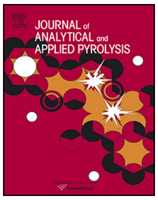
Journal of Analytical and Applied Pyrolysis 107 (2014) 211–223

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



The effect of different pyrolysis temperatures on organic microfossils, vitrain and amber—A comparative study between laser assisted- and Curie Point-pyrolysis–gas chromatography/mass spectrometry

Nadia Anna al Sandouk-Lincke[a], Jan Schwarzbauer[a,*], Christoph Hartkopf-Fröder[b], Herbert Volk[c,1], David Fuentes[c], Martin Young[c,2], Ralf Littke[a]

[a] *Institute of Geology and Geochemistry of Petroleum and Coal, Energy and Mineral Resources Group (EMR), RWTH Aachen University, Lochnerstr. 4-20, 52056 Aachen, Germany*
[b] *Geological Survey North Rhine-Westphalia, De-Greiff-Str. 195, 47803 Krefeld, Germany*
[c] *CSIRO Earth Science and Resource Engineering, P.O. Box 136, North Ryde, NSW 1670, Australia*

ARTICLE INFO

Article history:
Received 18 December 2013
Accepted 7 March 2014
Available online 22 March 2014

Keywords:
Curie Point-pyrolysis–GC/MS
Laser-pyrolysis–GC/MS
Sporopollenin
Prasinophytes
Scolecodonts
Amber

ABSTRACT

This study explores the comparability of results of two different pyrolysis methods applied to macromolecular geochemical material: laser-pyrolysis–gas chromatography/mass spectrometry (La-Py–GC/MS) and Curie Point-pyrolysis–gas chromatography/mass spectrometry (CP-Py–GC/MS). Six samples of different fossil (megaspores, prasinophytes, scolecodonts, amber, vitrain) and extant (sporopollenin) biomaterials were analysed at various pyrolysis temperatures by CP-Py–GC/MS and by La-Py–GC/MS. The qualitative composition of the pyrolysates obtained from both methods was similar. However, La-Py–GC/MS produced shorter aliphatic pyrolysis products in almost all samples. Results obtained from megaspores and prasinophytes indicate a laser temperature higher than the highest Curie temperature applied (920 °C). The application of La-Py–GC/MS was successful for material with a predominantly aromatic structure and/or a high thermal maturity (scolecodonts, vitrain). For extant or immature materials CP-Py–GC/MS appears to be a more suitable method as the applied temperature can be regulated much more accurately.

1. Introduction

The composition of many fossil biomacromolecules is highly complex and difficult to analyse. However, a better understanding of the chemical structure of biomaterials may have implications for their oil-generating potential, or may offer important insights into the taxonomic position of enigmatic species. In general, organic matter (OM) consists of an extractable and a predominant, non-extractable portion. The latter, however, usually contains the main structural information on the macromolecular material. Burial of strata containing OM leads to thermal maturation processes due to temperature and pressure increase, altering the original chemical structure and making it more difficult to reconstruct. Geochemical analyses may give insight into the composition of thermally altered OM which can be used to infer on its original structure. The application of analytical pyrolysis, i.e. the cracking of macromolecular substances into smaller compounds by heating under oxygen free conditions is an important tool to gain insight into the structure of macromolecules, especially if combined with other techniques (e.g. [1,2]). While higher pyrolysis temperatures convert a greater proportion of macromolecular matter into GC-amenable fragments, excessively high pyrolysis temperatures produce pyrolysates that are difficult to relate to the original biomaterial. A well established pyrolysis method is Curie Point-pyrolysis–gas chromatography/mass spectrometry (CP-Py–GC/MS). The method is based on the ballistic heating (20–30 ms) of a metal crucible or wire, containing a small amount of sample material, to its Curie temperature using magnetic induction. The Curie temperature is alloy-specific (150–1040 °C) and very accurate. In earth science studies CP-Py–GC/MS is mostly applied to homogeneous but not manually separated bulk sample material such as kerogen concentrates (OM in sedimentary rocks which is

---

[*] Corresponding author. Tel.: +49 241 80 95750; fax: +49 241 80 92152.
E-mail address: jan.schwarzbauer@emr.rwth-aachen.de (J. Schwarzbauer).

[1] Present address: BP Exploration Operating Company Ltd., Chertsey Road, Sunbury-on-Thames TW16 7LN, UK.

[2] Present address: Morgan-Goodall Palaeo Pty Ltd., Box 161, Maitland 5573, South Australia, Australia.

http://dx.doi.org/10.1016/j.jaap.2014.03.004
0165-2370/

insoluble in organic solvents) [3–6] or to fossil remains of plants and animals [7–9]. Common CP-Py–GC/MS set-ups require a minimum of ca. 0.25 mg of sample material.

A more recent and not widely available analytical method is laser-pyrolysis–gas chromatography/mass spectrometry (La-Py–GC/MS) [1,10–12]. This method uses a focussed laser beam that can be applied to target specific specimens under the microscope without prior separation, or may be used to target individual parts of larger specimens. The amount of material required is much lower than in other methods of flash pyrolysis, enabling the analysis of much smaller amounts of OM. In earlier studies La-Py–GC/MS was applied to a wide range of materials, e.g. oil-bearing fluid inclusions [11,13], in situ maceral analyses [10,12] as well as individual fossil bisaccate pollen [14]. However, the pyrolysis temperature induced by the laser and its spatial resolution depends on laser type and energy [1], optical lenses used in the system and the sample material itself.

In summary, both pyrolysis methods have advantages and disadvantages depending on the sample material and the analytical questions. The success of laser-pyrolysis analyses can be limited by the surface condition and colour of material itself. We expected that lower pyrolysis temperatures may give more insight into the structure of extant or immature fossil organic materials, while higher temperatures may be more suited to analyse more mature fossil organic matter. To explore this hypothesis in more detail, extant and fossil organic matter (hand-picked and optically clean under a binocular microscope) of different chemical composition, geological age and thermal maturity was analysed using CP-Py–GC/MS at several Curie temperatures and the results were compared to La-Py–GC/MS.

2. Materials and methods

2.1. Samples and sample preparation

Six samples of various fossil (megaspores, prasinophytes, scolecodonts, amber, vitrain) and extant (sporopollenin) biomaterials were analysed by CP-Py–GC/MS and La-Py–GC/MS (Table 1). All samples have different chemical compositions and show different chemo-physical characteristics (i.e. colour, surface conditions) leading to a wide variety of analytical results of different types of OM. Sporopollenin builds up the exine of pollen and spores. The Late Carboniferous megaspores of the genus *Calamospora* are ca. 310 Ma years old. Due to thermal maturity and geological age of the megaspores the original structure of sporopollenin is expected to be diagenetically modified. Prasinophytes are green algae and built of algaenan, a biomacromolecule based on long chain ester- and ether-linked hydroxyl fatty acids (Fig. 1, [15]). They can be a significant precursor material for kerogen generating petroleum Type I and Type II source rocks [16]. Scolecodonts are fossilised elements of the jaw apparatus of polychaetes. They may have some applications in palaeoecological and biostratigraphical studies. Amber is fossil resin of trees. Our sample has a geological age of ca. 40 Ma years (Eocene). Vitrains are bright layers in coal derived from wood. Smaller, microscopically visible particles are called vitrinites; their reflectance is commonly used to determine maximum palaeotemperatures experienced by sedimentary rocks during burial [17]. Increase in reflectivity is accompanied by an increase in relative abundance of large aromatic units [18]. Further information about the sampling localities and rank of thermal maturity [17,19] is given in Table 1.

Samples were processed using standard palynological and palaeontological techniques to isolate megaspores, prasinophytes and scolecodonts from the sediment [20]. Subsequently, well preserved palynomorphs with no adhering sediment or organic material were selected from the residue and handpicked under a dissecting binocular microscope. Vitrain particles were obtained from a pure vitrain layer. A small piece of amber was crushed and only fragments without the outer slightly weathered crust were selected. Extant sporopollenin, isolated from *Lycopodium* spores and distributed by Polyscience Inc. (Lot# 504496), was used for comparison with the fossil organic matter of megaspores. Isolated specimens of all samples were placed either in metal crucibles (CP-Py–GC/MS) or onto a 6 mm diameter glass slide (La-Py–GC/MS).

2.2. Curie Point–pyrolysis–gas chromatography/mass spectrometry

Ca. 0.4 mg of each sample material was collected in metal crucibles and pyrolysed at various pyrolysis temperatures for 10 s using a CP pyrolyser (Fischer GSG CPP 1040 PSC) coupled to a GC/MS system (GC Fisons 8065; Thermoquest MD 800). A 30 m non-polar GC capillary column (Zebron ZB-5, 0.25 mm I.D., 0.25 μm film thickness) was used and a cryofocussing trap (−70 °C) was installed directly behind the injector. The pyrolysis products were introduced onto the GC column using splitless injection (injector temperature 270 °C, splitless time 60 s) and the oven temperature was heated from 40 °C (held 3 min) at 3 °C/min to 310 °C (held 20 min). He was used as carrier gas. MS parameters included a source temperature of 200 °C, 70 eV EI and a scan range of m/z 35–550. Peak identification was based on comparison of MS data and retention times with those of reference material and mass spectral libraries (Wiley 7th Ed., NIST 05). Individual composition was analysed by integrating relevant extracted ion peak areas.

2.3. Laser-pyrolysis–gas chromatography/mass spectrometry

Analyses were carried out on a modified version of the instrumentation described in Greenwood et al. [11,21] and used by al Sandouk-Lincke et al. [14]. In brief, sample material was transferred onto a 6 mm diameter glass slide and pyrolysed by focusing a Nd:YAG laser (1064 nm) with a microscope onto the sample placed into a heated (ca. 100 °C) custom-built laser chamber and flushed with 100 mL/min He. The pyrolysis time varied between 0.1 and 0.4 s. Pyrolysis and thermal extraction products were then transferred with the use of valve switches and two cold traps immersed in liquid N_2 to an Agilent 6890 GC instrument interfaced to a quadrupole MSD 5973 (electron energy 70 eV, source temperature 250 °C). Full scan analysis (m/z 50–550) of the pyrolysates was performed after separation on a fused silica DB-5MS column (J&W, 60 m, 0.25 mm I.D., 0.25 μm film thickness) with He carrier gas at constant pressure. The GC oven was programmed from 10 °C (3 min hold) to 310 °C (30 min hold) at 3 °C/min. The pyrolysis products of 20–80 individual specimens were combined in a cryofocussing trap and measured in total. The laser spot size (20 μm to <40 μm) was sample dependent and controlled by adjusting the laser power and using appropriate magnification (10×, 20× or 50× long working distance). Where multiple shots were carried out on one single specimen, care was taken to avoid regions already pyrolysed or affected by the laser. Duplicate measurements were performed to increase representativeness.

Laser pyrolysis and its efficiency are strongly dependent on the sample composition. The laser penetrates a sample more easily where the surface is dark, such as coals and its macerals. However, if the sample is white or translucent such as glass, quartz, carbonates or resins (resinites), the coupling of laser (Nd:YAG) energy with the sample is far less efficient. A strategy to overcome this problem was to coat the sample with a thin layer of graphite to help the coupling of the laser power onto the sample. By shooting the laser at the graphite, pyrolysis products from graphite could be