 |
| 3 | " | 17.6 | 16.0 | − 9.1 | 62.2 | 61.3 | −14.0 | 7.6 | 7.6 | 0 |
| 4 | " | 18.7 | 19.0 | +1.6 | 63.2 | 61.0 | − 3.5 | – | 7.0 | – |
| 5 | Broadleaf (Elm, or Beech) | 16.6 | 16.0 | − 3.6 | 71.4 | 72.6 | +1.5 | 9.0 | 9.5 | +5.6 |
| 6 | " | 18.4 | 20.0 | +8.7 | 61.1 | 61.0 | − 0.2 | 11.1 | 8.3 | −25.2 |
| 7 | " | 19.1 | 17.0 | −11.0 | 71.2 | 73.0 | +2.5 | 9.8 | 9.6 | − 2.0 |
| 8 | " | 14.3 | 11.0 | −23.1 | 65.0 | 59.3 | − 8.8 | 7.7 | 7.5 | − 2.6 |
| 9 | " | 12.4 | 11.0 | −11.3 | 73.3 | 74.1 | +1.1 | 7.9 | | |

Analysis performed according to the 'TAPPI' method, described in previous papers [7, 9]. 'TAPPI' = Technical Association of the Pulp and Paper Indrustry

$$\Delta\,\% = \frac{\text{Value (by 'TAPPI') method} - \text{Value (by TG method)}}{\text{Value (by 'TG' method)}}$$

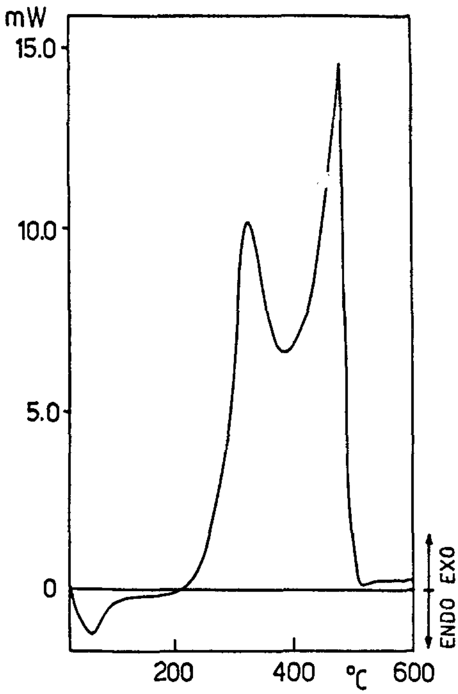


Fig. 5 DSC curve of fresh wood of larch. In air stream (100 $cm^3 \cdot min^{-1}$); heating rate 5 $deg \cdot min^{-1}$

samples, in the DSC curves, an exothermic peak is observed, which can be related to the lignin combustion. This peak is, for the fresh wood at about 460° and, for the ancient wood, at about 440°. The DSC curve of the dried sawdust of waterlogged wood differs strongly in the exothermic DSC peak, showing a single peak at about 410°, with two shoulders, one around 340° and the other at 450°, even more clearly separated from the main peak, probably due to combustion processes of residues of cellulose, still present in the sample, and of more degraded portion of lignin.

## Conclusions

As a conclusion it is possible to determine rapidly by TG the moisture, lignin, cellulose contents and ash residues of fresh and ancient woods with a reasonable accuracy and to approximately evaluate the same data for waterlogged wood samples. Especially for the latter one, it is possible to point to a strong chemical change of the cellulose and lignin content, due to the storing condition. This observation was confirmed by SEM micrographs of analogous wood samples reported in a previous paper [8]. The DSC curves of samples of different kinds of wood, reported in this note, under the qualitative profile, show, even more pronunciated by TG curves, the level of damagement of the wood, due both to the age and to the storing conditions. The almost disappearance of the peak of the cellulose is, for instance, very evident in the DSC curve of the sawdust of the waterlogged wood of 1st century A.D. on the other hand, also the temperature shifts and the enlargement of DSC peaks of lignin and cellulose, in the ancient and archeological samples, in comparison with fresh woods, are evident. These qualitative observations and other ones, such as the height/area ratio of the DSC peaks, relative to cellulose and lignin, will reveal interesting results, under the point of view of characterizing and dating the sample; as well as, in previous paper [8], lignin and cellulose content of wood was found in a qualitative, but well evident, correlation with the age of the sample.

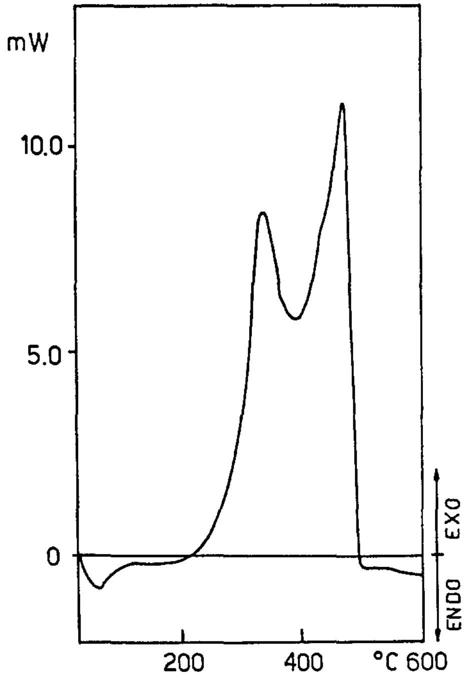


Fig. 6 DSC curve of ancient wood of larch (XIII A.D.). In air stream (100 $cm^3 \cdot min^{-1}$); heating rate 5 $deg \cdot min^{-1}$

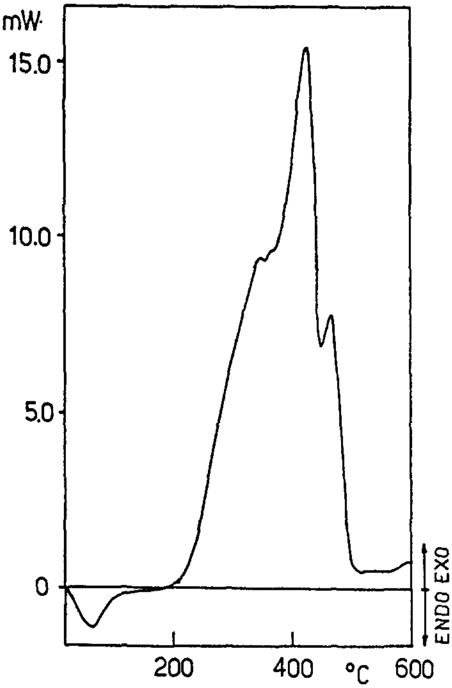


**Fig. 7** DSC curve of dried sawdust of waterlogged wood (I A.D.) In air stream (100 $cm^3 \cdot min^{-1}$); heating rate 5 $deg \cdot min^{-1}$

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**Zusammenfassung** – Die Differenzierung von historischen, neuzeitlichen und gewässerten Holzproben mit den Methoden der Thermogravimetrie und DSC wurde untersucht und diskutiert. Die Kriterien, nach denen der Gehalt an Lignin, Cellulose, Wasser und Asche (Rückstand nach Erhitzung auf 700°C) aus TG-Kurven abzuleiten sind, wurden erläutert und die Befunde mit den Resultaten einer nasschemischen Standardmethode verglichen. DSC-Kurven demonstrieren den chemischen Abbau der unterschiedlich gealterten respektive gewässerten Holzproben.