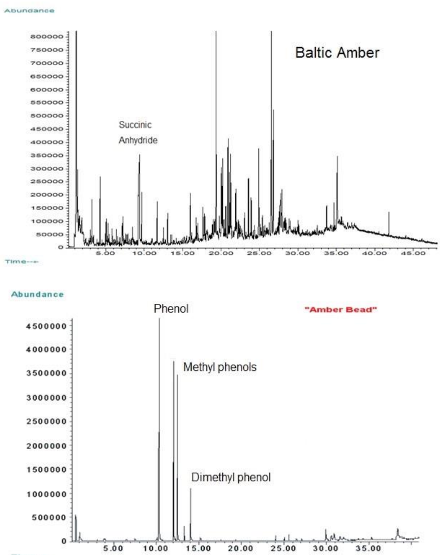
A Practical Applications Guide for Analytical Pyrolysis -GC/MS

Arts and Antiquities

Genuine and Imposter Ambers

Amber, fossilised tree resin, appreciated for its natural beautify, has often been made into decorative objects. There are different classes of ambers; identifying the type of amber can help us understand the history behind a certain object. In the following example, two artifacts were pyrolysed at 650°C. Natural ambers produce terpenes, and succinic anhydride is indicative of Baltic ambers. The second artifact, contains no terpenes, just phenols and methyl phenols, indicating that this artifact is not real amber, but just a phenolic resin.

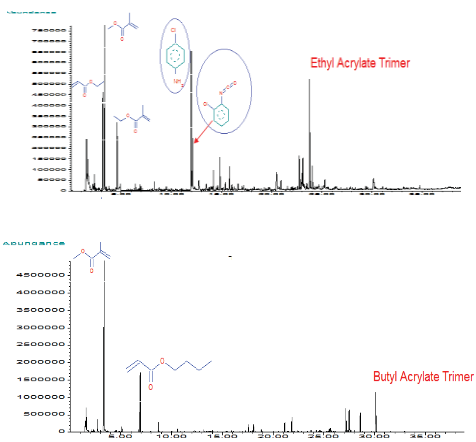


Baltic Amber (top) and Imposter Amber (bottom), 650°C.

Pyroprobe Setting	
Set-point:	**650°C for 15 s**
Valve Oven:	**300°C**
Transfer Line:	**325°C**
GC/MS Setting	
Column:	**5% Phenyl**
Carrier:	**Helium, 50:1 split**
Injector:	**325°C**
Oven:	**40°C for 2 min**
	8°C/min to 295°C
Scan Range:	**35-550 amu**

Acrylic Artist Paints

When caring for or restoring artwork, it's important to know the type of materials the artist used. Pyrolysis can be used to distinguish between different artists paints. The example are pyrograms of two yellow acrylic paints. The top pyrogram has peak for ethyl acrylates trimer, indicating poly ethyl acrylate is present. The bottom paint instead contains butyl acrylate, as evidenced by its trimer. Also, pyrolysis products from organic pigments can be seen in the Hansa yellow paint. Pyrolysis products of this yellow pigment are circled in blue.



Two yellow acrylic paints- yellow light Hansa (top) and cadmium (bottom).

Pyroprobe Setting

Set-point:	700°C 15s
Valve Oven:	300°C
Transfer Line:	325°C

GC/MS Setting

Column:	5% phenyl
Carrier:	Helium, 75:1 split
Injector:	300°C
Oven:	40°C for 2 min
	10°C/min to 325°C
Scan Range:	35-550 amu

Natural Dyes in Textiles

TMAH can be useful when analysing for natural dyes. Carminic acid is the active ingredient in a natural dye called cochineal. When trying to analyse it thermally, it simply disintegrates, and no useful information is obtained (Figure 1). When treated with TMAH, carminic acid breaks apart in much larger fragments, and distinct characteristic peaks appear at the end of the chromatogram. For derivatisation, 10 microliters of 25% TMAH in Methanol was added to about 100micrograms of sample prior to heating.

Figure 2 is a pyrogram of denim fabric containing Indigo dye. A small peak for the dye can be seen at about 31 minutes. However, when the dye is treated with TMAH (Figure 3), methylated indigo is seen as a sharp, dominant peak in the chromatogram.

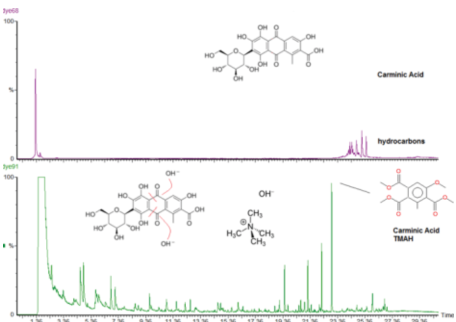


Figure 1: Carminic acid (top) and Carminic acid with TMAH (bottom)

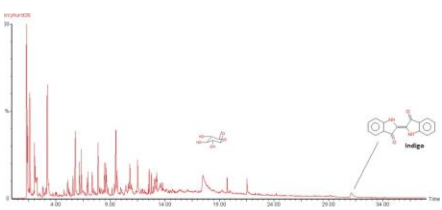


Figure 2: Denim Fabric

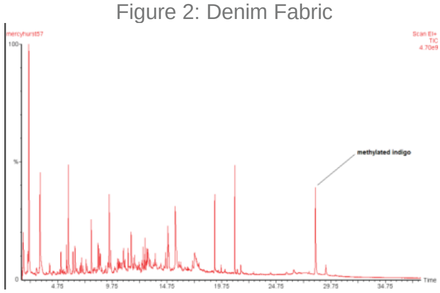
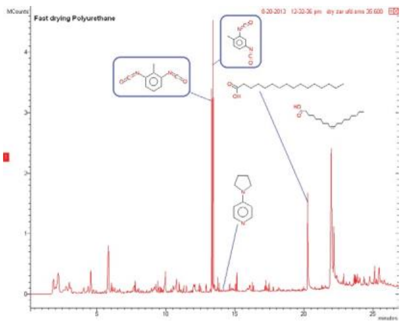


Figure 3: Denim Fabric with TMAH

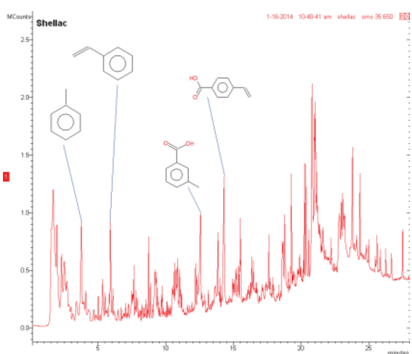
Pyroprobe Setting	
Set-point:	600°C for 15 s
Valve Oven:	325°C
Transfer Line:	325°C
GC/MS Setting	
Column:	5% Phenyl
Carrier:	Helium, 50:1 split
Injector:	325°C
Oven:	40°C for 2 min
	10°C/min to 300°C
Scan Range:	25-600 amu

Varnish Coatings

Frequently, antiquities are covered with hard coatings like varnishes. To best preserve the artifact, the coating must be identified properly. Coatings can be natural or synthetic. A synthetic coating, like a polyurethane always regenerates the diisocyanate it was made with. In the following example, this fast drying polyurethane was made with toluene diisocyanate (TDI), circled in blue. Shellac, however is made from a natural resin secreted by insects. When pyrolysed, it generates benzoic acids, and other aromatics like styrene and toluene.



Polyurethane Coating



Shellac Pyrogram

Pyroprobe Setting	
Set-point:	700°C for 15 s
Valve Oven:	325°C
Transfer Line:	325°C

GC/MS Setting	
Column:	5% Phenyl
Carrier:	Helium, 50:1 split
Injector:	325°C
Oven:	40°C for 2 min
	10°C/min to 300°C
Scan Range:	25-600 amu

Analysis of Pigments

Pyrolysis can be used to identify types of organic pigments used in paints. Pyrolysis of these pigments leave behind fragments which relate to the parent molecule. In this next example, blue and red pigments are pyrolysed. Phthalocyanine Blue, a nitrogen containing complex surrounding copper, produce aromatics with nitriles. While a Quinacridone (Red 122), also containing nitrogen, but in a much different configuration, produces aromatic amines.

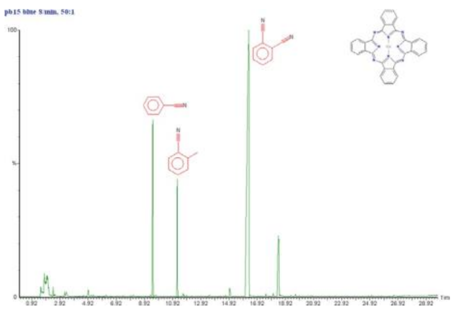


Figure 1. Phthalocyanine Blue Pigment, 700°C.

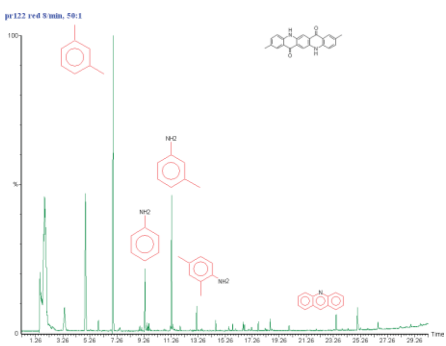
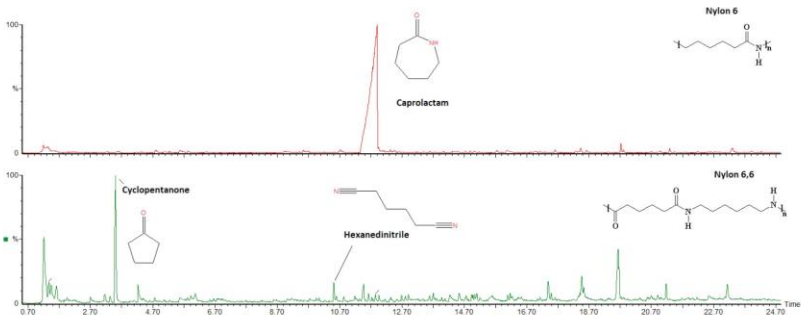


Figure 2. Red Pigment 122, 700°C.

Pyroprobe Setting	
Set-point:	**700°C for 15 s**
Valve Oven:	**325°C**
Transfer Line:	**325°C**
GC/MS Setting	
Column:	**5% Phenyl**
Carrier:	**Helium, 50:1 split**
Injector:	**325°C**
Oven:	**40°C for 2 min**
	8°C/min to 295°C
Scan Range:	**35-550 amu**

Distinguish between Similar Nylon Fibres

Materials in artwork which may have a similar look and feel could be either slightly, or entirely different, polymerically. In this example, two nylon fibers pyrolysed. The type of nylon will not be distinguished using FTIR, however pyrolysis GC-MS can easily characterise them. Nylon 6 produces a large peak for caprolactam, the monomer. Nylon 6,6 instead produces a peak for cyclopentanone and hexane dinitrile, both of which are related to Nylon 6,6 monomers.



Nylon 6 (top), Nylon 6,6 (bottom), 750°C.

Pyroprobe Setting

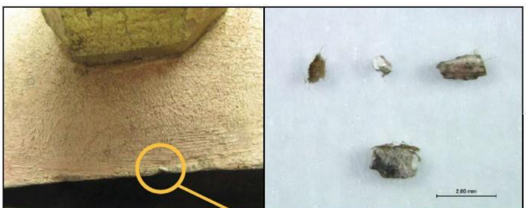
Set-point:	750°C for 15 sec
Valve Oven:	325°C
Transfer Line:	325°C

GC/MS Setting

Column:	5% Phenyl
Carrier:	Helium, 50:1 split
Injector:	325°C
Oven:	40°C for 2 min
	10°C/min to 300°C
Scan Range:	25-600 amu

Mask Materials from Opera Museum

In order to preserve items of cultural heritage, the type of material first needs to be known. Different components of masks from the Opera Museum of Paris, France were analysed using Pyrolysis GC-MS. Of these components, very tiny pieces of the mask coating were analysed. Methyl methacrylate monomer and ethyl acrylate oligomers were present, as well as dioctyl phthalate. So, the coating is composed of a methyl methacrylate and ethyl acrylate copolymer containing dioctyl phthalate plasticiser. Also, the presence of acetic acid and ethyl acetate indicate a polyvinyl acetate adhesive also exists.



Mask of the Opera Museum, Paris, France- created by the Company. Jules Ferry (1981, Houdart): theater copyright BNF.

Pyroprobe Setting

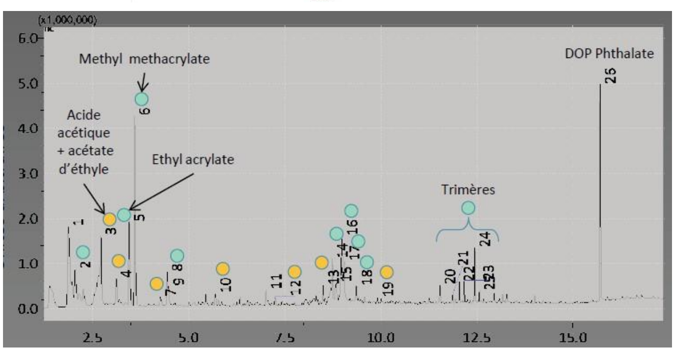
Set-point: 600°C

Valve Oven: 325°C

Transfer Line: 325°C

Analysis performed at the laboratory of the Bibliothèque nationale de France (BnF)

Physical chemistry center, Bussy Saint Georges site



Mask Coating, 600°C Peaks marked with blue indicate pyrolysis products of the paint. Peaks marked with yellow indicate pyrolysis products of the adhesive. Analysis performed at the laboratory of the Bibliothèque nationale de France (BnF)

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