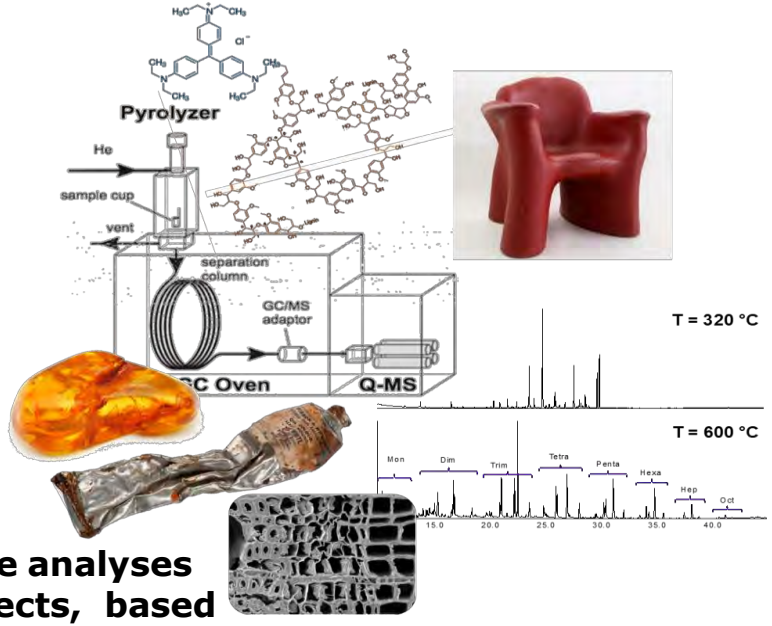
Analytical Pyrolysis to Investigate Organic Materials in Heritage Science

Webinar Invitation
Thursday, 17th of September 2020, 11:00am – 12:00pm (UTC+2h)

Speakers:

Dr. Michael Soll
EU Business Development Manager
Frontier Laboratories
michael@frontier-lab.com

Prof. Francesca Modugno
University Pisa
Department of Chemistry and Industrial Chemistry
francesca.modugno@unipi.it



TOPICS:

Analytical Pyrolysis & µFurnace Pyrolyzer Technology
Introduction of Analytical Method Map
Recent advances in the qualitative and semi-quantitative analyses of organic materials in ancient and modern heritage objects, based on analytical pyrolysis coupled to mass spectrometry.

Please follow registration link https://bit.ly/2XRNfMP to receive the confirmation & password !

1. Frontier Lab-a Brief History

- Frontier Laboratories, Ltd. was founded in 1991 by Dr. Chu Watanabe (Chu-san). Dr. Watanabe, with the support of polymer scientists at Nagoya University in Japan, developed a pyrolyzer based on a *vertical micro-furnace design.*
- We are a global corporation and our main products, supported by a number of accessories and software, include the EGA/PY-3030D Multi-Functional Pyrolysis System, the PY-3030S Single-Shot Pyrolyzer, the 3050 series of Rapid Screening Reactors for catalyst screening, and a line of Ultra ALLOY® stainless steel capillary columns.

Office Locations:

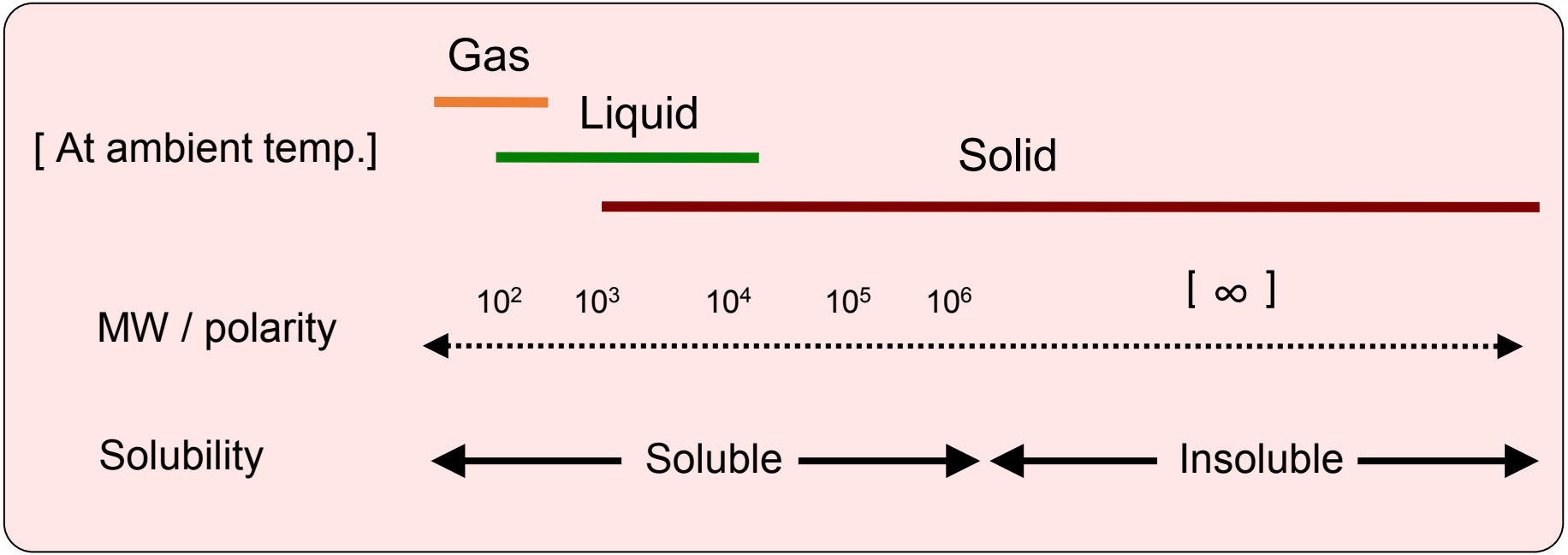
- **Japan (Headquarters)**
- **North America**
- **Germany (Europe)**
- **Singapore (Asia/Oceania)**
- **India**
- **China**
- **Russia**

Frontier Laboratories Europe, Essen, Germany: +49 1716488148 / michael@frontier-lab.com

30 Years of Passion for Analytical Pyrolysis

Leading the Way in Material Characterization

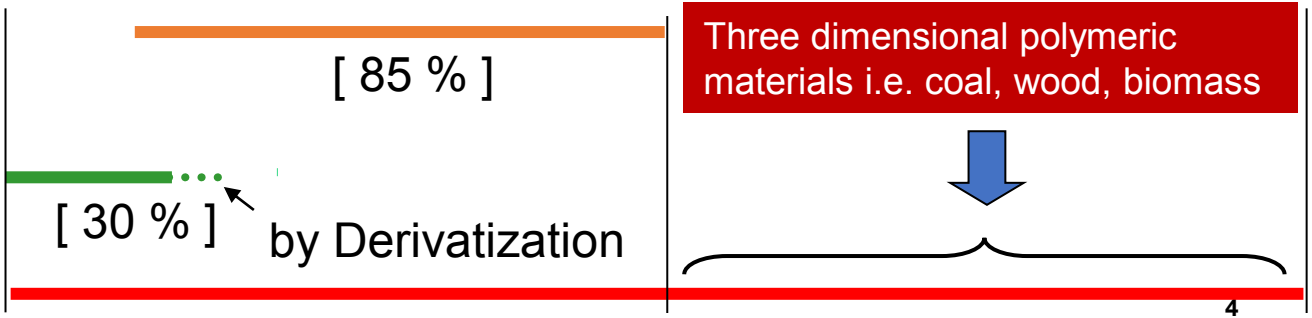
Expansion of Application Areas with Py-GC/MS



LC, LC/MS

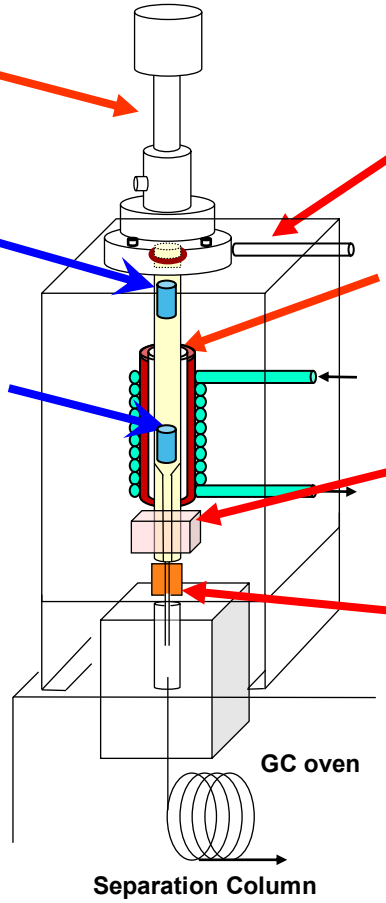
GC, GC/MS

Py-GC, Py-GC/MS



EGA-MS, Thermal Desorption (TD), Reactive Pyrolysis (RxPy)

Schematic diagram of Multi-Shot pyrolyzer EGA/PY-3030D



Sample cup

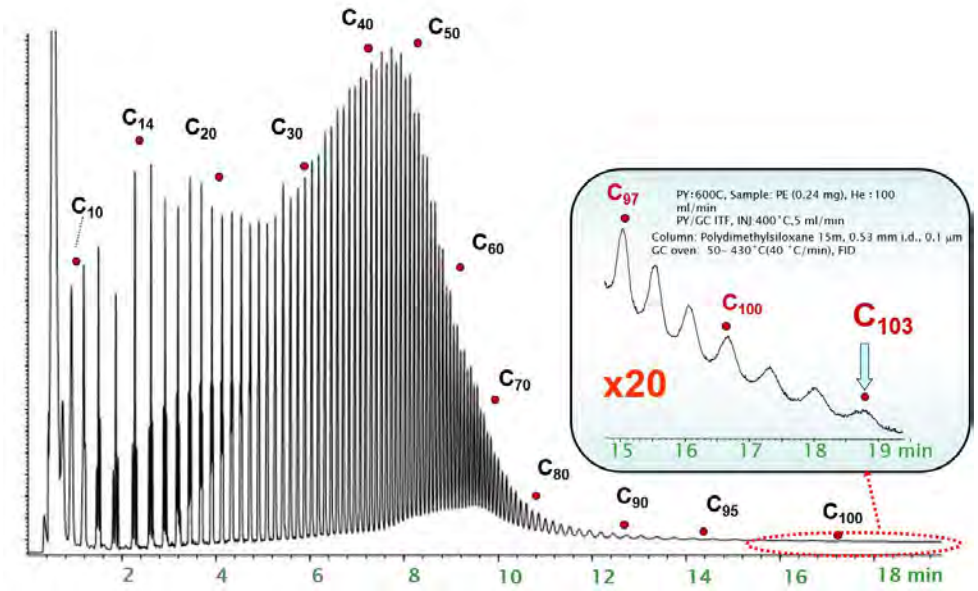
- Stainless steel with deactivated coating
- Put liquid and solid samples

Volume: 50µL 80µL

Micro-Furnace Technology

Full Range Analysis (low MW, high MW, and Polar Compounds)

FID pyrogram of Polyethylene at 600℃



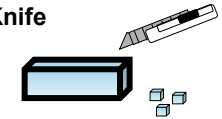
Micro-Furnace Technology:

- Directly deposits all pyrolyzates on-column in a single step process
- No switching valves
- No trap
- No transfer line
- No Pre-heating Prior to Pyrolysis
- Heavy and polar compounds are directly placed on-column and light compounds are never lost.

Easy Sample Preparation

Step 1

Knife

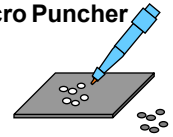


Polymer Prepper

Filed; Cryo milled

Micro Syringe

Micro Puncher



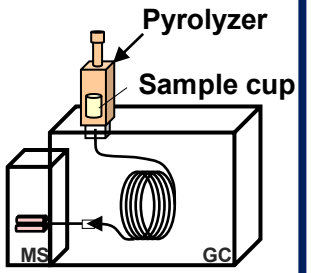
Step 2

Weigh the sample into the sample cup

No Solvent Extraction

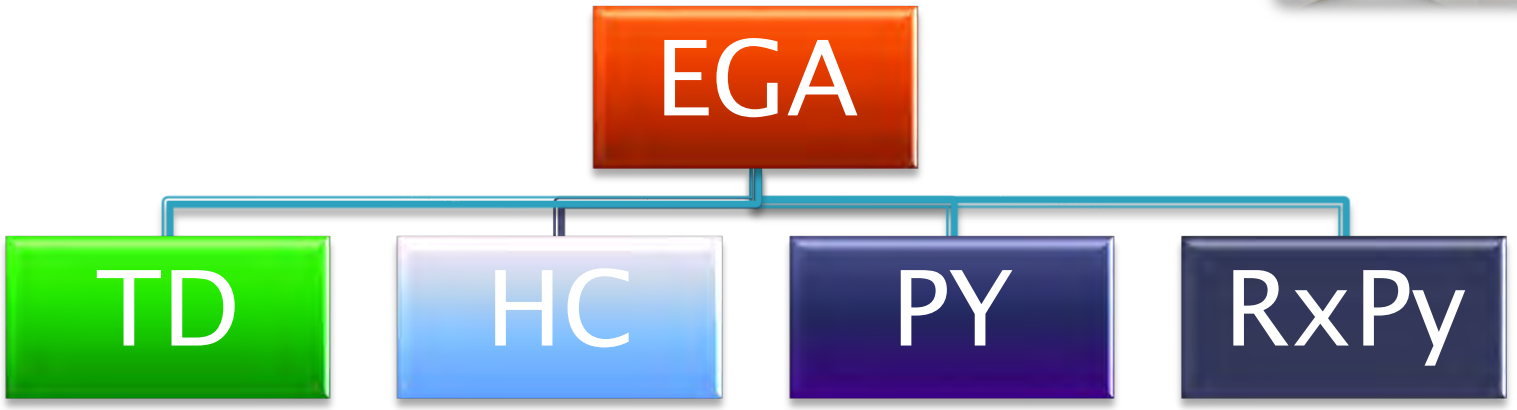
Sample

Step 3



Ready for Analysis !!

“Method Map” for Materials Characterization

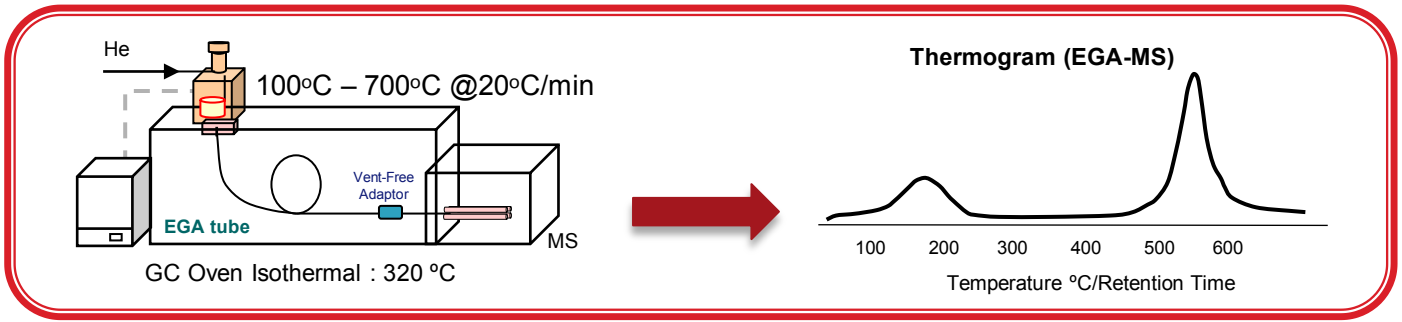


EGA	Evolved Gas Analysis
TD	Thermal Desorption
HC	Heart-Cutting
PY	Pyrolysis
RxPy	Reactive Pyrolysis

Evolved Gas Analysis: Rapid Screening

1st step in the "Method Map"

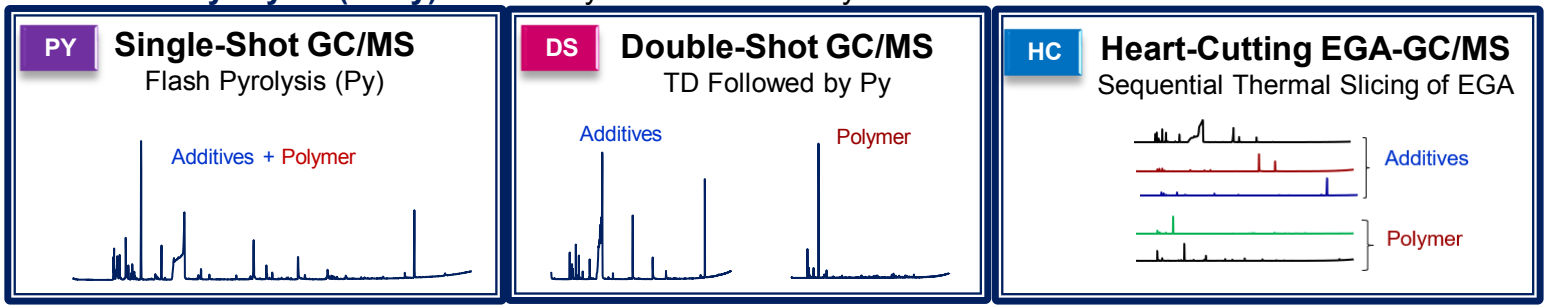
- No column is used; a short, small diameter (2.5m, 0.15 mm id.) deactivated tube connects the injection port to the detector
- The sample is dropped into the furnace which is at a relatively low temperature (*ca.* 40-100˚C). The furnace is then programmed to a much higher temperature (*ca.* 600-800˚C)
- Compounds "evolve" continuously from the sample as the temperature increases. A plot of detector response versus furnace temperature is obtained



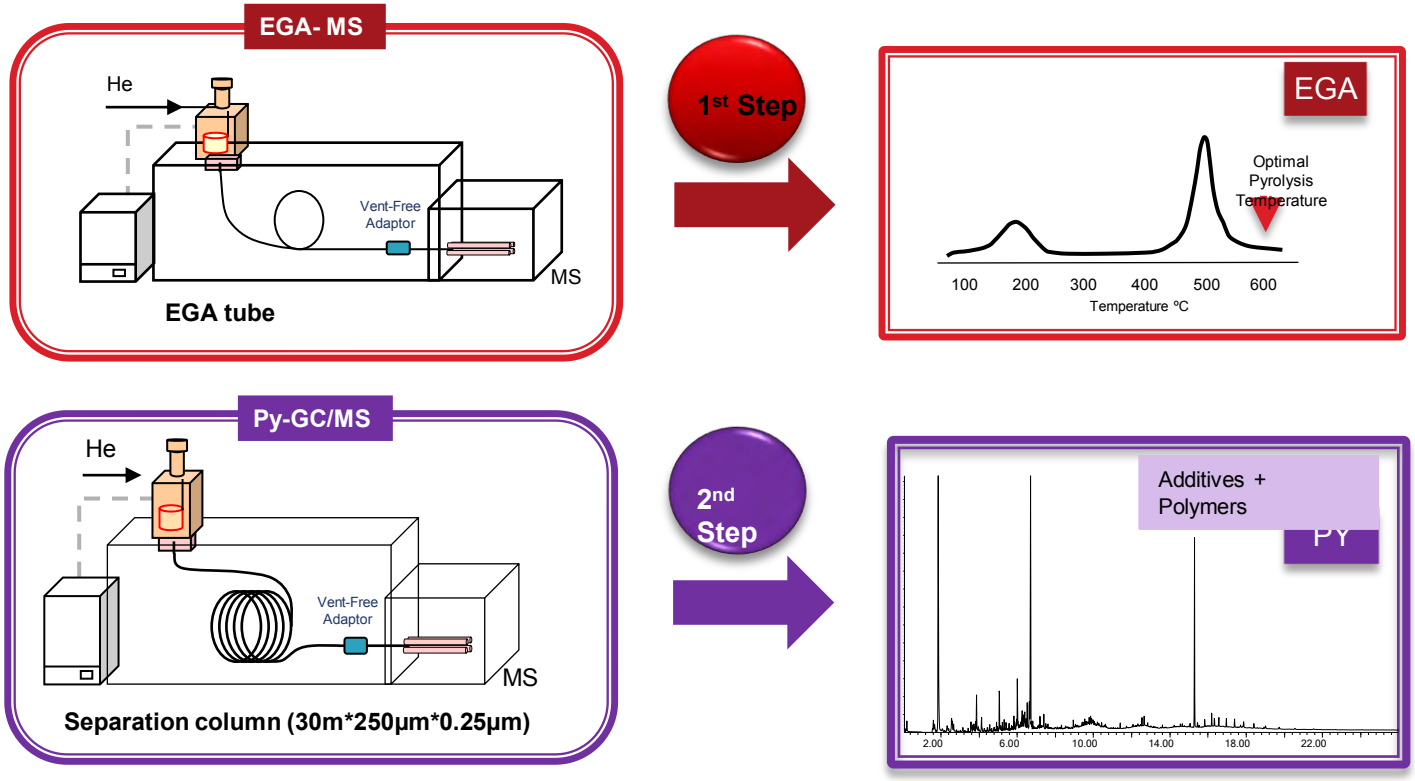
Isothermal &Temperature Programmed Micro Furnace Techniques

2nd step: Use the EGA thermogram and selected ion chromatograms (EIC) to define the thermal zones of interest and then perform one or combination of the following techniques:

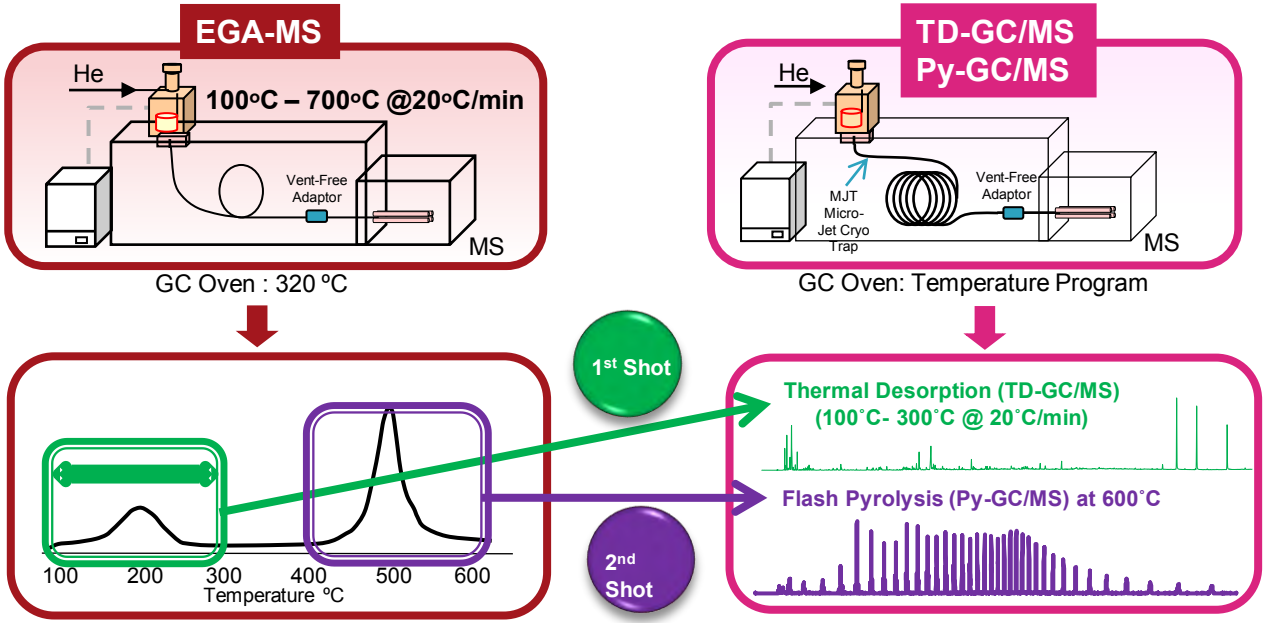
- **Thermal Desorption (TD):** Thermal Extraction of additives & volatiles (No solvent extraction or sample pretreatment)
- **True Flash Pyrolysis (Py):** Single-Shot GC/MS; polymer analysis
- **Double-Shot GC/MS:** Thermal Desorption followed by Flash Pyrolysis on one sample
- **Heart Cutting (HC):** Thermally slicing EGA thermogram (up to 8 programmable temperature zones); deformulation/reverse engineering, failure, “Good vs. “Bad”, and contamination analysis
- **Reactive Pyrolysis (RxPy):** Thermally assisted thermolysis & derivatization



Flash Pyrolysis (Single-Shot GC/MS)



Double-Shot: Thermal Desorption + Pyrolysis



- EGA-MS is the recommended first step to characterize a sample and uses an uncoated metal tube **(2.5m x 0.15mm i.d.)** to connect the GC inlet to the MS. **TD followed by PY on a single sample is called a Double-Shot.**
- Subsequent analyses (TD-GC/MS and Py-GC/MS) are performed using an analytical column **(30m x 0.25mm x 0.25µm).** Switching from the tube to the column takes only minutes using the Vent-free Adapter (VFA).

Heart-Cutting-GC/MS: Sequential Thermal Slicing of EGA-MS

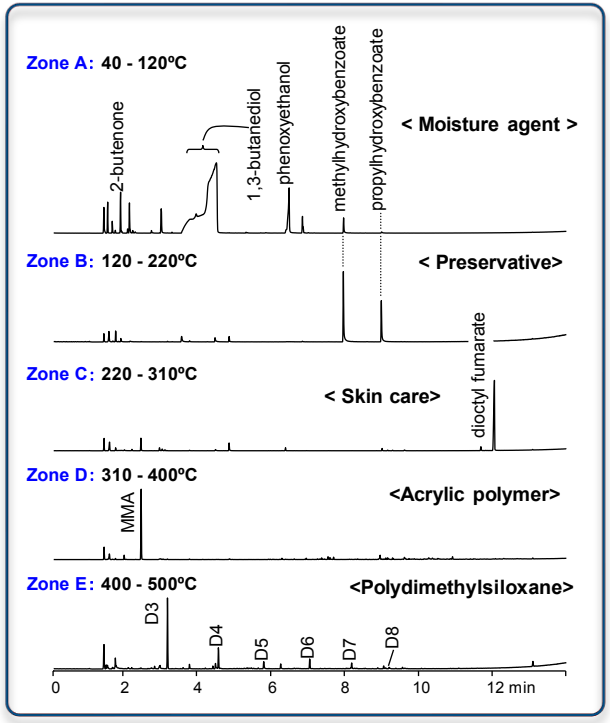
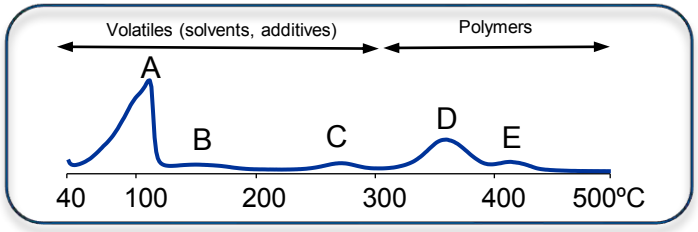
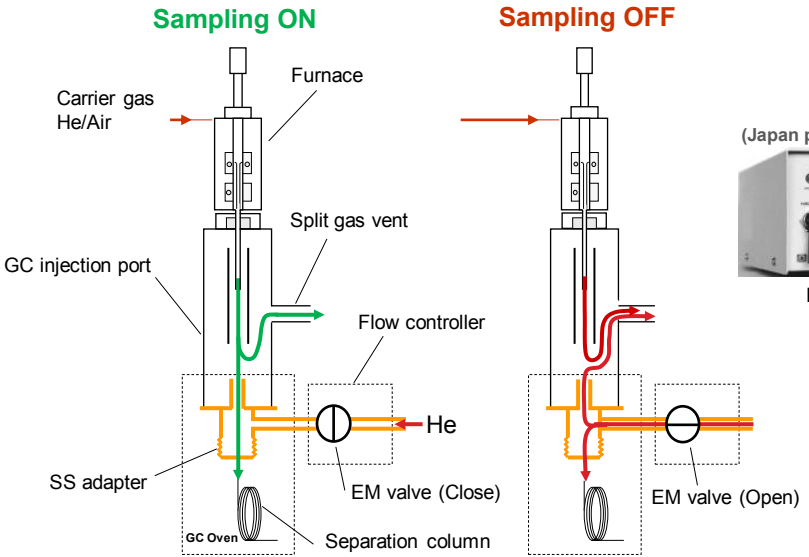


Figure.1: Heart-cut EGA-GC/MS analysis of zones A to E of EGA thermogram of an eyeliner.



Selective Sampler



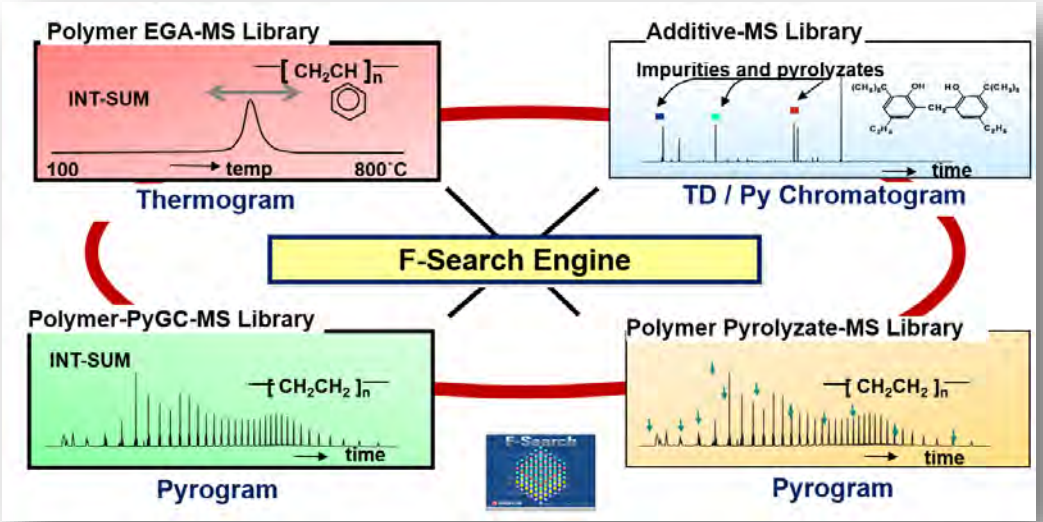
(Japan patent No.3290893)

Flow controller

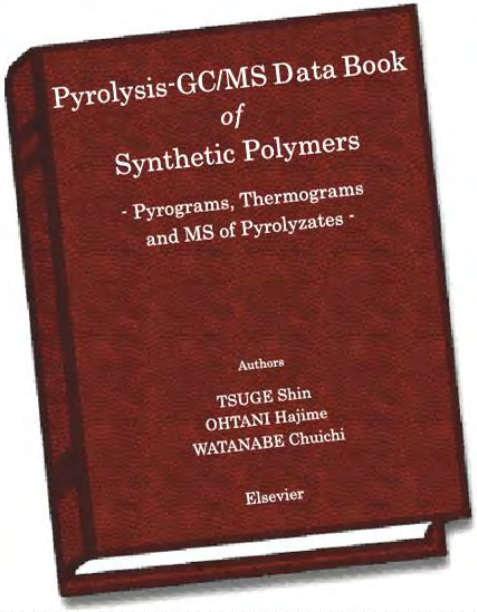
Simplify and Improve Data Interpretation Using F-Search

Identification of polymers and additives from data obtained by evolved gas analysis, thermal desorption, or pyrolysis GC/MS analysis. User library can also be created.

1) EGA-MS polymer library : 1000 polymers stored (300 newly added)
2) PyGC-MS polymer library : 1000 polymers stored (300 newly added)
3) Pyrolyzate-MS library : 268 polymers stored (103 newly added)
4) ADD-MS library : 494 additives stored



Pyrolysis GC/MS Data Book of Synthetic Polymers



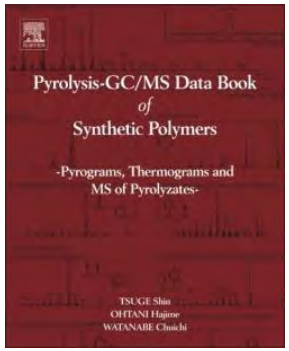
- ***TSUGE Shin, Nagoya University***
- ***OHTANI Hajime, Nagoya Institute of Technology***
- ***WATANABE Chuichi, Frontier Laboratories Ltd.***

Features:

- **Data compilation of pyrograms, thermo- grams and MS data of major pyrolyzates for 163 typical polymer samples with detailed peak assignment Tables and Thermograms for each polymer.**
- **Data compilation of pyrograms of 33 condensation polymers through reactive pyrolysis (RP) in the presence of tetramethyl ammonium hydroxide (TMAH) with the detail detailed peak assignment.**

Search ISBN “9780444538925” in Amazon books

Multi-functional pyrolysis system 3030



PY Data book

Pyrolysis - GC/MS Data Book of Synthetic Polymers

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WATANABE Chuichi,
Frontier Laboratories Ltd.

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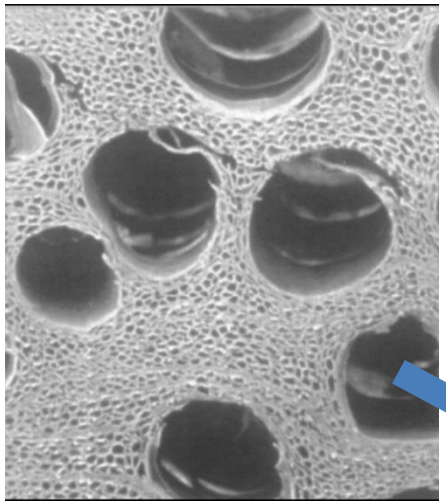
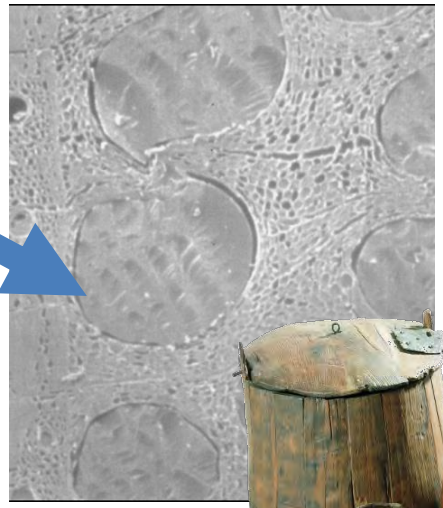
Analytical Pyrolysis to Investigate Organic Materials in Heritage Science

Francesca Modugno

[1] SCIBEC , Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy
http://www.scich.it francesca.modugno@unipi.it





Frontier Lab Webinar
September 17th 2020

Organic materials in **heritage objects**

Chromatography

Mass spectrometry

Analytical pyrolysis

To investigate **organic materials** in **cultural heritage** objects: their **composition**, their **ageing processes**, their **interactions**…to support the knowledge of heritage objects and the development of **conservation** strategies

Outline

- Analysis of **organic materials in heritage objects**: **what, why, how**
- The **role of analytical pyrolysis**: why and when using analytical pyrolysis to investigate polymers in heritage objects
- What kind of information can be obtained using different analytical assets - Py-GC-MS, EGA-MS, multi-shot Py-GC-MS - applications to case studies: **archaeological wood** and **plastic design objects**

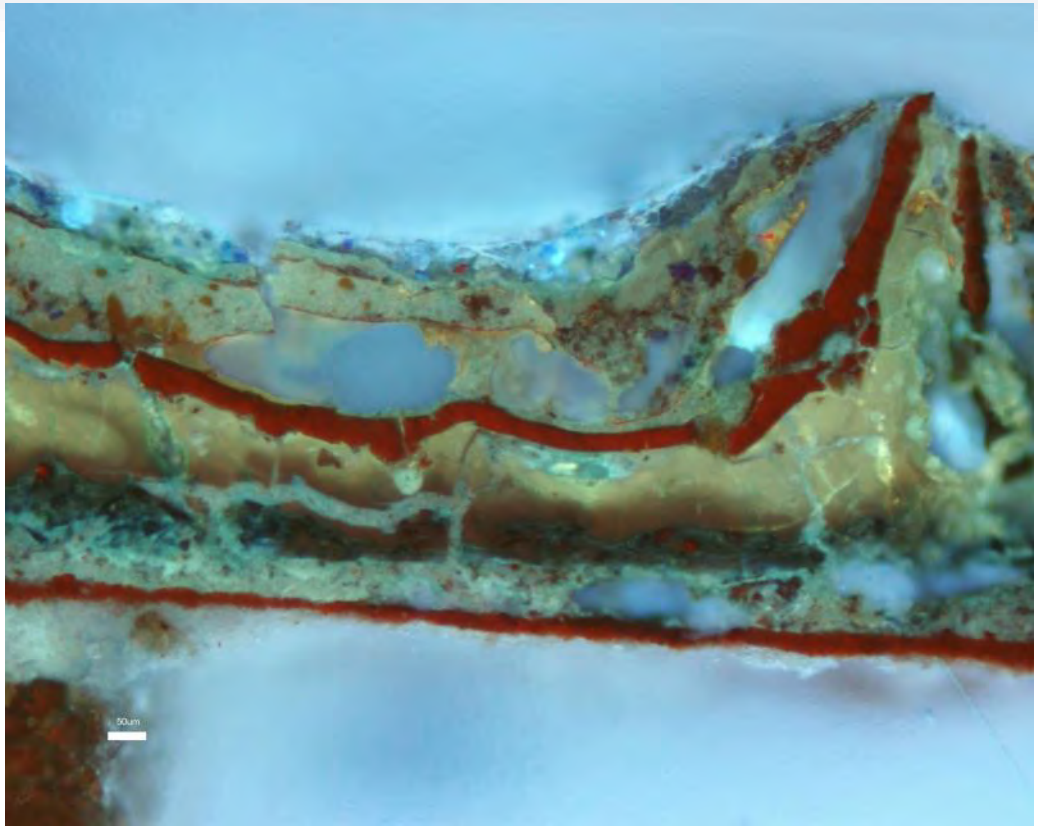
La Nasa et al., 2020 Molecules, 25(7), 25071705

Tamburini et al., 2016, Journal of Analytical and Applied Pyrolysis 122, 429-441

Degano et al., 2018 , Angewandte Chemie - International Edition 57(25), pp. 7313-7323

Organic materials in heritage objects: what

- **Paints and varnishes**



Cross-section of a paint sample

Annunciazione, Beato Angelico, San Marco, Firenze

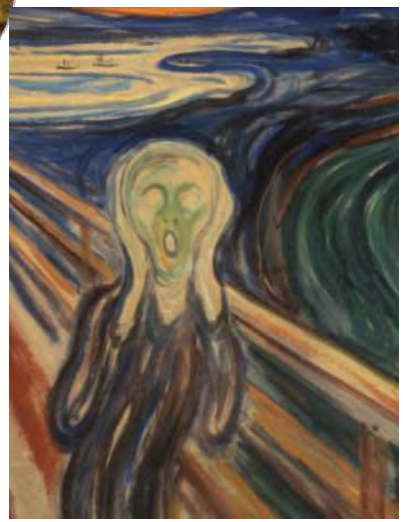
Stravinsky fountain, Niki de Saint Phalle, paris

Organic materials in heritage objects: why?

Edvar Munch palette from the artist's atelier , Munch Museum, Oslo

Organic materials in heritage objects: why?

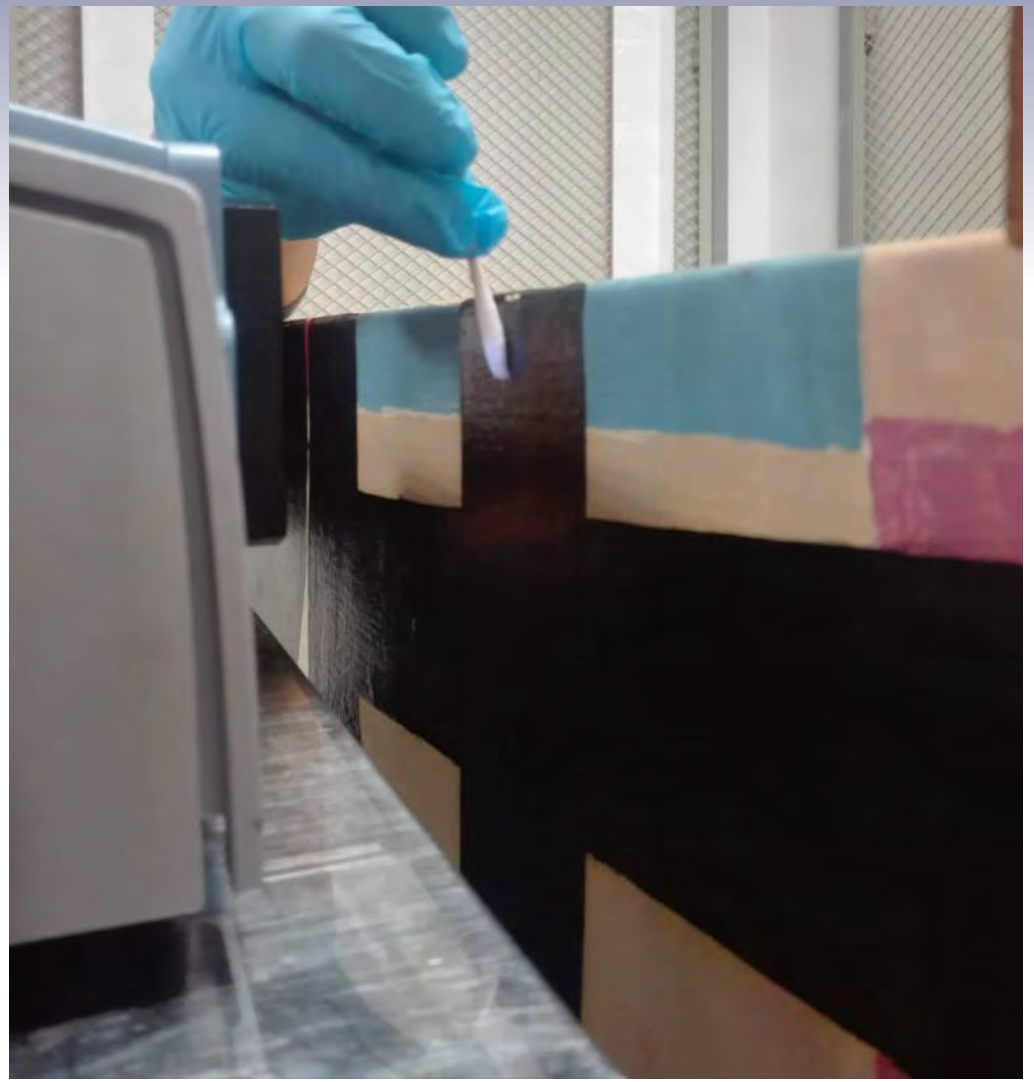
To study paint techniques and paint materials art history, authentication, attribution



Atelier materials from Edvar Munch studio, Munch Museum, Oslo

Organic materials in heritage objects: **why?**

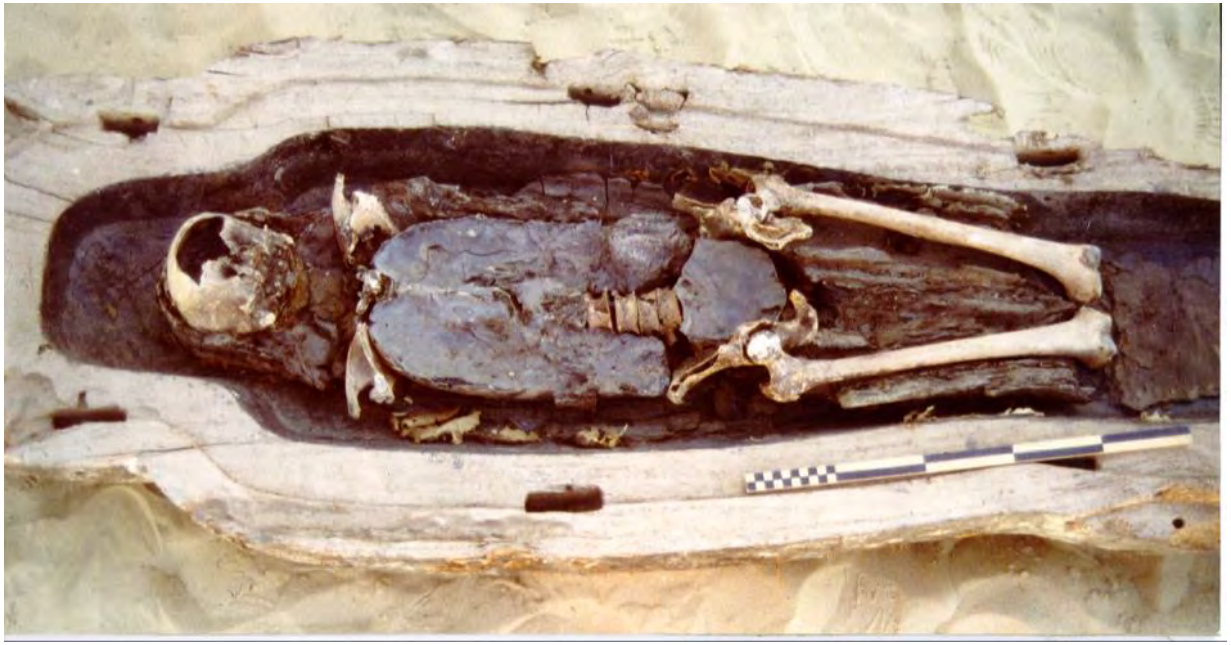
To investigate degradation processes and to select the best preventive conservation condition, cleaning or restoration procedures



The cleaning of a painting by Giuseppe Capogrossi, GNAM, Rome

Organic materials in heritage objects: what

- Paints and varnishes, laquers e.g. urushi
- **Archeological amorphous residues**



Merneith mummy, Fayyum, Egypt, 7th century BC

Balms in Roman unguentaria from Oplontis (1h century AD)

Organic materials in heritage objects: **why?**

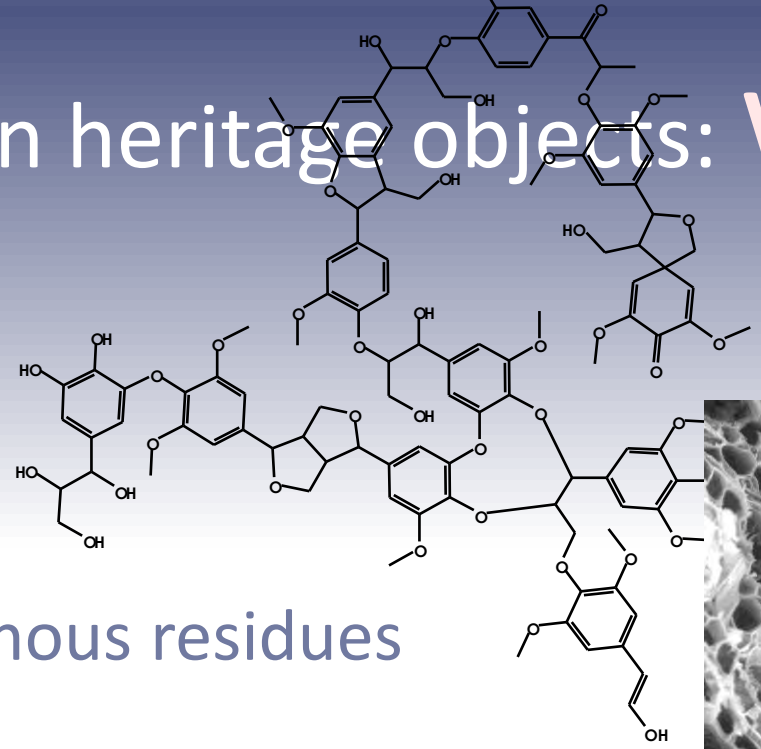
Archeological organic residues:

- technologies and practices in past societies
- use of vessels and trade routes

Roman ship, Pisa

Coptic Egyptian lamp, Egyptological Museum, Florence

Organic materials in heritage objects: what

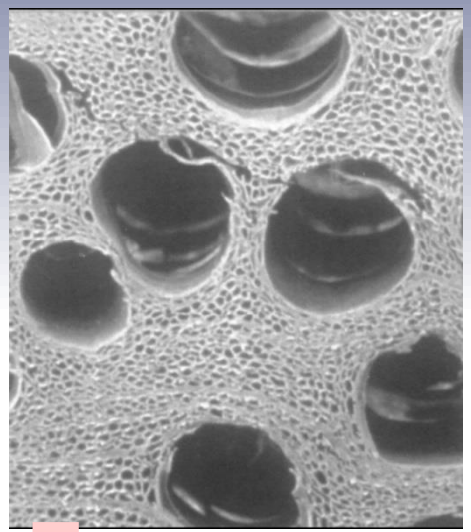


- Paints and varnishes
- Archeological amorphous residues
- **Lignocellulosic materials (wood, paper)**

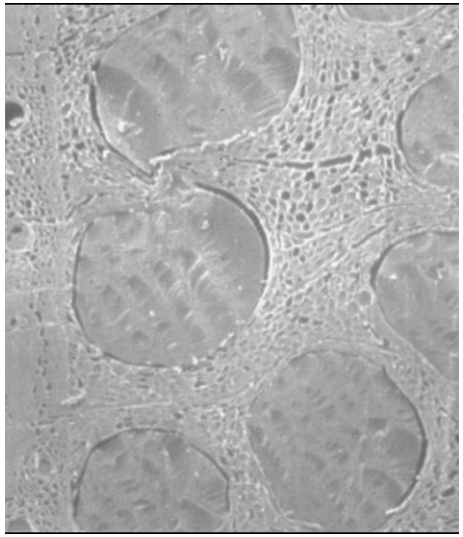
Oseberg Viking ship and findings, Oslo

Organic materials in heritage objects: what

- Paints and varnishes, laquers
- Archeological amorphous residues
- Lignocellulosic materials (wood, paper)
- **Conservation materials (consolidants, coatings, adhesives..)**



MMA polymerised in-wood



Organic materials in heritage objects: what

- Paints and varnishes
- Archeological amorphous residues
- Lignocellulosic materials (wood, paper)
- Conservation materials (consolidants, coatings,..)
- **Modern plastic objects**

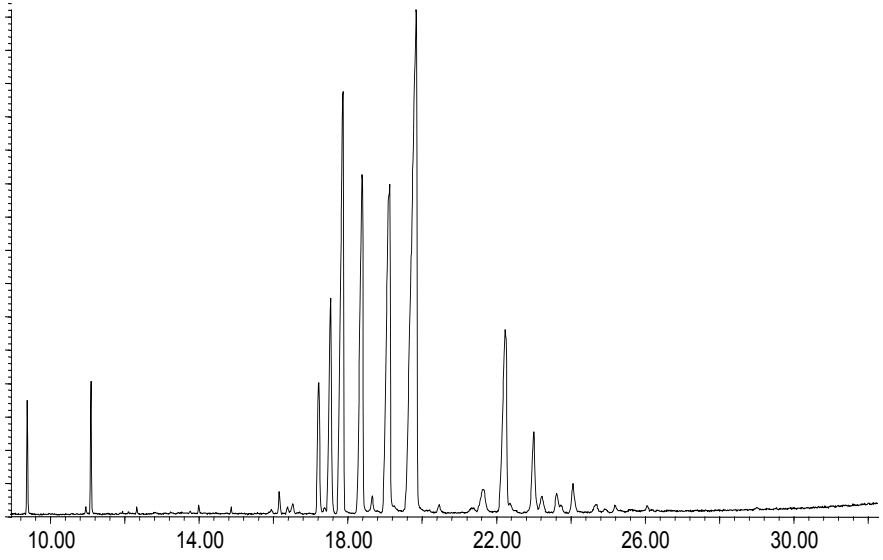
Chair Dalila1 1975 , Gaetano Pesce

Phone Grillo 1966 Marco Zanuso

1910-1920 cellulose nitrate sculptures by Naum Gabo

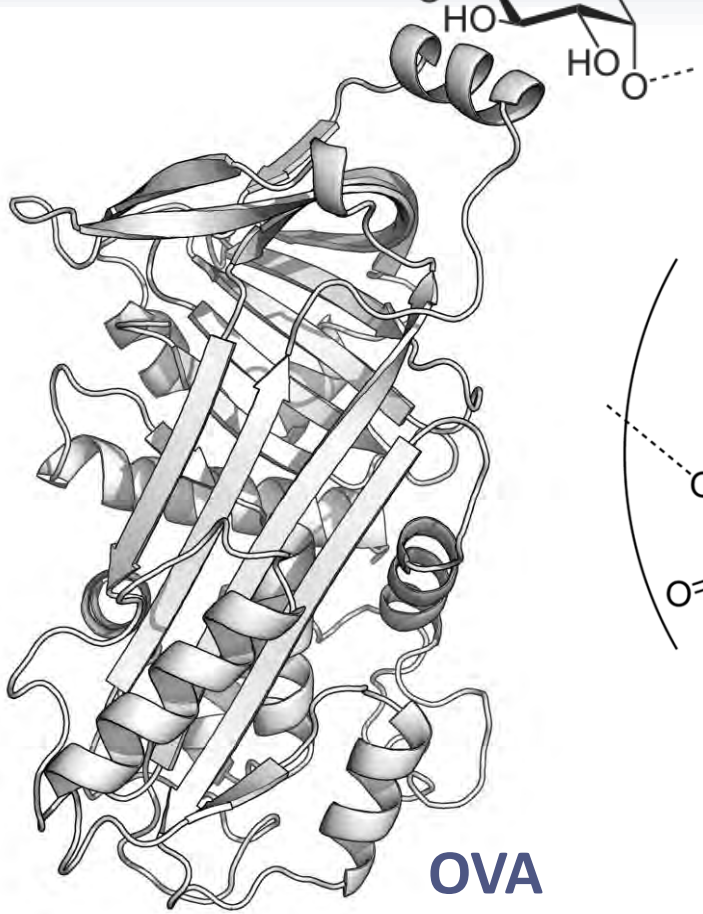
Organic materials in heritage objects: how

- Spectroscopic techniques
- **Molecular** analysis by **chromatographic techniques** coupled with analytical pyrolysis and **mass spectrometry**



starch

PET



OVA

nitrocellulose

alkyd paint

Organic materials in heritage objects: how

Chromatography

Mass spectrometry

Analytical pyrolysis

Characterisation at a molecular level of low-medium mw molecules and polymers in heritage objects

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  Py-GC/MS and Py-MS ?

GDCh Minireviews Angewandte International Edition Chemie

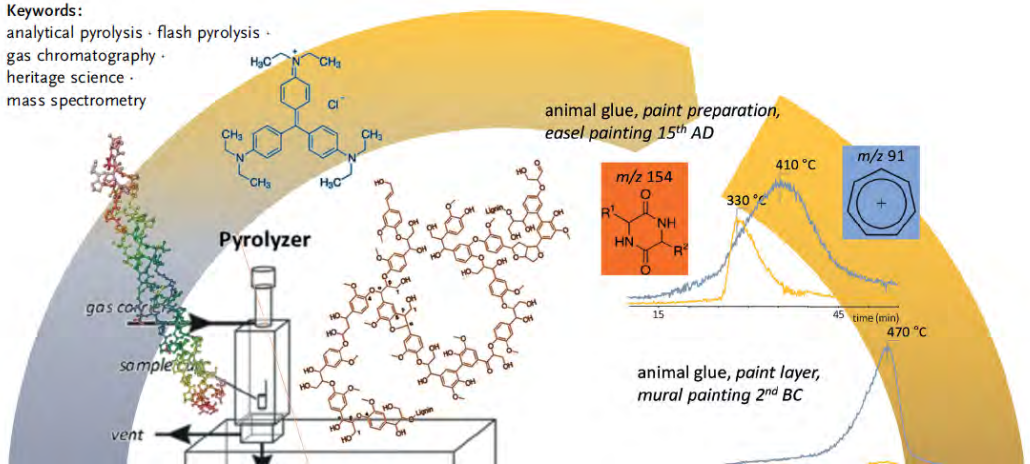
Analytical Pyrolysis

International Edition: DOI: 10.1002/anie.201713404
German Edition: DOI: 10.1002/ange.201713404

Recent Advances in Analytical Pyrolysis to Investigate Organic Materials in Heritage Science

*Ilaria Degano, Francesca Modugno, Ilaria Bonaduce, Erika Ribechini, and Maria Perla Colombini**

Keywords:
analytical pyrolysis · flash pyrolysis · gas chromatography · heritage science · mass spectrometry




A. GORKY

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  **Py-GC/MS and Py-MS** ?

- **minimum amount of sample** **sampling artworks** is a critical step

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  **Py-GC/MS and Py-MS** ?

- **minimum amount of sample** **sampling artworks** is a critical step

- **Minimum sample pre-treatment** – risk of contamination is a major issue when **samples are unique**

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  **Py-GC/MS and Py-MS** ?

- **Non-specific sample pretreatment**– you do not have to know in advance what is in the sample

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  **Py-GC/MS and Py-MS** ?

- **Non-specific sample pretreatment**– you do not have to know in advance what is in the sample
- **Suitable for a wide range of analytes in a wide range of molecular weights** – unexpected components can be present

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  **Py-GC/MS and Py-MS** ?

- **Non-specific sample pretreatment**– you do not have to know in advance what is in the sample
- **Suitable for a wide range of analytes in a wide range of molecular weights** – unexpected components can be present
- **Suitable for mixtures** - Art and historic objects are often mixtures of many different materials, and often they are **polymers** (lignocellulosic, proteins, polymerised drying oils, resins, conservation materials)

Analytical pyrolysis in Heritage Science

WHY do heritage scientists  **Py-GC/MS and Py-MS** ?

- **Fast analysis time** - some historical objects are **highly heterogeneous in composition**, and many samples need to be compared to obtain **representative chemical information**

Analytical pyrolysis in Heritage Science

First application : **Analysis of organic materials in Egyptian cartonnages from 2000-4000 years old mummies**

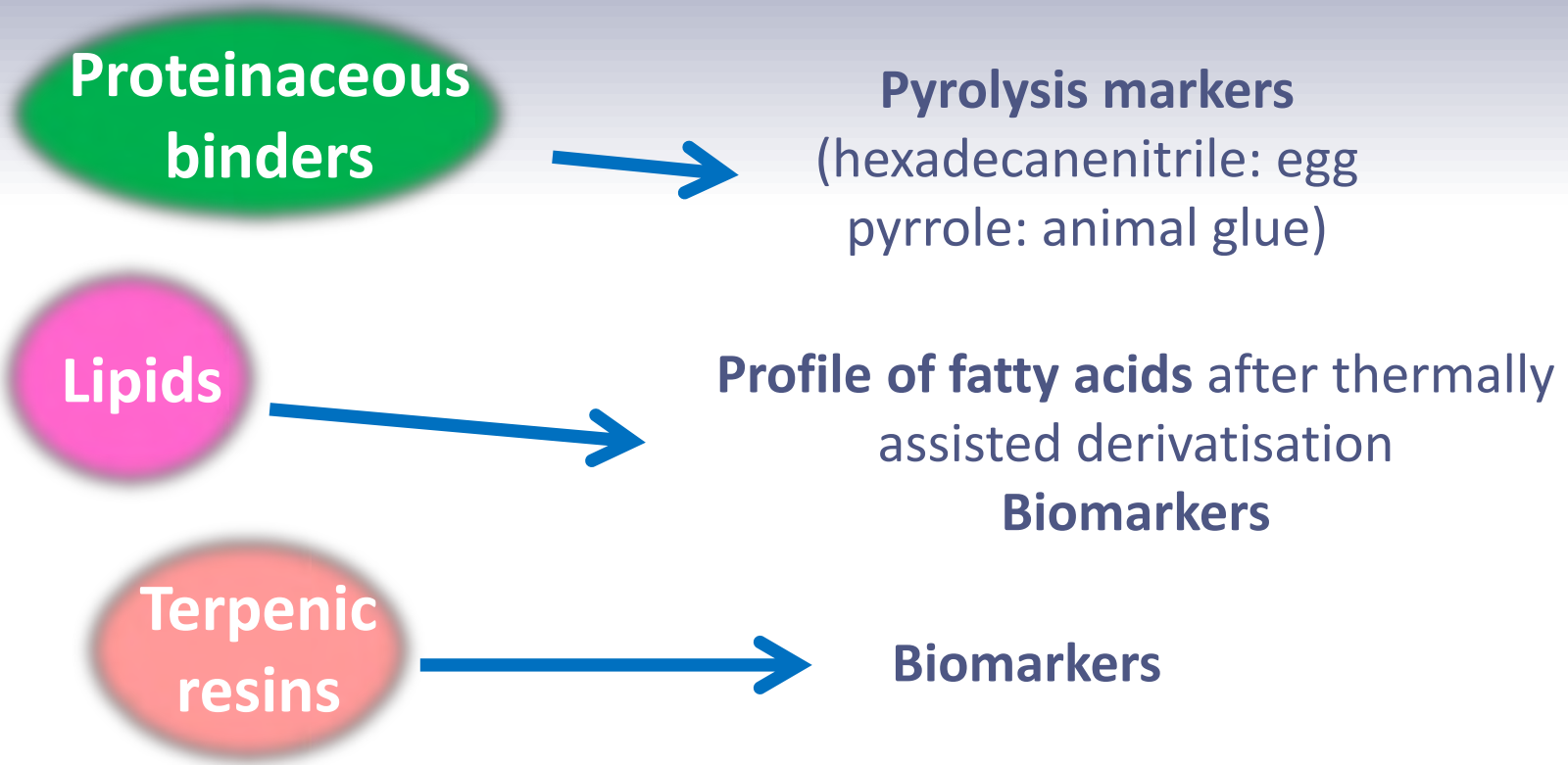
M.M. Wright and B.B. Wheals, J. Anal. Appl. Pyrolysys 11 (1987) 195

Comparison with reference natural substances of known origin

Identification of polysaccharide gums, waxes and terpenic resins

Analytical pyrolysis in Heritage Science

Qualitative identification



Colombini et al, *Accounts of Chemical Research* 43, 2010, 715-727

Moldoveanu, S.C., *Analytical pyrolysis of natural organic polymers*. Vol. 20. 1998: Elsevier

Linn et al.,, 2018 , *Angewandte Chemie* , 57(40), pp. 13257-13260

Orsini et al., 2017, *Journal of Analytical and Applied Pyrolysis* 124, 643-657

Tamburini et al. 2017, *Journal of Analytical and Applied Pyrolysis* 124, 51-62

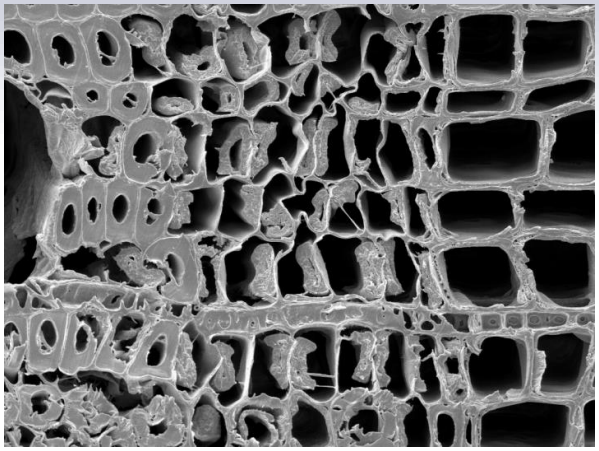
Analytical pyrolysis in Heritage Science

- Archeological wooden objects

- Synthetic polymers in modern art and design

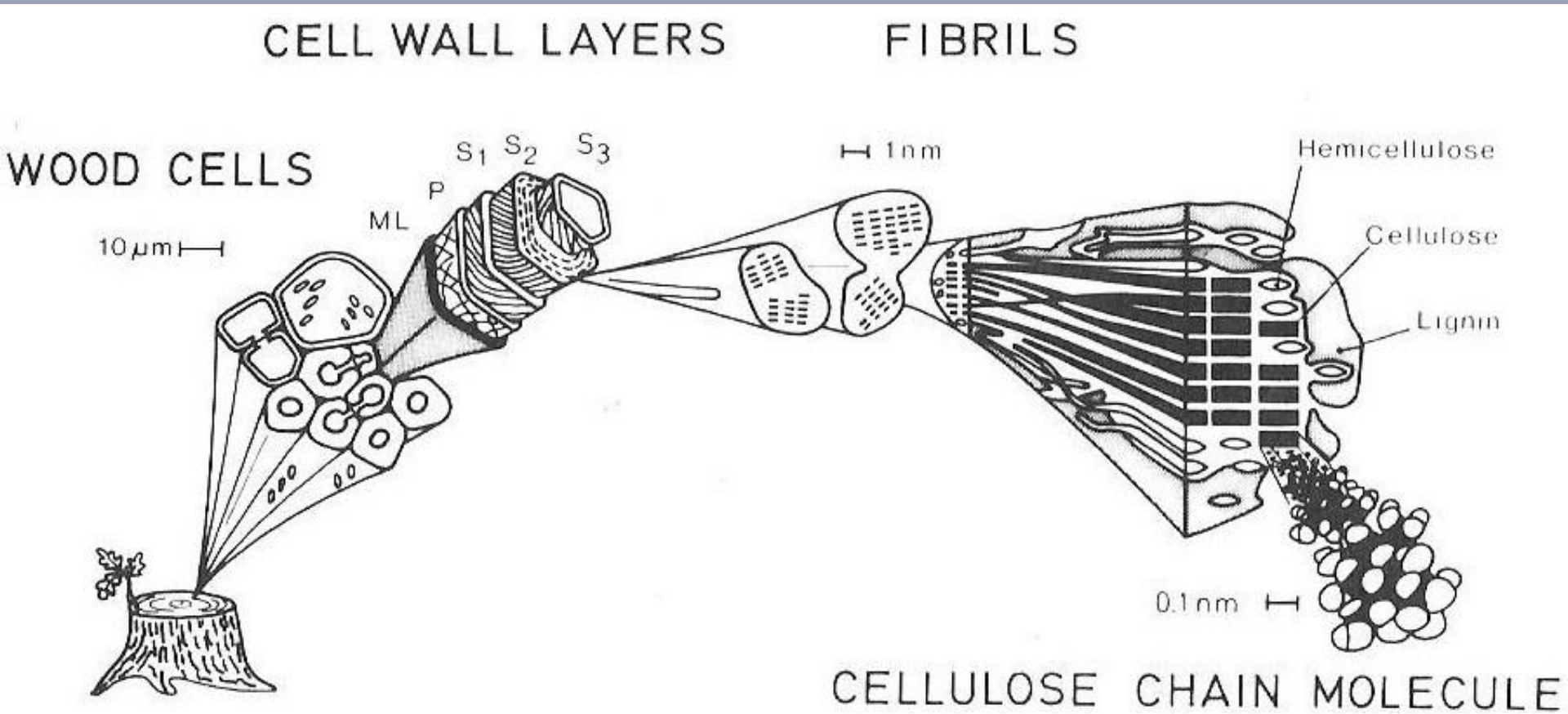
McQueen et al., 2019 Heritage Science 7(1),78
Ghelardi et al, *Analytical and Bioanalytical Chemistry* 407, 2015, 1415-1431
Learner, *Analysis of Modern Paints*, 2005, Getty Conservation Institute

Chemical analysis of archaeological degraded wood



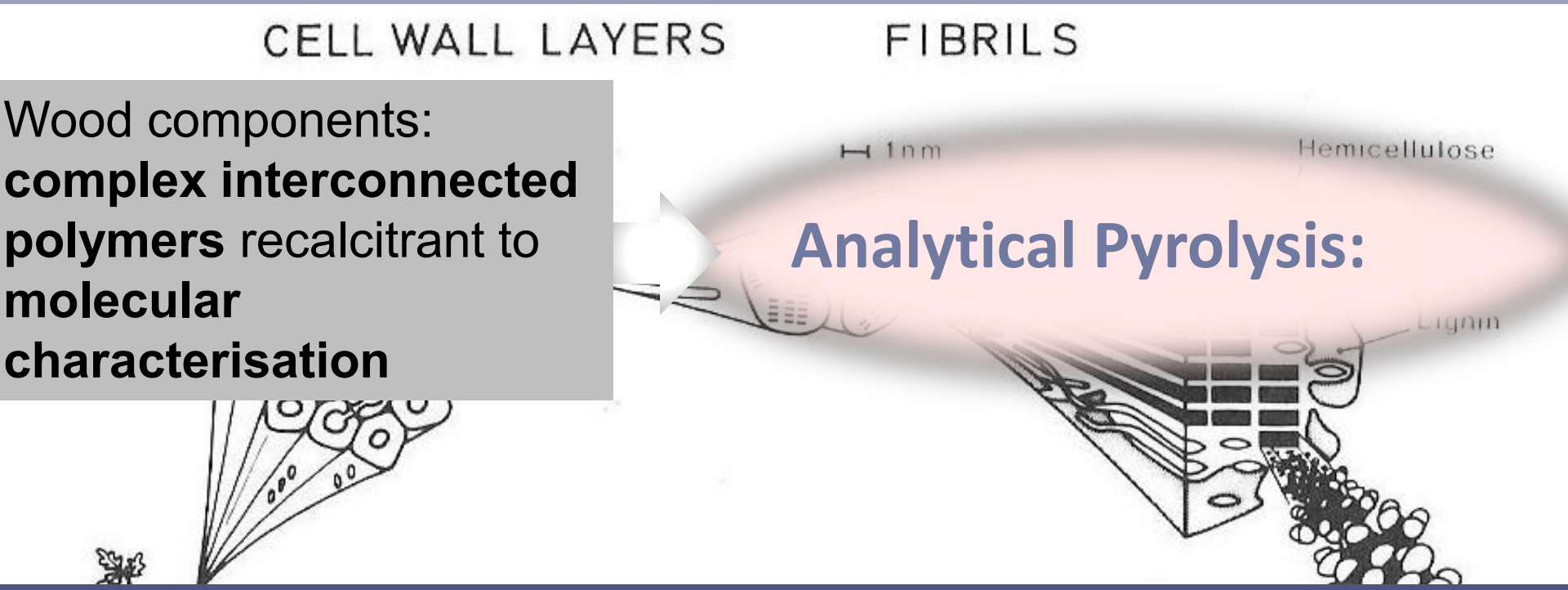
Wood archaeological objects: rare, preserved only in peculiar environments as underwater, deeply degraded, need consolidation **composite objects**: degraded **wood** + **conservation materials** + inorganic **salts**

Chemical analysis of archaeological degraded wood



Wood components: complex interconnected polymers recalcitrant to molecular characterisation

Chemical analysis of archaeological degraded wood



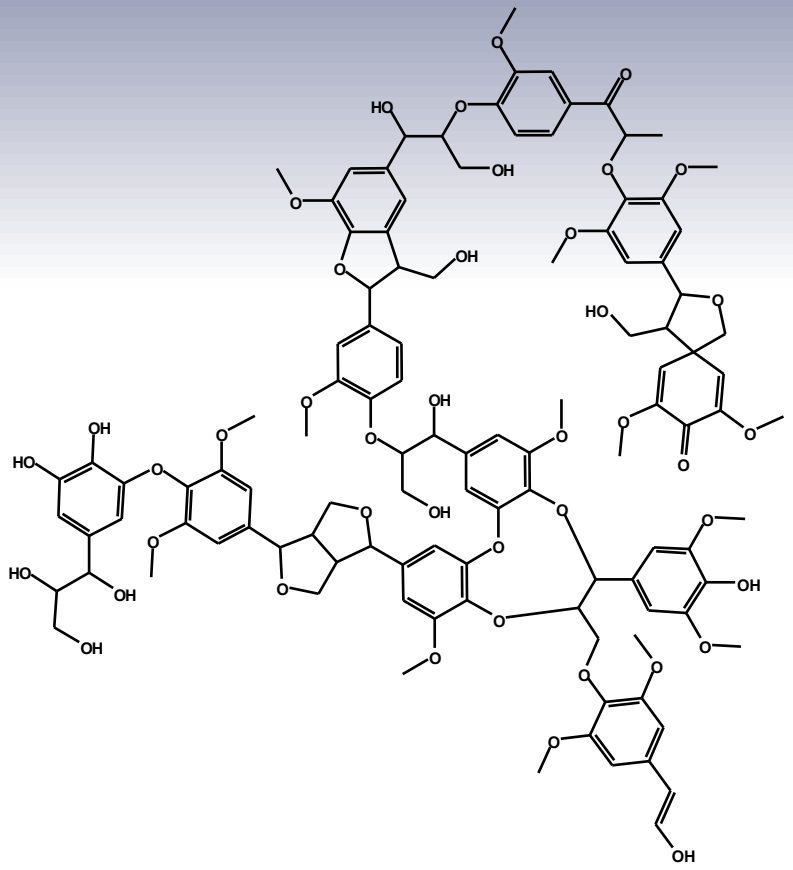
Wood components: **complex interconnected polymers** recalcitrant to **molecular characterisation**

Analytical Pyrolysis:

Thermal cracking of lignocellulosic polymers in reproducible conditions in order to obtain a pool of small fragments (**pyrolysis products**) that can be **analysed, identified and quantified**

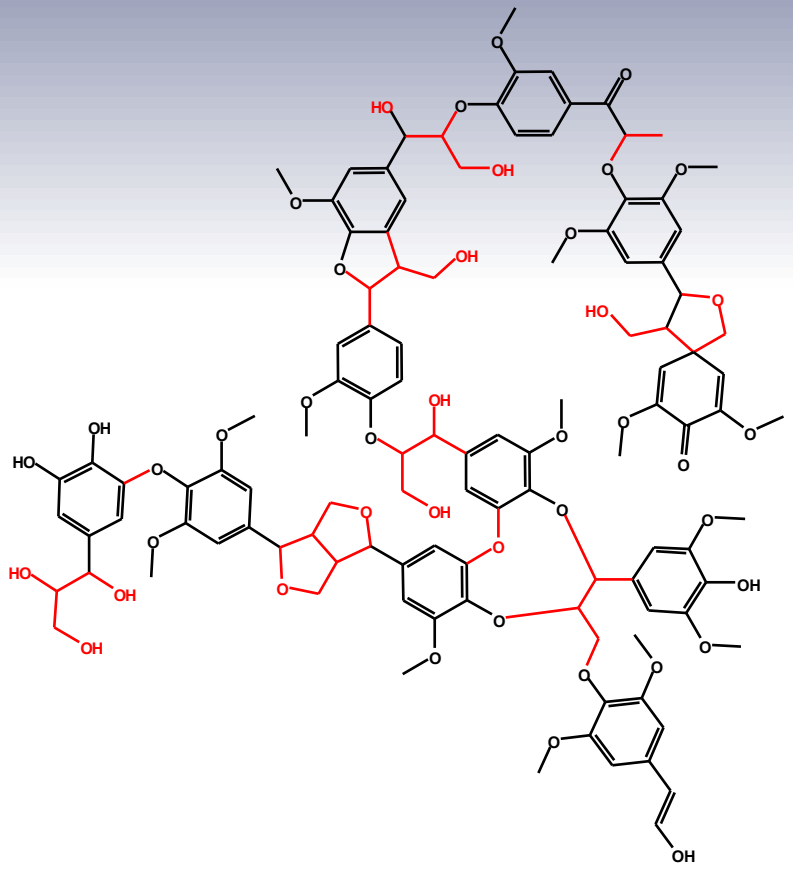
Analytical pyrolysis of lignocellulosic materials

Py-GC/MS

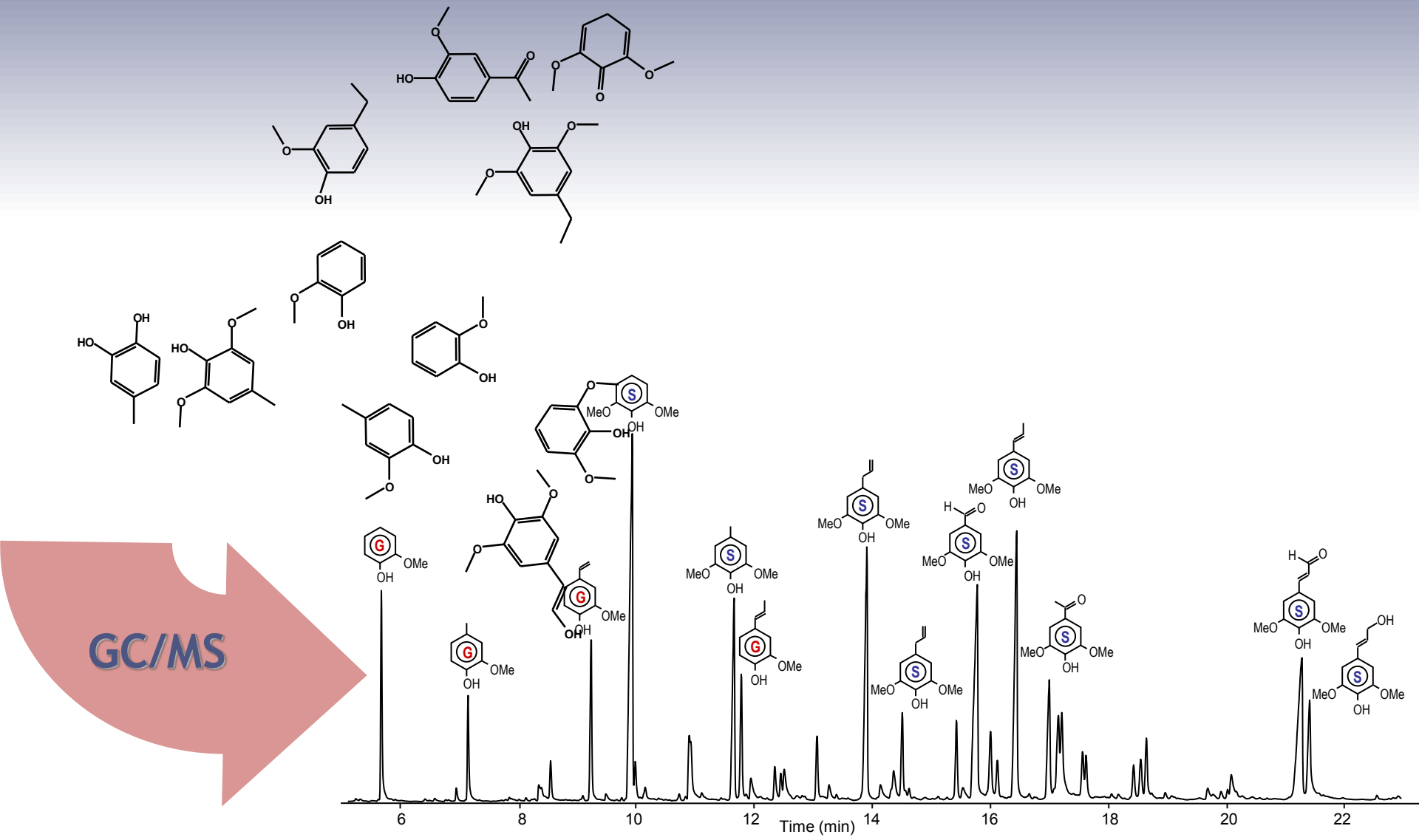


Microsamples (50-100 µg) are analysed without any sample pretreatment or adding a silylating agent to derivatise –OH and –COOH functionalities

Analytical pyrolysis of lignocellulosic materials



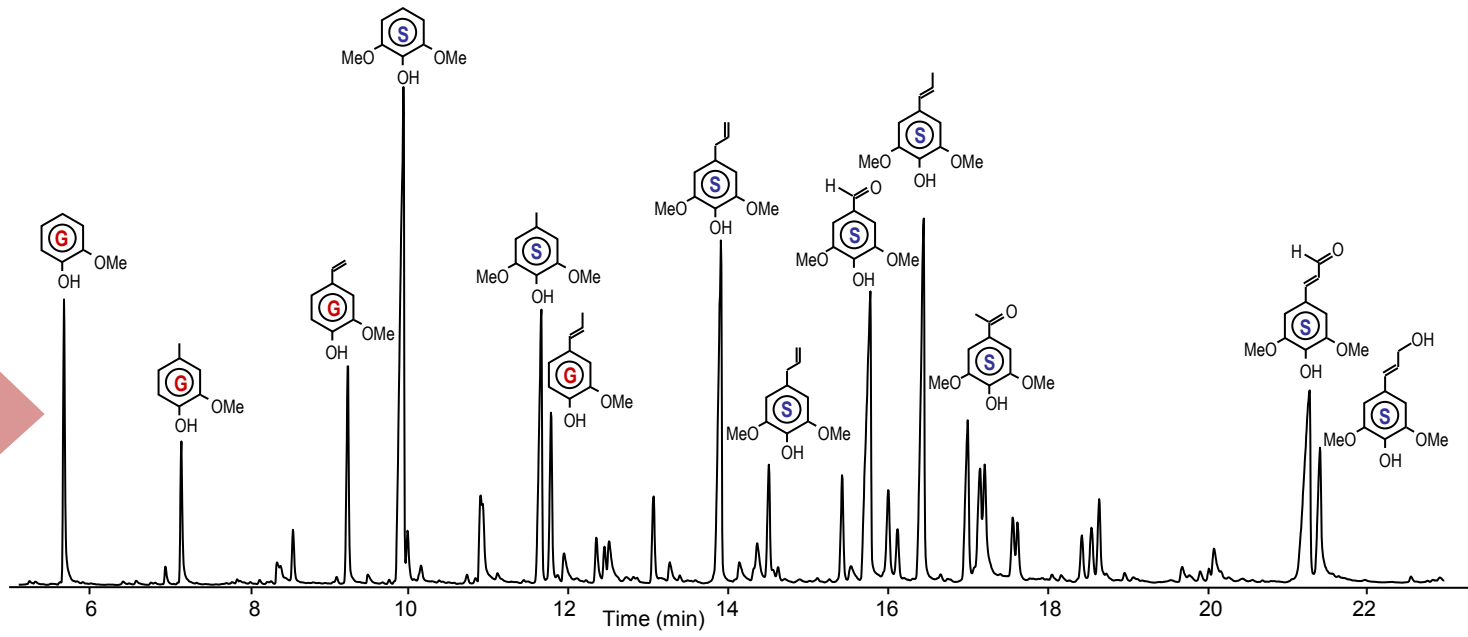
Analytical pyrolysis of lignocellulosic materials



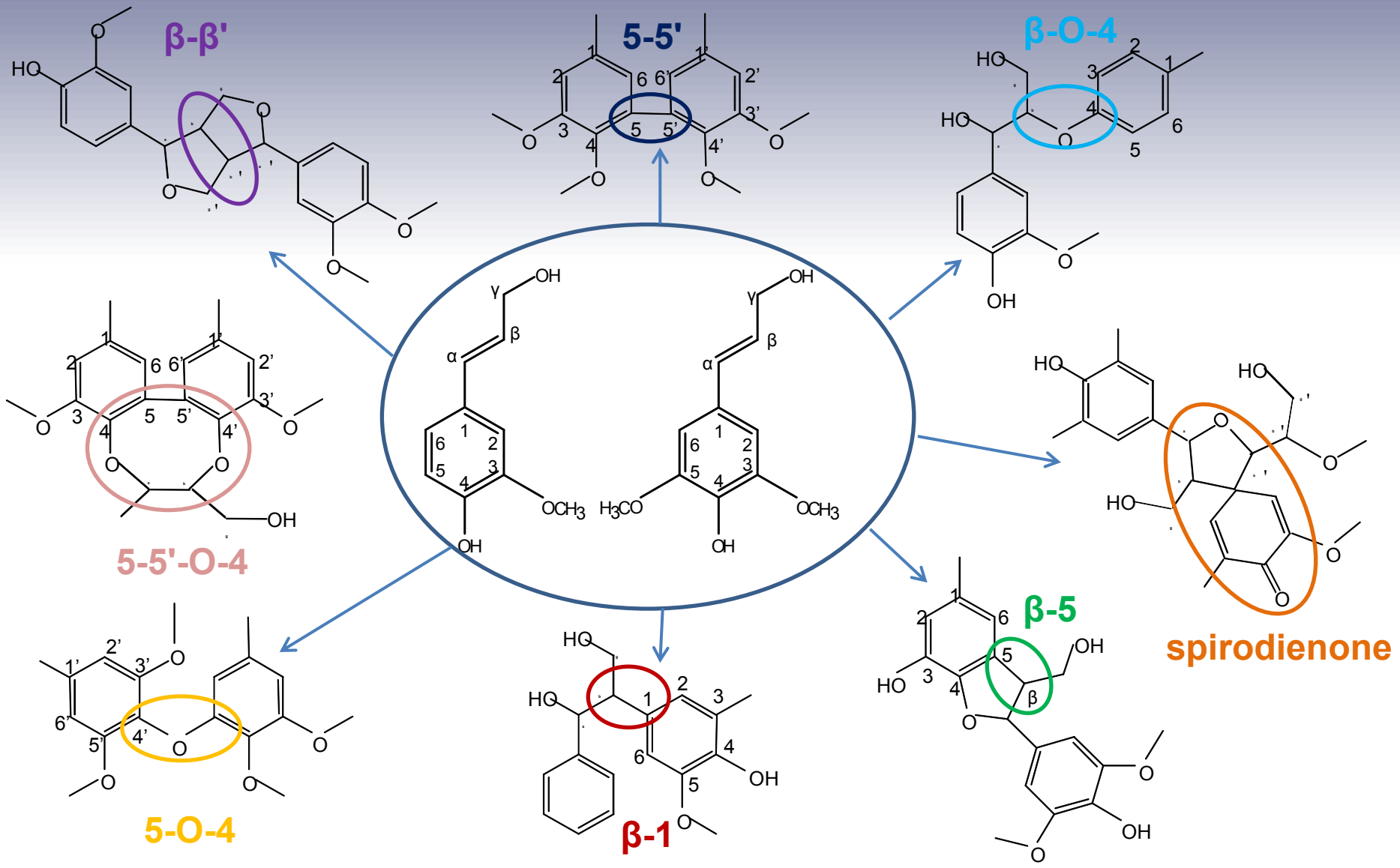
Analytical pyrolysis of lignocellulosic materials

The **pyrolysis products of lignin, cellulose and hemicellulose** are qualitatively and semi-quantitatively analysed

GC/MS

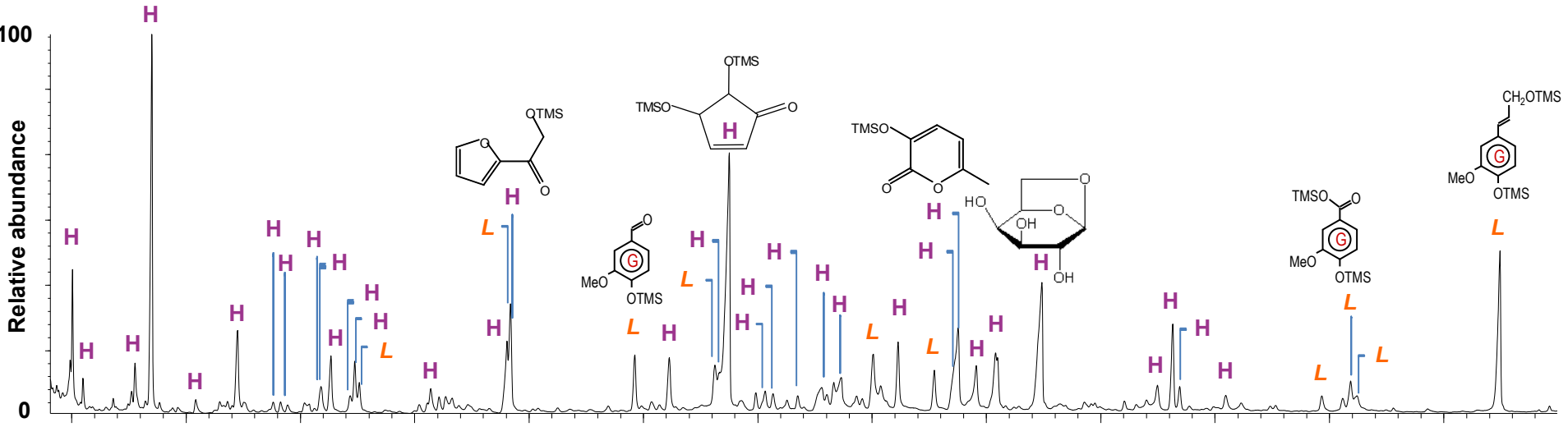


Many intermonomeric bonds in lignin: many pyrolysis reactions



Analytical pyrolysis of wood

Pyrolytic profiles obtained by Py(HMDS)-GC/MS of **pine reference wood** In presence of hexamethyldisilazane (HMDS) for the in-situ thermally assited silylation of polar pyrolysis products

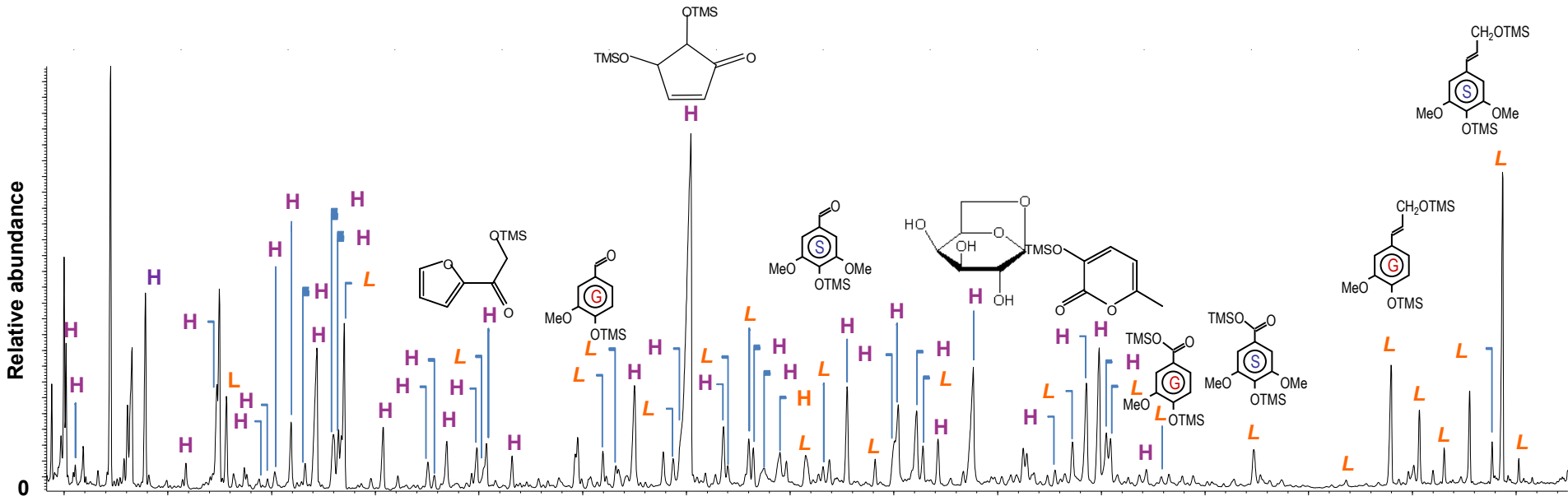


L – guaiacyl pyrolysis products

H – holocellulose pyrolysis products

Analytical pyrolysis of wood

Pyrolytic profiles obtained by Py(HMDS)-GC/MS of **oak reference wood** In presence of hexamethyl disilazane (HMDS) for the in-situ thermally assited silylation of polar pyrolysis products

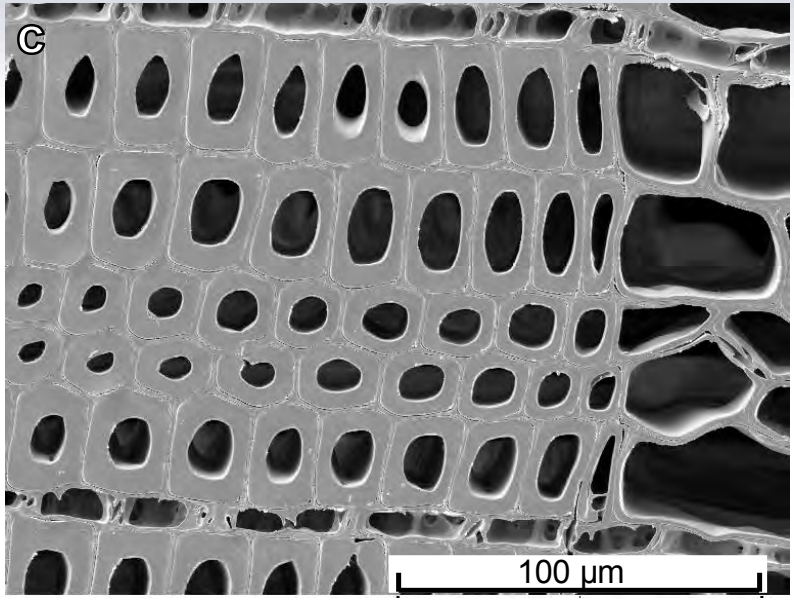


L- guaiacyl- and syringyl-lignin pyrolysis products

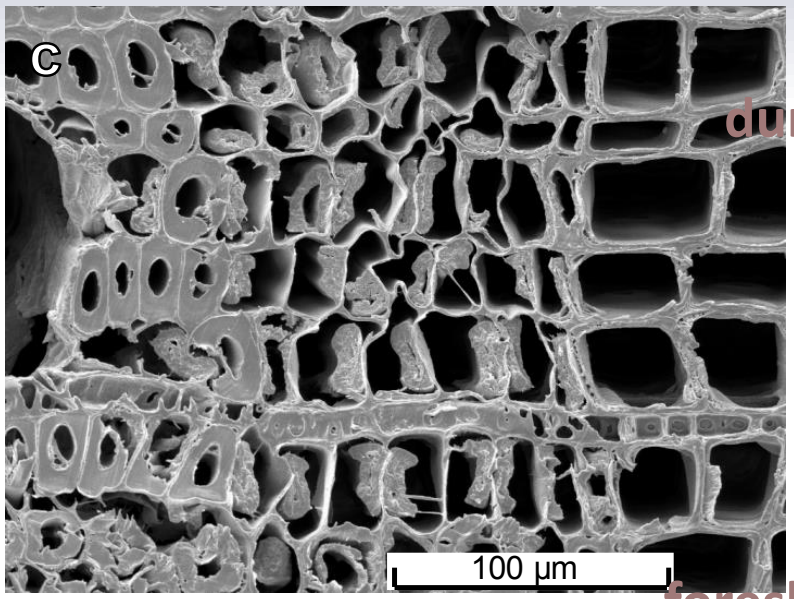
H- holocellulose pyrolysis products

Chemical analysis of archaeological degraded wood

Reference pine wood



Pine wood after 8 years in wet peat



dunes

foreshore

Conservation of waterlogged wood

Drastic dimensional changes with **structural distortions and crackings** may occur during drying, because of the shrinkage and collapse of weakened cell walls

Conservation treatments of waterlogged archaeological wood: **impregnation with a consolidant material**

Composite waterlogged wood artifacts containing inorganic components and conservation materials

- **The Oseberg collection, Norway** samples from an **alum-treated** fragment the Museum of Cultural History (Oslo) from the alum rich **surface** (**O1**) and from the **core** (**O2**) of the same fragment. Hypothesized specie: birch.

SAVING OSEBERG

Alum treatment
$KAl(SO_4)_2 \cdot 12H_2O$

UiO : Museum of Cultural History
University of Oslo

Composite waterlogged wood artifacts containing inorganic components and conservation materials

French shipwrecks:

"**L'Aimable Grenot**", corsair boat dating 18th century (oak)

"**Lyon ship**", Roman boat dating 2nd century AD (oak and softwood)

A post-treatment using a solution of **PEG** 20% and **disodium sebacate** 10% was tested to solve conservation issues related to the acidity of the wood

Samples from French shipwrecks were provided by ARC-nucleART Grenoble)

Composite waterlogged wood artifacts containing inorganic components and conservation materials

French shipwrecks

Genoese shipwreck "**La Lomellina**" (cargo ship 1516 AD), discovered in 1979 near Villefranche sur Mer, and treated with **PEG 4000** and **disodium sebacate .**
Comparison of the **external surface** (Lo-3), **core** (Lo-4) and **internal surface** (Lo-5) of the same fragment, Hypothesized specie: pine

Samples from French shipwrecks were provided by **Arc Nucleart** (Grenoble)

Guérout Max, 2007 – *La Lomellina , une nave génoise de la Renaissance*, dans *Sauvé des Eaux*, (dir. Pierre Vaudaine, ARC-Nucleart), Villeurbanne , p.118-126.

Composite waterlogged wood artifacts containing inorganic components and conservation materials

Viking ships, Denmark :

Skuldelev ships (Viking Ship Museum of Roskilde, Denmark), **Sk**. Surface of a fragment treated with **PEG 4000**.

- **Nydam Boat** (Gottorf Castle in Schleswig, Germany), **Ny**, treated with **PEG 2000**.

Wood species: oak

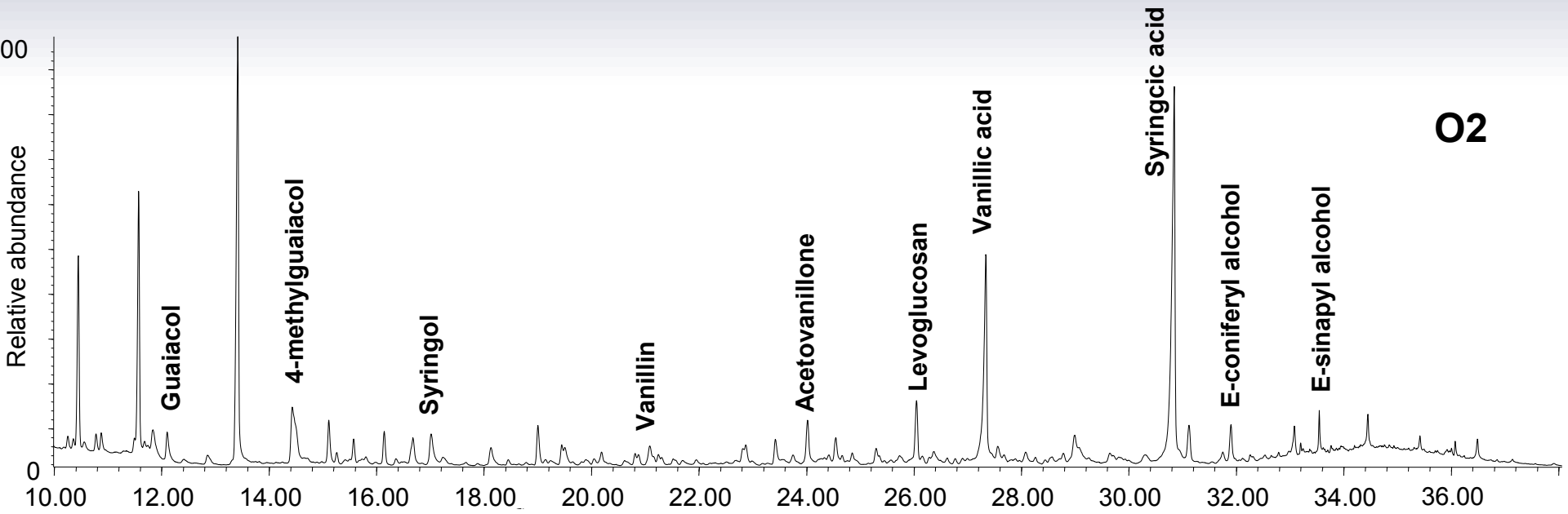
Provided by NatMus (Denmark)

Mange museer i ét

Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

Oseberg O2
alum rich sample



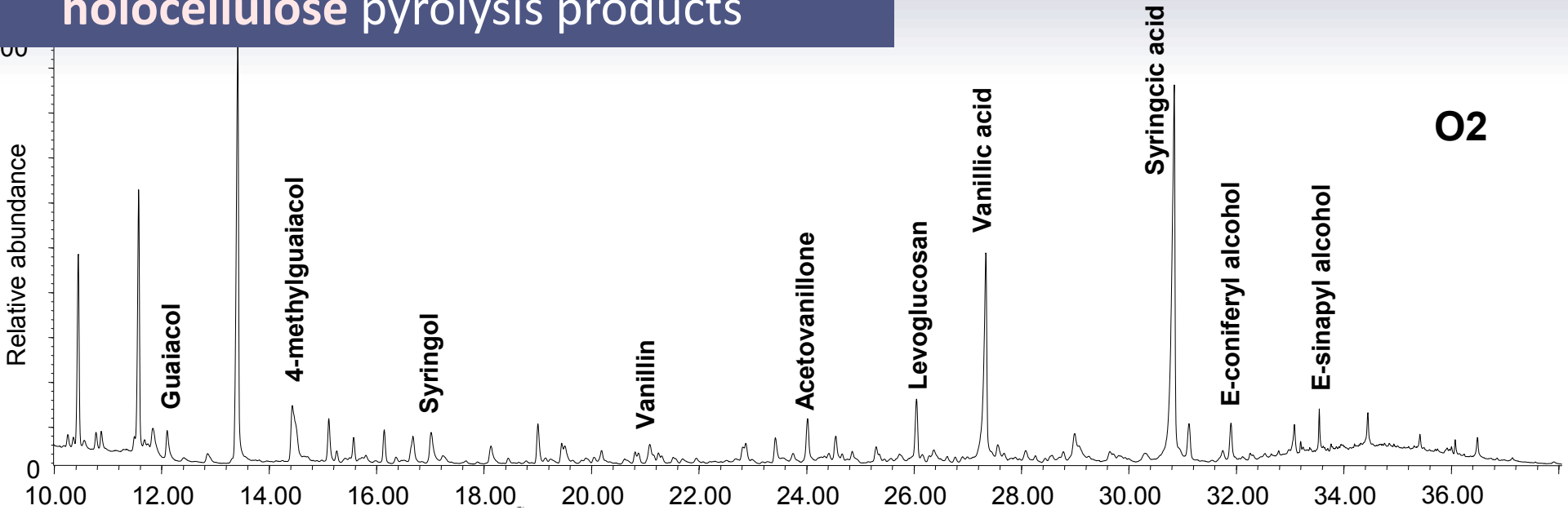
A **Multi-Shot Pyrolyzer EGA/Py-3030D** (Frontier Lab) was used for the experiments and **HMDS** was used as derivatising agent

Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

Oseberg O2
alum rich sample

- very **low relative abundance of holocellulose** pyrolysis products



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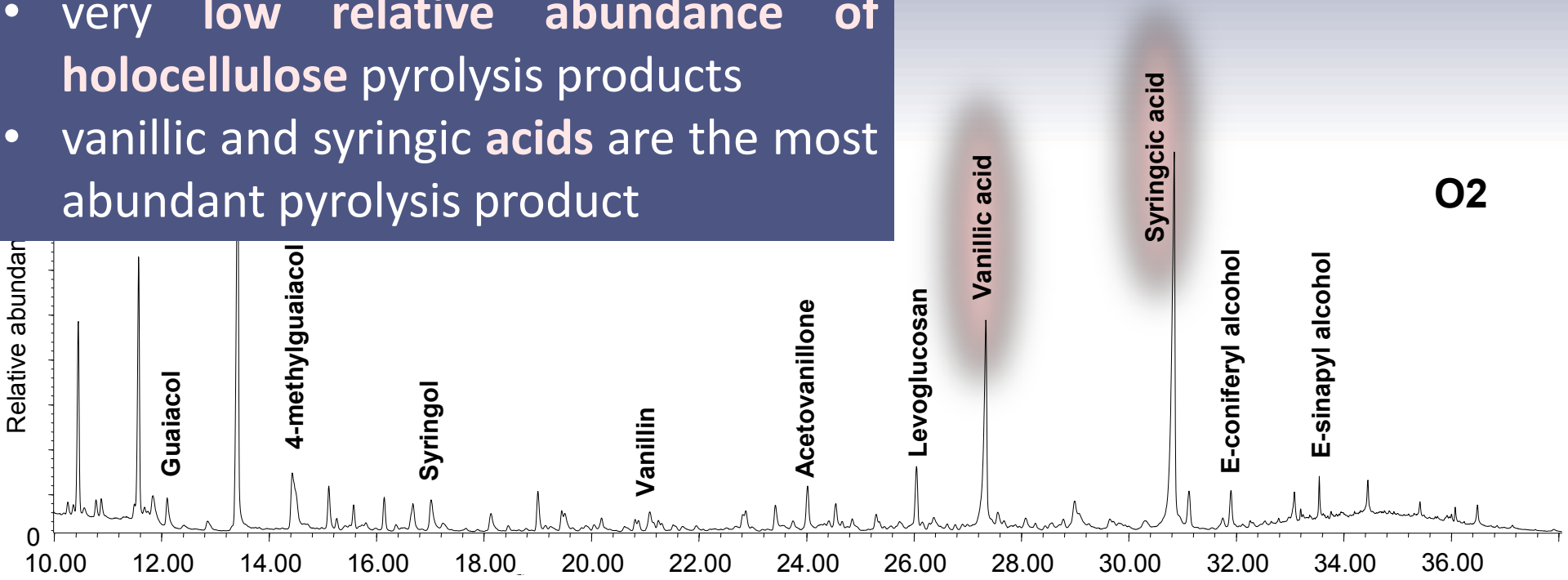
Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

Oseberg O2
alum rich sample

- very **low relative abundance of holocellulose** pyrolysis products
- vanillic and syringic **acids** are the most abundant pyrolysis product



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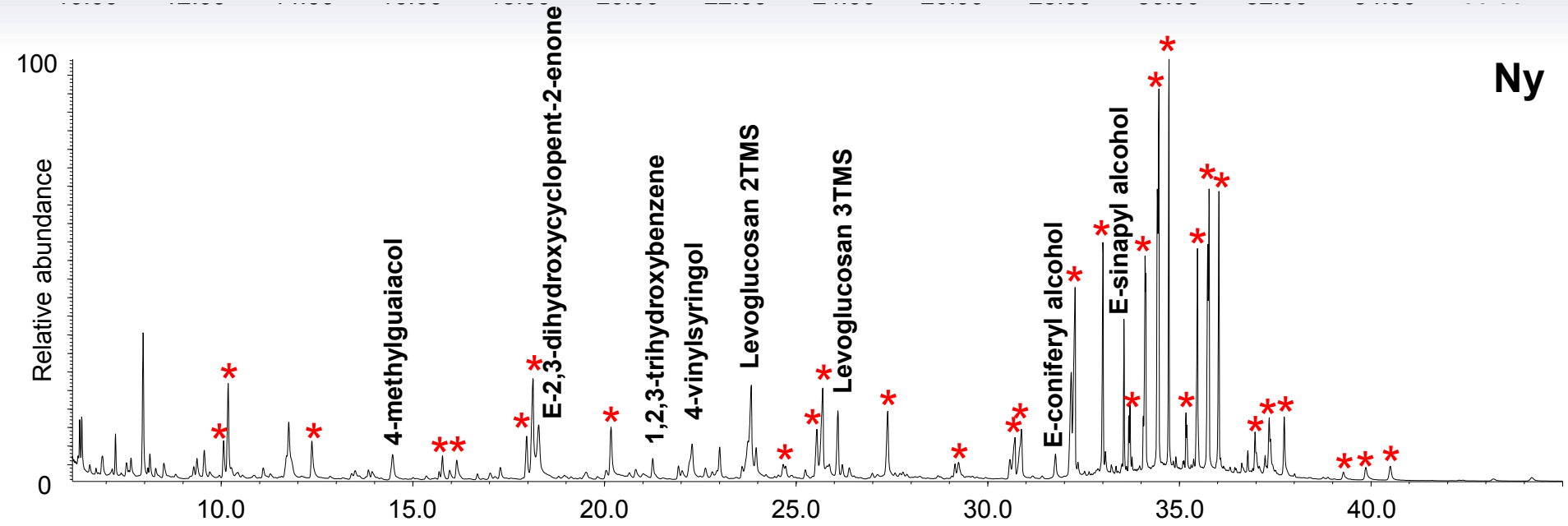
Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

Viking ship Nydam boat
treated with **PEG 4000**



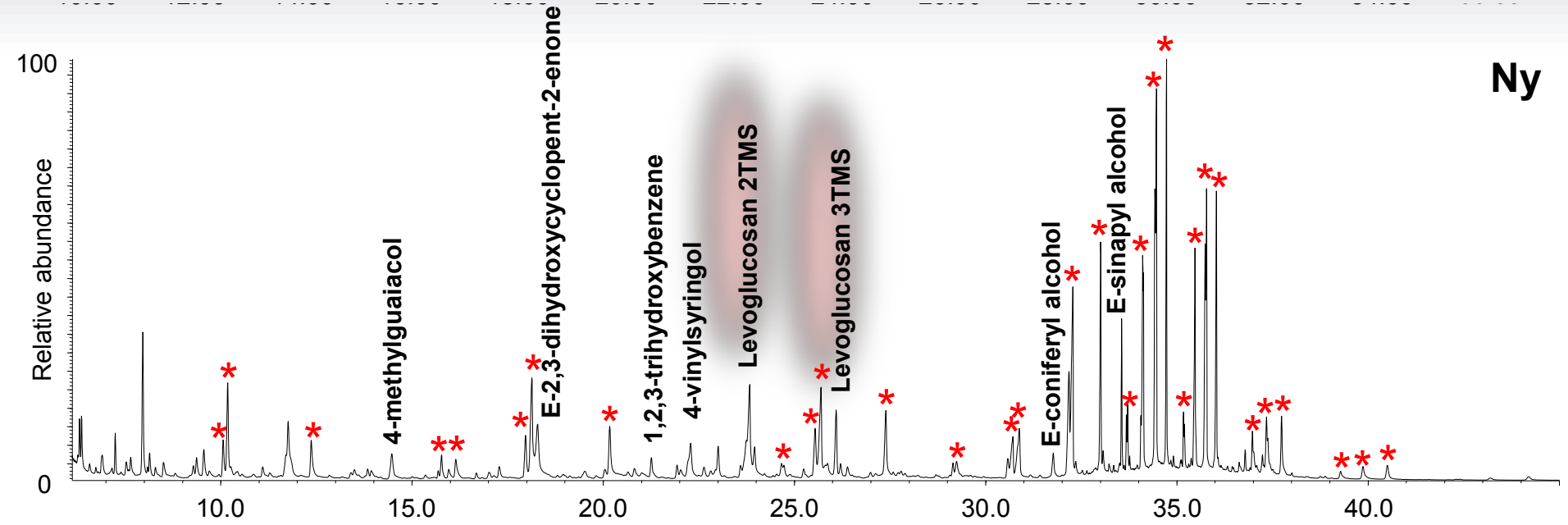
* PEG pyrolysis products

Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

Viking ship Nydam boat
treated with **PEG 4000**

- **holocellulose** pyrolysis products are still present



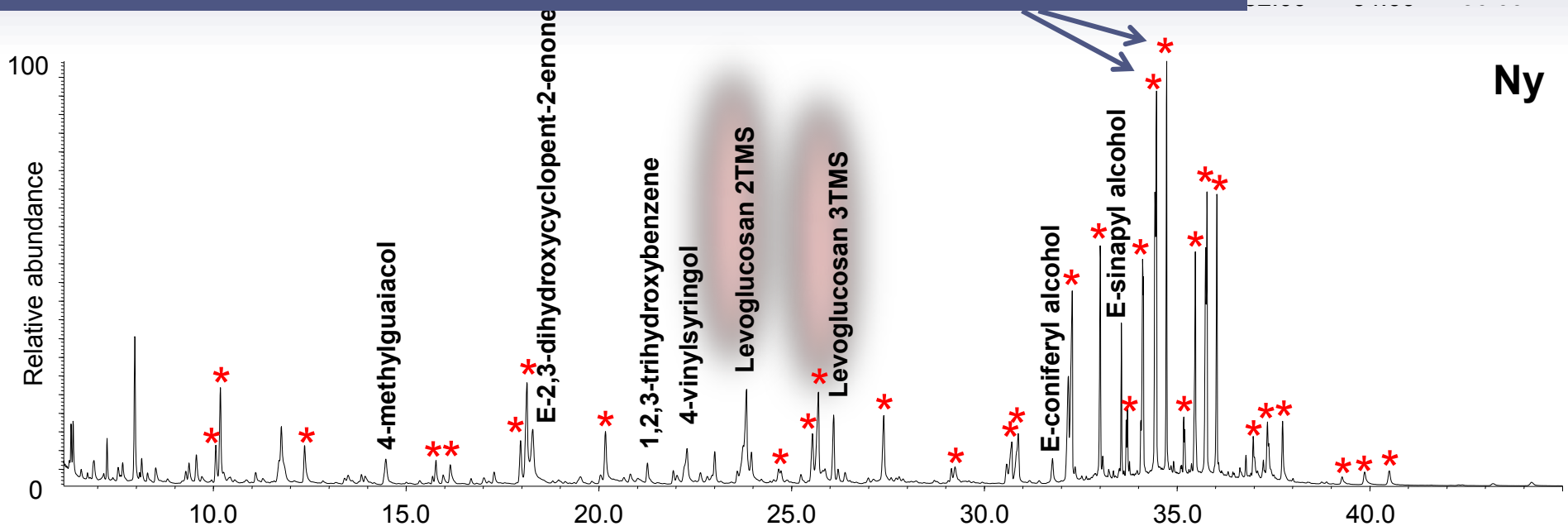
* PEG pyrolysis products

Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

Viking ship Nydam boat
treated with **PEG 4000**

- **holocellulose** pyrolysis products are still present
- **PEG pyrolysis products** are the most abundant

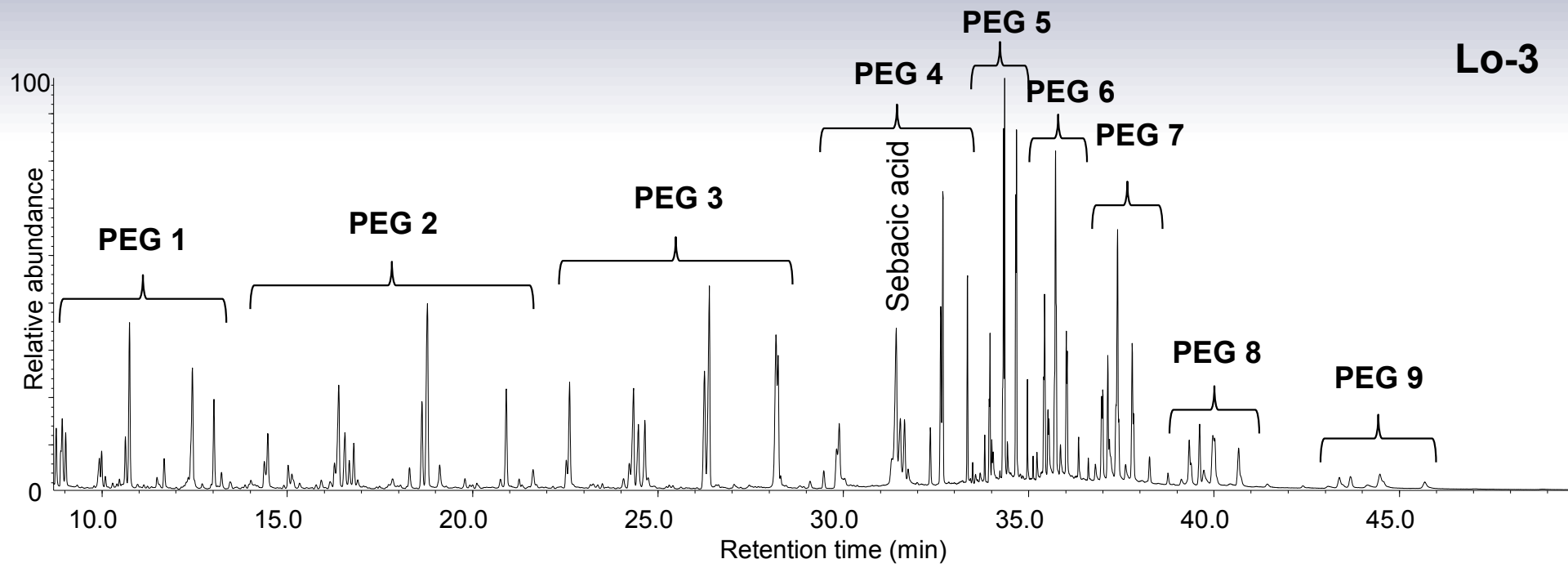


* PEG pyrolysis products

Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

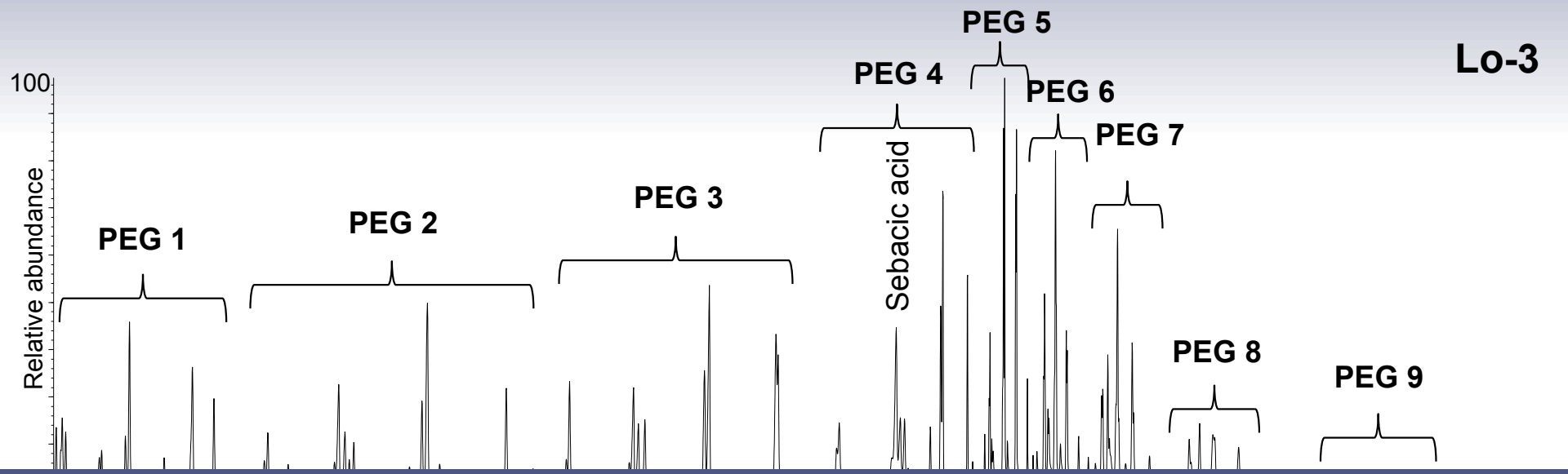
La Lomellina treated with **PEG 4000**



Py(HMDS)-GC-MS

T_{pyr} 550°C, 100 µg sample, 5 µL HMDS

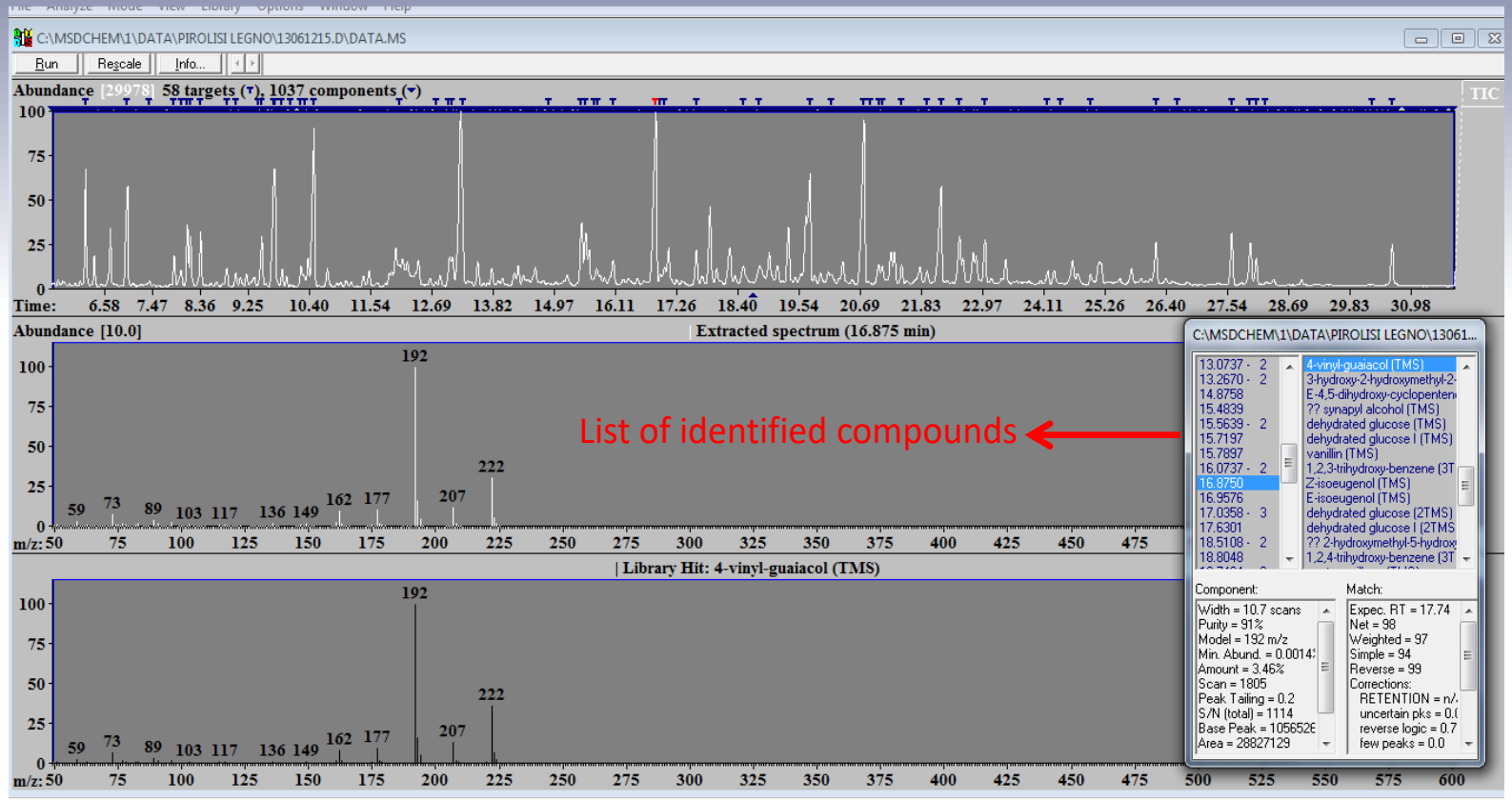
La Lomellina treated with **PEG 4000**



PEG pyrolysis products: **clusters** of six/seven compounds differentiated on the basis of their terminal groups. The clusters have the same structure but they increase in size and weight by one monomeric unit (–CH_2–CH_2–O–) , 44 uma

Analytical pyrolysis of wood

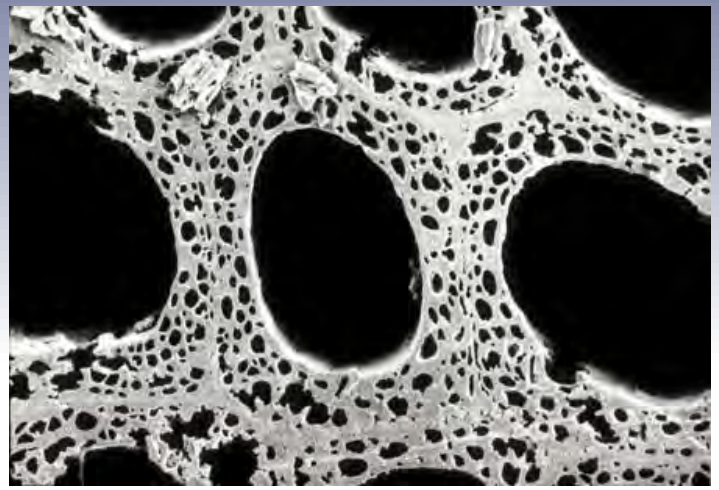
The AMDIS (Automated Mass spectral Deconvolution and Identification System) software



- Construction of a library of the mass spectra of all the original and degradation wood pyrolysis products.
- Possibility to deconvolute the pyrograms eliminating overlapping
- Automatic recognition and integration (areas) of the peak whose spectrum matches with those in the library.

Py-GC-MS analysis of archaeological degraded wood:

Evaluation of the degradation state of wood:



- comparison between **archaeological and sound wood** of the same species

- comparison between **different samples from the same object**
- evaluation of the pyrolytic **H/L ratio: ratio between the sum of the areas of the pyrolysis products of holocellulose and of lignin**

Lucejko JJ, Zborowska M, Modugno F, Colombini MP, Pradzynski W (2012). Analytical pyrolysis vs. classical wet chemical analysis to assess the decay of archaeological waterlogged wood. Analytica Chimica Acta 745, pp. 70-77

Py-GC-MS analysis of archaeological degraded wood: Determination of the ratio between the amount of holocellulose and the amount of lignin : H/L ratio

- H/L is a common parameter to evaluate the degradation state of waterlogged archaeological wood
- Evaluation of the **degradation/preservation state** of waterlogged wood in terms of **loss of polysaccharides**
- The difference between the H/L ratio obtained for sound and waterlogged archaeological wood of the same specie can be used to estimate the **extent of degradation**

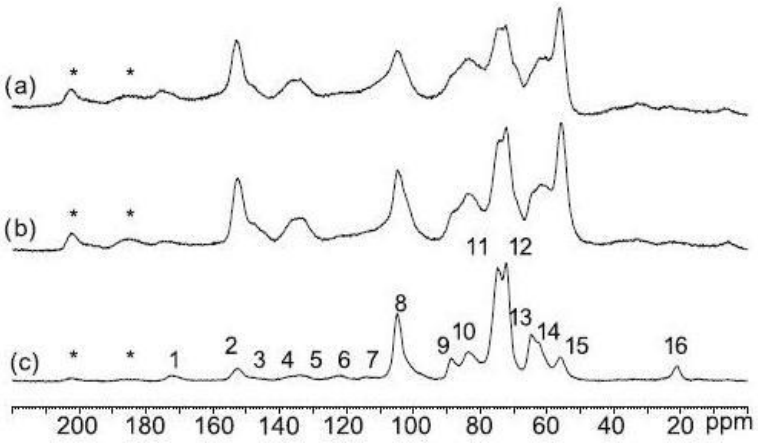
Determination of H/L ratio

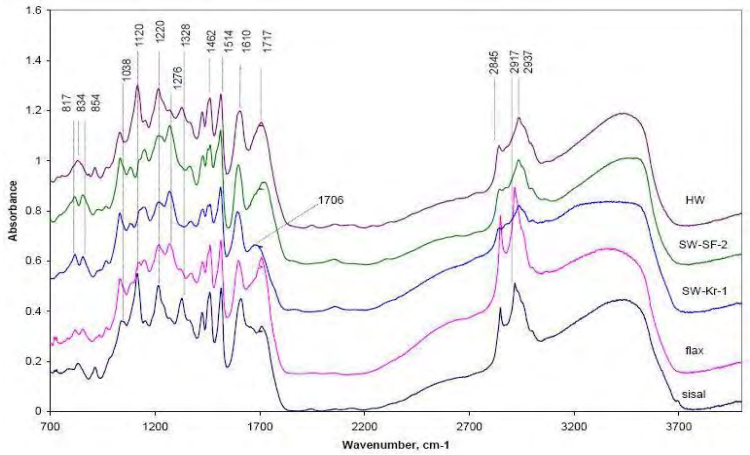
- Classical **wet-chemical** methods (TAPPI methods): based on **weighted amounts of isolated wood components after hydrolysis and extraction.**

Determination of H/L ratio

- Classical **wet-chemical** methods (TAPPI methods): based on **weighted amounts of isolated wood components after hydrolysis and extraction**

- **Spectrofotometric methods**: based on the comparison of intensity of **FTIR**, **Raman** or **NMR** bands related to lignin and polysaccharides





Łucejko,J.J. et al., Analytical instrumental techniques to study archaeological wood degradation. Applied Spectroscopy Reviews, 2015 50(7): p. 584-625

Determination of H/L ratio

- Classical **wet-chemical** methods (TAPPI methods): based on **weighted amounts of isolated wood components after hydrolysis and extraction**

- **Spectrofotometric methods**: based on the comparison of intensity of **FTIR**, **Raman** or **NMR** bands related to lignin and polysaccharides

- Methods based on the molecular identification of **pyrolysis products of lignin and polysaccharides** (< 100 µg of sample): sum of chromatographic areas of pyrolysis products deriving from polysaccharides and lignin are compared

Łucejko,J.J. et al., Analytical instrumental techniques to study archaeological wood degradation. Applied Spectroscopy Reviews, 2015 50(7): p. 584-625

Determination of H/L ratio

Pyrolytic H/L ratios obtained for the archaeological and sound wood samples

			Oseberg: Alum treated		Lomellina: internal and external fragments			Viking ships	
	Pine ref	**Oak ref**	**O1**	**O2**	**Lo-3**	**Lo-4**	**Lo-5**	**Sk**	**Ny**
Sum H %	73.6	75.0	4.0	7.0	30.0	40.6	18.5	18.1	18.5
Sum L %	26.4	25.0	96.0	93.0	70.0	59.4	81.5	81.9	81.5
H/L	**2.8**	**3.0**	**0.04**	**0.08**	**0.4**	**0.7**	**0.2**	**0.2**	**0.2**

Determination of H/L ratio

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Significant **loss of carbohydrates**: The archaeological wood samples showed a drastic reduction of the H/L ratio, if compared with sound wood

Determination of H/L ratio

Pyrolytic H/L ratios obtained for the archaeological and sound wood samples

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Oseberg wood treated with alum shows almost **no residual carbohydrates**

Determination of H/L ratio

Pyrolytic H/L ratios obtained for the archaeological and sound wood samples

			Oseberg: Alum treated		Lomellina: internal and external fragments			Viking ships	
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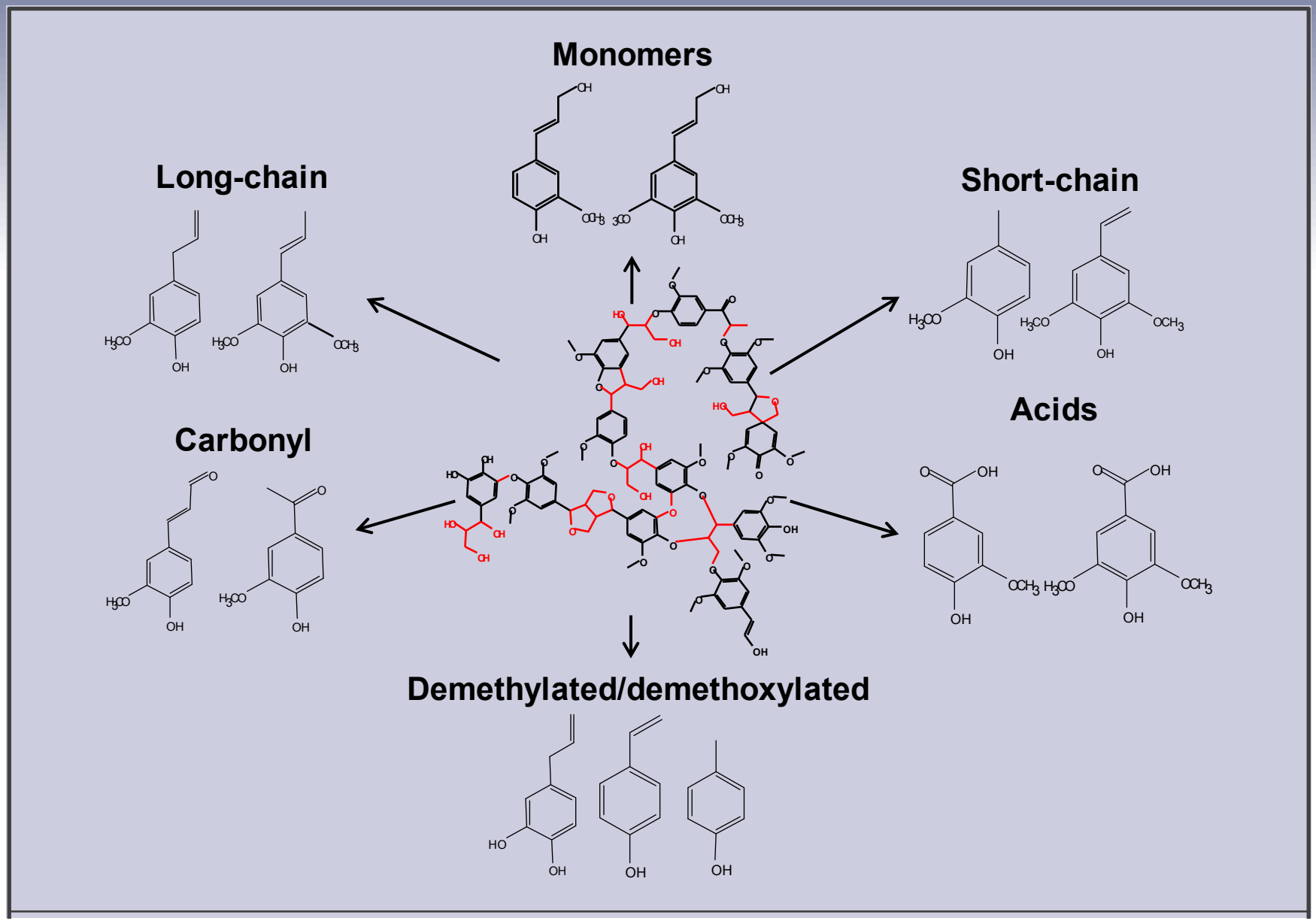
H/L	**2.8**	**3.0**	**0.04**	**0.08**	**0.4**	**0.7**	**0.2**	**0.2**	**0.2**

Among the samples from **La Lomellina, Lo-4,** from the **middle part of the fragment**, showed a **better preservation** of carbohydrates

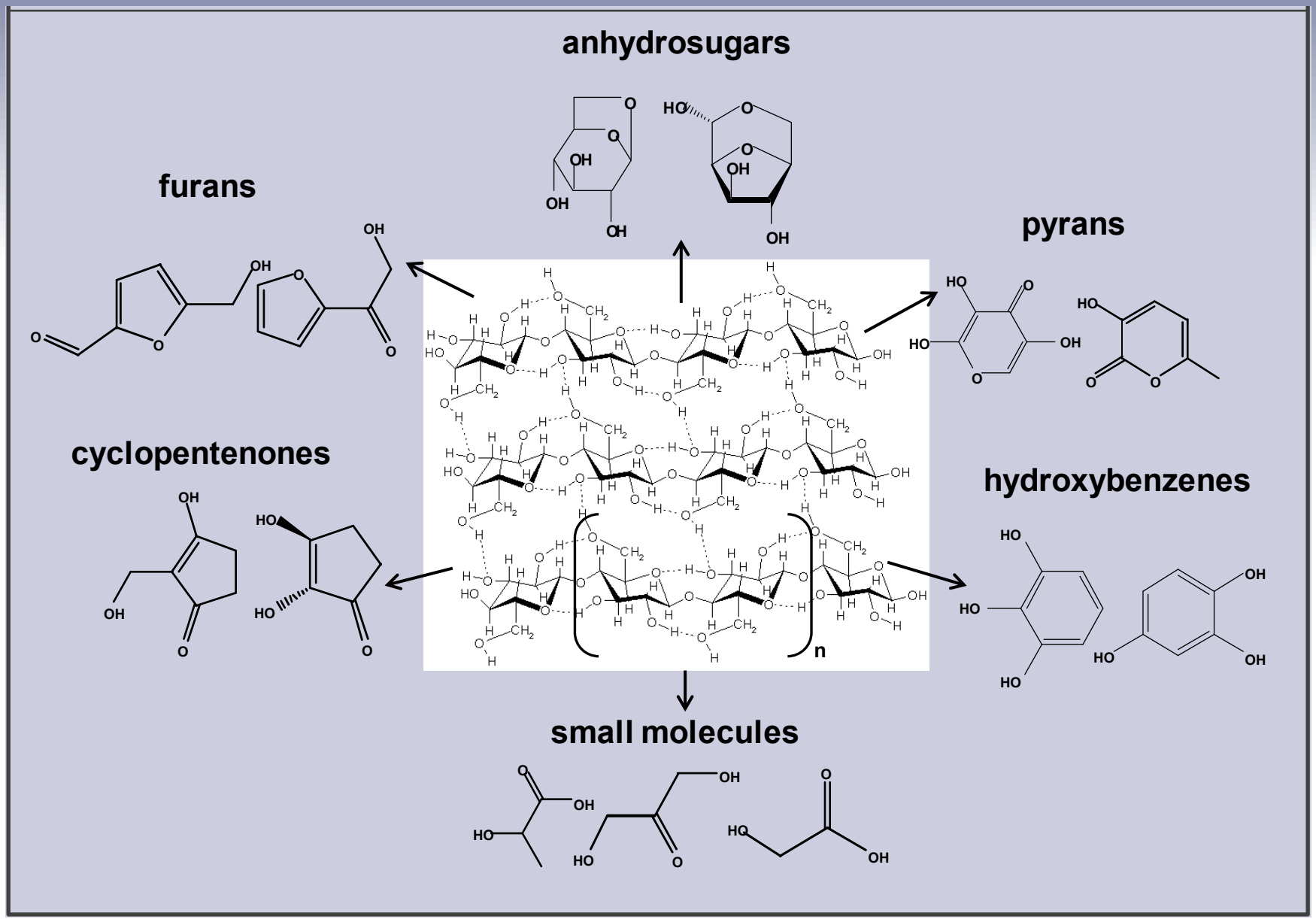
Py-GC-MS analysis of archaeological degraded wood:

information about the specific chemical changes occurred in wood components is needed : molecular information on lignin, cellulose and hemicelluloses

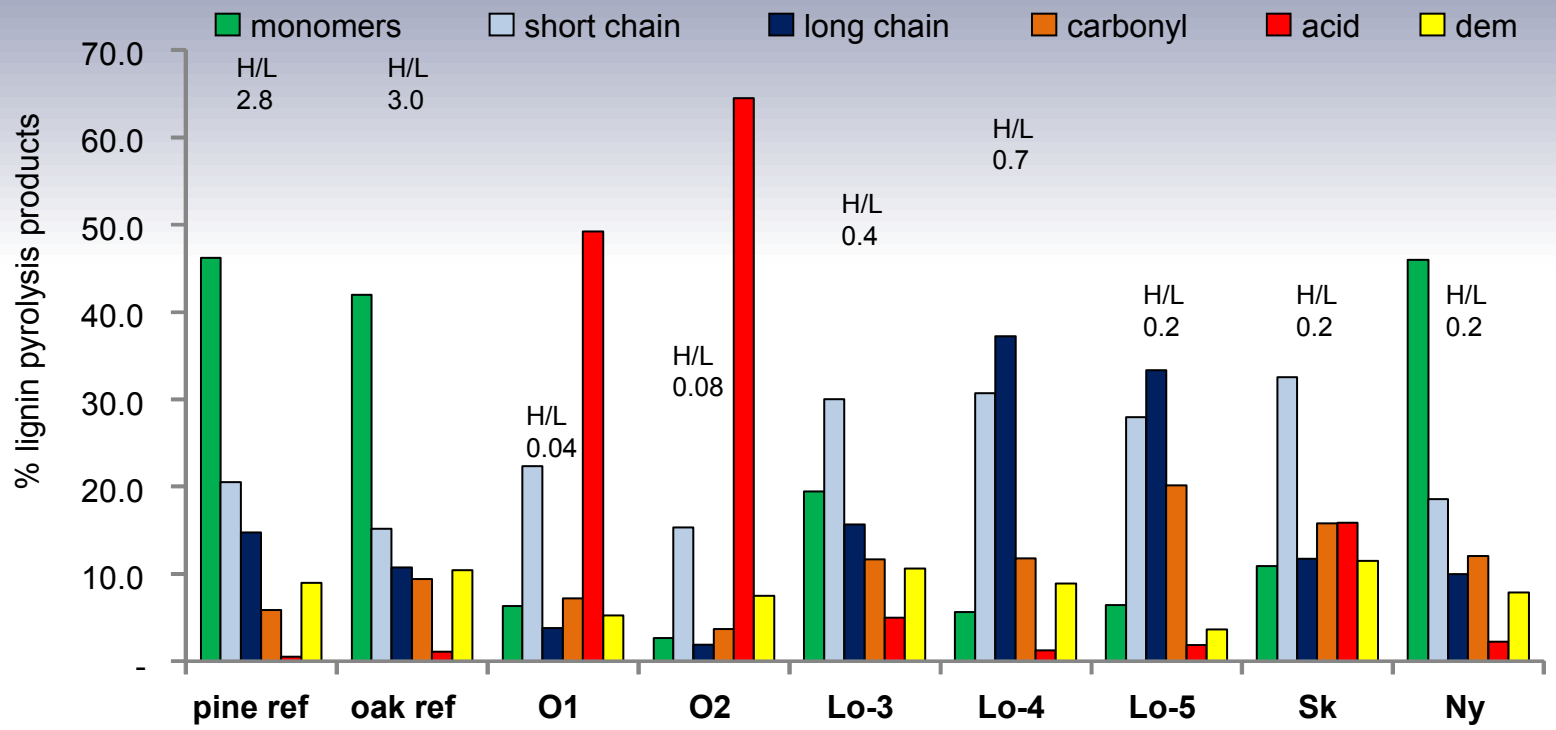
Pyrolysis products can be grouped into classes for semi-quantitative analysis: lignin



Pyrolysis products can be grouped into classes for semi-quantitative analysis: polysaccharides

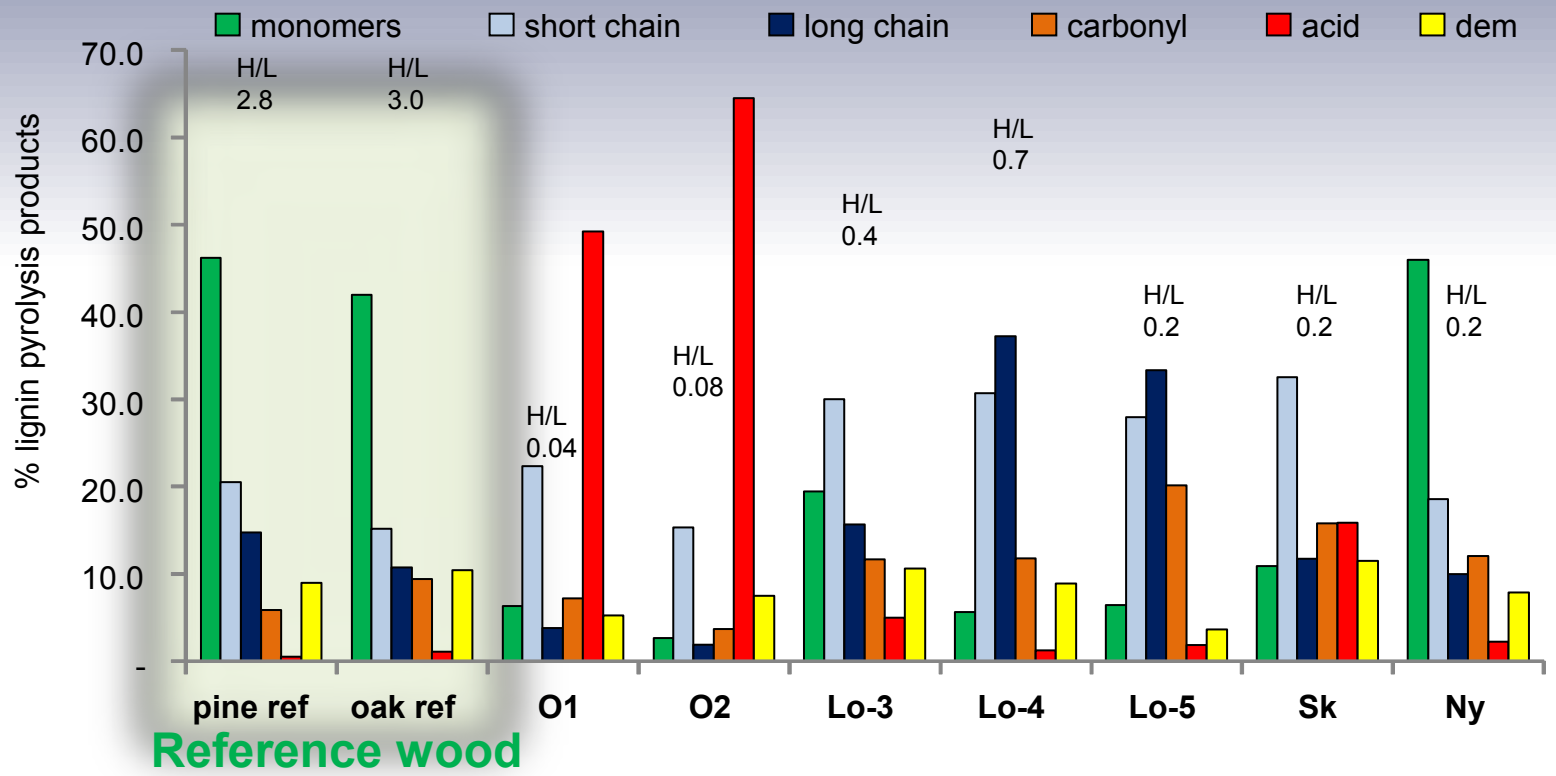


Relative amounts of lignin pyrolysis products in archaeological samples



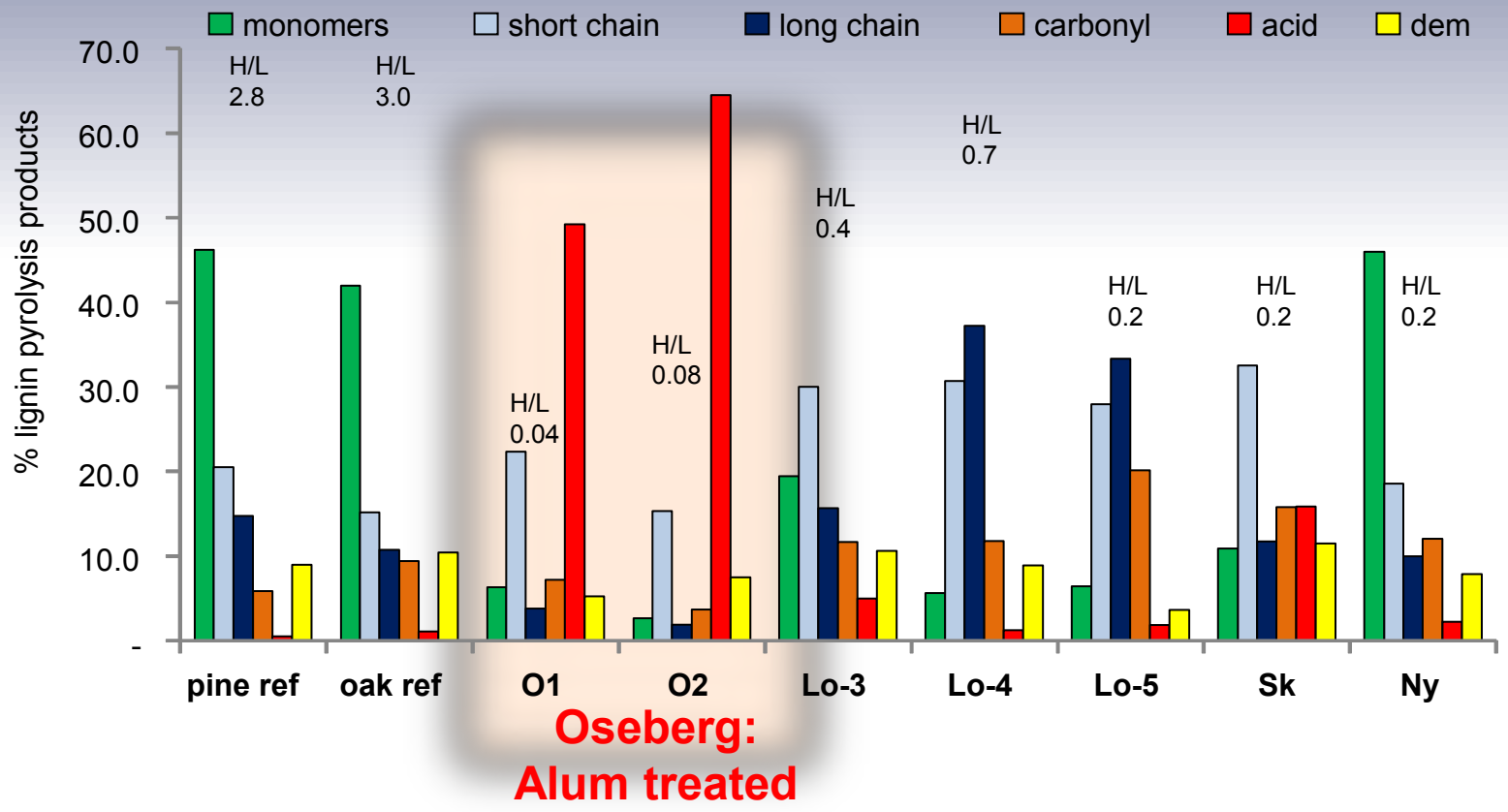
Calculation of the **percentage abundance** of each category with respect to the total lignin: information on **lignin alteration processes**

Relative amounts of lignin pyrolysis products in archaeological samples



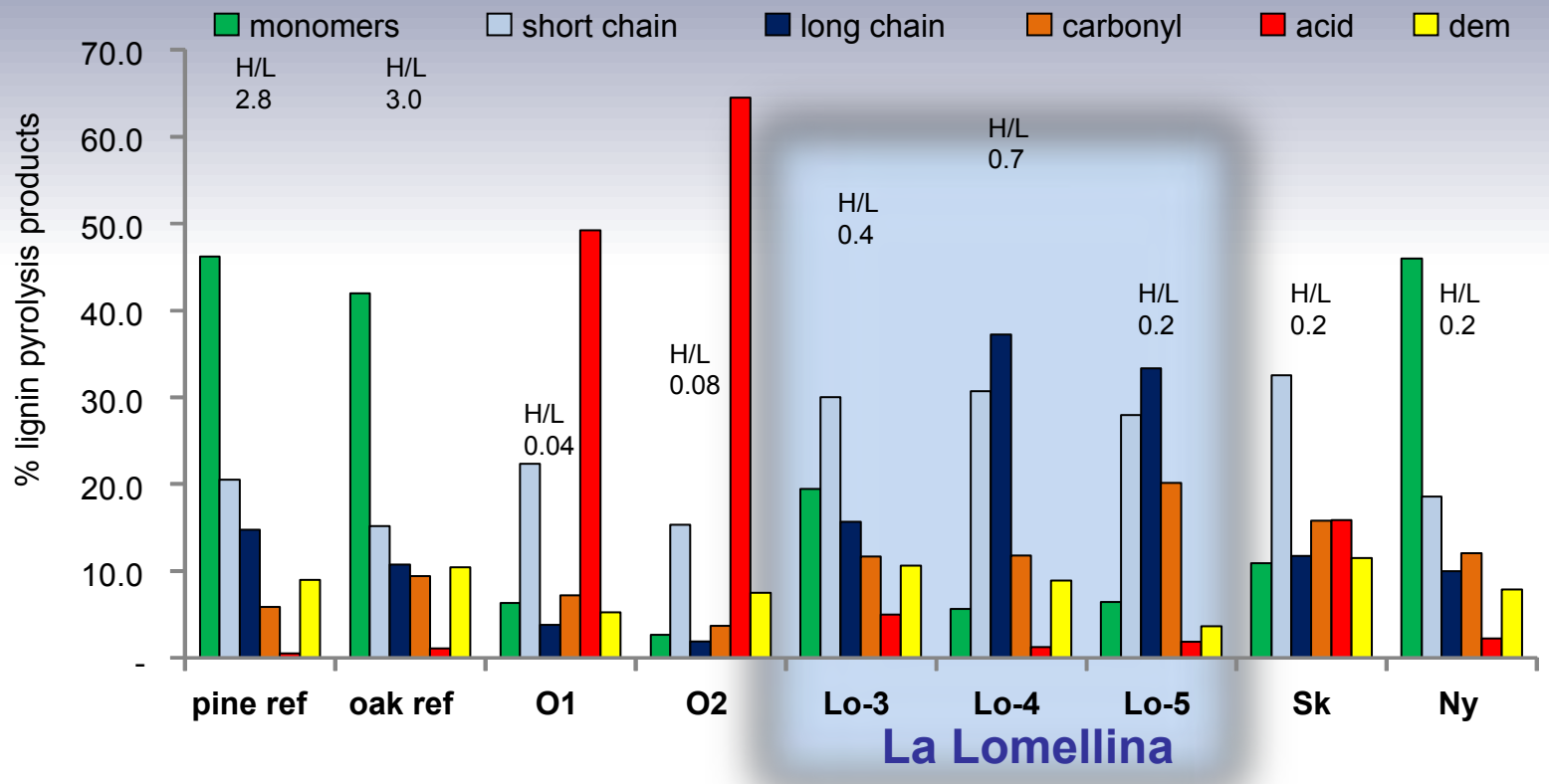
Undegraded reference wood samples show similar distribution of lignin pyrolysis products: **monomers** 50%, short-chain ca. 15-20 %, **long-chain** ca. 10 %, **carbonyl** ca. 5-10 %, **acids** 1-2 % and **demethylated/demethoxylated** 5-10%

Relative amounts of lignin pyrolysis products in archaeological samples



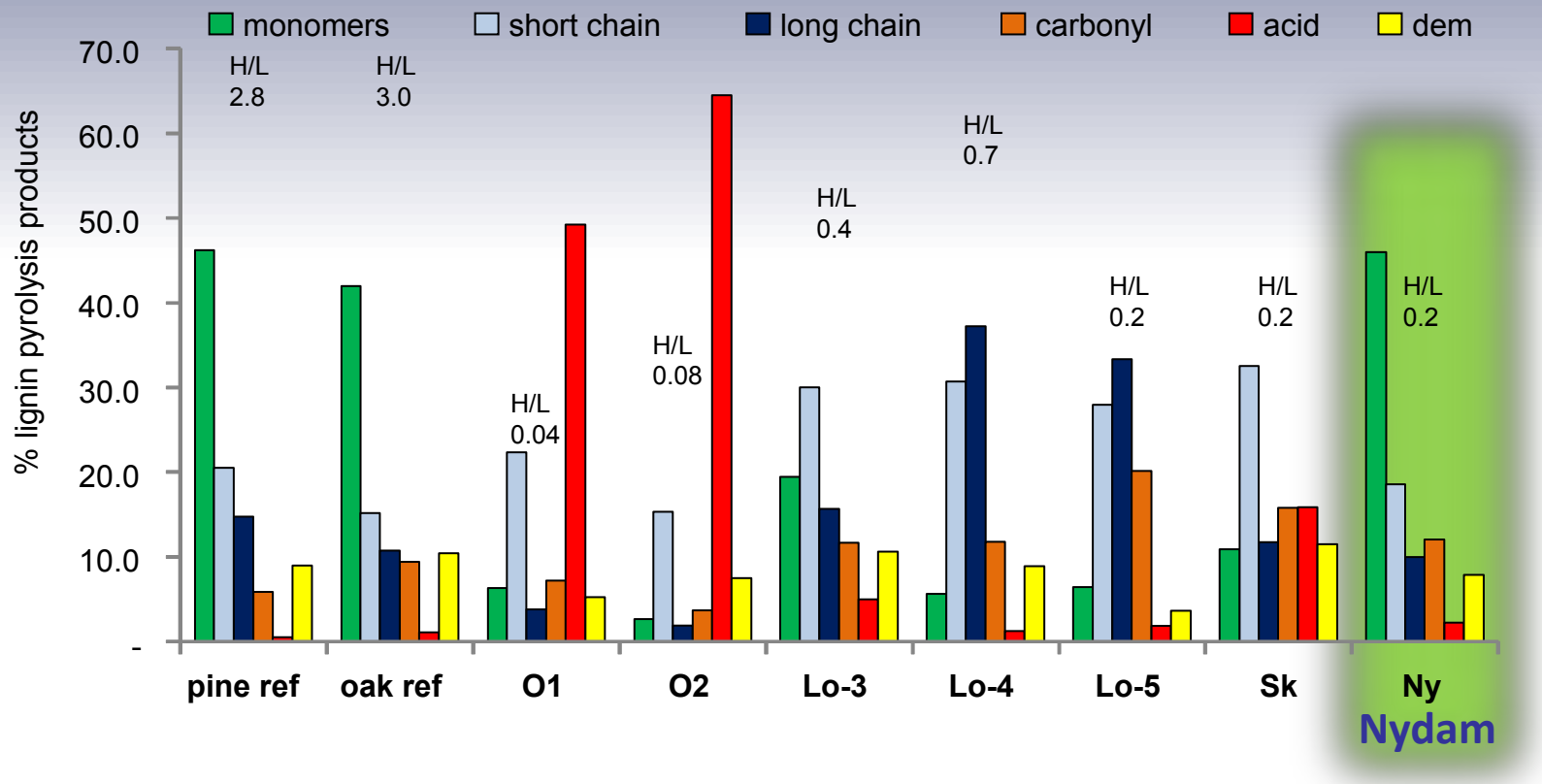
Oseberg alum treated material: lignin units with carboxylic groups up to 50-60% extreme oxidation of lignin

Relative amounts of lignin pyrolysis products in archaeological samples



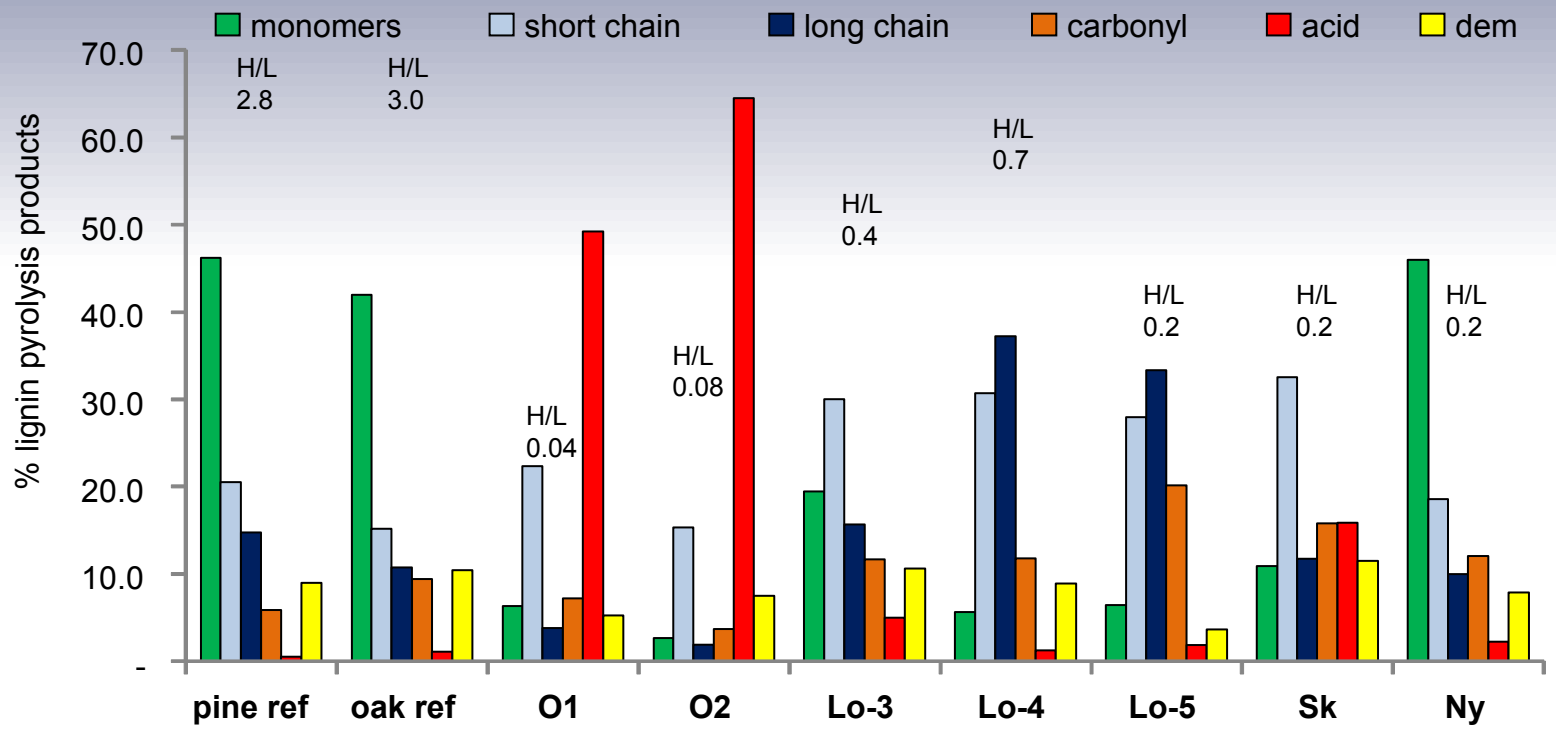
La Lomellina: reduction in **monomers** ⬇ and increase in short-chain ⇧ and **long-chain** ⬆ pyrolysis products: alteration of the lignin side chains.
Medium preservation level .

Relative amounts of lignin pyrolysis products in archaeological samples



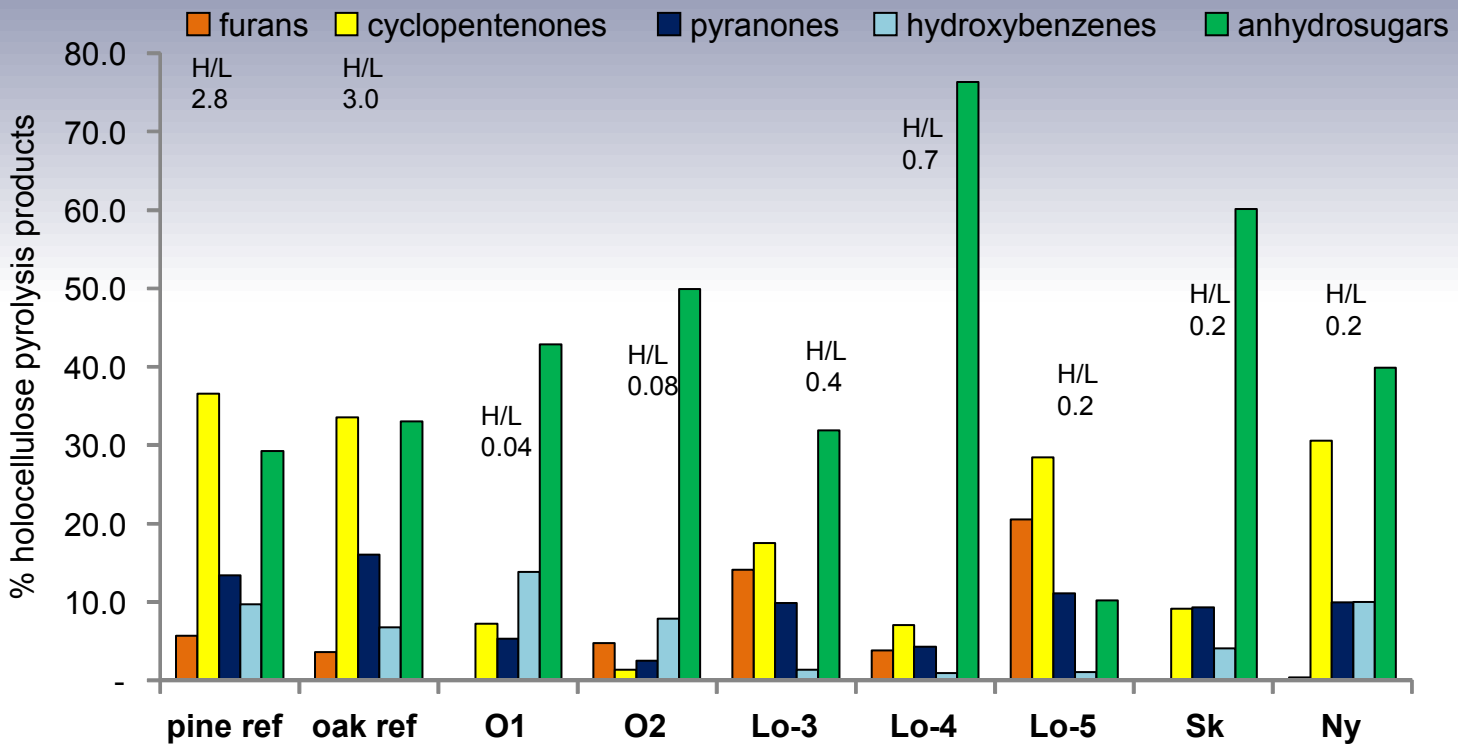
Nydam boat: distribution of categories almost identical to oak reference sample perfect conservation of lignin

Relative amounts of lignin pyrolysis products in archaeological samples



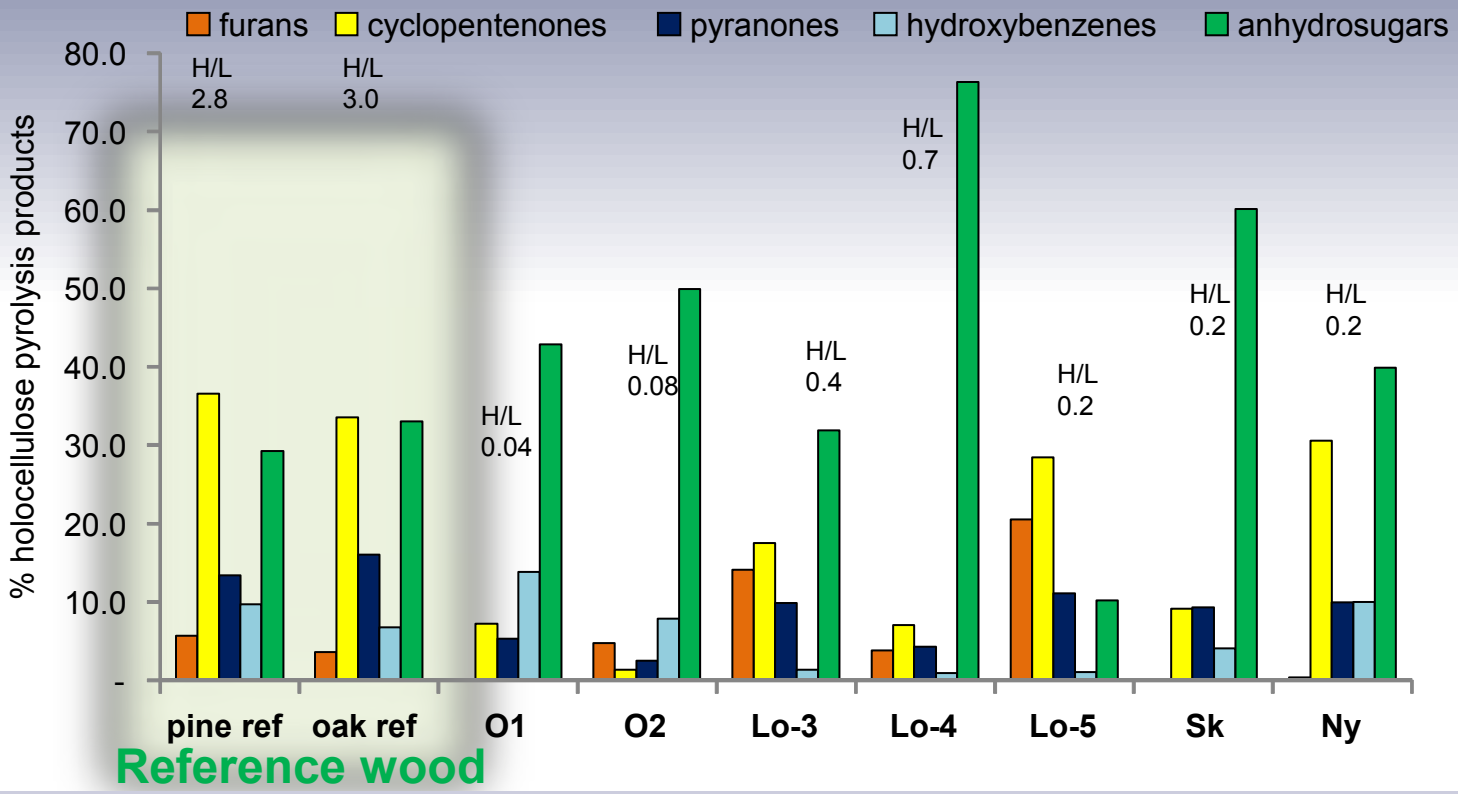
Despite **very similar H/L ratios**, all the samples highlighted a **very different preservation state of lignin**

Relative amounts of polysaccharides pyrolysis products in archaeological samples



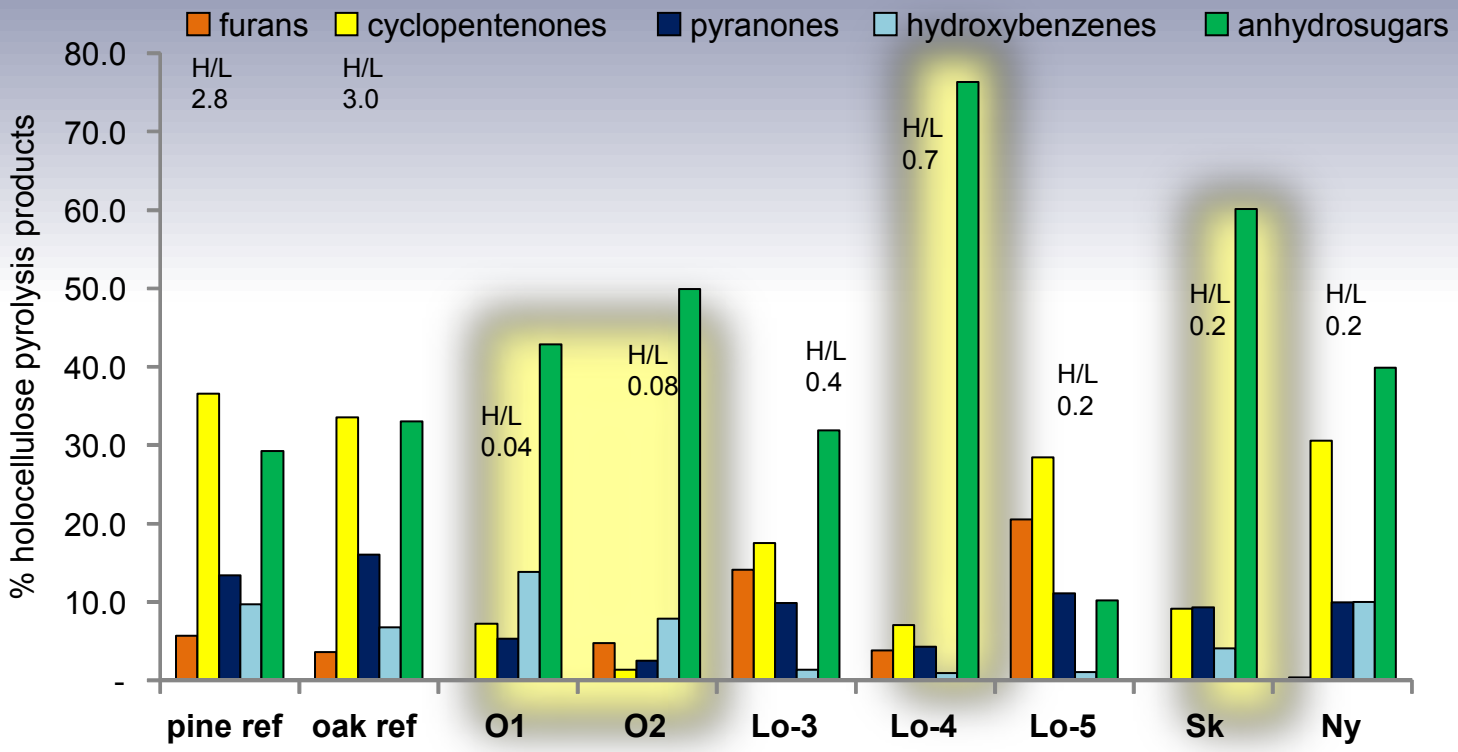
Although residual holocellulose is present in low amount in the samples, it is possible to evaluate differences in the **preservation state of the residual carbohydrates** examining their pyrolysis products.

Relative amounts of polysaccharides pyrolysis products in archaeological samples



Undegraded pine and oak woods: similar distribution of holocellulose pyrolysis products. Comparable abundances of anhydrosugars and cyclopentenones (30-35 %), pyranones *ca.* 15 %, furans *ca.* 5 % and hydroxybenzenes *ca.* 5-10 %

Relative amounts of polysaccharides pyrolysis products in archaeological samples



Oseberg collection, **Lo-4** and **Skuldelev**: increase in **anhydrosugars partial depolymerisation of cellulose**, a decay phenomena that <u>cannot</u> be evaluated on the basis of the H/L ratio and of spectroscopic data

The thermal degradation ranges of the components can be studied by Evolved Gas Analysis – Mass Spectrometry

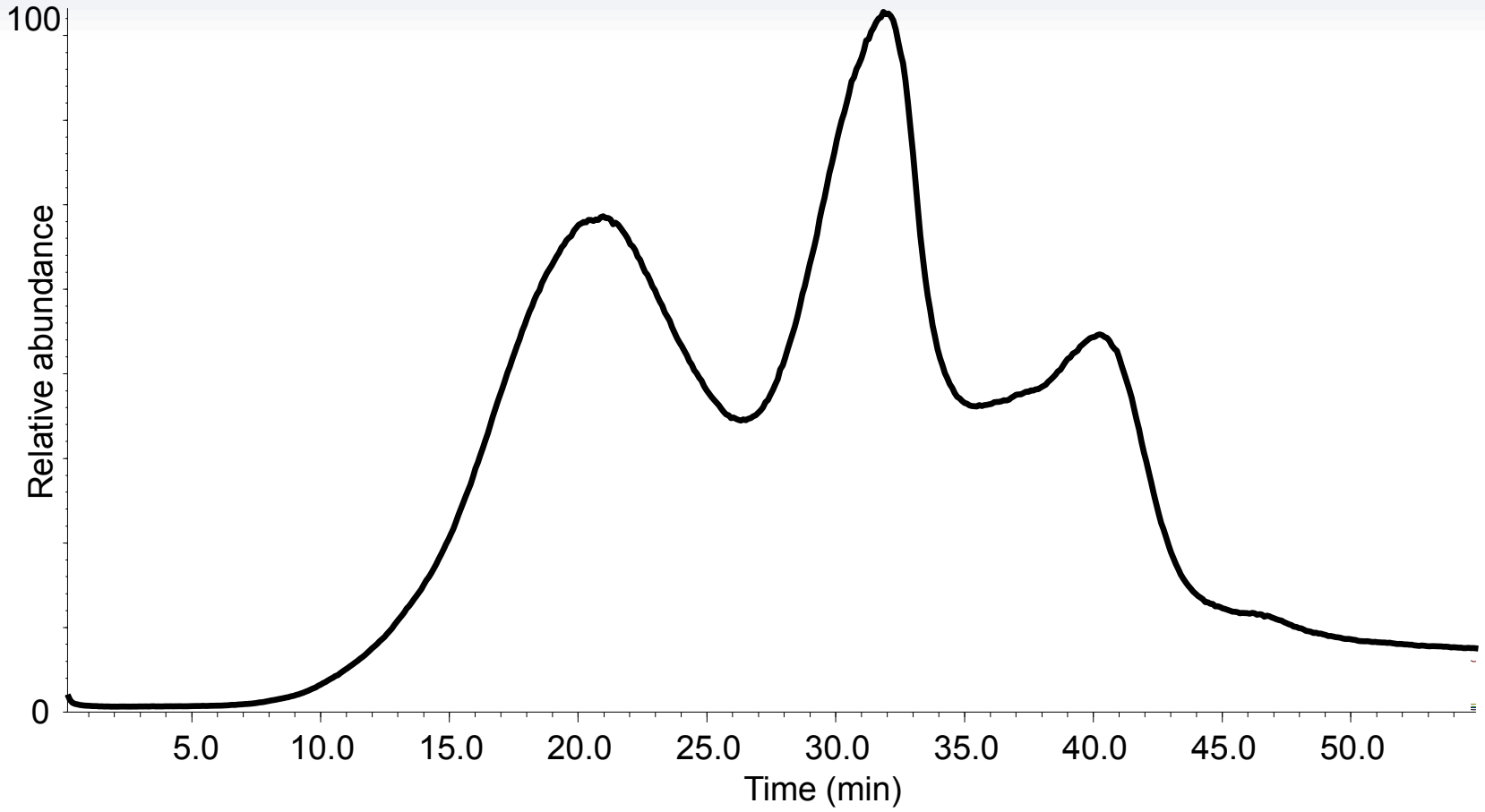
EGA-MS

T_{pyr} = 50-200°C (20°C/min), 200-500°C (8°C/min), 500-700°C (20°C/min)

Tamburini D, Łucejko JJ, Modugno F, Colombini MP (2016). Combined pyrolysis-based techniques to evaluate the state of preservation of archaeological wood in the presence of consolidating agents. *Journal of Analytical and Applied Pyrolysis* 122, pp. 429–441

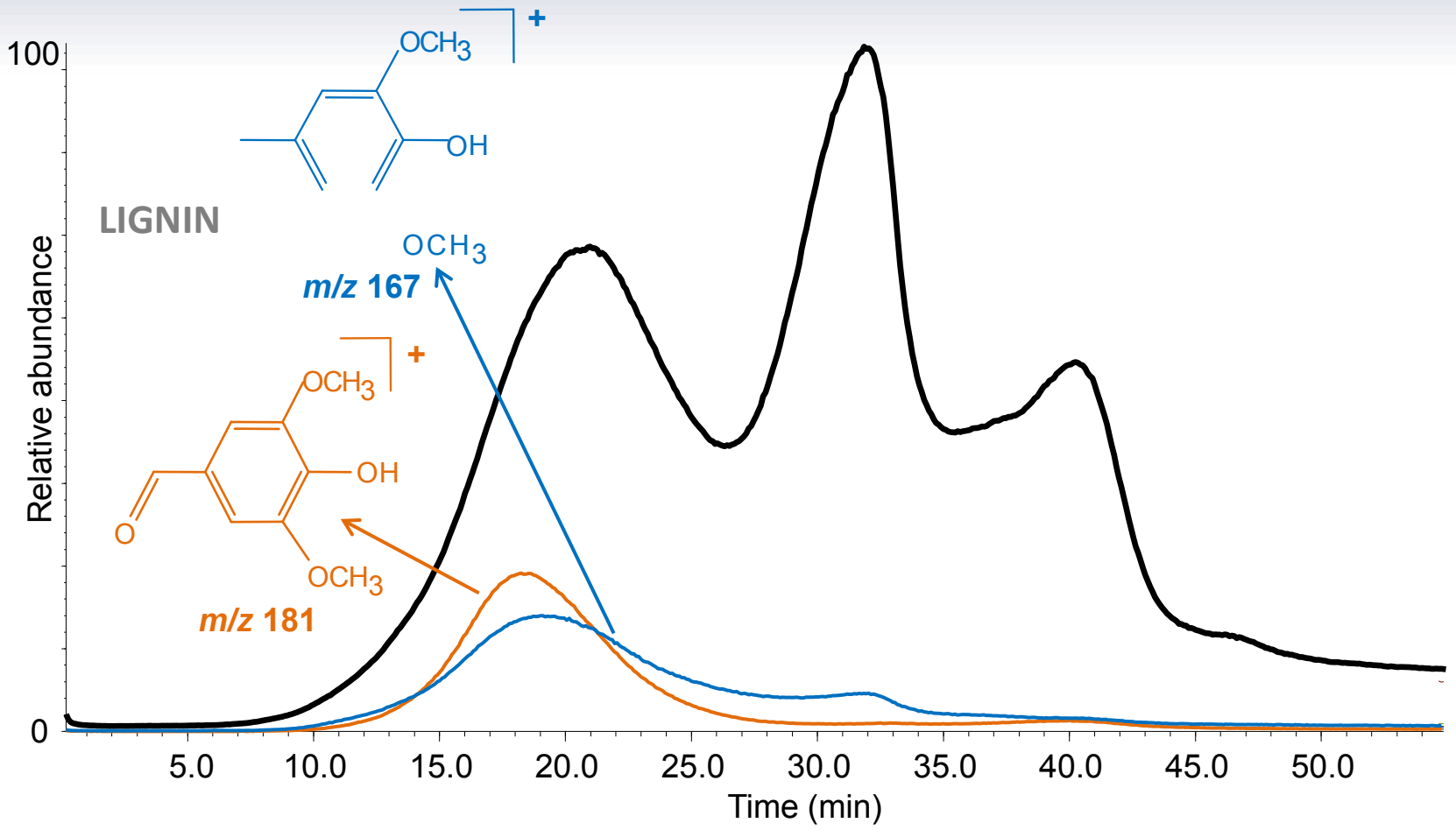
EGA-MS T_{pyr} = 50-200°C (20°C/min), 200-500°C (8°C/min), 500-700°C (20°C/min)

Total Ion Thermogram Lyon ship: treated with PEG and Na_2Seb



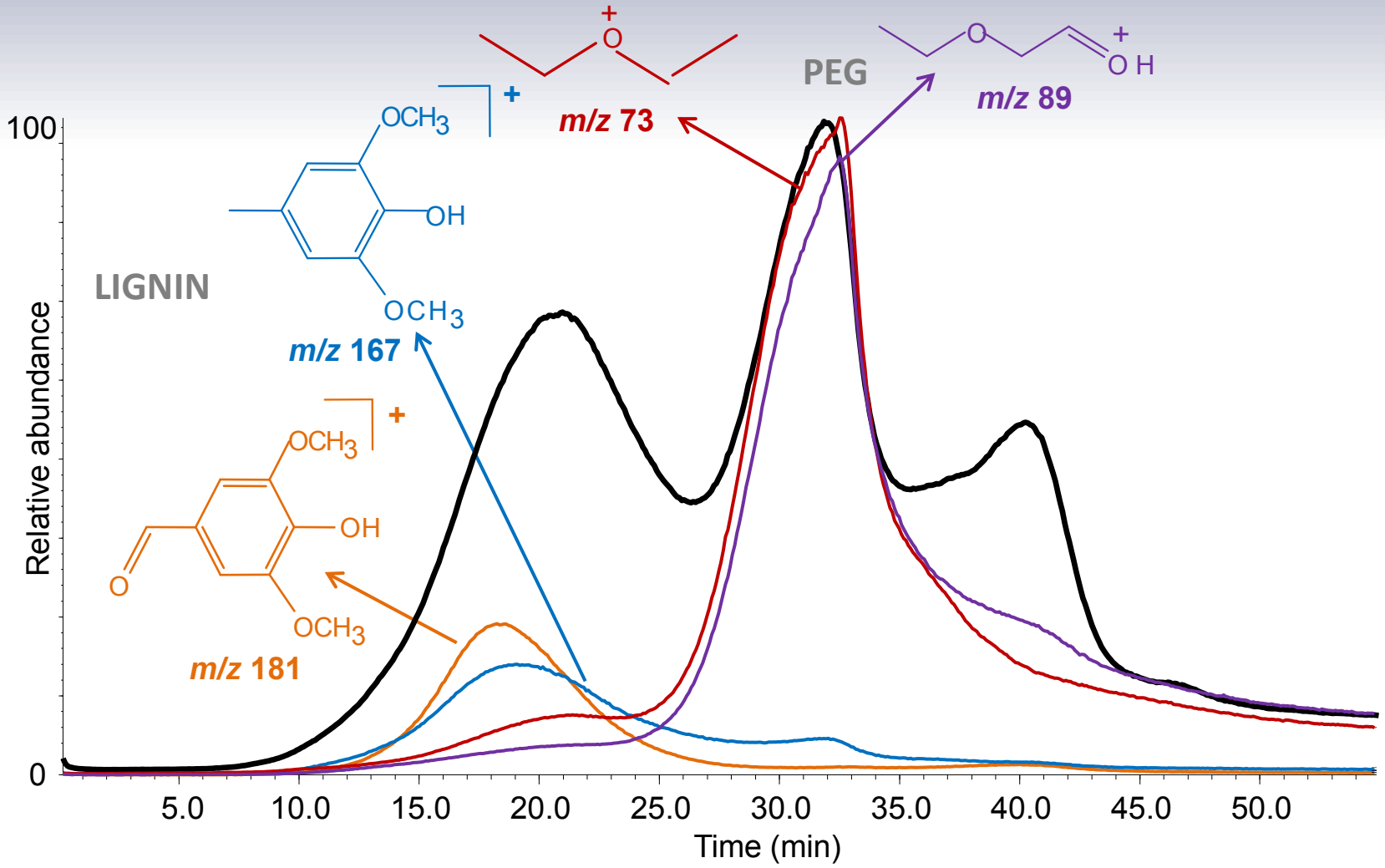
EGA-MS T_{pyr} = 50-200°C (20°C/min), 200-500°C (8°C/min), 500-700°C (20°C/min)

Total Ion Thermogram Lyon ship: treated with PEG and Na_2Seb



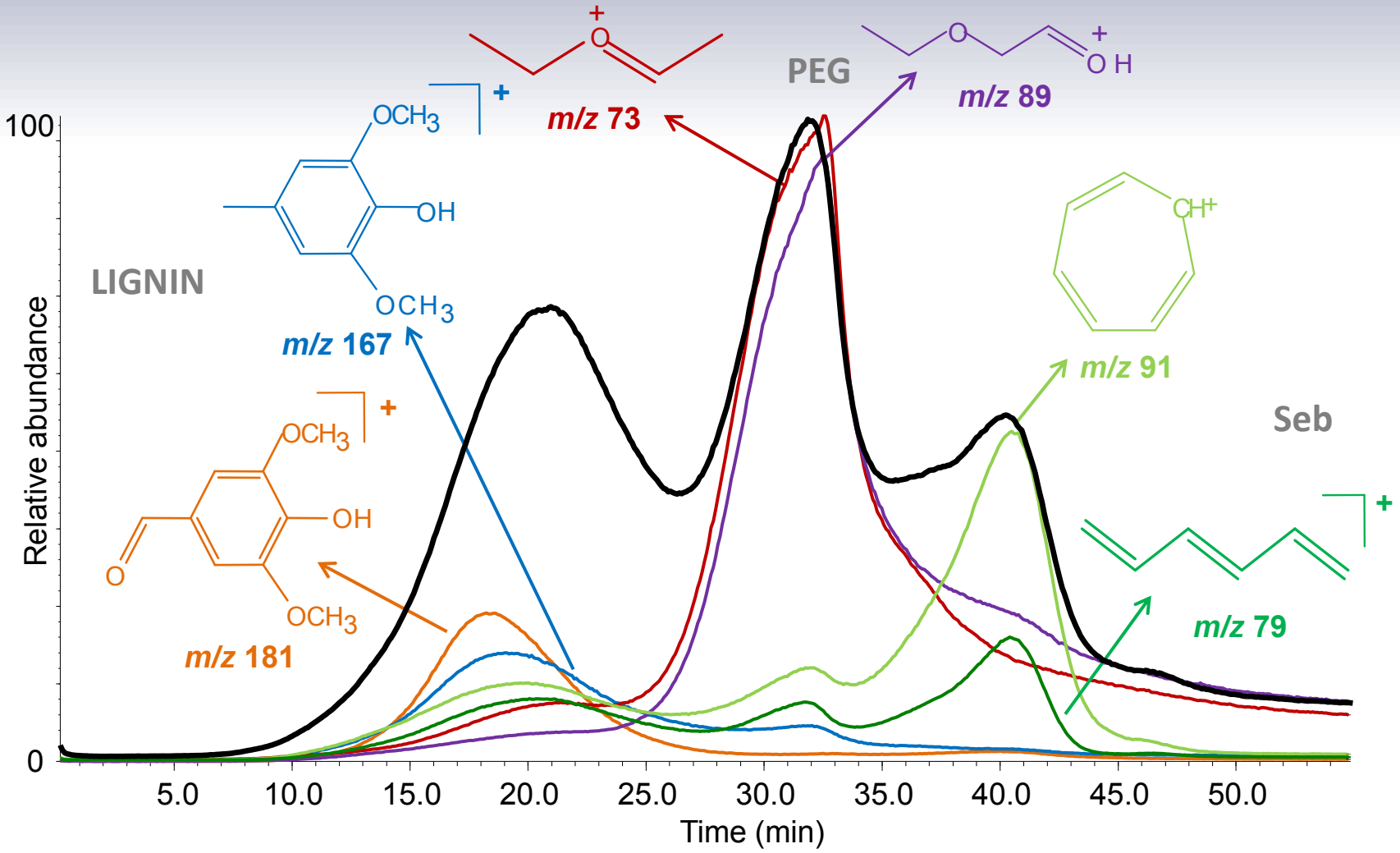
EGA-MS T_{pyr} = 50-200°C (20°C/min), 200-500°C (8°C/min), 500-700°C (20°C/min)

Total Ion Thermogram Lyon ship: treated with PEG and Na_2Seb



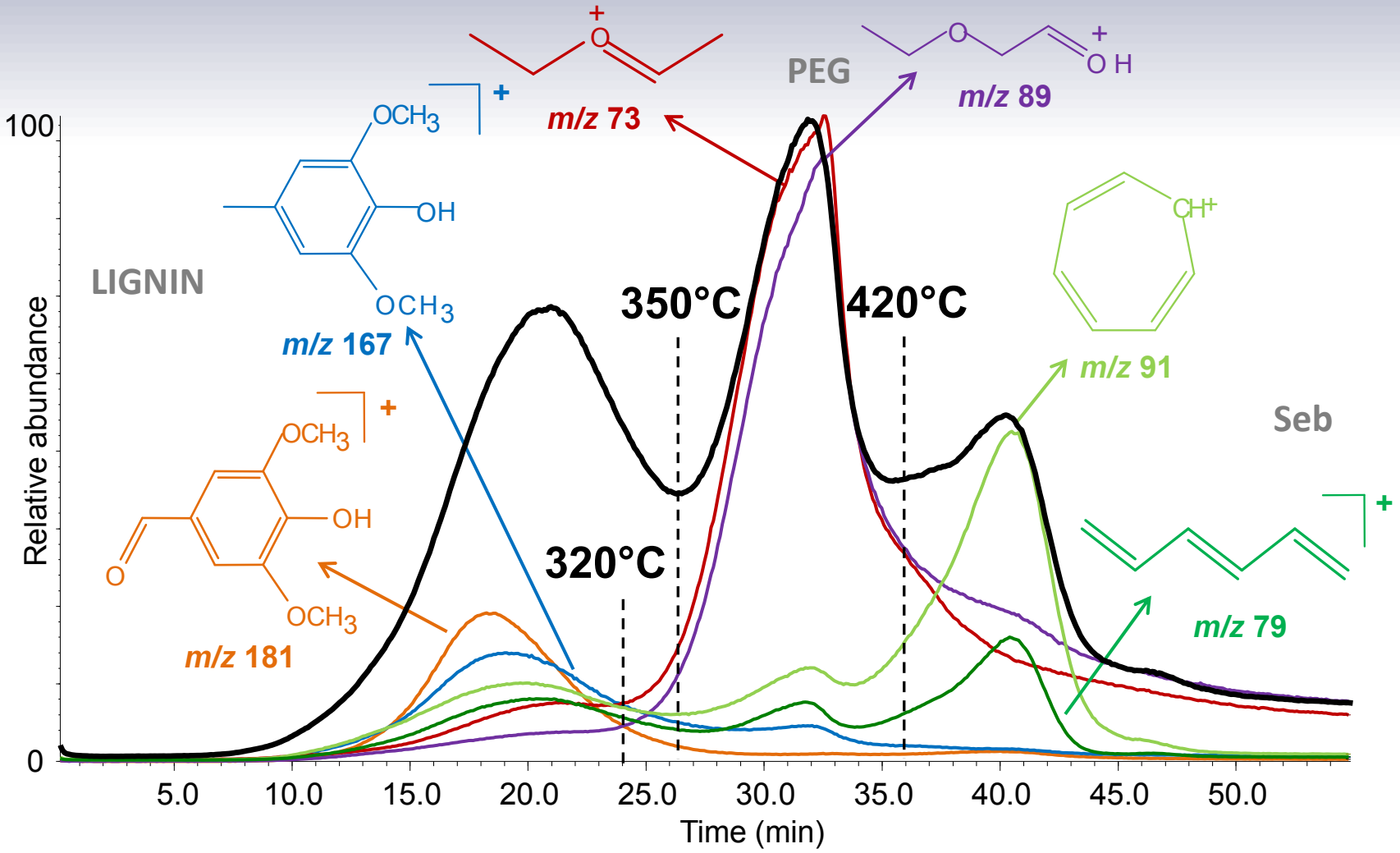
EGA-MS T_{pyr} = 50-200°C (20°C/min), 200-500°C (8°C/min), 500-700°C (20°C/min)

Total Ion Thermogram Lyon ship: treated with PEG and Na_2Seb

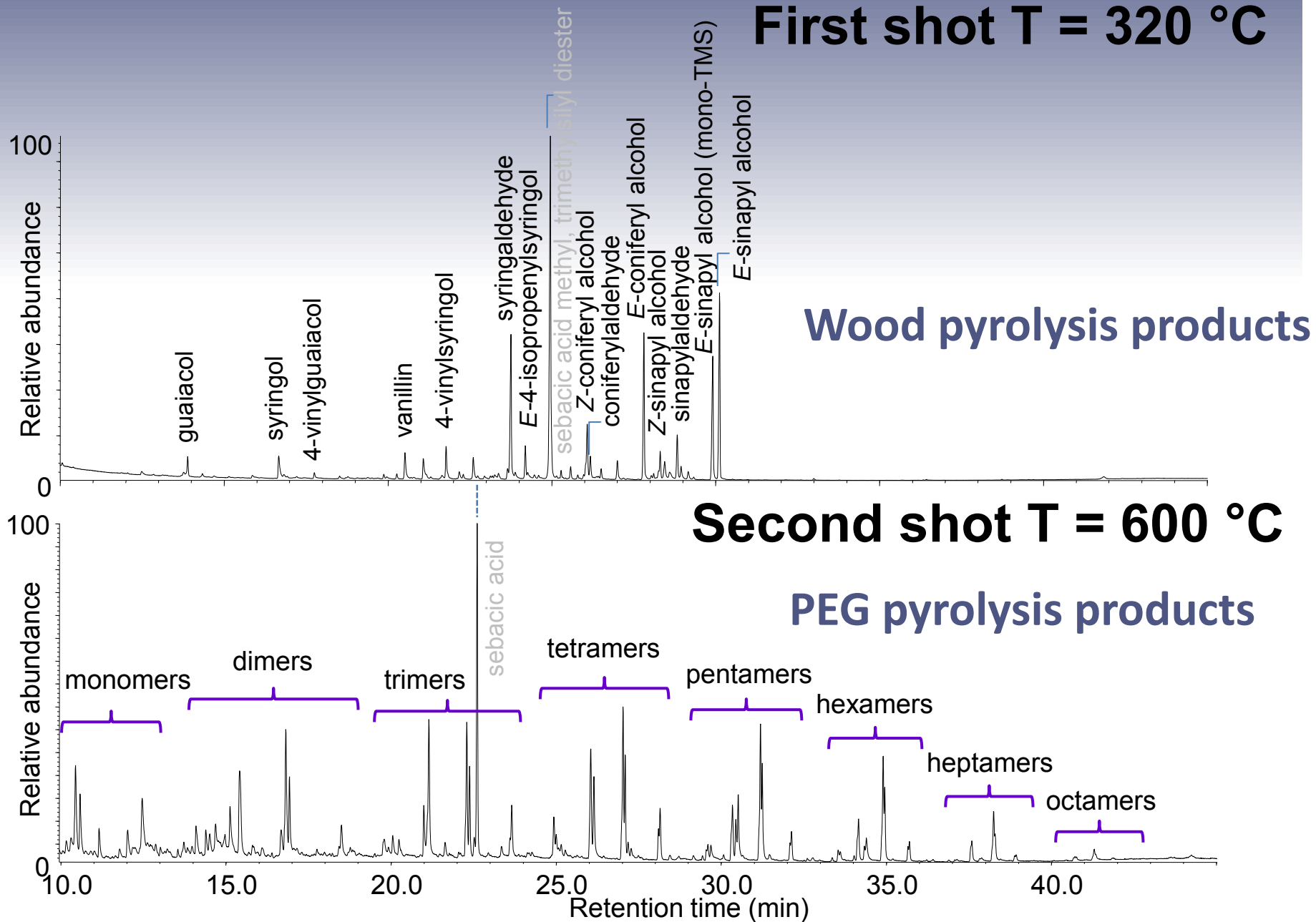


EGA-MS T_{pyr} = 50-200°C (20°C/min), 200-500°C (8°C/min), 500-700°C (20°C/min)

Total Ion Thermogram Lyon ship: treated with PEG and Na_2Seb



Double Shot Py-GC/MS Lyon ship treated PEG and $SebNa_2$



Analytical pyrolysis of archaeological degraded wood:

- Analytical pyrolysis-based techniques Py(HMDS)- GC/MS, EGA-MS, double shot Py(HMDS)-GC/MS permit to evaluate the degradation state **of composite archaeological wooden** artefacts in presence of consolidant materials

- The **categorisation of a high number of wood pyrolysis** products and the evaluation of their distribution allows to obtain a high molecular detail, going **beyond the simple estimation of the H/L ratio** and highlighting **new potentialities** of analytical pyrolysis in the analysis of archaeological wood.

- **EGA-MS** and double shot **Py-GC/MS** can be exploited to better investigate separately wood and consolidant materials

Similar approaches allow:

- Analysis of biomass for green chemistry and renewable energy
- Study of pyrolysis mechanisms of lignocellulosic polymers
- Study of composite materials containing lignocellulosic polymers

Mattonai, M., Ribechini, E. , A comparison of fast and reactive pyrolysis with in situ derivatisation of fructose, inulin and Jerusalem artichoke (Helianthus tuberosus), 2018, Analytica Chimica Acta 1017, 66-74

Mattonai et al., Timing in Analytical Pyrolysis: Py(HMDS)-GC/MS of Glucose and Cellulose Using Online Micro Reaction Sampler 2016 Analytical Chemistry 88(18), 9318

Pyrolysis -GC/MS and Py-MS

Detailed chemical information to investigate

Synthetic polymers in art

Pyrolysis -GC/MS and Py-MS
Detailed chemical information to investigate
Synthetic polymers in art

1847: **polyester** resins production

1901: first **alkyd resin**

Synthetic paint binders

1947: acryl paint binder in solvent (Magna paint)

1954: **PVAc** emulsion (Flashe paint)

1956: **acryl paint in emulsion** (Liquitex)

Morris Louis, Veil Paintings (1954)
Magna acrylic paint on canvas

Relation between preservation condition and binder composition in different Keith Haring public paintings

Tuttomondo (1989) Pisa

Excellent state of preservation

Py-GC/MS

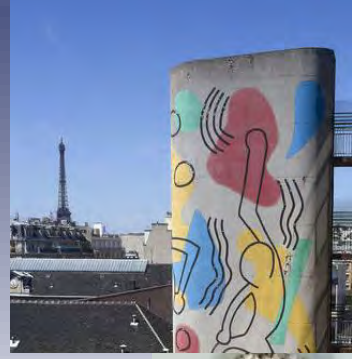
Paint binder: styrene/*n*-butylacrylate copolymer

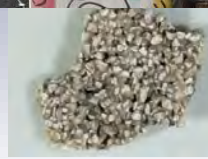
La Nasa et al, A chemical study of organic materials in three murals by Keith Haring: A comparison of painting techniques, *Microchemical Journal* 124, 2016, 940-948

Keith Haring

Necker Hospital mural (1987) in Paris

Necker Hospital mural





Sample 1

Relative Abundance

Acetic acid

Benzene

Toluene

Styrene

Indene

VeoVa + aromatic pyrolysis products

Butyl Phthalate

Sample 2

Sample 3

Wrinkling and detachments especially in the black paint

Vinyl resin plasticized with phthalate and VeoVa (vinyl ester of versatic acid)

La Nasa et al, *Microchemical Journal* 124, 2016, 940-948

LA GALLERIA

NAZIONALE

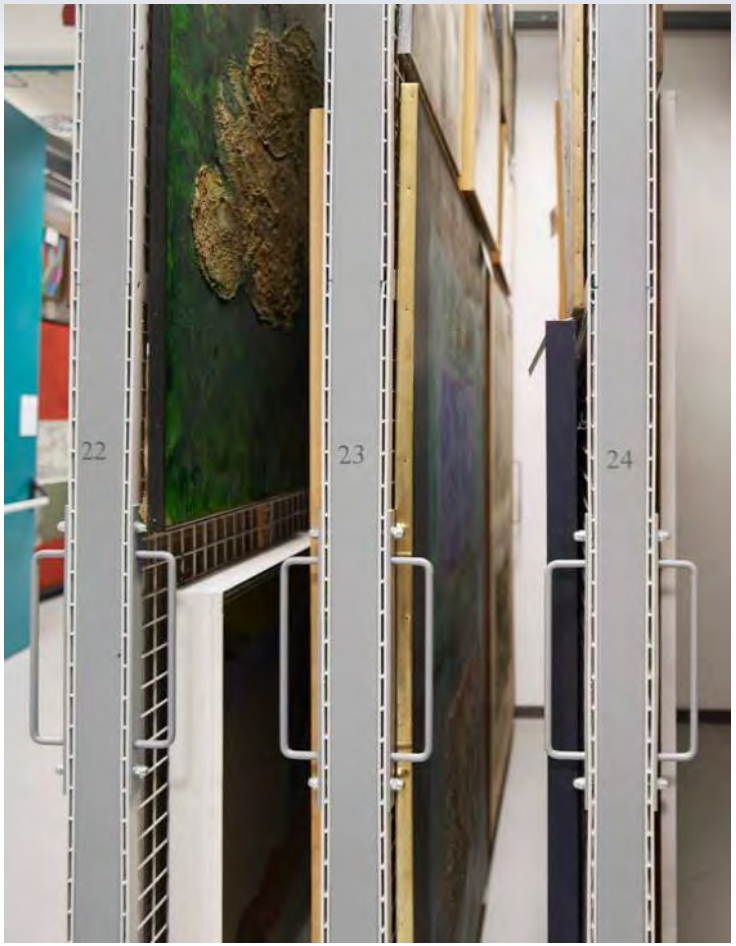
Galleria Nazionale Di Arte Moderna e Contemporanea (Rome)

LA GALLERIA

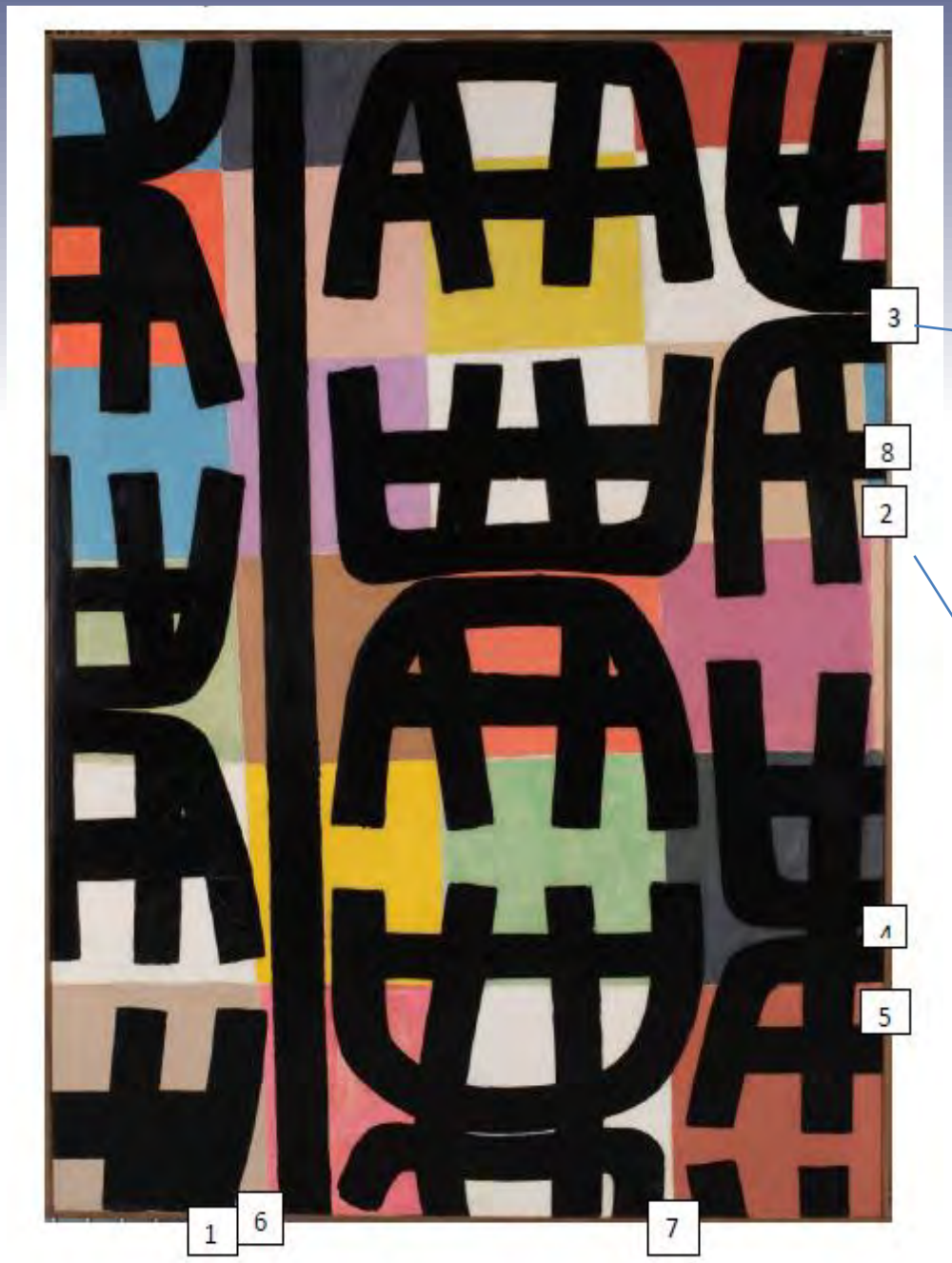
NAZIONALE

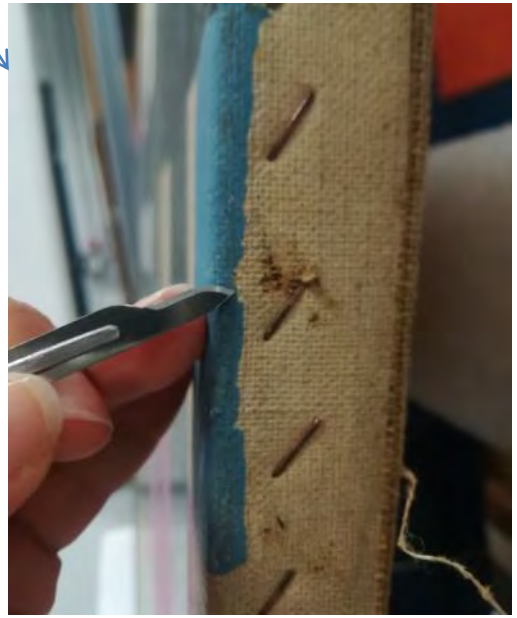
Galleria Nazionale Di Arte Moderna e Contemporanea (Rome)

Basement storage rooms: Giuseppe Capogrossi paintings



«Superficie 207» Capogrossi non inv. FTIR + microdestructive analysis





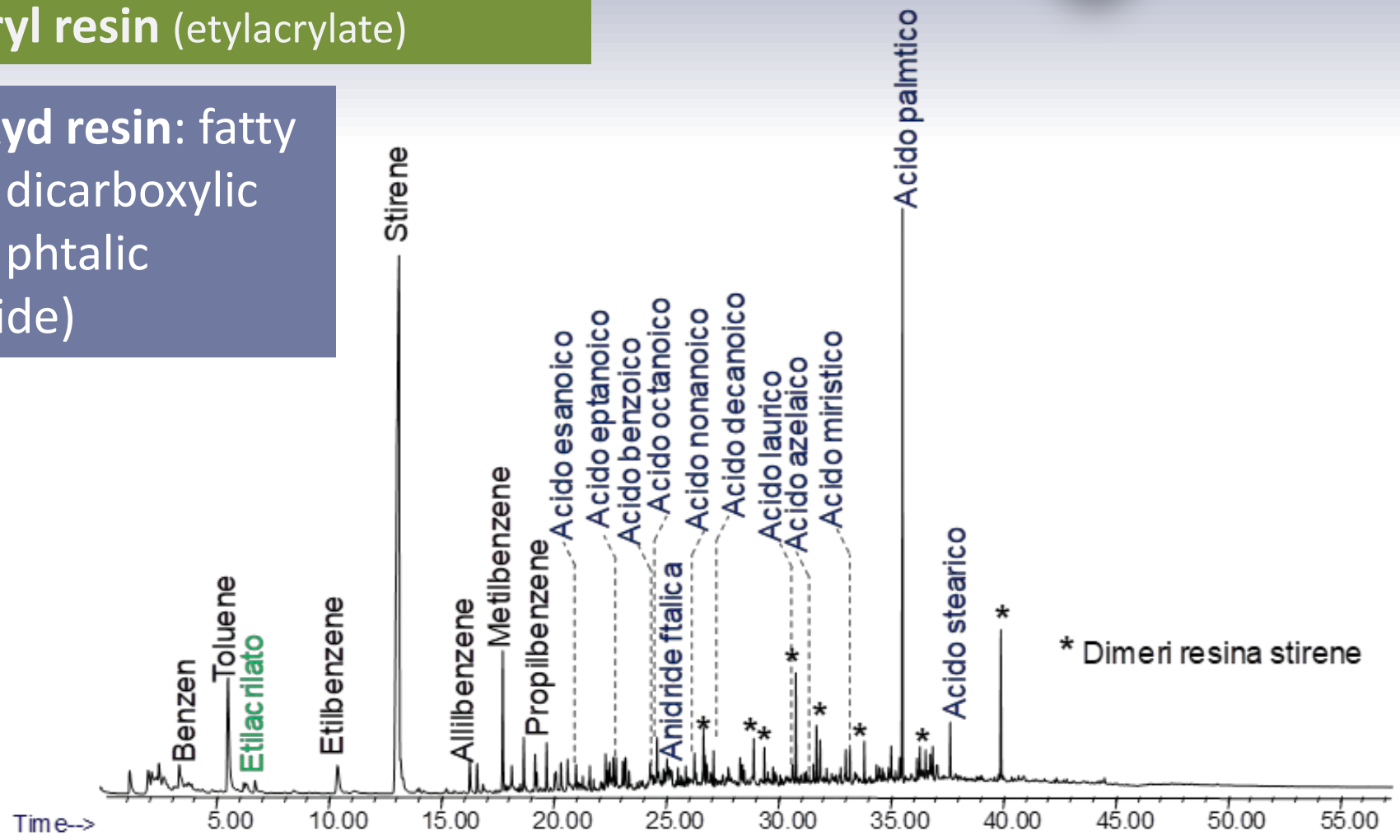
Superficie 207 sample 3 (fucsia)

pyrolysis-gas chromatography /mass spectroscopy Py(HMDS)-GC/MS

Polystyrene (styrene and dimers)

Acryl resin (etylacrylate)

Alkyd resin: fatty acids, dicarboxylic acids, phtalic anydride)



"Pratone" (1971), polyurethane and polyurethane foam, by Ceretti, Derosso and Rosso in the exhibition "*Giro Giro Tondo Design for Children",* 2018, Triennale Design Museum, Milan

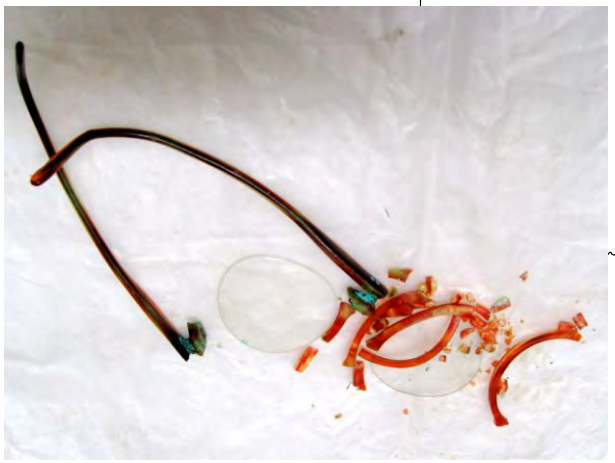
the preservation of synthetic polymer-based plastics is an urgent challenge for conservators and conservation scientists

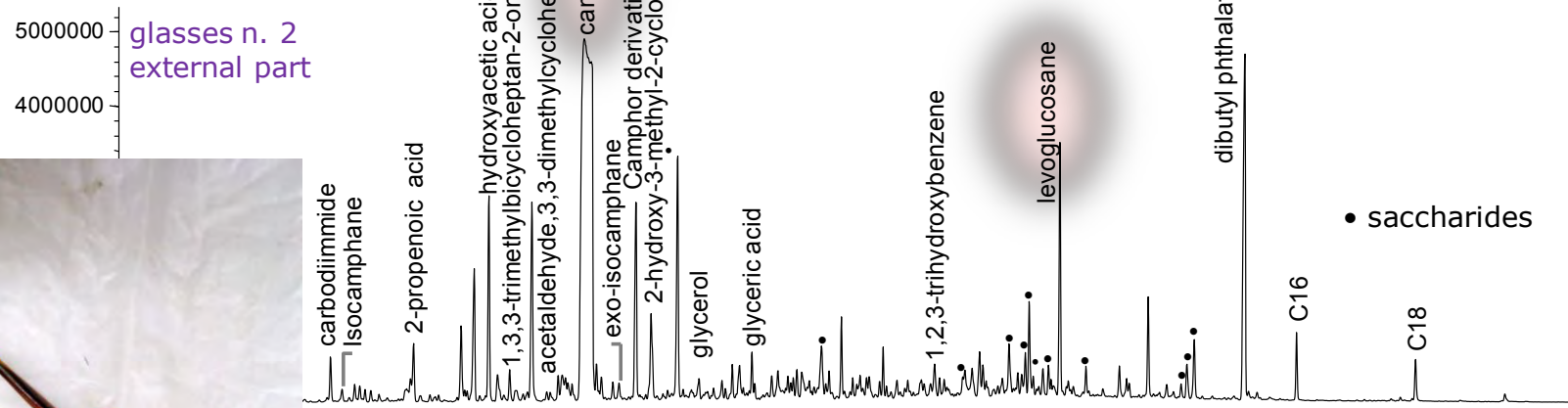
Y. Shashoua, Conservation of Plastics: Materials Science, Degradation and Preservation, Oxford: Butterworth-Heinemann, 2008

19th century celluloid objects from Czech museum collections

Alena Otmarova, Jeannette Łucejko

When sampling for Py-GC/MS does not compromise the integrity of the object





Comparison of relative abundances of camphor and levoglucosane in internal and external portions

Case studies

Triennale Design Museum

Design objects at Triennale Design Museum, Milan

Case studies: analysis of plastic objects in art

Triennale Design Museum

Design objects at Triennale Design Museum, Milan
Barbara Ferriani, Silvana Annicchiarico, Rafaela Trevisan

In collaboration with MOLAB CNR-ISTM (Perugia)
non-invasive *in situ* analysis
Francesca Rosi, Costanza Miliani





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Iperion CH: *European Research Infrastructure For Restoration And Conservation of Cultural Heritage*

Py-GC/MS Identification of unknown plastic materials

Triennale Design Museum

Design objects at **Triennale Design Museum**, Milan

Barbara Ferriani, Silvana Annicchiarico, Rafaela Trevisan

"Angel Lamp"

project and production 1994

by Gaetano Pesce

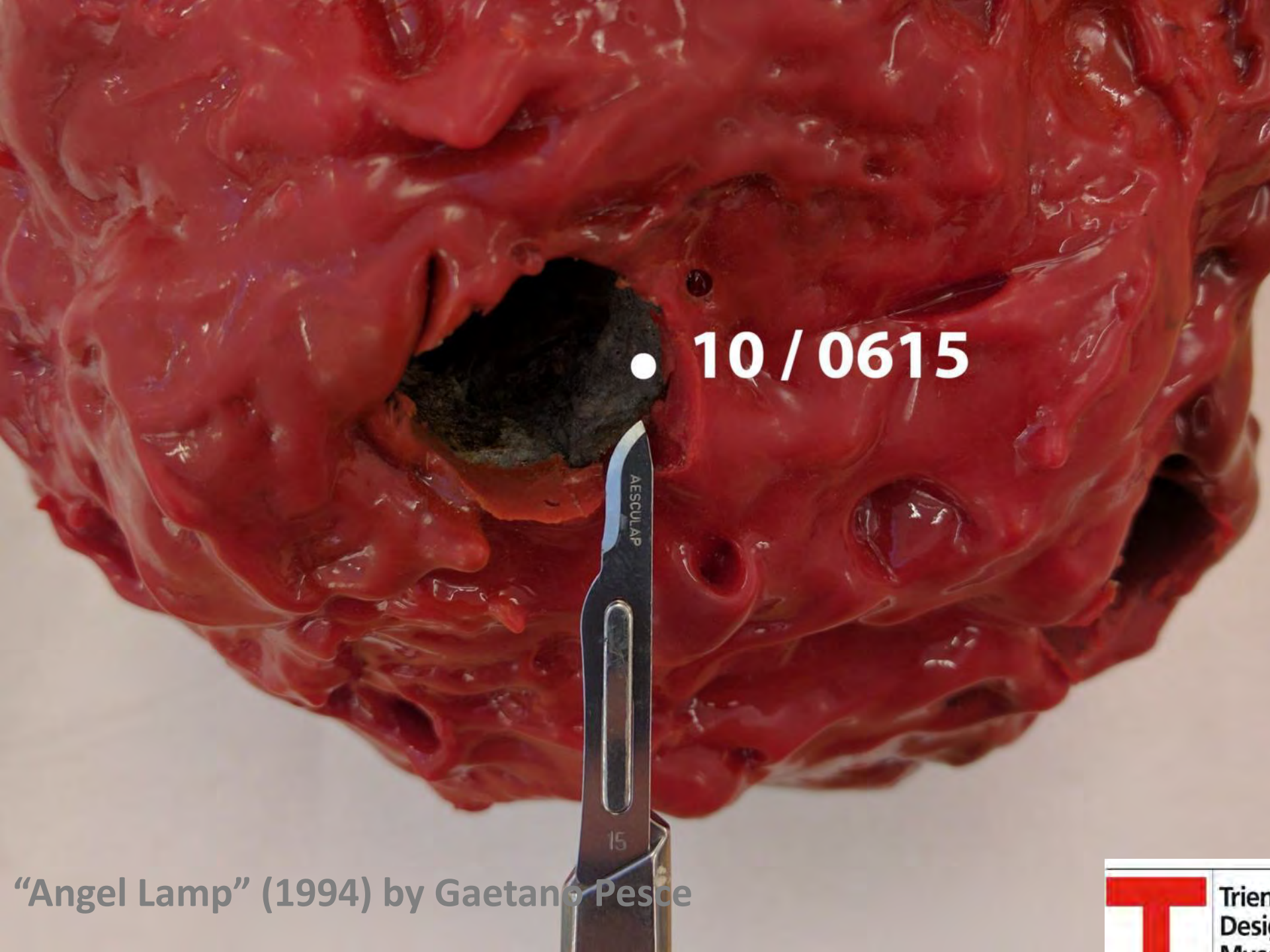
IPERION CH.it

Iperion CH: *European Research Infrastructure for Restoration and Conservation of Cultural Heritage*

The **morphology** does not allow non-invasive spectroscopic testing sampling for Py-GC-MS analysis

• 09 / 0615

“Angel Lamp” (1994) by Gaetano Pesce

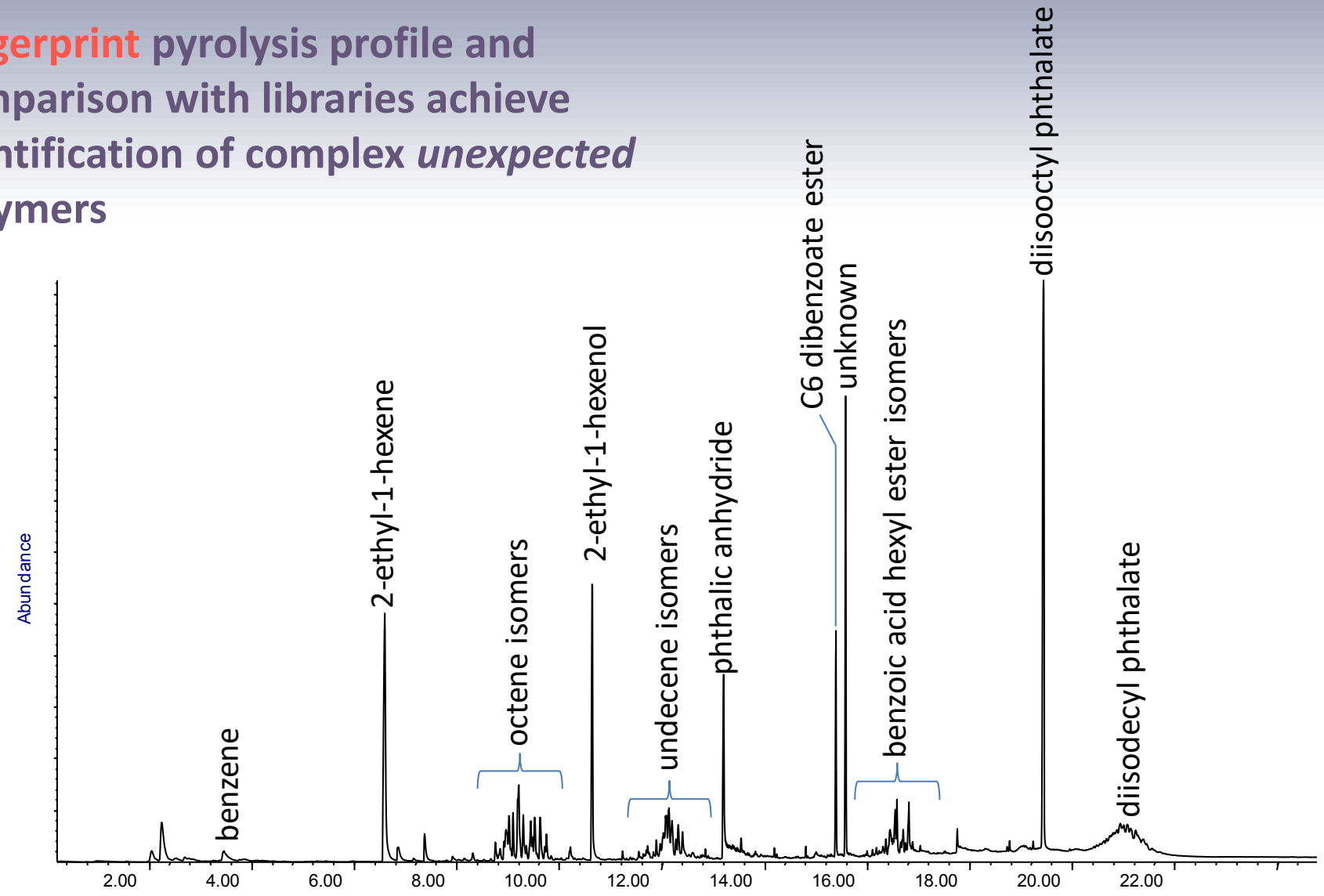


“Angel Lamp” (1994) by Gaetano Pesce

Py-GC/MS Angel Lamp (1994), Gaetano Pesce

Triennale Design Museum

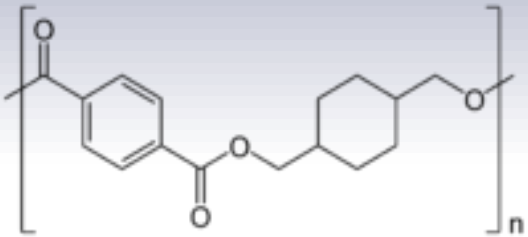
Fingerprint pyrolysis profile and comparison with libraries achieve identification of complex *unexpected* polymers

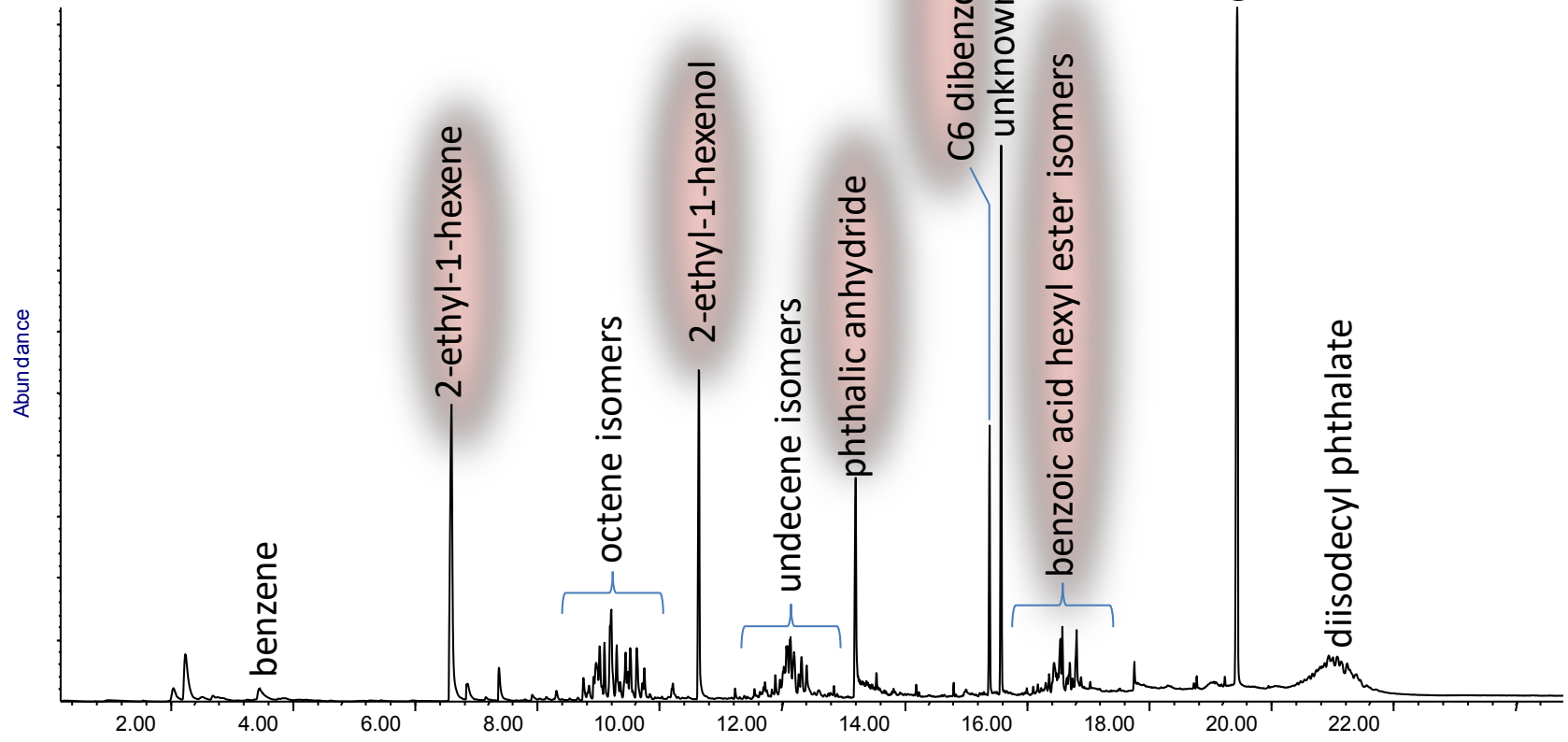


Py-GC/MS Angel Lamp (1994), Gaetano Pesce

Triennale Design Museum

Polycyclohexylenedimethylene terephthalate (PCT)

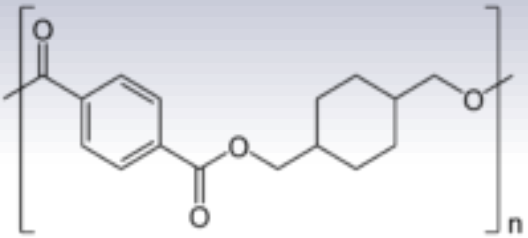




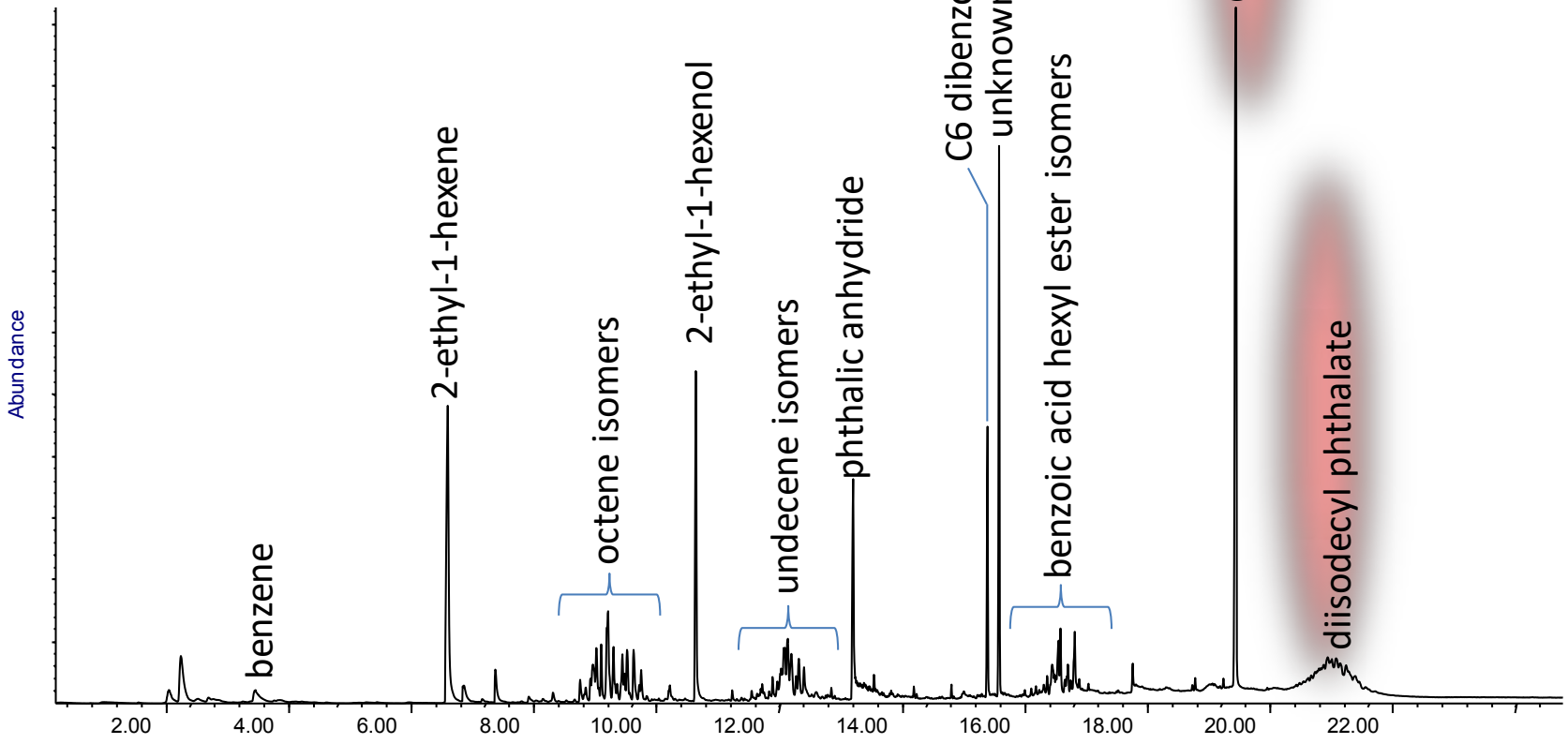
Py-GC/MS Angel Lamp (1994), Gaetano Pesce

Triennale Design Museum

Polycyclohexylenedimethylene terephthalate (PCT)

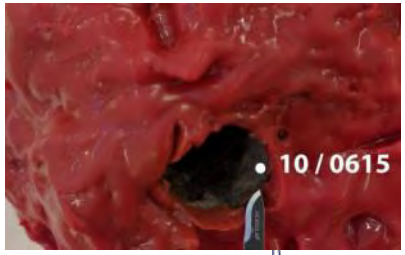


Plasticizers



Py-GC/MS Angel Lamp (1994), Gaetano Pesce

Triennale Design Museum



TDM8AL

TDM9AL

TDM10AL

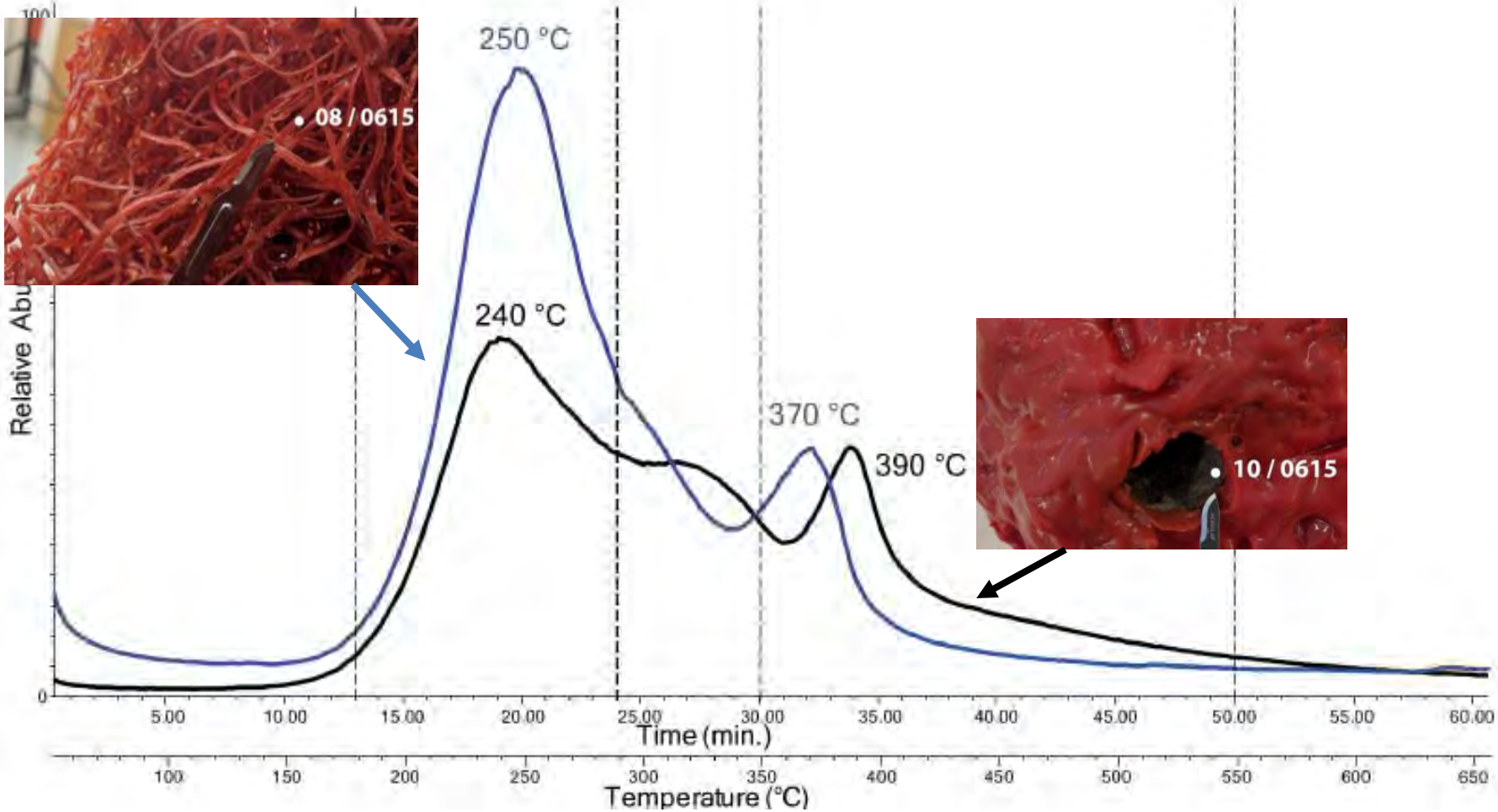
Plasticizers

Time--> 2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00

Evaluation of degradation processes: loss of plasticizers due to heating in the *head* of the lamp

EGA-MS Angel Lamp (1994), Gaetano Pesce

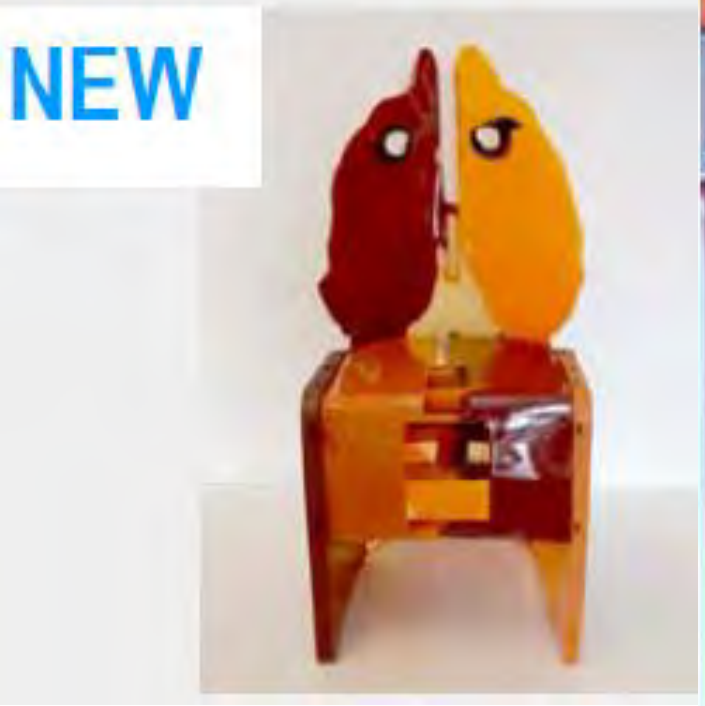
Triennale Design Museum

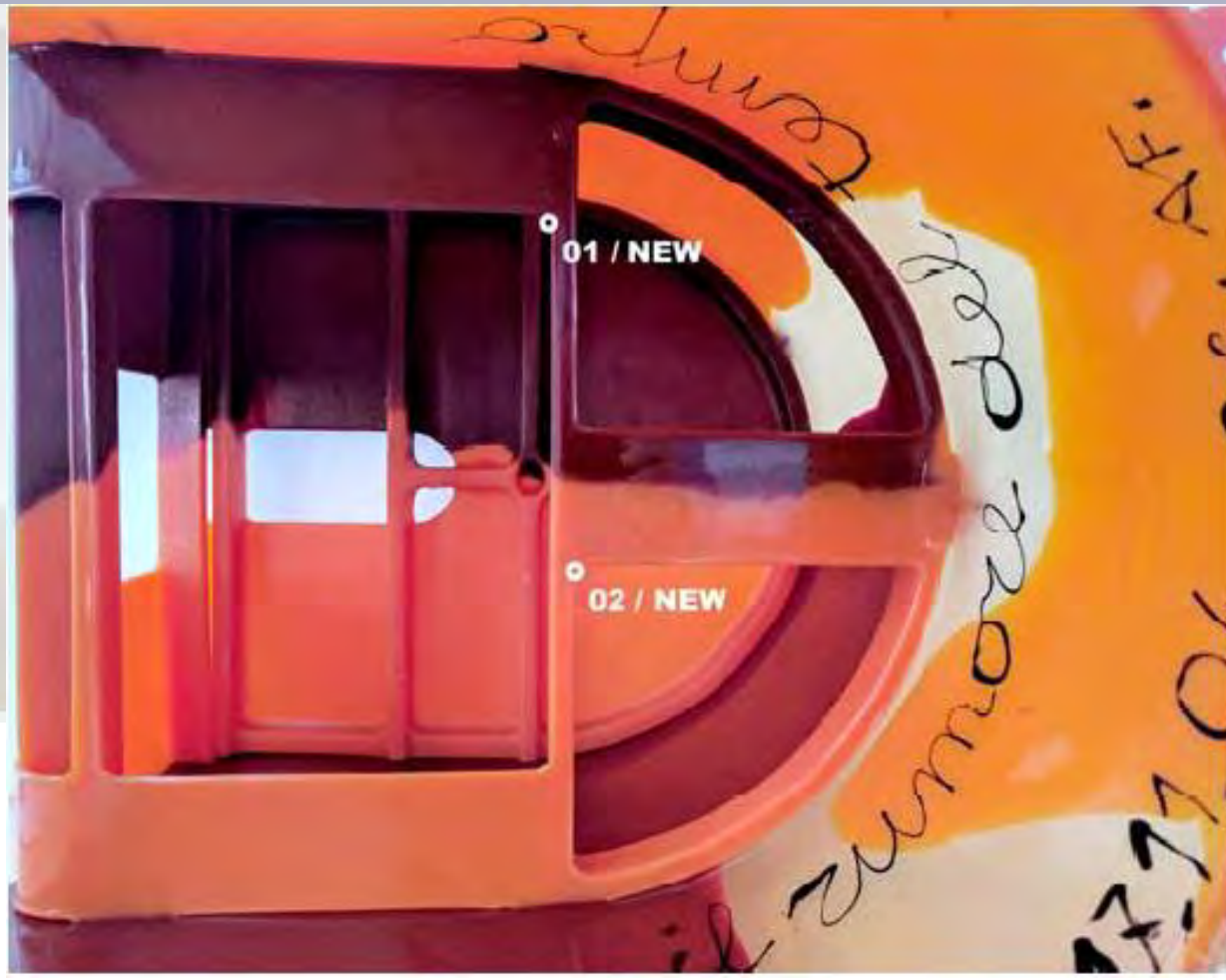


Comparison of the thermal profiles to investigate alteration processes

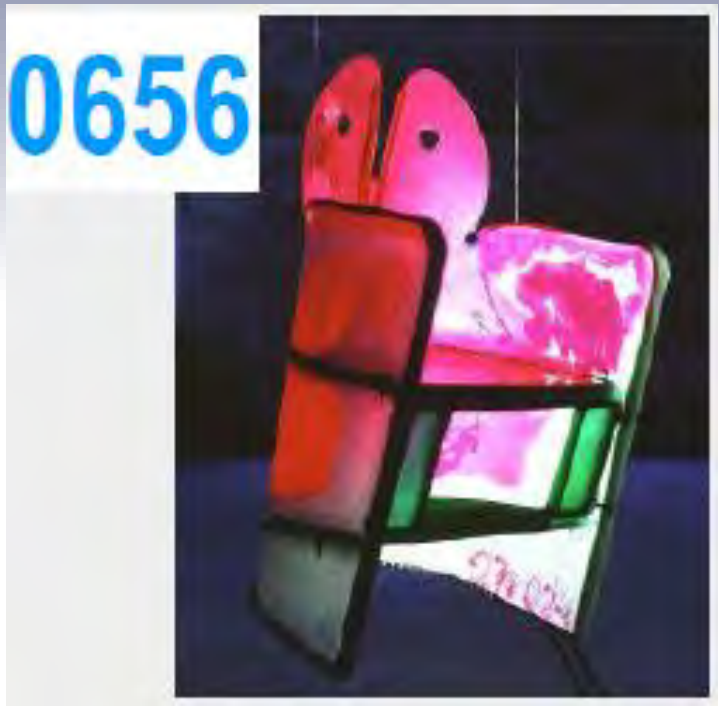
“Nobody’s perfect” chairs Gaetano Pesce (project and production 1993)

Triennale Design Museum





“Nobody’s perfect” chairs Gaetano Pesce



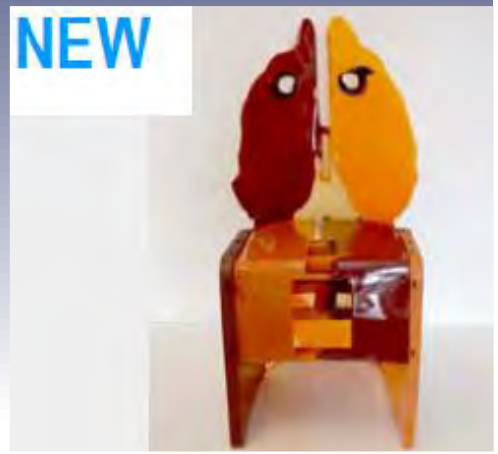
Triennale Design Museum

“Nobody’s perfect” chairs Gaetano Pesce

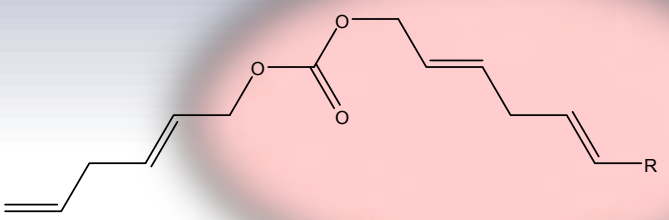
Triennale Design Museum

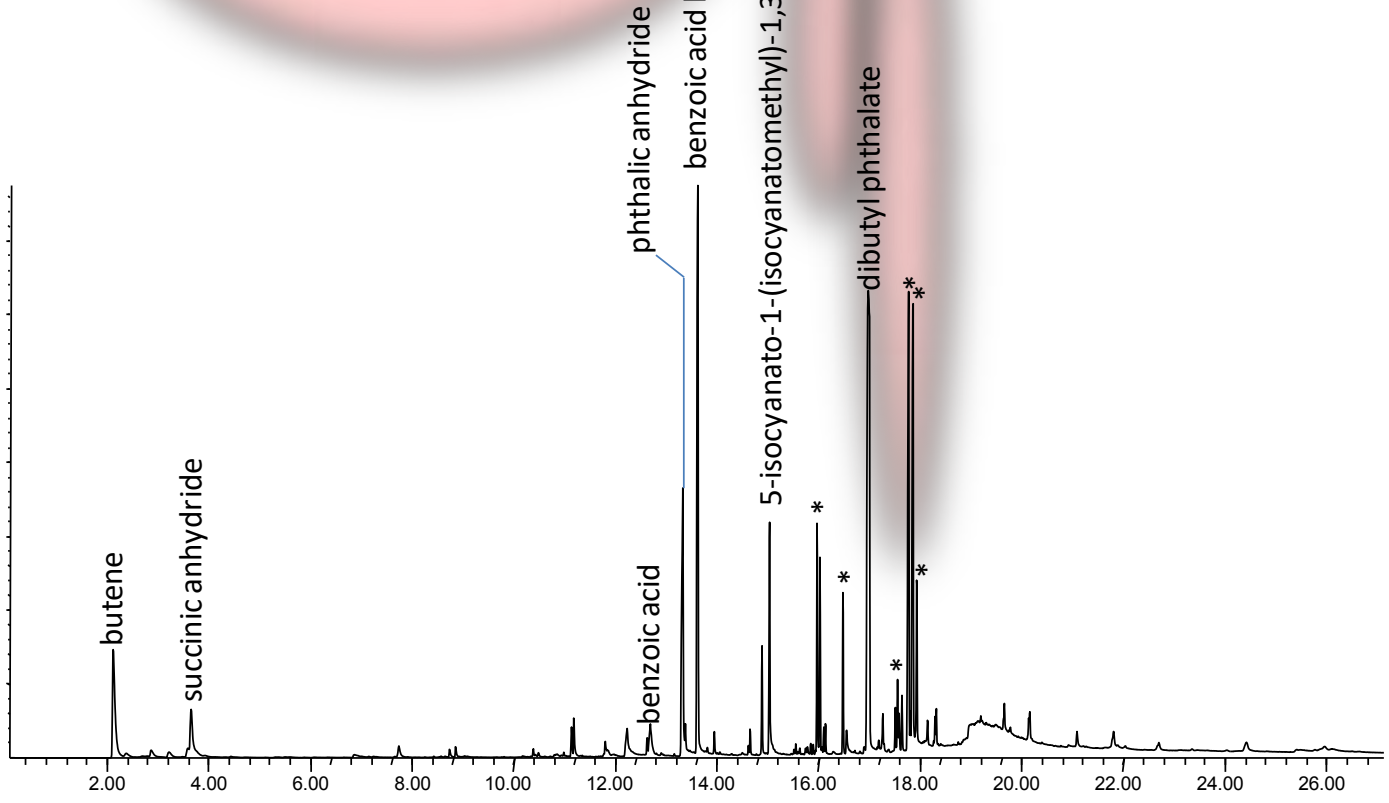
Py-GC/MS "Nobody's perfect" chairs Gaetano Pesce

polycarbonate polyester modified with isocyanate



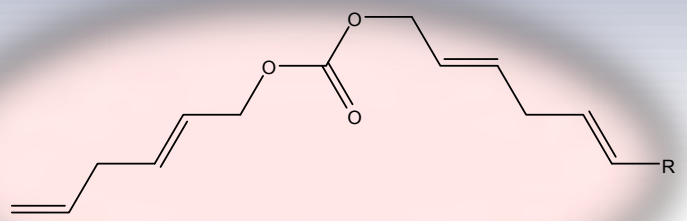
*m/z 80-81 carbonate di-esters structures





Py-GC/MS "Nobody's perfect" chairs Gaetano Pesce

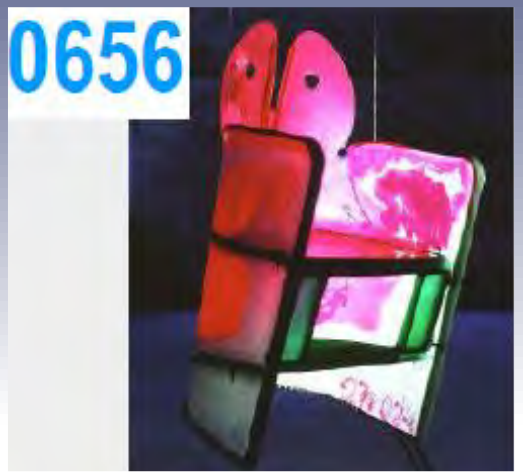
Same formulation as "New" chair: polycarbonate polyester modified with isocyanate



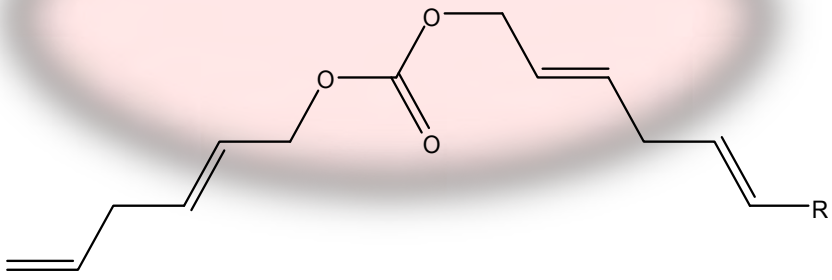
Py-GC/MS "Nobody's perfect" chairs Gaetano Pesce

Different formulation from "New" and "1092" chair:

- **Polycarbonate polyester**
- **Isocyanate peak is not present**



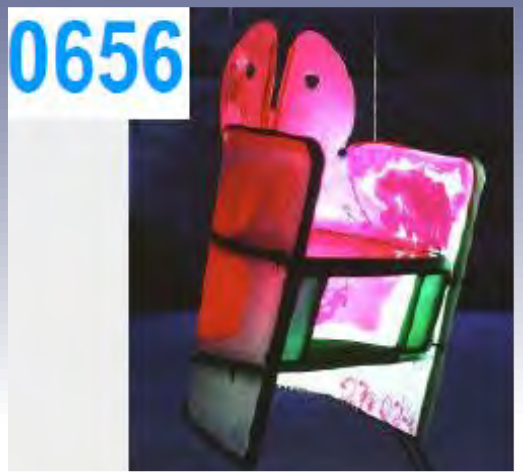
*m/z 80-81 carbonate di-esters structures



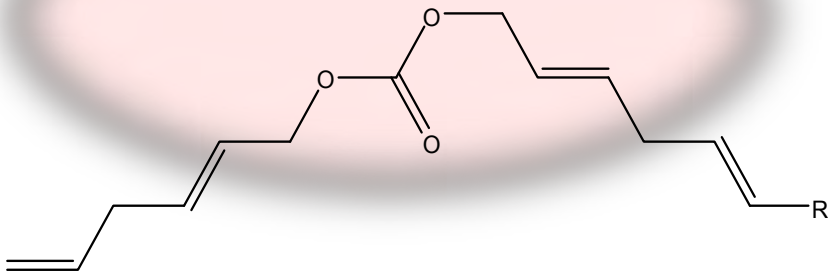
Py-GC/MS "Nobody's perfect" chairs Gaetano Pesce

Different formulation between "New" and "1092" chair:

- **Polycarbonate polyester**
- **Isocyanate peak is not present**



*m/z 80-81 carbonate di-esters structures



benzoic acid butyl ester

dibutyl phthalate

*

*

Possibility to differentiate among similar formulation

01/0656

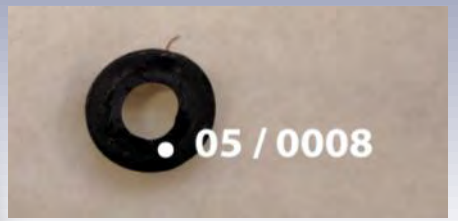
VE505 (Zerowatt), Ezio Pirali (project and production 1954)

Triennale Design Museum

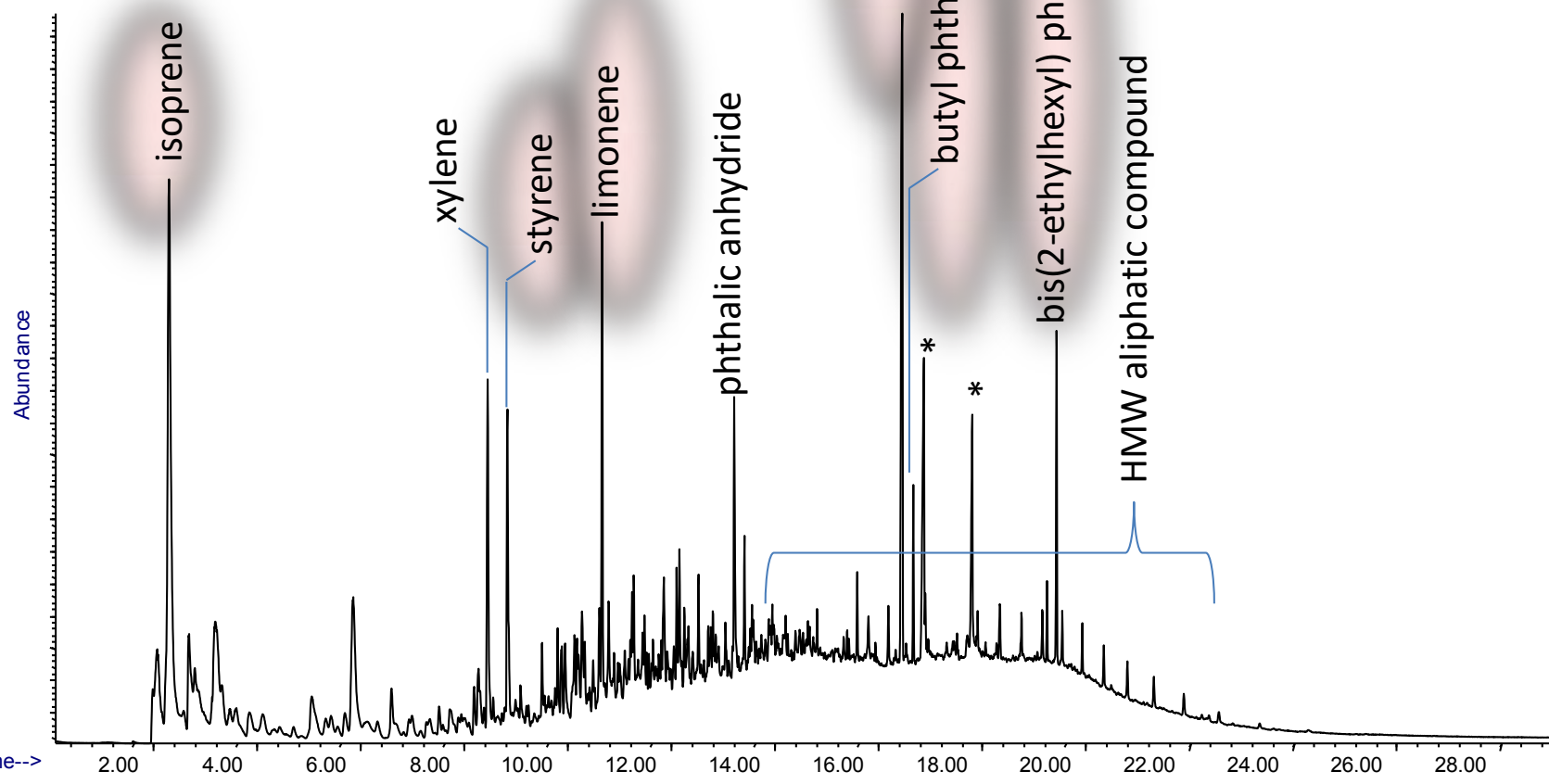
Black plastic surfaces

Py-GC/MS VE505 (Zerowatt), Ezio Pirali

Triennale Design Museum



Isoprene-styrene synthetic rubber
Specific formulation of additives and plasticizers




GALLERIA NAZIONALE D'ARTE MODERNA
TIME IS OUT
OF JOINT.

Investigation of **polyurethane foams** with different state of degradation in in **1960s Italian pop artworks**

"Contenitoreumano n.1"
Ico Parisi and Francesco Somaini, 1968

Tappeto Natura "Disgelo"
Piero Gilardi, 1968

T. van Oosten, PUR Facts: Conservation of Polyurethane Foam in Art and Design, Amsterdam University Press, 2011

Triennale Design Museum

CONSERVATION AND RESEARCH DEPARTMENT

IPERION CH.it

BRINGING THE CONTENITOREUMANO BACK TO LIFE

The *Contenitoreumano n.1,* Ico Parisi and Francesco Somaini, 1968,

polyurethane foam in a metallic case, 1250 x 1575 x 92 cm

Ferriani B., Annicchiarico S., Trevisan R., La Nasa J., Modugno F., Bringing back to life the Contenitoreumano, Future Talks 017, Munich, 11-13 October 2017


interni
la rivista dell'arredamento
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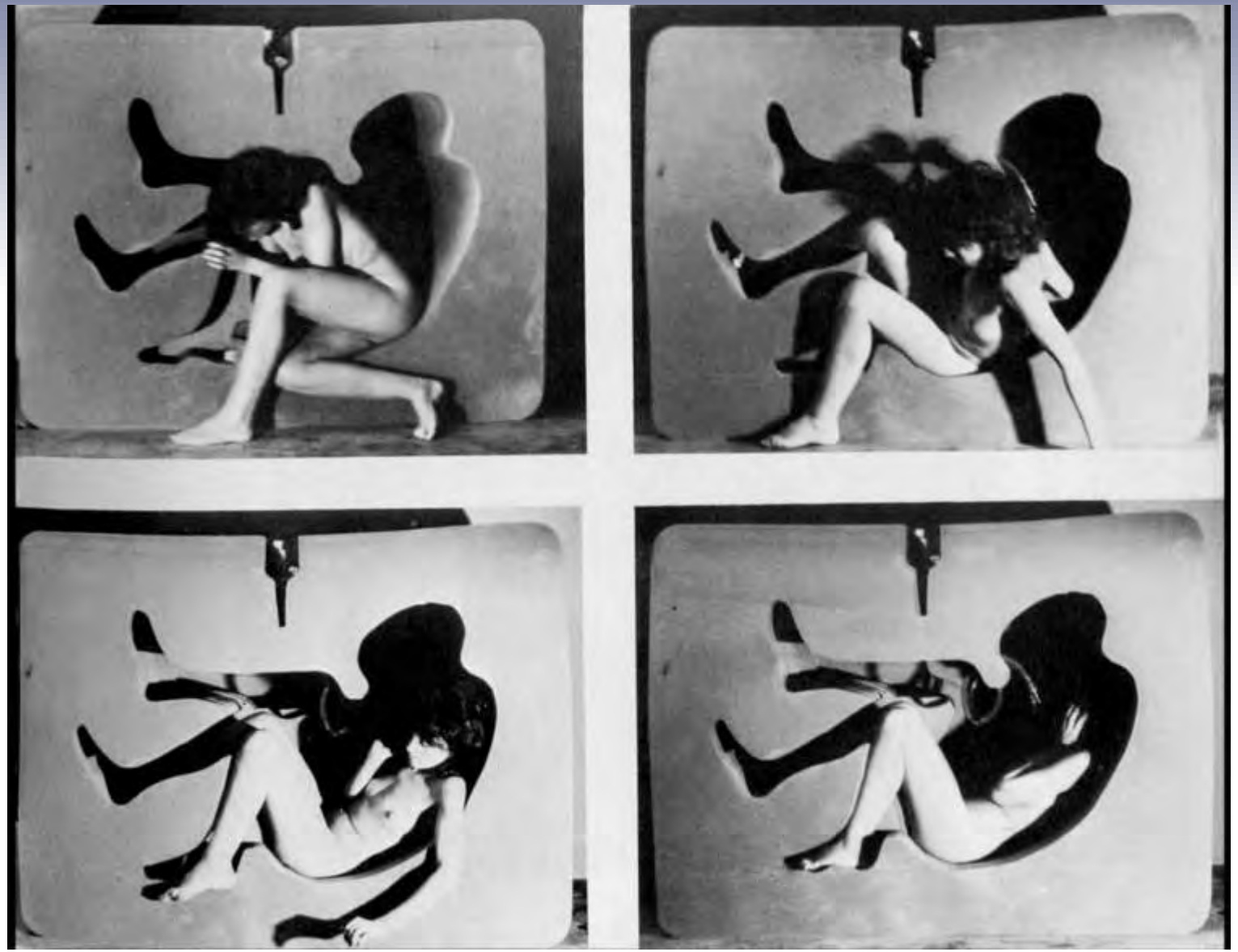
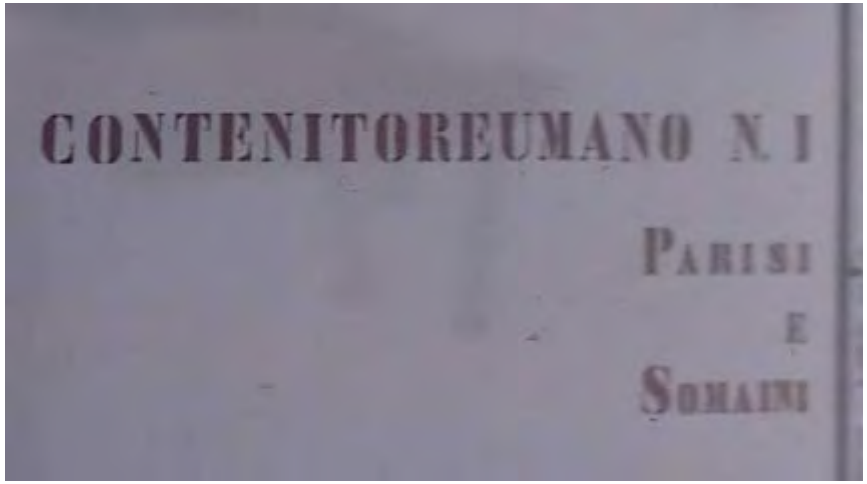
arredo:
soggiorno
pranzo
cucina
letto
studio
la nuova
produzione
all'ottavo salone
del mobile
görlich editore milano


proponiamo · contenitoriuma
ni · perchè la casa di oggi e di
domani sia diversa · perchè
sia una casa aperta e libera
da schemi · perchè da questa
libertà sorgano nuove e mi
gliori città · perchè l'uomo ab
bia un rapporto nuovo con la
sua casa · perchè l'uomo ritro
vi l'ambiente fantastico · per
chè l'uomo viva nei suoi so
gni · sappiamo che i · conteni
toriumani · sono oggi solo una
idea una proposta ma siamo
sicuri che domani in qualche
modo anche diverso saranno
una realtà ·
ico parisi · francesco somaini

STAREMO DENTRO I CONTENITORI




CONTENITOREUMANO N.I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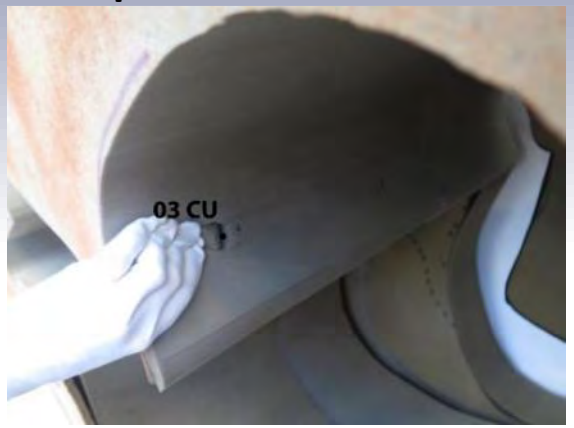
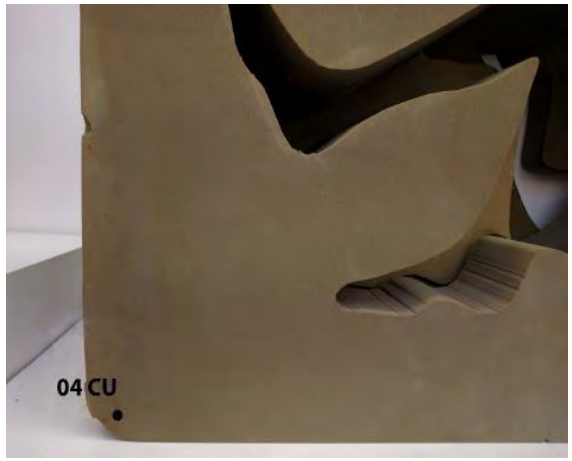
Evolved gas analysis – mass spectrometry EGA-MS

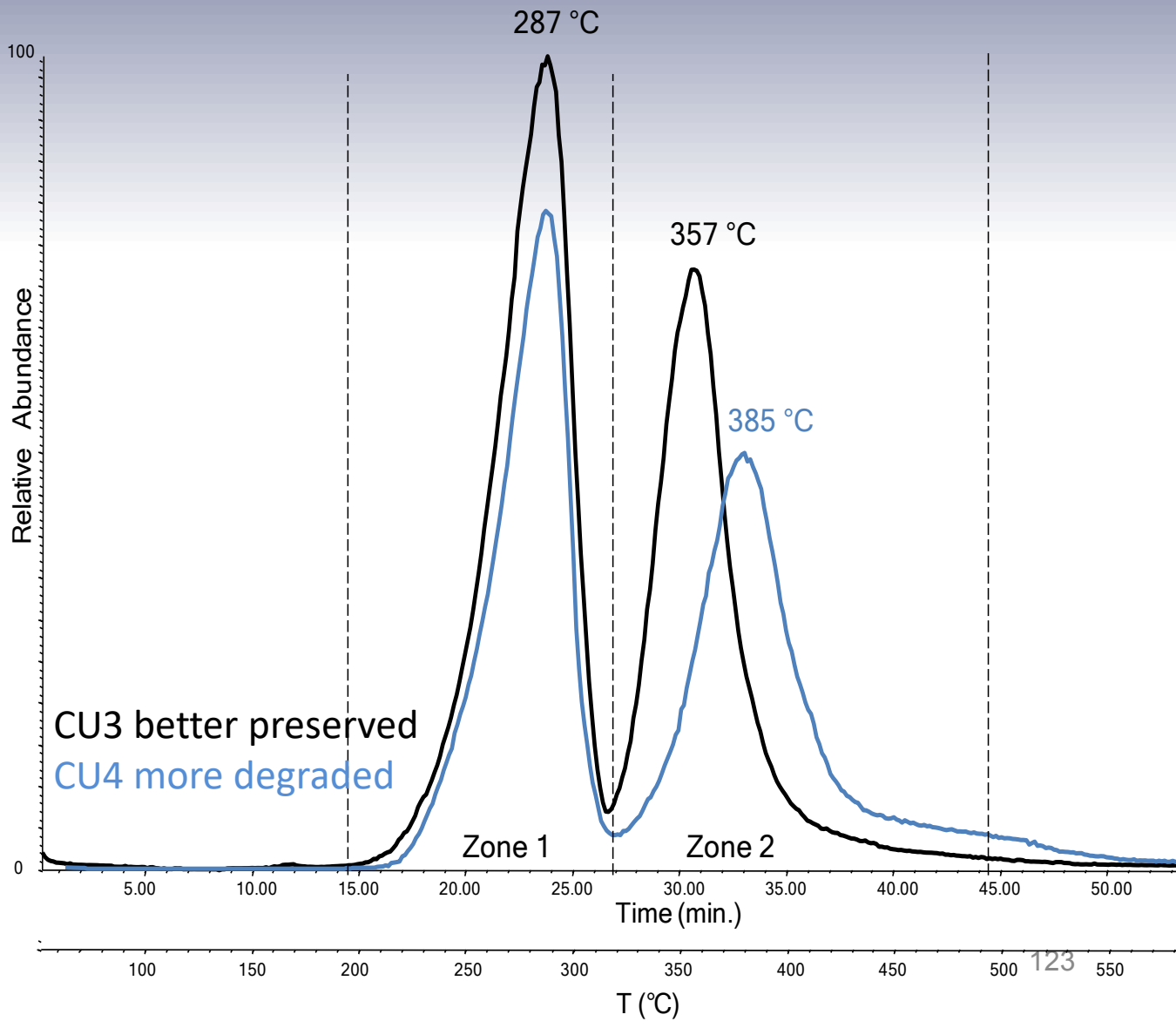
sample CU03, foam bulk well preserved



sample CU04, foam surface degraded

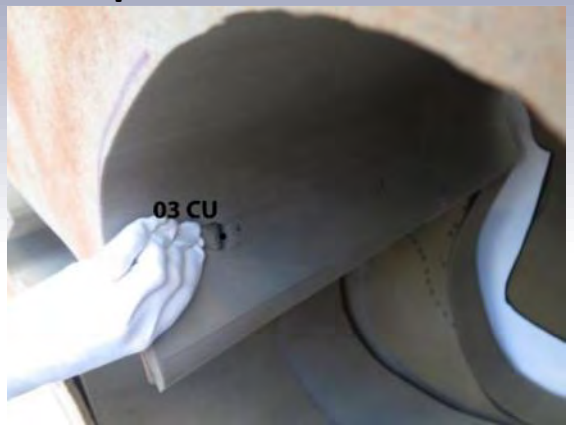


Two thermal degradation zones

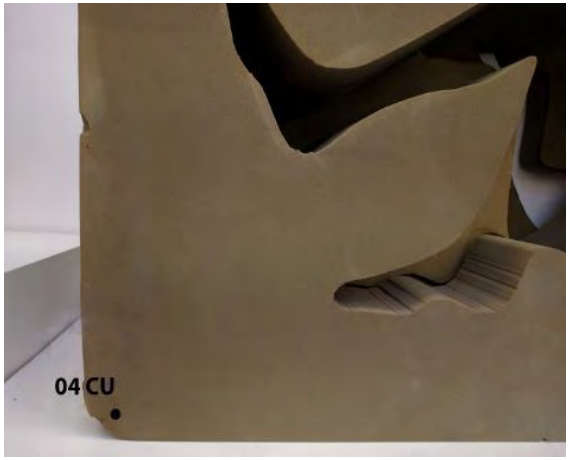


Evolved gas analysis – mass spectrometry EGA-MS

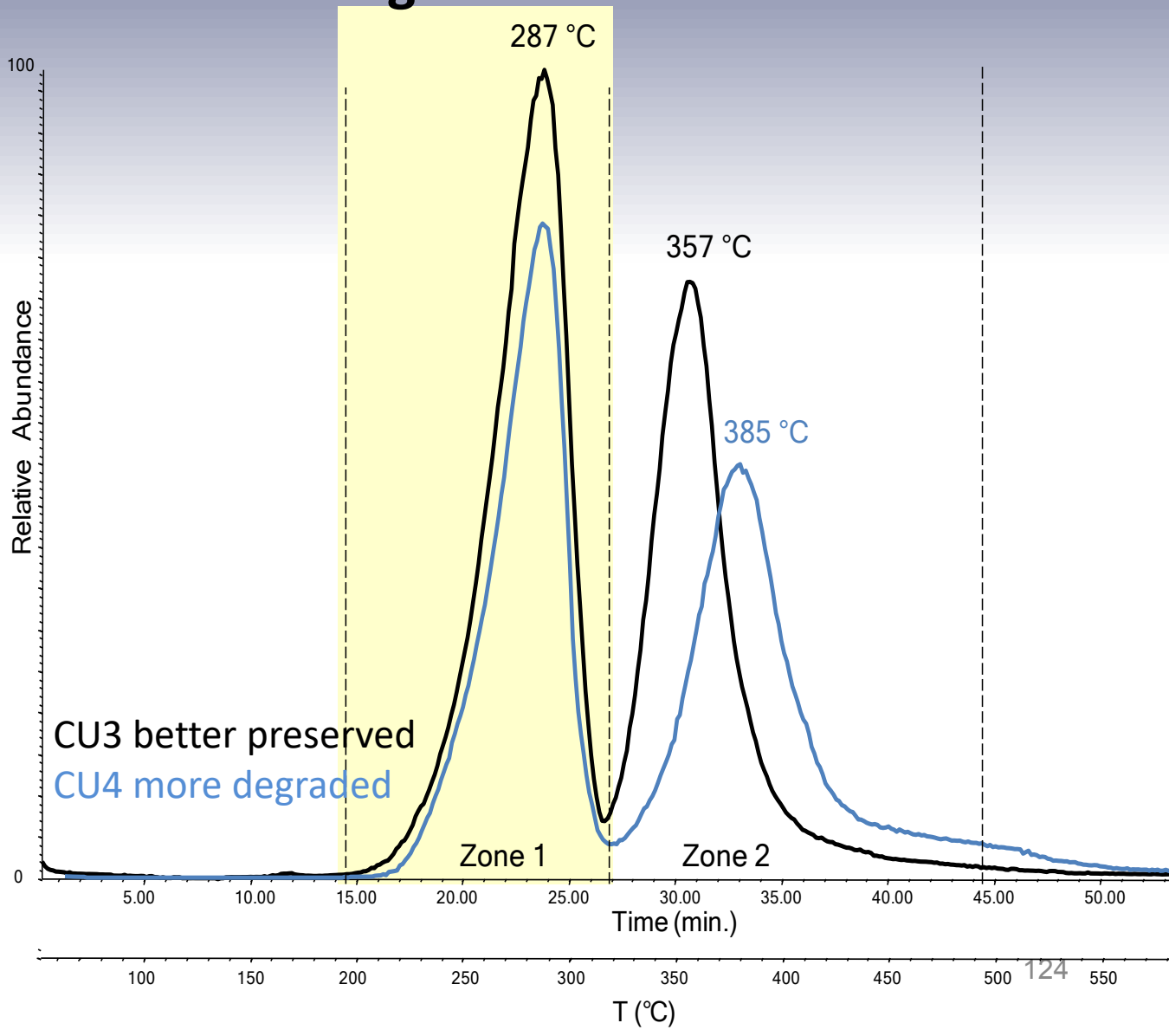
sample CU03, foam bulk well preserved



sample CU04, foam surface degraded



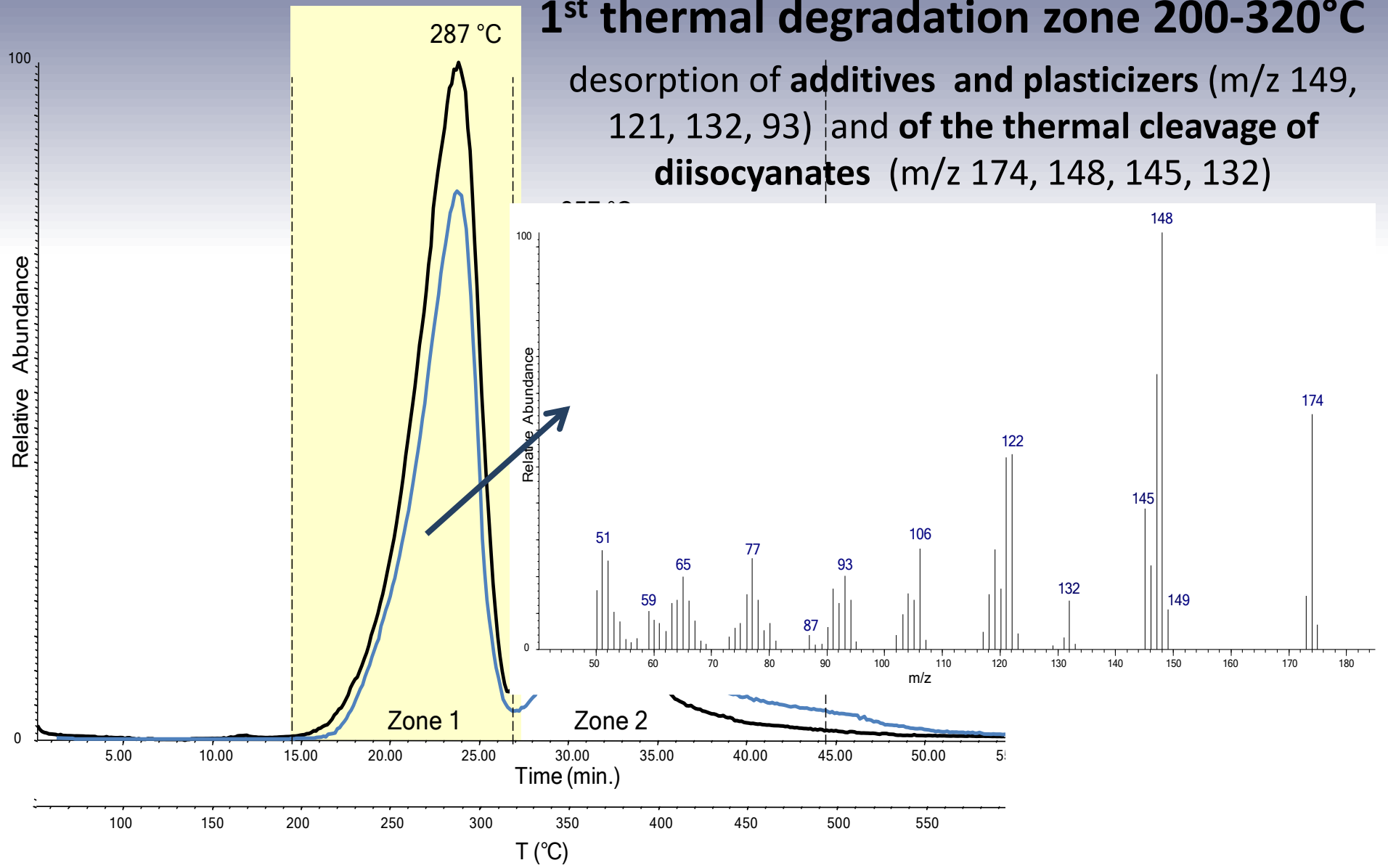
1st thermal degradation zone 200-320°C



Evolved gas analysis – mass spectrometry EGA-MS

1st thermal degradation zone 200-320°C

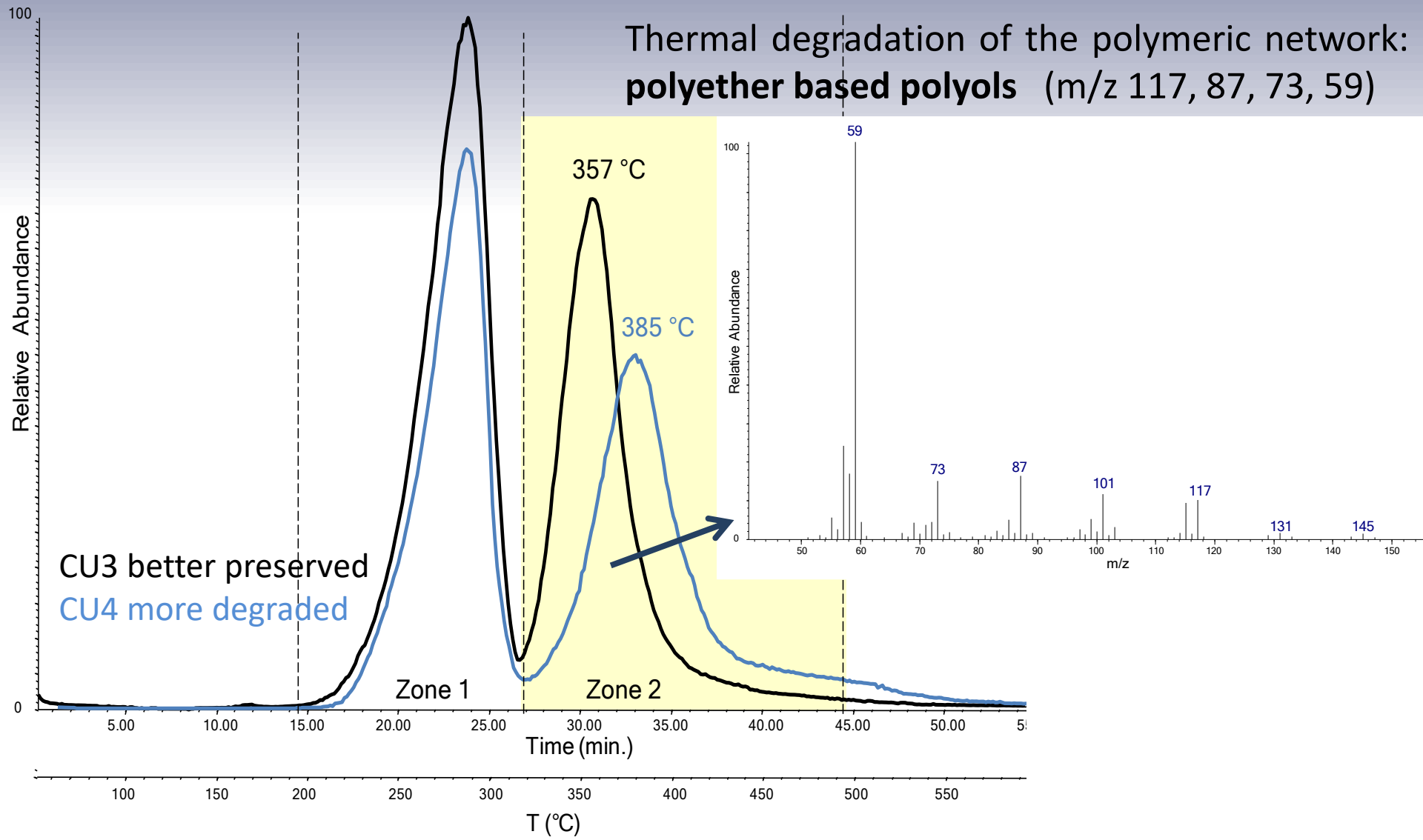
desorption of **additives and plasticizers** (m/z 149, 121, 132, 93) and **of the thermal cleavage of diisocyanates** (m/z 174, 148, 145, 132)



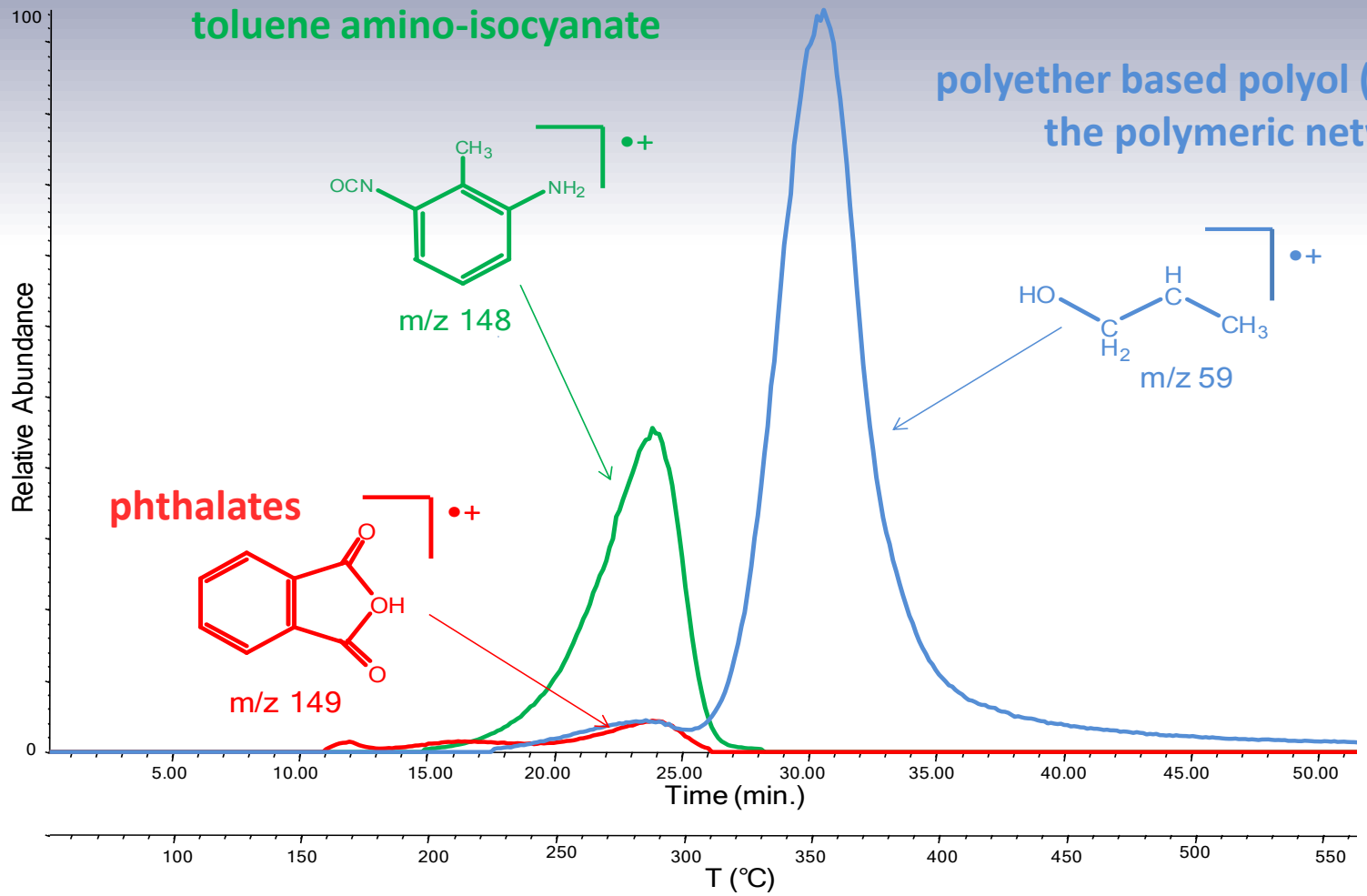
Evolved gas analysis – mass spectrometry EGA-MS

2nd thermal degradation zone 320-500 °C

Thermal degradation of the polymeric network:
polyether based polyols (m/z 117, 87, 73, 59)



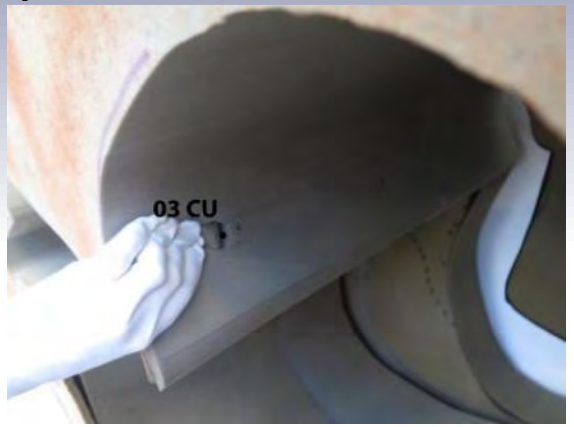
EGA-MS extract ion



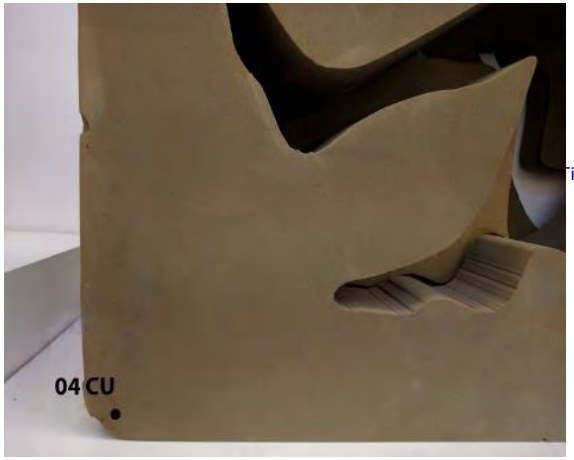
La Nasa J, Biale G, Ferriani B, Colombini MP, Modugno F (2018). A pyrolysis approach for characterizing and assessing degradation of polyurethane foam in cultural heritage objects. Journal of Analytical and Applied Pyrolysis 134, pp. 562-572

Evolved gas analysis – mass spectrometry EGA-MS

sample CU03, well preserved foam bulk

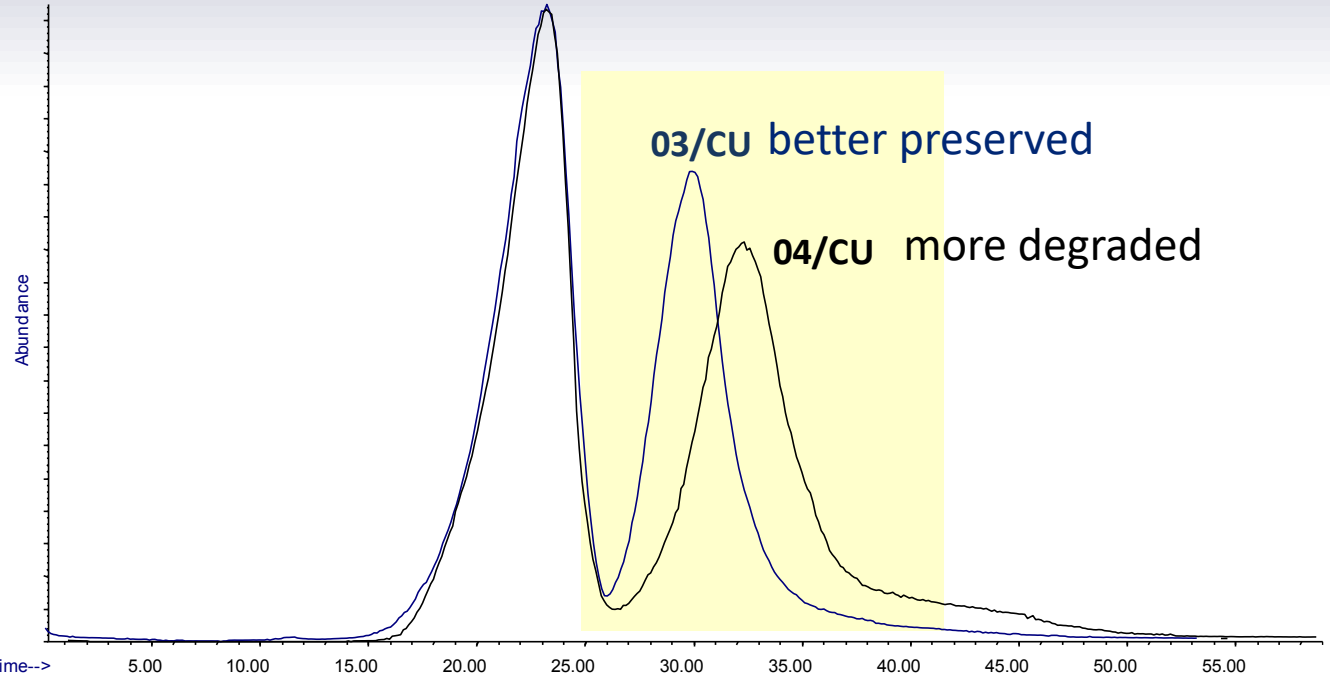


sample CU04, degraded foam surface



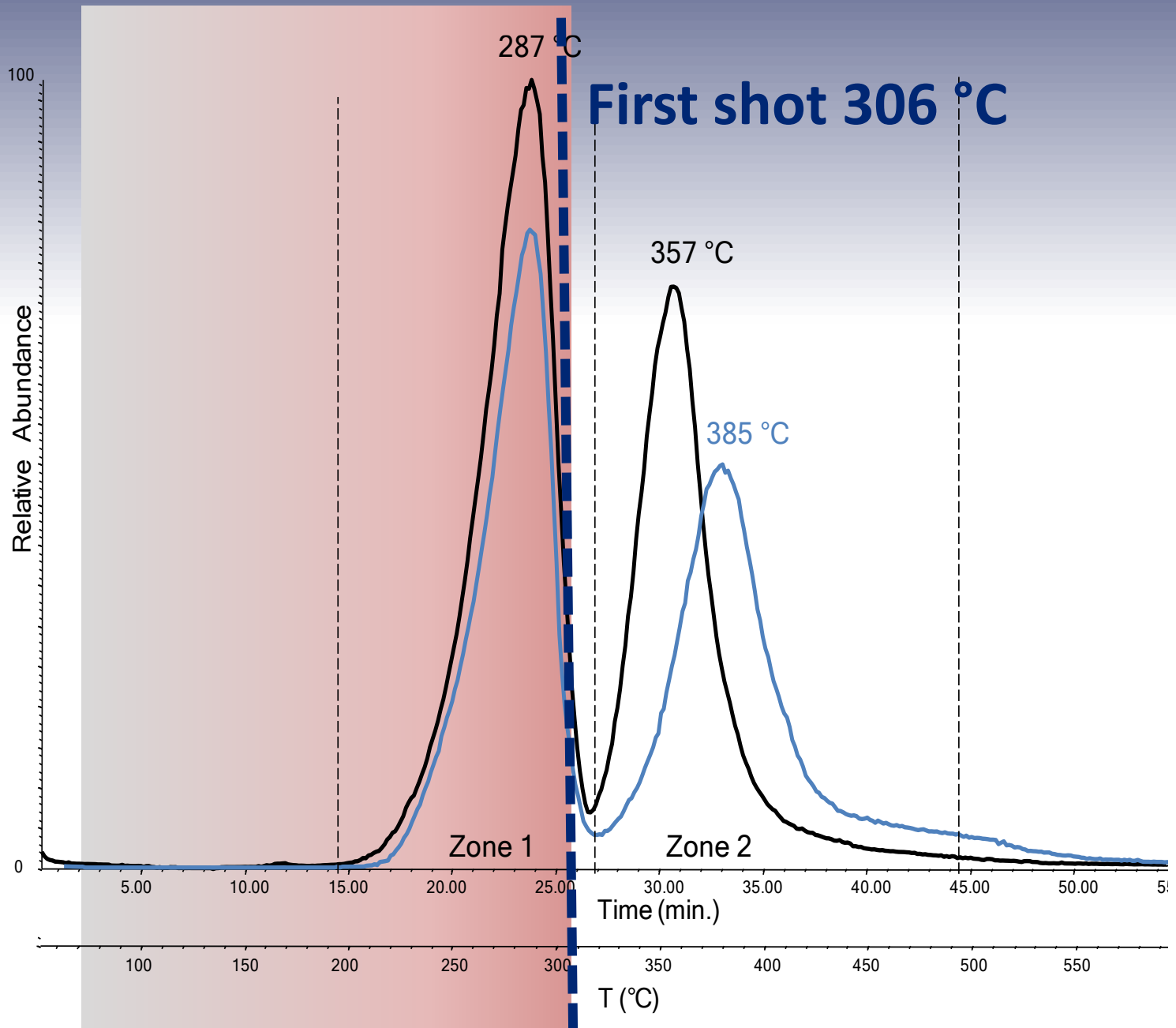
EGA-MS profiles:

increase in the degradation temperature of the polymeric network of sample 04/CU (50°C)

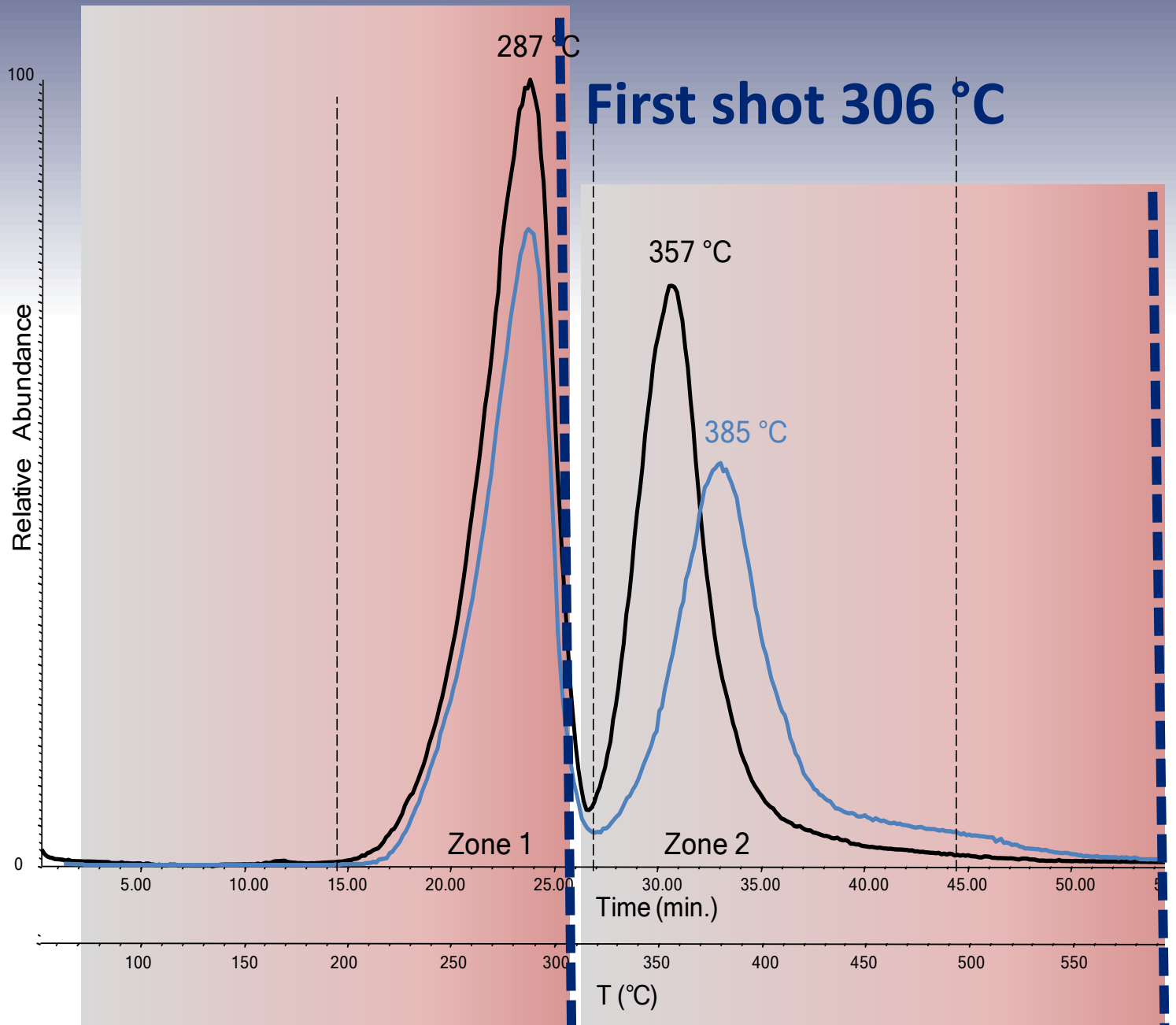


crosslinking process involving the polyurethane polymeric network: this **reticulation process leads to an increase in the hardness/brittleness** of the polymer

Double -shot Py-GC/MS



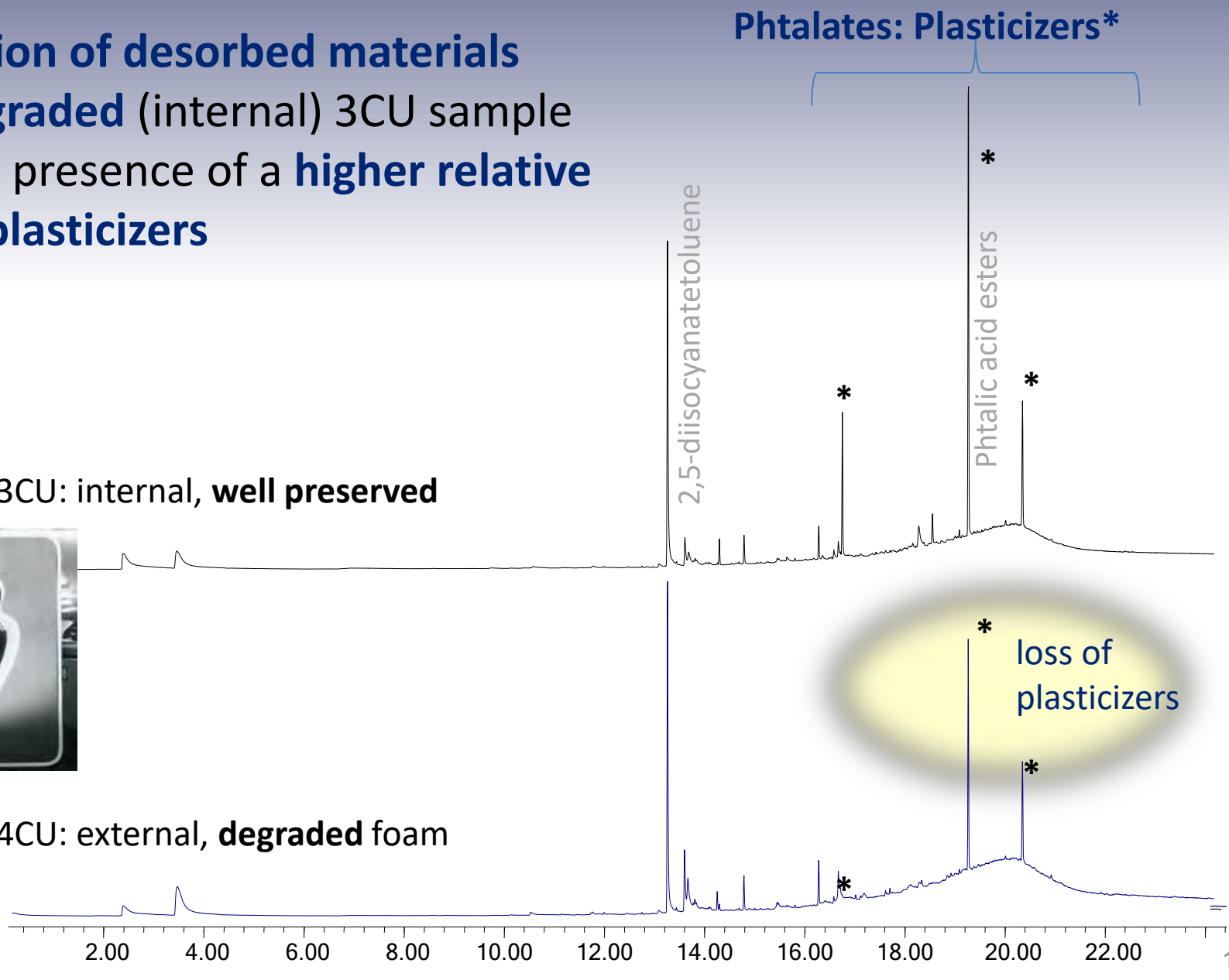
Double -shot Py-GC/MS



First shot 306°C

Determination of desorbed materials

The **less degraded** (internal) 3CU sample features the presence of a **higher relative amount of plasticizers**



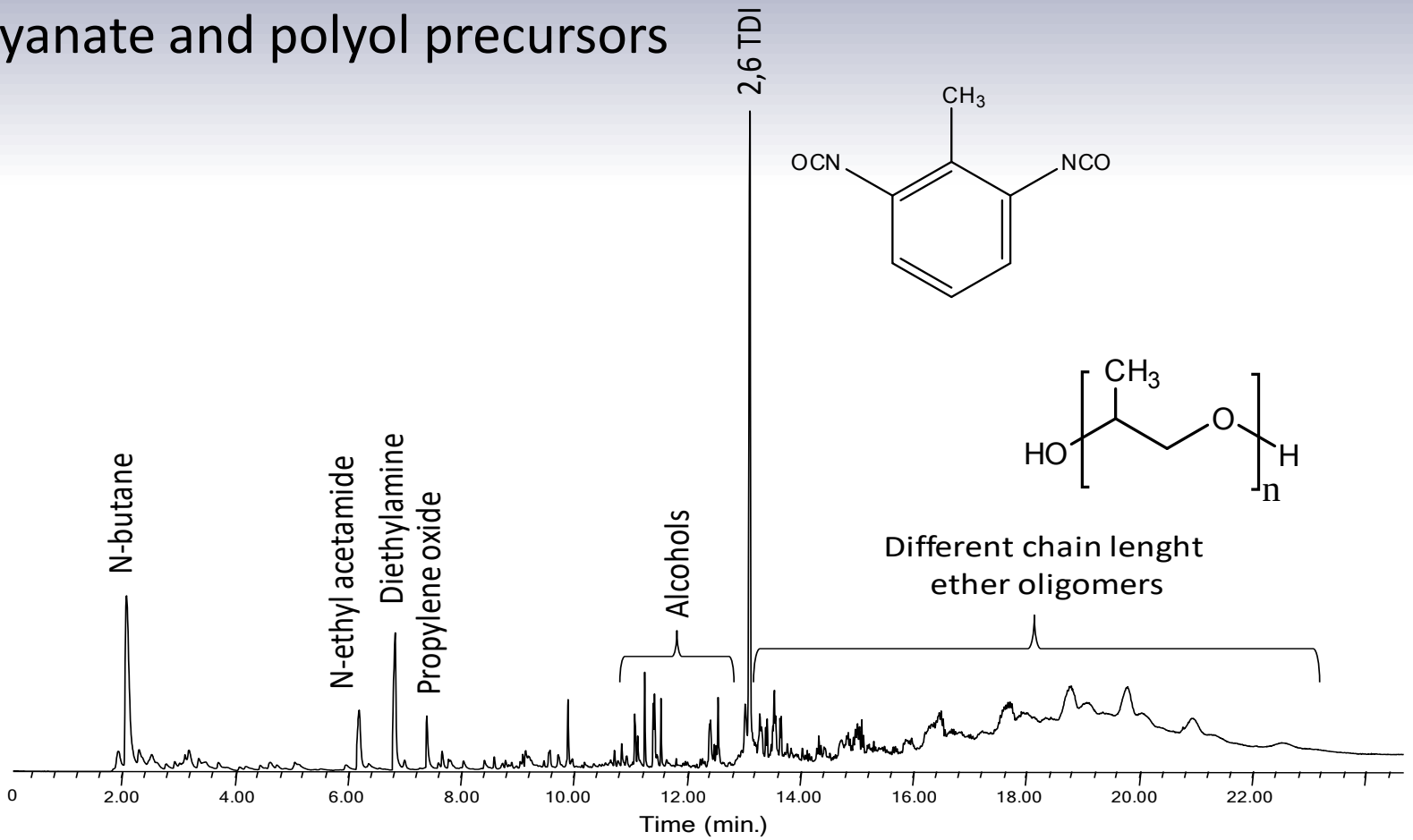
Second shot 600°C

Characterisation of the polymeric network :

polyether-based polyurethane

with **2,6-toluenediisocyanate** and **polypropylene glycol**

as diisocyanate and polyol precursors



La Nasa J, Biale G, Ferriani B, Colombini MP, Modugno F (2018). A pyrolysis approach for characterizing and assessing degradation of polyurethane foam in cultural heritage objects. Journal of Analytical and Applied Pyrolysis 134, pp. 562-572

Tappeto Natura “Disgelo”

Piero Gilardi, 1968, private collection

A. Rava, La conservazione di opere in poliuretano espanso. Il lavoro di Piero Gilardi, Kermes 98,, 2015, 14-22

13 aprile 2017 - 15 ottobre 2017

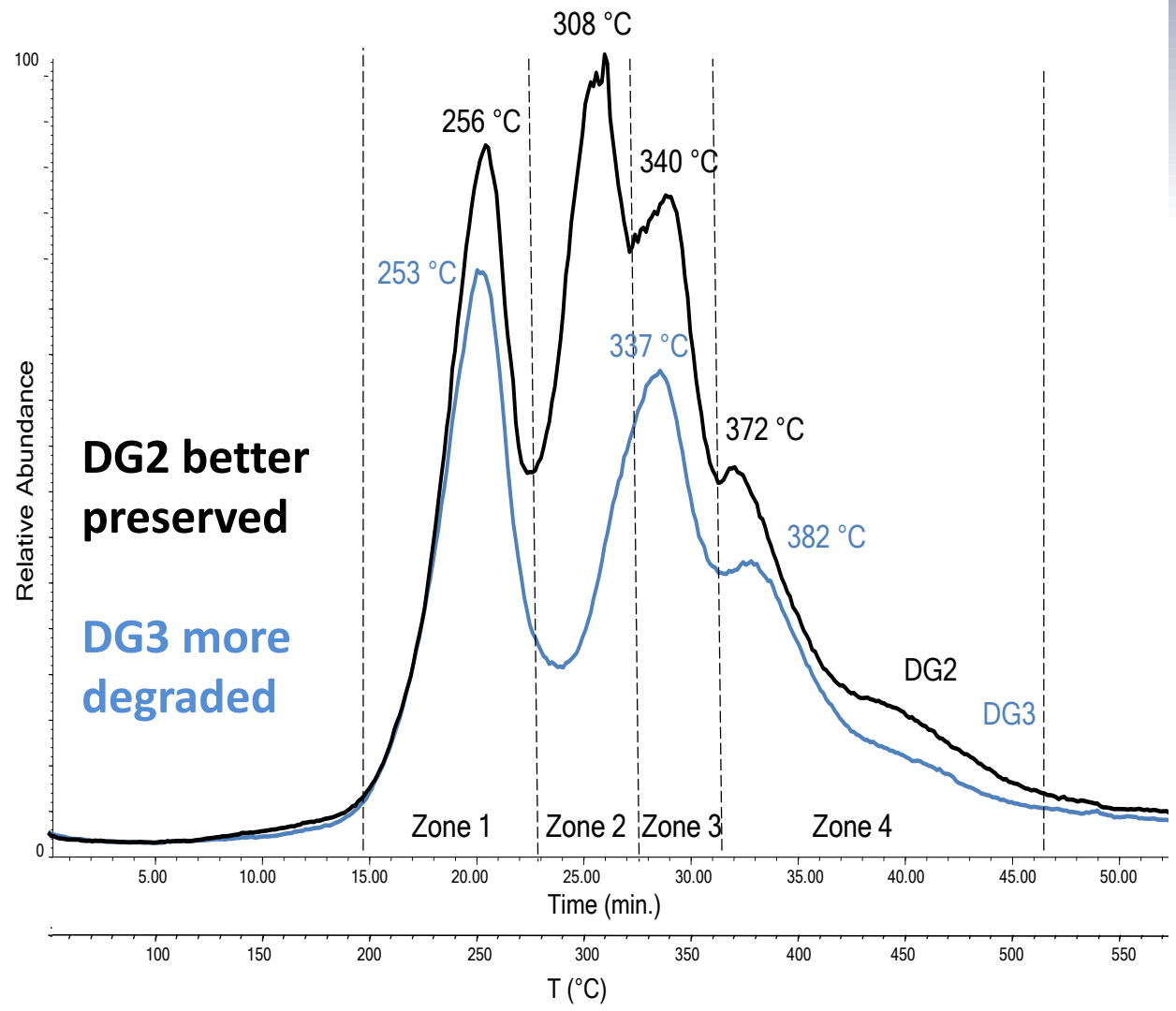
NATURE FOREVER. PIERO GILARDI

Galleria 3

a cura di Hou Hanru, Bartolomeo Pietromarchi e Marco Scotini

L'Arte deve entrare nella vita, ma dato che la vita è alienata, occorre impegnarsi

EGA-MS “Disgelo”



DG2 better preserved

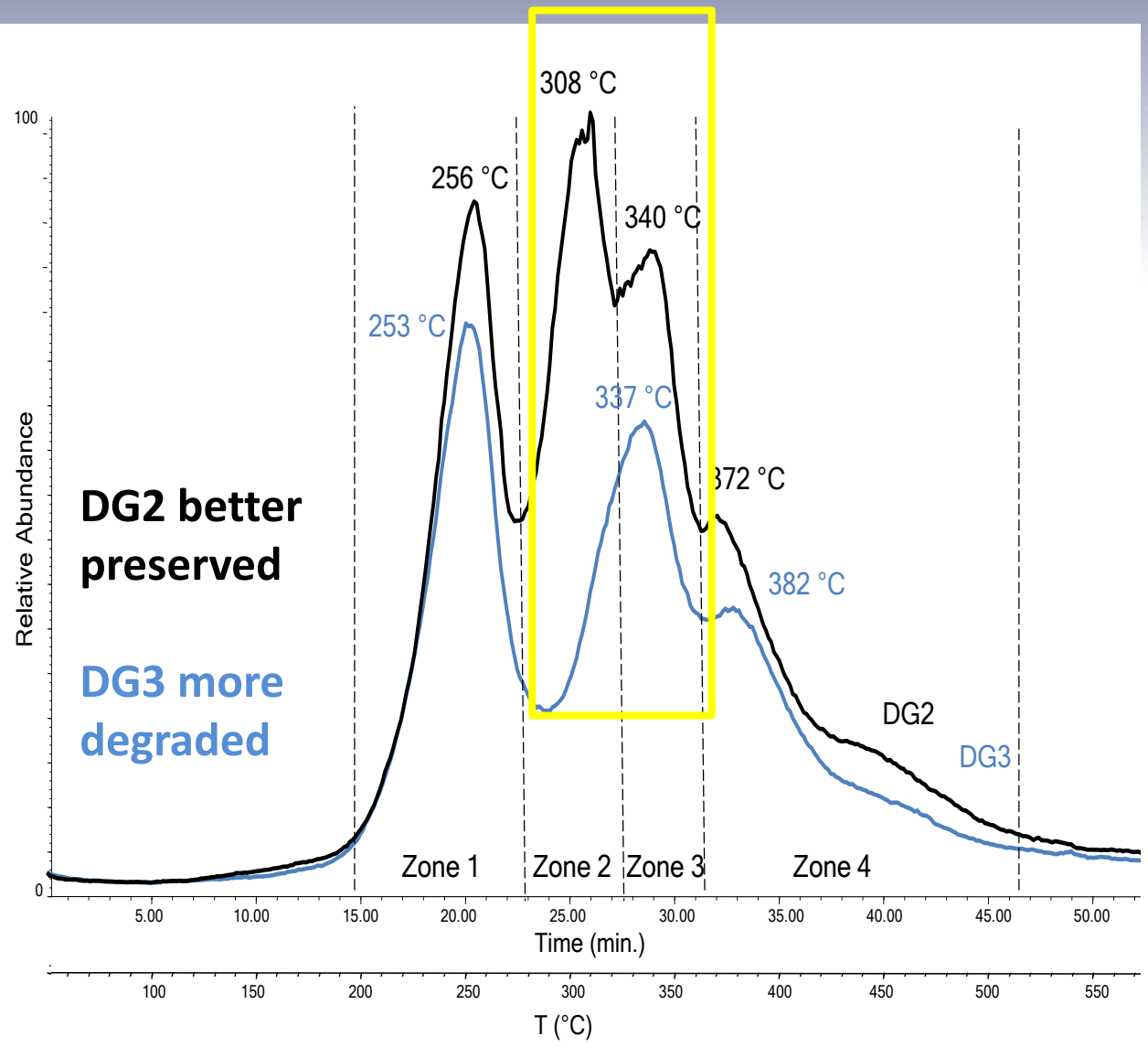
DG3 more degraded

Zone 1:
desorption of additives and of non-reticulated precursors

Zone 2 and zone 3:
Partial pyrolysis of the polymeric network

Zone 4:
Complete thermal degradation of the PU network and of the paint

EGA-MS “Disgelo”



DG2 better preserved

DG3 more degraded

Zone 2-3 : 270-360 °C

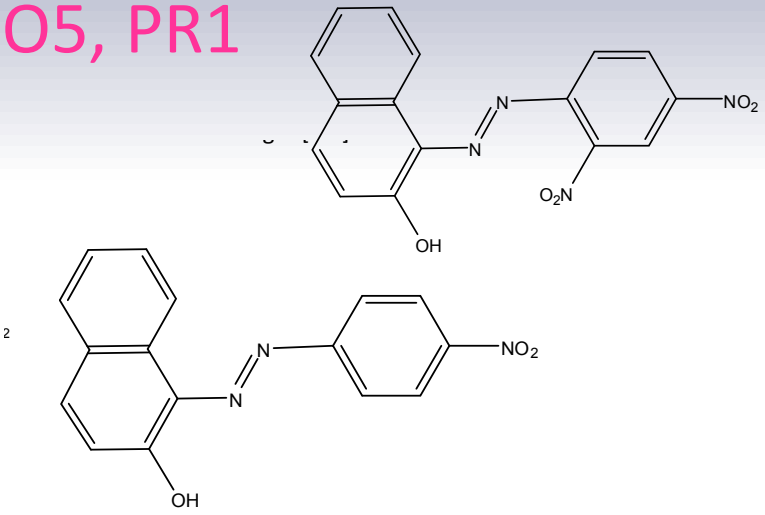
Loss of detail and higher degradation temperature of the degraded foam sample:
cross-liking phenomena

Multi-shot Py-GC-MS experiment

Multi-shot Py-GC/MS "Disgelo" (1968), sample DG3

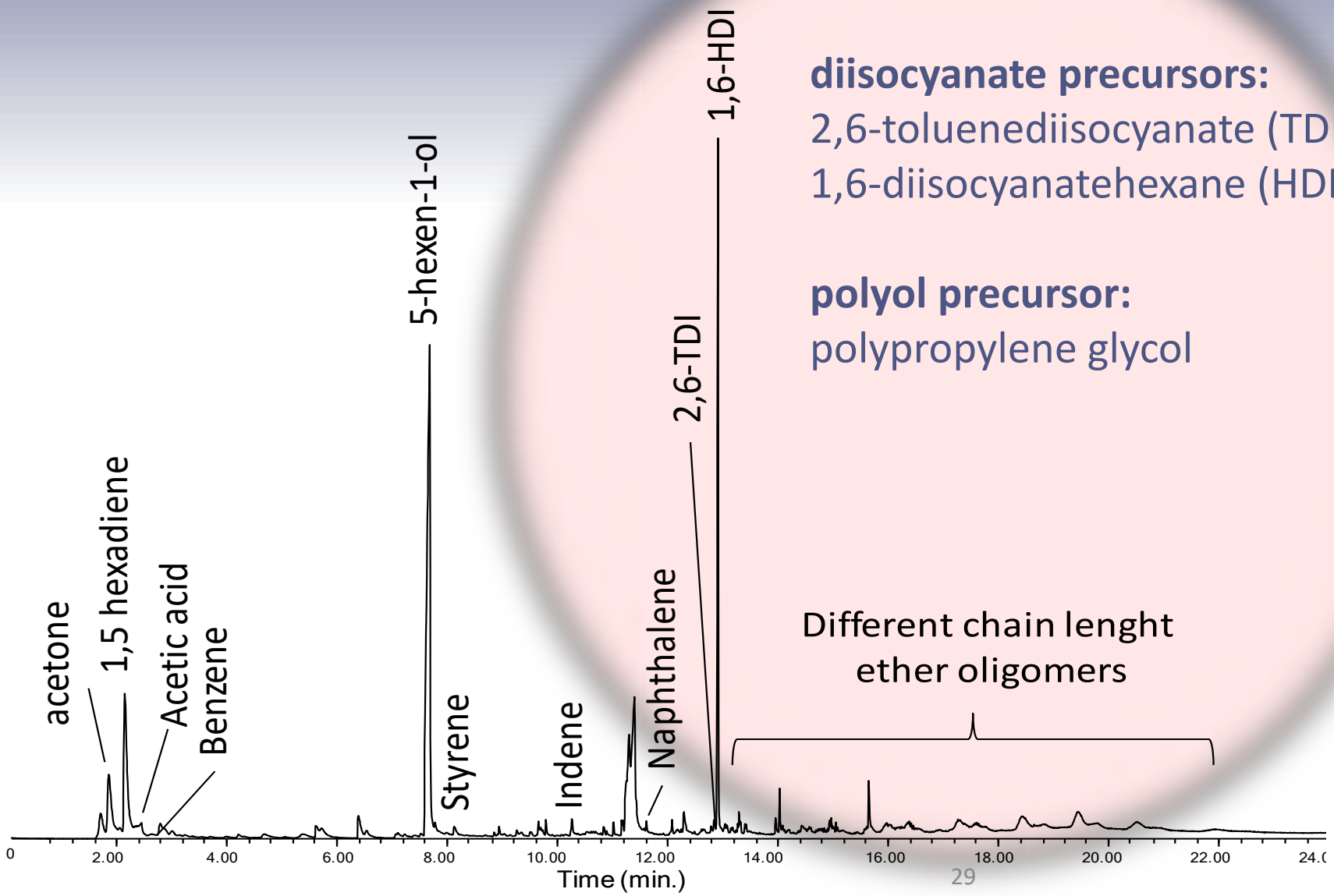
Third shot 340°C:
pyrolysis products of **organic pigments** in the paint

β-naphthol pigments
PO5, PR1



Multi-shot Py-GC/MS "Disgelo" (1968), sample DG3

Fourth shot 600°C : pyrolysis of the polymeric network



diisocyanate precursors:
2,6-toluenediisocyanate (TDI)
1,6-diisocyanatehexane (HDI)

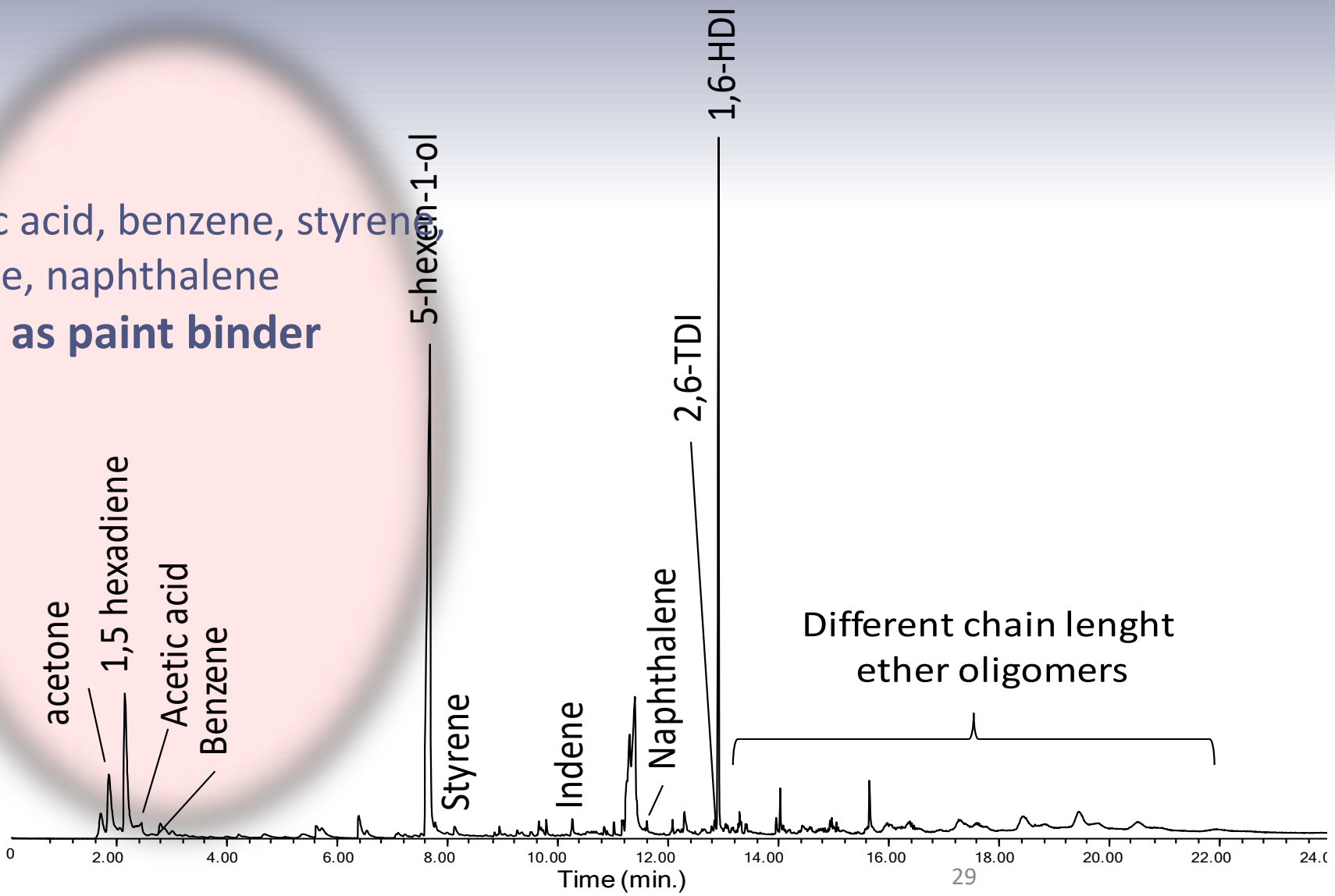
polyol precursor:
polypropylene glycol

Multi-shot Py-GC/MS "Disgelo" (1968), sample DG3

Fourth shot 600°C : pyrolysis of the polymeric network

Acetic acid, benzene, styrene, indene, naphthalene

PVAc as paint binder



Conclusions

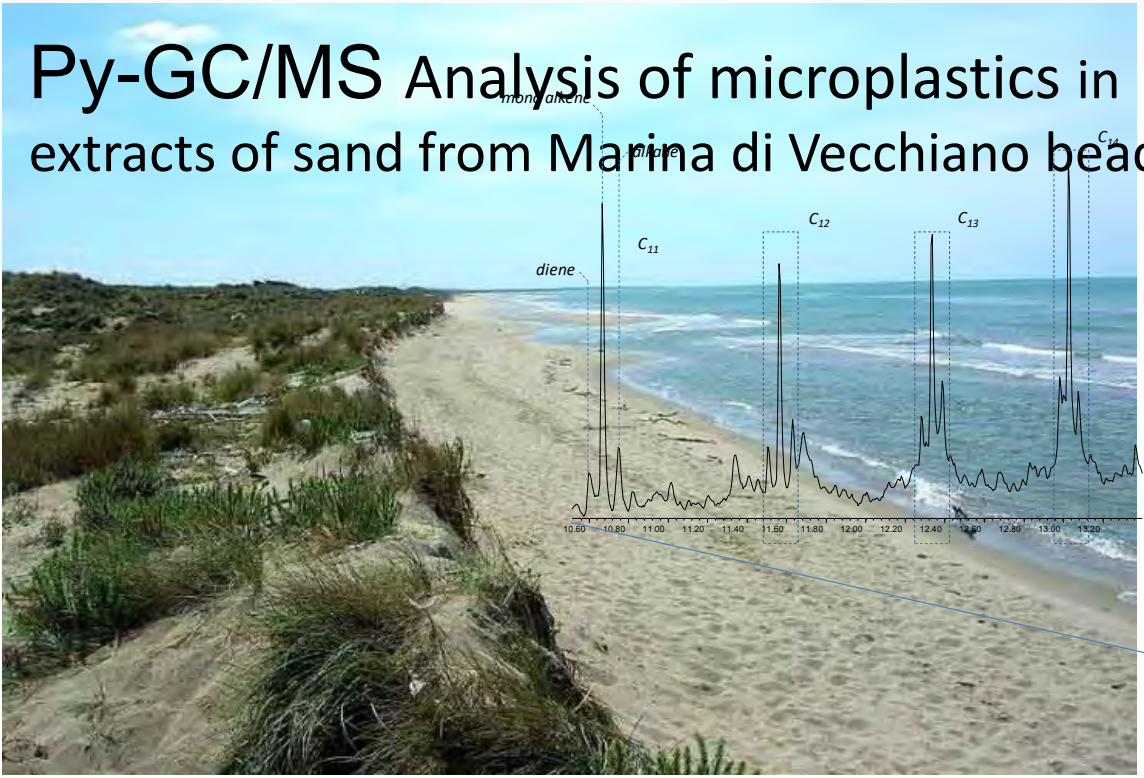
Evolved gas analysis mass spectrometry (EGA-MS) and multi-shot Py-GC/MS allow us to characterize synthetic polymers in art at a molecular level, selectively studying the different fractions evolved at different temperatures

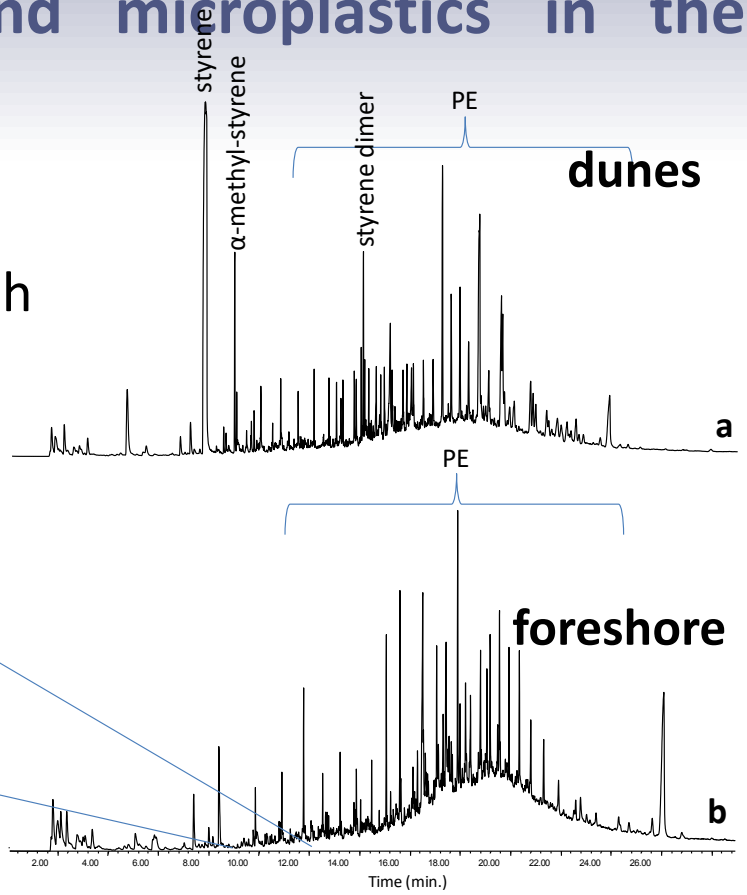
Information on different components of mixtures can be achieved including additives and organic pigments, separating them on the basis of their thermal degradation temperature

The evaluation of the relative amounts of evolved materials during thermal degradation goes beyond simple qualitative information and identification, and permits to investigate degradation mechanisms and to obtain semi-quantitative data on cross-linking, chain scission phenomena, formation or loss of low molecular weight components

Parallel approaches find application in:

- Material science
- Study of degradation processes of polymers, coatings, paints
- Investigation of plastic debris and microplastics in the environment





La Nasa et al, 2020 , Journal of Analytical and Applied Pyrolysis 149,104841

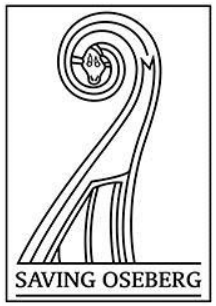
La Nasa et al, 2021 Journal of Hazardous Materials 401,123287

Credits

“ArCo” Project: Ageing Study of Treated Composite Archaeological Waterlogged Artifacts (2014-2016), funded as JPI-JHEP Joint Pilot Transnational Call

WOAM 2016

ARCHA



UiO : Museum of Cultural History
University of Oslo

“Saving Oseberg” Project (2014-2020) funded by the Norwegian State and the University of Oslo - Museum of Cultural History

Mange museer i ét

ARC-nucle ART

Credits

MOLAB CNR-ISTM (Perugia)
Francesca Rosi, Annalisa Chieli, Costanza Miliani

Triennale Design Museum

Triennale Design Museum, Milan
Silvana Annicchiarico, Rafaela Trevisan

LA GALLERIA NAZIONALE

Galleria Nazionale di Arte Moderna Roma
Paola carnazza, Luciana Tozzi

Antonio Rava, **Will Shenck**: investigations on the Keith Haring murals and on Gilardi's Tappeto Natura "Disgelo"

IPERION CH.it

Iperion CH: European research infrastructure for restoration and conservation of Cultural Heritage

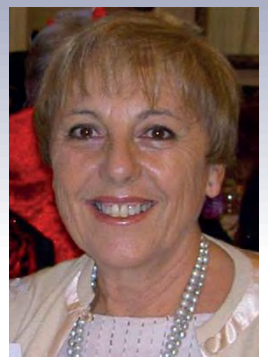
Alena Otmarova, Museum of Decorative Arts in Prague

1506 UNIVERSITÀ DEGLI STUDI DI URBINO CARLO BO

FONDAZIONE ARCHIVIO CAPOGROSSI

Daphne de Luca, University of Urbino, Italy

Credits my research group

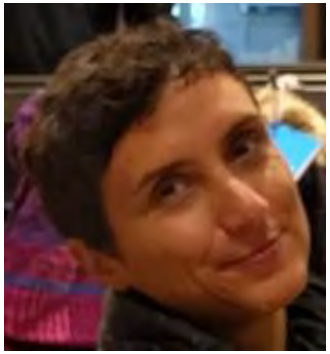


Prof. M.P. Colombini

Prof. E. Ribechini

Prof. I. Bonaduce

Dr J.J. Łucejko



Prof. I. Degano

Dr J. La Nasa

Dr. M. Mattonai

Dr. D. Tamburini (former, now at Smithsonian, Washington)

and UniPI-DCCI students

Thank you for your attention