

## PY/GC/MS ANALYSES OF HISTORICAL PAPERS

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The thermal degradation of cellulose is an important process in several fields such as the paper industry, biomass combustion, fire retardation, etc. Paper consists mostly of cellulose fibres. Although the fibre source has changed continuously from cotton or linen rags to wood, its nature is still vegetal. Pyrolysis in combination with gas chromatography and mass spectrometry has been used to identify the structures of thermal degradation products with the aim to characterize papers used in different centuries. Pyrolysis of cellulose has also been studied in the presence of the methylating reagent tetramethylammonium hydroxide (TMAH).

*Keywords:* Pyrolysis; Gas chromatography; Mass spectrometry; Ancient paper

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### INTRODUCTION

In the modern era of digitized information, it is sometimes forgotten that paper is one of the oldest and most used media. Paper consists mostly of cellulose fibers. Although the fiber source has changed from cotton or linen rags to wood (after many centuries), its nature is still vegetal (Grant 1978). The renewable character of vegetable material ensures a potentially unlimited supply (Havermans 1995). Although fibrous matter from different vegetative sources differ from each other, they all consist in great part of cellulose. Cotton contains ca. 95% cellulose, linen ca. 80%, wood ca. 45%, and grasses ca. 30%. Cellulose is a linear homopolysaccharide composed of  $\beta$ -D-glucopyranoside units linked by (1 $\rightarrow$ 4) bonds. Cellulose is one of nature's major building materials, found in algae, bacteria, plants, and animals. Recently it has been found also in space (Griffith, 2008). The kinetics of paper degradation has been reviewed (Calvini and Gorassini 2006). These authors, re-elaborating the literature data, found many questionable statements pertaining to the science of paper conservation. In particular, it was shown that accelerated ageing techniques do not allow any prediction of the life expectancy of paper, owing to the exponential structure of the Arrhenius relationship.

Py/GC/MS applications have been the subject of several review articles (Irwin 1981; Liebman 1983; de Angelis 2004; Shafizadeh 1982; Syverud 2003) and books (Wampler 1995; 2007; Irwin 1982). Pyrolysis is the thermal decomposition of macromolecules in the absence of oxygen into volatile and semivolatile molecules that can be easily analyzed, combining gas chromatographic and mass spectrometric (GC/MS) techniques. The observed fragments provide a fingerprint of the spectral characteristic of a particular sample, in terms of both fragment nature and relative distribution. Pyrolysis of cellulose has a potential application for converting woody biomass into fuels and chemicals (Shafizadeh 1982; Antal 1985, 1989). Understanding the mechanism of pyrolysis of

woody biomass on a molecular basis can provide useful information for improving product selectivity. Many kinetic models of cellulose pyrolysis have been proposed to predict product formation (Broido and Nelson 1975; Bradbury et al. 1979). However, the molecular basis of the pyrolysis mechanism, focusing on product formation, is not yet clear. During cellulose pyrolysis at temperatures above 300°C, anhydromonosaccharides are known to form. The formation of levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) and 1,6-anhydro- $\beta$ -D-glucofuranose is an important process. Levoglucosan is a key initial intermediate for cellulose pyrolysis. Levoglucosan and cellulose gave similar pyrolysis products (Broido and Nelson 1975).

The technique has been used also for lignins (see De Angelis 2004 and the references therein). PY/GC/MS is an analytical technique useful in characterization of paper. The method is widely used in qualitative analysis of residual lignin (Martinez 2001). Pyrolysis under controlled conditions has proven to be a fast and reproducible method to degrade papers into volatile thermal dissociation products, which are amenable to chromatographic and mass spectrometric analysis.

The present project involving conservation and preservation of ancient papers has started recently and intends to study many examples of different papers and the influence of different compounds, i.e., inks with very different compositions on papers. By such an approach, a large and useful database will be formed for conservation and preservation field specialists. This paper reports only preliminary work done in that direction. We have more than hundred inks with different composition prepared by different recipes and analysed alone, marked on Whatman paper by calamus, in fresh and aged form.

The goal of this study is to identify the structures of thermal degradation products of papers used in different centuries. Pyrolysis has been also studied in the presence of the methylating reagent tetramethylammonium hydroxide (TMAH)

## EXPERIMENTAL

### Materials

The analysed papers were Whatman 1/ Cat. 1001 185, i.e. pure cellulose, two samples of ancient paper dated 1567 and 1885. TMAH for methylation (tetramethylammonium hydroxide), 25% solution in methanol, was purchased from Aldrich.

### Methods

Pyrolysis performed in this study was carried out using a SGE's Pyrojector II microfurnace pyrolyser directly connected to the GC/MS system, which consisted of a Clarus 500 Gas Chromatograph interfaced by direct coupling to the Mass Spectrometer (Perkin-Elmer). The gas chromatograph was equipped with a 30m x 0.25mm I.D. fused-silica column coated with a 0.25 $\mu$ m film of RTX<sup>®</sup>5 (Cross bond 5% diphenyl 95% dimethyl polysiloxane). The carrier gas was helium with a head pressure on gas chromatograph of 7.6 psi and 5 psi more in the pyrolyser head. The velocity of the carrier was 37ml/s. The injector and transfer line temperatures were set at 250 °C and 220°C. Samples were injected in the splitless mode, and the oven was programmed as follows: 45°C during 3 min, then 10°C/min to 250°C, hold for 20 min. The operating conditions

for the electron impact mass spectrometer consisted of a source temperature 220°C, a filament emission current of 3.7 $\mu$ A, an ionizing voltage of 70eV, and a scan range from m/z 25 to m/z 1200 with a scan time 0.2s. The mass spectra identifications were carried out by comparison to the NIST 2002 (National Institute of Standard and Technology) as well as to the NBS (N.Y., USA) and Pflieger (Germany) mass spectral libraries. Solid samples were inserted directly into the pyrolyser through a septumless injector.

Reproducible sample sizes are easily achieved. The sample amounts were about 30  $\mu$ g. In case of methylation they were mixed with 5 $\mu$ l of TMAH solution. The same amount of sample was pyrolysed in three replicates, and the variability between replicate pyrograms was minimal. Due to the relatively large surface area of the interface between the GC instrument and the pyrolyser, a memory effect is often obtained, where high molecular weight compounds from previous analysis still produce traces during a subsequent experiment. A blank run (sometimes two or three) was inserted between each pair of actual analyses to be able to rule out such influences.

Pyrolysis of macromolecules produces a wide range of chemical compounds ranging in polarity from non-polar, alkanes and alkenes, to highly polar, e.g. alcohols and carboxylic acids. The polar compounds in particular give useful diagnostic information about the structure of the material. The polar pyrolysis products are normally difficult to measure by GC due to their partial or complete adsorption in the pyrolysis zone, injection system or capillary column. Polar pyrolysates often show peak tailing characteristics, poor reproducibility, long elution times or, in some cases, no chromatographic peaks are obtained. The solution to this problem in conventional gas chromatograph is the derivatization of the polar compounds externally or by co-injection to give compounds which may be efficiently separated. One procedure involves alkylation with derivatising reagents which include TMAH (Fabbri and Helleur 1999). Under high temperatures of pyrolysis and in the presence of strong base (TMAH) it is now generally believed that the chemical reactions involved are a combination of thermally assisted base hydrolysis, pyrolytic bond cleavage and methylation of acidic functional groups as weakly acidic as aliphatic hydroxyl.

### Analytical Pyrolysis

There are three general events that can occur at different temperatures during pyrolysis; mild temperatures (ca. 250°C and below) cause the release or thermal desorption of adsorbed volatile compounds from a substrate. No new compounds are formed. Pyrolysis occurs when a sample is heated to higher temperatures, typically 300°C or higher, rising to more than 650°C. At yet higher temperatures, e.g. 700°C, polycyclic aromatic hydrocarbons are mainly formed by cellulose and similar compounds, due to secondary pyrolysis (Antal 1989).

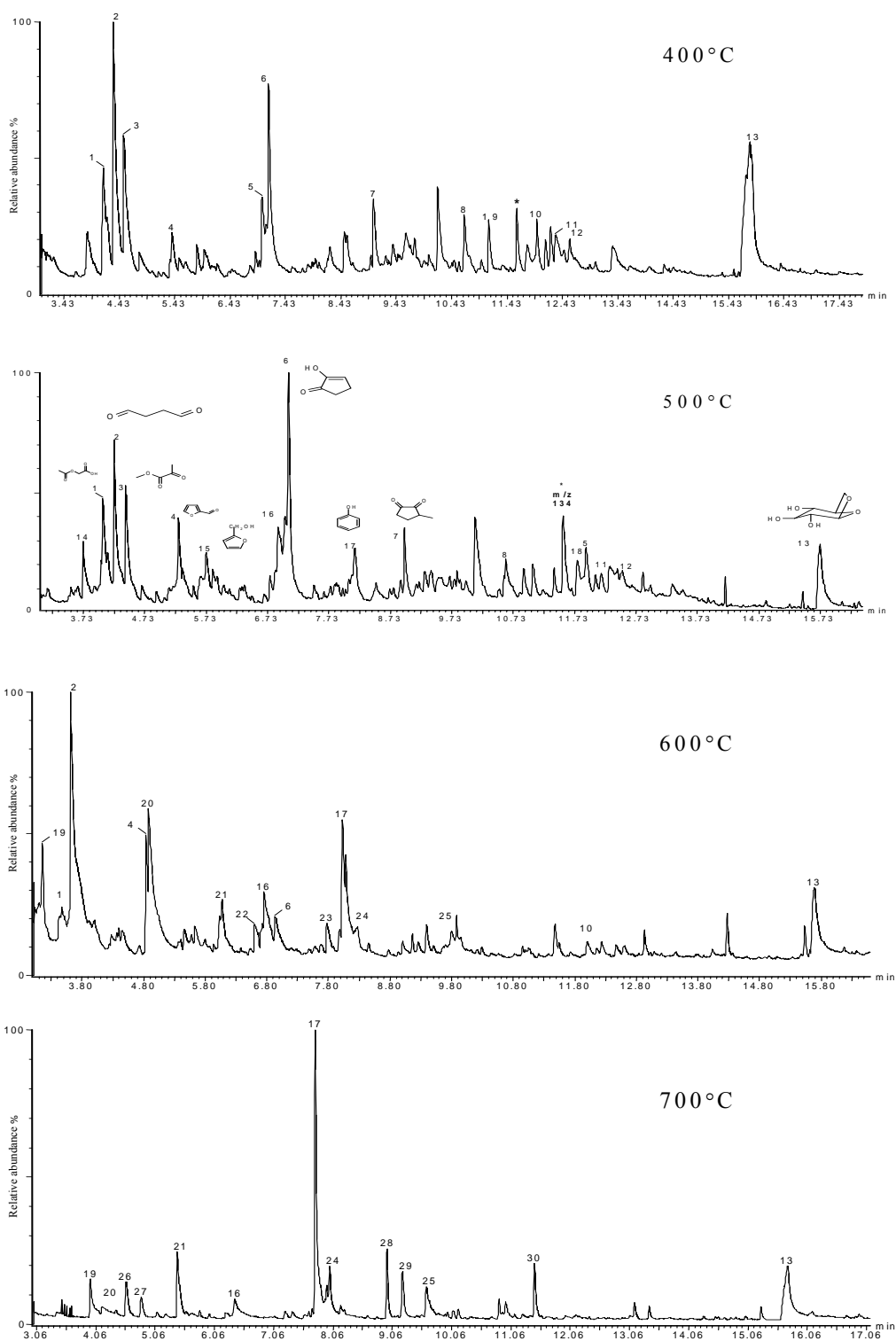
## RESULTS AND DISCUSSION

Characterization of the pyrolysis products revealed minor amounts of the compounds known from pyrolysis of cellulose, i.e. acetic acid, 2-furfural, (2H)-furan-3-one, formic acid, 5-methyl-2-furfural, (5H)-furan-2-one, levoglucosenone, phenol, 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose, 1,6-anhydro- $\alpha$ -D-glucofuranose, levoglucosan, 1H-indol and 2,5-pyrrolidindione (Challinor 1989). The total ion chromatograms obtained by pyrolysis of Whatman filter paper at 4 different temperatures are reported in Fig. 1. They reveal very different major compounds, i.e. at 400°C methylglyoxylate (1), butanedial (2), ethylpyruvate(3), 2-hydroxy-cyclopenten-1-one(6), 1,4-dioxaspiro (2.4) heptan-5-one, 7-methyl- (9) and levoglucosan (13). At 500°C the main fragmentation products were 2-cyclopenten-1-one, 2-hydroxy-(6), followed by glyoxylic acid(1), butanedial (2), methylpyruvate(3), furfural (4), 3-methyl-cyclopentanedione1,2,(7) and levoglu-cosan (13). The Whatman paper pyrogram at 500°C was very similar to the results of Moldoveanu (2001) for non-derivatized cellulose, i.e. furfural and 2-hydroxy 2-cyclopenten-1-one were the main products. At 600°C the main peak has been assigned to butanedial (2), and an increased content of phenol (17) has been observed. At this temperature some aromatic compounds begin to form as toluene (19), styrene (21) and benzofuran (24). The aromatic compounds included toluene (19), xylene (26,27), styrene (21), 1-ethynyl-2methyl-benzene, (28), naphthalene (30), dimethylphenol (29) and a large amount of phenol (17). These compounds correspond to the main peaks in the pyrogram at 700°C.

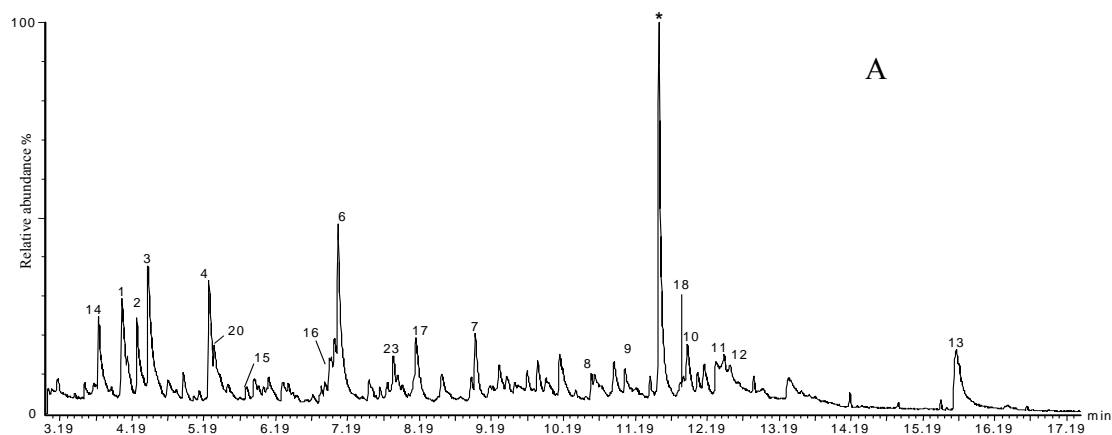
Comparing the analyses at different temperatures of paper, we decided to carry out analysis of real samples at 500°C. This temperature seems to be the best one under our conditions because it gives the formation characteristic and well defined peaks. For sake of simplicity the structures also have been applied only on this pyrogram.

Figure 2 reports the pyrograms obtained by the pyrolysis and chromatographic analysis of different samples of papers of different periods. The pyrograms were very similar and reflect the fragmentation pathway of paper at 500°C, where a large amount of 2-hydroxy-2-cyclopenten-1-one, (6) has been detected. Comparing the ancient samples with standard Whatman paper, the main difference is the high amount of a compound eluted at about 11.50 minutes in the chromatogram A and B. It has been marked by an asterisk, probably is hexopyranose derivative of m/z 128, and has the formula C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>.

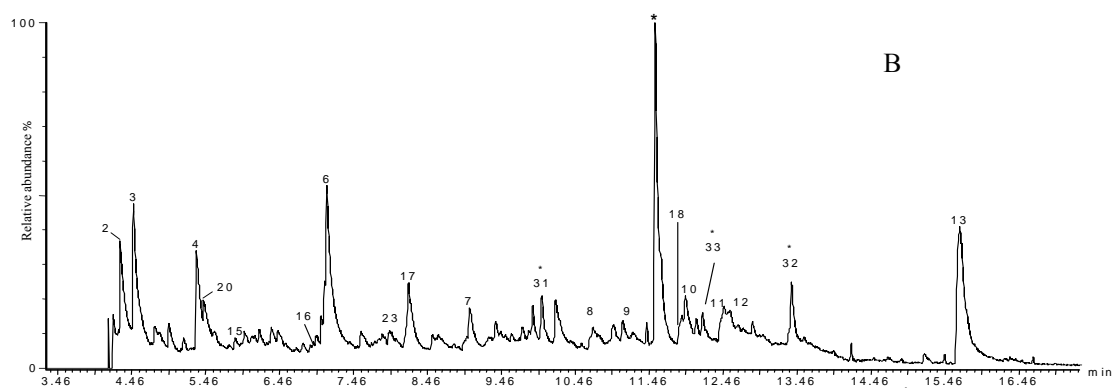
The differences between the papers of the 16<sup>th</sup> and 19<sup>th</sup> centuries are the presence of the peaks in the later marked by \* and namely the presence of methoxyphenol- (31), 2-methoxy-4-vinylphenol(32) and 2,3-anhydro-D-Galactosan(33).



**Figure 1.** Total ion chromatogram obtained from pyrolysis of Whatman paper at four different temperatures. In y-axis relative intensities have been reported, i.e., most abundant ions obtain a relative abundance of 100% and all other ions are shown as a percentage of that most abundant ion. On horizontal x-axis are retention times in minutes.



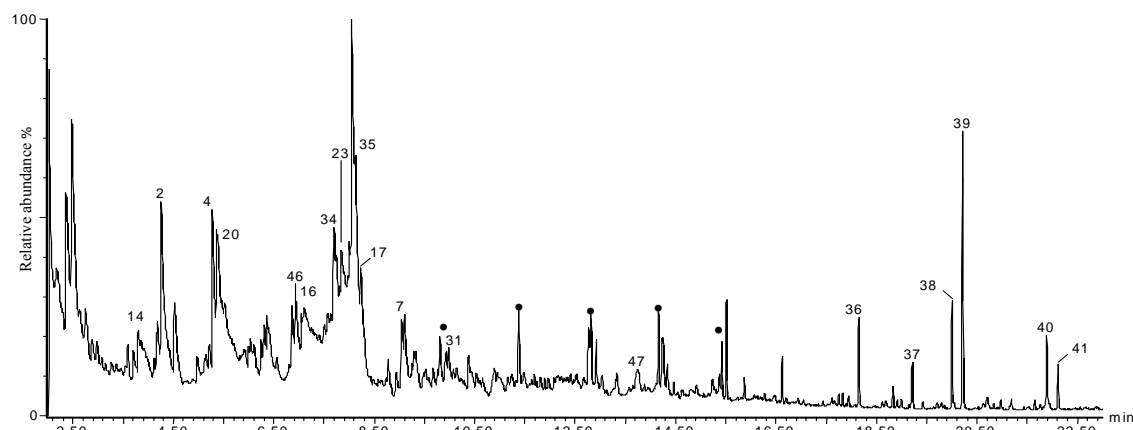
**Figure 2A.** Total ion chromatogram obtained from pyrolysis of an ancient paper of the 16<sup>th</sup> century



**Figure 2B.** Total ion chromatogram obtained from pyrolysis of a paper of 19<sup>th</sup> century

### Pyrolysis in the Presence of TMAH

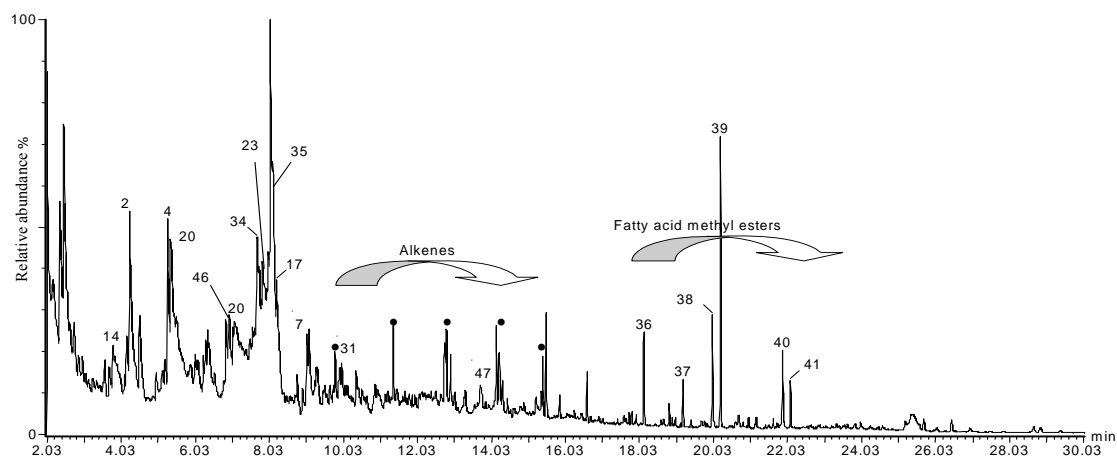
Since the above pyrolysis results afford little information about polar molecules, we performed pyrolysis in the presence of tetramethylammonium hydroxide (TMAH). This method was first developed for the analysis of phenolic polymers (Moldoveanu 2001). It was used for both an efficient cleavage of polar bonds and the subsequent methylation of OH and NH<sub>2</sub> groups. Figure 3 reports the total ion chromatogram obtained from pyrolysis and methylation of Whatman paper at 500°C.



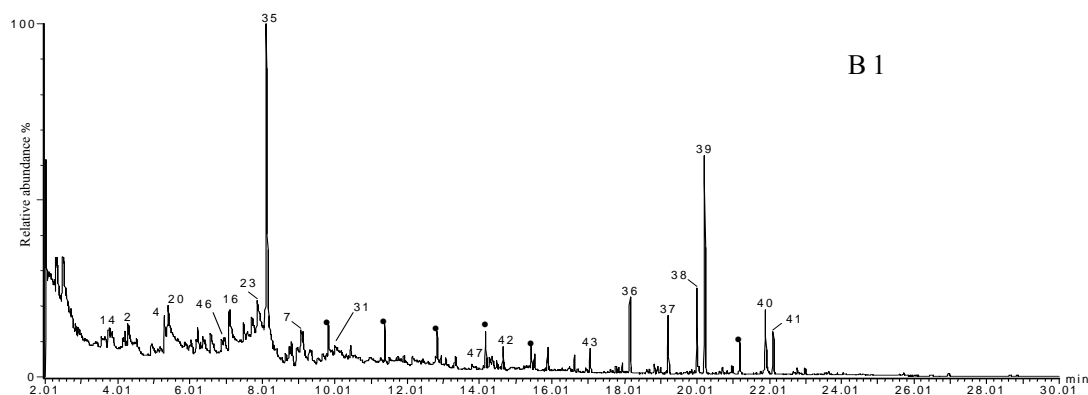
**Fig. 3.** Total ion chromatogram obtained from pyrolysis and methylation of Whatman paper at 500°C.

The chromatograms obtained from the pyrolysis and methylation of paper dated 1567 and 16<sup>th</sup> century are shown in Figs. 4 and 5. They seem very similar to each other, but they differ significantly from the previous analysis without derivatisation. The main compound in the two pyrograms of the ancient paper has been identified as methoxy-methylbenzene (35), while in the pyrogram of paper the most intense peak eluted at 7.05 minutes and has been identified as 2-hydroxy-3-methyl-2-cyclopenten-1-one.

The chromatograms of the ancient paper differ from that of Whatman paper also because of the presence of two compounds eluted at 14.65 min and 17.05 min. Even comparing their mass spectra with those of NIST 2002 library, their identification is not clear. They could probably be methyl-4,6-decadienyl ether (42) and methyl-6,8-dodecadienyl ether (43), respectively. Adopting the methylation technique a series of alkenes (marked by •) and fatty acids methylesters (36-41) were detected. Peak 34 present in paper has not been detected in ancient paper.



**Figure 4.** Total ion chromatogram obtained from pyrolysis of paper dated 1567 in the presence of TMAH



**Figure 5.** Total ion chromatogram obtained from pyrolysis of paper of 16<sup>th</sup> century in the presence of TMAH

## CONCLUSIONS

Although only preliminary results have been reported this study shows that THM in connection with GC/MS can be effectively used to specify different kind of papers. Through the analysis of whatman paper as model compound, a series of methylated benzenecarboxylic acid derivatives were tentatively identified. In conclusion, the Py-GC/MS technique considered to be useful tool in characterizing paper and the naturally aged papers.

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