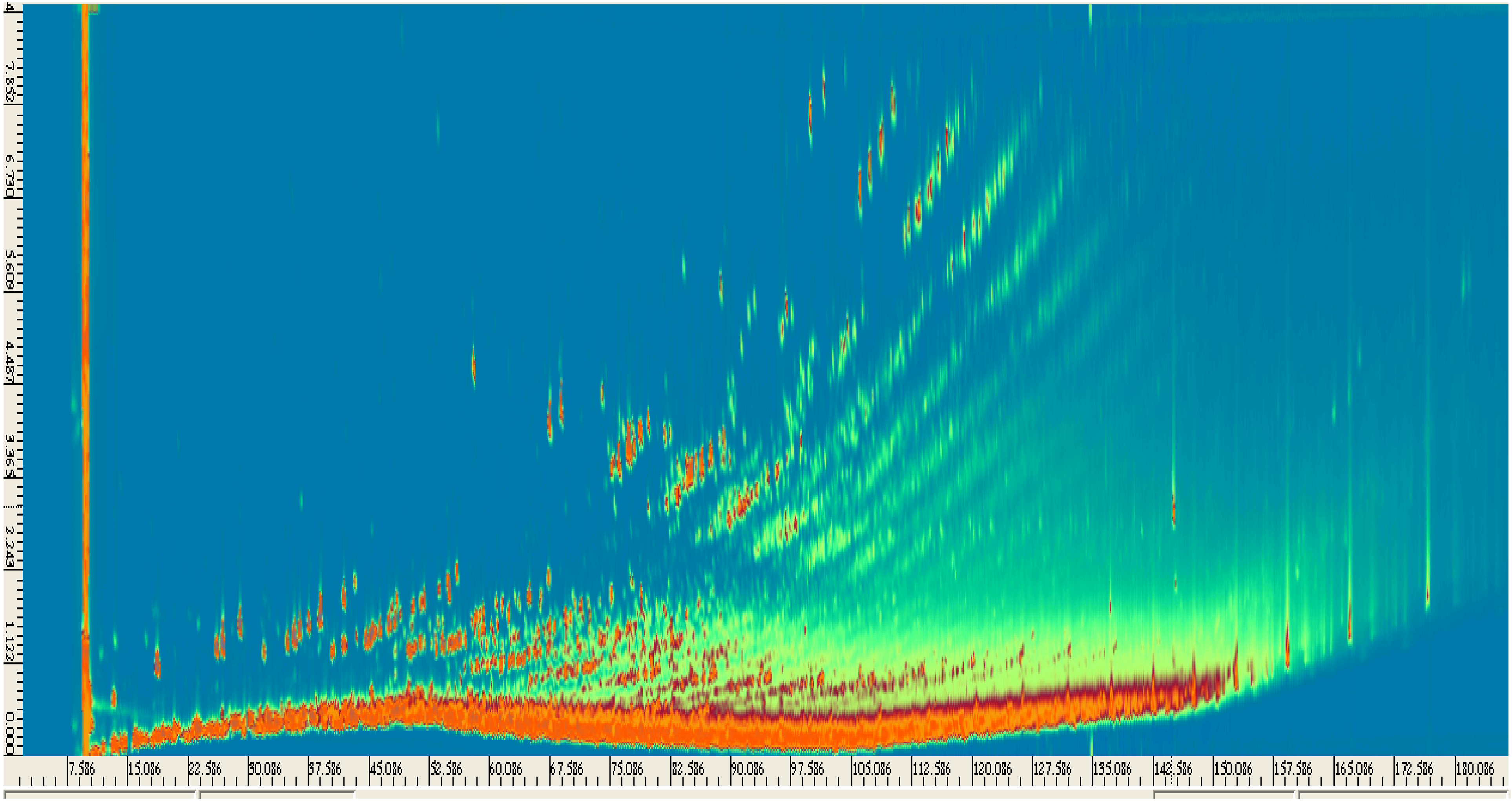
Characterization of Hydrocarbons in petroleum fractions using Comprehensive Gas-Chromatography GCxGC coupled with Fast Scan Quadrupole MSD

Marc Gibert - Ingenieria Anal´ñitica s.L.

Why GCxGC-MSD in petrochemistry



Which information is in this picture

- Fingerprint of crude oils (based on bidimensional distribution of more than 1000 compounds)

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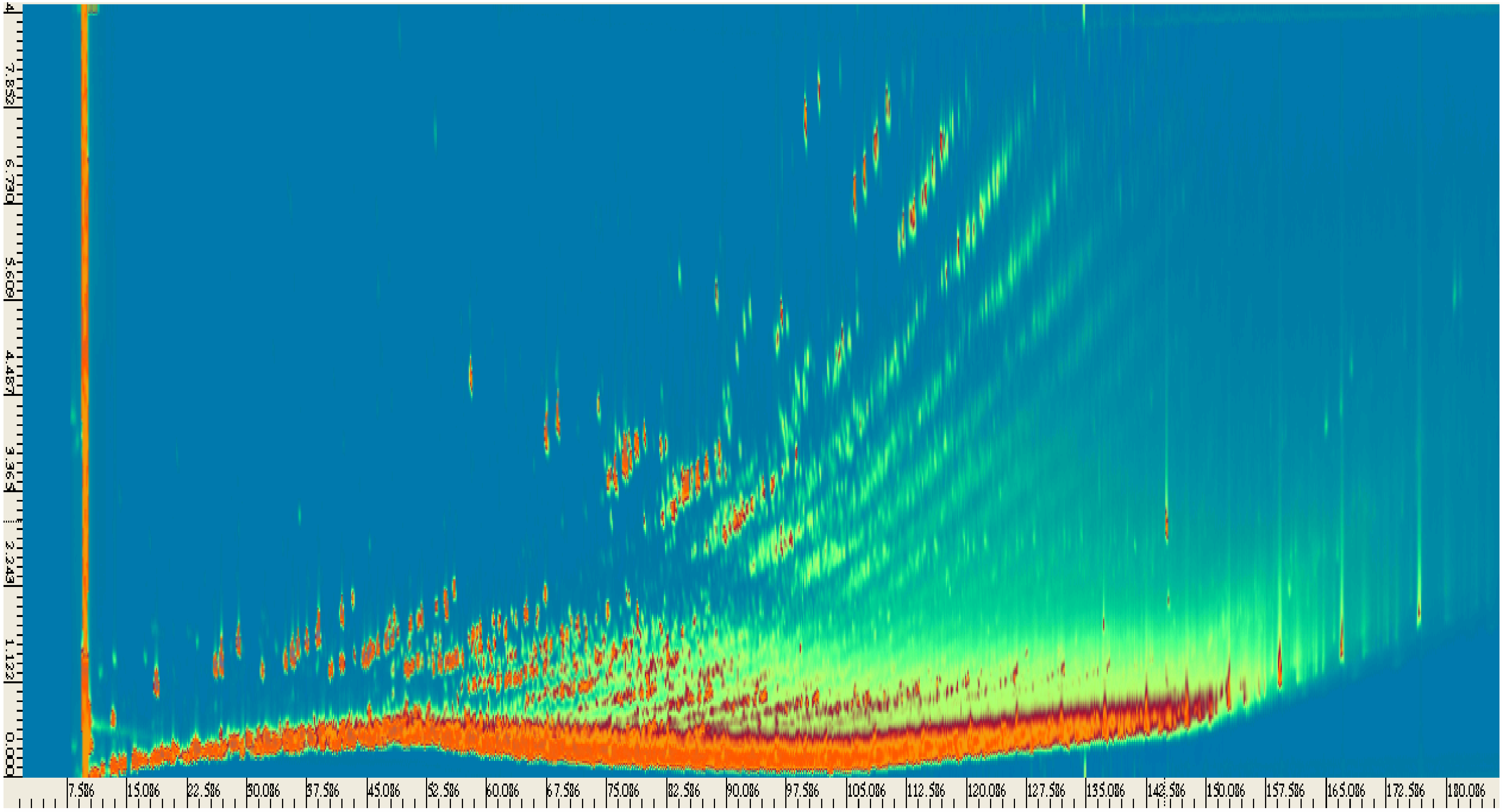
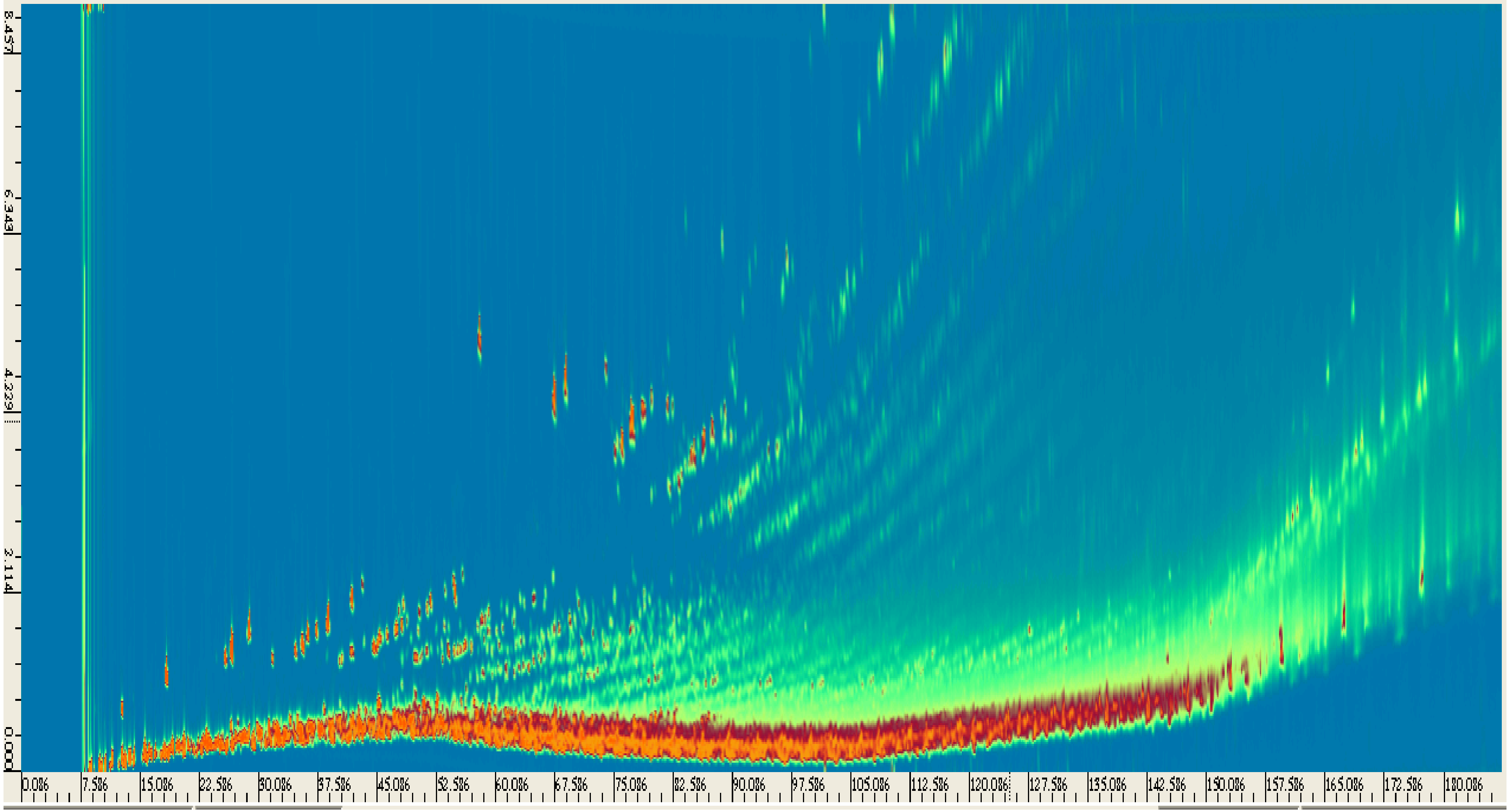
Light crude oil A

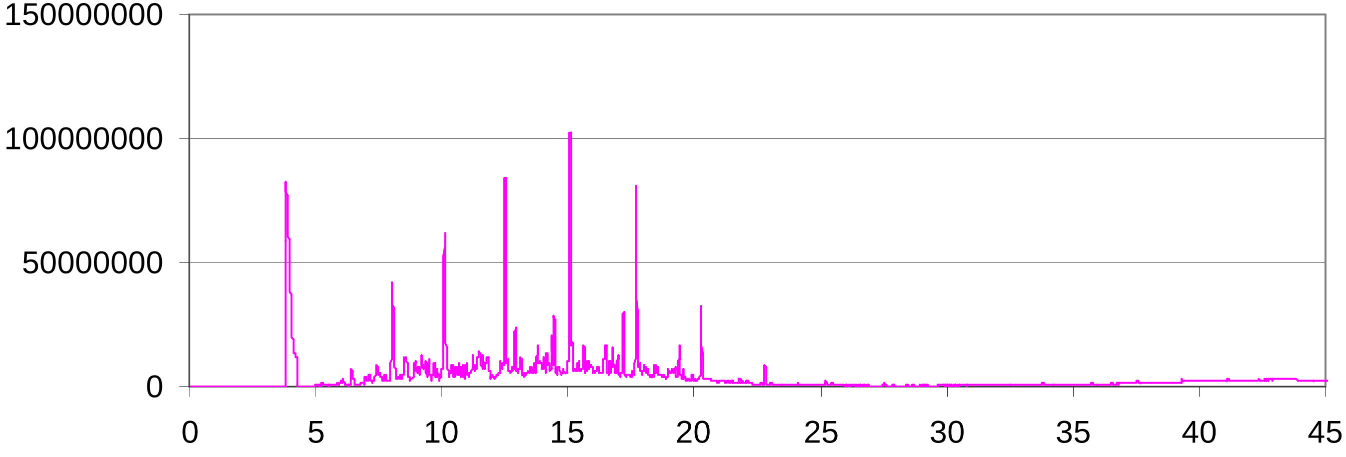


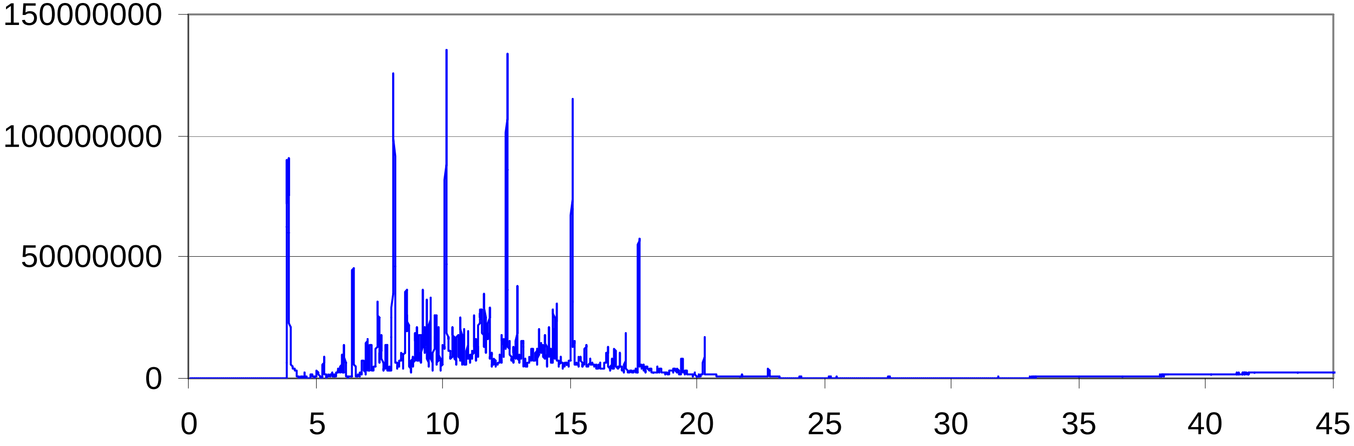
ZOEX CORPORATION

Light crude oil C



Light crude oil GC-MS chromatograms comparison

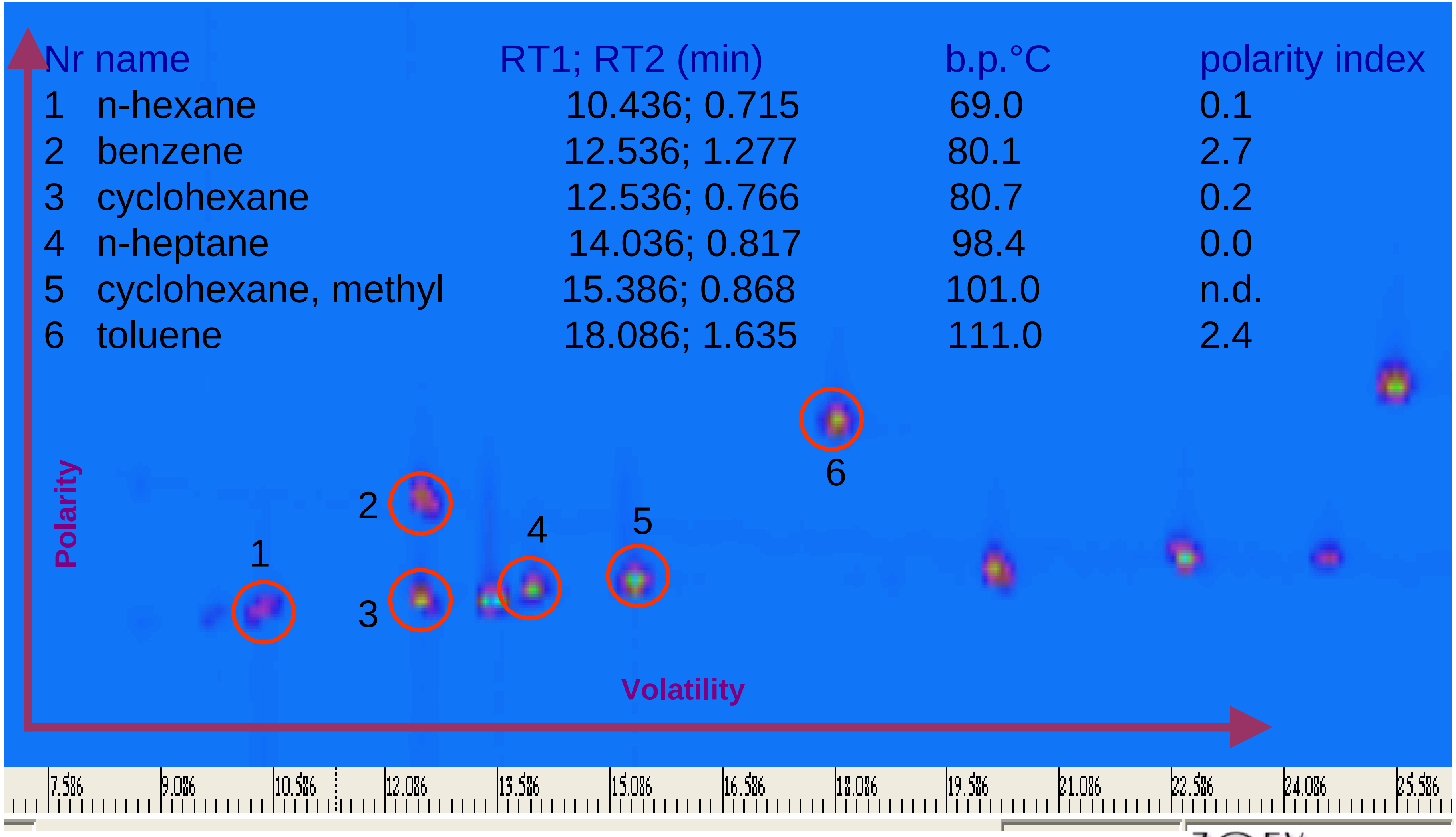




Which information is in this picture

- Fingerprint of crude oils (based on bidimensional distribution of more than 1000 compounds)
- Chemical information (chemical structure, volatility, polarity, etc.)

Volatility vs. Polarity



Nr	name	RT1; RT2 (min)	b.p.°C	polarity index
1	n-hexane	10.436; 0.715	69.0	0.1
2	benzene	12.536; 1.277	80.1	2.7
3	cyclohexane	12.536; 0.766	80.7	0.2
4	n-heptane	14.036; 0.817	98.4	0.0
5	cyclohexane, methyl	15.386; 0.868	101.0	n.d.
6	toluene	18.086; 1.635	111.0	2.4

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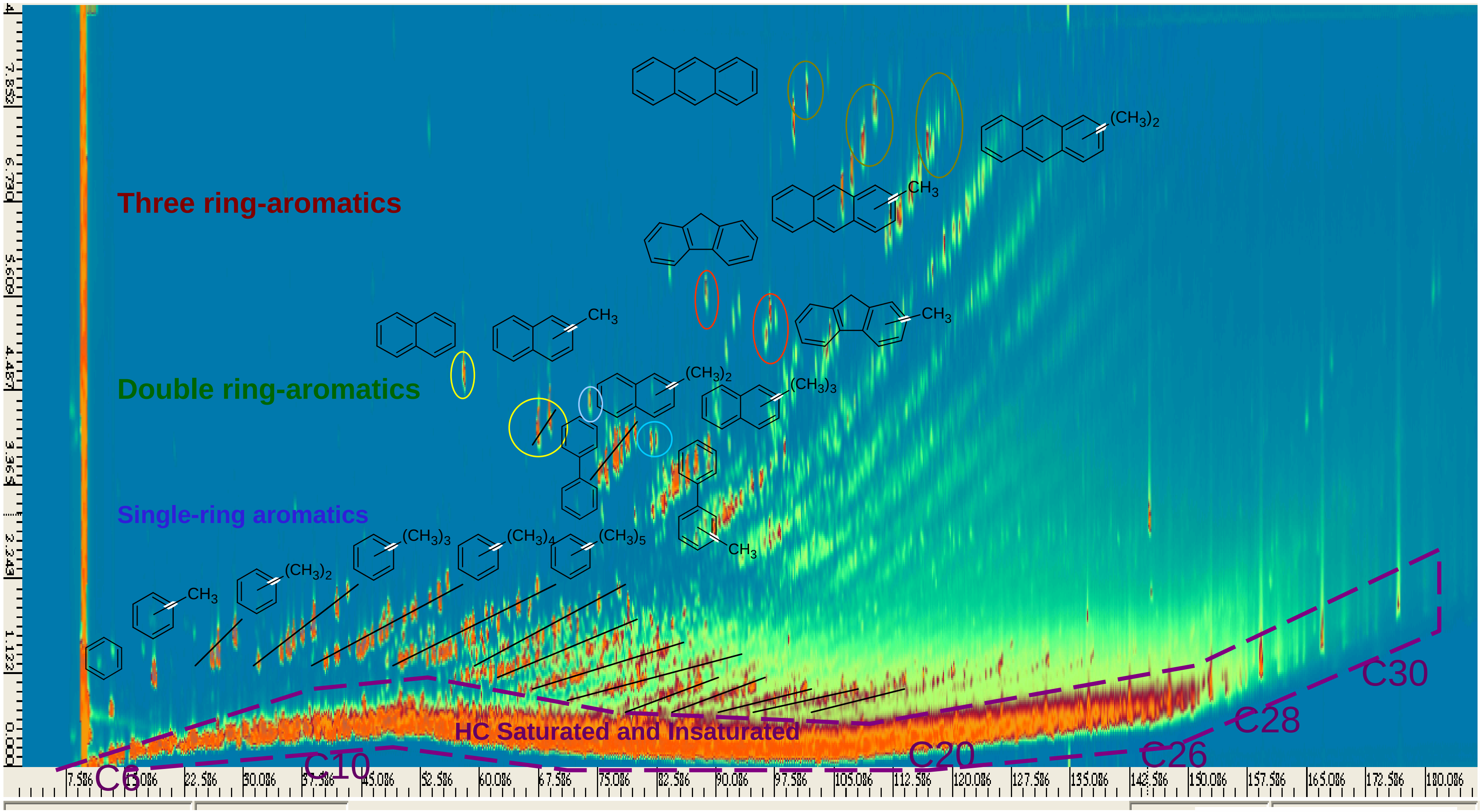
Which information is in this picture

- Fingerprint of crude oils (based on bidimensional distribution of more than 1000 compounds)
- Chemical information (chemical structure, volatility, polarity, etc.)
- Information for application purposes (compound identification for geological exploration and process refinery uses)

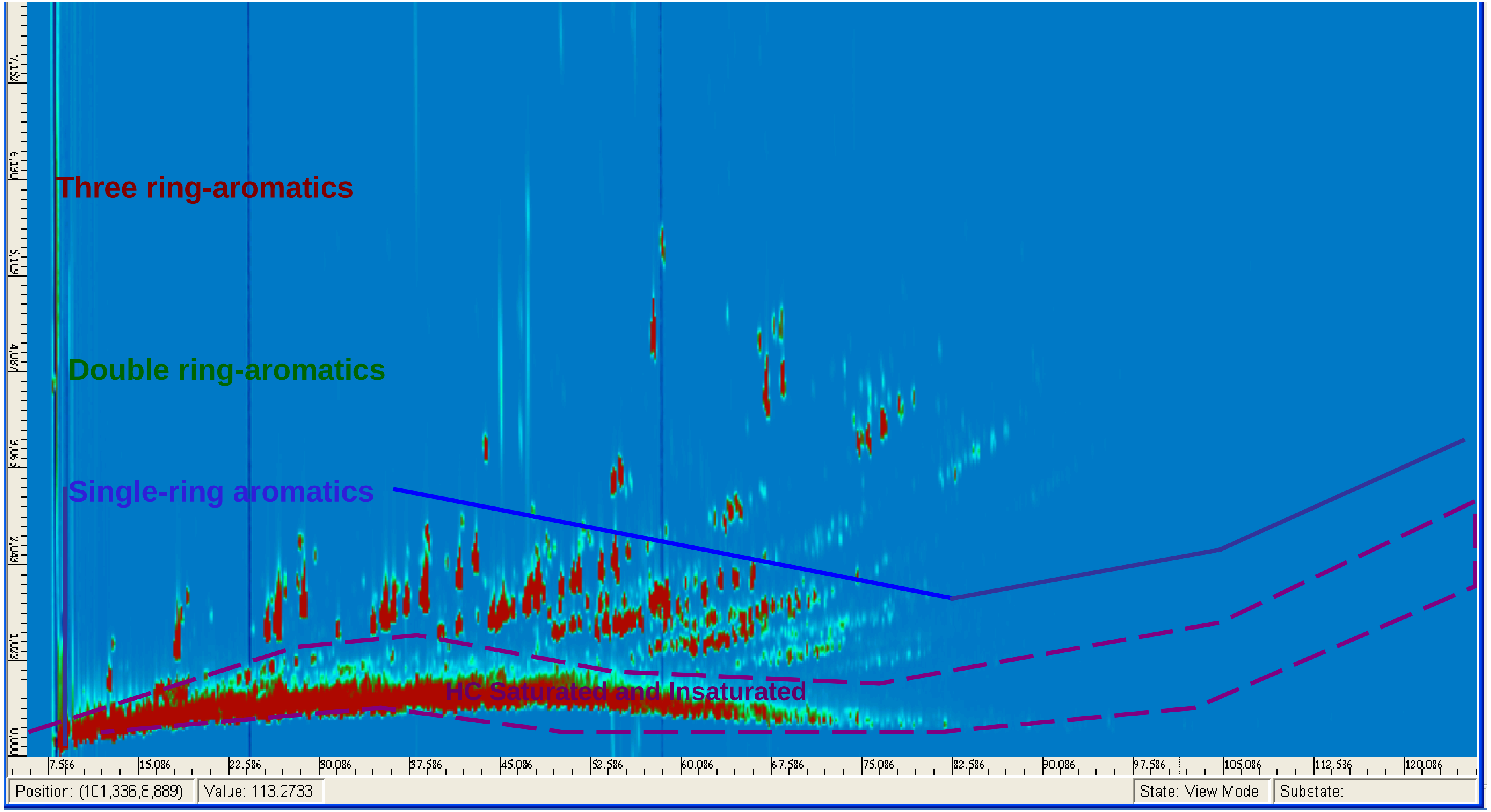
GC x GC method approach

- Goal: use the potentiality of the GCxGC to obtain as much as possible information and semplify instrument use for routine analysis
- One GCxGC method is here described:
  - to optimise the separation among classes;
  - to discrimine among information the more interesting ones:
    - Hydrocarbons group type
    - S-containing compounds
    - N-containing compounds

Hydrocarbons in light crude oil A



GCxGC analysis of light petroleum distillate

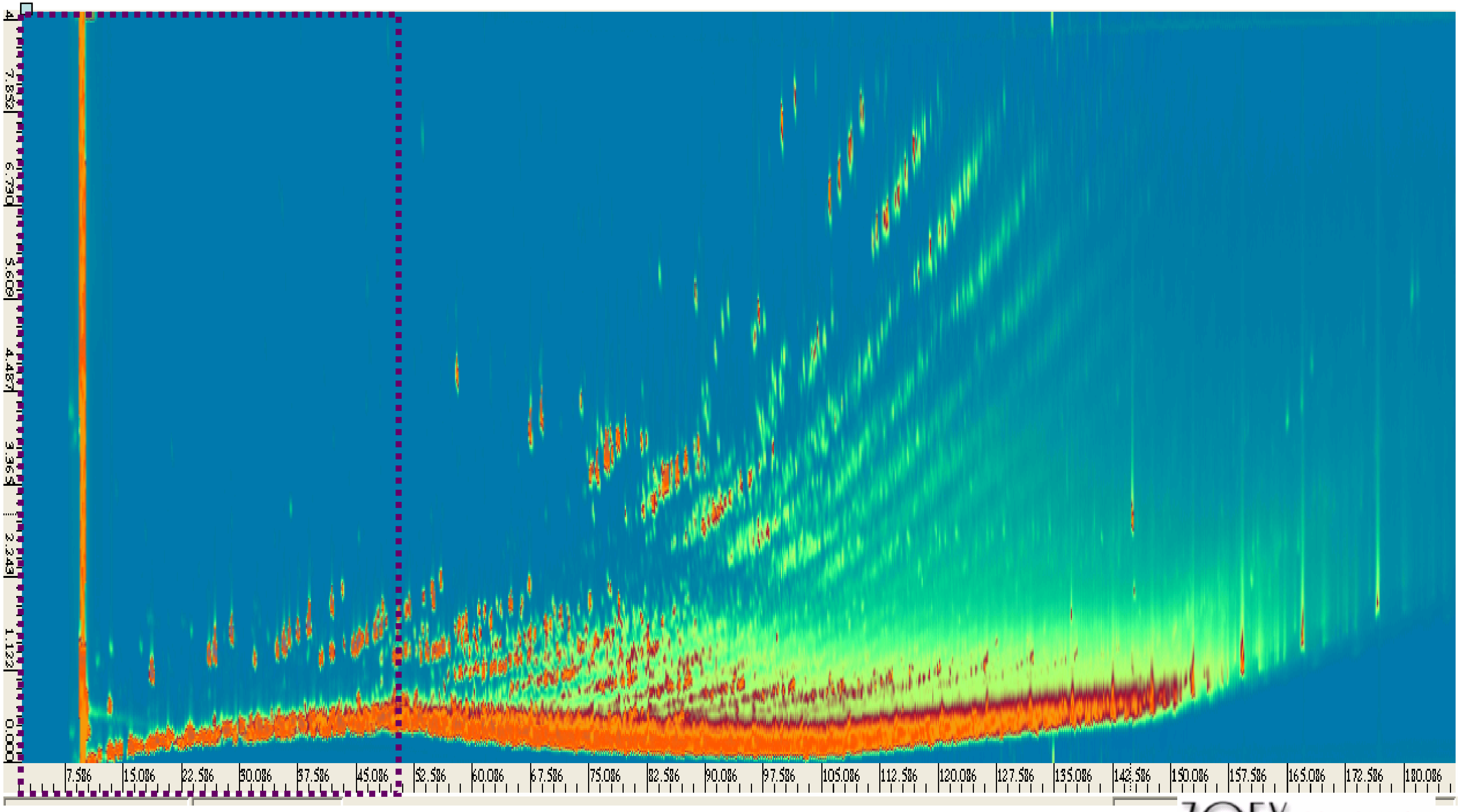


Position: (101,336,8,889) | Value: 113.2733 | State: View Mode | Substate:

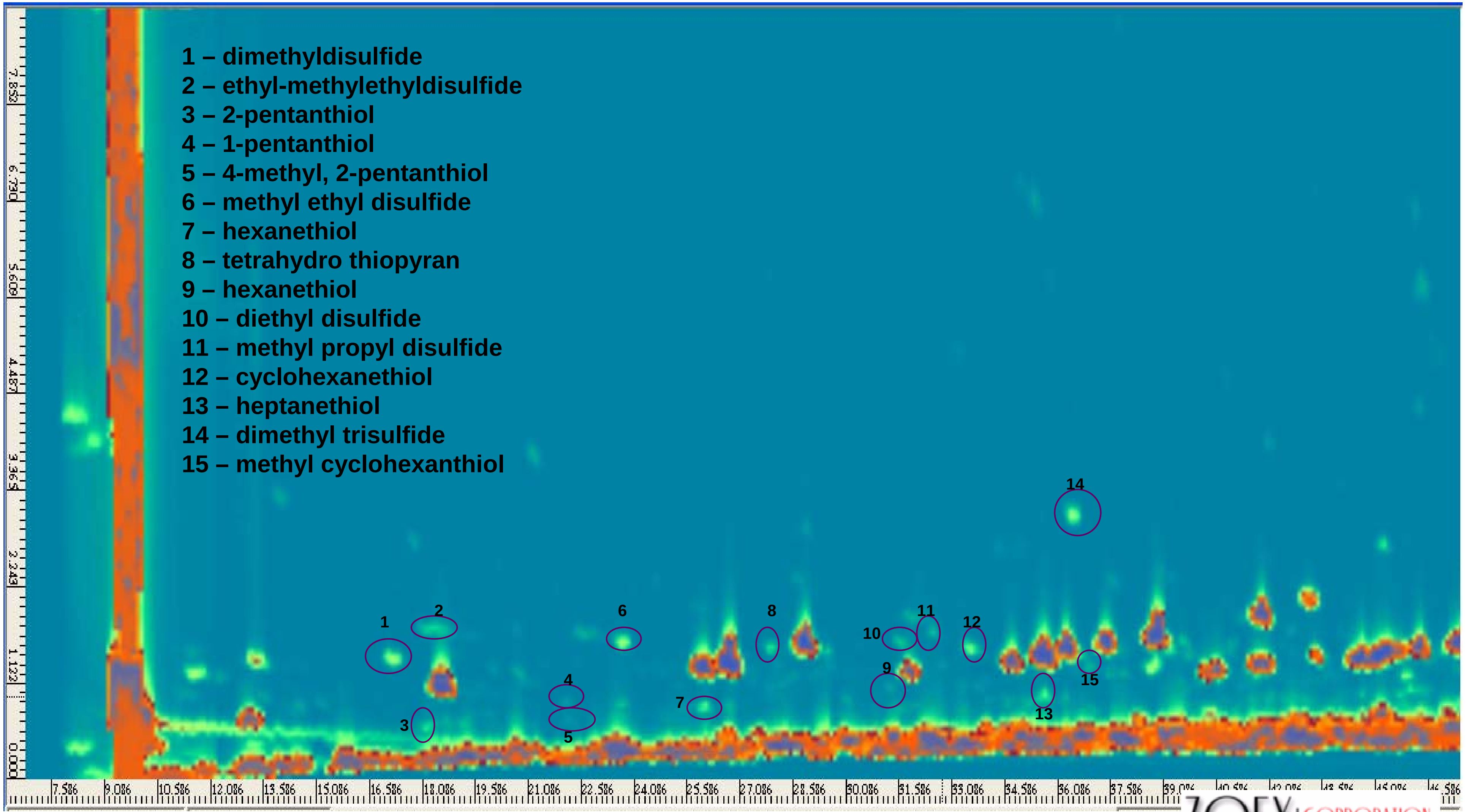
Why to study sulphur compounds

- The increasing concern on the environmental conditions requires to limit the sulphur level in diesel fuel and gasoline (e.g. the specification in Europe for S content is lower than 10 ppm S).
- Very deep conversion of sulphur compounds is therefore required to produce extremely clean transportation fuel. Nature and amount of the sulphur compounds strongly influence the conditions of desulphurisation treatments.
- The understanding and mapping of these species is of vital importance for the further treatment of oil and oil derivatives.

S-containing compounds in light crude oil A

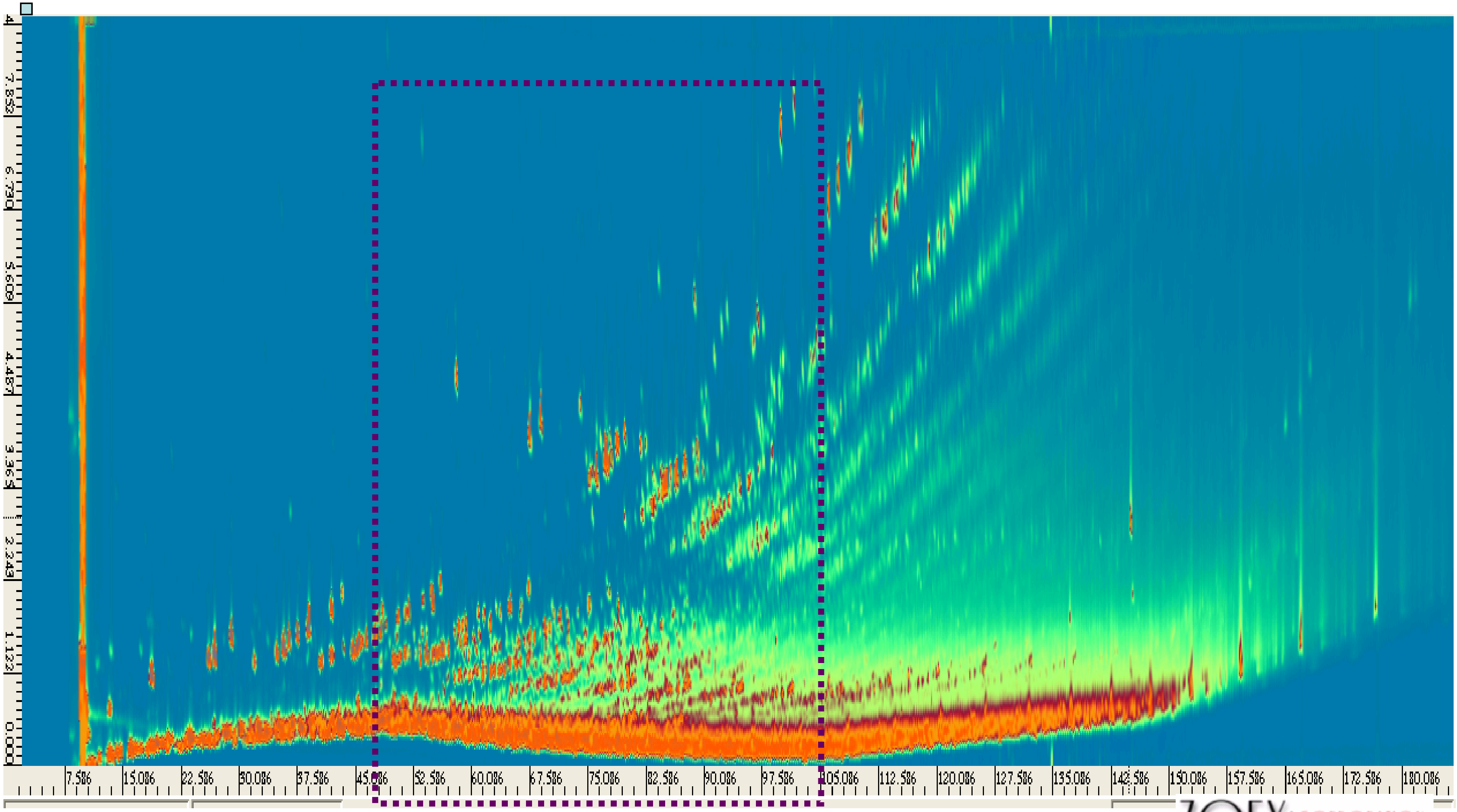


Thioles and sulfides in light crude oil A



1 – dimethyldisulfide
2 – ethyl-methylethyldisulfide
3 – 2-pentanthiol
4 – 1-pentanthiol
5 – 4-methyl, 2-pentanthiol
6 – methyl ethyl disulfide
7 – hexanethiol
8 – tetrahydro thiopyran
9 – hexanethiol
10 – diethyl disulfide
11 – methyl propyl disulfide
12 – cyclohexanethiol
13 – heptanethiol
14 – dimethyl trisulfide
15 – methyl cyclohexanthiol

S-compounds in light crude oil A



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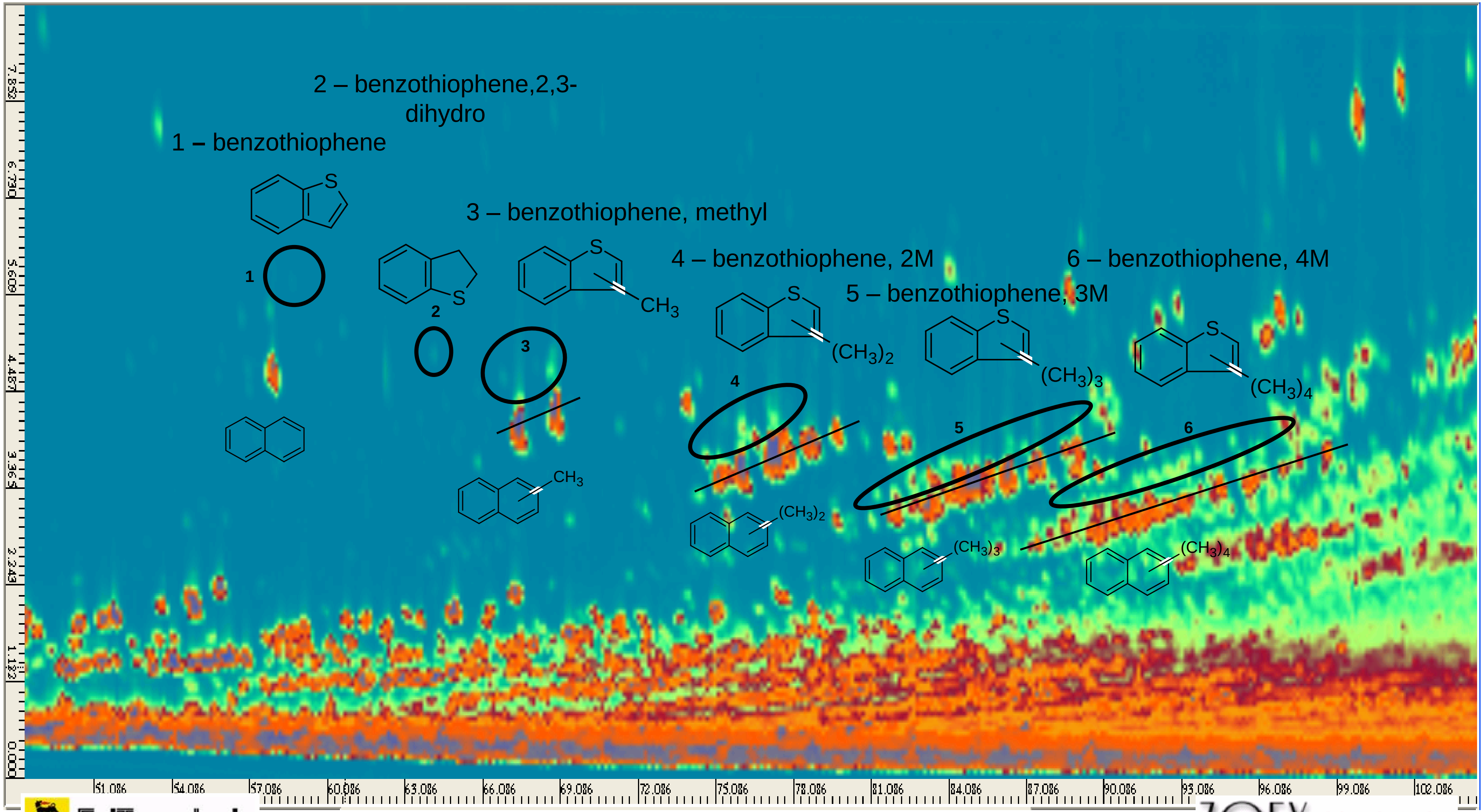
Benzothiophenes in light crude oil A



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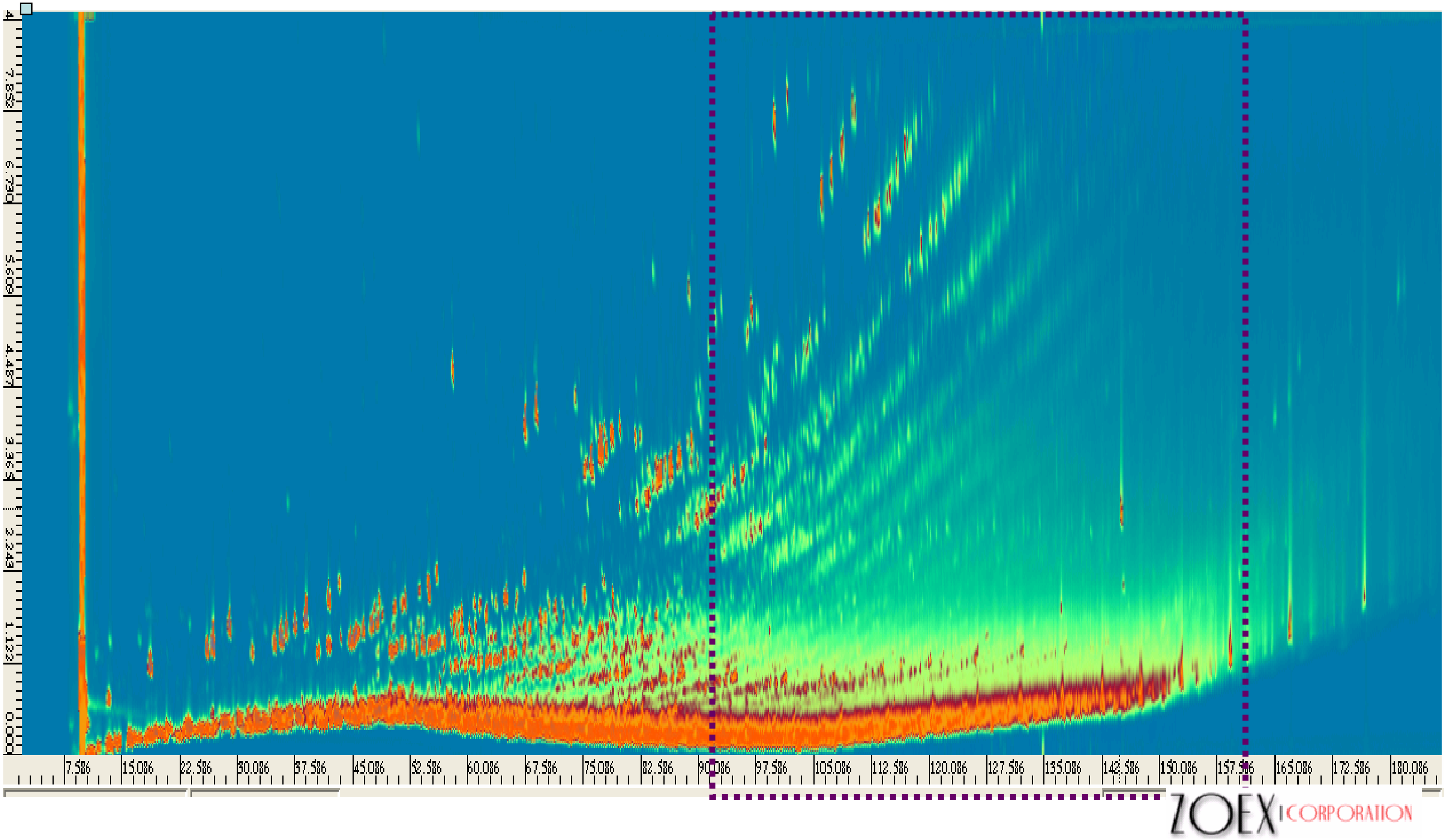
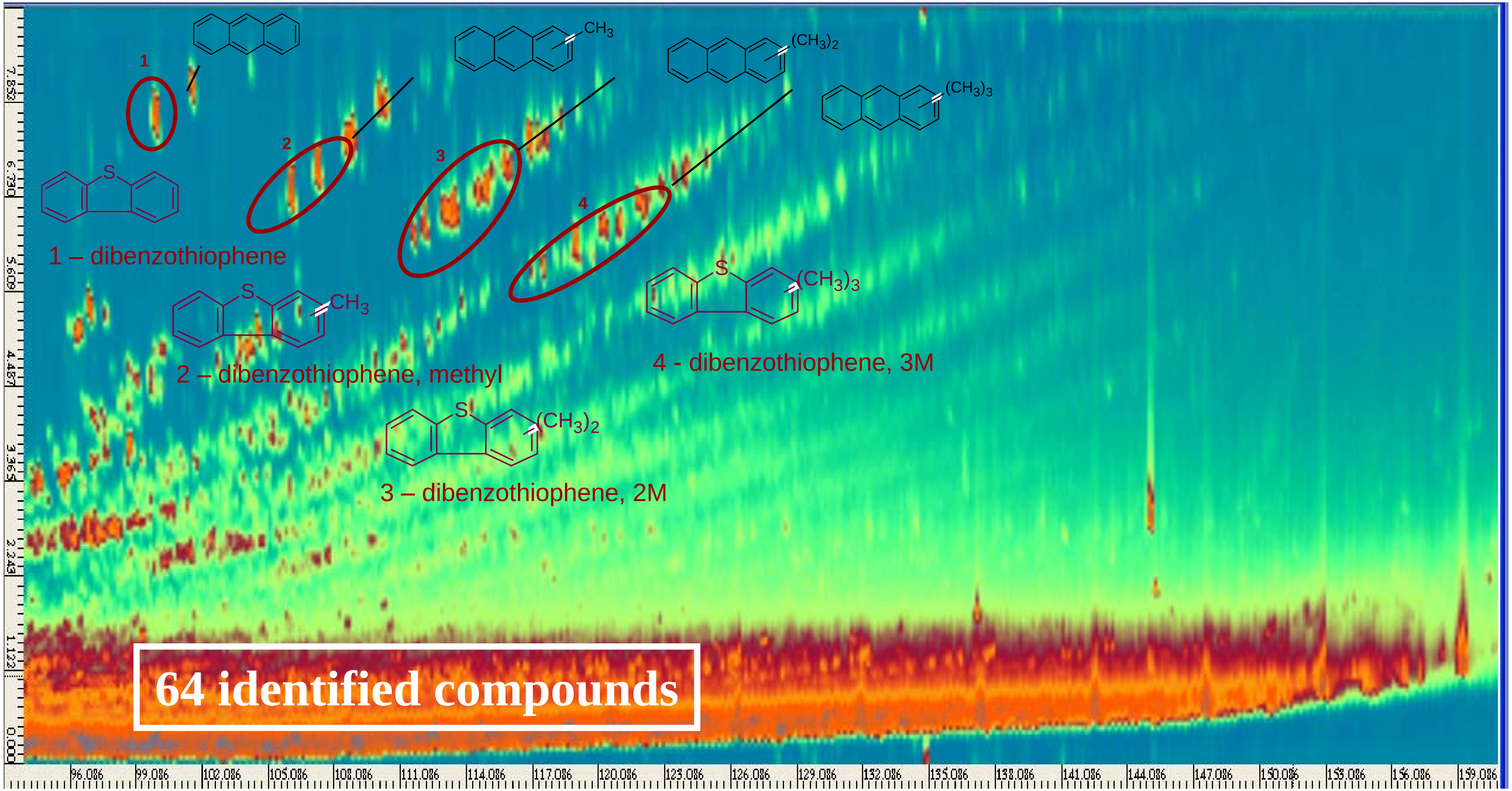
S-compounds in light crude oil A

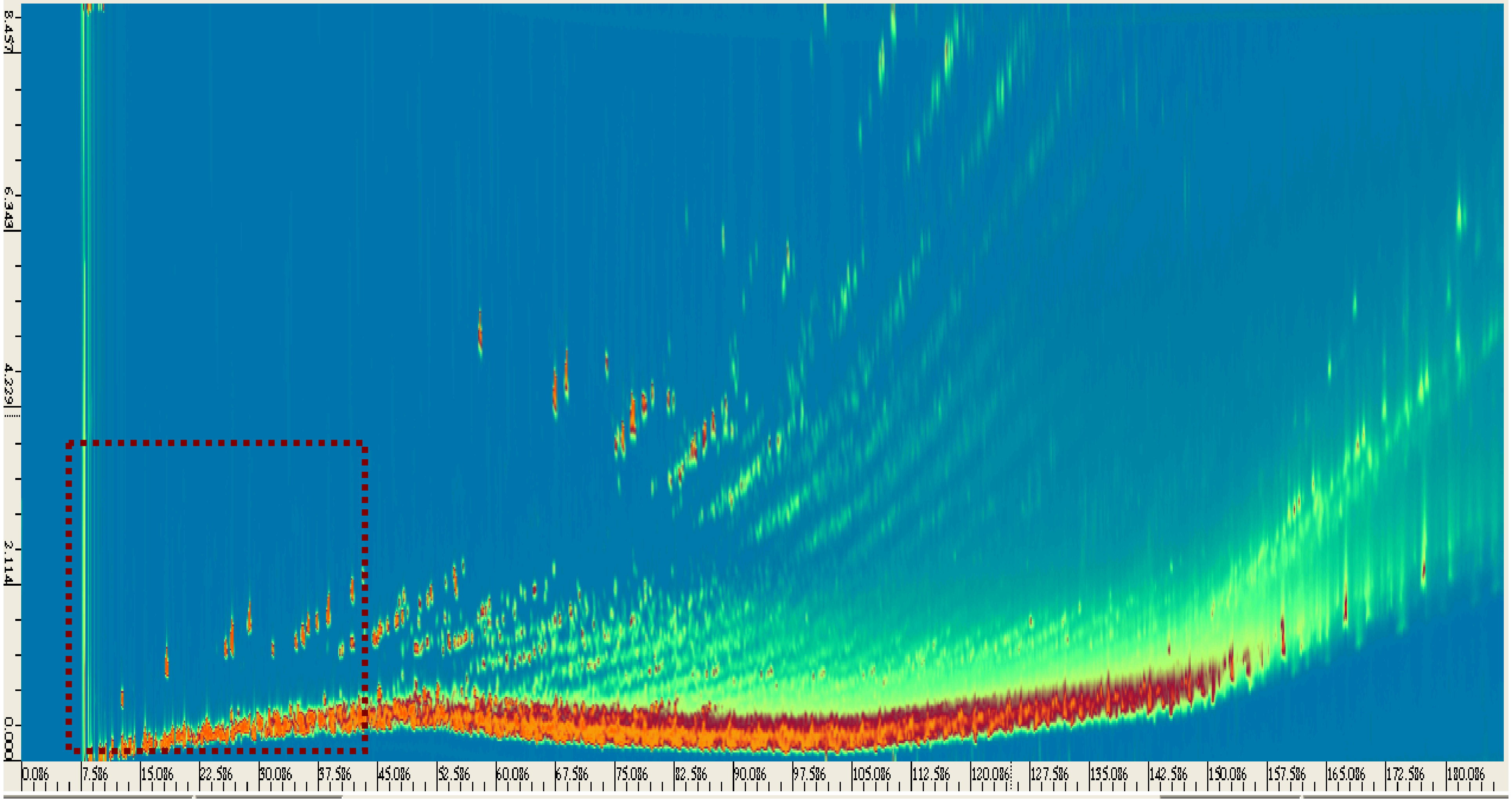


Dibenzothiophenes in light crude oil A

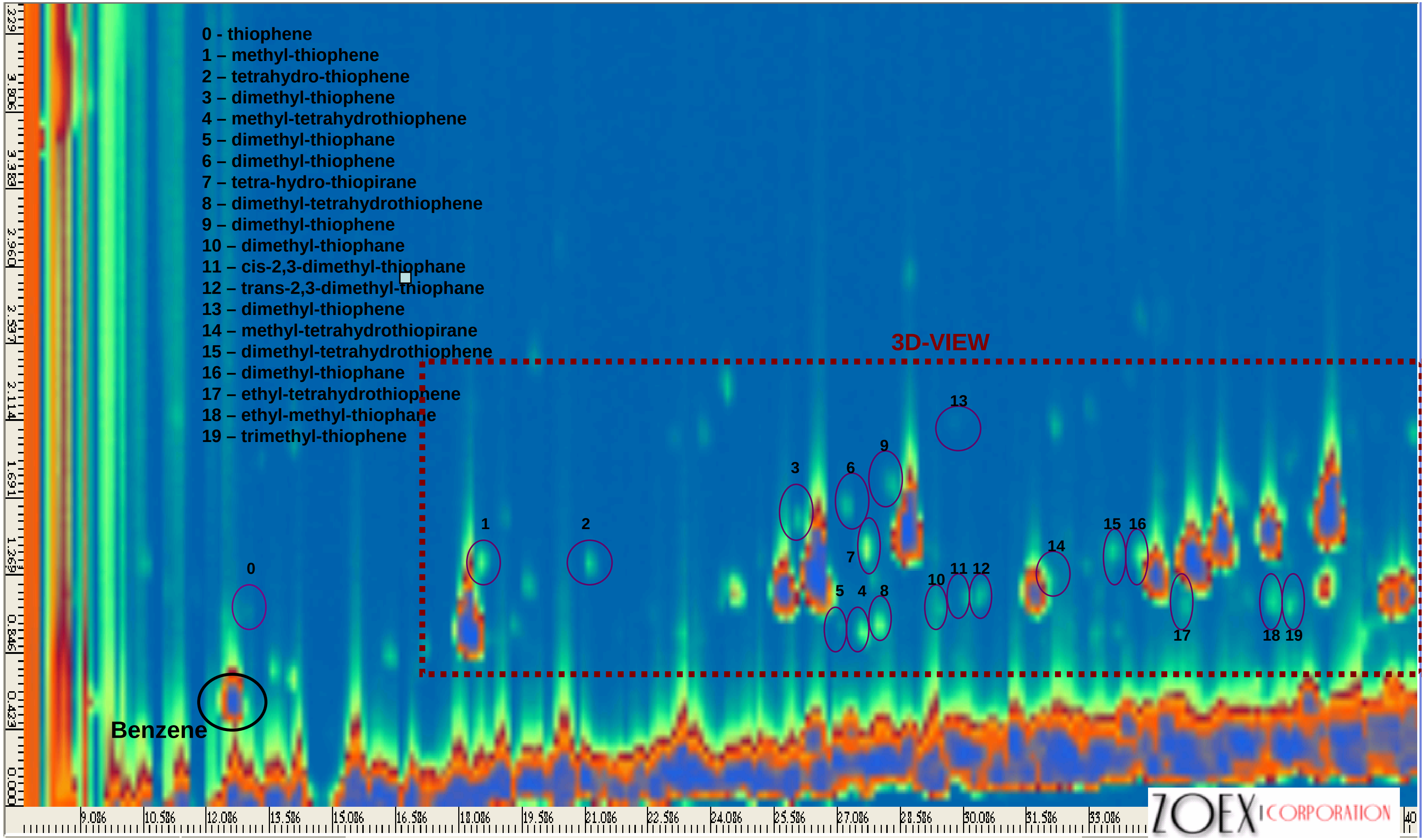


64 identified compounds

S-compounds in light crude oil C

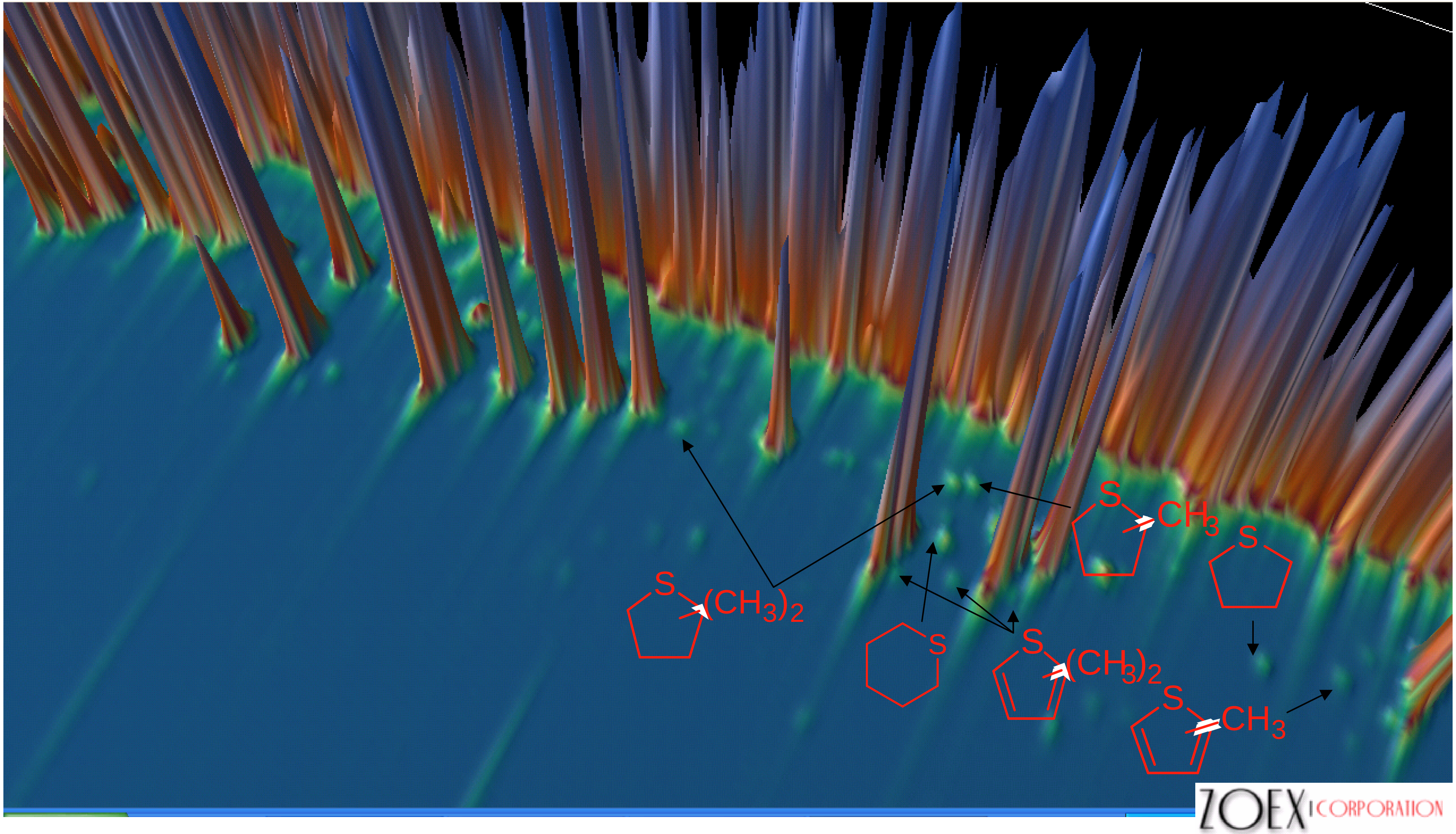


Thiophenes in light crude oil C



0 - thiophene
1 – methyl-thiophene
2 – tetrahydro-thiophene
3 – dimethyl-thiophene
4 – methyl-tetrahydrothiophene
5 – dimethyl-thiophane
6 – dimethyl-thiophene
7 – tetra-hydro-thiopirane
8 – dimethyl-tetrahydrothiophene
9 – dimethyl-thiophene
10 – dimethyl-thiophane
11 – cis-2,3-dimethyl-thiophane
12 – trans-2,3-dimethyl-thiophane
13 – dimethyl-thiophene
14 – methyl-tetrahydrothiopirane
15 – dimethyl-tetrahydrothiophene
16 – dimethyl-thiophane
17 – ethyl-tetrahydrothiophene
18 – ethyl-methyl-thiophane
19 – trimethyl-thiophene

3D-view: Thiophenes in light crude oil C



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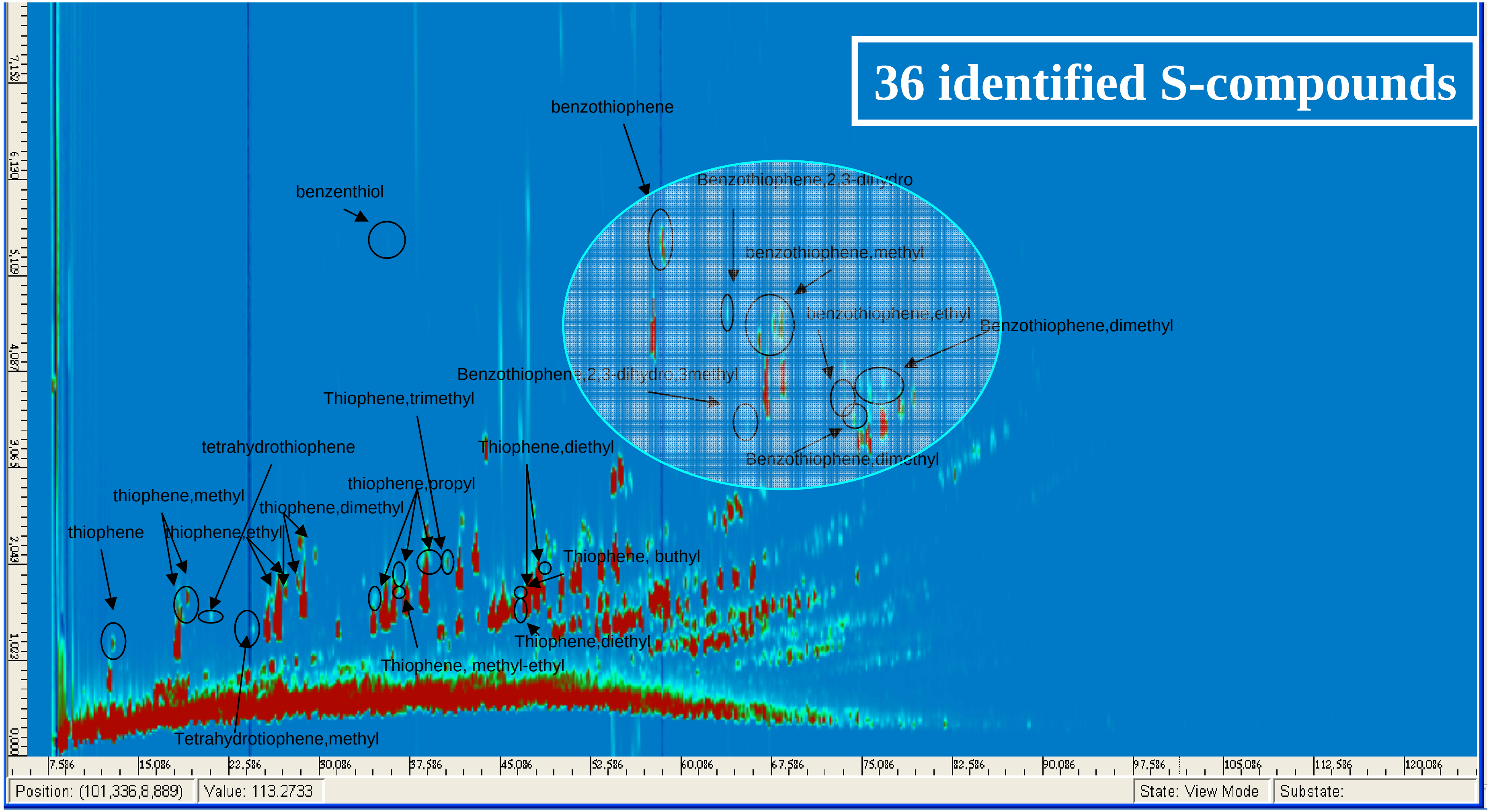
GCxGC S-compound map of light petroleum distillate (527 ppm S)



36 identified S-compounds

Position: (101,336,8,889) | Value: 113.2733 | State: View Mode | Substate:

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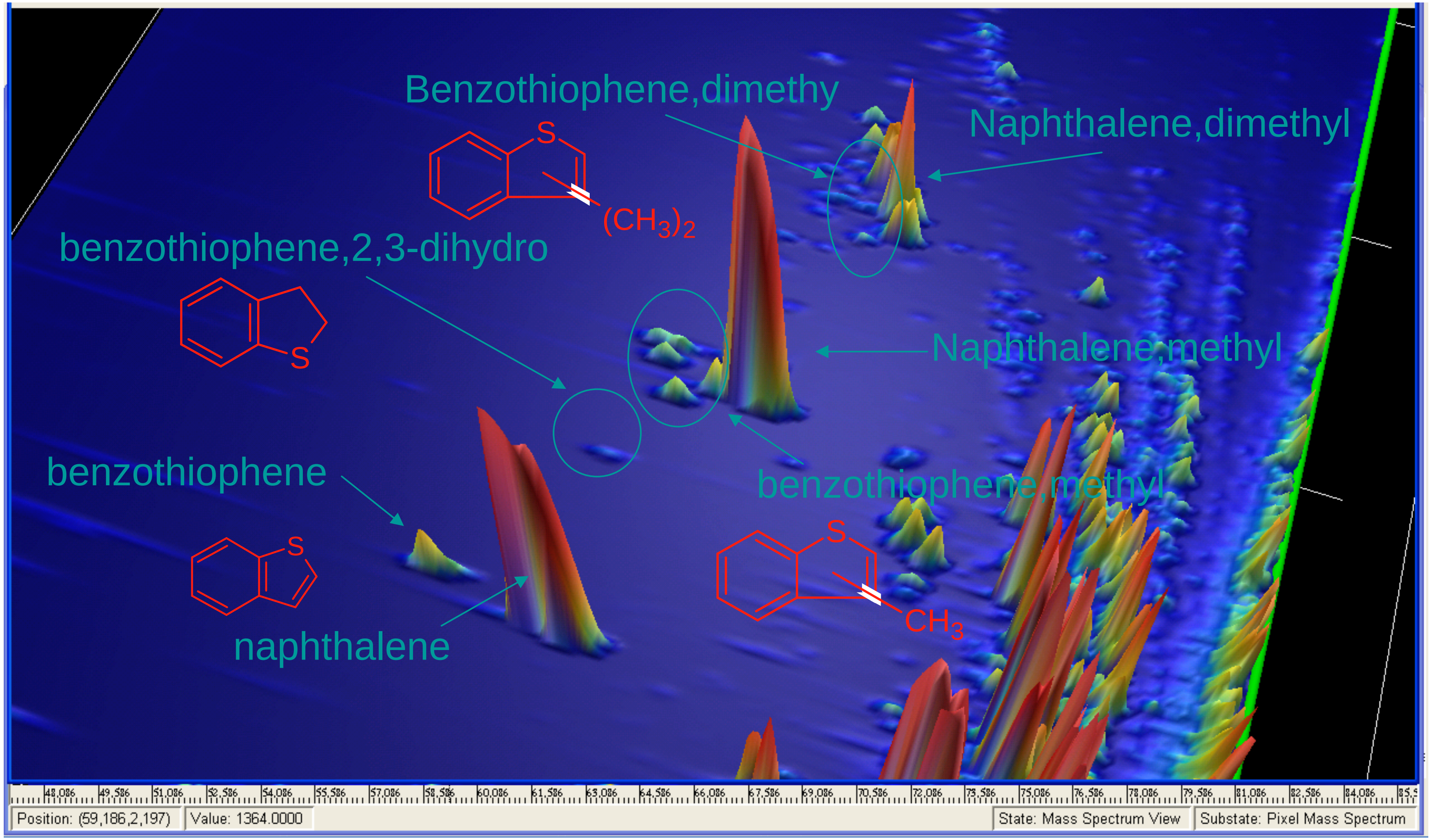
Benzothiophenes 3D-view



Position: (59,186,2,197)

Value: 1364.0000

State: Mass Spectrum View

Substate: Pixel Mass Spectrum

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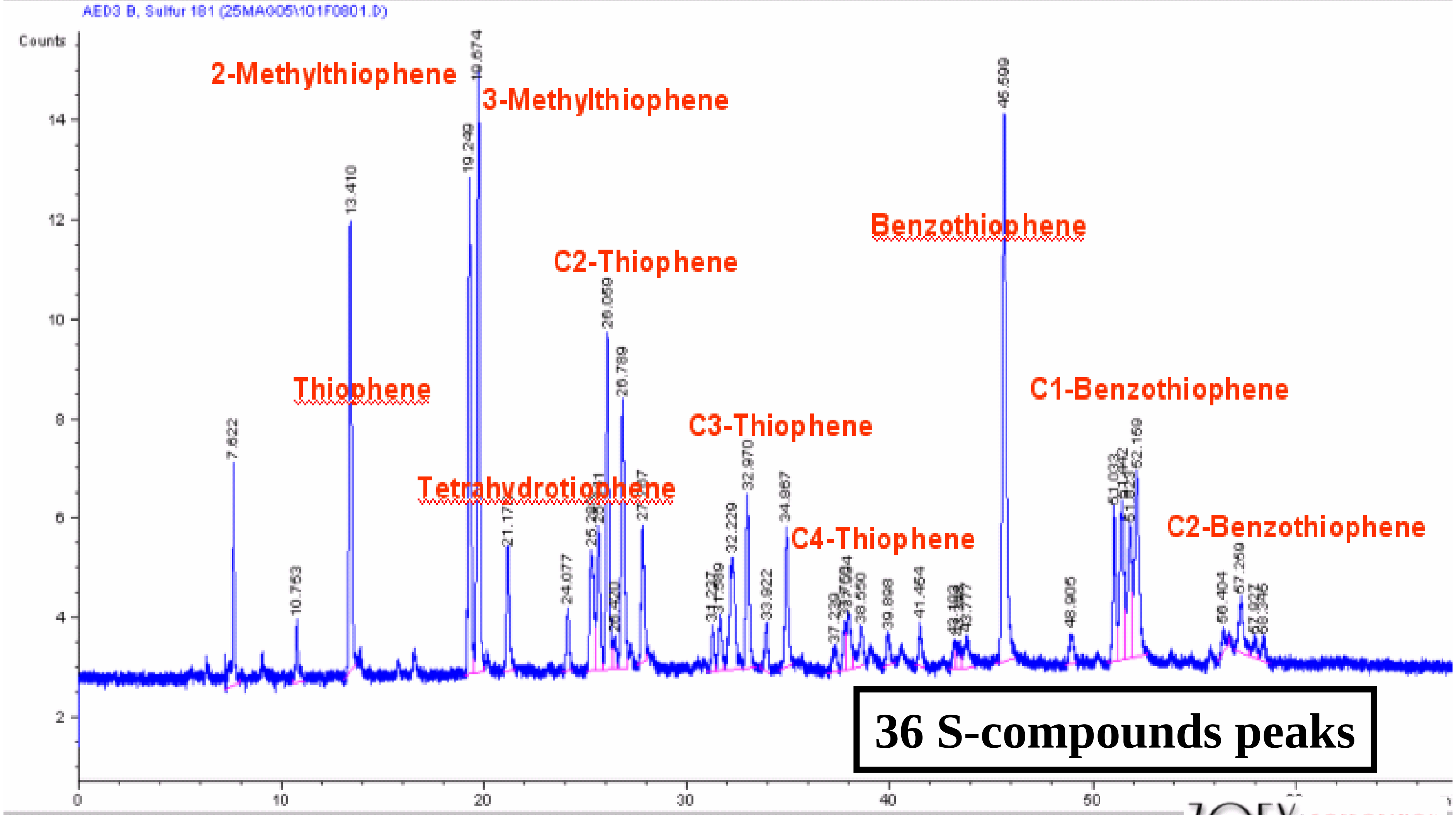
S-compound identification: comparison with GC-AED data



36 S-compounds peaks

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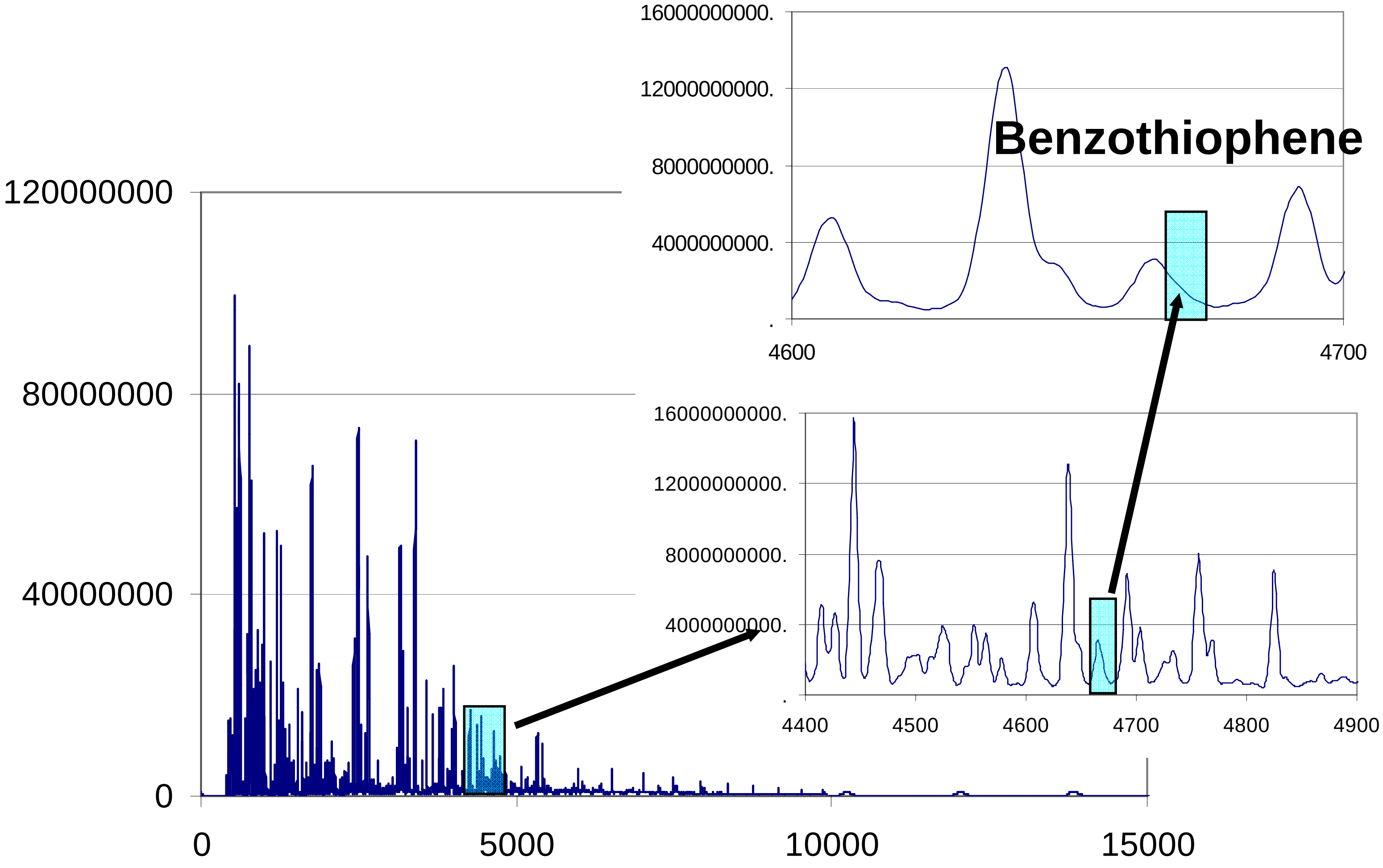
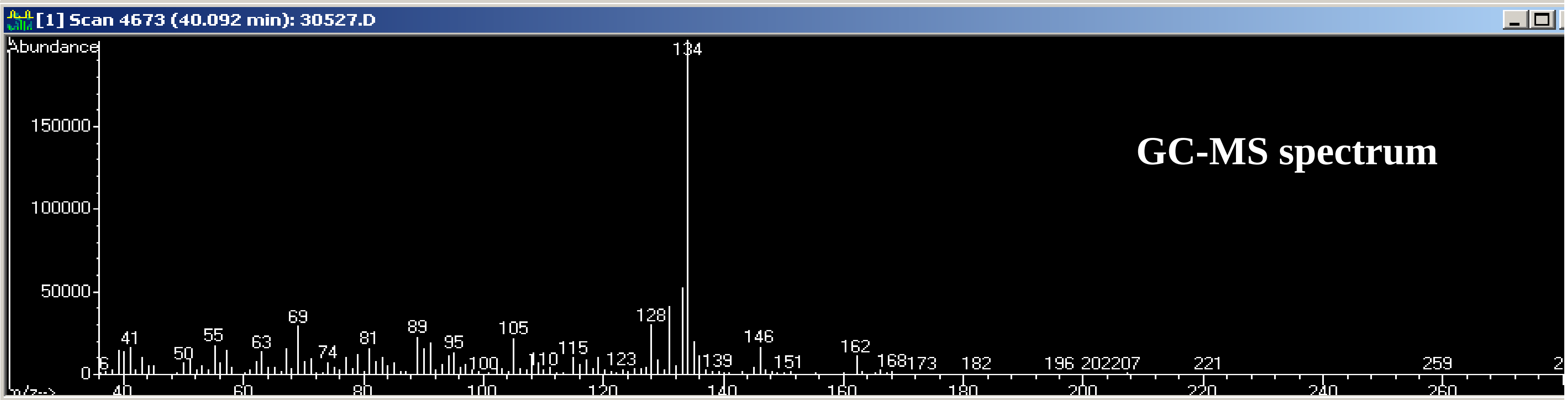
GC-MS analysis



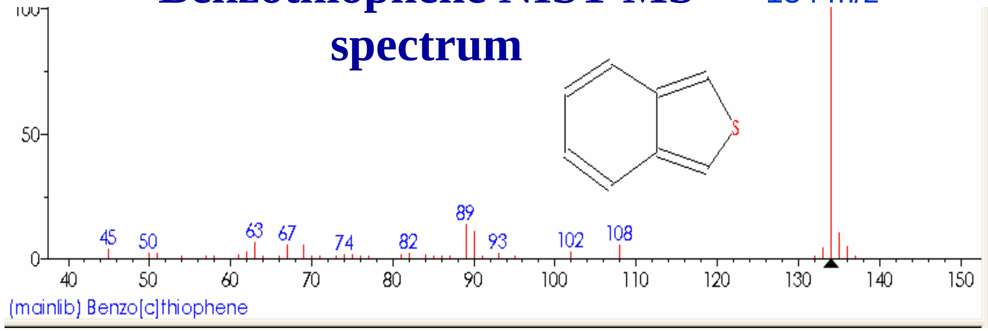
Benzothiophene GC-MS



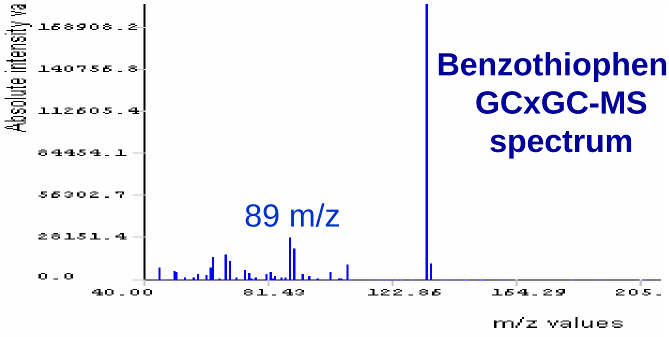
GC-MS spectrum

Benzothiophene NIST MS spectrum

134 m/z



134 m/z



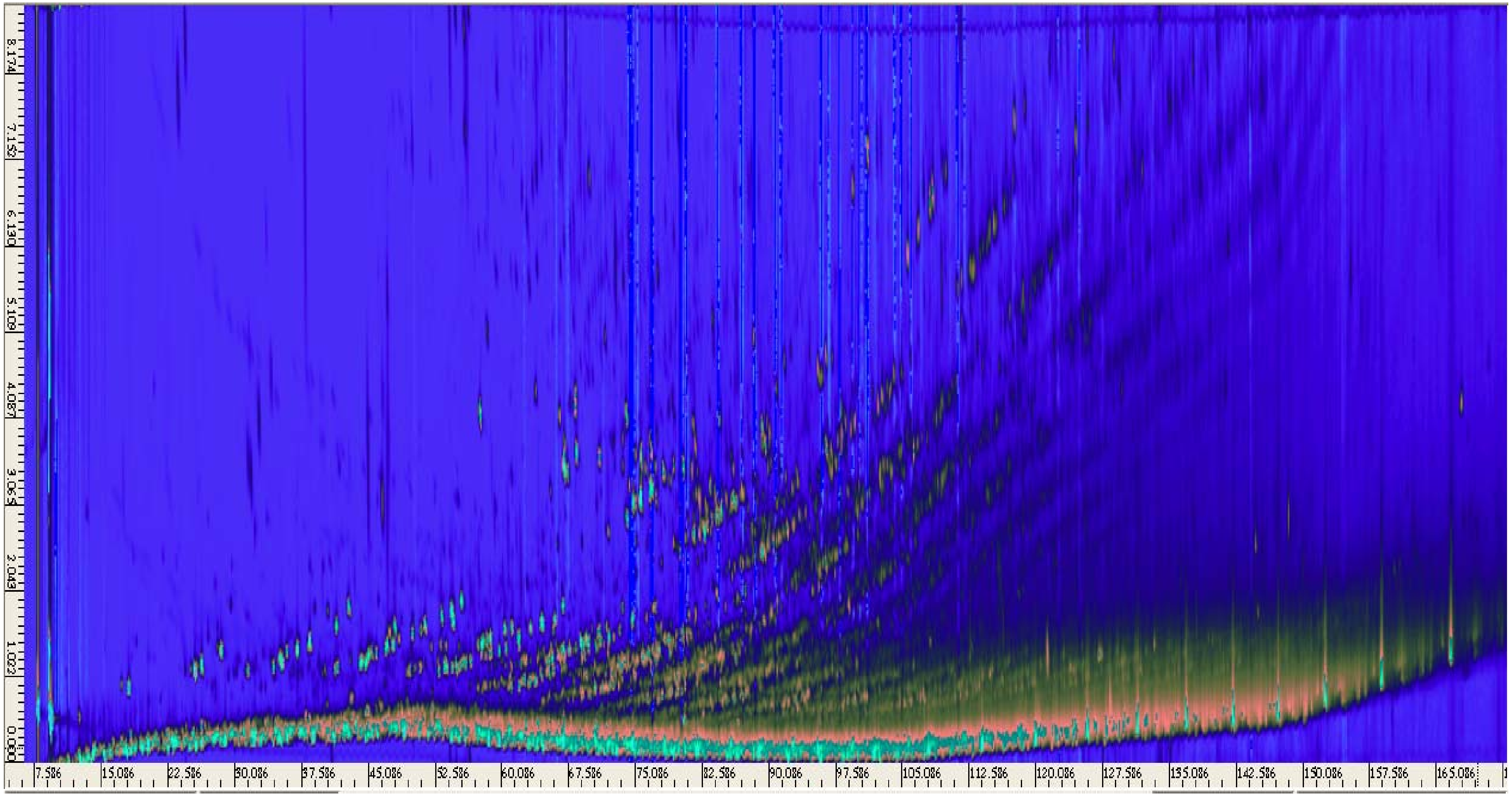
Benzothiophene GCxGC-MS spectrum

89 m/z

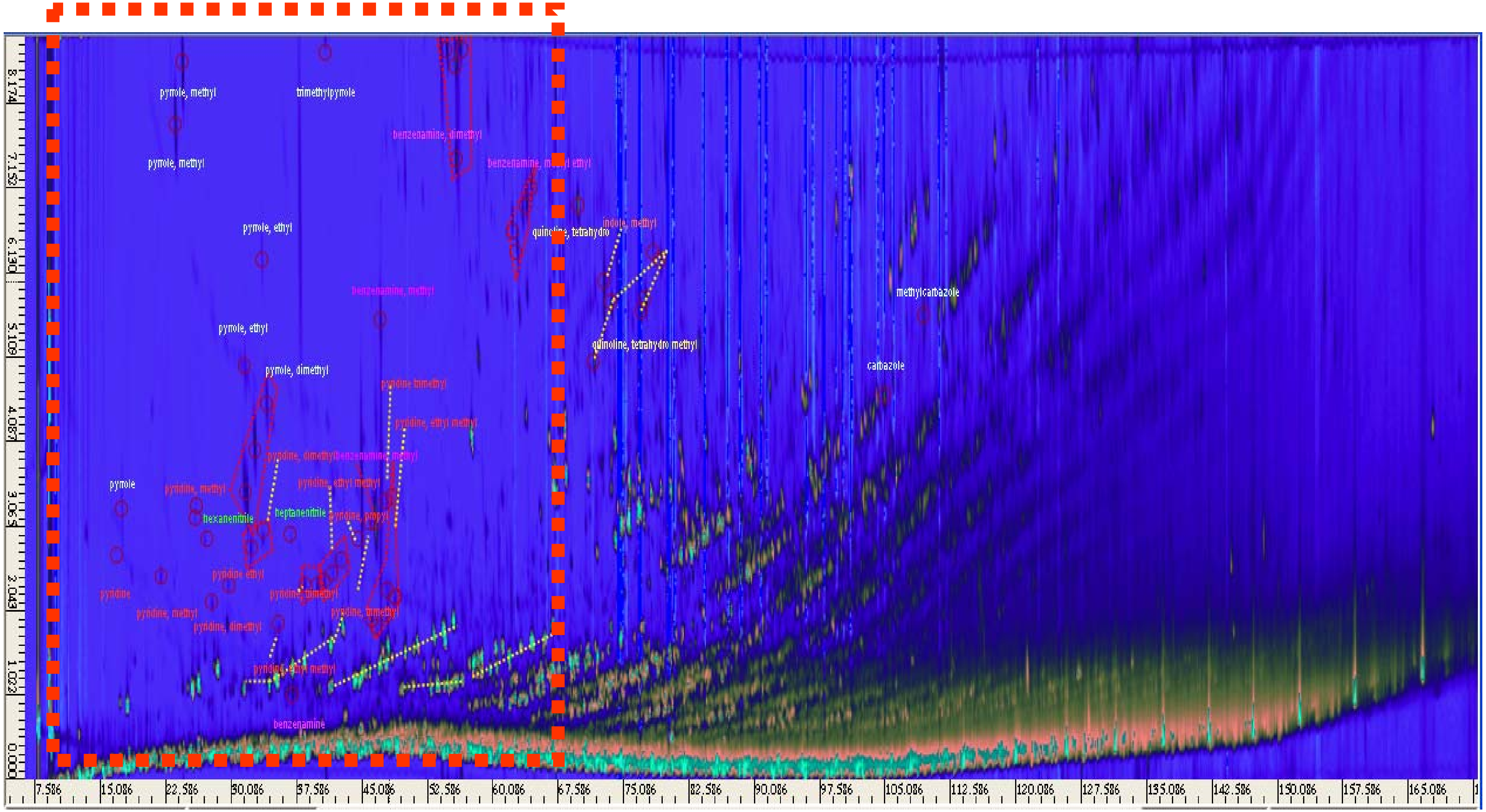
Why to study nitrogen compounds

- During desulphurisation, the presence of refractory and competitive species as nitrogen compounds is highly detrimental, due to their effect as inhibitors for HDS (hydrodesulphurisation) catalysts.
- Neutral (e.g. carbazole), slightly basic (e.g. quinoline) and basic (e.g. pyridine) nitrogen compounds are present in gas oil and cracked oil stream. The need to pre-remove these species is a function of their nature, the more stringent the removal the more basic are the species.
- The mapping of the nitrogen species is of vital importance for the further treatment of oil and oil derivatives.

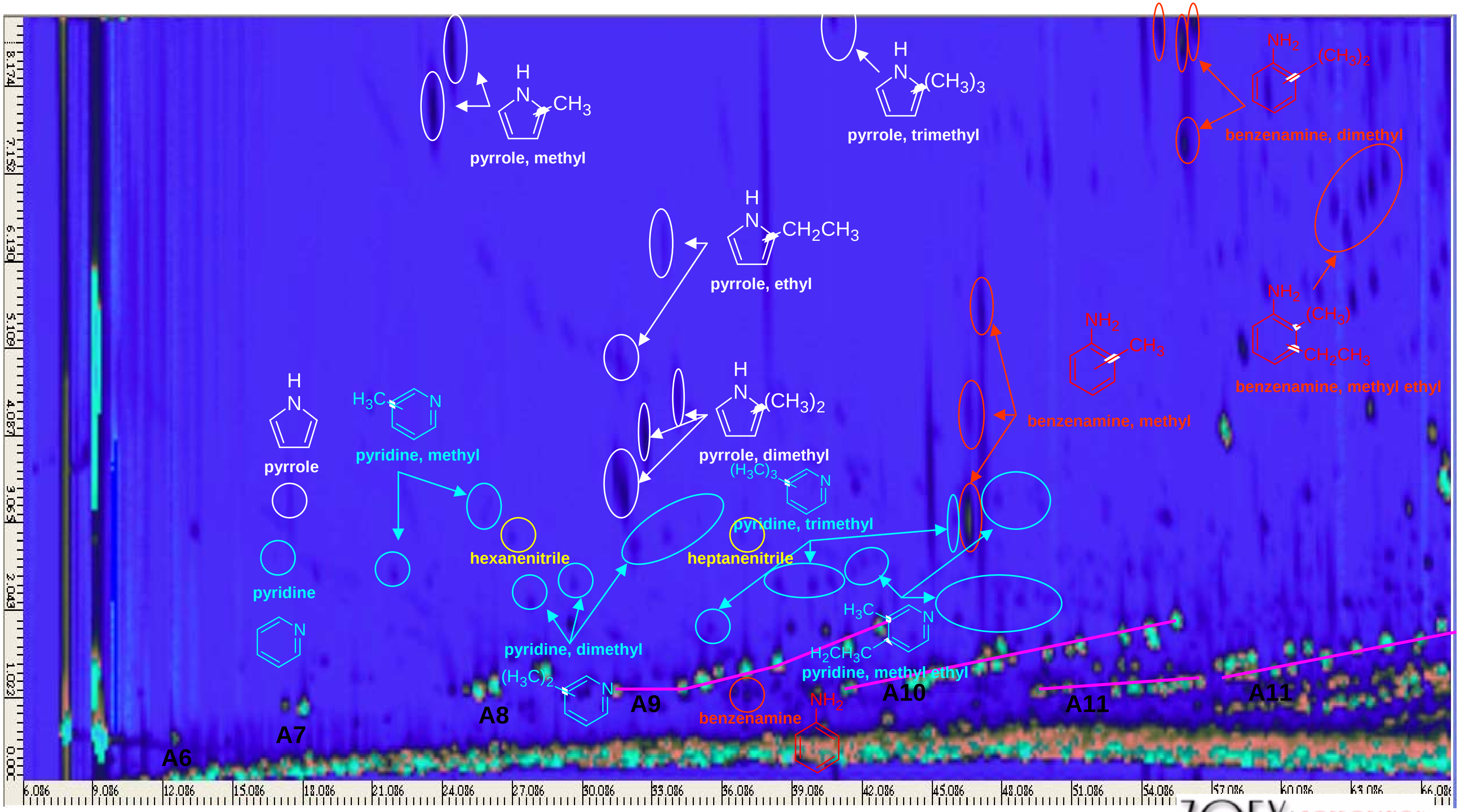
N-compounds in Naphtha



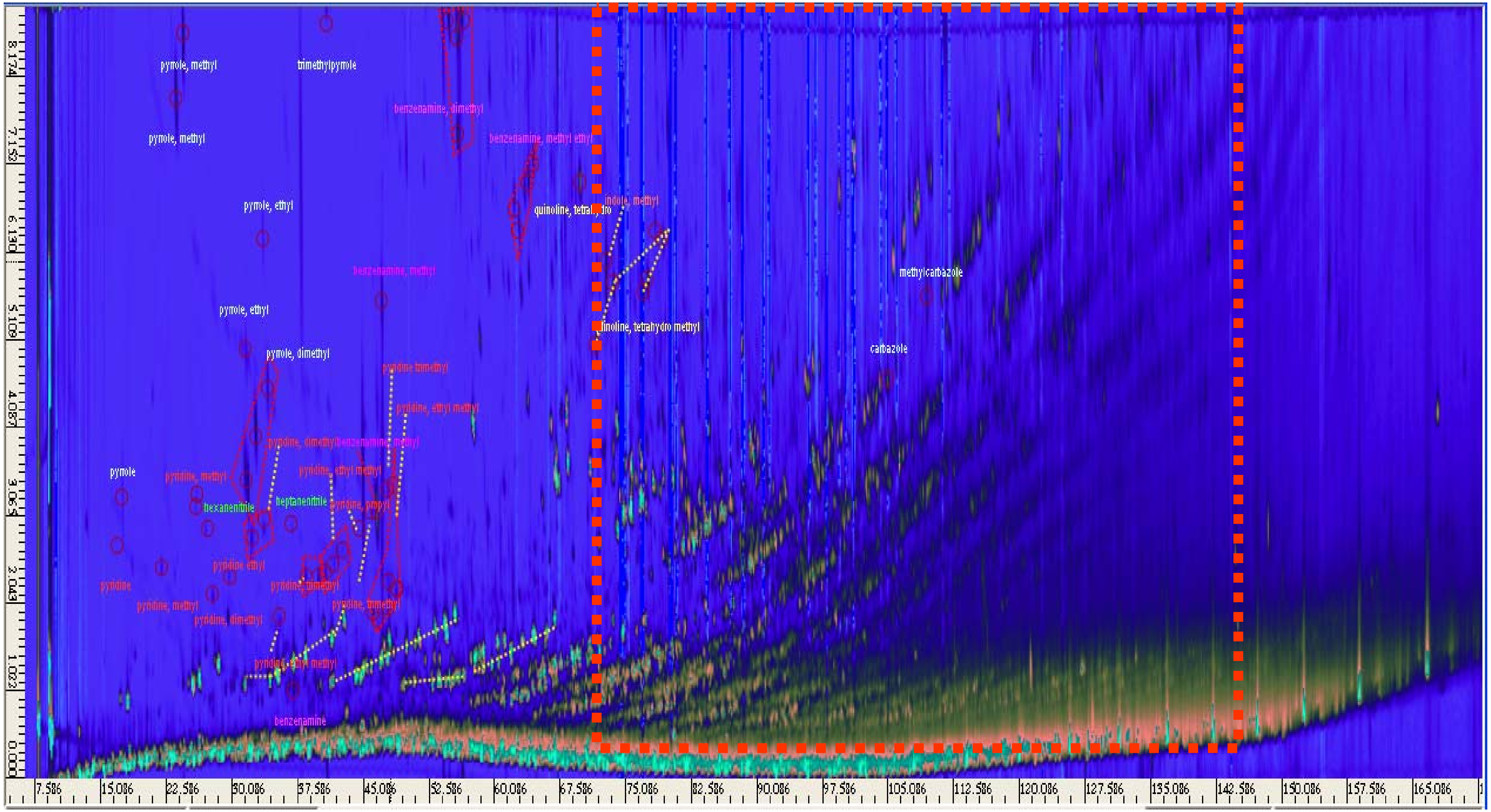
N-compounds in Naphtha



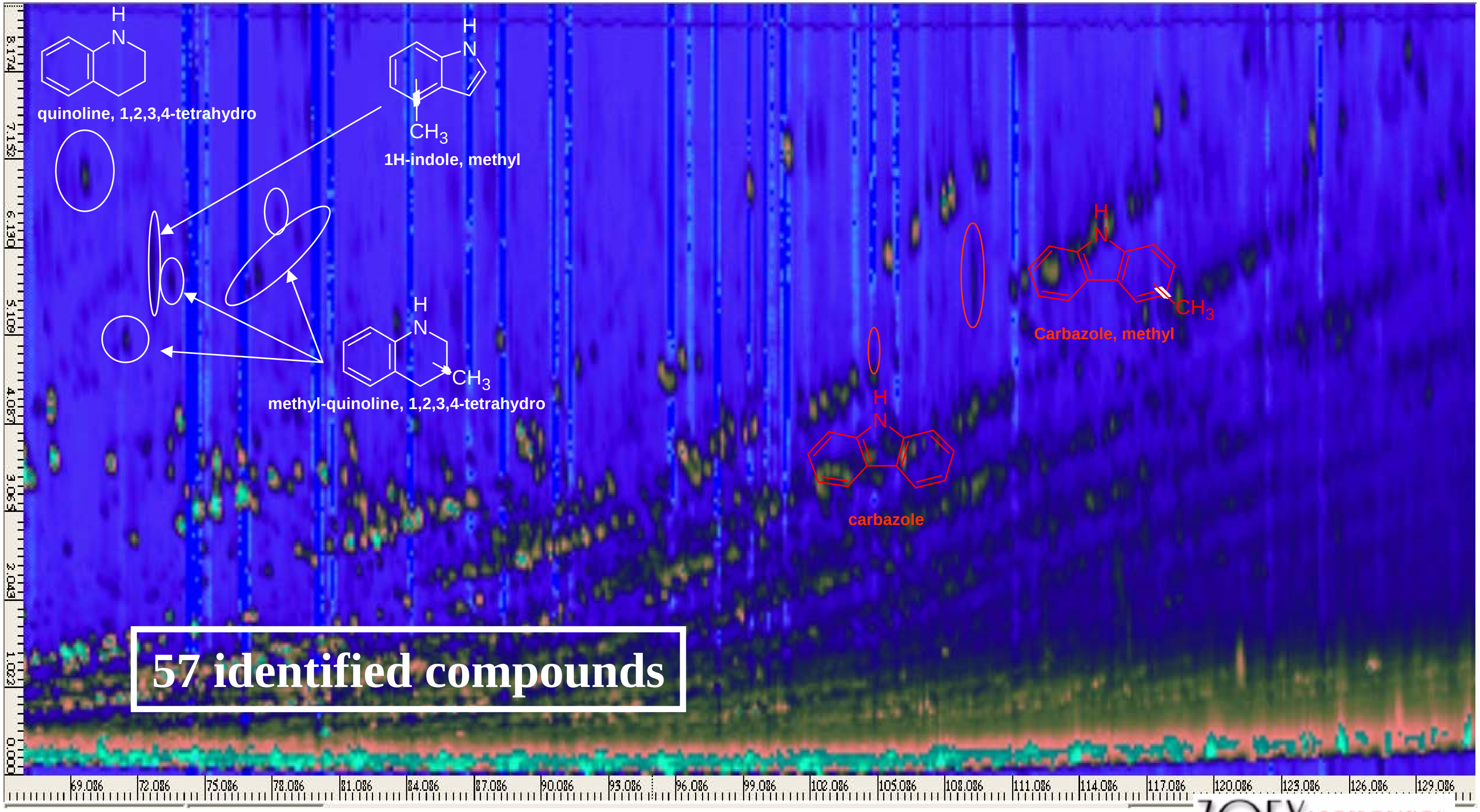
N-compounds in Petroleum fraction



N-compounds in Petroleum fraction



N-compounds in Petroleum fraction



57 identified compounds

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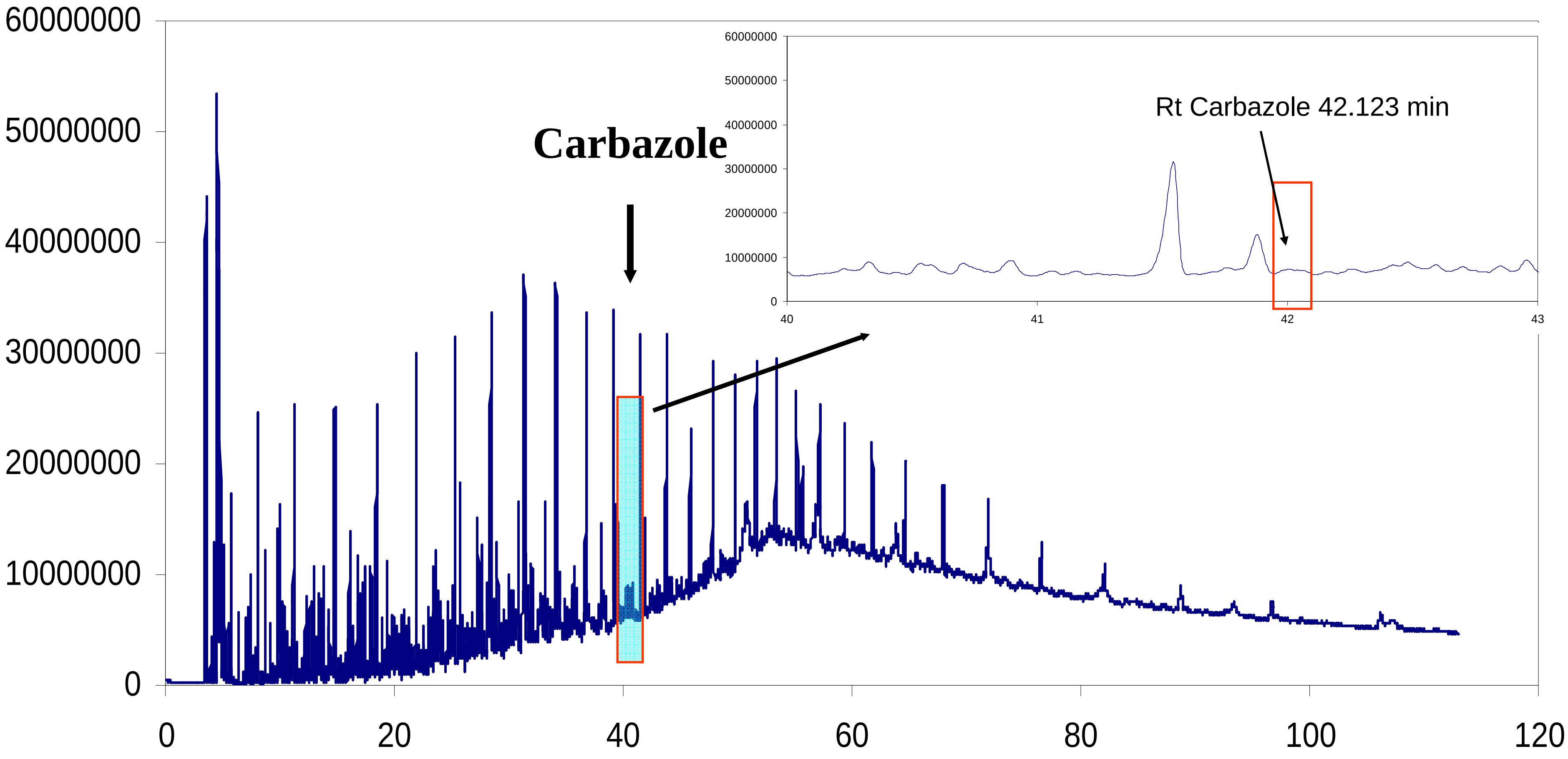
GC-MS analysis



Carbazole

Rt Carbazole 42.123 min

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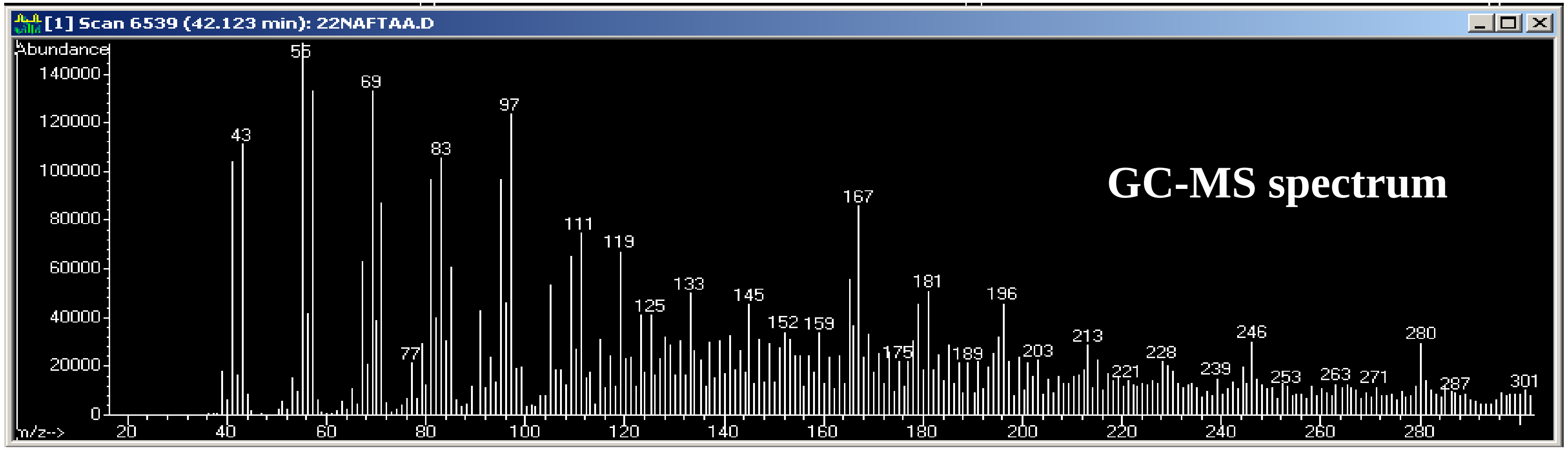
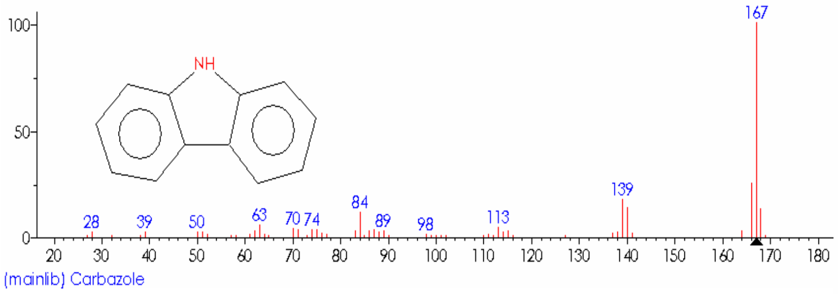
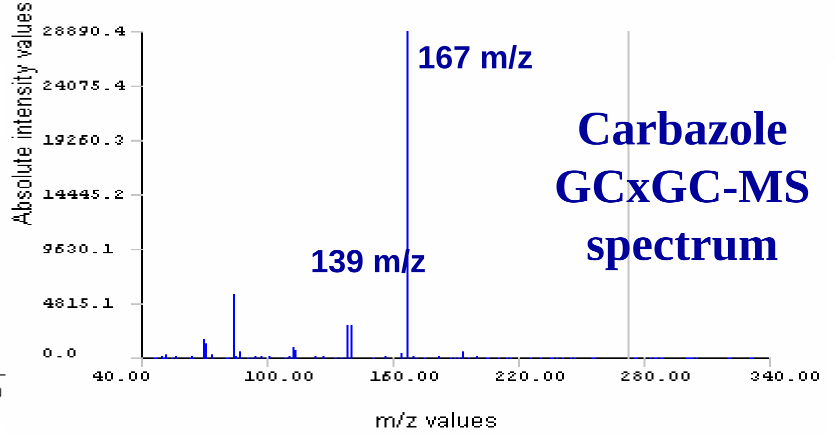
Carbazole MS Spectra



GC-MS spectrum

Carbazole NIST MS spectrum



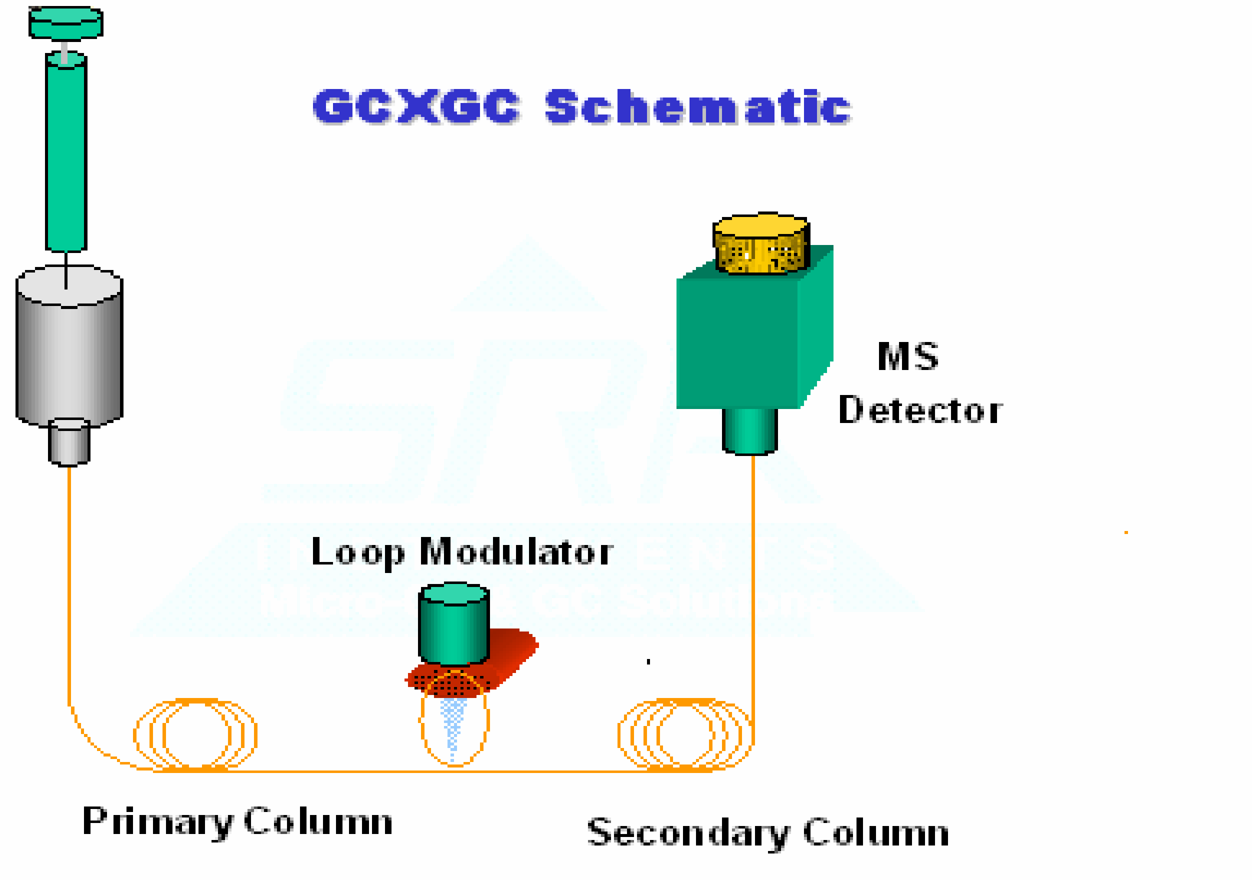


167 m/z

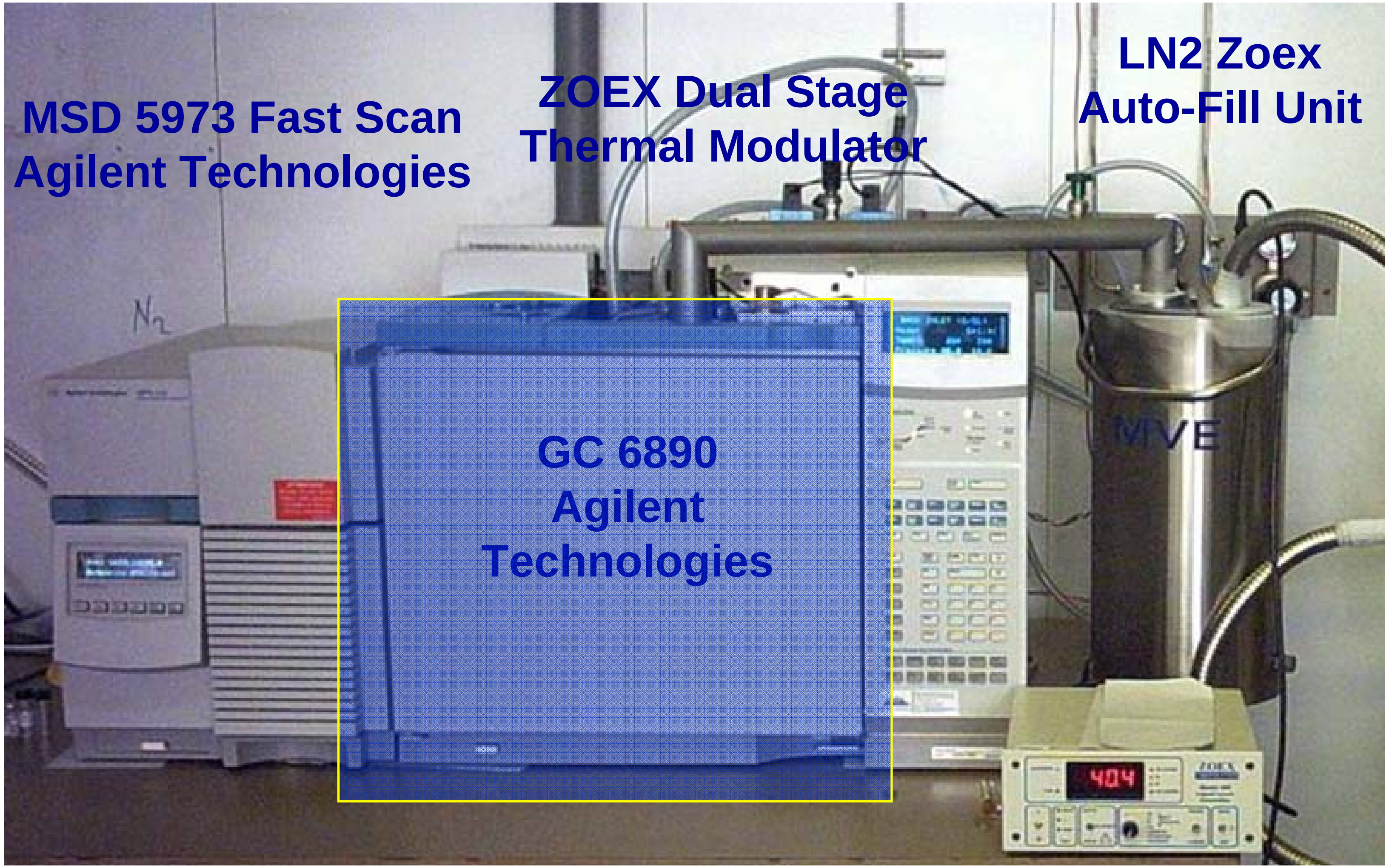
139 m/z

Carbazole GCxGC-MS spectrum

Development of one GCxGC method for petrochemical analysis



GCxGC-MSD System



MSD 5973 Fast Scan
Agilent Technologies

ZOEX Dual Stage
Thermal Modulator

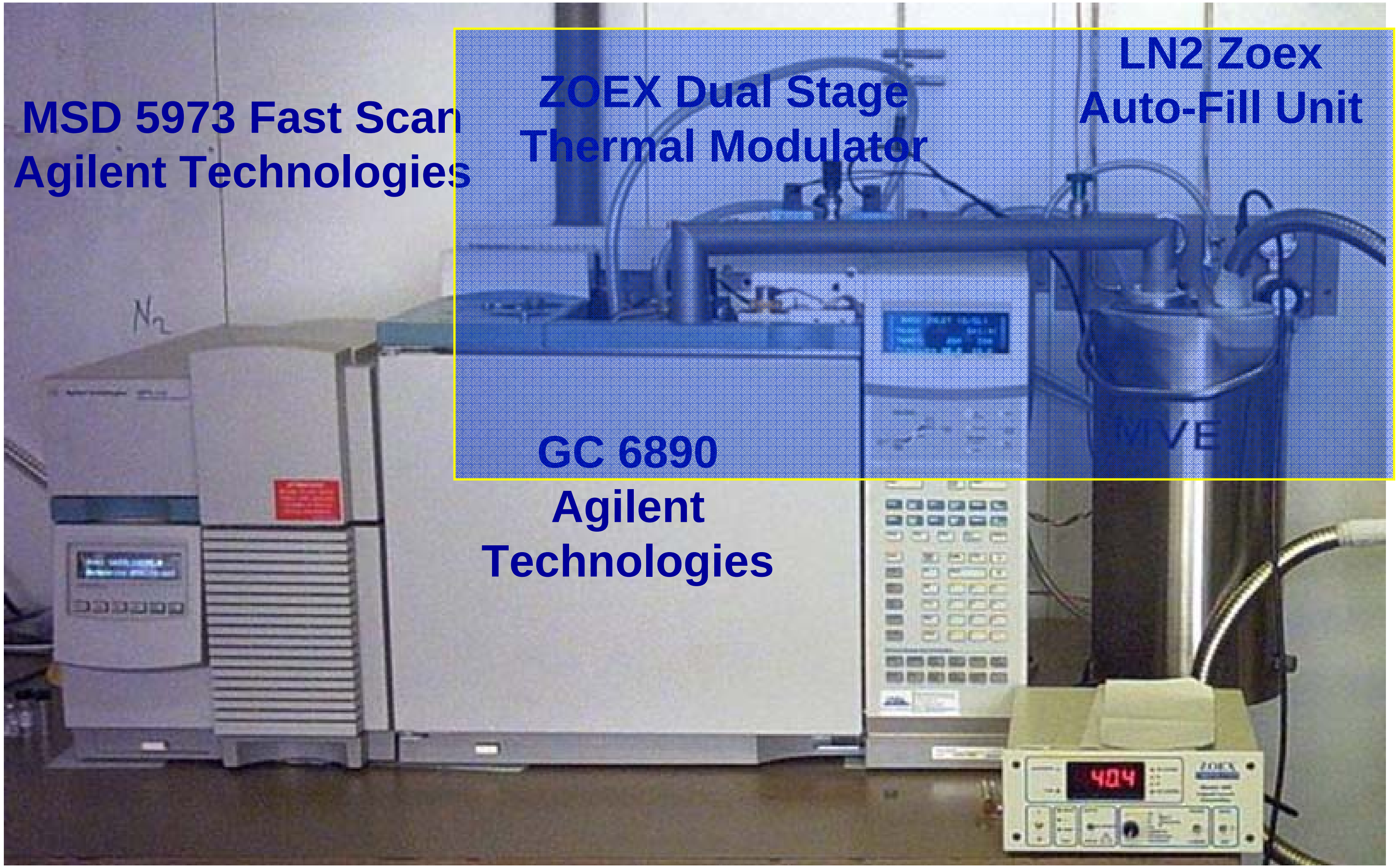
LN2 Zoex
Auto-Fill Unit

GC 6890
Agilent
Technologies

GC Agilent Technologies 6890N

- Injector Split/Splittless with EPC
- Split 1:100, carrier Helium
- Primary column: HP-5 MS (25m x 0.25mm ID, df=0.25μm)
- Secondary column: HP-WAX (0.7m x 0.1mm ID, df=0.1μm)
- Oven: 40°C x 0.5min, 1.5°C/min to 260°C, 260°C for 40 min (run time 187 min)
- Ramp Pressure: 20psi, 0.1psi/min to 25psi, 0.55psi/min to 55psi

GCxGC-MSD System



MSD 5973 Fast Scan
Agilent Technologies

ZOEX Dual Stage
Thermal Modulator

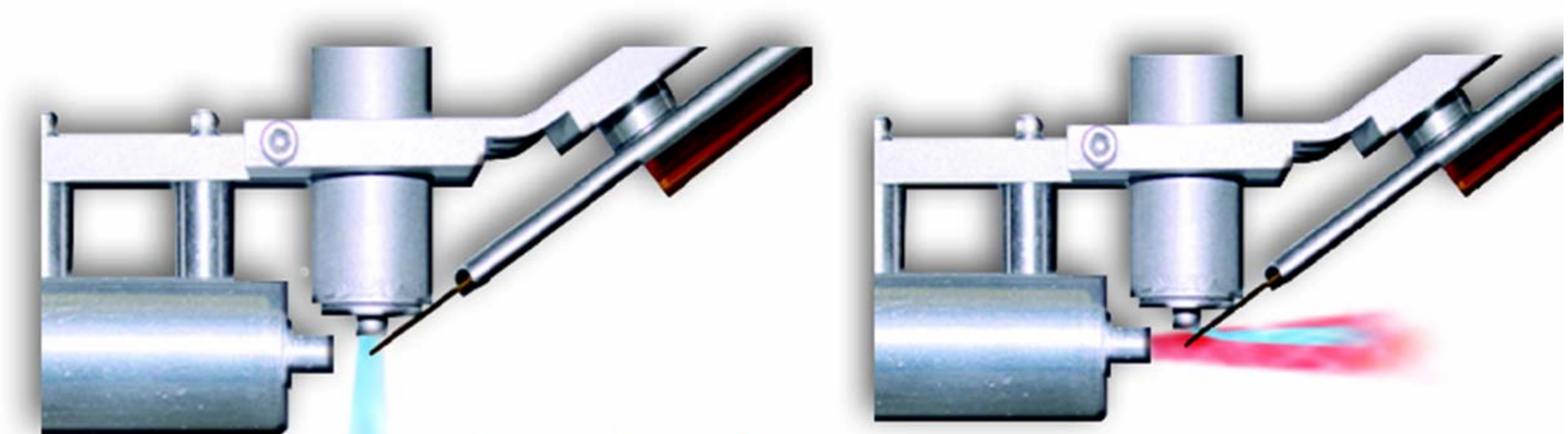
LN2 Zoex
Auto-Fill Unit

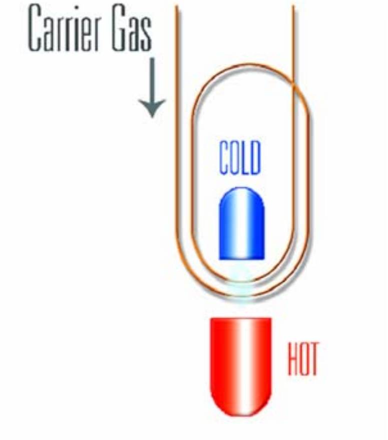
GC 6890
Agilent
Technologies

ZOEX dual stage thermal modulator

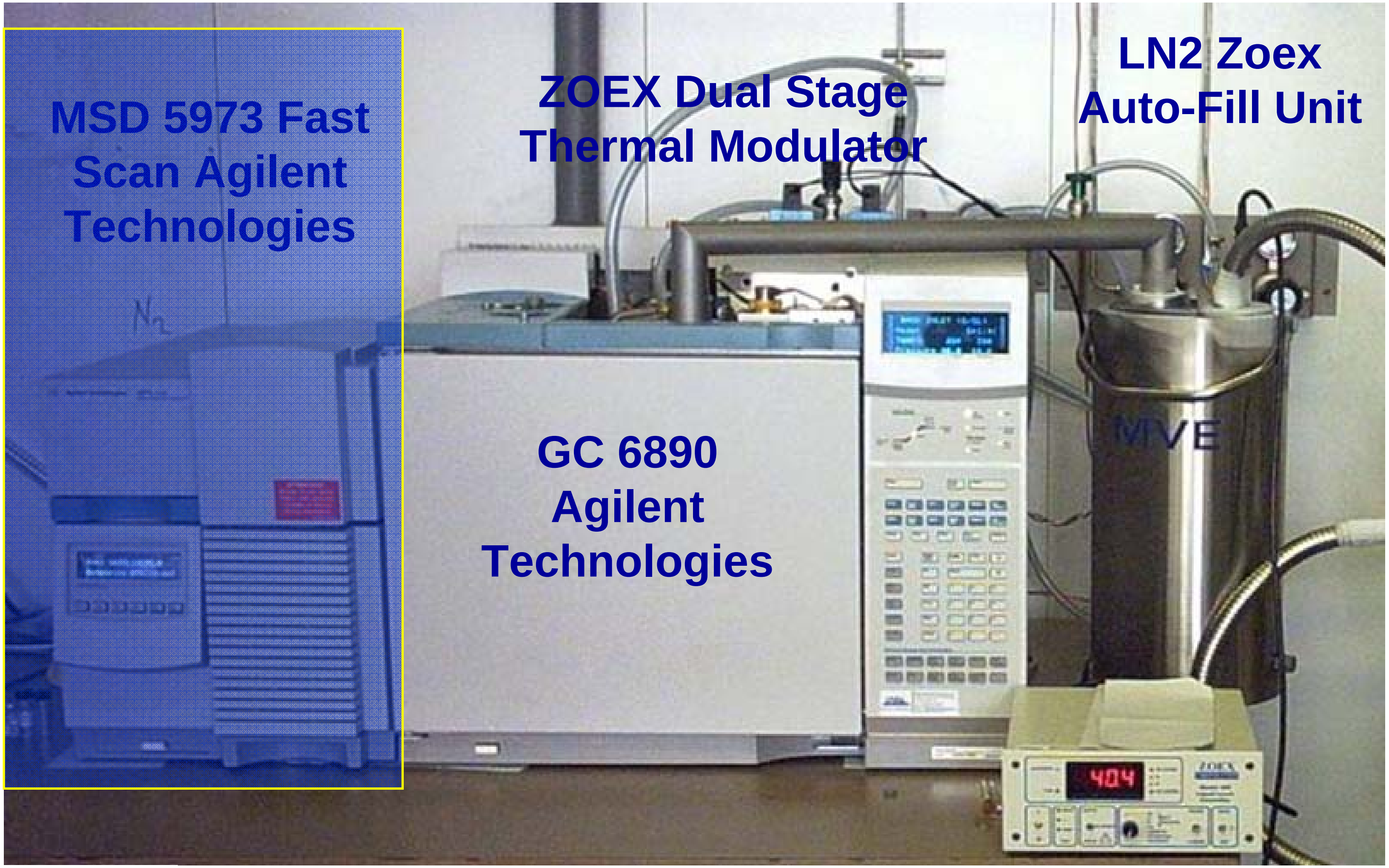
- KT-2004 Zoex Dual Stage Thermal Modulator
- LN2 Zoex Auto Fill Unit
- Zoex GC-Image Software
- Modulator Tube: uncoated fused silica tube 2mt X 0.1mmID
- Modulation period: 9 seconds
- Modulation duration: 450 msec
- Hot Jet Temperature: 350°C

ZOEX modulator operation





GCxGC-MSD System



MSD 5973 Fast Scan Agilent Technologies

- In order to maximize the spectral information, full-scan mass spectra acquisition mode (EI) was used
- MSD 5973 inert with Performance Electronics for Fast Scan Capabilities (10,000 amu/sec) and improved sensitivity
- Range 45-350 amu (19.80 scan/sec)
- MS Transfer line: uncoated fused silica tube (0.8m x 0.25mm ID, temperature 280°C)

Development of one GCxGC method for petrochemical analysis

How many variables in setting up a GCxGC method?

Columns choice (stationary phase and lenght)

Main oven temperature and/or secondary oven temperature

Column flow

Modulation period and duration

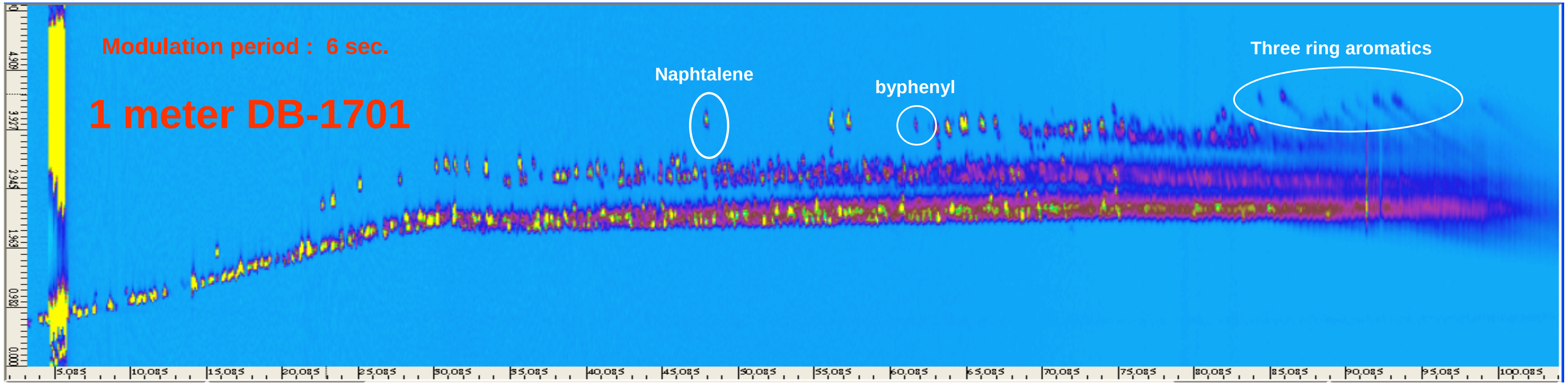
Cold and Hot jet flows

Simplify the user operation maintaining fixed the conditions for all type of compounds in oil-derivatives

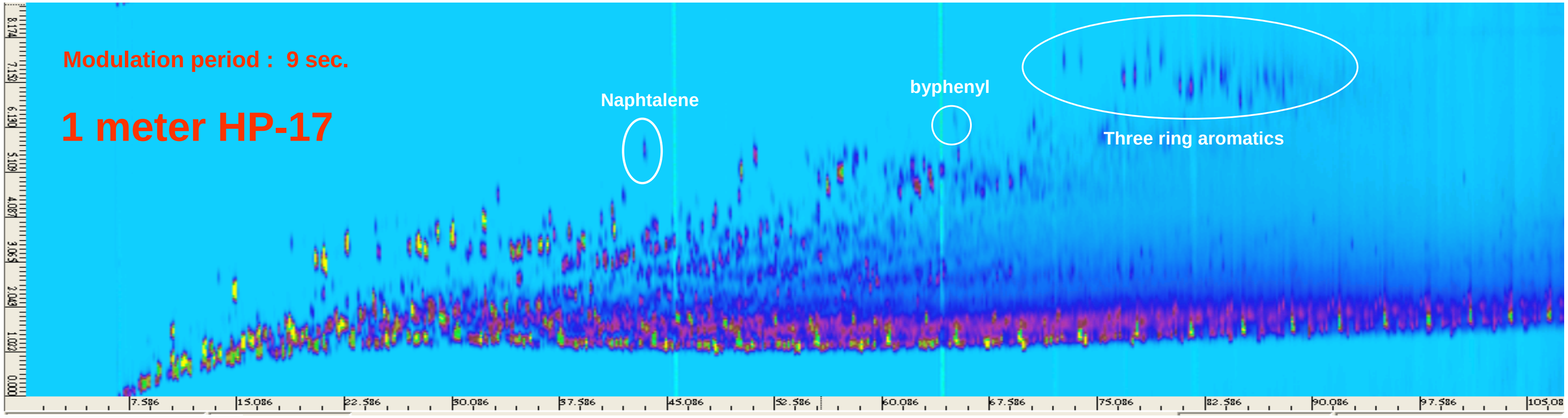
Column choice

- Column combination to maximize GCxGC potentiality: the most “bi-dimensional” stationary phases must be used
  - Primary column: apolar
  - Secondary column: polar
- Separate wide variety of hydrocarbon compounds (saturate/insaturate, light up to heavy aromatics and heteroatom compounds)
- Which stationary phase and column lenght?
- Wax : polyethylene glycol
- DB-1701: 14% cyanopropyl-phenyl, 86% dimethylpolysiloxane
- HP-17: 50% phenyl, 50% dimethylpolysiloxane

Secondary column 1 mt x 0.1 mmID x 0.1 um DB-1701
Oven: 35°Cx0min, incr. 2°C/min to 300°C for 10 min
No secondary oven



Secondary column 1 mt x 0.1 mmID x 0.1 um HP-17
Oven: 40°Cx0.5min, incr. 2°C/min to 300°C for 10 min
No secondary oven



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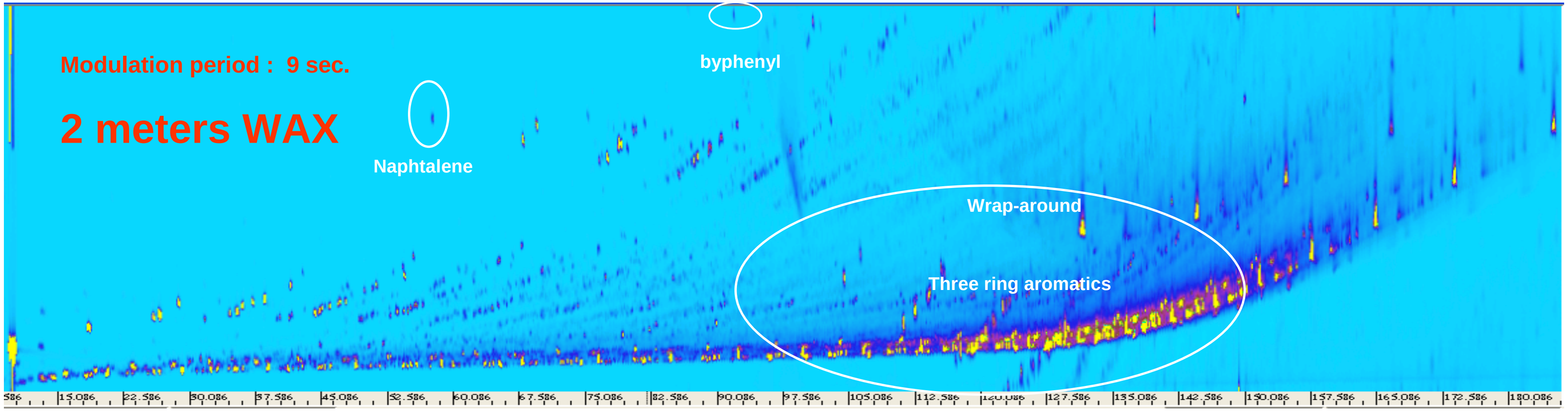
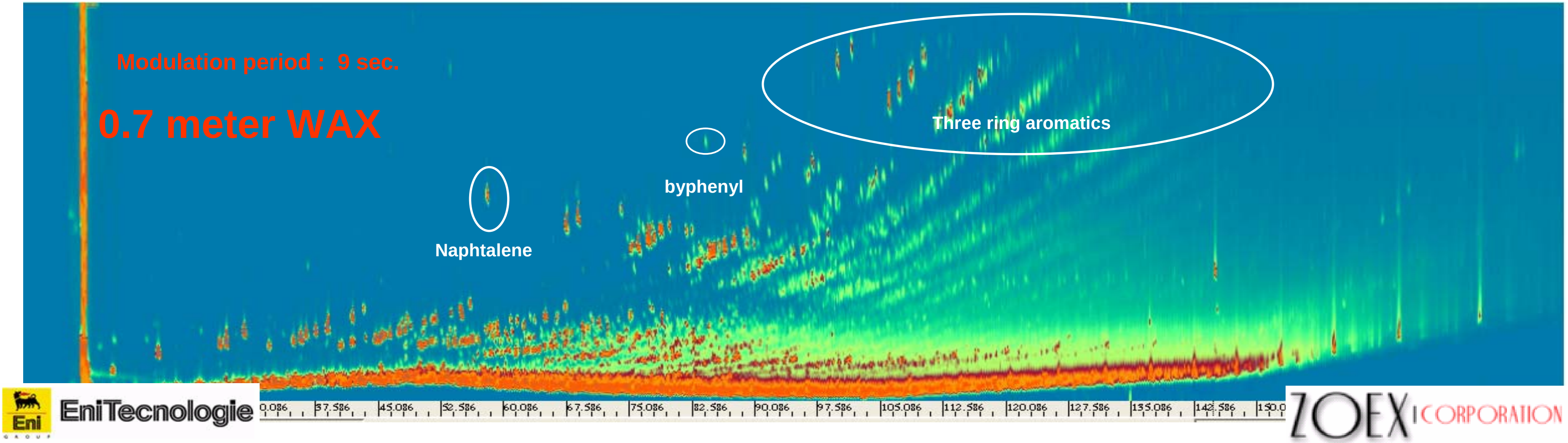
Secondary column <u>2 mt x 0.1 mmID x 0.1 um WAX</u>
Oven: 40°Cx0.5min, incr. 0.5°C/min to 260°C for 40 min
<u>Secondary Oven</u>: 30°C above main oven



Secondary column <u>1 mt x 0.1 mmID x 0.1 um WAX</u>
Oven: 40°Cx0.5min, incr. 0.5°C/min to 260°C for 40 min
<u>Secondary Oven</u>: 30°C above main oven



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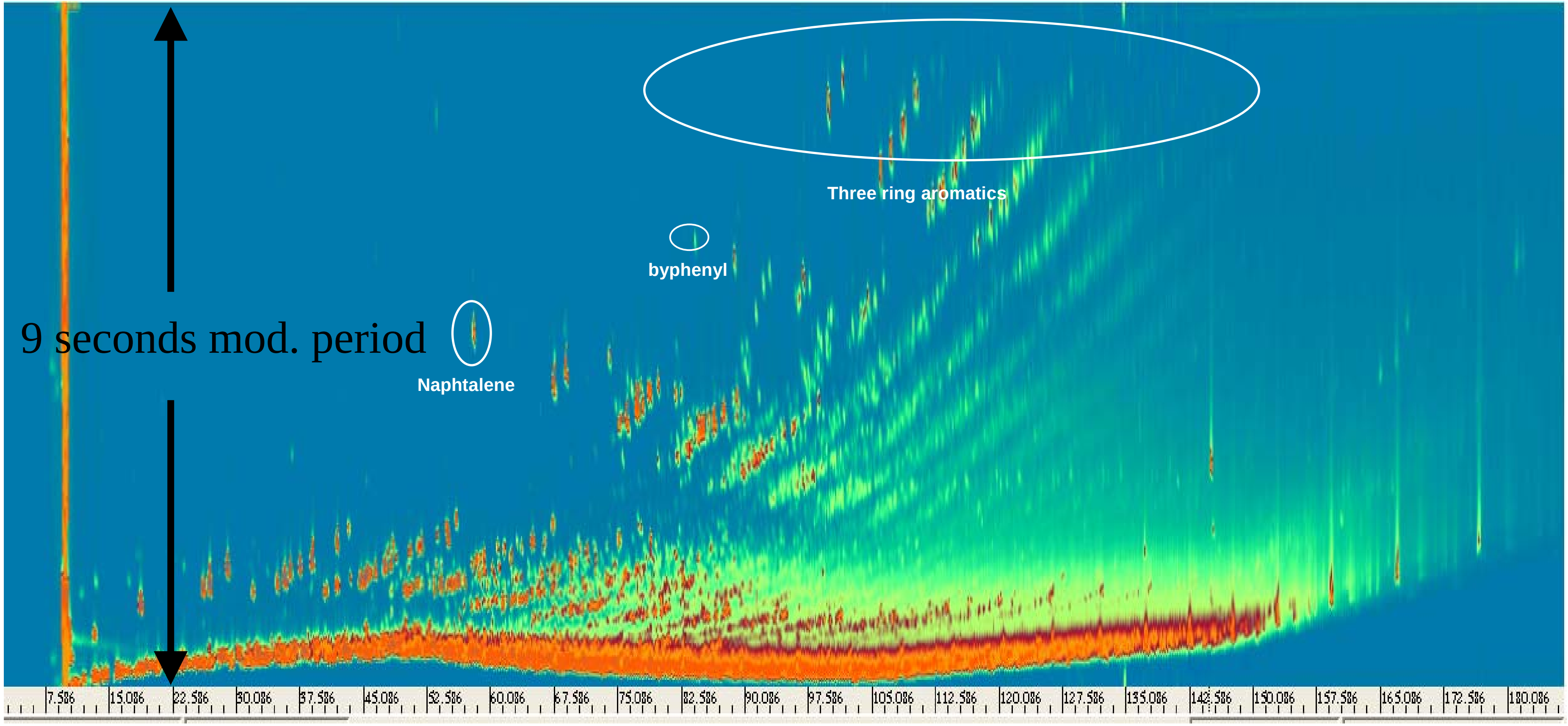
Modulation period

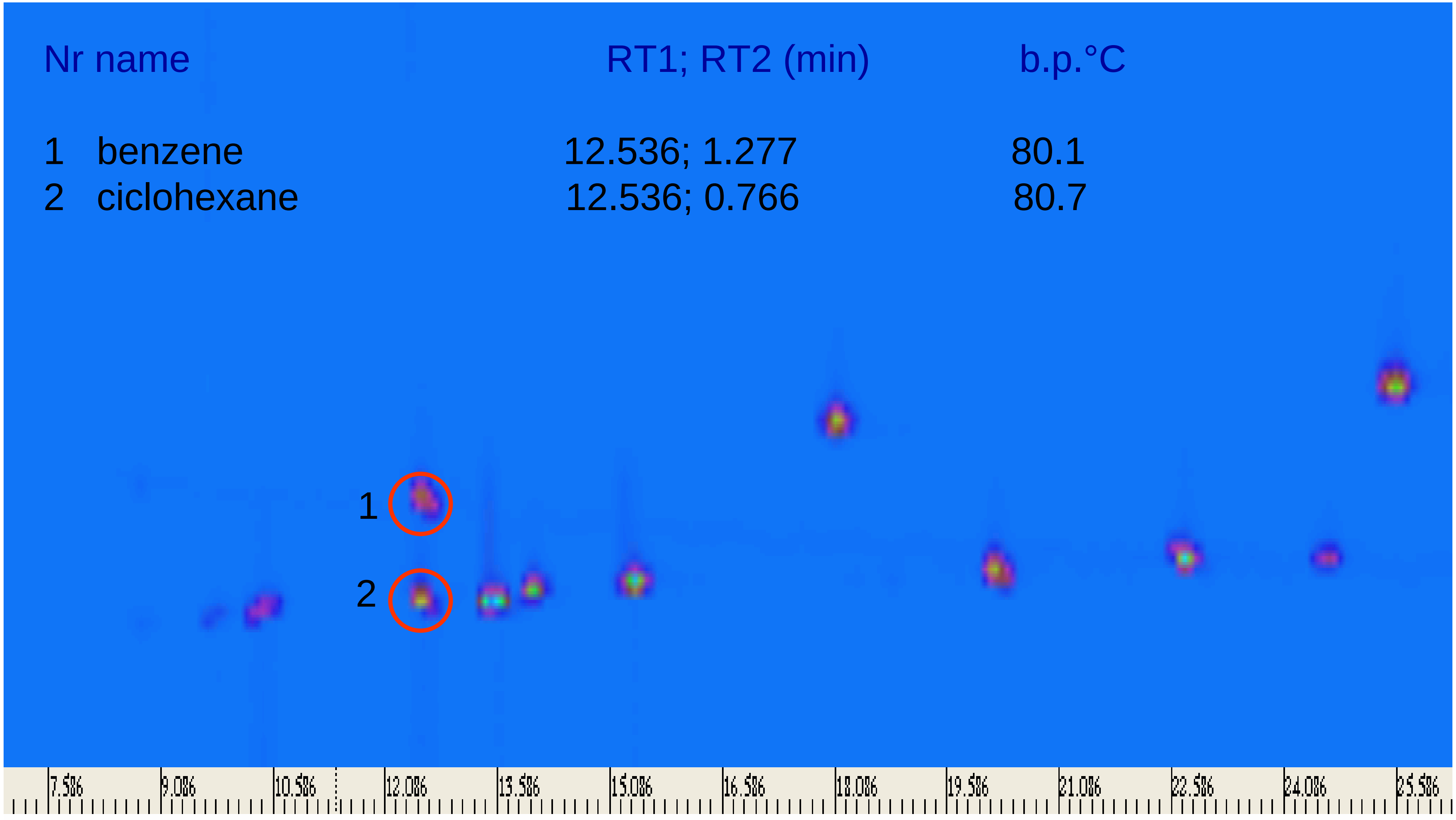
- Large enough to permit the elution of all the components from the secondary column (y- axis, separation by polarity)
- Should be tuned to collect at least three fraction of the eluting primary column peaks (high modulation period values require wide primary column peaks)

Modulation period



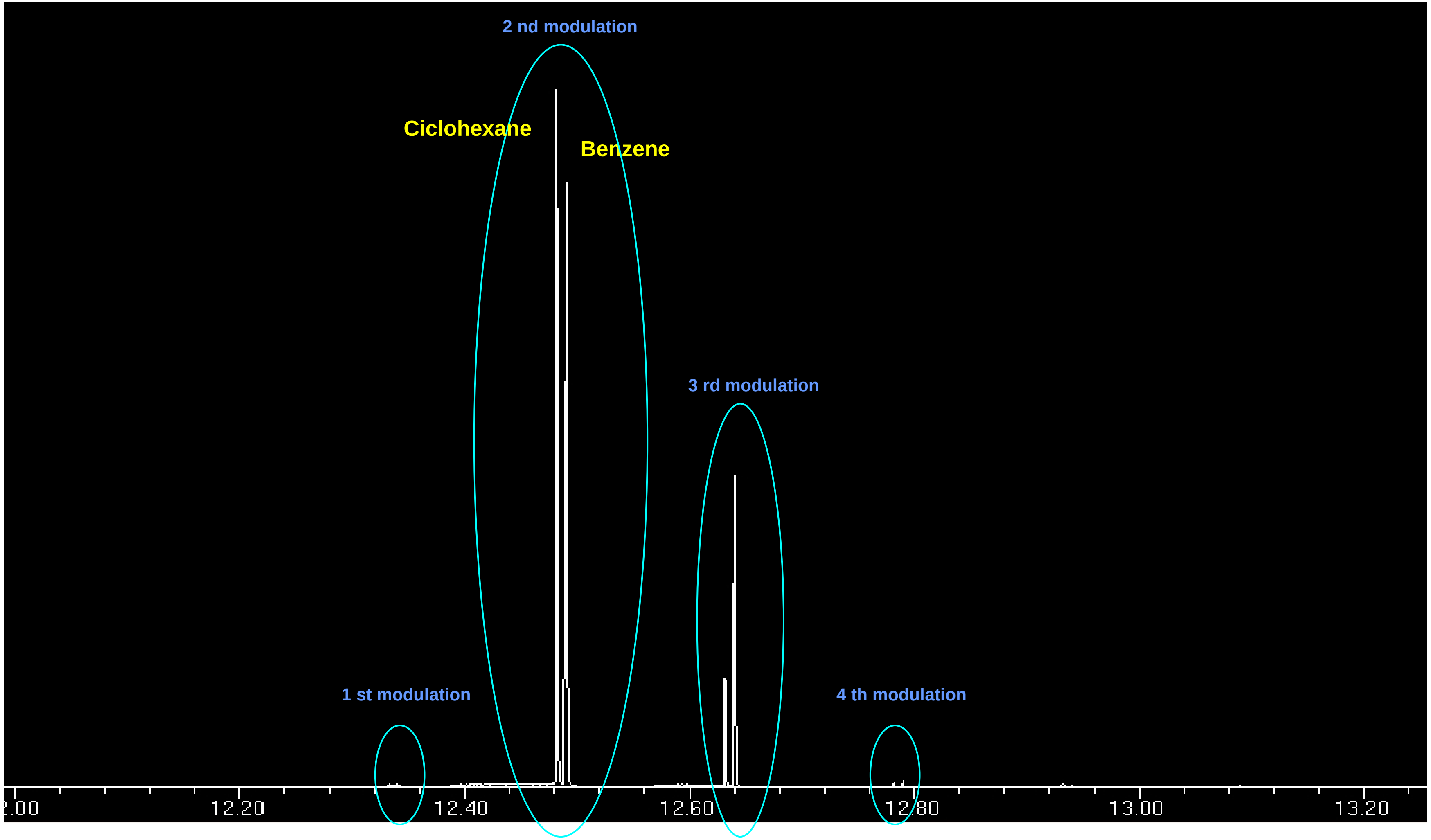
9 seconds mod. period

Modulation period



Nr	name	RT1; RT2 (min)	b.p.°C
1	benzene	12.536; 1.277	80.1
2	ciclohexane	12.536; 0.766	80.7

Modulation period



Conclusions

- The GCxGC-qMSD showed to be a powerful tool in light petroleum fraction investigation. Its use allows the separation and identification of different polarity hydrocarbons (aromatic vs aliphatic) together with unique identification of heteroatom compounds, with a single sample run and without changing any analytical set up and parameters.

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Thank you for your attention