Kerogen thermal destruction

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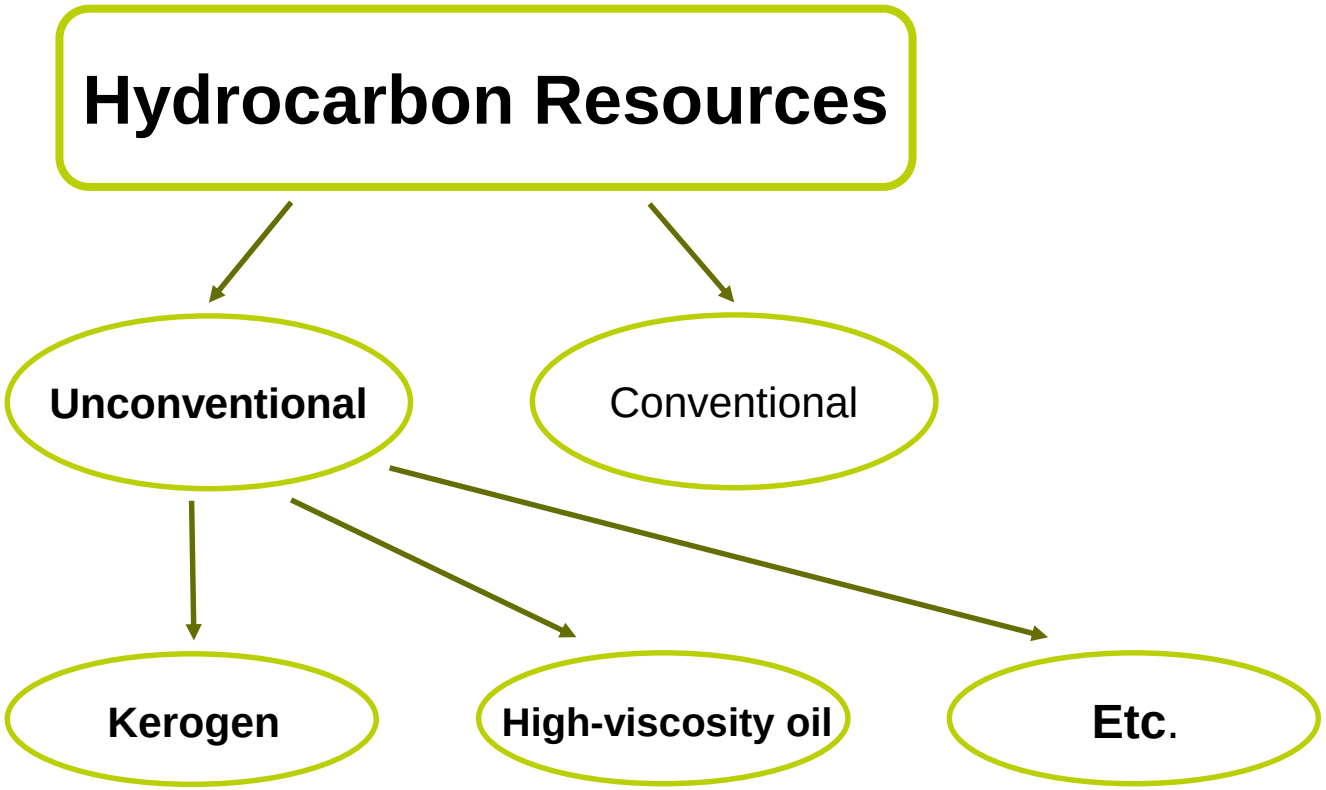
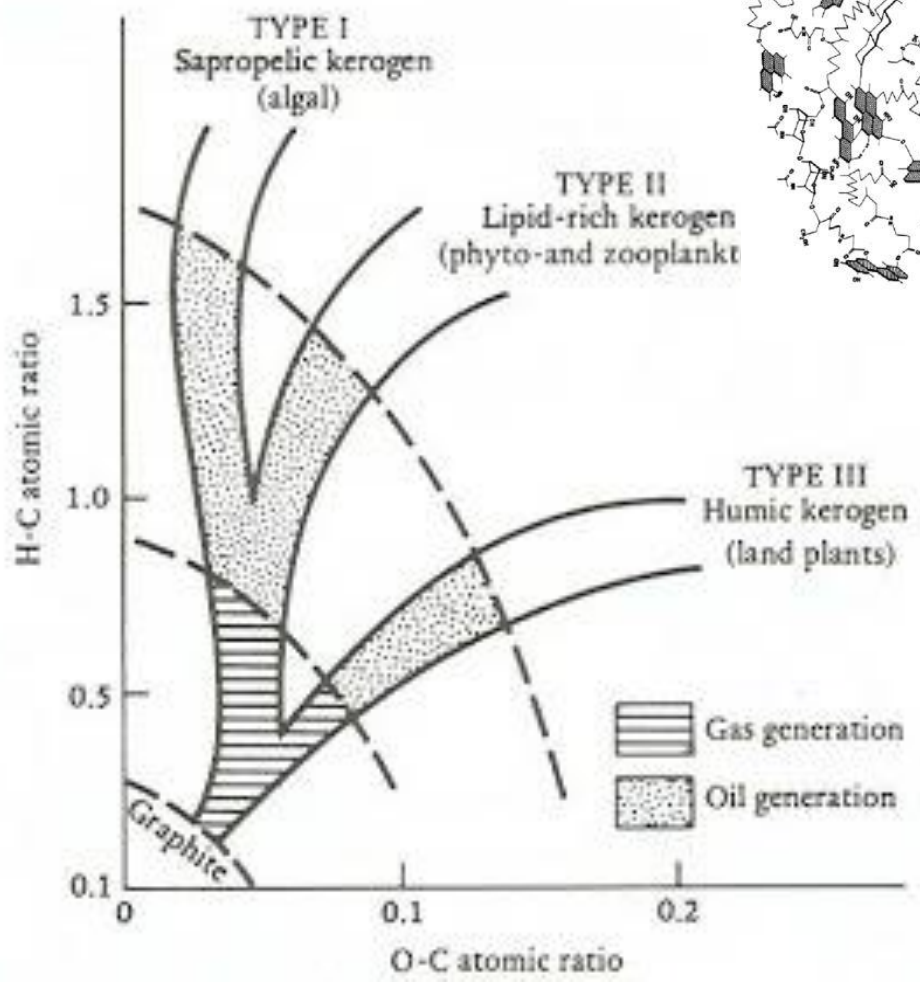
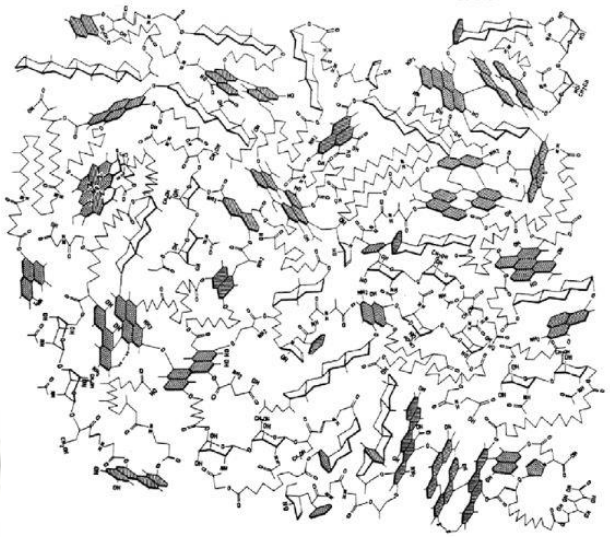


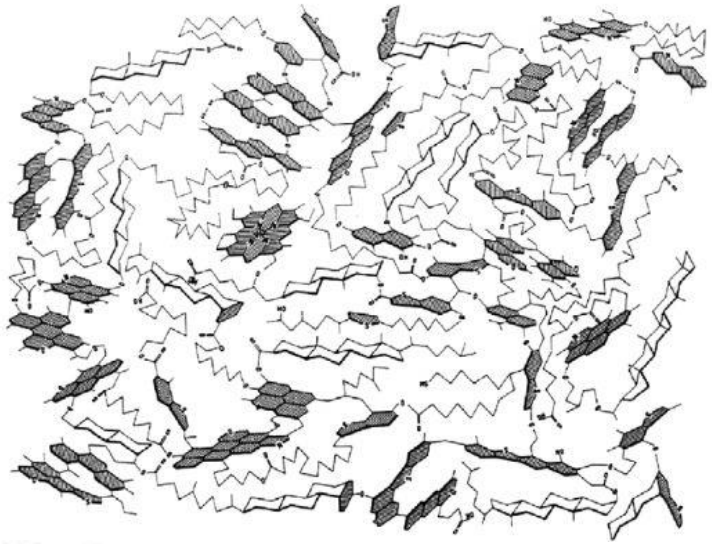
Tasks

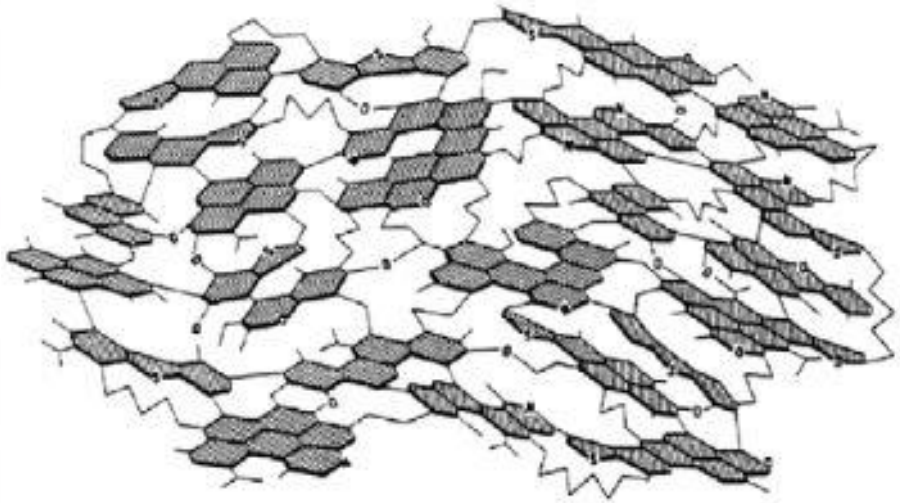
- What is kerogen? Is there any difference between samples from different wells?
- What structure kerogen has? What's the mechanism of its decomposition?
- How to learn is it worth it to make production from certain kerogen?
- How efficiently obtain hydrocarbons from it? Which types of HC will we get?

Kerogen



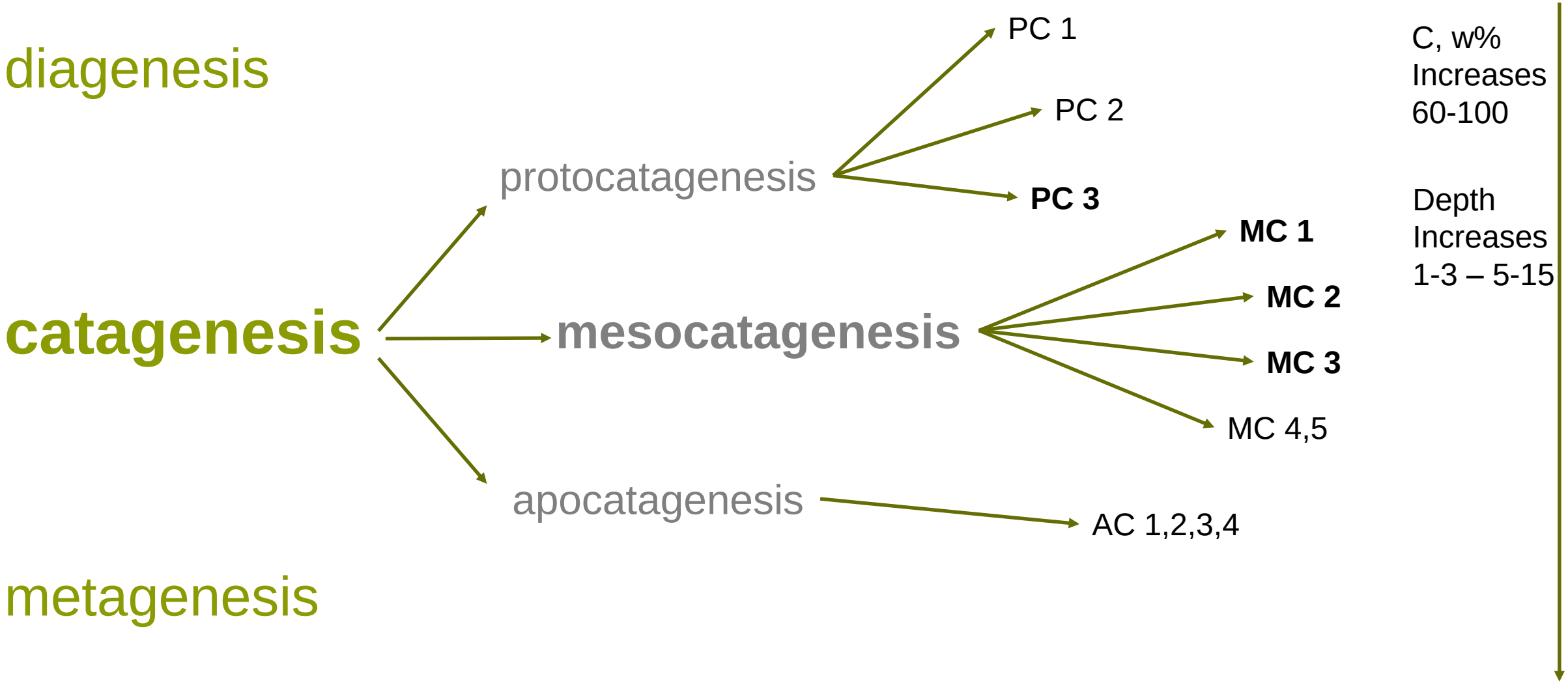






M. Vandenbroucke, C. Largeau / Organic Geochemistry 38 (2007) 719–833

Kerogen genesis



The main oil window exists at within range from PC3 till MC3

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Methods

- **Analysis of kerogen structure**

  Nuclear magnetic resonance (NMR)
  X-ray photoelectron spectroscopy (XPS)
  CHNS analysis

- **Kerogen properties investigation and analysis of thermal destruction products**

  Pyrolysis
  Kinetic experiments
  Coupled two-dimensional gas chromatography with mass spectrometry

Solid State Nuclear Magnetic Resonance

3 Main Problems

Sensitivity

^{1}H-^{13}C dipole-dipole interactions

Long-spin lattice relaxation times

Resolution

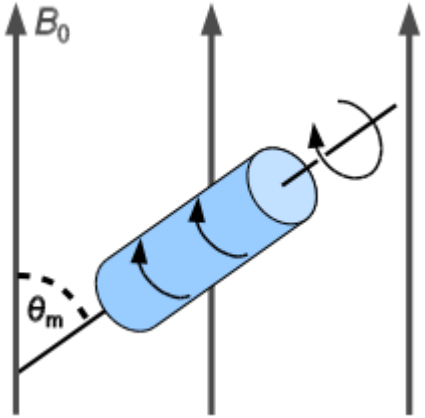
Chemical shift anisotropy

High-power decoupling

$$H_{loc} \propto \mu_h (1 - 3\cos^2\phi)/r^3$$

Nonspherical electron density around ^{13}C nuclei

Magic angle spinning



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NMR techniques

^{1}H MAS NMR

Main drawback of this method – too broad signals, which makes impossible detailed structure investigation. Can be used to analyze relative contribution of aromatic and aliphatic fragments.

^{13}C CP MAS NMR

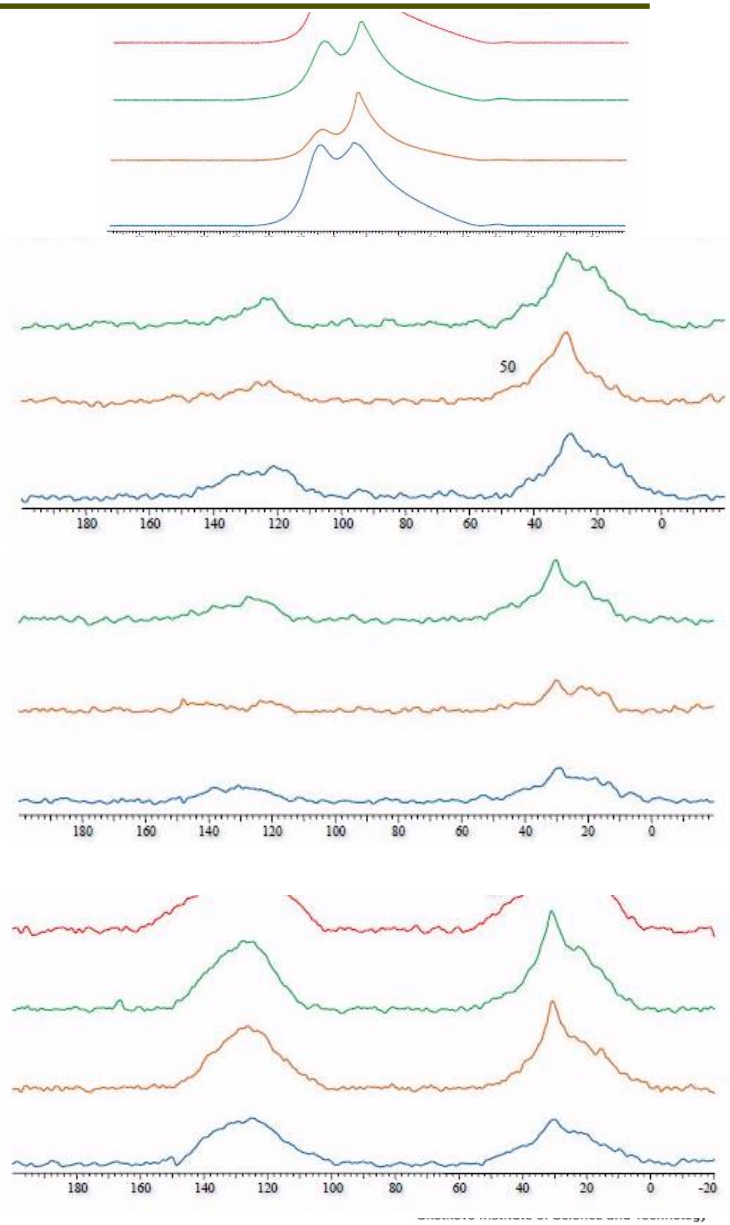
Cross-polarization NMR relies on the presence of an abundant spin system (^{1}H) to enhance the observation of a signal from a dilute spin system (^{13}C). The idea is to transfer polarization (hence signal intensity) from the abundant ^{1}H spins to the dilute ^{13}C spins.

^{13}C CP DD MAS NMR

This modification (dipolar dephasing) of cross-polarization technique is used for selective observation of tertiary ^{13}C atoms, due to their low dipole-dipole interactions, and mobile aliphatic chains with low effective cp.

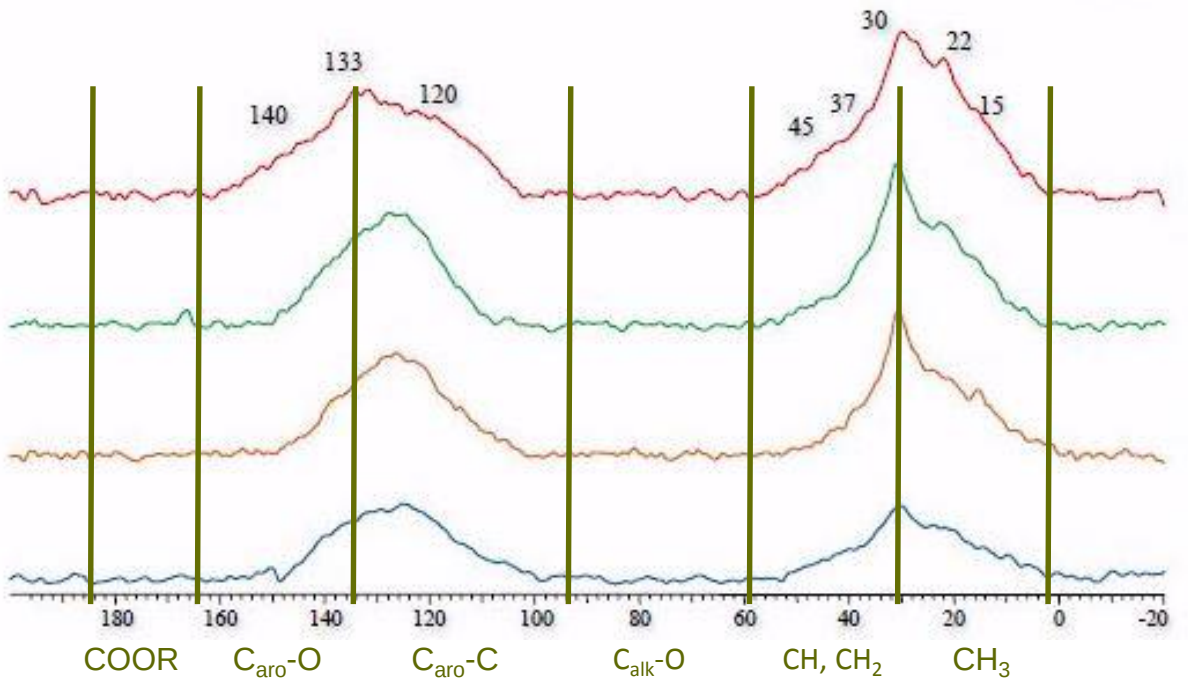
^{13}C DP MAS NMR

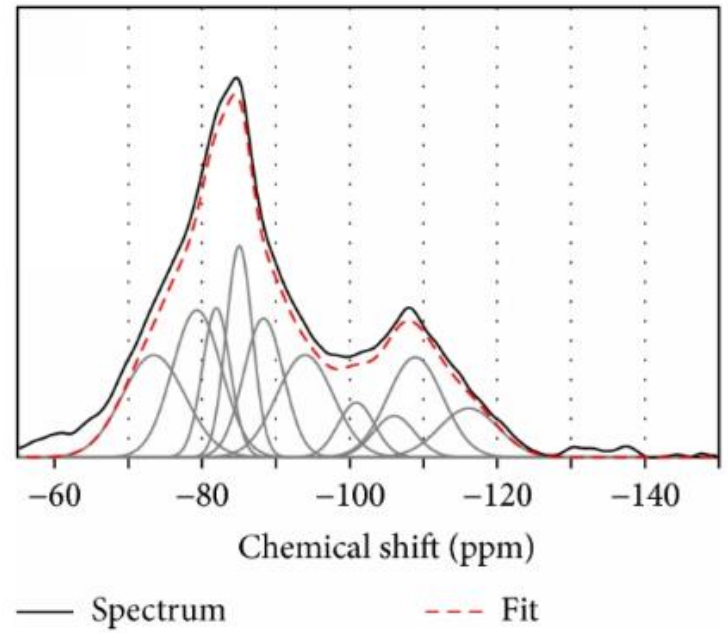
Experiments with direct polarization of ^{13}C atoms. Can be used for quantitative analysis. However, due to low natural abundance of ^{13}C and long-spin relaxation times, time of experiment increases significantly



Spectrum deconvolution

Direct Polarization ^{13}C Spectrum





deconvolution of spectrum

COOR	C_{aro}-O	C_{aro}-C	C_{alk}-O	CH, CH_2	CH_3
1.4%	7.5%	38.5%	0%	25.2%	27.3%
0%	12.6%	32.2%	0%	23.8%	28.4%

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Kinetics Theory: Reaction rate

$$aA + bB \rightarrow cC + dD$$

A,B,C,D – substances; a,b,c,d – stoichiometric coefficients

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Reaction rate **r** – change of substance amount in time

$$r = k\,[A]^x[B]^y$$

Reaction constant **k** – every aspect of reaction except [C]

$$\boldsymbol{x}, \boldsymbol{y} - orders\ of\ reaction, with\ respect\ to\ substances\ (A, B), not\ related\ with\ a, b$$

$$n = x + y$$

n - reaction order

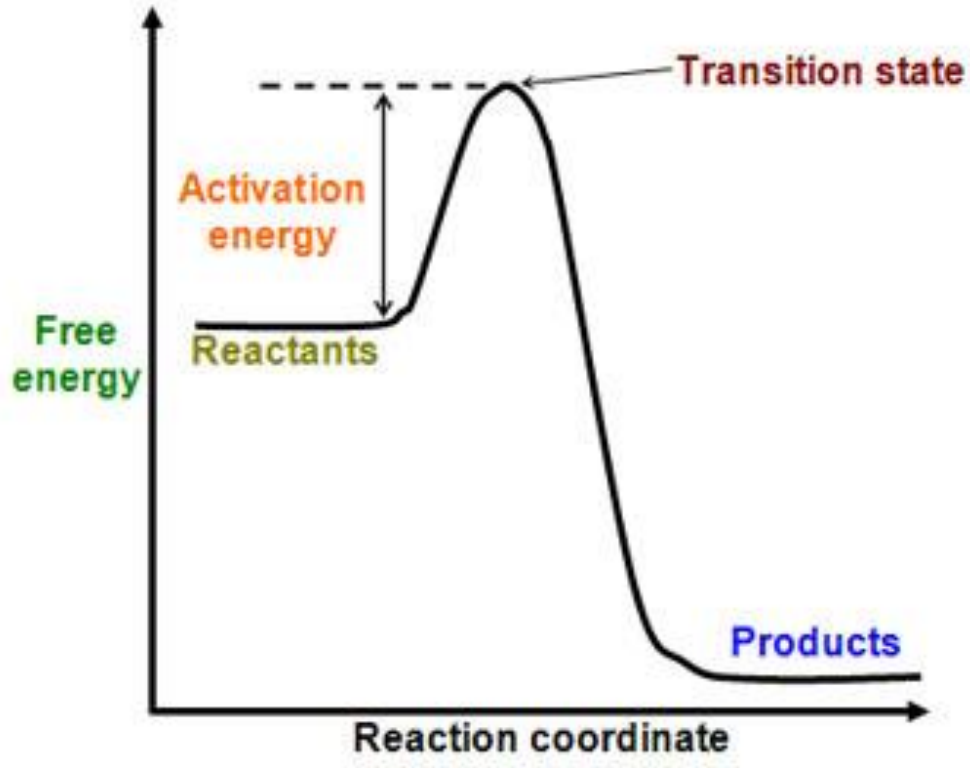
Arrhenius equaiton

$$k = Ae^{-\frac{E_a}{RT}}$$

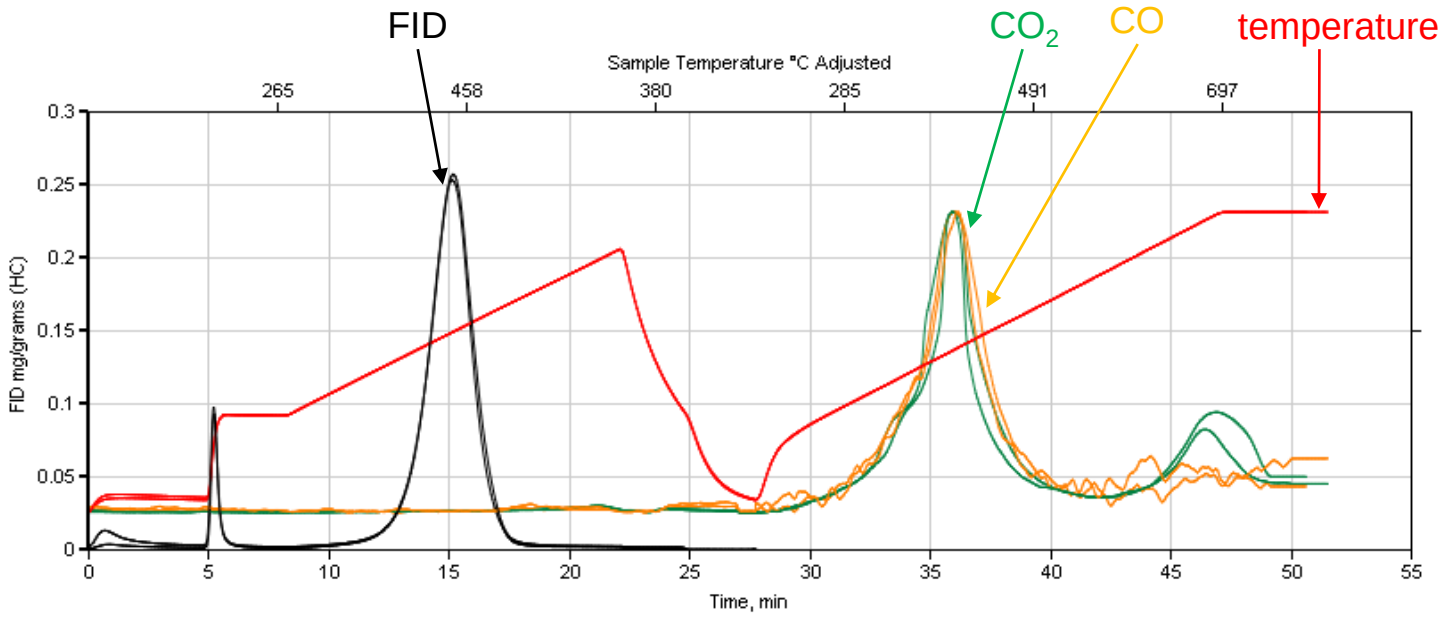
A – frequency factor (probability of a favorable collision between two atoms)

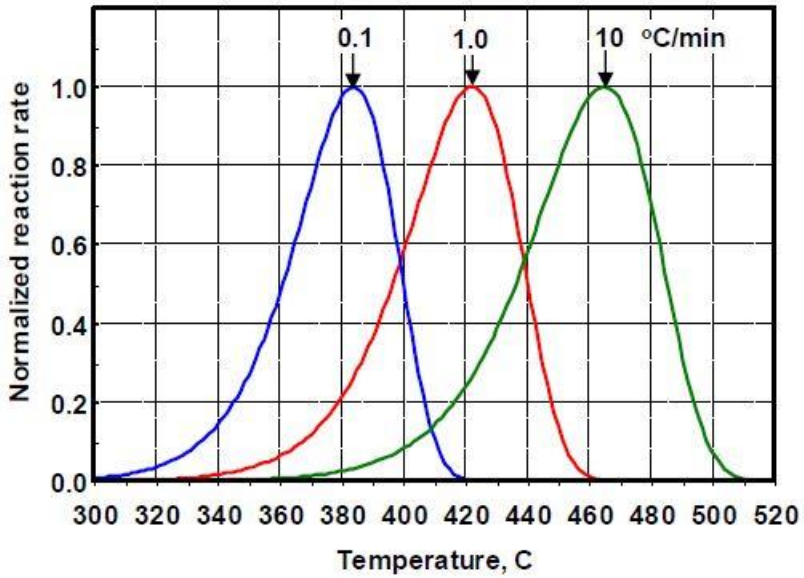
Kerogen $\xrightarrow{\Delta} B + C + D + \cdots$

$$\frac{d[Kerogen]}{dt} = -kt = -Ae^{-\frac{E_a}{RT}}t$$



HAWK pyrolysis instrument





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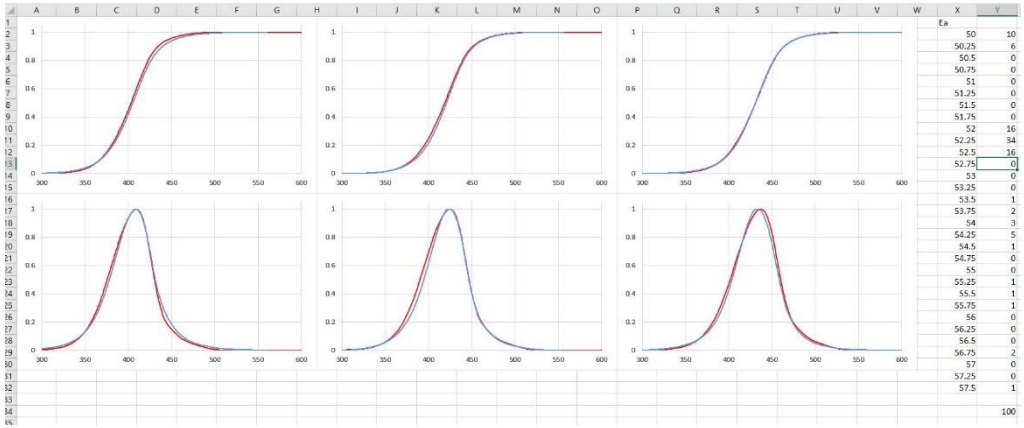
Energy activation distribution

$$\alpha = -\frac{dC}{dt} = \sum_i \frac{dC_i}{dt} = \sum_i -Ae^{\frac{-E_{a_i}}{RT}} t$$



E_a	kJ/mol
50	5
52	15
52.25	35
53.25	5
53.5	15
53.75	10
54	5
55.25	2
55.5	2
55.75	2
56	2
57.25	1
57.5	1

1 млн лет											
T, °C	200	210	220	230	240	250	260	270	280	290	300
%	0,3	0,8	2,4	6,2	14,4	29,3	51,9	74,2	87,9	94,5	97,5

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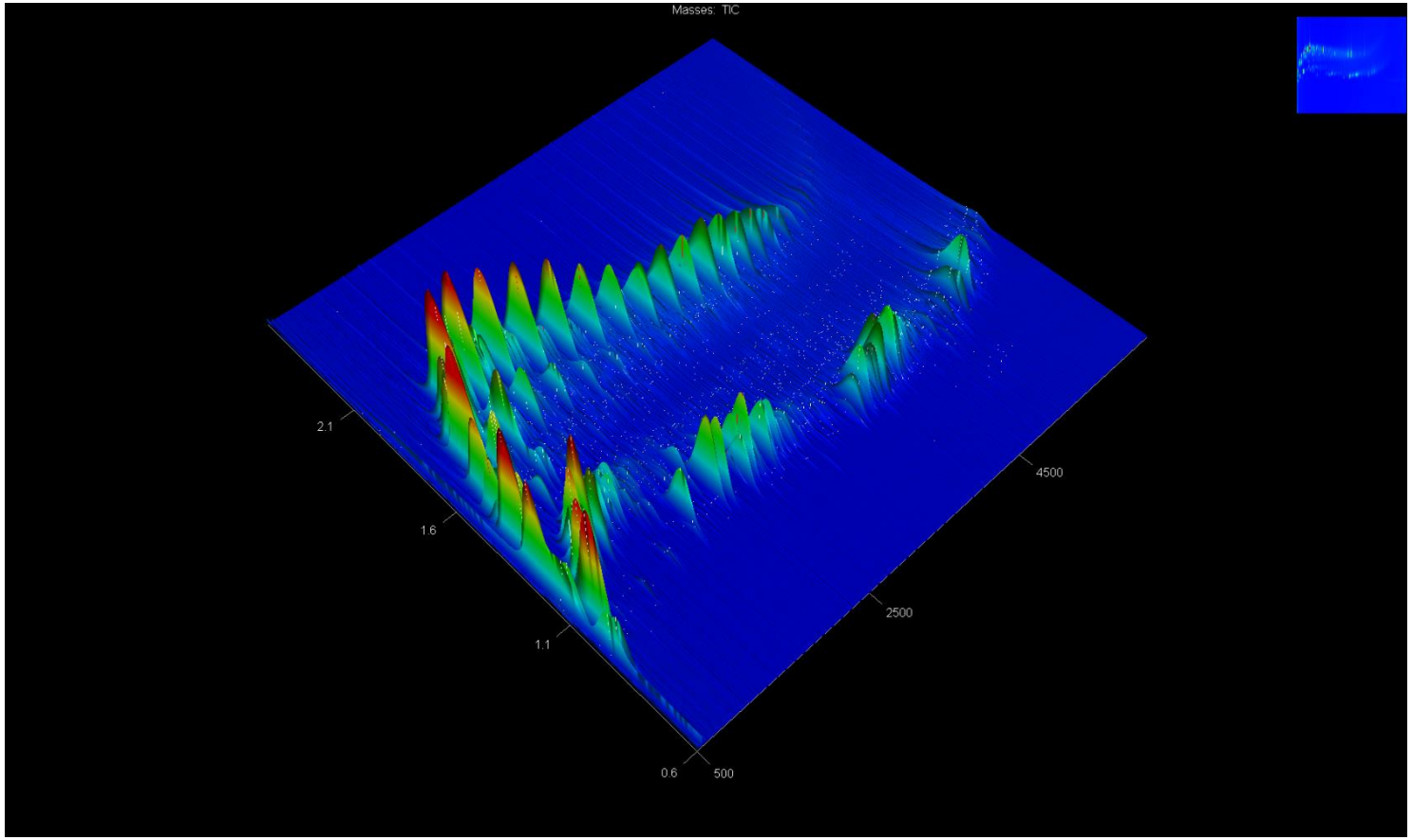
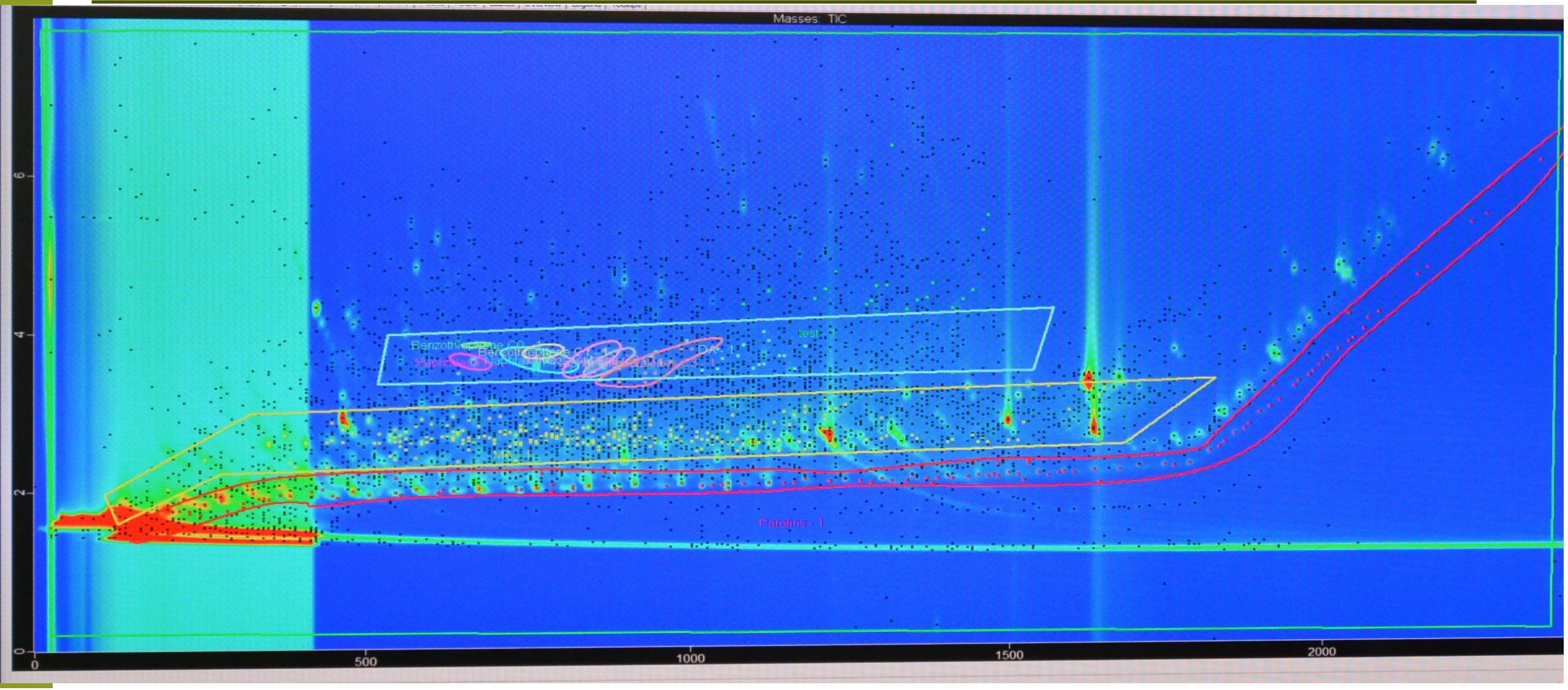
GC-GC-ToFMS

High resolution time of flight mass spectrometer provides
Two-dimensional gas chromatography divides

GC-GC-HRT ToFMS LECO



Two-dimensional gas chromatogram



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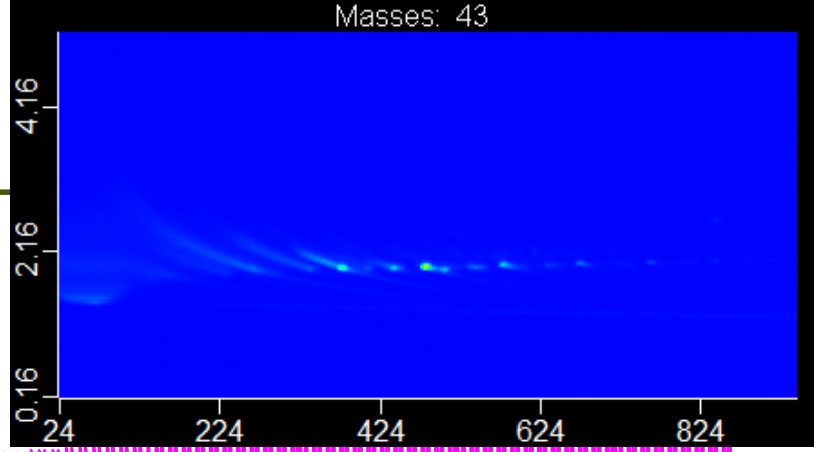

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400000
350000
300000
250000
200000
150000
100000
50000

1st Time (s) 496 1000 1496 2000 2496
2nd Time (s) 4 0 4 0 4

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