



# *In Situ* analysis by Pyrolysis – Mass Spectrometry of the macromolecules in heartwood of *Q. robur* L.

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**Abstract:** The technique of pyrolysis coupled with Mass Spectrometry (PYR/MS) makes it possible, using an adequate temperature ramping program, to gain access to the macromolecules of the wood. We attributed the main peaks in the spectra obtained to the products of depolymerisation and thermal degradation of carbohydrates and lignins.

**Key words:** Pyrolysis / Mass Spectrometry, heartwood, oak, *Q. robur*, lignins, carbohydrates.

## INTRODUCTION

The study of the constituents of wood is often carried out once they have been extracted and purified. But in situ study would also appear to be an interesting approach to analysis.

The methods most often used are based either on the <sup>13</sup>C NMR of the solid (CPMAS <sup>13</sup>C NMR, KOŁODZIEJSKI *et al.*, 1982; HAW *et al.*, 1984; FRUND and LUNDEMAN, 1989), or on the combination of pyrolysis with mass spectrometry (PYR/MS, MEUZELAAR *et al.*, 1982; GUTTERIDGE *et al.*, 1984; DE GROOT *et al.*, 1987). These two techniques are relatively recent and prove to be of interest when studying macromolecules which would undergo marked structural modification during extraction (TOLLIER *et al.*, 1986; MANDERS, 1987) due to the partial depolymerisation which is indispensable if they are to be isolated.

PYR/MS is based on the depolymerisation of the macromolecules by heat followed by identification of the fragments by MS. For the sub-units of the polymers which are not, or are only a little volatile, the increase in temperature leads to their thermal degradation and then to the identification of the products formed (VITELLO, 1982).

## MATERIAL AND METHODS

The analysis was carried out on a series of samples of *Q. robur* L. from the Limousin region (France). The samples were in the form of sticks of 5 x 1 mm. The weight of the wood was close to 1 mg ( $\pm 0.05$  mg). They were placed in a tube using a quartz vial located at the tip of the programmable-temperature probe of a Fisons AutoSpec EQ mass spectrometer. Pyrolysis was carried out in a vacuum, directly in the ion source of the spectrometer. The probe temperature was programmed from 50°C to 650°C, rising by 50°C/min. Mass spectra were recorded at regular intervals (one per second), so as to identify the compounds formed at the exact moment when they were volatilised. The collection and processing of the data (thermograms and mass spectra) were carried out by the OPUS system installed on a Digital Equipments VaXstation 3100. Computer processing consisted in tracing pyrograms representing the quantities of products released according to the temperature during the reaction, as well as mass spectra enabling these products to be identified.

## RESULTS

### I – GENERAL APPEARANCE OF THE PYROGRAMS.

The total ion flow of the pyrogram is presented in figure 1. We observed that, even at quite low temperatures ( $< 100^\circ\text{C}$ ), molecules were already released from the mass of the wood. Two maximum values were observed at temperatures of 150°C and 195°C. From 200°C to about 300°C, we detected the main products of pyrolysis.

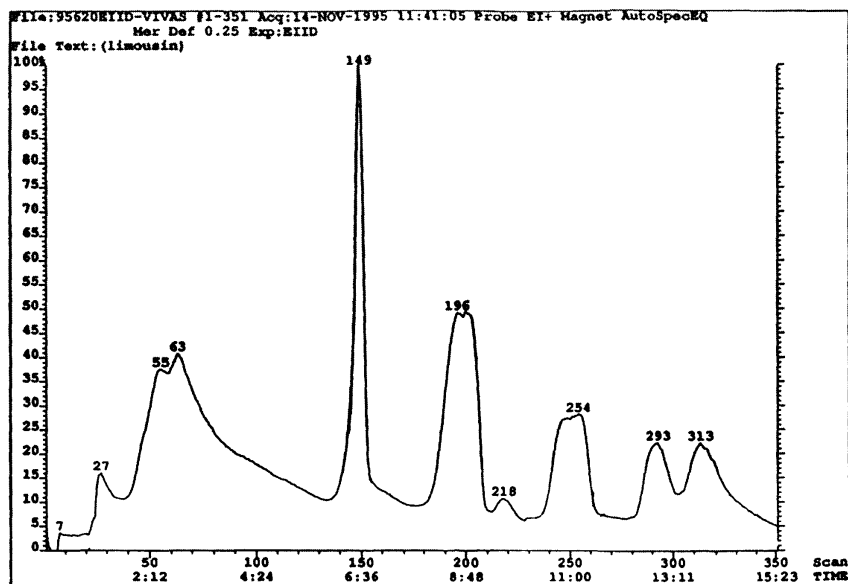


Figure 1 - Total ionic current of *Q. robur* pyrogram

Beyond 350°C, few products were formed and the total ion flow showed only low variations in density.

## II – IDENTIFICATION AND ATTRIBUTION OF THE PRODUCTS OF PYROLYSIS

On the basis of the recording of the total ion flow, we selected a certain number of zones of the pyrogram in which the number of ions formed was high. These were the spectra obtained at 27, 63, 149, 196, 218 and 250°C (figure 2). In accordance with the works of Reid *et al.* (1993), the ions observed at  $m/z$  124, 135, 151-152 and 180-181 were attributed to elements released by the depolymerisation of lignins, and those at  $m/z$  84, 96, 114, 126 and 144 to those of carbohydrates. The ions with  $m/z$  of 60 and 73 are characteristic fragments of fatty acids. In the course of the pyrolysis process, macromolecule depolymerisation reactions were observed at around 150°C. At this temperature, the quantity of products detected was at its highest. Beyond, at higher temperatures, the fragments attributed to lignins decreased sharply, whereas the presence of carbohydrate fragments decreased only very gradually.

Various molecules derived from carbohydrates were identified. They were fragments of 2-, 3- and 2,5-furaldehydes ( $m/z$ : 96), 4-hydroxy-5,6-dihydro-(2H)-pyrane-2-one ( $m/z$ : 114), 5-hydroxymethyl-2-furaldehyde or hydroxymethyl-pyarone ( $m/z$ : 126). The 2-, 3- and 2,5-furaldehydes are due to the pyrolysis of the pentose units of hemicellulose, whereas the 5-hydroxymethyl-2-furaldehyde comes from the glucose units of cellulose. The ratio between the heights of the  $m/z$  96 and  $m/z$  126 peaks was, on average,  $1.9 \pm 0.2$ . Although cellulose is more abundant in wood, hemicellulose is more easily thermally degraded.

The main products originating from the pyrolysis of lignins are classified as guaiacyl “G” units (monomethoxylated) and syringyl “S” units (dimethoxylated). Among the “G” units, we identified 2-methoxyphenol ( $m/z$ : 124), a fragment of 4-formyl-2-methoxyphenol ( $m/z$ : 151) and 4-formyl-2-methoxyphenol (vanillin,  $m/z$ : 152). Among the “S” units, we identified 4-vinyl-2,6-dimethoxyphenol ( $m/z$ : 180) and a fragment of 4-formyl-2,6-dimethoxyphenol (syringaldehyde,  $m/z$ : 181). The S/G ratio varied during the course of pyrolysis; it was 1.25 at around 150°C, 1.8 at 195°C, 2.2 at 220°C and 0.77 at around 250°C. This result would suggest that, for temperatures below 220°C, pyrolysis degrades the “S” units of the lignins selectively whereas, at higher temperatures, the phenomenon is reversed and it is the lignins which are richer in “G” units which are affected.

## DISCUSSION

Cellulose, although much more abundant in oak wood than hemicellulose, is degraded less, whatever the temperature. The crystalline structure of a part of the cellulose explains its resistance (BARNOUD, 1980). During pyrolysis, the furanic derivatives released by the thermal degradation of arabinose and xylose are predominant. Depolymerisation of lignin is high at temperatures of around 150°C; beyond this temperature, we can note a sharp decrease in these products of thermal degradation. In accordance with the works of LAPIERRE *et al.*, (1986), the increase in temperature causes depolymerisation at first, followed by cross-linkage of the lignin at higher temperatures. The new polymers produced have higher molecular masses and fusion

points. Attentive examination of the S/G ratio shows that different types of lignins are transformed during pyrolysis. From 150 to 220°C, the S/G ratio is greater than 1 and, above 250°C, it becomes less than one. During the first phase of thermolysis, the lignins located in the secondary walls, rich in "S" units, are degraded; at higher temperatures, thermal degradation concerns more particularly the primary walls containing lignins rich in "G" units (MONTIES, 1992).

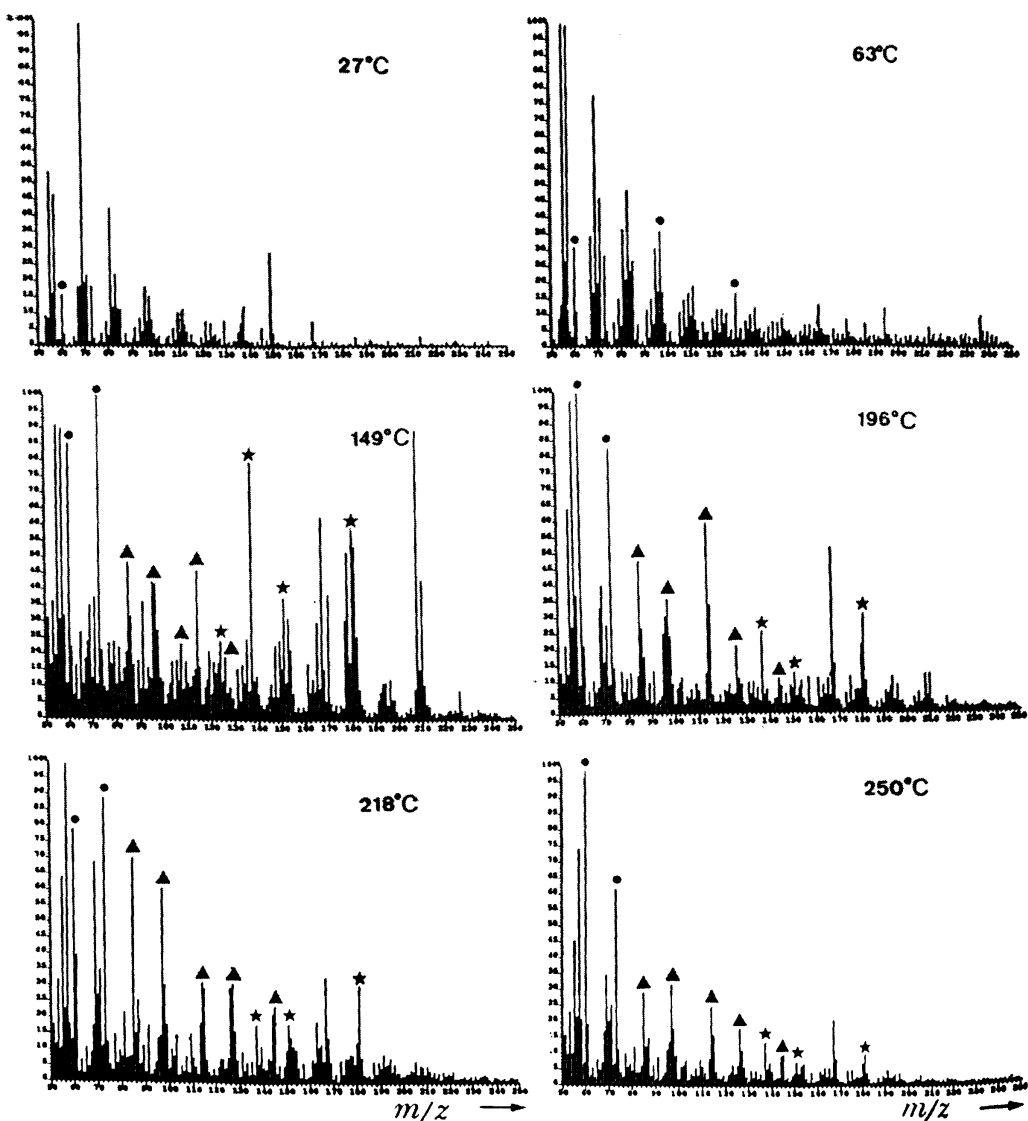


Figure 2 - Mass spectra recorded at different temperatures

These first results demonstrate the interest of such a technique, on the one hand in studying wood macromolecules and, on the other, in modelling heating operations in cooperage. We can also envisage the possibility of rapid estimation of wood quality based on such criteria as carbohydrate or lignin contents. This may be assessed by identifying the fragments produced on pyrolysis, thus making it possible to evaluate the capacity of the wood sample to produce thermal degradation products of real olfactory interest (REID *et al.*, 1993).

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