Univerzita Palackého v Olomouci

# Py GC-MS analysis of organic binders in Cultural Heritage


**<u>Paola Lucero</u>, Petr Barták, Jana Michalčáková, Karel Lemr**

Department of Analytical Chemistry, Palacký University

paola.lucero@upol.cz



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# Motivation for the analysis of art materials

***Art material analysis important in order to:***

- Better understand the Master's technique, her/his artistic, socio-cultural, economic background, and the resources and materials available to him
- Identify any alterations, modifications or later conservative intervention
- Assess the authenticity of a particular piece of art
- Reveal potential changes of the materials used by the artist over time, or under the influence of light and environmental conditions

[1] J. Mills, R. White, *The Organic Chemistry of Museum Objects*, Second Ed. Butterworth-Heinemann, Oxford (1994).

# Organic materials in art objects

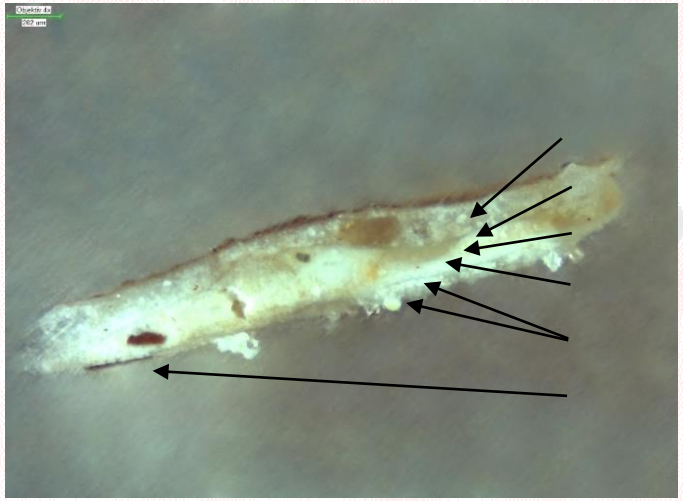
Different binder reveal different painting technique

- Encaustic painting: wax
- Oil paint: siccative oil (mainly linseed oil)
- Tempera painting: based on a proteinaceous component (egg, gelatin, animal glue, casein, or mixture of these) lipid additives, as siccative oils (if present in higher amounts the technique is called tempera grassa)
- Aquarelle painting: mainly arabic gum
- Modern painting: synthetic resins

# Challenges in the analysis of organic paint constituents

Critical consideration of the following factors necessary when planning an analytical investigation:

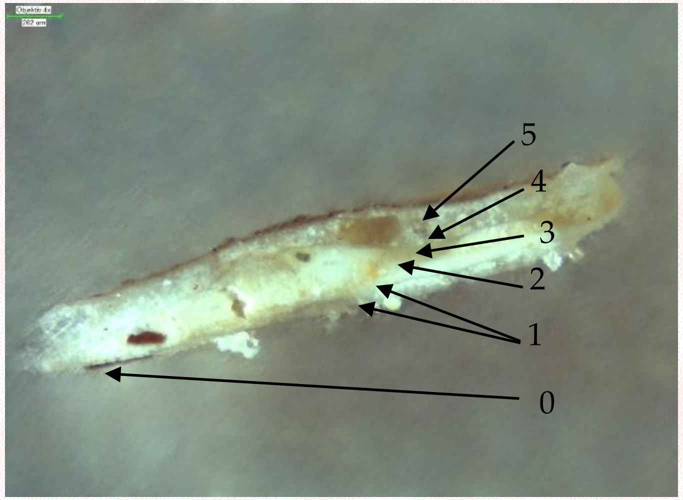
- Several organic natural and synthetic substances are often simultaneously present in the layered structure;
- Non-original compounds, formed as a result of aging or introduced by restoration treatments and pollution, are generally also present;
- A very low amount of organic matter (a few percent in the overall weight or even lower) is generally encountered in a minute heterogeneous paint sample (<<1 mg)

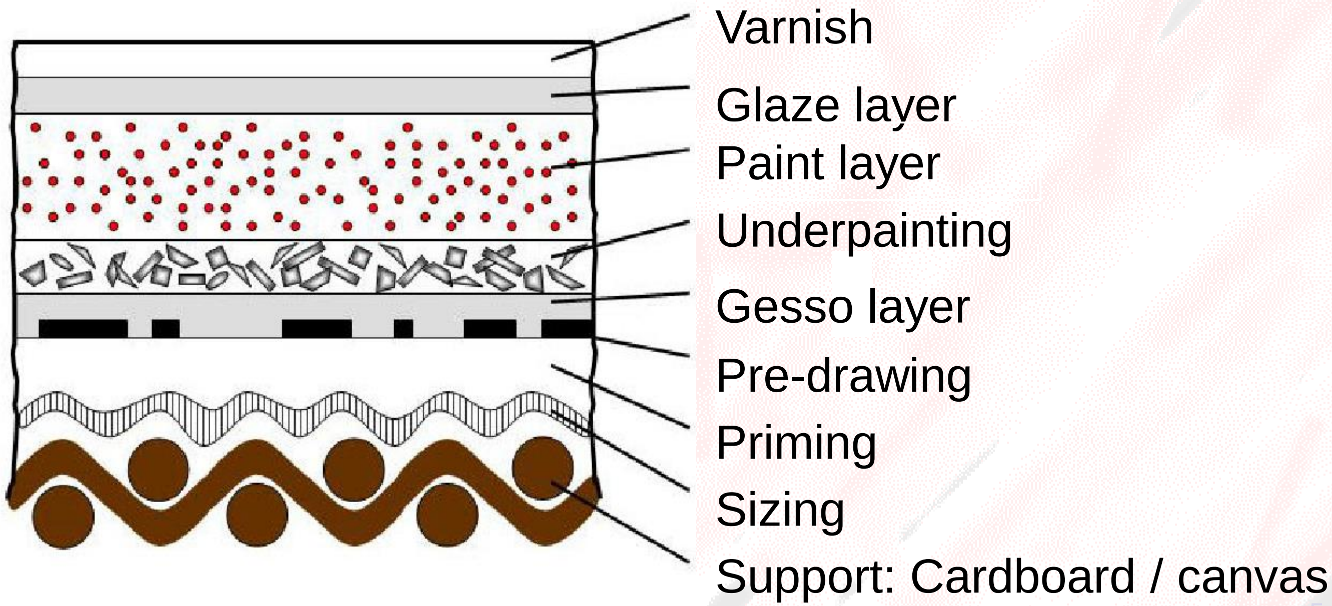


Paint sample under the microscope 50x

# Organic materials in art objects

- Binders if used as a matrix of the paint
- Varnishes if applied as a protective layer
- Consolidants if used for the conservation of a fragile paint (⇒ can complicate the understanding of the original painting technique !)



# Organic materials used in artworks

| Category | Organic materials | Uses |
| --- | --- | --- |
| Proteins | Egg, milk and casein, animal glue, silk, wool, vegetable proteins (e.g. garlic, beans), human and animal tissues (e.g. mummies) | Paint binders, adhesives, textiles, commodities, parchment |
| Glycerolipids | Animal fats, vegetable oils (e.g. palm oil, olive oil) including drying oils (e.g. linseed, walnut, poppy seed) | Paint binders, varnishes, illuminants, commodities, ingredients of cosmetic and pharmaceutical preparations |
| Waxes | Beeswax, spermaceti, Chinese wax, lanolin (animal waxes); carnauba, candelilla, Japan wax, esparto (vegetable waxes); paraffin, ozokerite (fossil waxes) | Paint binders, coatings, sealants, writing tablets, ingredients of cosmetic and pharmaceutical preparations, sculptures |
| Natural resins | Pine resins, sandarac, copals, mastic, dammar, amber, frankincense, benzoe, styrax, myrrh, (plant resins); shellac (animal resin); tar and pitch (from thermal treatment of plant resins or wood) | Varnishes, coatings, waterproofing materials, paint binders, ingredients of cosmetic and pharmaceutical preparations |
| Polysaccharide materials | Starch, cellulose, plant gums (arabic gum, tragacanth, karaya, ghatti, guar, locust bean, fruit tree gum) | Paper, paint binders, adhesives |
| Bituminous materials | Bitumen, asphalt | Moulding materials, adhesive, pigment |
| Organic dyes | Cochineal, madder, kermes, saffron, purple, indigo, synthethic dyes | Colourants for dyeing textiles, paint materials |
| Synthetic polymers | Polyacrylates, cellulose nitrate, phenolic resins, polyethylene, poly(vinyl acetate), polystyrene | Paint binders, varnishes, coatings, consolidants, sculptures |

these materials are characterized by a macromolecular nature: in some cases they are natural polymers, others undergo oligomerization or cross-linking reactions as an effect of exposure to light and air . Due to their macromolecular nature, analytical pyrolysis is a fast and efficient approach for identifying such organic materials in samples from works of art.

Natural polymers

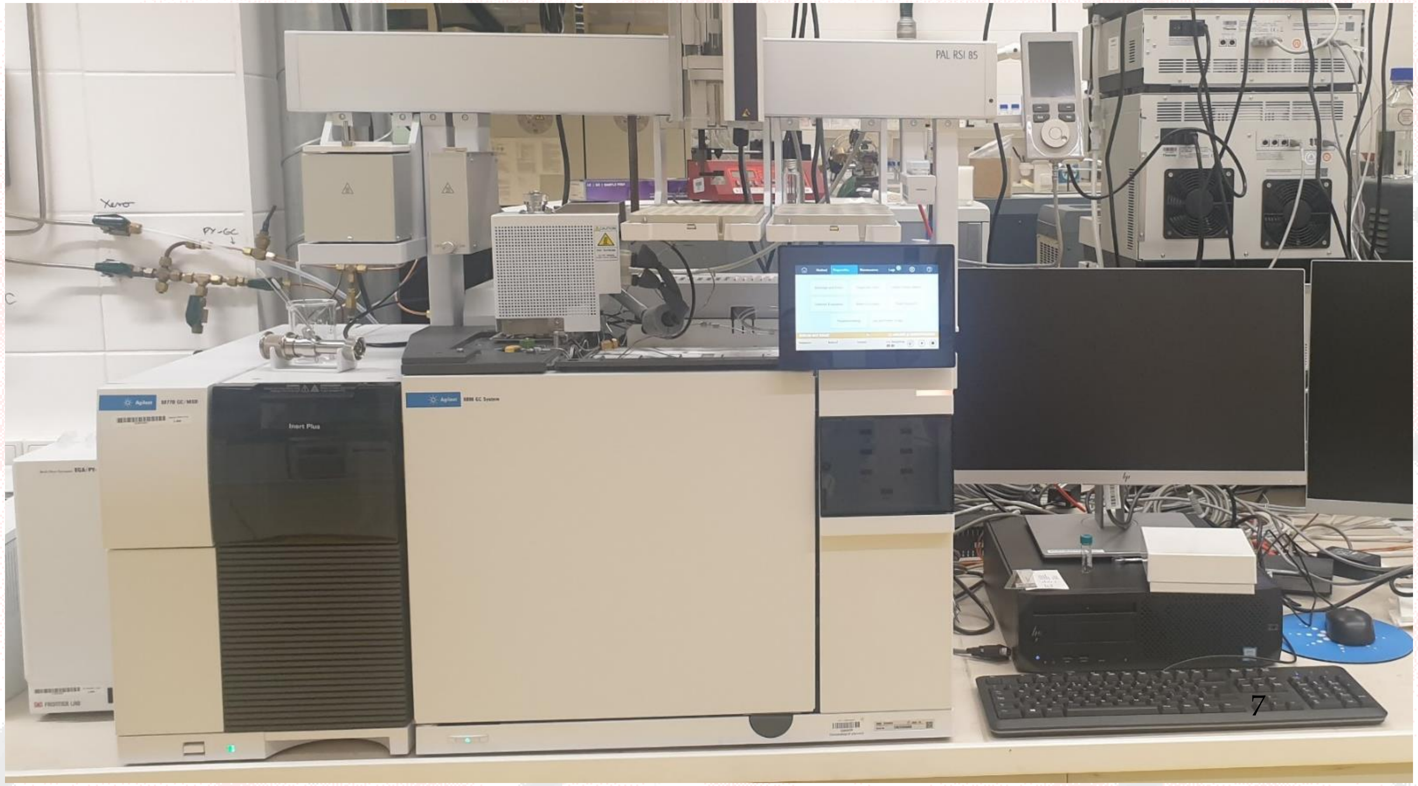
Undergo polymerization

(M.P. Colombini and F. Mondugno in: M.P. Colombini, F. Mondugno (eds.) *Organic Mass Spectrometry in Art and Archaeology*, Wiley, Chichester (2009), p. 4)

# Materials and Methods

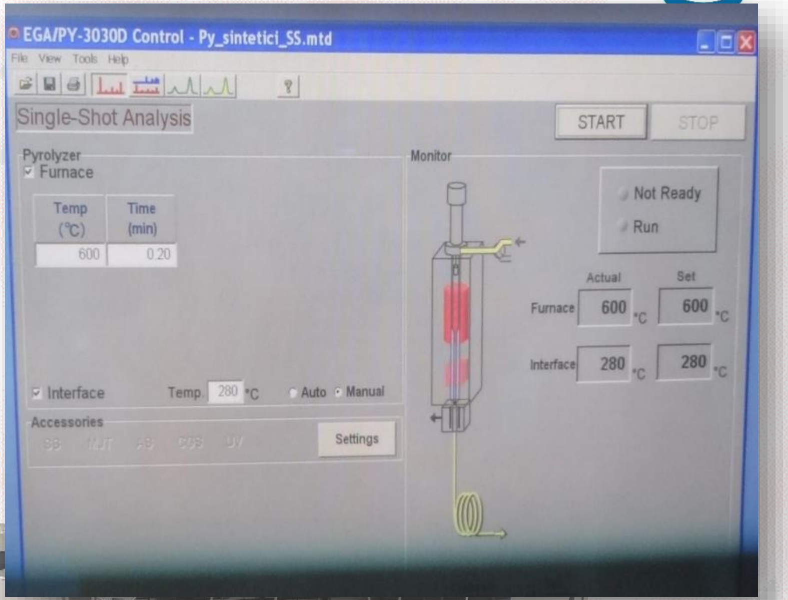
- The instrumentation consisted of a micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab, Japan) connected to an Agilent chromatograph 8890  and a single quadrupole MSD Agilent 5977B

This technique was selected due to its minimum sample size and pre-treatment requirements



# Materials and Methods

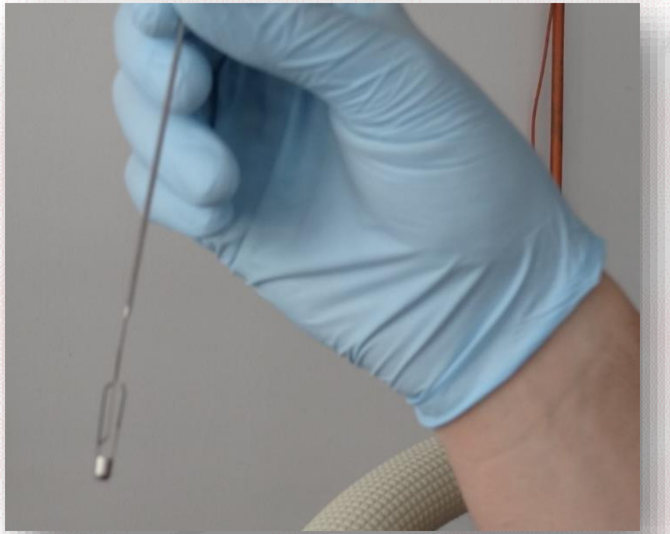
- Single shot pyrolysis was used, pyrolysis conditions were optimized as follows: pyrolysis chamber temperature 550 °C, time: 1 min, T interface 280 °C. The GC injector Temperature was 280 °C. The GC injection port was operated in split mode with a split ratio of 1:10

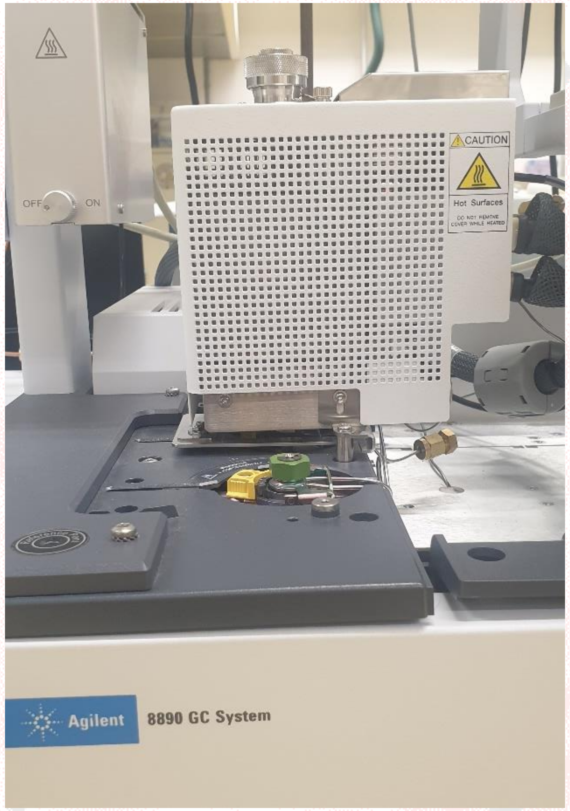



- MSD ChemStation (Agilent Technologies) software was used for data analysis, and peak assignment was based on a comparison with mass spectra libraries (NIST )

# Sample preparation and Pyrolysis Conditions

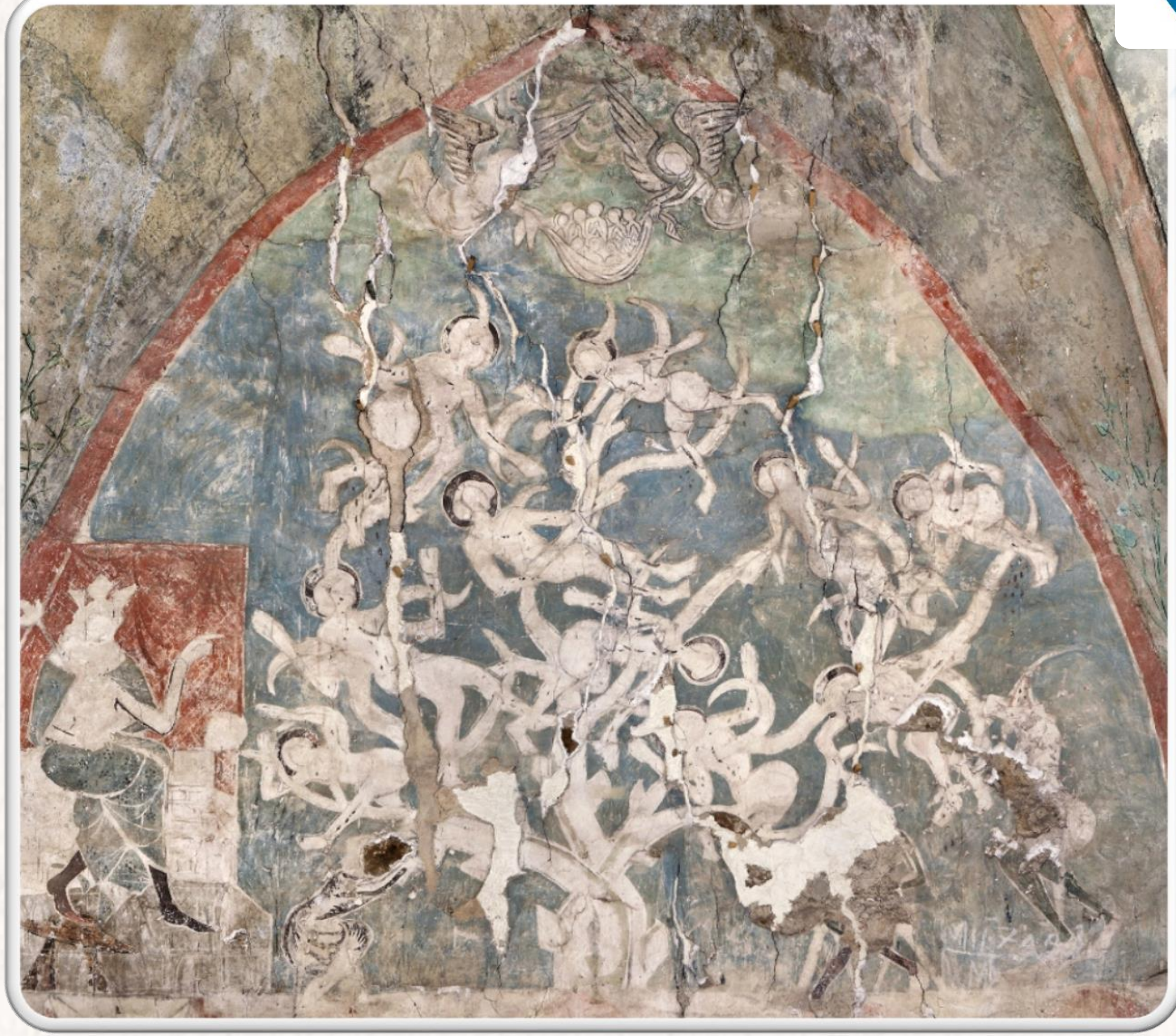
The samples (~0.2 mg) were placed in platinum sample cups and then derivatized with 5 µl of HMDS.
The cups were placed on top of the pyrolyzer at ambient temperature and then placed into the furnace.



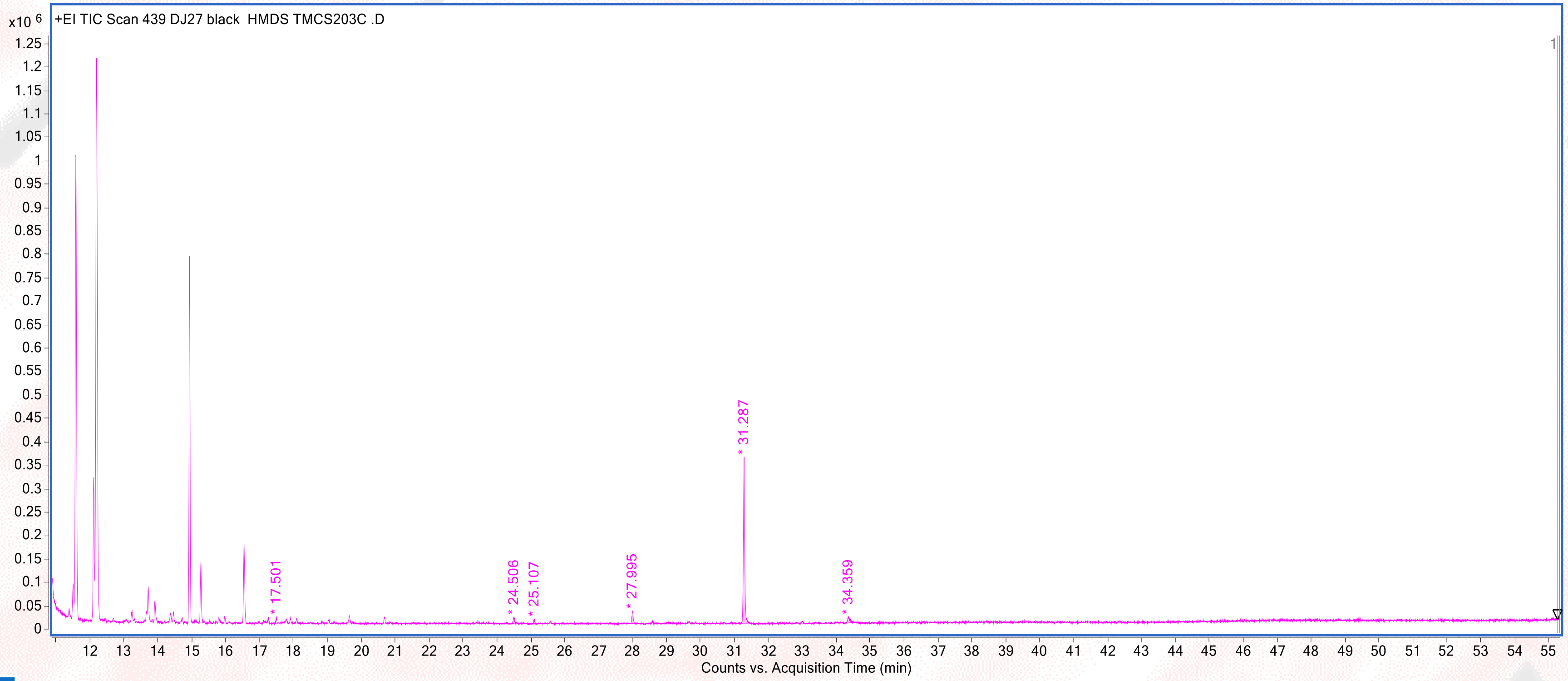
# Py/GC-MS Application

## Case Studies Wall painting $16^{th}$ Century



# Sample 1

- Picture of the sample under microscope 50x

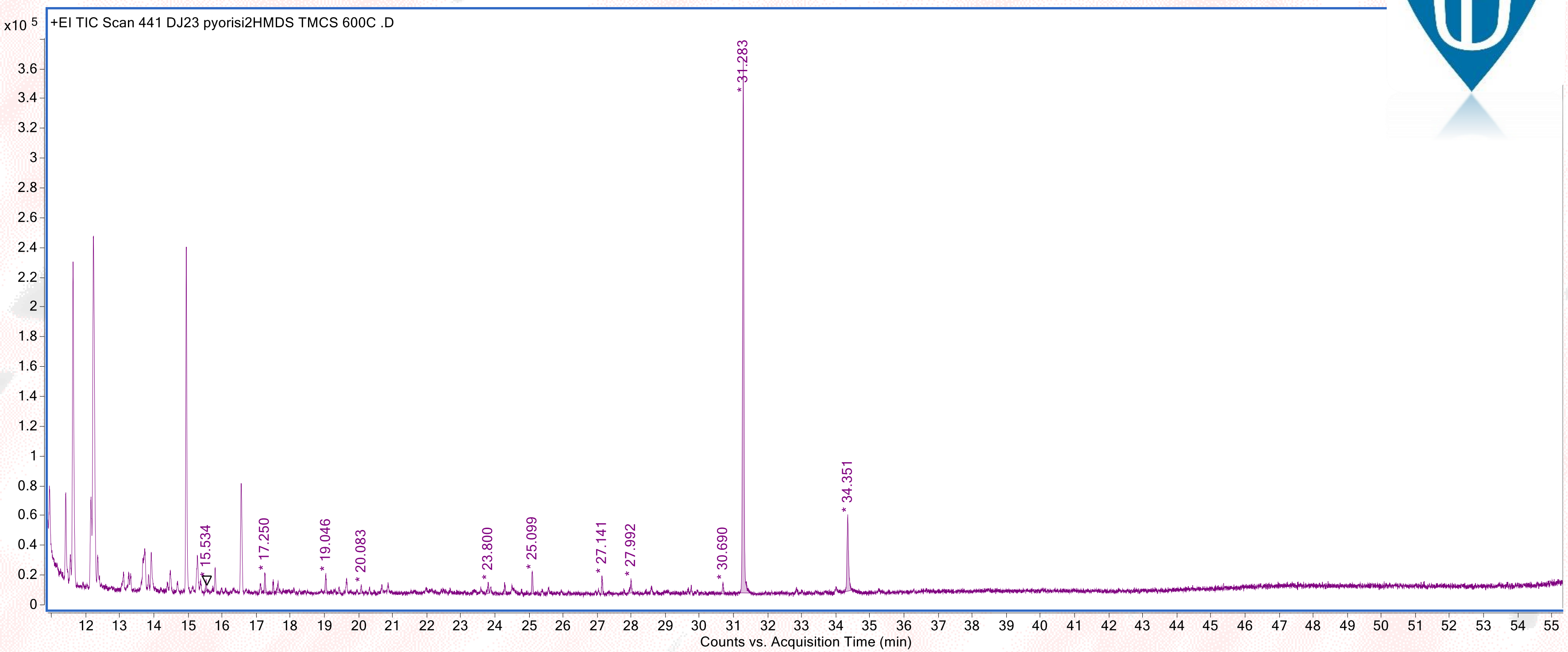



| No | Ret Time | Compound |
|---|---|---|
| 3 | 17.5 | Glycerol |
| 8 | 24.5 | Octadecanoic acid |
| 10 | 27.9 | Tetradecanoic acid |
| 11 | 31.3 | Hexadecanoic acid |
| 12 | 34.3 | Stearic acid |

Proteinaceous tempera

# Sample 2

- Picture of the sample under microscope 50x

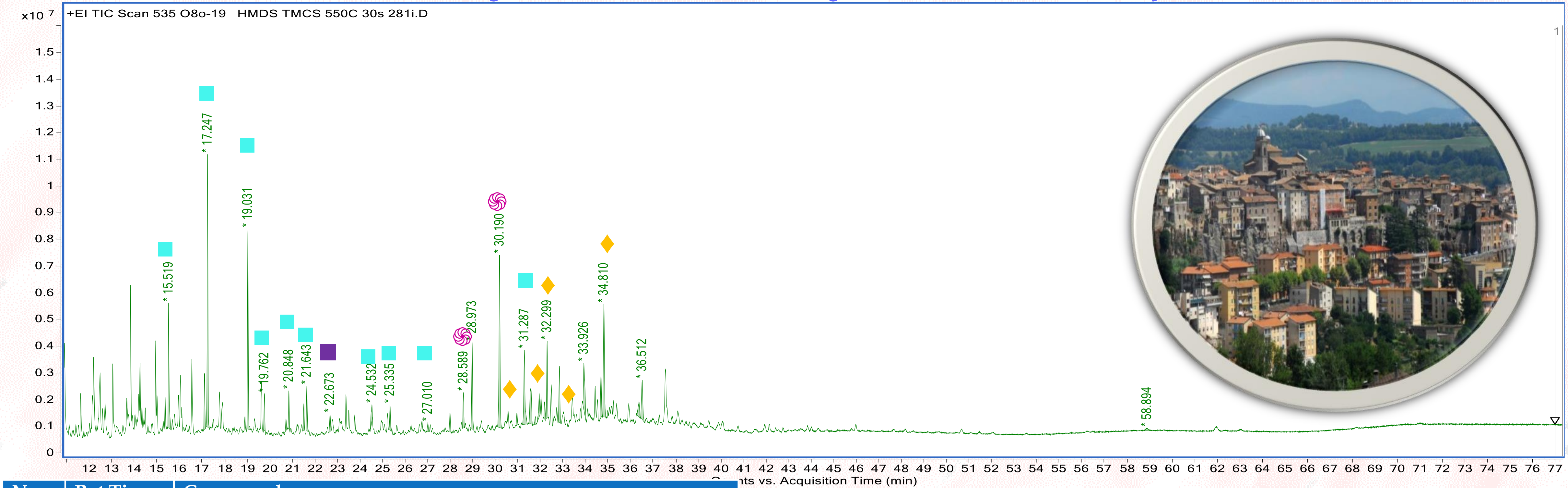



| No | Ret Time | Compound |
|---|---|---|
| 1 | 15.5 | heptanoic acid ■ |
| 2 | 17.2 | octanoic acid ■ |
| 3 | 17.5 | glycerol ▲ |
| 4 | 17.6 | silanol, trimethyl-, phosphate (3:1) ▲ |
| 5 | 19 | nonanoic acid ■ |
| 6 | 23.8 | Silane, [1,2,3-benzenetriyltris(oxy)]tris[trimethyl- |
| 7 | 24.5 | Octadecanoic acid ■ |
| 8 | 27.1 | Azelaic acid ■ |
| 9 | 27.9 | Tetradecanoic acid ■ |
| 10 | 31.3 | Hexadecanoic acid ■ |
| 11 | 34.3 | Stearic acid ■ |

# Py/GC-MS Application

## Orte polychrome objects

# Case study 2: Orte Polychrome objects

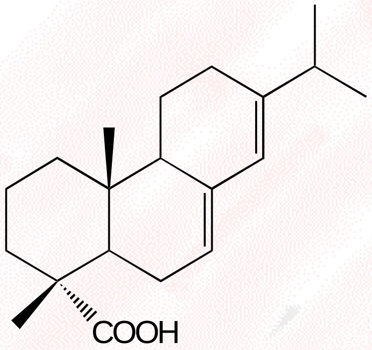



| No | Ret Time | Compound |
|---|---|---|
| 1 | 15.5 | heptanoic acid |
| 2 | 17.2 | octanoic acid |
| 3 | 19.0 | nonanoic acid |
| 4 | 20.8 | decanoic acid |
| 5 | 21.69 | pentadecane |
| 6 | 22.6 | undecenoic acid |
| 7 | 24.5 | dodecanoic acid |
| 8 | 25.3 | octanedioc acid |
| 9 | 27.1 | nonadioic acid (azelaic) |
| 10 | 28.5 | phtalic acid deriv |

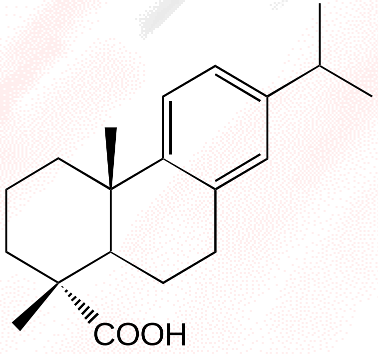
| No | Ret Time | Compound |
|---|---|---|
| 11 | 30.2 | dibutyl phthalate |
| 12 | 30.9 | dehydroabietic acid |
| 13 | 31.3 | hexadecanoic acid (palmitic) |
| 14 | 31.5 | pimaric acid |
| 15 | 32.2 | phenanthrene,2,7-dimethyl |
| 16 | 32.8 | 10,18-Bisnorabieta-5,7,9(10),11,13-pentaene |
| 17 | 34.8 | phenanthrene, 1-methyl-7-(1-methylethyl)- |

# Diterpenic molecules in resins from conifer plants order

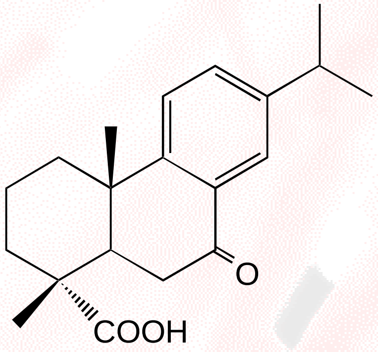
**Abietane squeleton**




*Abietic acid*

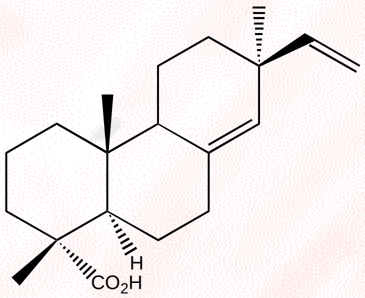



*Dehydroabietic acid*

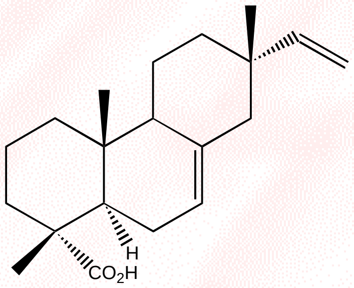



*7-oxodehydroabietic acid*

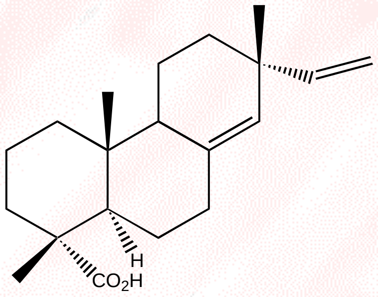
**Pimarane squeleton**




*Pimaric acid*




*Isopimaric acid*




*Sandaracopimaric acid*

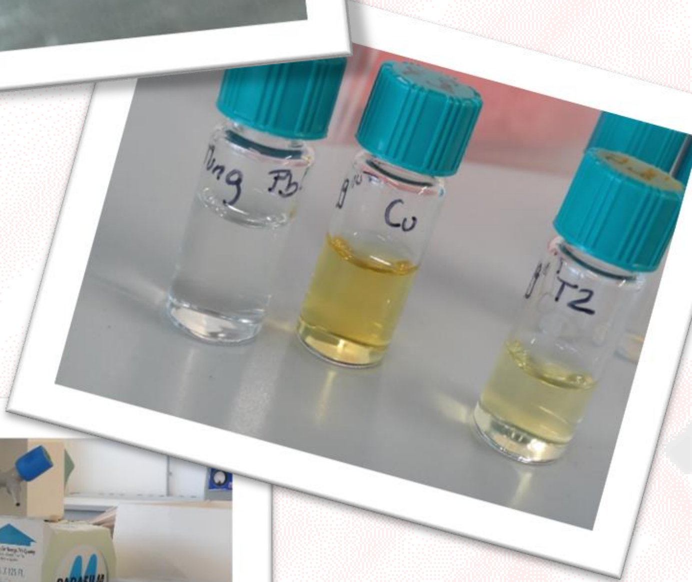
# Conclusions

Py-GC/MS is rapid, avoids sample wet chemical workup, avoiding sample loss and contamination, and has a low sample requirement.

It allows the determination, in a single step, of polymeric materials and low molecular weight components

Pyrolysis is a relatively inexpensive technique, especially if compared with the classical wet analytical procedures that are required prior to GC/MS analyses.

Py-GC/MS technique overcomes the major disadvantages encountered in GC/MS, i.e. undetectability of synthetic polymers and unpredictable interferences

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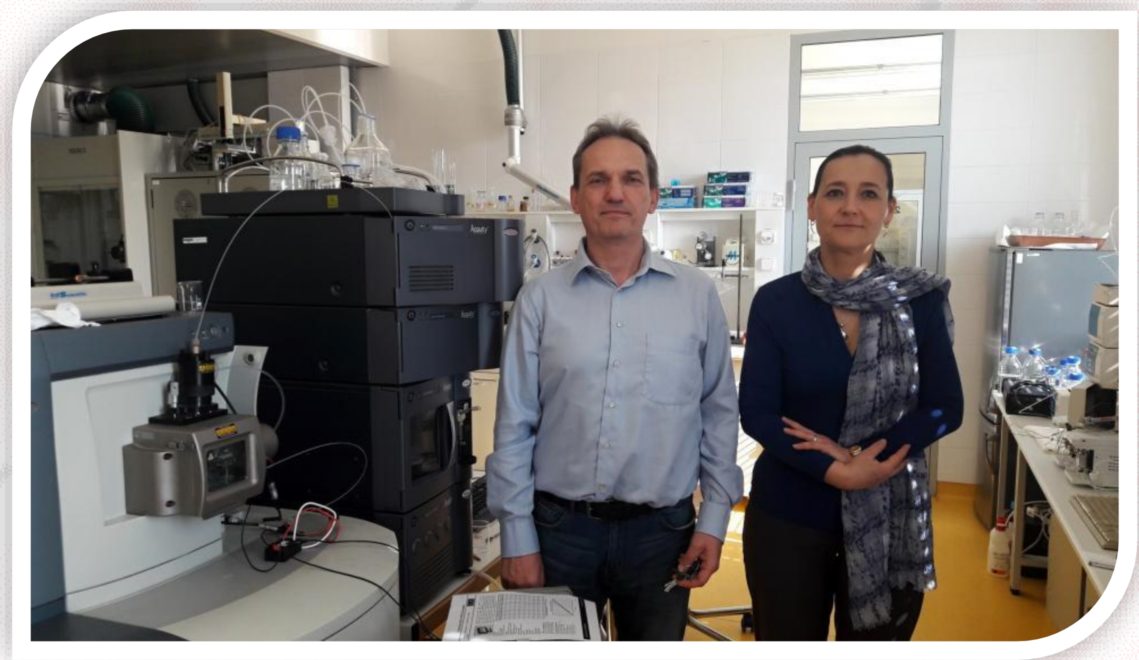

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**Thank you for your attention!**

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Department of Analytical Chemistry, Palacký University

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