

LmPy-GCMSMS and Other Alternative Methodologies in the Screening for Source Rocks*

João Graciano Mendonça Filho¹

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¹Palynofacies and Organic Facies Laboratory, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil (graciano@geologia.ufrj.br)

Abstract

Pyrolysis gas chromatography-mass spectrometry (Py-GCMS) is a hyphenated analytical technique applied using a Pyrolyzer (Laser Source), Microscope, Gas Chromatograph (GC), and Mass Spectrometer (MS). Pyrolysis has been used extensively over the last 20–30 years as an analytical technique, in which large molecules are degraded into smaller volatiles species using thermal energy only (Hanson et al., 1975). For improvement of the analytical process, this technique uses the chromatographic information to determine the composition or structure of the original sample (Sobeih et al., 2008). Gas chromatography-mass spectrometry (GC-MS) detection provides molecular analysis of gaseous species and its combination with the laser system has resulted in a relatively new technique termed Laser Micropyrolysis-Gas Chromatography–Mass Spectrometry (LmPy-GCMS) (Greenwood et al., 1996, 1998). Among pyrolysis techniques, laser micropyrolysis has relatively succeeded in providing important molecular data on organic fossils such as coals, source rocks, oil shales and kerogen, and has also been useful in assessing the oil-proneness and maturity of maceral materials (Greenwood et al., 1993; Stout and Lin, 1992; Stout, 1993; Vanderborgh and Jones, 1983; Yoshioka and Takeda, 2004; Silva et al., 2016). Previous works showed studies with laser micropyrolysis were primarily focused on instrumental development and the authors listed a number of factors that could explain this setting as: the sensitivity limitations of chromatographic technologies required for small product concentrations; the interdisciplinary skills needed; the financial expense of the different instruments; the difficulties involved with interfacing these instruments; the lack of understanding of the interactions between laser and material; and the issue that not all samples are compatible with laser radiation to produce pyrolysis products (see Sobeih et al., 2008). Nevertheless, the LmPy-GC-MS method

has been successfully applied to different organic components. For example, Greenwood et al. (1998) demonstrated the credibility in the LmPy-GCMS through the analysis of micro-sized quantities of various organic fossils. Their results were confirmed by the favorable comparison from the laser derived molecular data to corresponding data obtained from more traditional methods. Arouri et al. (1999) performed laser pyrolysis on small populations (≤ 10) of acritarch specimens and showed that laser pyrolysates reflect a significant aliphatic and aromatic content of the studied acritarchs, a result consistent with the thermal desorption-mass spectrometry data exposed in the same paper. Greenwood et al. (2000) studied the hydrocarbon composition of a Tasmanite oil shale and isolated Tasmanites that were separately investigated by LmPy-GCMS and concluded that the very similar tricyclic content of both samples strongly supports the proposal of an inherent relationship between the Tasmanites and tricyclic terpenoid production. Meruva et al. (2004) describes the design, construction and applications of UV laser pyrolysis-GC/TOF-MS for characterization of synthetic polymer samples, observing that laser pyrolysis requires little or no sample preparation and reduces sample size requirements. Jacob et al. (2007) provided LmPy-GCMS on individual and well-preserved chitinozoan specimens extracted from Silurian marine rocks. They observed that organic structures of chitinozoans appear to be a kerogen network dominated by aromatic units with few aliphatic groups. Saundouk-Linke et al., (2013) compared micro- and macroscale spectroscopic and pyrolysis methods demonstrating that both micro-Fourier transform infrared (μ -FTIR) spectroscopy FTIR analysis and LmPy- GCMS provide similar trends with maturation, whereas the results from Curie Point-Py showed wide differences, especially at higher stages of maturity. They concluded that both IR spectroscopy and LmPy-GCMS are suitable for studying the alteration of palynomorphs during maturation, whereas for immature materials Curie Point-Py-GC/MS appears to be a more suitable method as the applied temperature can be adjusted much more accurately (Saundouk-Linke et al., 2014). Silva et al. (2016) used LmPy-GCMSMS to compare the chemical composition of both *Botryococcus* and *Gloeocapsomorpha prisca* microfossils and to evaluate the similarities and differences between their chemical compositions, once the chemical structure of these microorganisms has long been a topic of debate in geochemistry. All these studies show that laser pyrolysis has a high potential to improve our understanding of the organic composition of heterogeneous materials and isolated organic-walled microfossils, allowing to individually analyze, on an isolated way, very small components within complex mixtures. In Palynofacies and Organic Facies Laboratory (LAFO-UFRJ), the micropyrolysis system refers to a laser and an optical device; a sample chamber and cold trap; and a gas chromatographer coupled with triple quadrupole mass spectrometer (LmPy-GCMS) to separate and detail the composition of molecular pyrolysis products. This system was assembled exclusively for LAFO/UFRJ by CSIRO Division of Petroleum Resources (Sydney, Australia) with financial support from PETROBRAS/Brazil.

AAPG HEDBERG Conference

*The Evolution of Petroleum Systems Analysis:
Changing of the Guard from Late Mature Experts to
Peak Generating Staff*

2019



LmPy-GCMSMS and other alternative methodologies in the screening for source rocks

Prof. Dr. João Graciano Mendonça Filho

Prof. Dr. Tais Freitas da Silva

Dr. Antonio Donizeti de Oliveira

MSc. Jaqueline Torres de Souza

BSc. Milton Cesar Silva

BSc. Luiz Guilherme Costa dos Santos

LAFO-UFRJ

Palynofacies and Organic Facies Lab

ImPyGCMS is a hyphenated analytical technique composed by:



Laser Source: Nd: Y₃Al₅O₁₂

(neodymium-doped yttrium aluminium garnet)

Nd-YAG laser is a solid-state laser emission device that has yttrium oxide and crystalline aluminum ("host") doped with neodymium ("guest"), forming a variety of garnet. These are one of the most common types of laser, emitting light in the infrared spectrum (wavelength of 1064 nm)

Mendonca Filho et al. (2019)



Nd: YAG Laser System
Control Panel



ImPyGCMS is a hyphenated analytical technique composed by:

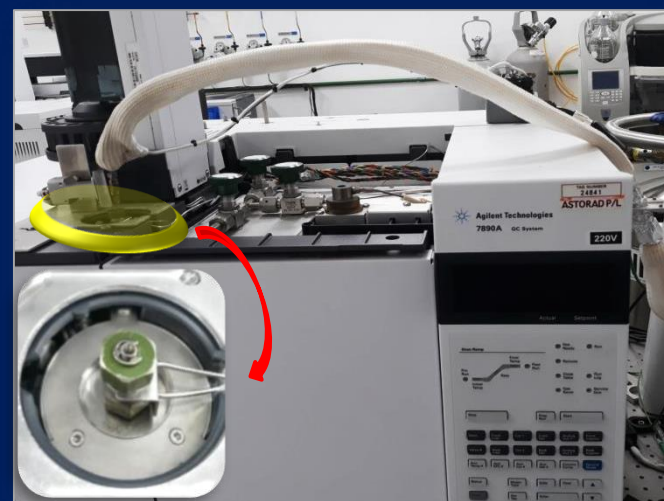
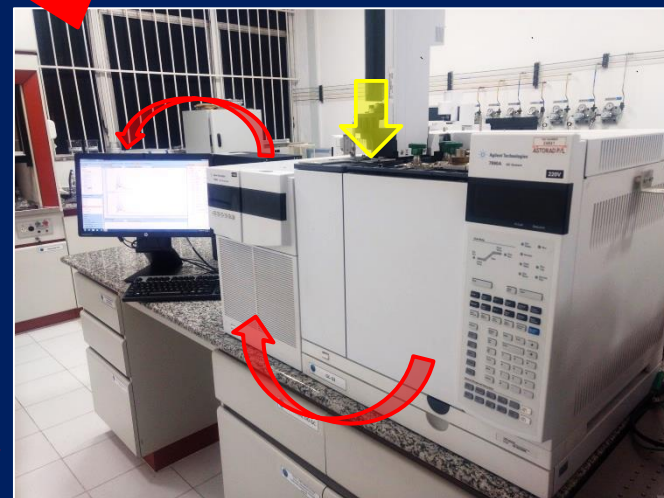


Zeiss Axio, Imager (D2m)



The system also has an **Optical Device** with a **Custom Built Laser Chamber** (sample chamber)

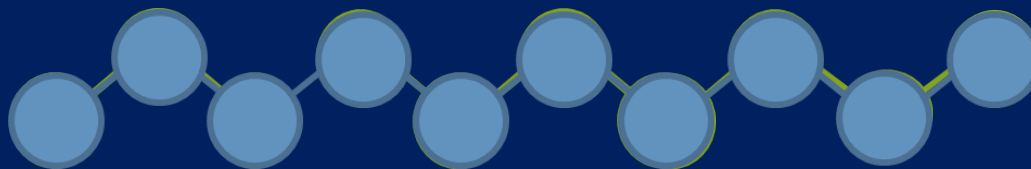
ImPyGCMS is a hyphenated analytical technique composed by:



GCMS: gas chromatography equipment (Agilent 7890A) coupled to a triple quadrupole mass spectrometer (7000B series)

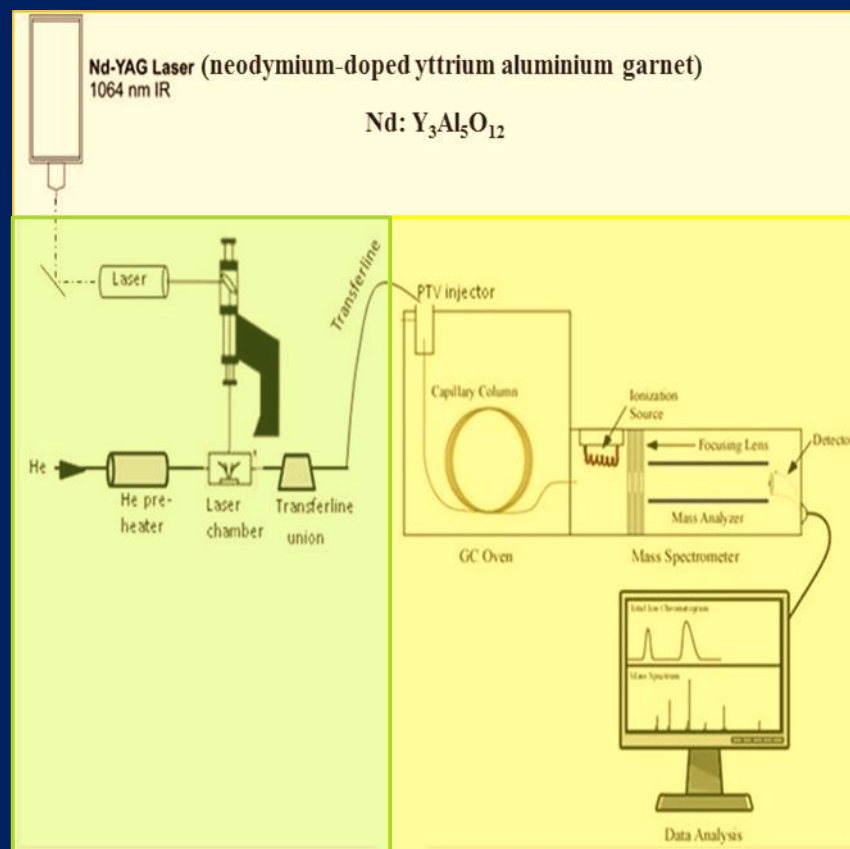
Cold Trap: Cryogenic entrapment (Cryol Collecting) Liquid N (-80°C)

- ▶ Pyrolysis has been used extensively over the last 40-50 years as an analytical technique in which large molecular weight polymer carbon chains are degraded into smaller volatile species using only thermal energy under an oxygen free environment;



- ▶ Pyrolysis studies of organic material have proven to be an excellent mean in which the chemical composition of these heterogeneous materials is examined;

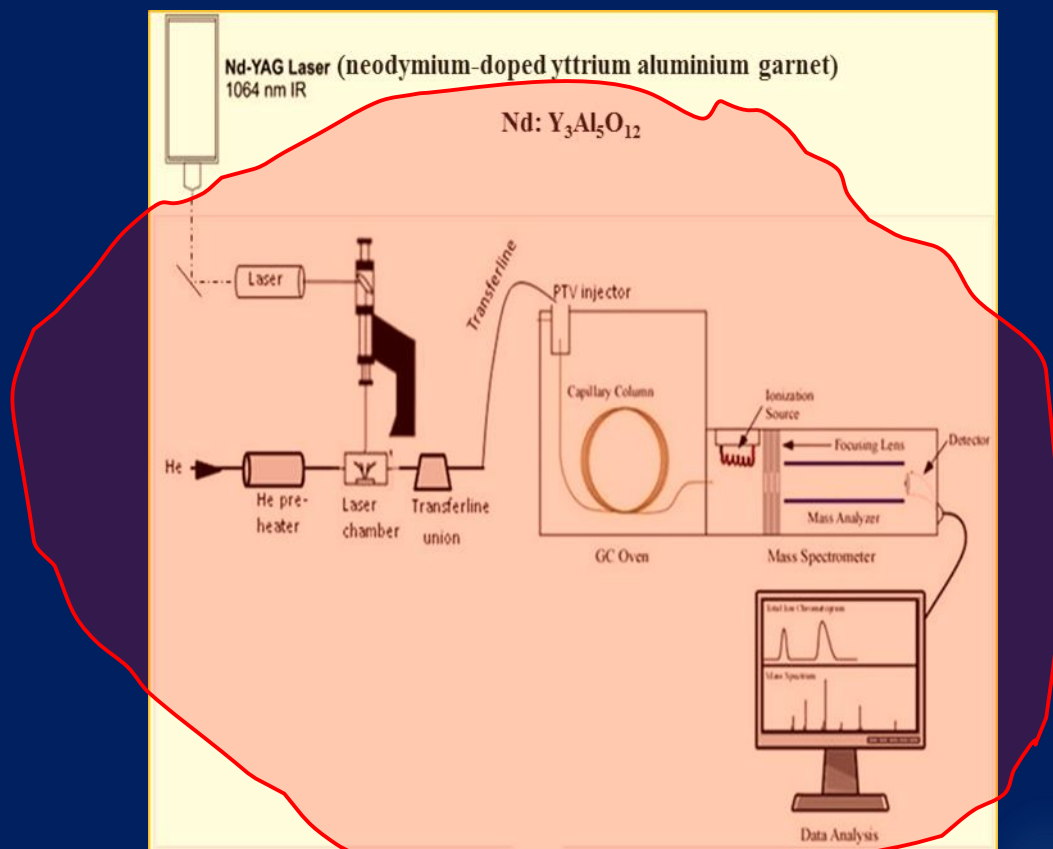
- For analytical process improvement, pyrolysis techniques (LmPy) were associated with chromatographic techniques to determine the composition or structure of the original sample;



LmPy-GCMS System (LAFO-UFRJ)

Mendonça Filho et al. (2019)

- ▶ A combination of GC-MS with the laser system has resulted in a technique called Laser Micropyrolysis - GCMS (LmPy-GCMS);



LmPy-GCMS System (LAFO-UFRJ)

Mendonça Filho et al. (2019)

- Among pyrolysis techniques the LmPy has had some success in providing important molecular data on organic fossils, such as:

Coals

Vastola and McGahen (1987); Stout (1993); Greenwood et al. (1993; 1998)

Kerogen

Arouri et al. (1999); Greenwood et al. (2000); Dutta et al. (2006); Jacob et al. (2007); Sandouk-Lincke et al. (2013; 2014); Silva et al. (2016)

Synthetic Organic Polymers

Stout and Hall (1991); Meruva et al. (2004)

Source Rocks

Derenne et al. (1990); Greenwood et al. (1995); Vanderborgh and Jones (1983)

Oil Shales

Stout and Lin (1992); Greenwood et al. (1996; 1998)

► Previous works have shown that studies with LmPy were mainly focused on instrumental development and the authors listed a number of factors that could explain this setting, such as:

Vastola and McGahan (1987)

Stout and Lin (1992)

Stout (1993)

Greenwood et al. (1996)

Meruva et al. (2004)

Metz et al. (2008)

Greenwood (2011)

Mendonça Filho et al. (2014)

the sensitivity limitations of chromatographic technologies required for small product concentrations

the interdisciplinary skills needed

the financial expense of the different instruments

the difficulties involved with interfacing these instruments

the lack of understanding of the interactions between laser and material

the issue that not all samples are compatible with laser radiation to produce pyrolysis products

- ▶ Many other studies have applied LmPy-GCMS and other detection methods to determine the molecular chemical composition of different organic materials:

Derenne et al. (1990) examined the kerogen of an Ordovician Estonian Kukersite sample by spectroscopic NMR and FTIR, and pyrolytic ("off-line", flash) methods

Stout and Hall (1990) investigated two synthetic organic polymers (poly-para-tert-butylstyrene:graphite (1:1) and linear polyethylene: graphite (1:1) mixtures) using LaPy-GCMS

Dutta et al. (2006) analysed prasinophyte specimens from a Silurian-Devonian sedimentary sequence in South-East Turkey using CPPy-GCMS

Greenwood et al. (1995, 1998, 2000, 2001 and 2002) demonstrated the credibility in the LmPy-GC/MS through the analysis of micro-sized quantities of various organic fossils

Arouri et al. (1999) performed LmPy on small populations of acritarch specimens

Yoshioka and Takeda (2004) published a paper about the use of IR laser micropyrolysis to analyze organic compounds in three macerals of an immature, sub-bituminous coal

Jacob et al. (2007) provided LmPy-GCMS on individual and well-preserved chitinozoan specimens extracted from Silurian marine rocks

Saundouk-Lincke et al. (2013; 2014) compared micro- and macroscale spectroscopic and pyrolysis methods (μ -FTIR; CP-Py-GCMS; NMR and FTIR-spectroscopy analysis; and LmPy-GCMS)

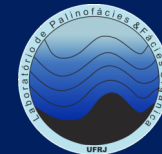
Silva et al. (2016) used LmPy-GCMS to compare the chemical composition of both *Botryococcus* and *G. prisca* microfossils and to evaluate the similarities and differences between their chemical composition

Results of all these studies have been confirmed by the favorable comparison from the laser derived molecular data to those corresponding data obtained from more traditional methods, suggesting that laser energy is a suitable source of pyrolysis for the molecular investigation of organic macromolecules

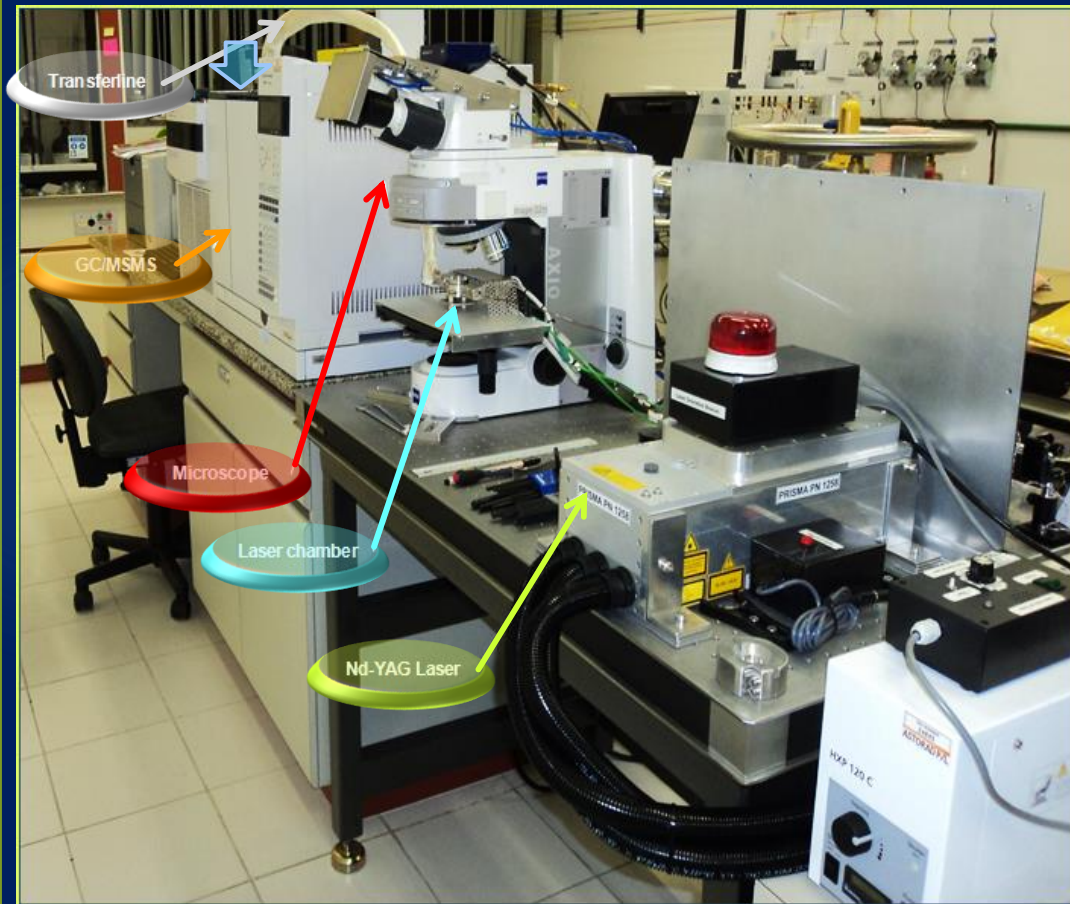
All these studies have shown that LmPy-GCMS and other micro-macroscale spectroscopic methods (FTIR, μ -FTIR, NMR, and CP-GCMS) have a high potential to improve the understanding of the composition of heterogeneous organic materials and isolated OWM, allowing to individually analyzing and on an isolated way, very small components within complex mixtures

- In the LAFO-UFRJ, the LmPy system refers to a laser source (Nd: $\text{Y}_3\text{Al}_5\text{O}_{12}$), an optical device; a sample chamber; a transfer line and a GCMS with a cold trap to separate and detail the composition of molecular pyrolysis products;

- This system was assembled exclusively for LAFO/UFRJ by CSIRO (Commonwealth Scientific and Industrial Research Organisation), Division of Petroleum Resources (AUS) with financial support from PETROBRAS/Brazil;



- The performance of the LmPy system installed in LAFO-UFRJ can be demonstrated with the analysis of isolated particles of *B. braunii* microfossils;



LmPy-GCMS system LAFO-UFRJ, Brazil

Mendonça Filho et al. (2019)

LmPy-GCMS system Performance

- ▶ For a good work involving LmPy-GCMS techniques is necessary an efficient and appropriate method of sample preparation;
- ▶ The pattern of sample collection, the type of sample, and the sample processing technique strongly affect the utility of LmPy analysis data;
- ▶ The quality of the result interpretations can be strongly influenced by the quality of the samples and their preparation proceedings;
- ▶ This study can be carried out in WR and KC;



WR polished section



KC

Sample Preparation

- For analyzing individual organic components, a standard non-oxidative method is applied for the isolation of kerogen, where the rock sample is crushed into fragments of size from 2-5 mm;



Rock Sample



The crushed fraction (2-5mm) must be treated with HCl and HF acids to remove carbonates and silicates

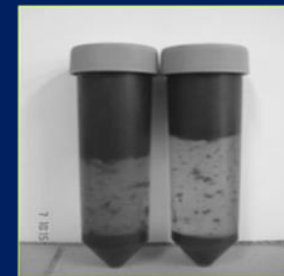
Crushed sample is pre-extracted in Soxhlet Extraction Apparatus using CH_2Cl_2 for at least 24 hs



Isolated kerogen is the fraction retained in the sieve



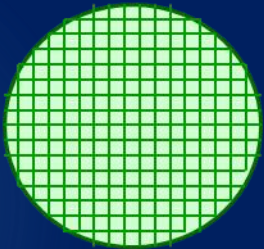
The organic residue is sieved through a 10 mm nylon mesh using distilled water



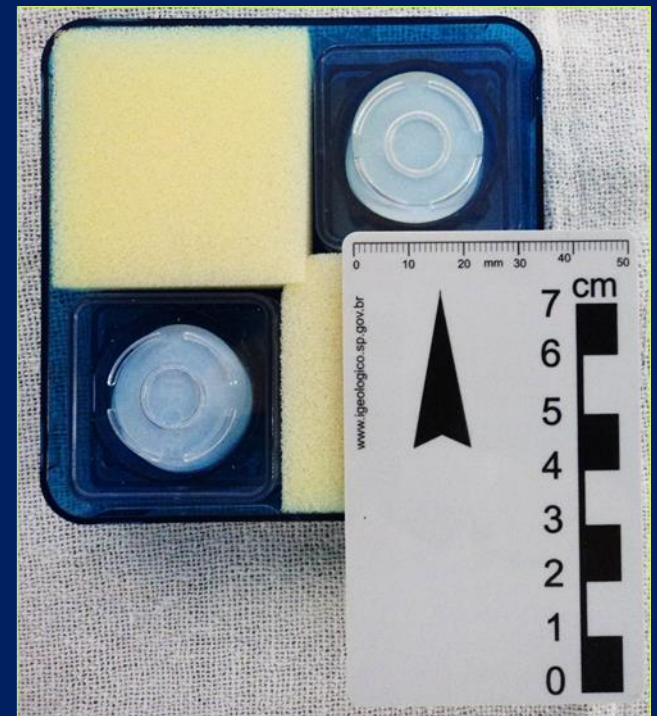
Heavy liquid (ZnCl_2) is applied in order to concentrate the kerogen

Sample Preparation

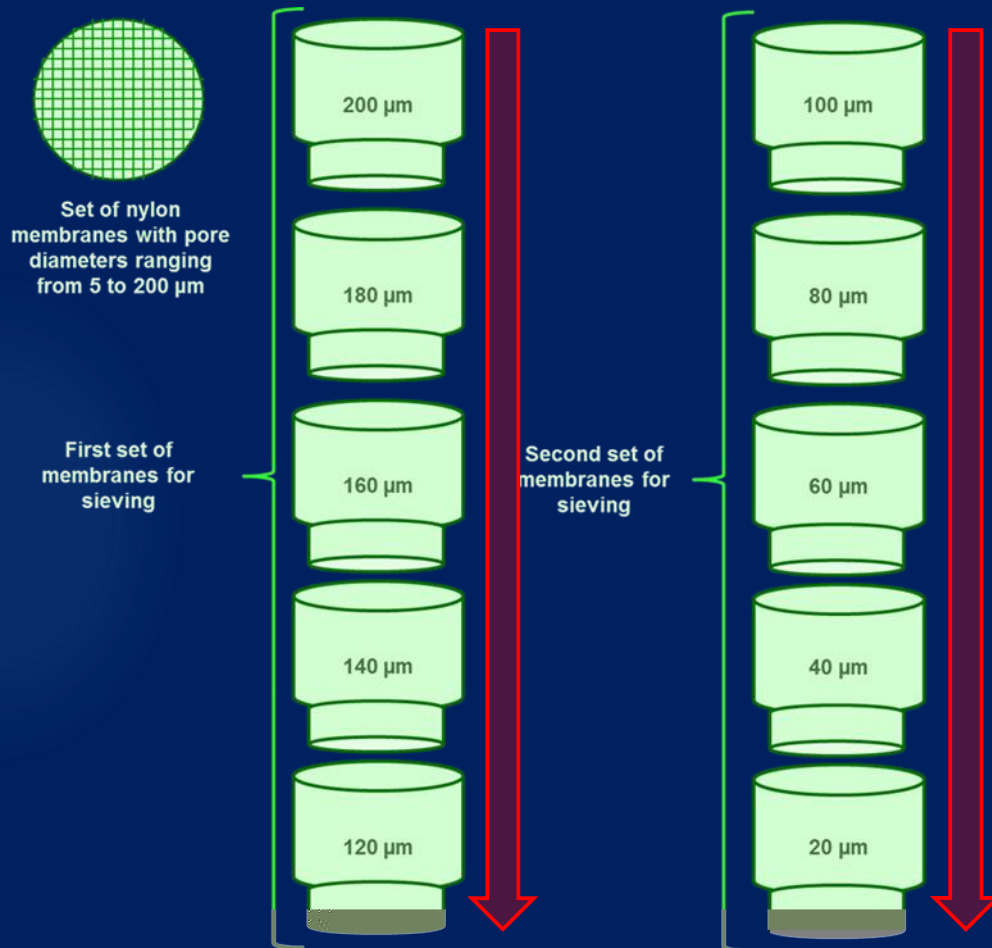
- ▶ Particulate organic components are separated by size using a set of nylon membranes;



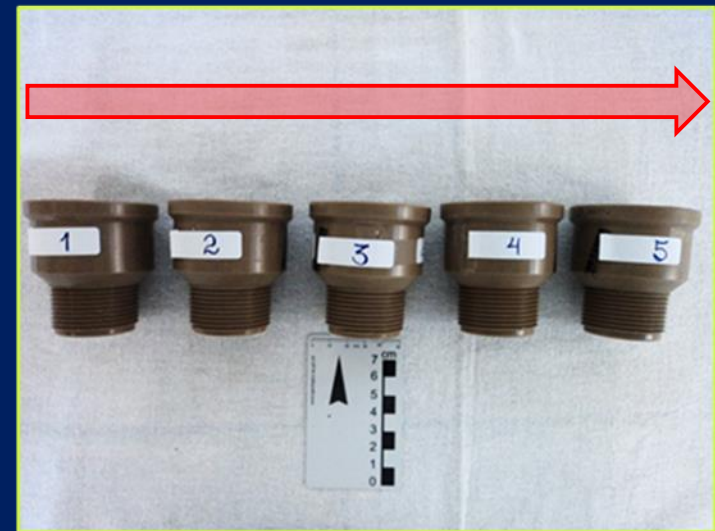
Set of nylon membranes with pore diameters ranging from 5 to 200 μm



Sample Preparation



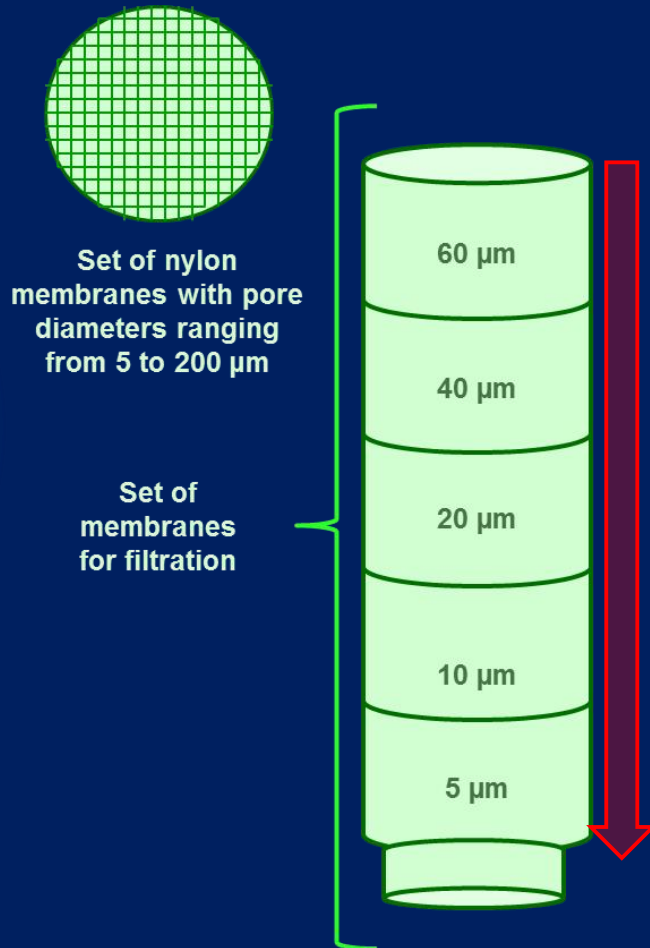
The sieving process follows the arrangement the sieves (membranes) in a sequential nest: smallest mesh number (largest aperture) at the top and largest mesh number (smallest aperture) at the bottom.



Set of sieves with nylon membranes

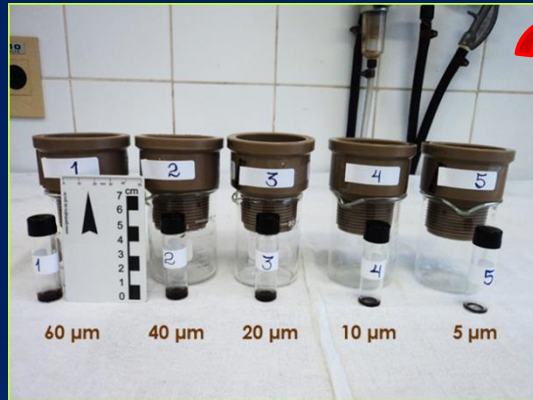
Sample Preparation

- ▶ The set of smallest aperture nylon membranes is used for filtration process using an apparatus fitted with a kitasato flask and a vacuum pump;



Set Filtration of Kitasato flask, Nylon Membrane filter, and Vacuum pump

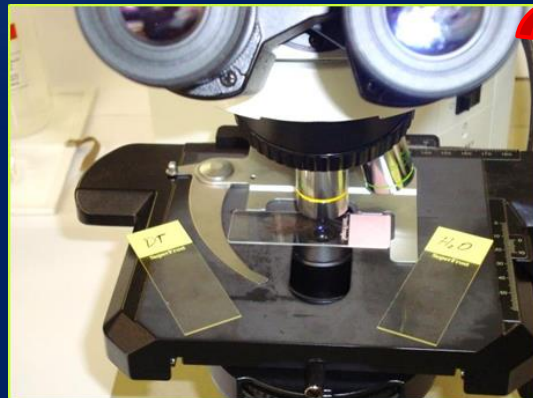
Sample Preparation



Organic residue separated by size after the filtration process is spread on slides using different solutions



- KC strewn slide is placed under the microscope and, with the aid of a histological needle, the organic particles are then separated from each other, one by one, using the hand-picking technique:



Kc strewn slides



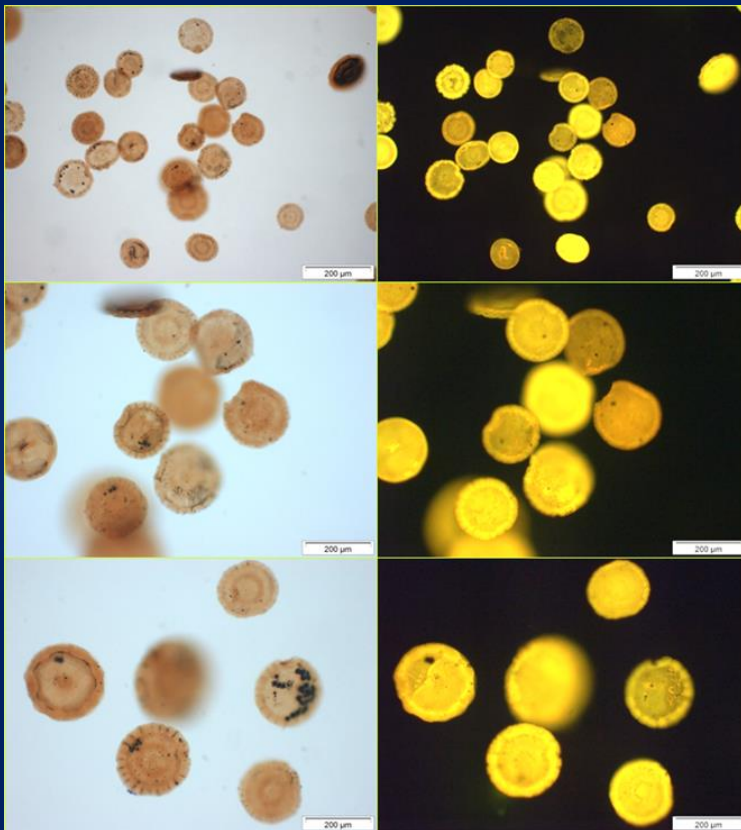
Histological needle



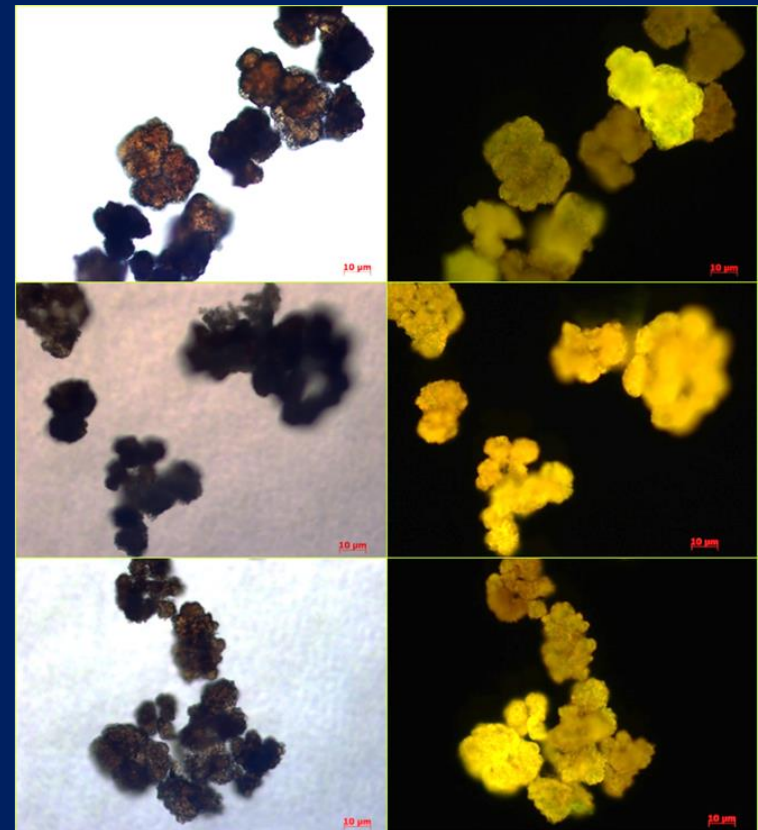
Hand-picking technique

Sample Preparation

- ▶ The components of the heterogeneous mixture are then identified and individually separated from each other;



hand-picked *Tasmanites* algae



hand-picked *Botryococcus* algae

Assembling the LmPy-GCMS system unit for analysis performing

- ▶ **Sample Chamber Assembly:** The hand-picked organic material is transferred to a 6 mm diameter glass slide and placed inside the sample chamber compartment (6 mm is the inner diameter of the sample chamber);



KC strewn slide



KC or WR polished section

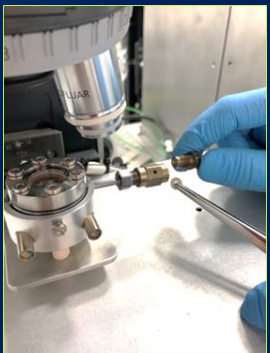


Seal the chamber with Copper Gasket Seal



Close the Chamber with a Fused Silica Coating*

* VAR coating reduce reflectance from around 10% to 1%



Connect the Gas line

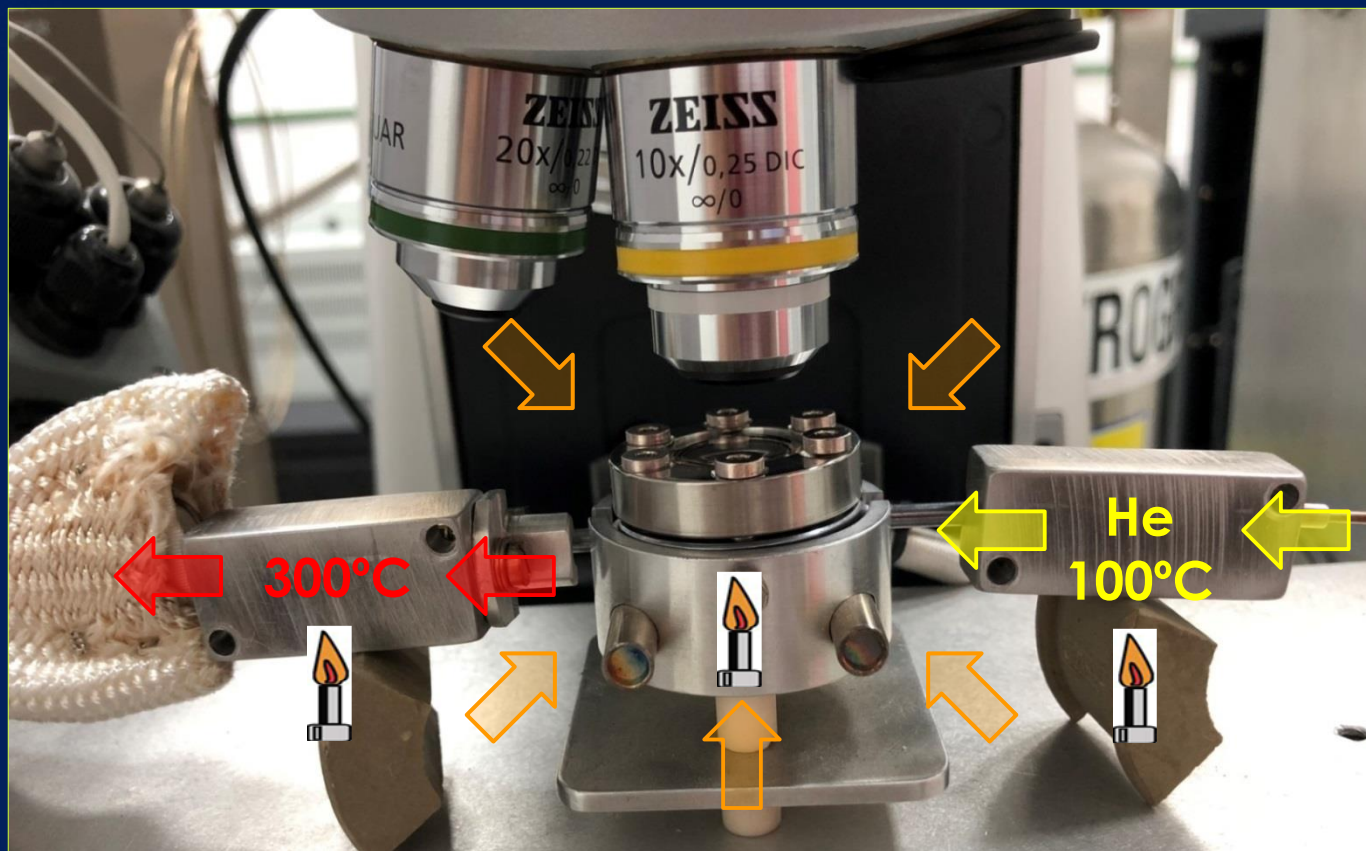


System assembled and ready

Mendonca Filho et al. (2019)

Thermal Extraction

- Organic material is subjected to Thermal Extraction inside the sample chamber by heating at 100°C and the extracted products are transferred online to a PTV injector, using He as carrier gas, via a transfer line heated at 300 °C;



Establishment of laser power conditions

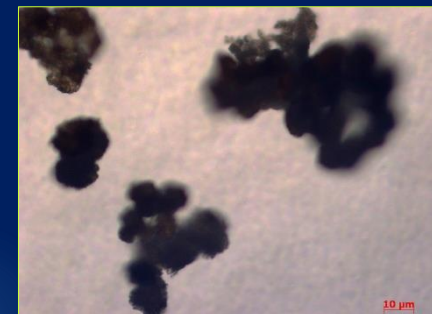
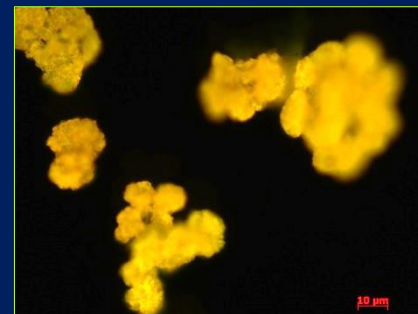
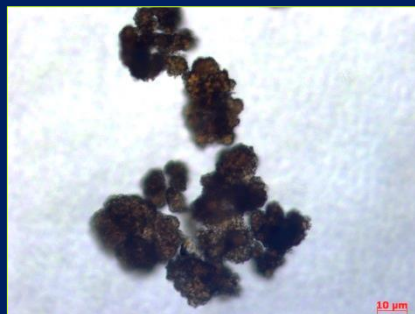
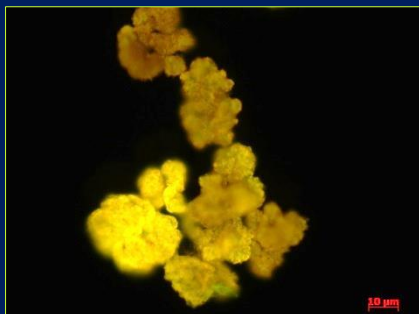
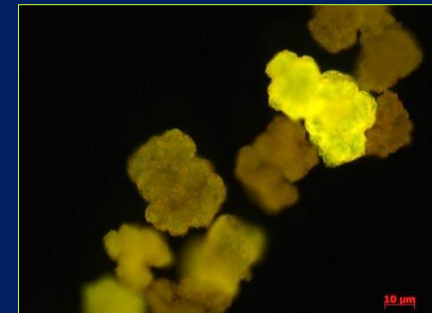
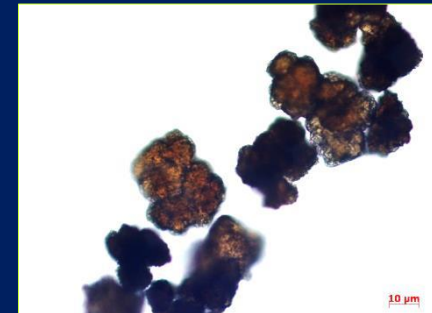


Nd:YAG Laser System
Control Panel

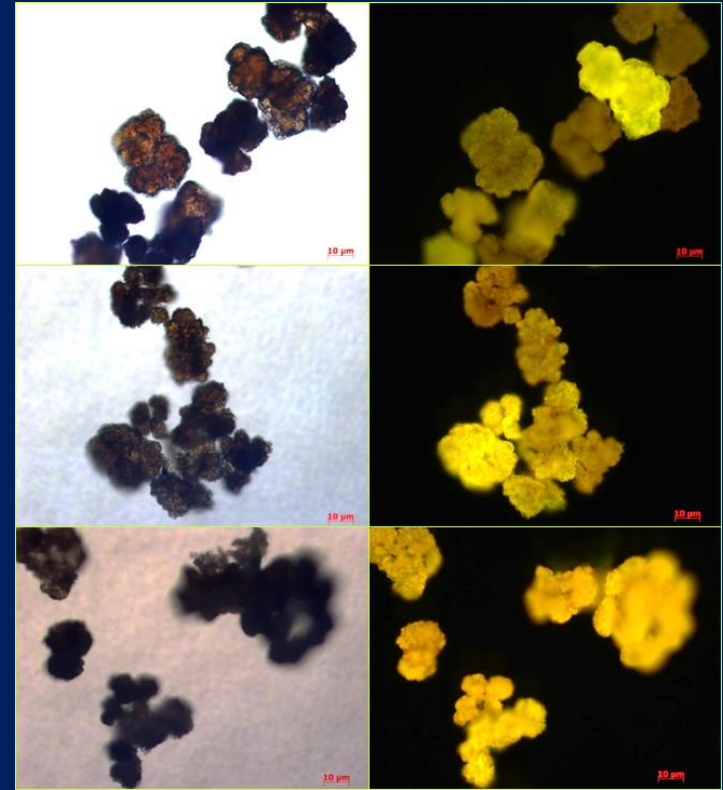


The laser conditions (laser energy, irradiation time, etc.) must be varied in order to establish the most favorable parameters for the generation of primary pyrolysates, as well as provide an initial characterization of their performance and influence on the technique;

Identification and selection of organic particles for pyrolysis

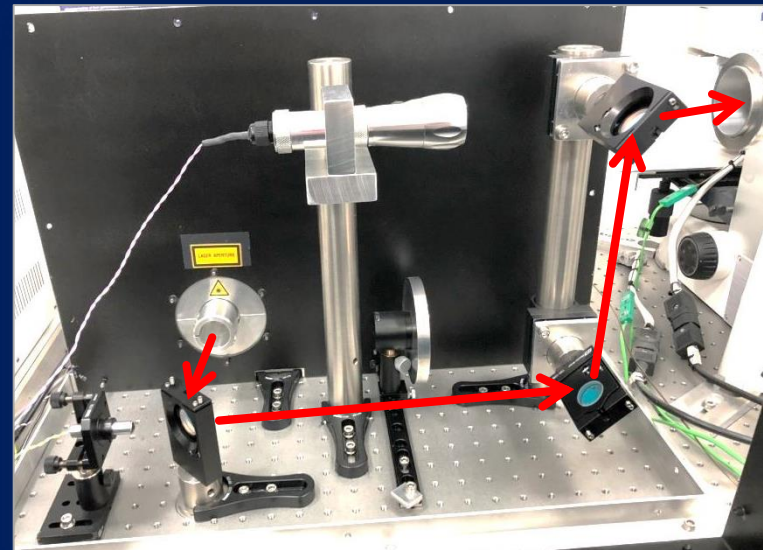


LmPy-GCMS system Performance



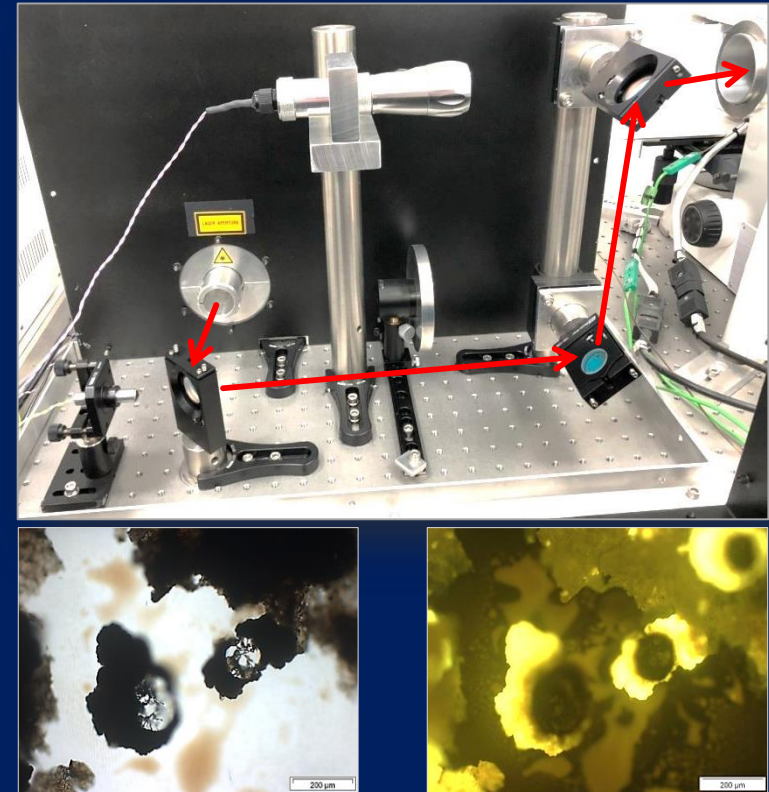
The organic particles are identified, selected and marked with a spot size of range diameter of up to 100 μm . The laser spot size is sample dependent and controlled by adjusting the laser power and appropriate magnification in the microscope objective lens (10X, 20X, 40X or 50X);

LmPy-GCMS system Performance



Laser-radiation is triggered and the laser beam is then directed through out the prisms (lens) of the system until the entrance of the microscope;

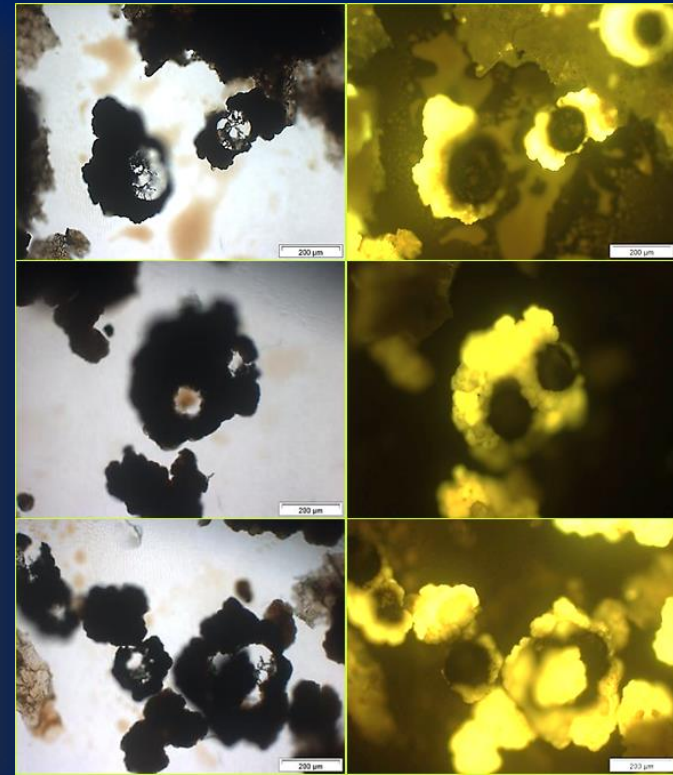
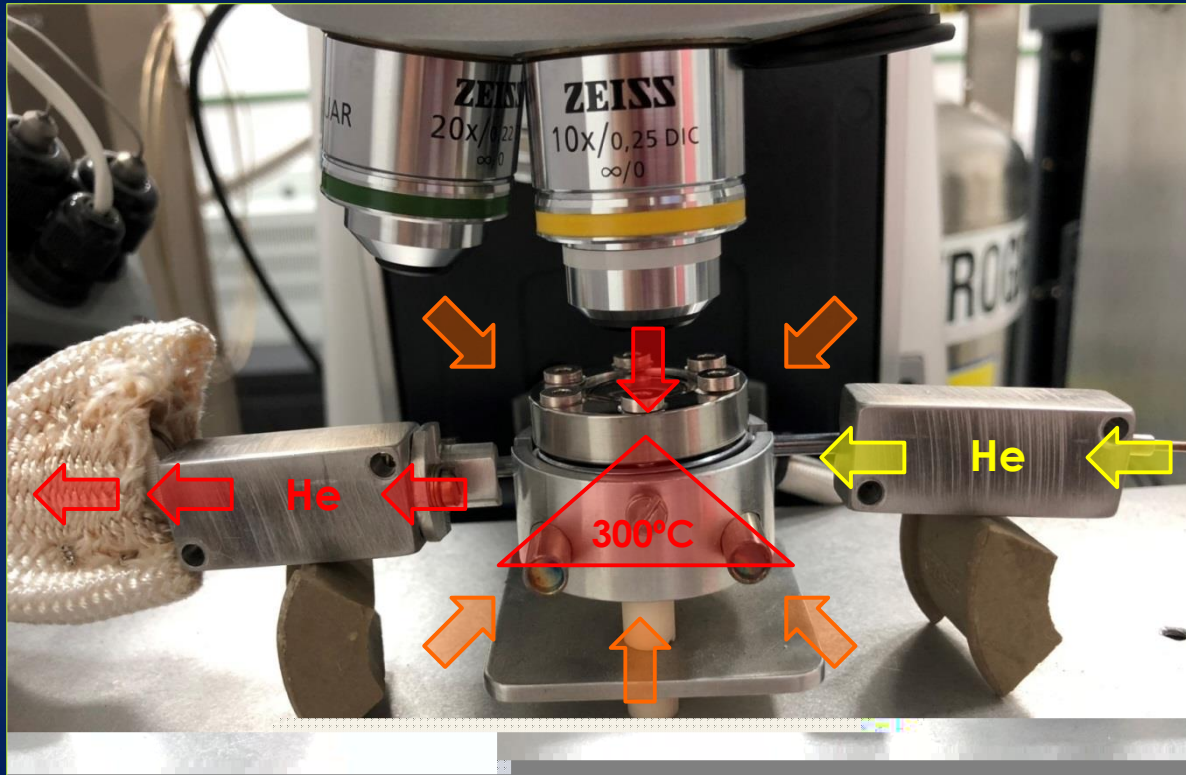
LmPy-GCMS system Performance



The organic particles packed inside the sample chamber are pyrolysed by focusing the laser radiation directly through the objective of the microscope, originating the pyrolysis products;

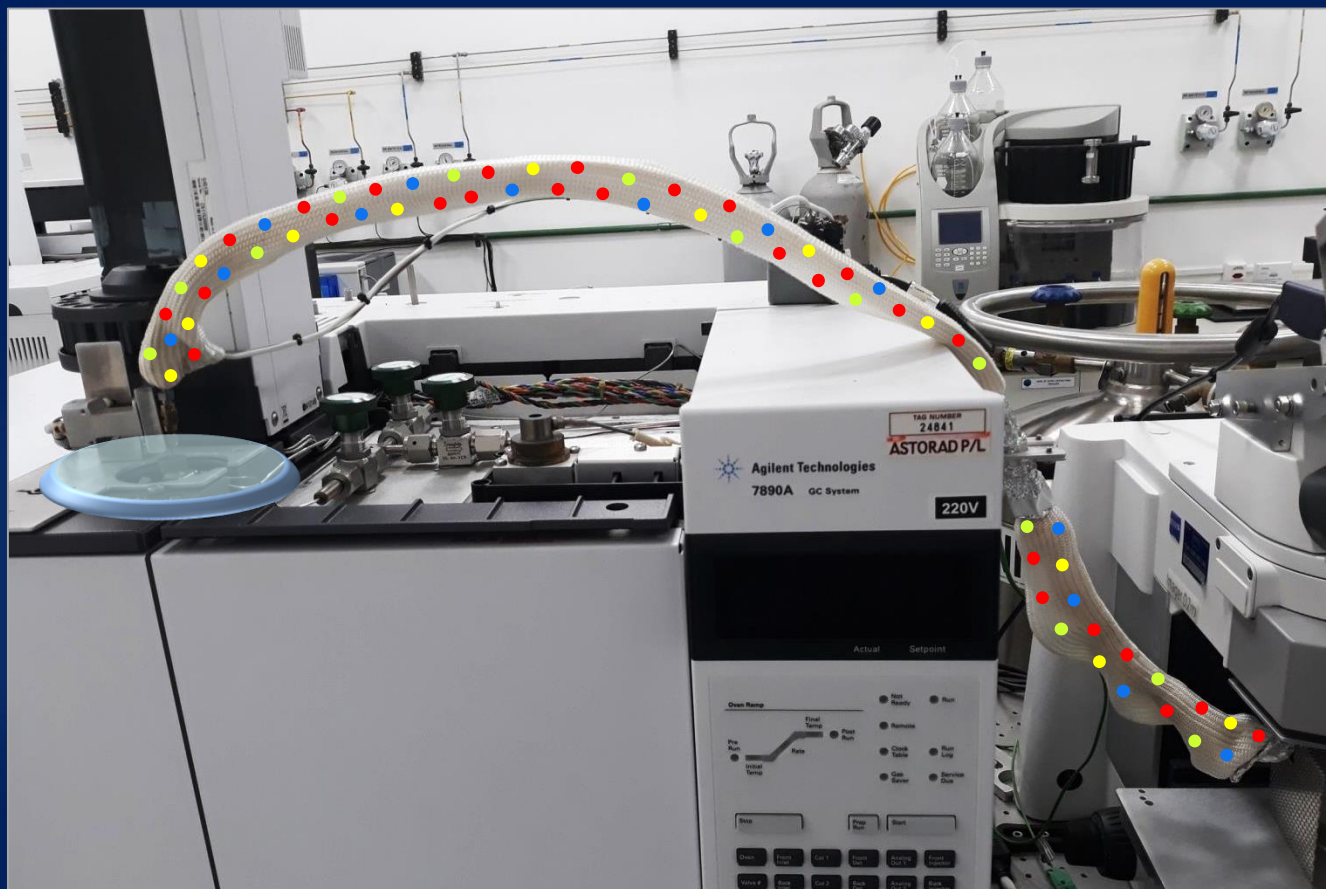
Multiple shots are carried out on the particles;

LmPy-GCMS system Performance



Pyrolysis products are then transferred online to interfacing between sample chamber and GC system via a heated transfer line at 300 °C, using He as carrier gas;

LmPy-GCMS system Performance



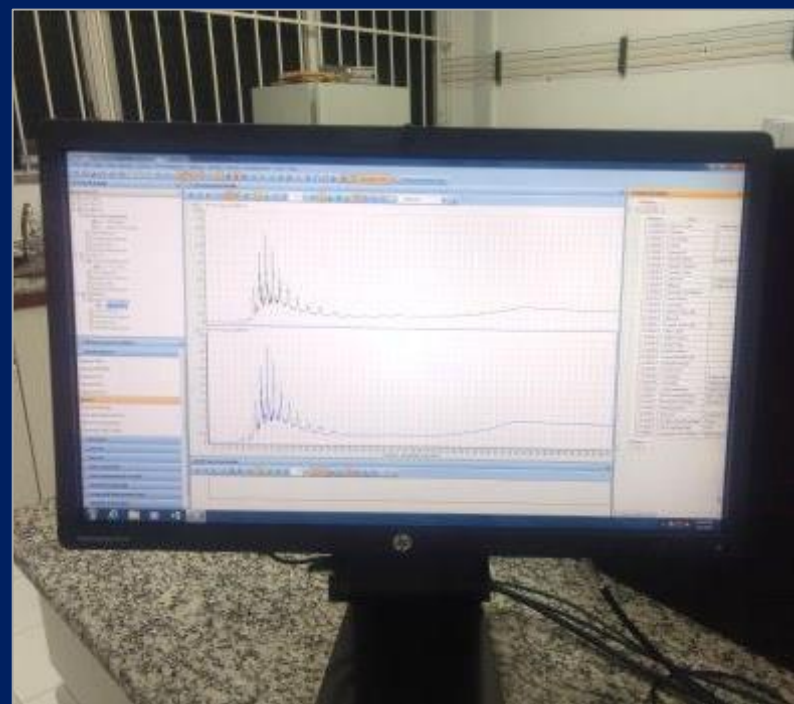
Pyrolysis products continue to be transferred online to the PTV injector via a heated transfer line at 300 °C (He), and they are cryogenically entrapped in a cold trap (cryol collecting) using Liquid N at - 80°C;

LmPy-GCMS system Performance



In the GC PTV injector (Programmed Temperature Vaporization) the pyrolysis products are cryogenically entrapped. The time of cold trapping is long enough to ensure complete trapping of the pyrolysis products, effluent from the sample cell;

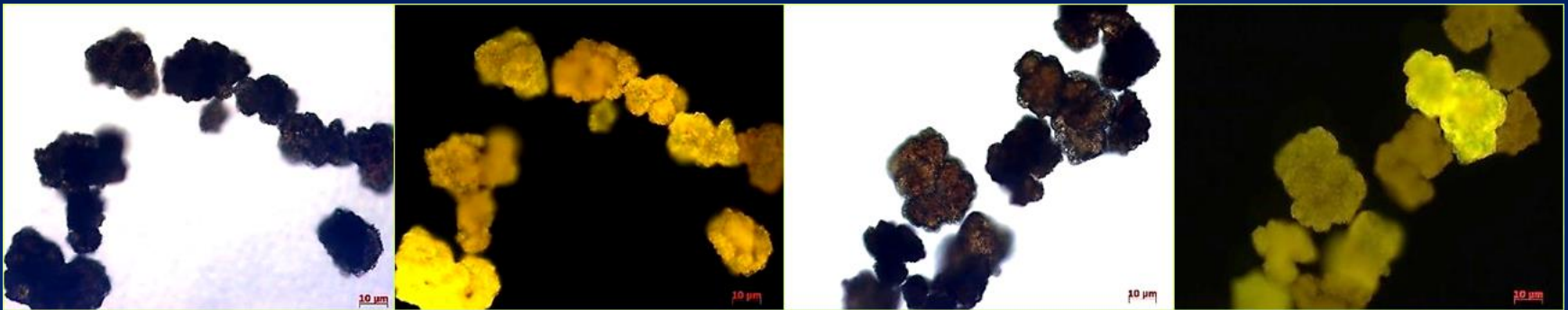
LmPy-GCMS system Performance



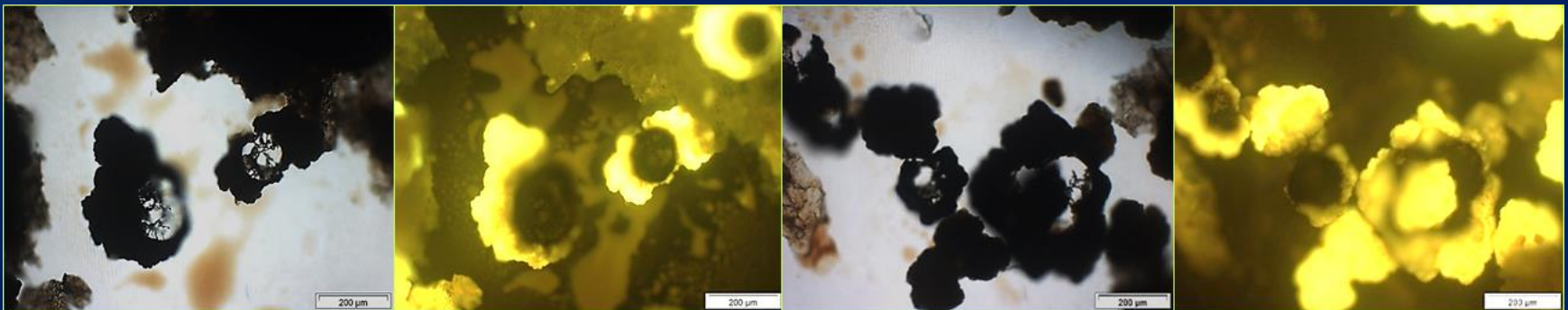
Then, the inlet temperature rapidly rises to vaporize the compounds and causes their transfer to the Capillary GC Column. Thus, the pyrolysis products cryogenically entrapped at -80°C are heated up to 350°C (Cryol Analysis) and analysed by GCMSMS system;

LmPy-GCMS system Performance

- ▶ The hand-picked *Botryococcus* OWM were analyzed to check its molecular organic composition;



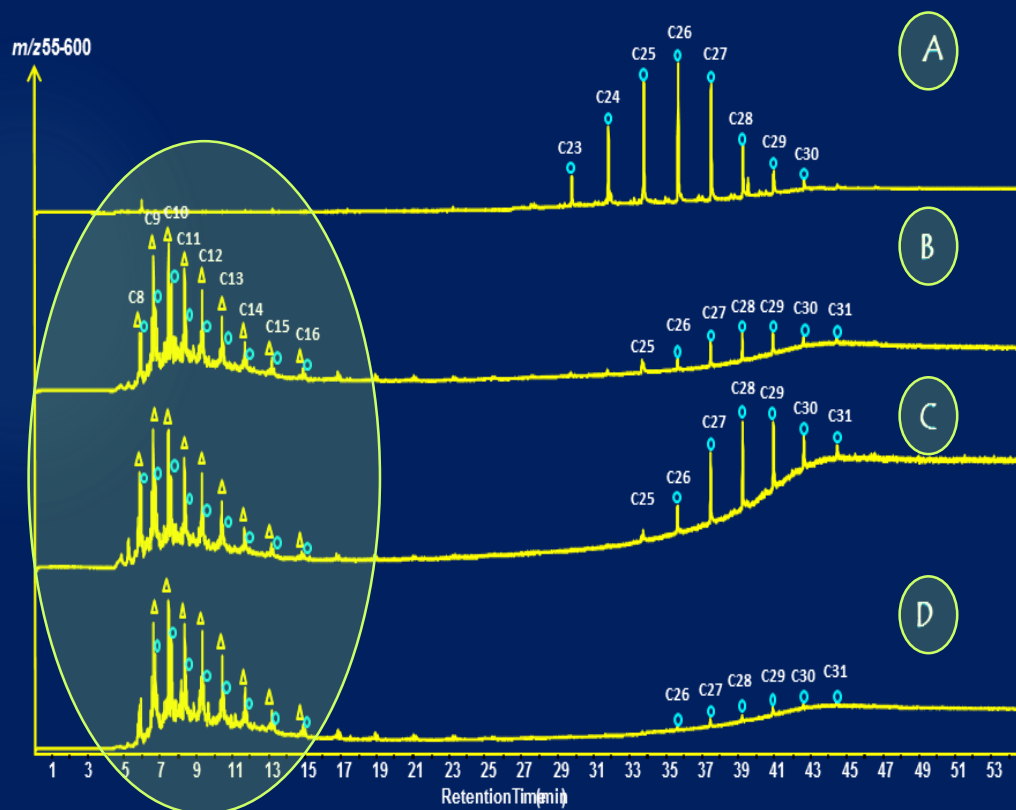
Isolated particles of *Botryococcus Braunii* (Tremembé Formation, Taubaté Basin, Oligocene, Brazil) from the total organic residue using a Hand-picking technique (LAFO-UFRJ)



Isolated particles of *Botryococcus Braunii* displaying craters generated by the laser radiation and drops of oil yielded

LmPy-GCMS system Performance

- ▶ Total ion chromatograms from the LmPy-GCMS analysis of the *B. braunii* showing the distribution of *n*-alkanes (○) and *n*-alkenes (Δ);
- ▶ (A) Analysis of compounds desorption before laser pyrolysis; (B, C, D) different analysis of the same sample;

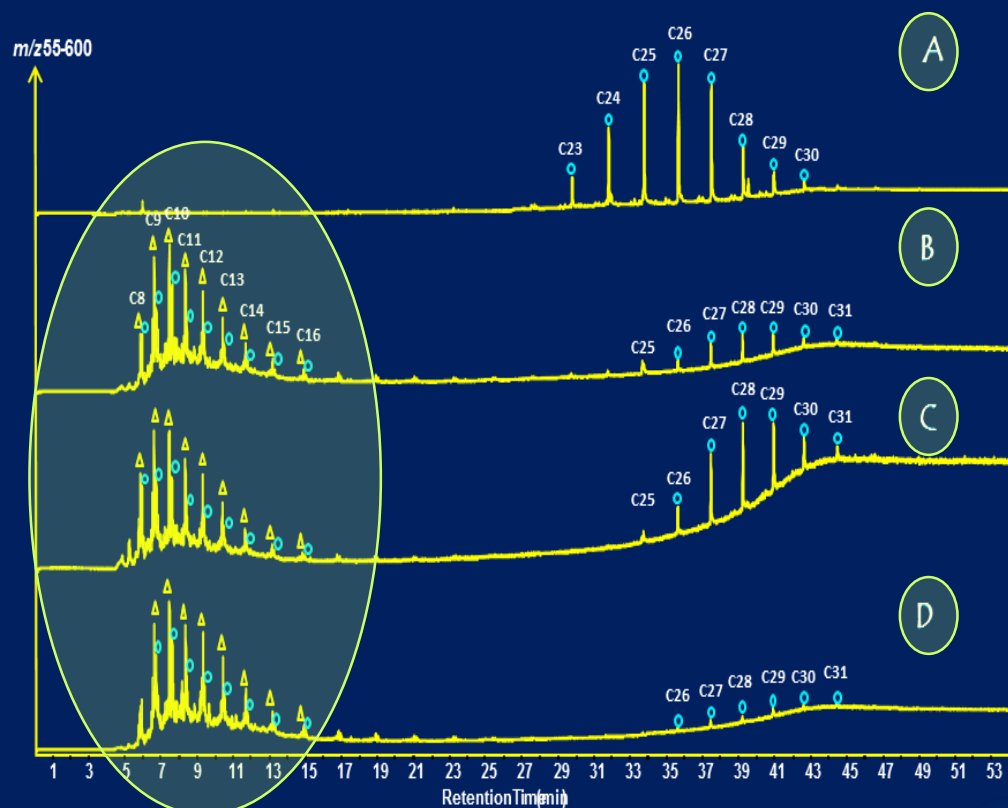


▶ TIC A corresponds to molecules that were adsorbed in the sample and released by heating the laser chamber at 100°C before LmPy analysis (thermal extraction);

▶ TICs B, C and D correspond to separated analysis from 6-8 particles of *Botryococcus* to check the reproducibility of the analyses;

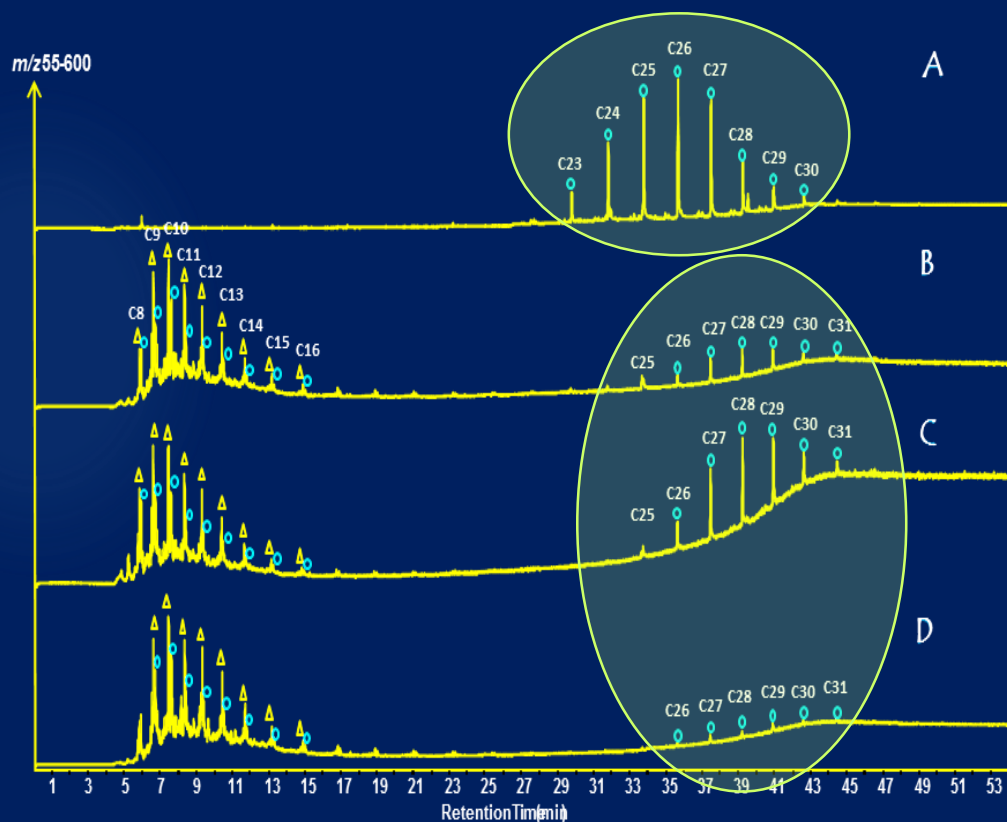
LmPy-GCMS system Performance

- The main pyrolysis products were ***n*-alkanes/*n*-alkenes** from C8 to C25, without the presence of cyclic or aromatic compounds;



LmPy-GCMS system Performance

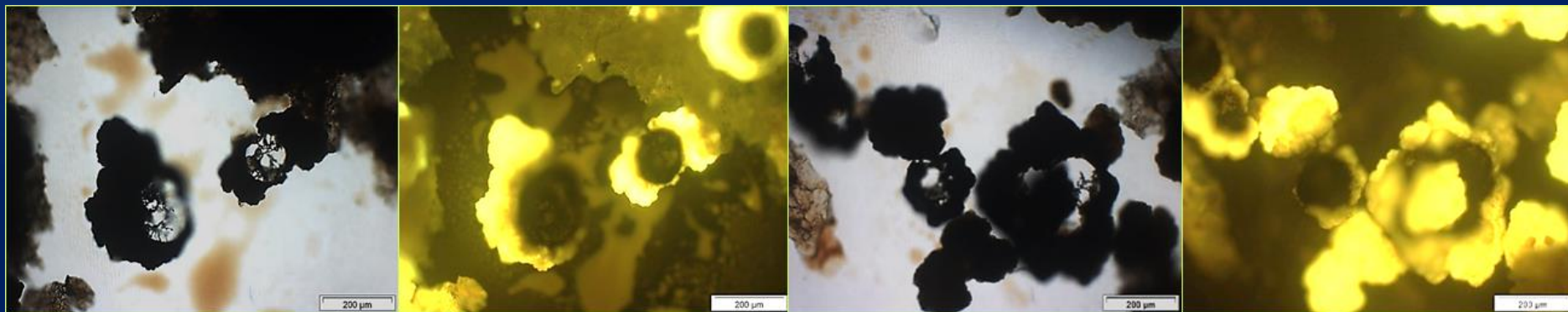
- The laser experiments also produced **n-alkanes** (○) with higher molecular weight (from C25 to C31);



- However, these compounds were also observed in bitumen and could not have been completely removed using solvent during sample pre-extraction/thermal extraction;
- The absence of aromatic compounds suggests non-severe conditions of analysis, avoiding secondary processes such as hydrogen loss and the cleavage of alkyl moieties;

LmPy-GCMS system Performance

- It is also observed that apart from variation of laser parameters no considerable difference, in the relative proportion of the hydrocarbon products, was observed between analyses of the same sample;
- However, it was observed that the size of the craters formed and thus the intensity of pyrolyzate distribution is dependent to the degree of focusing, the time span, and laser's energy settings;



Isolated particles of *Botryococcus Braunii* displaying craters generated by the laser radiation and drops of oil yielded

Final Considerations

In LmPy system the laser beam may impact an area of less than 100 μm through the use of focus lenses and this allows individual analysis of very small components within complex mixtures

The short duration laser beam is collimated by enabling thermal cleavage of isolated components or a macromolecule into smaller components with an immense amount of energy

This thermal interaction between laser and material initiates a shock, which in turn produces a series of pyrolysis products that are analyzed by GCMS

To any pyrolysis technique a certain higher temperature must be sufficient to break molecule bonds, but a low temperature of degradation is not analytically useful

Consequently, when exposed at very high temperatures the molecule degrades extensively, creating very small (and frequently nonspecific) products only

Therefore, the key in analytical pyrolysis is to select a temperature at which a macromolecule is degraded to produce a wide array of products, but quickly enough to be compatible with GC (Wampler, 1999)

In LmPy analyzes is not possible to control the temperature. On the other hand, the laser provides a sufficient thermal flux to heat polymeric materials as high as 1000°C/s in a very short time (2s or less)

These extreme heating rates are a characteristic of laser pyrolysis and also serve as great purpose in minimizing secondary pyrolysis reactions and thus producing pyrolysis fragments characteristic of original polymers (Stout and Lin, 1992; Stout and Hall, 1991)

Another aspect in laser pyrolysis is that the temperature corresponds to the energy needed to break certain covalent bonds, which can change the stereochemical features of molecules during pyrolysis experiment

Consequently, the laser radiation contains high collimated and coherent energy, which can deliver very large amounts of thermal energy on a specific area of small dimension

This means that the directional coherent and monochromatic attributes of high powered laser irradiation can be focused to pyrolysis very small or small parts of consolidated organic materials, which enables this technique to investigate non-volatile, thermally labile materials at a microscopic level (Greenwood et al., 1993)

Thus, LmPy-GCMS is not commonly used because of its high cost. Laser-material interactions are still not well understood neither all samples efficiently coupled with laser radiation to produce thermal degradation products

Nevertheless, the LmPy-GCMS and related methods have been successfully applied to different organic components in the source rock characterization, and therefore their use have improved the studies to chemical characterization of small components in heterogeneous material, as well as an identification of specific biomarkers in isolated OWM



Thank you for your attention!