LCT

Processes for the future

Detailed Crude Oil Analysis:

GC×GC, Field Ionization Mass Spectrometry and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Join Forces

Prof. Kevin Van Geem

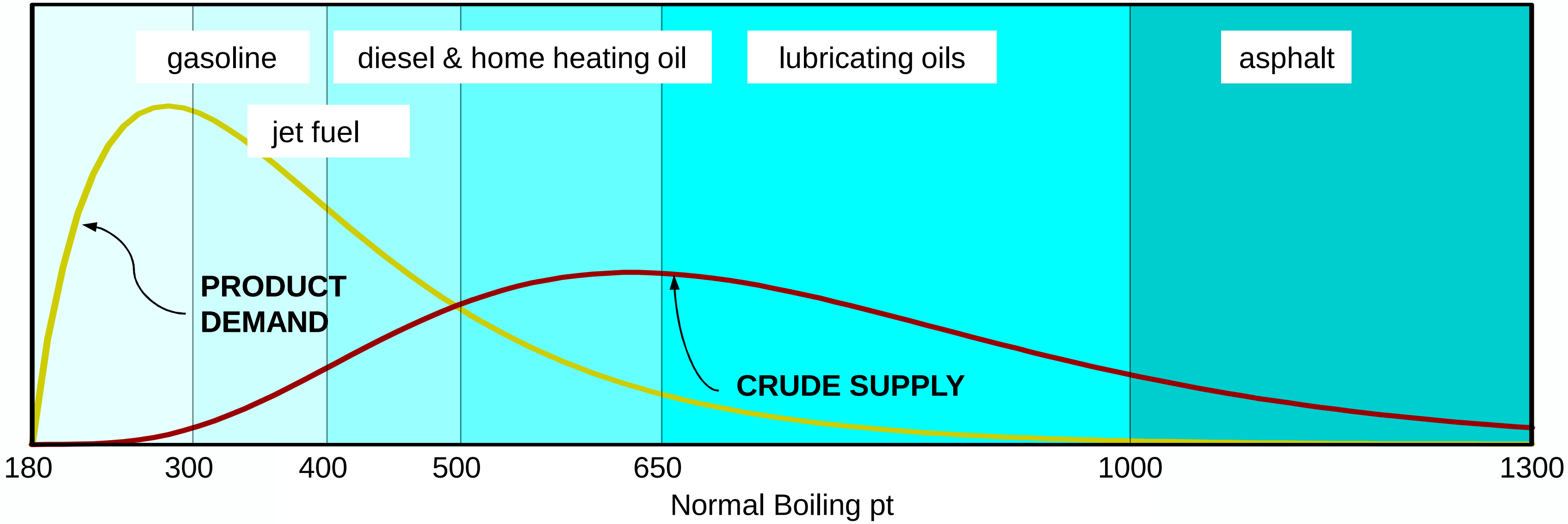
Outline

- Molecule driven process optimization
- GC-FIMS
- Comprehensive 2D GC analysis using FID/SCD/NCD/TOF-MS
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Conclusions

Outline

- Molecule driven process optimization
- GC-FIMS
- Comprehensive 2D GC analysis using FID/SCD/NCD/TOF-MS
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Conclusions

Petroleum as a Mixture of Chemicals



paraffins

naphthenes

benzenes

benzo-thiophenes

naphthalenes

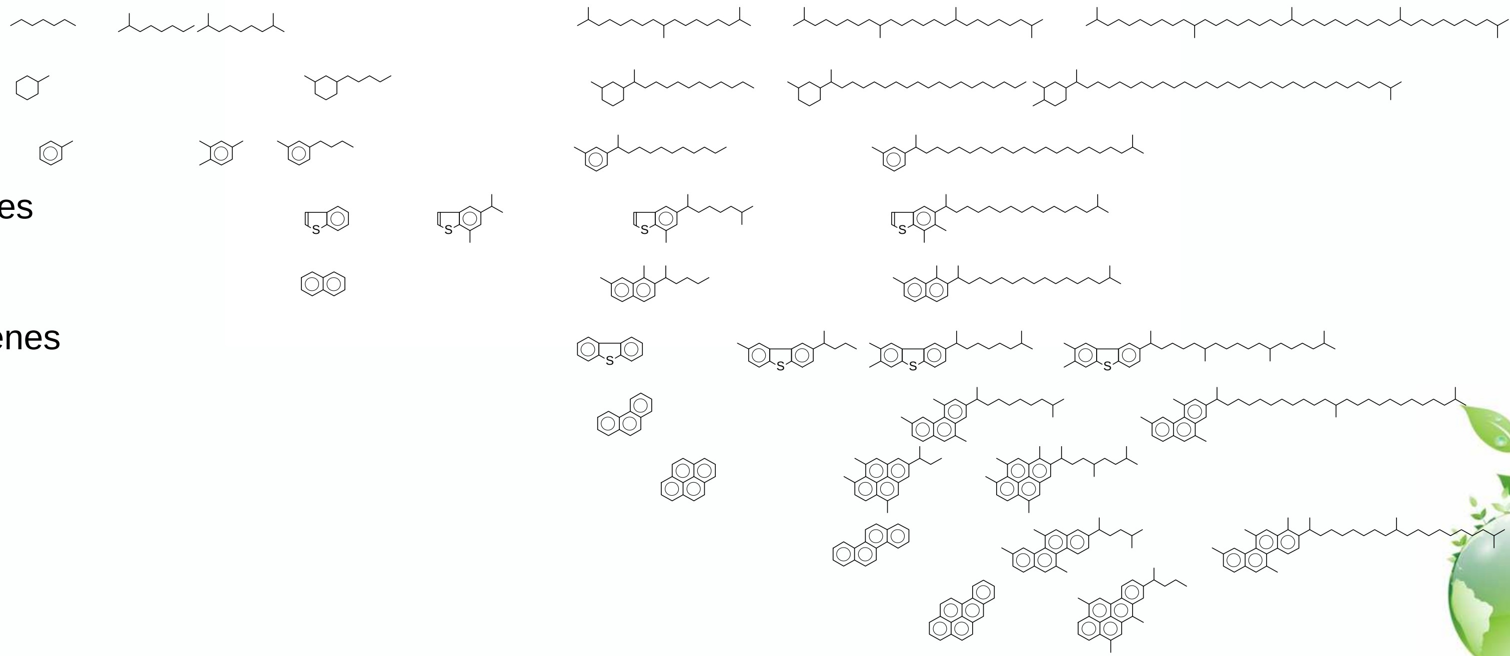
di-benzothiophenes

phenanthrenes

pyrenes

chrysenes

benzo-pyrenes



Molecule driven process optimization

Compositional information = crucial petroleum/petrochemical industry

Key is knowing the molecules:
- What they are
- Their performance
- Product impact
- Properties

Requirements:
- Characterization
- Detailed process models
- Business decision making

Blending & Schedulling

Real Time Optimization

Planning

Raw material Valuation

Molecule driven process optimization

Compositional information = crucial petroleum/petrochemical industry

Key is knowing the molecules:
- What they are
- Their performance
- Product impact
- Properties

Requirements:
- Characterization
- Detailed process models
- Business decision making

Blending & Schedulling

Real Time Optimization

Planning

Raw material Valuation

Molecule based management

Fluctuating and unpredictable oil market

- In 2014

Fluctuating and unpredictable oil market

- In 2016

What happened?

Bloomberg, 2016

Outline

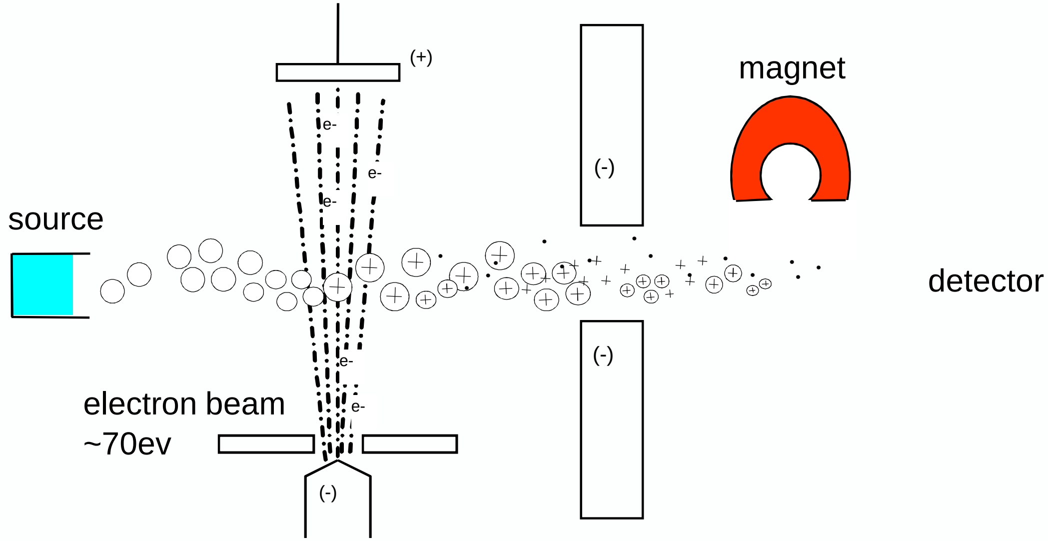
- Molecule driven process optimization
- GC-FIMS
- Comprehensive 2D GC analysis using FID/SCD/NCD/TOF-MS
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Conclusions

Dealing with Petroleum Complexity:

Organize **Composition** by homologous series

ELECTRON IMPACT IONIZATION mass spec

available ca. 1955

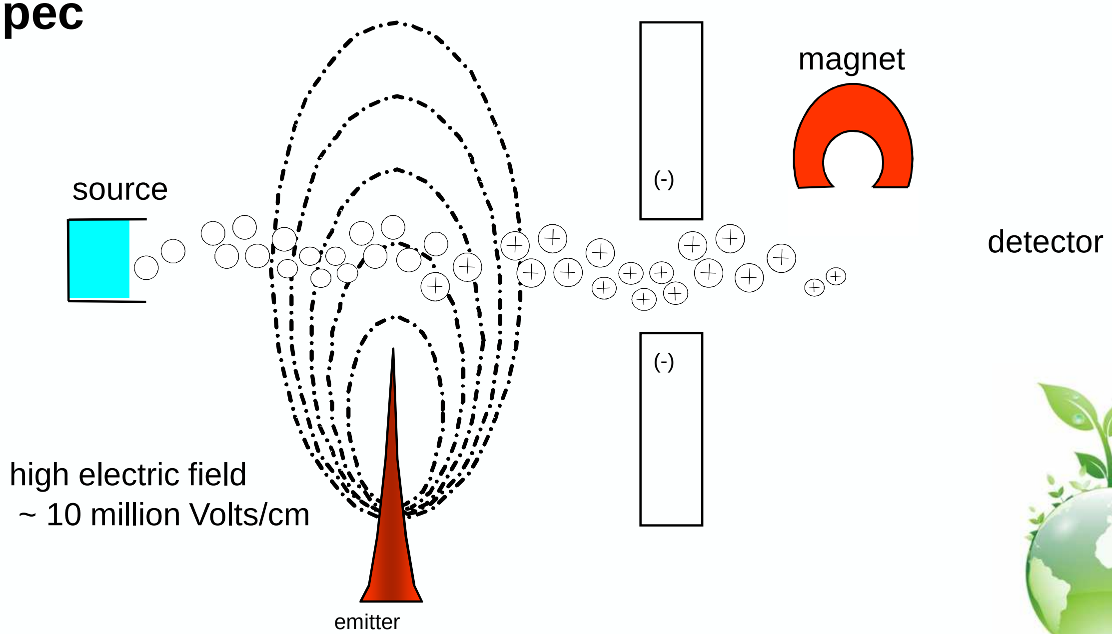


FI produces dominant molecular ions with little or no fragmentation

FIELD IONIZATION mass spec

available ca. 1985

As the gas molecules pass near the emitter, they are ionized by electron tunneling.



FI

Benefits

- simple mass spectra, typically one molecular or molecular-like ionic species per compound.
- FI is the only ionization method that can ionize both saturates and aromatics without fragmentation.
- little or no chemical background
- works well for small organic molecules and some petrochemical fractions

Limitations

- The sample must be thermally volatile. Samples are introduced in the same way as for electron ionization (EI)

Mass range

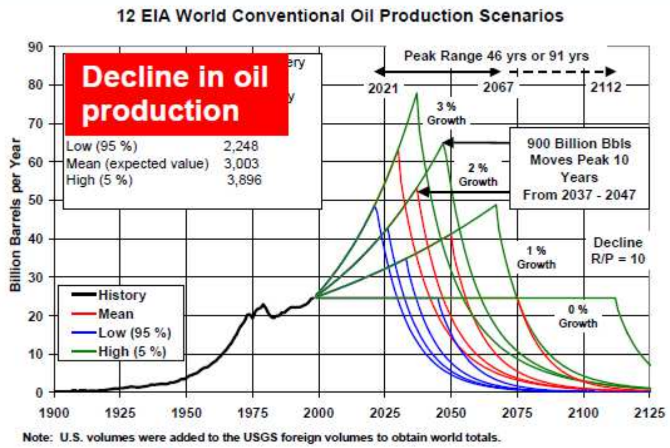
- Typically less than 1000 D

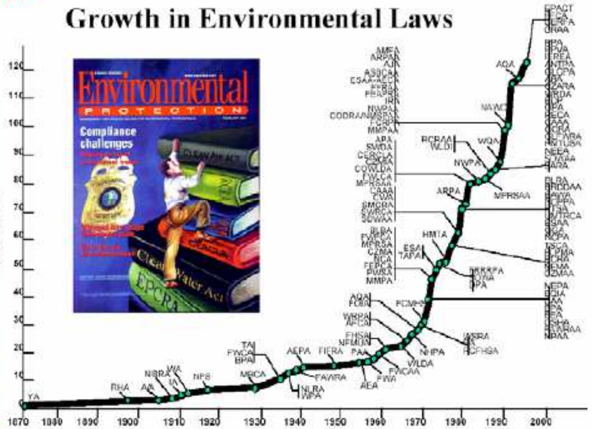
Outline

- Molecule driven process optimization
- GC-FIMS and SFC FI-TOF MS
- Comprehensive 2D GC analysis using FID/SCD/NCD/TOF-MS
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Conclusions

Issues of concern for the chemical industry

- Energy and availability of resources
- Material efficiency
- Safety
- Cost competitiveness
- Environment
- Public image





Main drivers

- Reserves of sweet crude oils are declining
- Reduction of CO_2 emissions
- Alternative sources
- Political and policy changes

Our drivers

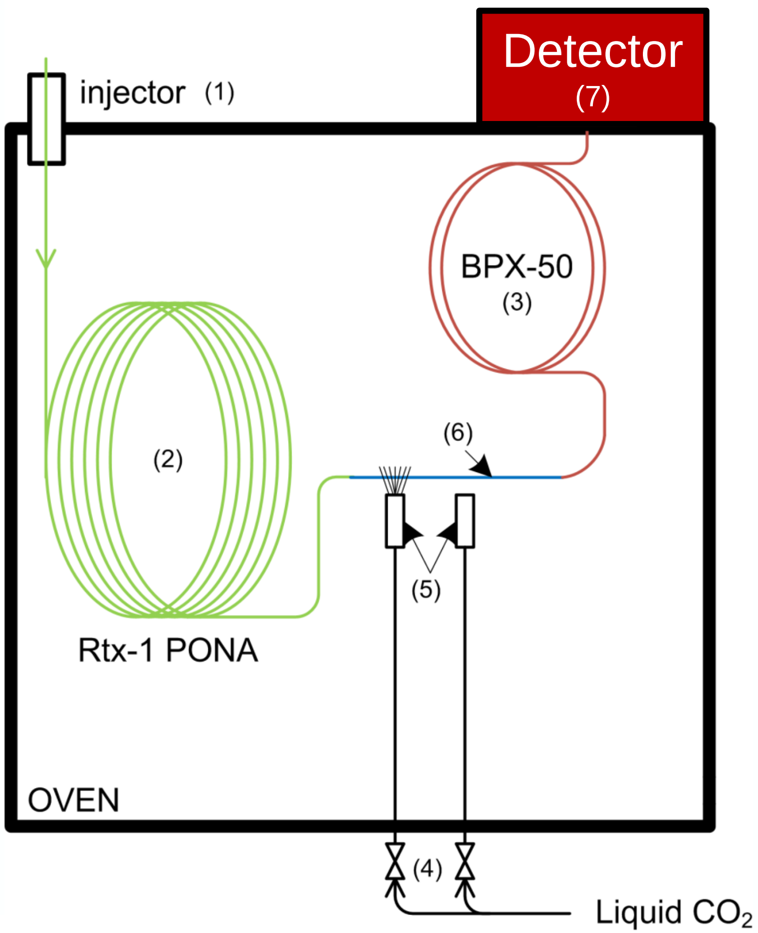
- Efficiency

- Speed-up of development

- More detail and need for advanced models

- Atom efficiency and sustainable production

GC × GC (1)

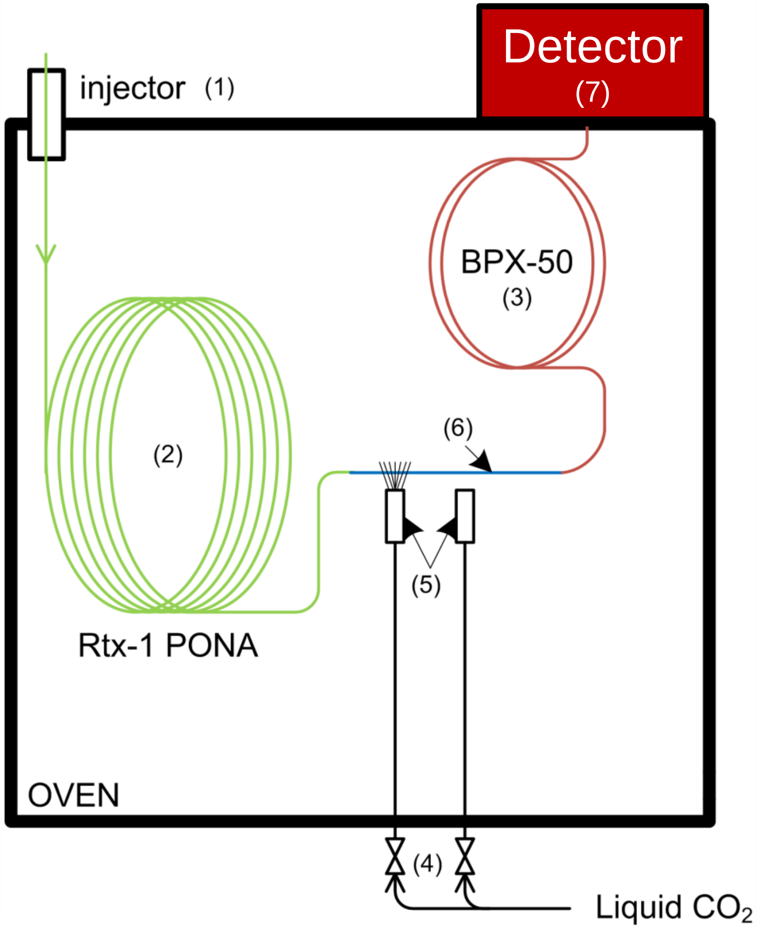


1. Injector
   - Split/Splitless injector
   - Cold-on column injector
   - PTV injector
   - Online Split/Splitless injector

2. 1st dimension column
   - Apolar column (normal phase)
   - Polar column (reverse phase)

3. 2nd dimension column
   - Medium polar column (normal phase)
   - Apolar or medium polar column (reverse phase)

GC × GC (2)



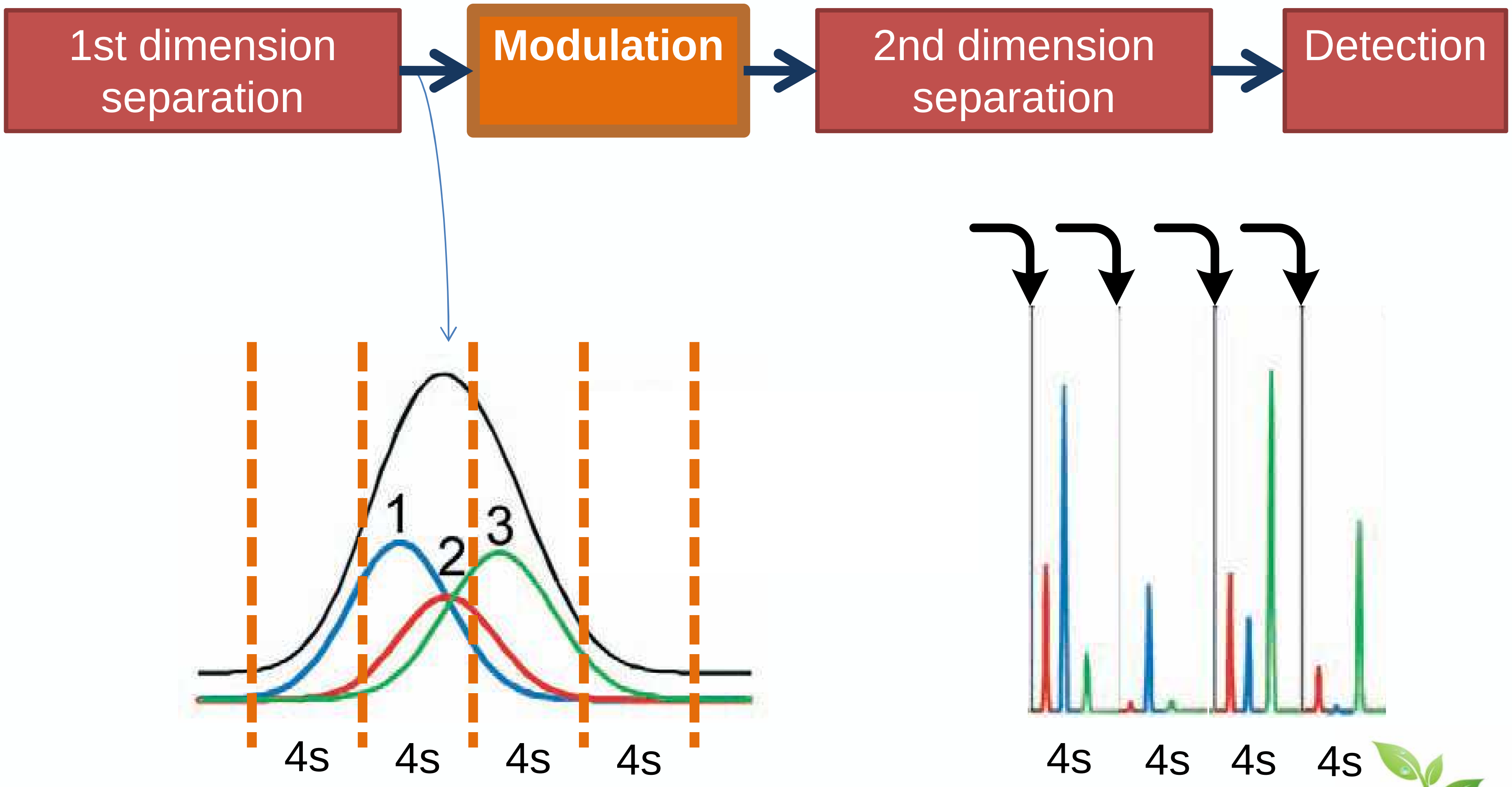
4. Cryo valves for modulator

5. Modulator

6. Piece of deactivated column

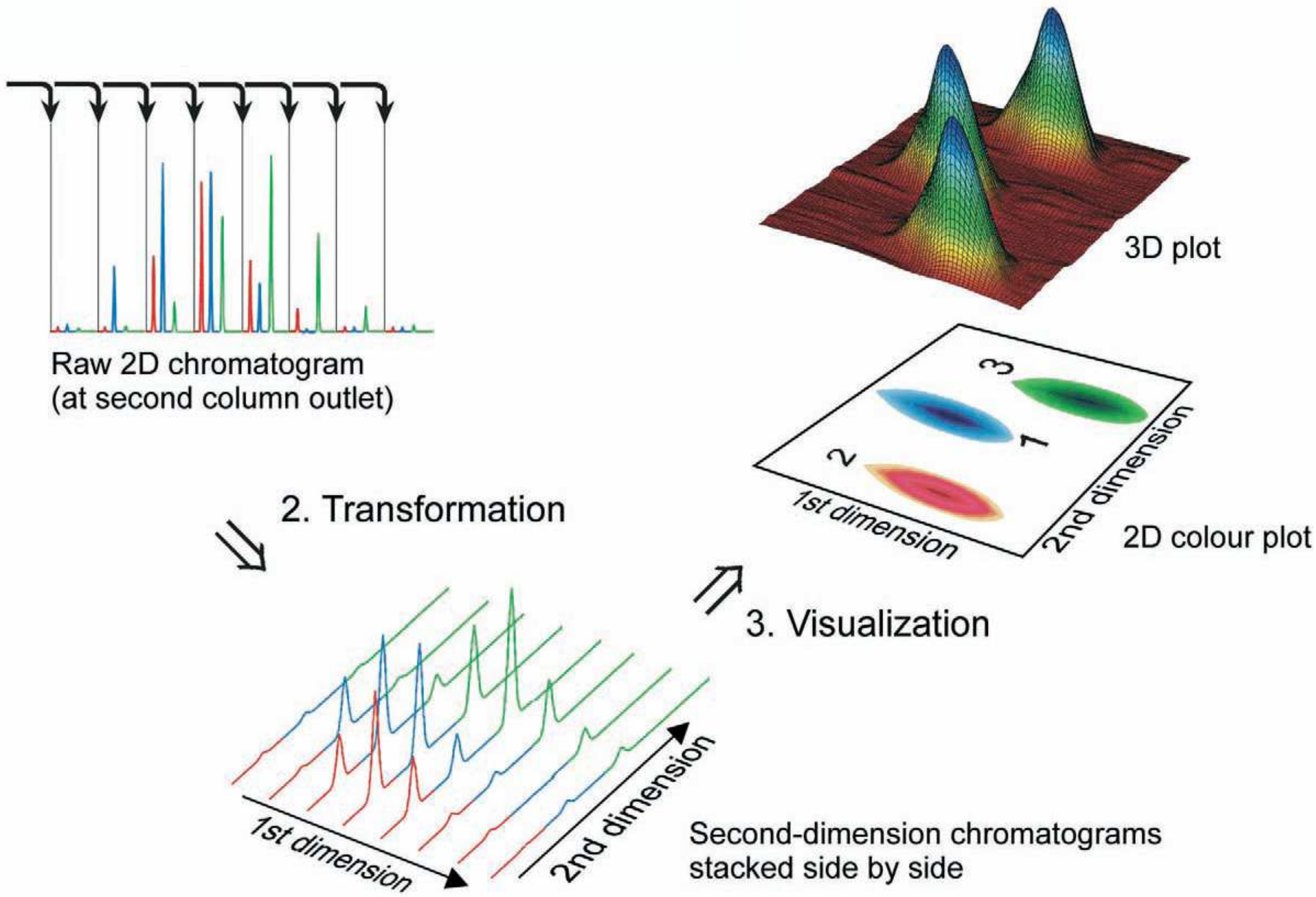
7. Detector
   - Flame ionization detector (FID)
     = universal and quantitative
   - Sulfur chemiluminescence detector (SCD)
     = Sulfur selective and quantitative
   - Nitrogen chemiluminescence detector (NCD)
     = Nitrogen selective and quantitative
   - TOF-MS
     = universal and mainly qualitative but also quantitative analysis are possible (but difficult)

GC × GC modulation



✓ Enhanced Resolution
✓ Enhanced Signal/Noise Ratio

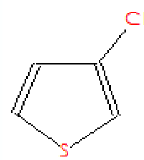
GC × GC data processing



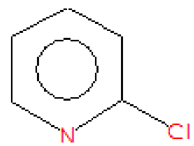
Dallüge et al., *J. Chrom. A* 2003

GC×GC analyses methodology

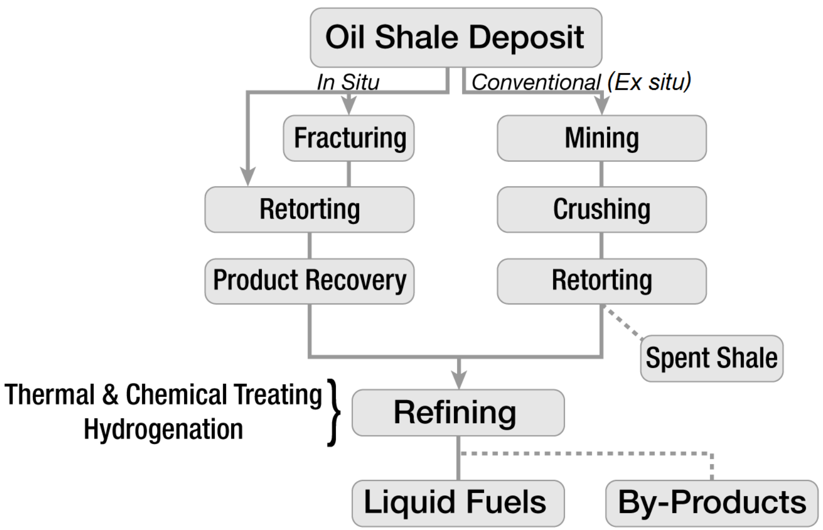
- Quantitative characterization via GC×GC-NCD/SCD with internal standards
- Internal standards (IS):
  - Not being a part of the sample itself
  - Not overlapping with other N- or S-compounds present in the pyrolysis oil
  - S-compounds quantification: 3-chlorothiophene

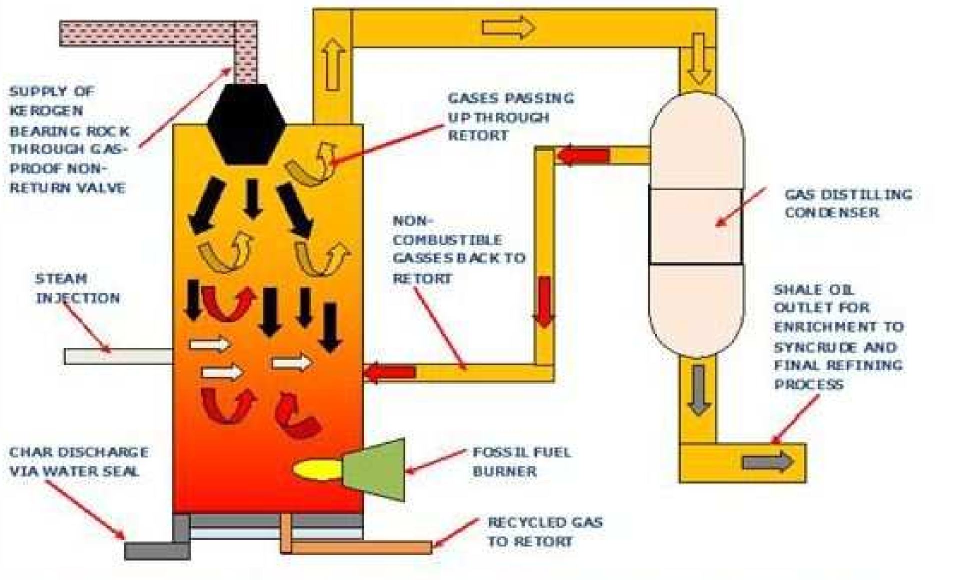


  - N-compounds quantification: 2-chloropyridine

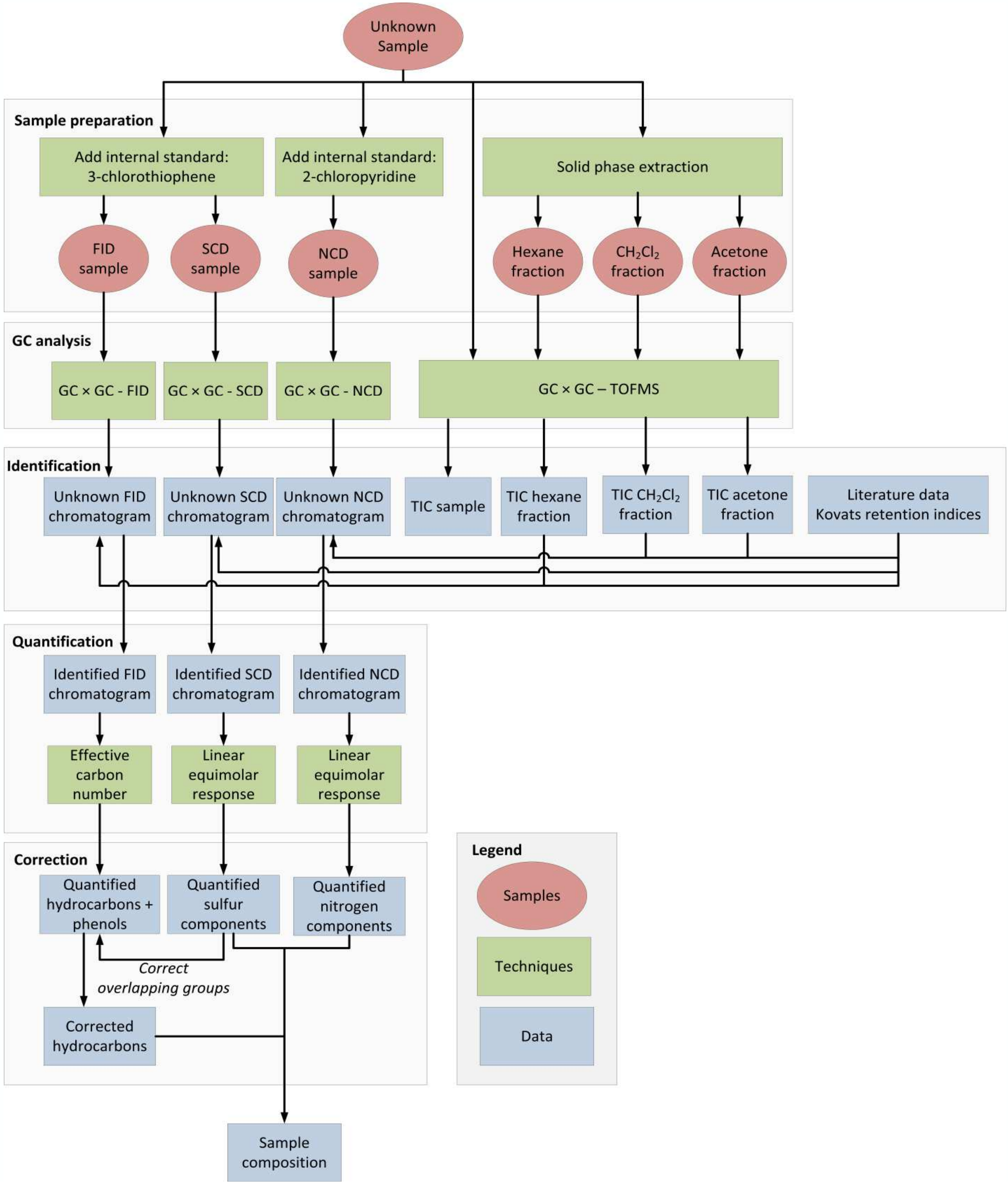


Shale oil analyisis



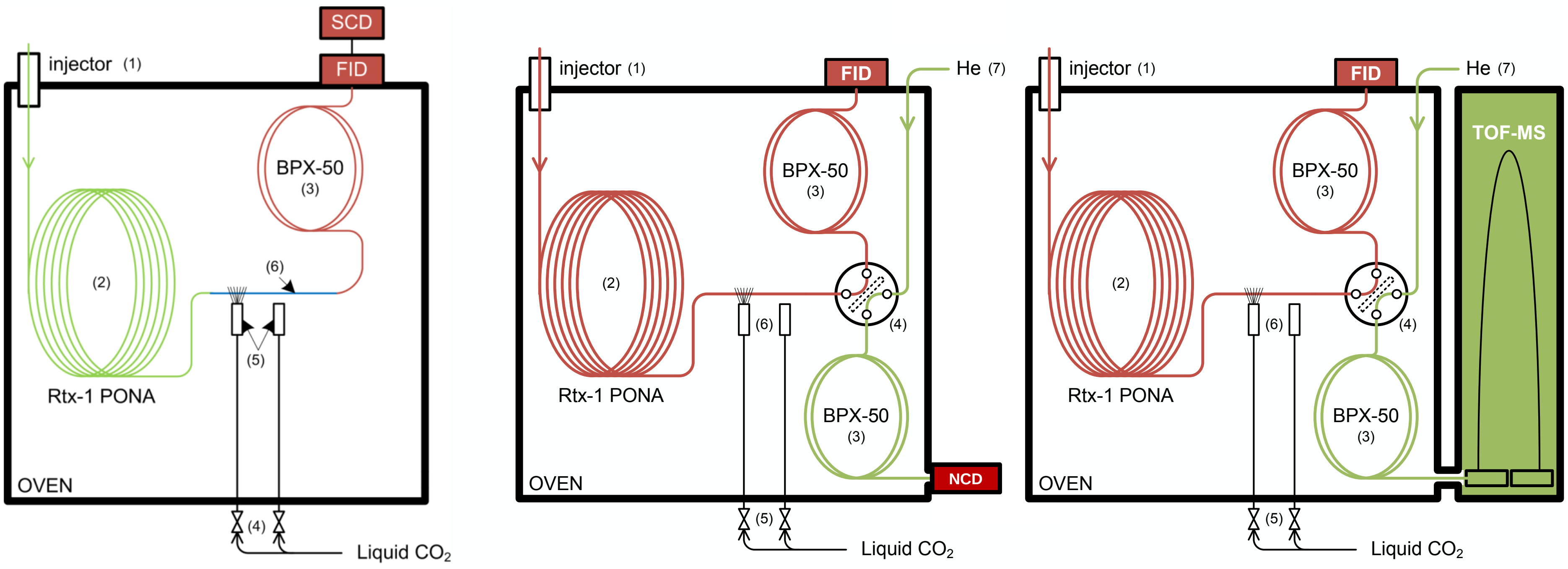


BASIC KIVITER TYPE PYROLYSIS RETORT PRODUCING 40T/hr OF SHALE OIL FROM KEROGEN BEARING ROCK
Drawn by Willie Scott 13/04/2010



Unknown Sample
Sample preparation
Add internal standard: 3-chlorothiophene
Add internal standard: 2-chloropyridine
Solid phase extraction
FID sample
SCD sample
NCD sample
Hexane fraction
CH_2Cl_2 fraction
Acetone fraction
GC analysis
GC × GC - FID
GC × GC - SCD
GC × GC - NCD
GC × GC – TOFMS
Identification
Unknown FID chromatogram
Unknown SCD chromatogram
Unknown NCD chromatogram
TIC sample
TIC hexane fraction
TIC CH_2Cl_2 fraction
TIC acetone fraction
Literature data Kovats retention indices
Quantification
Identified FID chromatogram
Identified SCD chromatogram
Identified NCD chromatogram
Effective carbon number
Linear equimolar response
Linear equimolar response
Correction
Quantified hydrocarbons + phenols
Quantified sulfur components
Quantified nitrogen components
Correct overlapping groups
Corrected hydrocarbons
Sample composition
Legend
Samples
Techniques
Data

GC × GC setups



Combination of 3 devices

Correction method

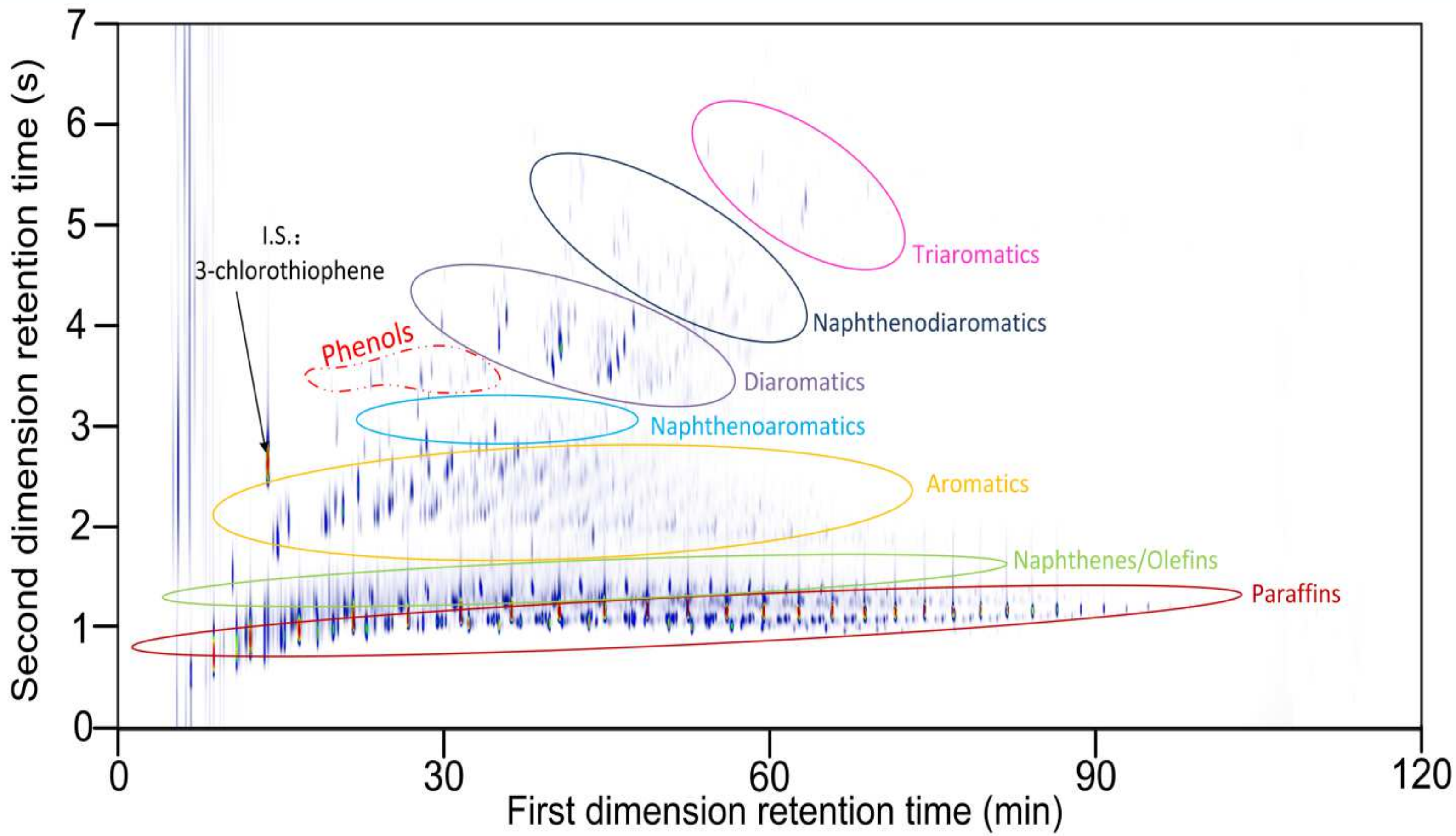
S and N compounds are visible on the FID

⇒ Bias in the prediction of the hydrocarbons

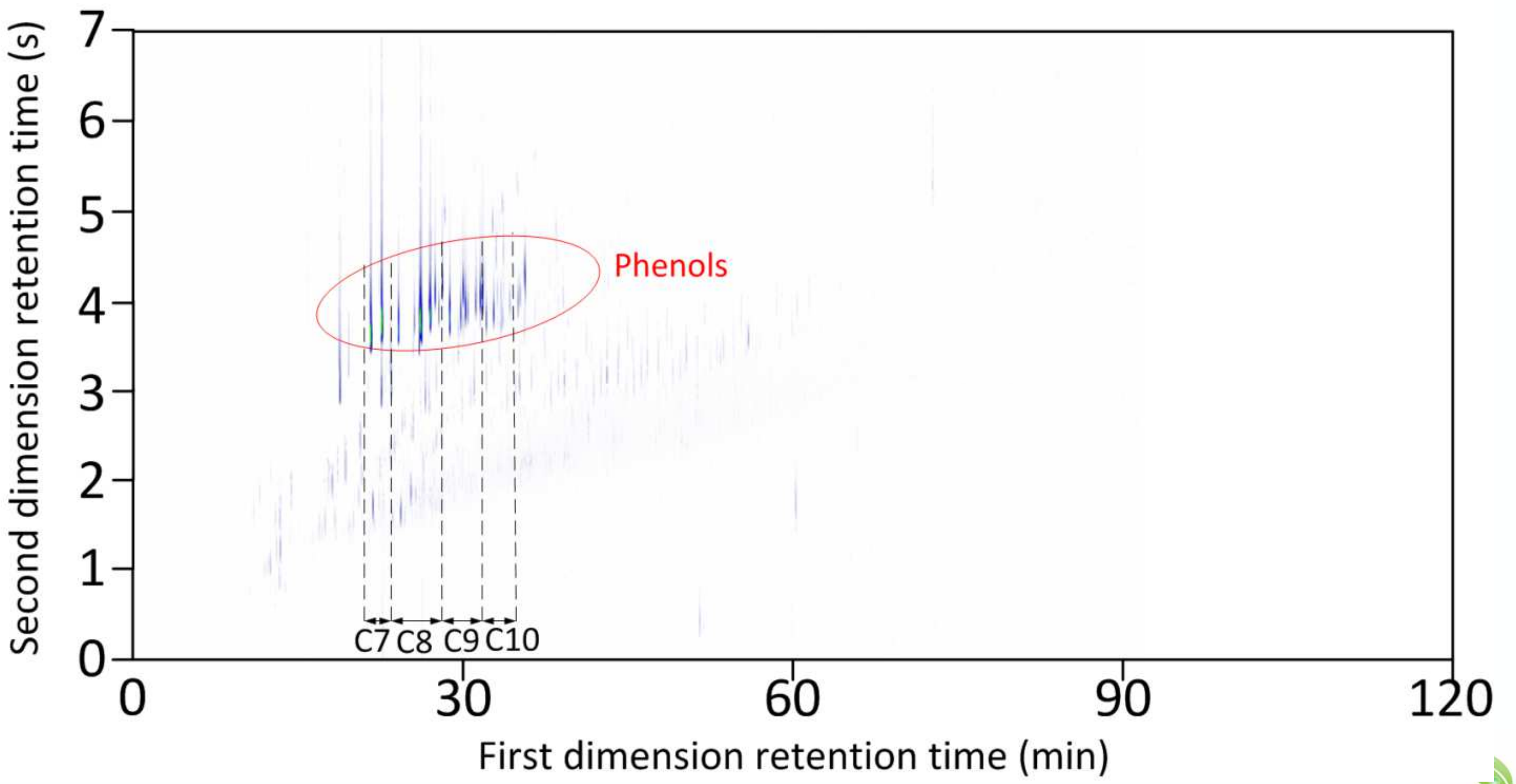
⇒ Need for a correction procedure

⇒ GC × GC allows to define overlapping groups and a correction procedure can be derived

GC × GC – FID chromatogram

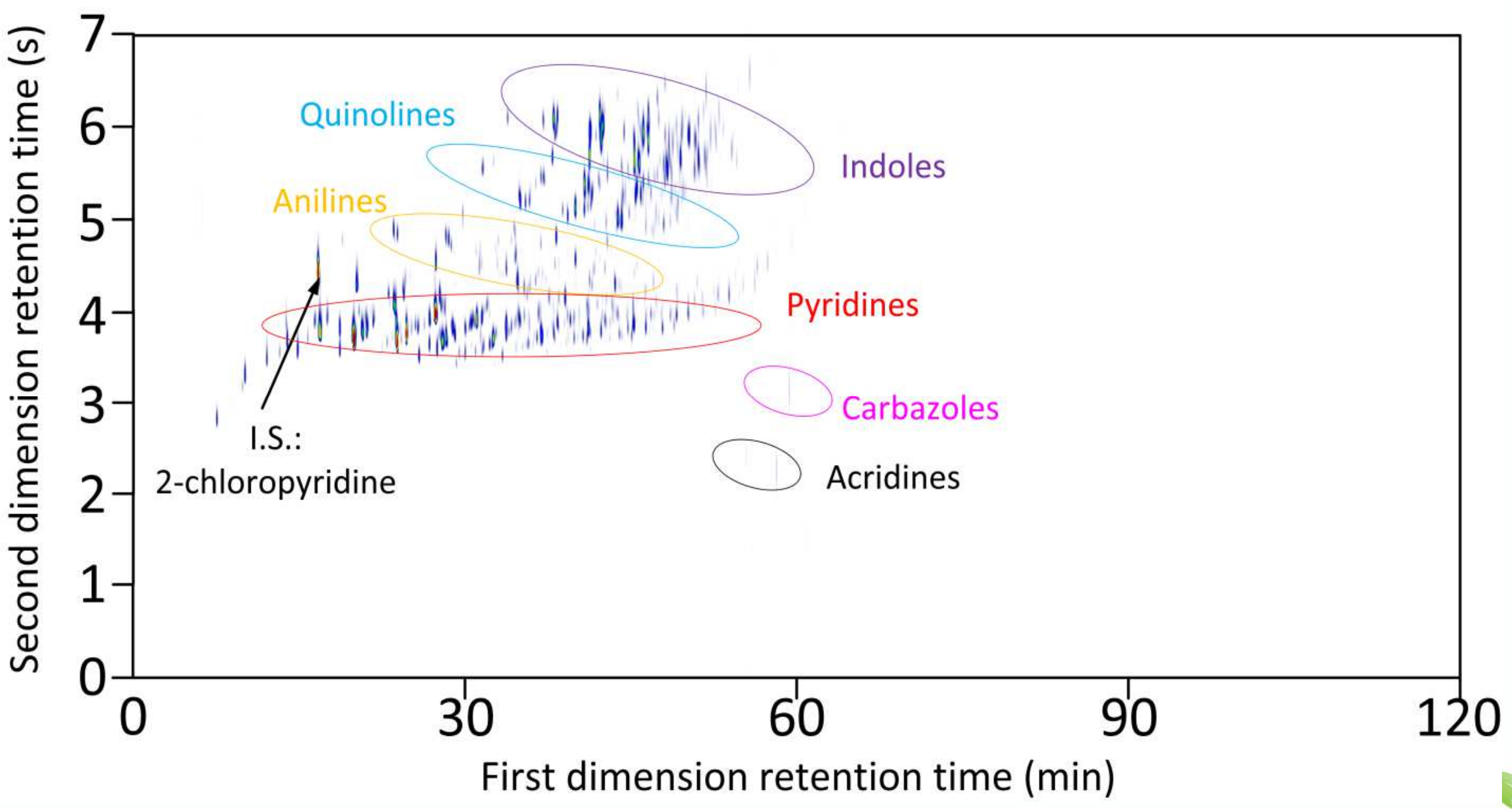


GC × GC – TOF-MS SIC chromatogram

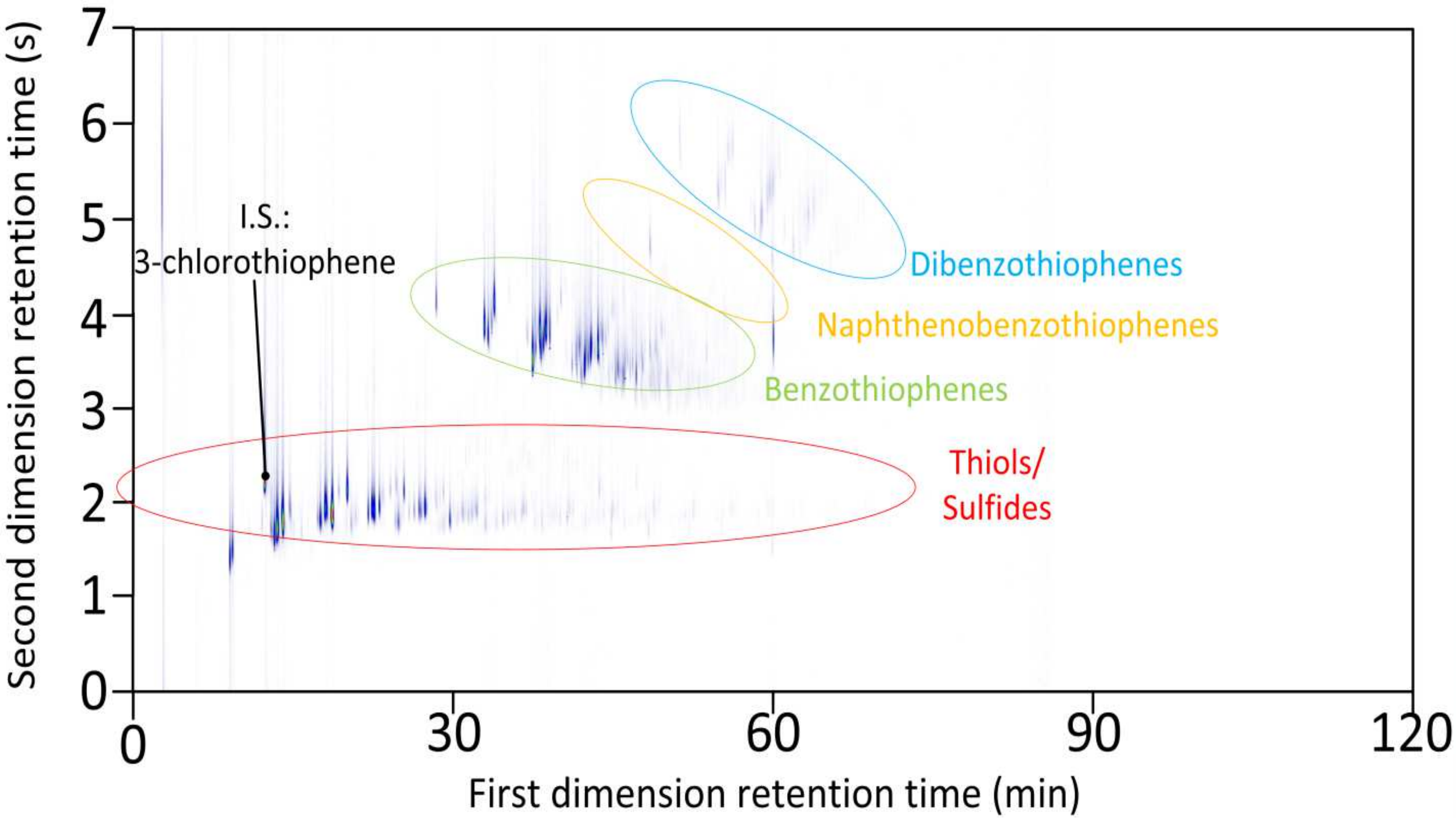


Selected ions: 108, 122, 136, and 150

GC × GC – NCD chromatogram



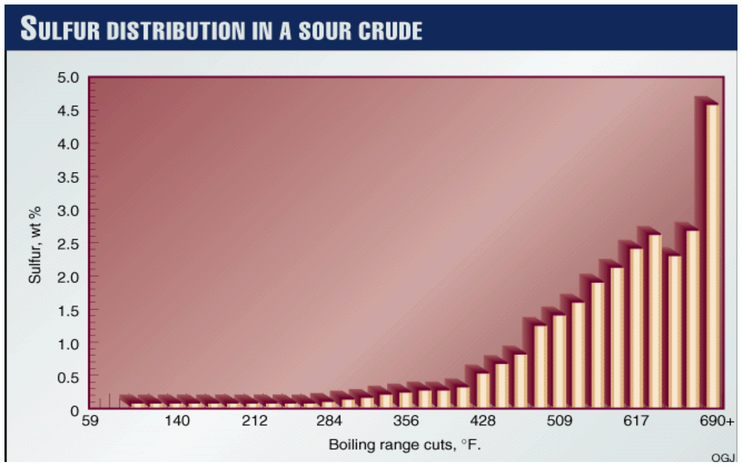
GC × GC – SCD chromatogram



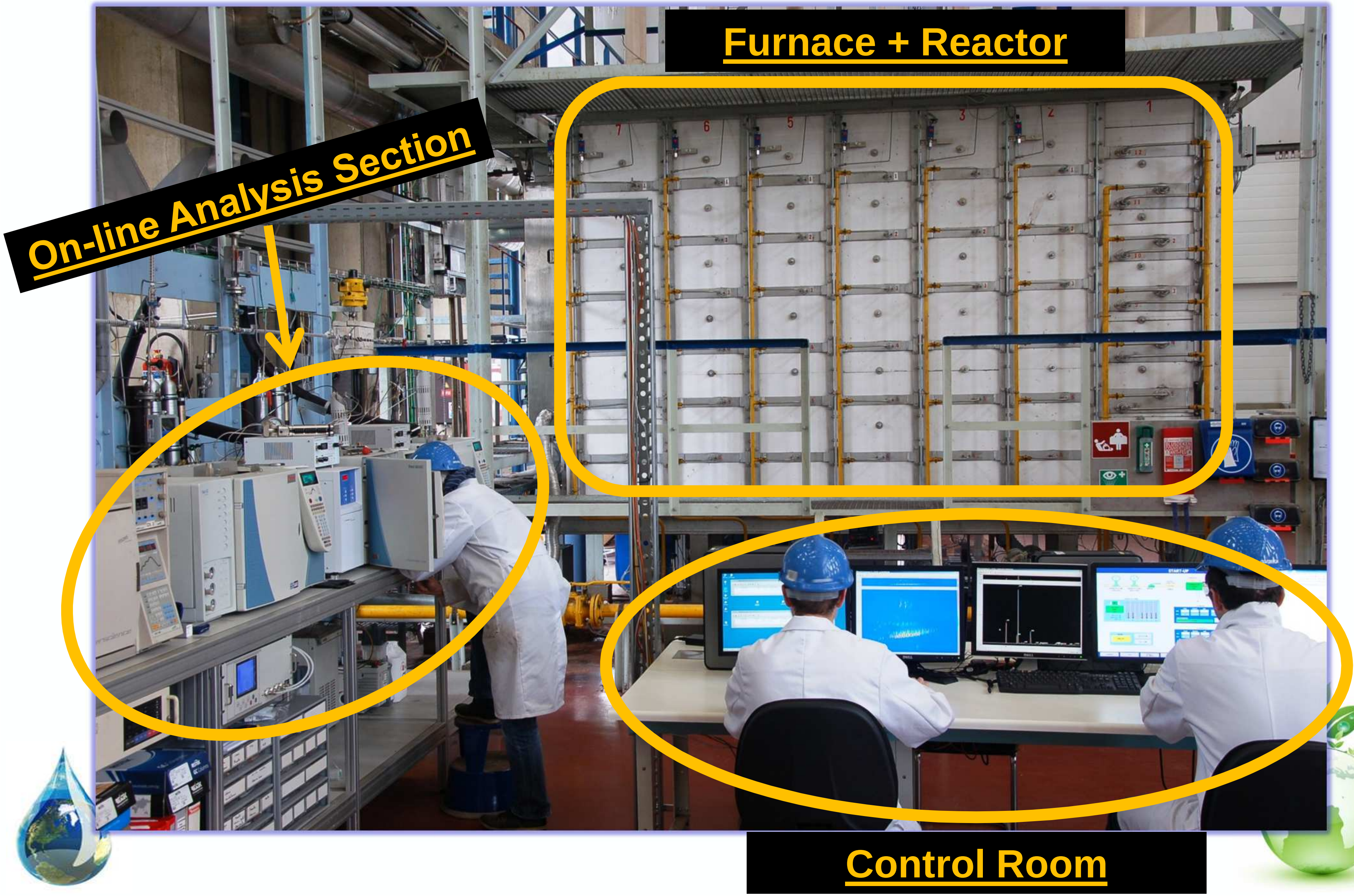
#C	P	I	MN	DN	MA	NA	DA	NDA	TA	Pd	An	Q	In	Ac	Ca	T	BT	NBT	DBT	Ph	Total
5	0	0	0	0	0	0	0	0	0	0.01	0	0	0	0	0	0.24	0	0	0	0	0.25
6	1.61	2.28	0	0	0	0	0	0	0	0.04	0	0	0	0	0	0.25	0	0	0	0.03	4.21
7	2.24	1.47	0	0	0.11	0	0	0	0	0.11	0.02	0	0	0	0	0.16	0	0	0	0.13	4.24
8	2.18	1.96	0	0	0.69	0	0	0	0	0.26	0.05	0	0.01	0	0	0.10	0.02	0	0	0.27	5.55
9	2.34	2.22	0.57	0	1.67	0	0	0	0	0.47	0.07	0.01	0.06	0	0	0.07	0.14	0	0	0.33	7.94
10	2.31	1.52	0.85	0	1.77	0.39	0.05	0	0	0.15	0.11	0.08	0.17	0	0	0.04	0.33	0	0	0.15	7.91
11	2.31	1.17	1.08	0	1.35	0.33	0.40	0.01	0	0.18	0.11	0.17	0.28	0	0	0.03	0.33	0	0	0	7.74
12	2.34	0.97	1.20	0.01	0.94	0.26	1.00	0.16	0	0.12	0.08	0.19	0.30	0	0	0.03	0.20	0.01	0.01	0	7.82
13	2.29	1.40	1.13	0.13	0.87	0.42	1.07	0.20	0	0.18	0.03	0.12	0.16	0	0.02	0.02	0.06	0	0.03	0	8.13
14	2.26	1.08	1.05	0.14	0.62	0.34	0.75	0.40	0.03	0.17	0	0.03	0.14	0.01	0.02	0	0.03	0	0.08	0	7.14
15	2.22	1.05	0.90	0.26	0.80	0.26	0.41	0.33	0.17	0.13	0	0	0	0.02	0	0	0.01	0	0.04	0	6.60
16	2.20	0.70	0.77	0.18	0.50	0.16	0.24	0.16	0.40	0.10	0	0	0	0	0	0	0	0	0	0	5.41
17	2.07	0.84	0.87	0.10	0.49	0.11	0.14	0.10	0.14	0.05	0	0	0	0	0	0	0	0	0	0	4.91
18	1.98	0.80	0.91	0.09	0.30	0.09	0.03	0.07	0	0.03	0	0	0	0	0	0	0	0	0	0	4.31
19	1.64	0.72	0.58	0.09	0.26	0.09	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.37
20	1.54	0.48	0.75	0.06	0.20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.03
21	1.36	0.38	0.58	0.07	0.18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.56
22	1.35	0.37	0.43	0.05	0.10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.29
23	1.12	0.32	0.28	0.04	0.05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.81
24	0.89	0.25	0.20	0.01	0.03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.38
25	0.77	0.07	0.16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.00
26	0.60	0.08	0.09	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.76
27	0.46	0.06	0.08	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.60
28	0.31	0.05	0.05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.41
29	0.21	0.03	0.03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.27
30	0.13	0.03	0.03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.19
31	0.05	0.02	0.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.09
32	0.03	0.02	0.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.07
33	0.02	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.03
Total	38.85	20.36	12.63	1.22	10.92	2.43	4.09	1.42	0.73	1.98	0.47	0.60	1.11	0.03	0.04	0.93	1.11	0.01	0.16	0.91	100

On-line analysis

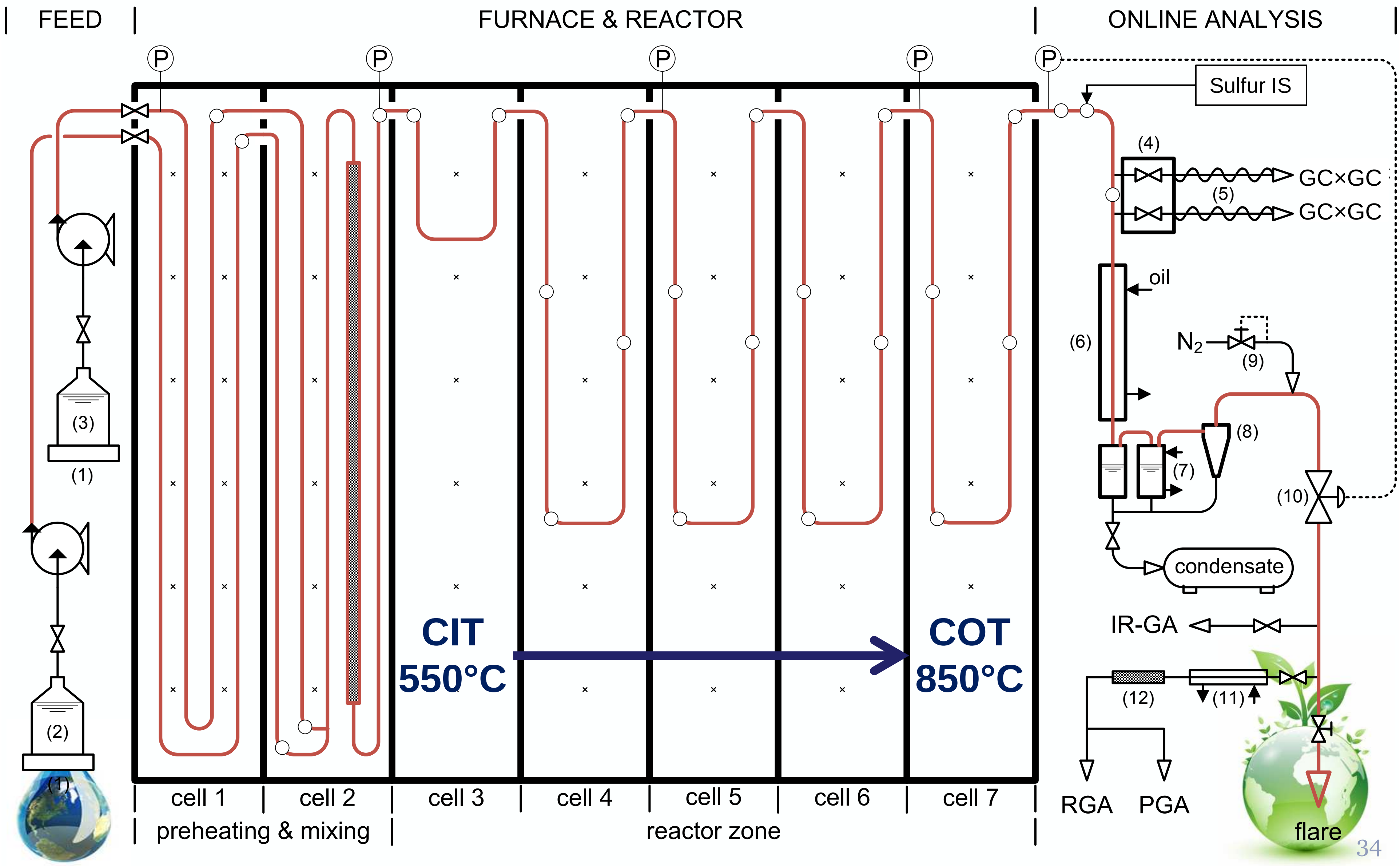
- Importance of sulfur and nitrogen containing compounds on steam cracking is two folded
  - **High S and N** content in **heavier petroleum fractions** (becoming more attractive as steam cracking feedstocks)
  - **Significant** influence on **steam cracking** performance
    - **Trace analysis** of sulfur and nitrogen an important challenge
    - **SCD** and **NCD** are the most suitable for analyzing S and N amount (**ppb** level)



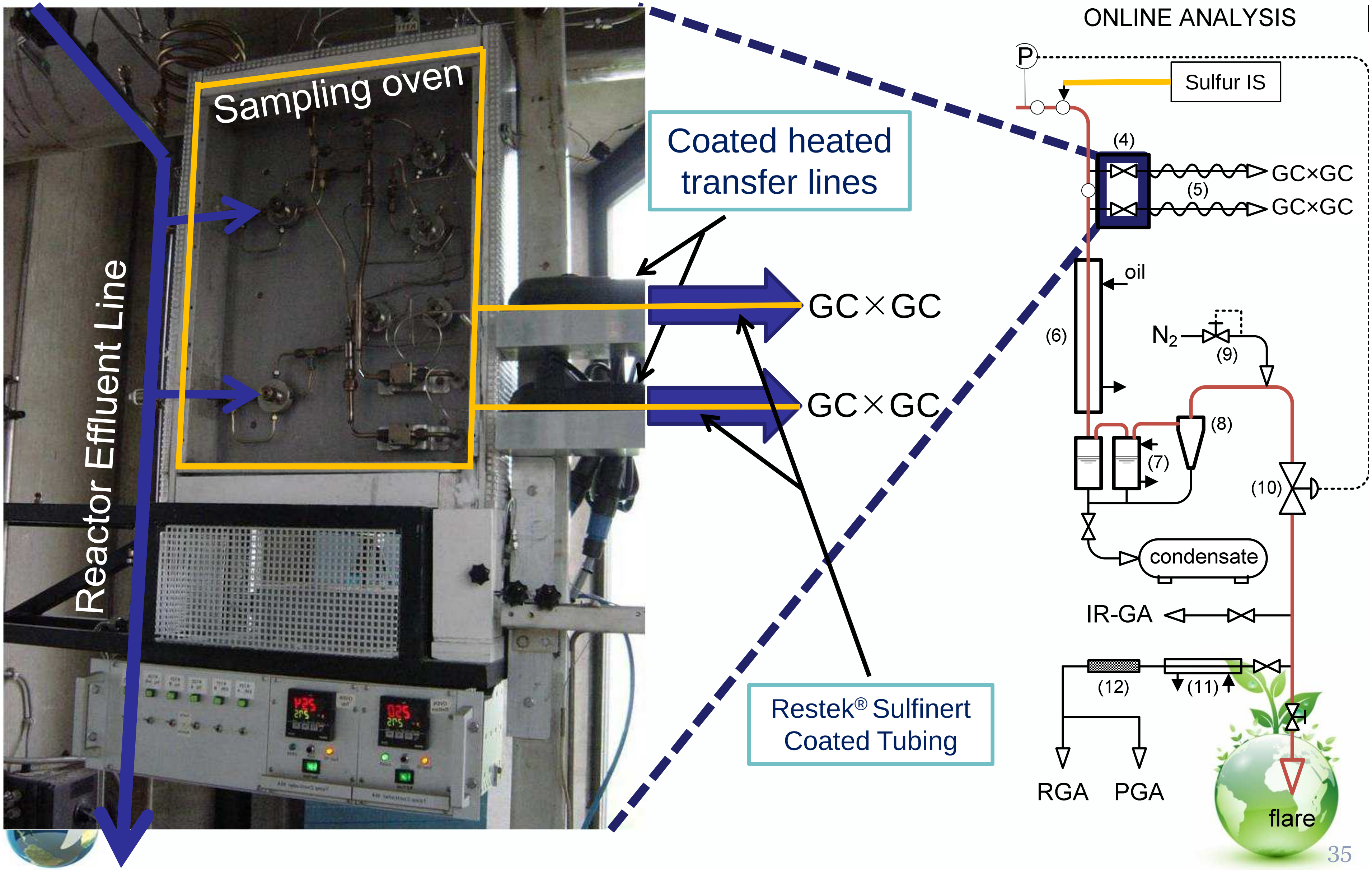
Pilot plant steam cracking setup



Pilot plant setup



Pilot Plant: On-line effluent sampling



Universal On-line quantification

Nitrogen = Internal Standard

RGA (TCD): H_2 CO_2 C_2H_4 C_2H_6 C_2H_2 **N_2** CH_4 CO

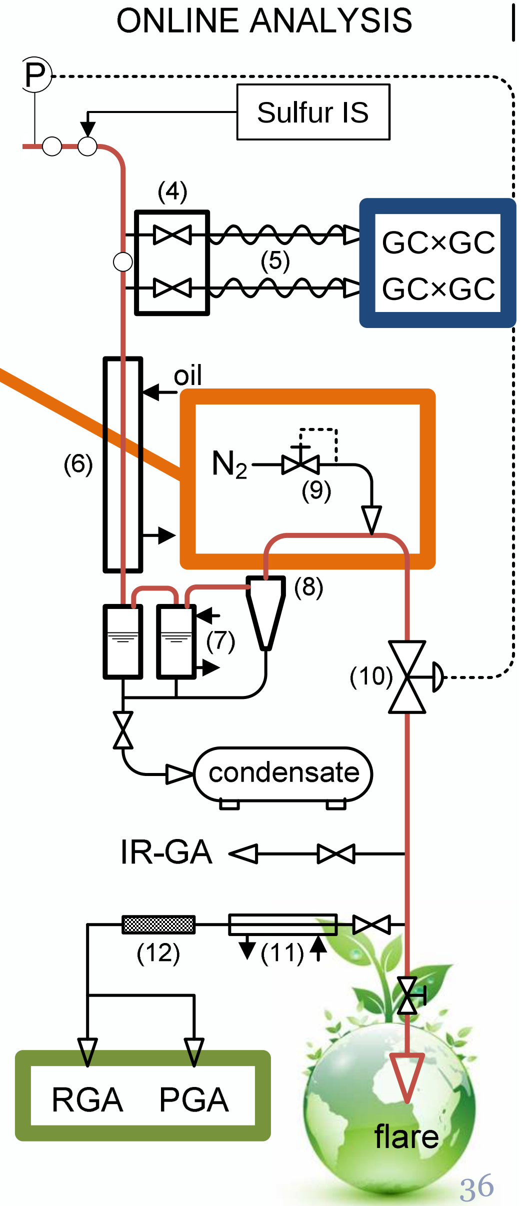
RGA (FID): **CH_4** C_2 C_3 C_4

check

PGA (TCD): CO_2 C_2H_4 C_2H_6 C_2H_2 **N_2** CO CH_4

GC×GC (FID): **CH_4** C_2 C_3 C_4 C_5 C_6 … C_{16}

GC×GC (FID): **CH_4** … C_{25}



Methane = Reference Component

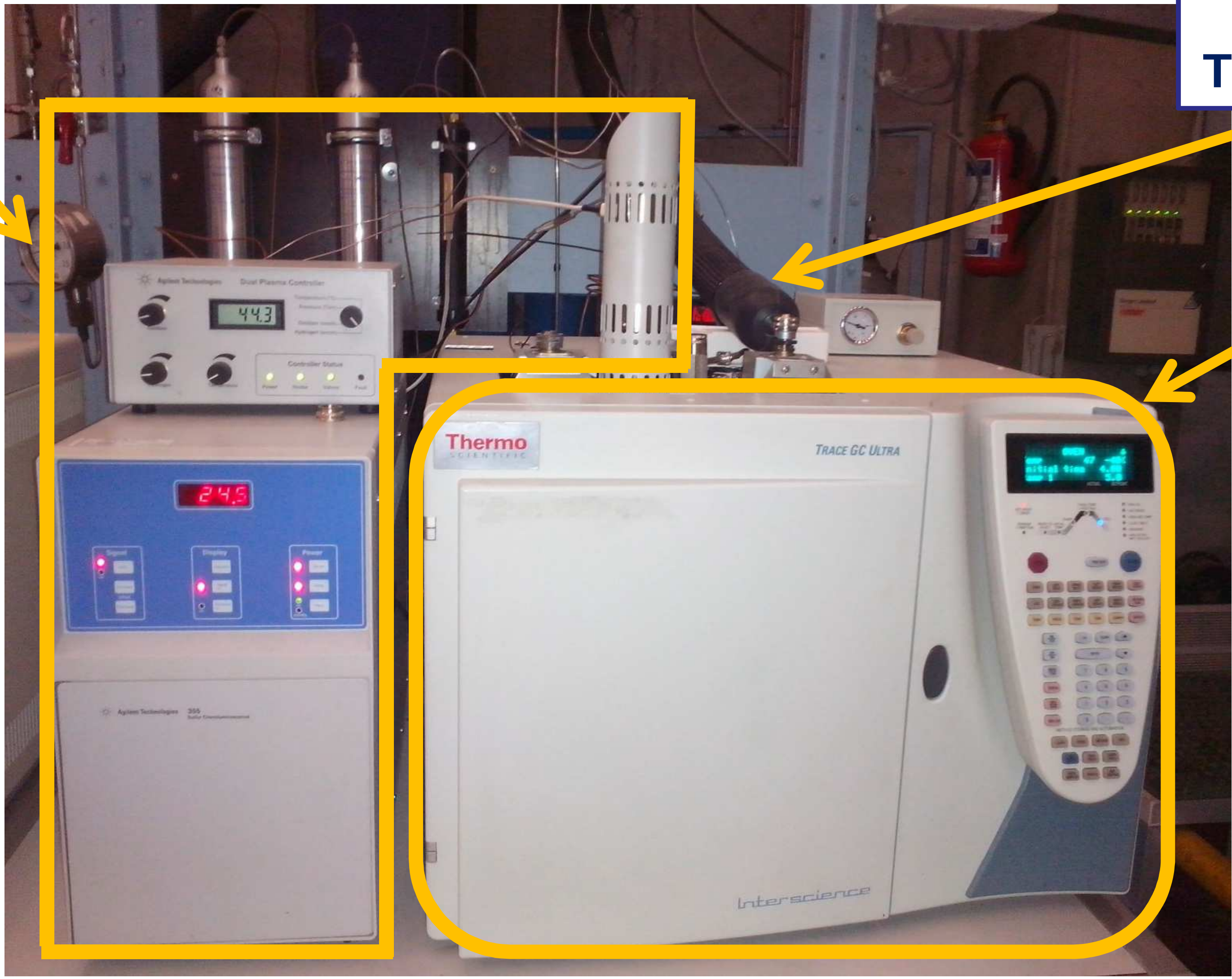
GC×GC temperature program: -40°C → 300°C

GC×GC-FID/NCD setup

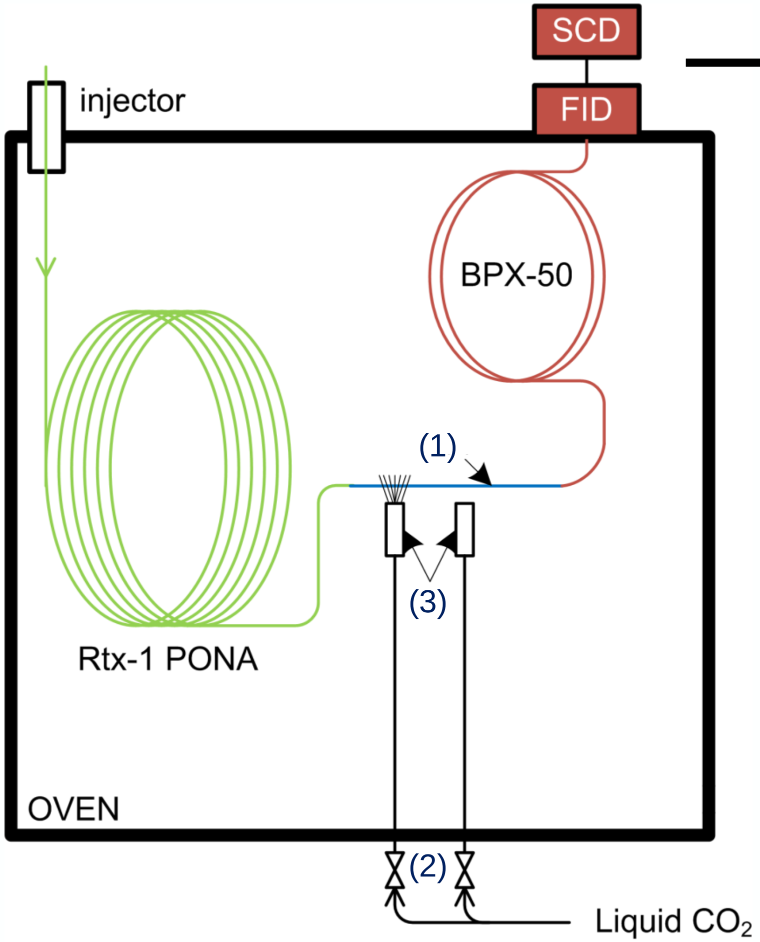
NCD

Heated Transfer-line

GC×GC



GC×GC-FID/SCD setup

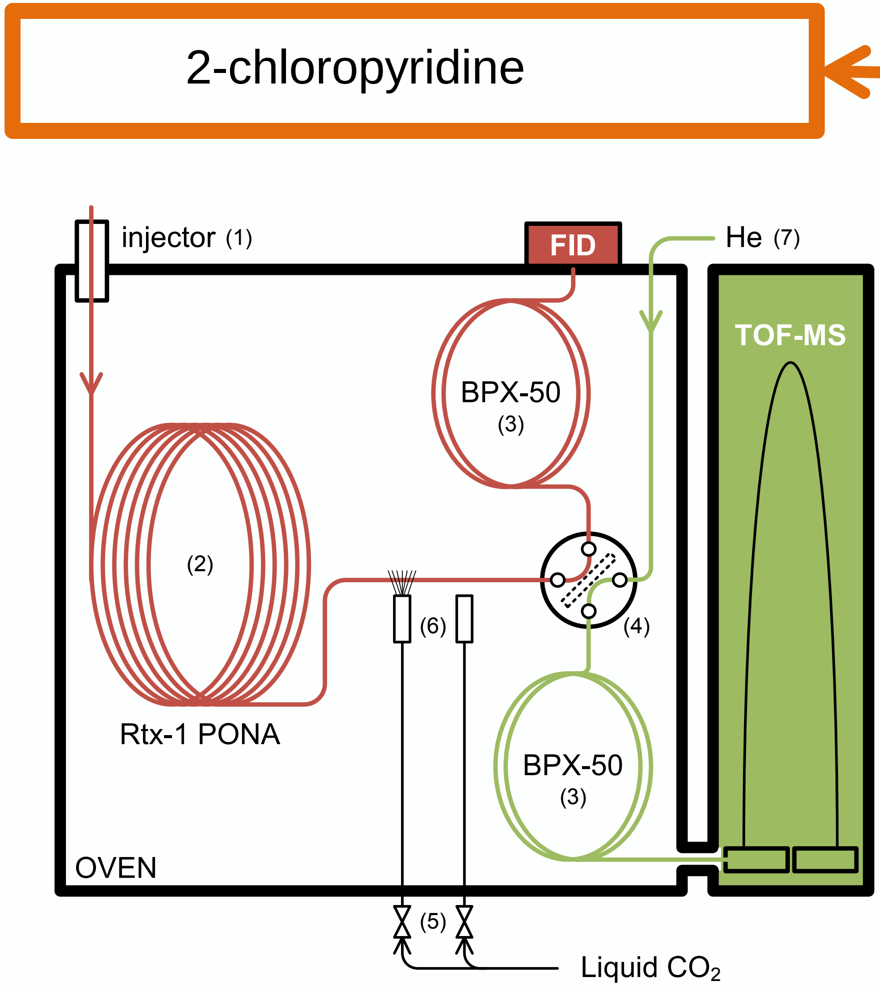


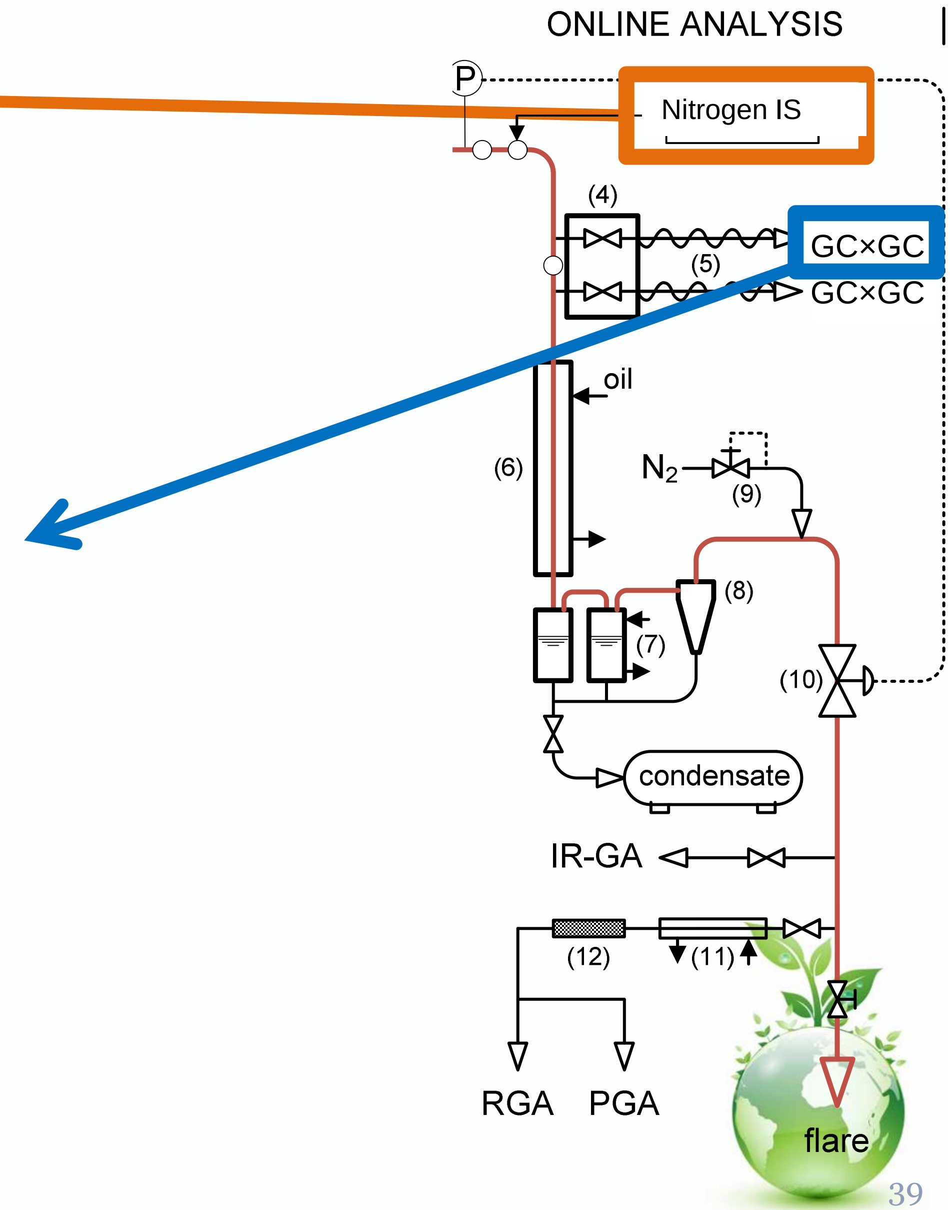
1) deactivated column
2) valves for liquid CO_2
3) cryogenic modulator

- SCD and FID are in series
- Both simultaneous and separate analyses are possible

Simultaneous	Separate
Single analysis (85 min)	Double analysis (2×85 min)
Maximum sensitivity for either FID or SCD	Maximum sensitivity for both FID and SCD

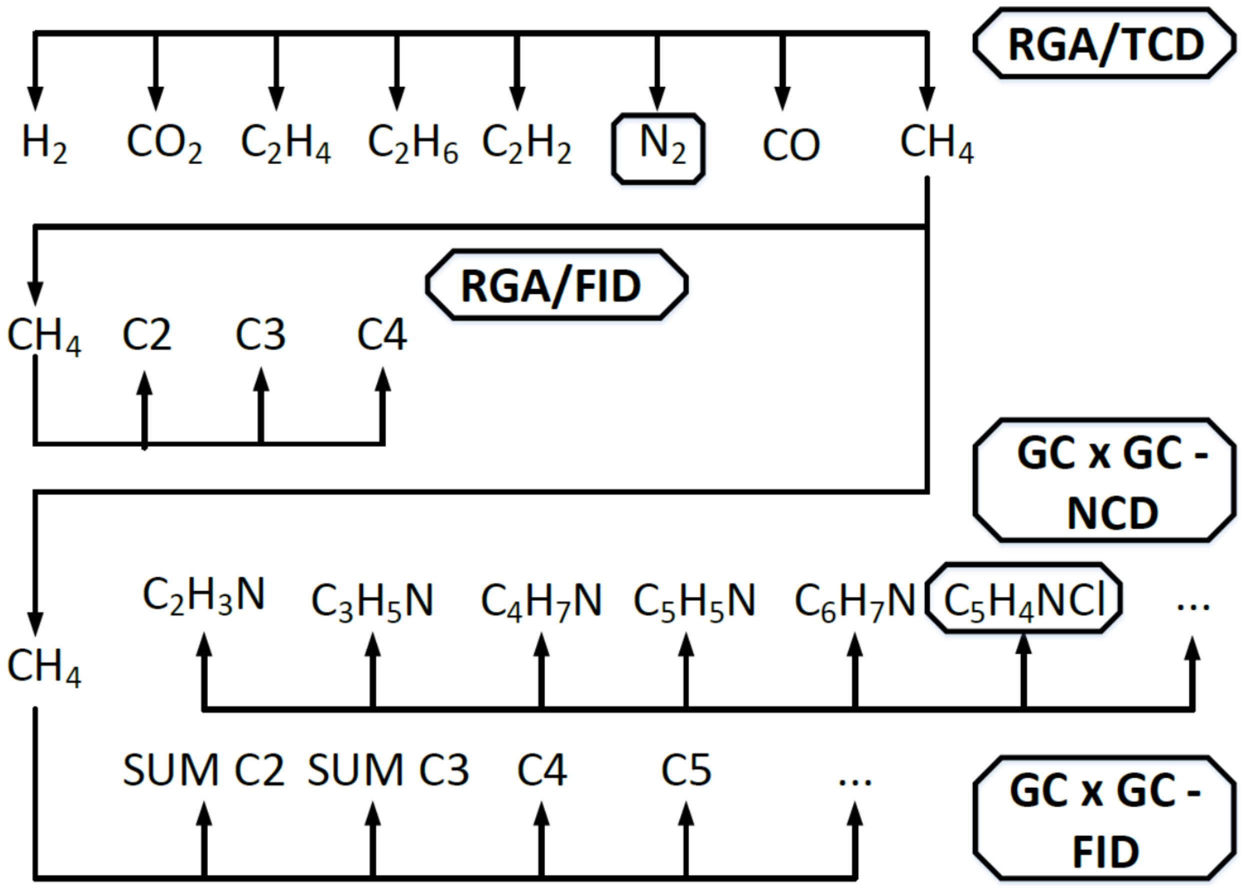
Nitrogen On-line quantification



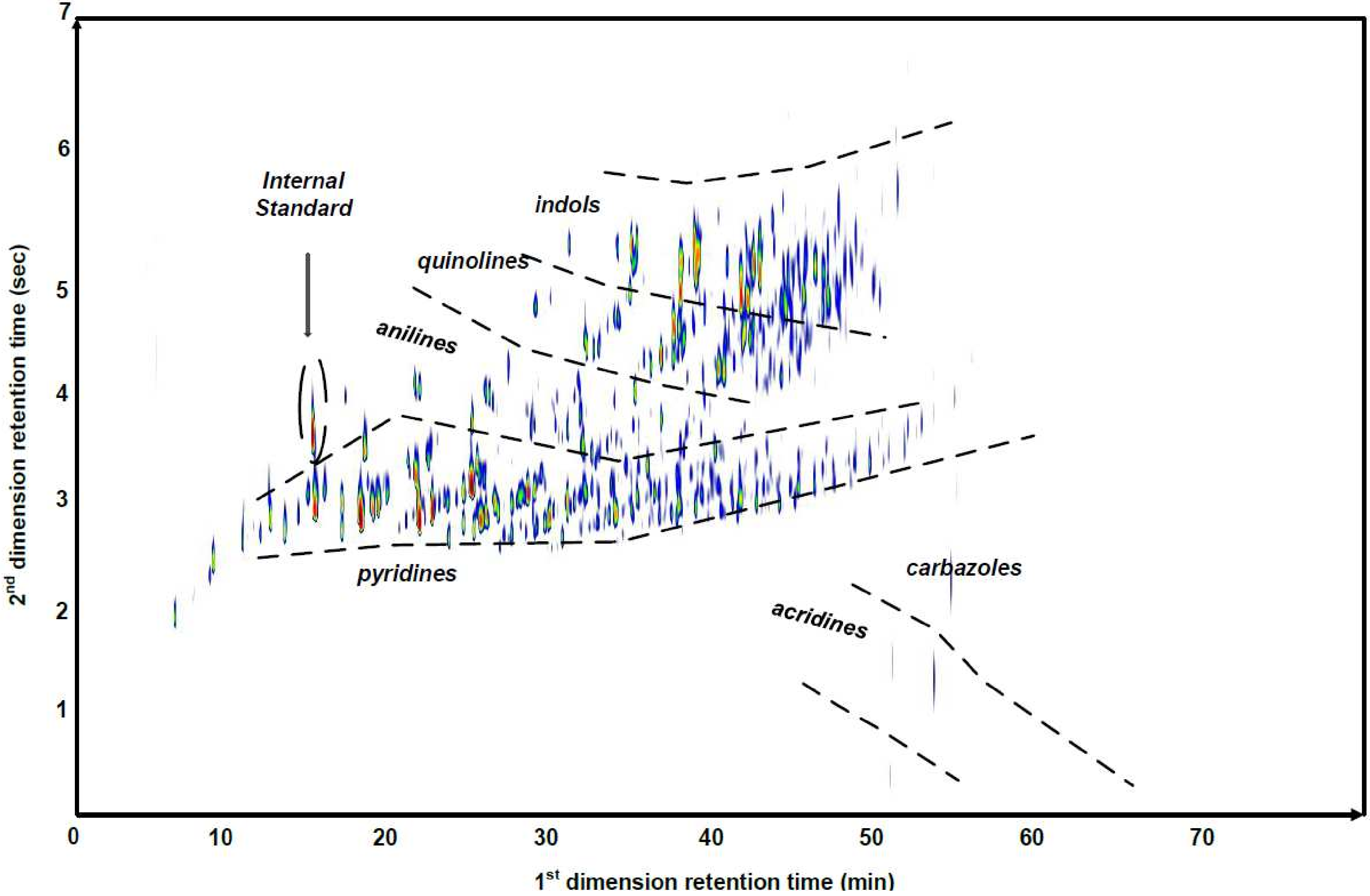


1) deactivated column
2) valves for liquid CO_2
3) cryogenic modulator

Experimental conditions



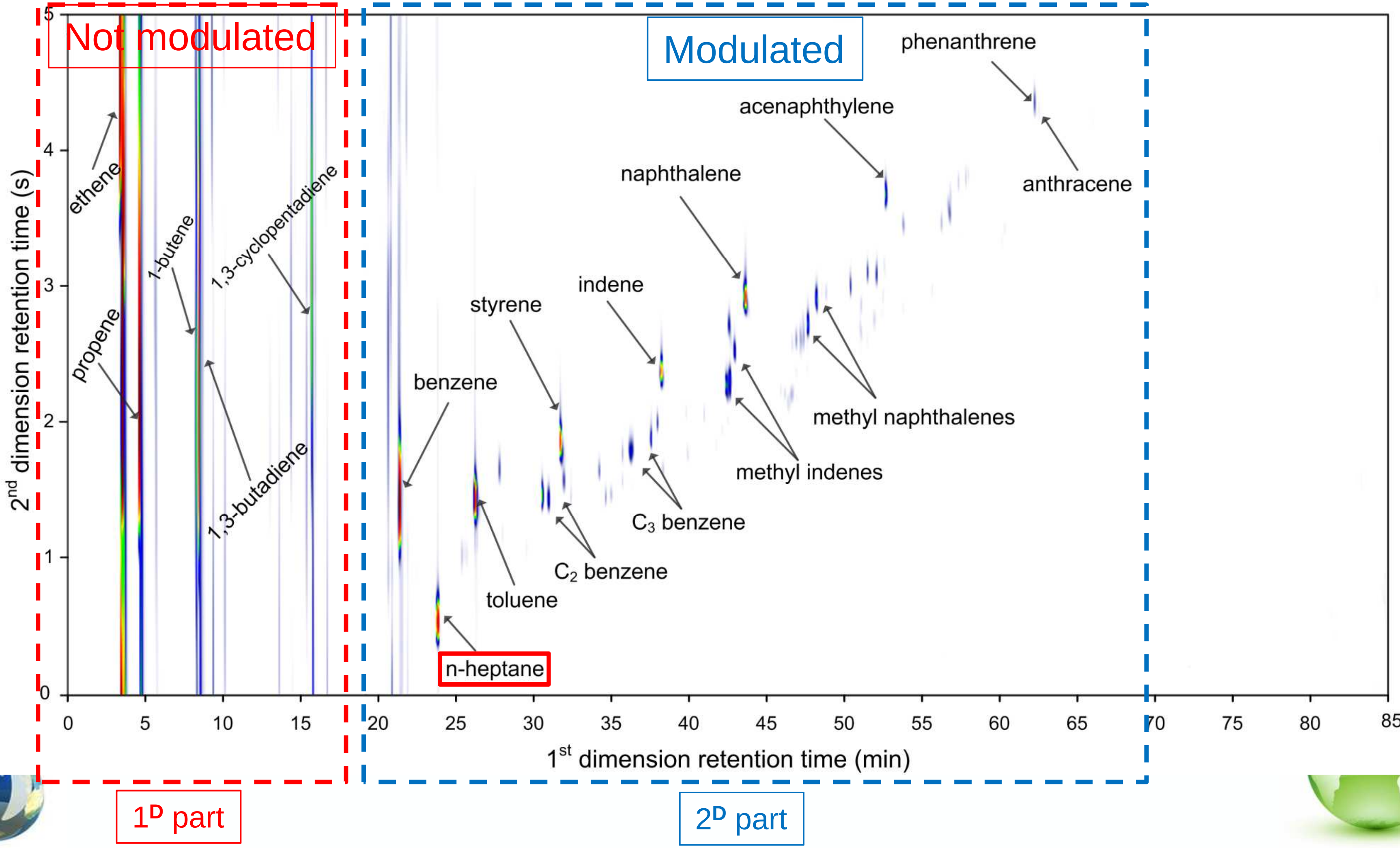
Nitrogen compounds



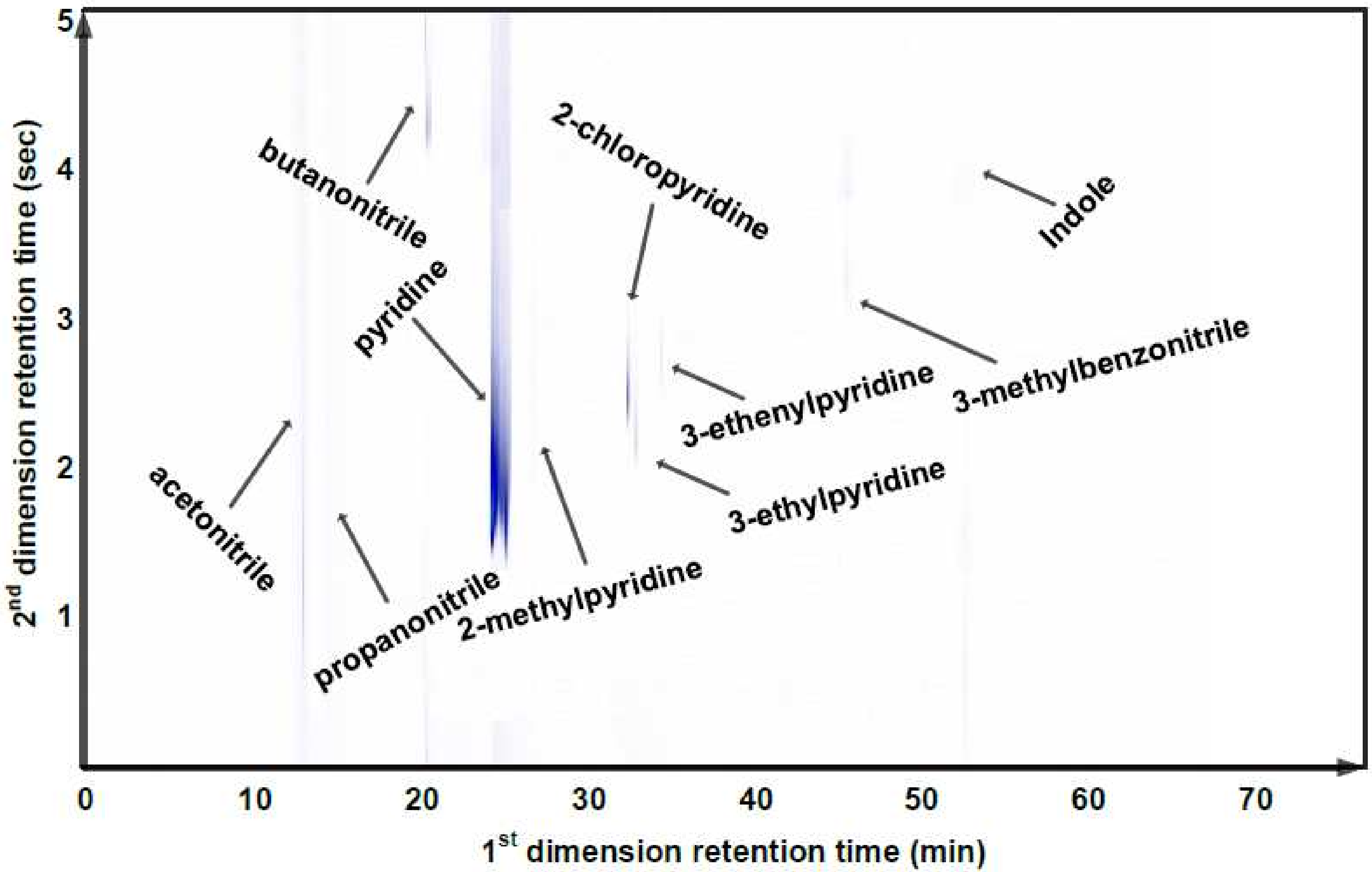
On-line FID analysis

Ethylene : 43 wt%
Propylene : 15 wt%

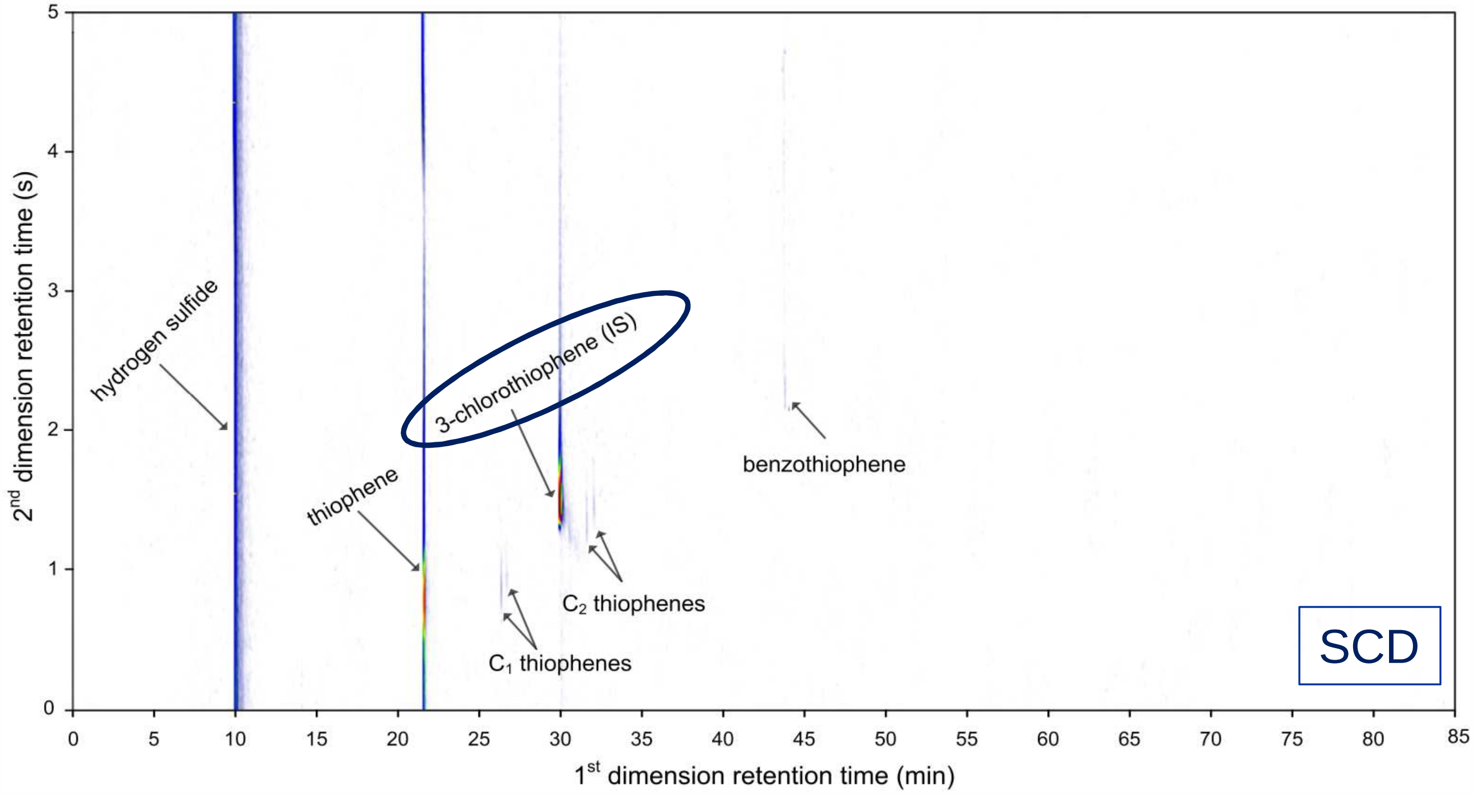
Benzene : 4 wt%
Heptane : 1 wt%



pyridin addition



Thiophene addition



- **Thiophene** slightly decomposes – **stable** under tested conditions (**COT, tau**)
- **H_2S** is the **major** product in the effluent (**DMDS** responsible for its production)
- Methyl-, ethyl- substituted thiophenes, benzothiophene at higher ppmwS/HC

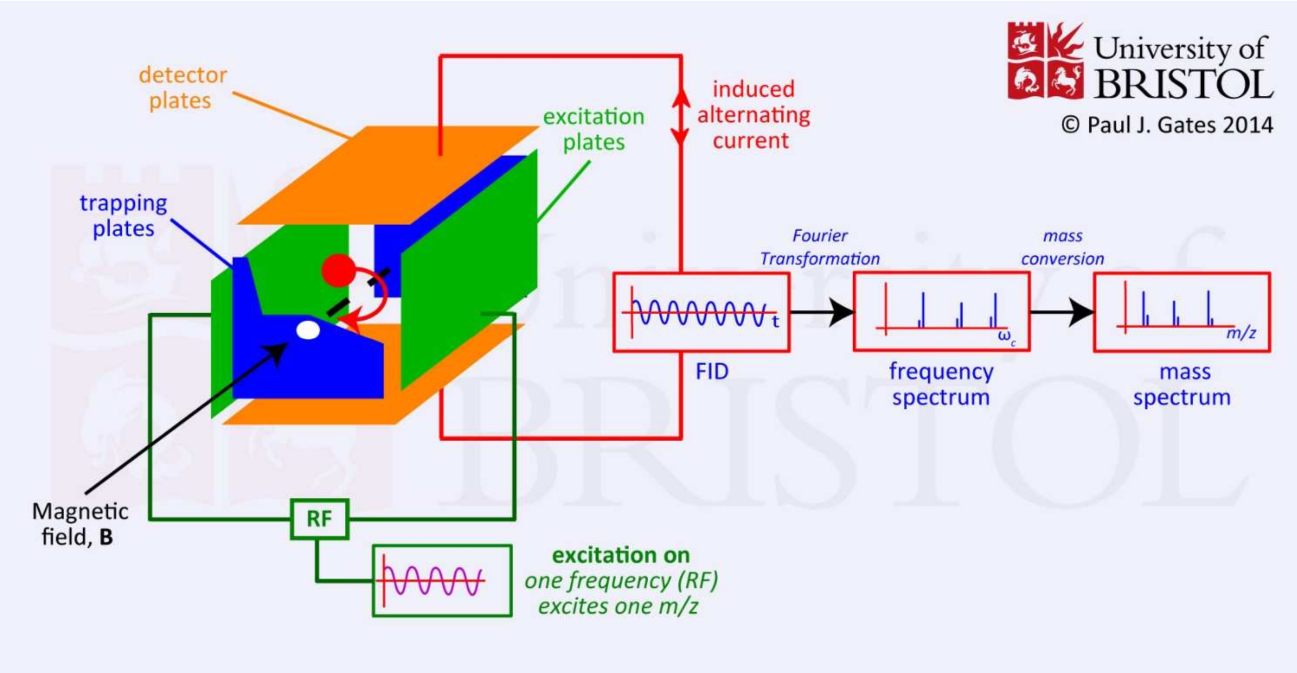
Outline

- Molecule driven process optimization
- GC-FIMS
- Comprehensive 2D GC analysis using FID/SCD/NCD/TOF-MS
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Conclusions

Fourier-transform ion cyclotron resonance (FT-ICR) MS

- It enables the acquisition of high-resolution mass spectra with high accuracy (developed in 1950's and 1970's)
- Almost unlimited resolution - >10^7
- Quantification is not easy
- Other limitations of FT-ICR MS are that it cannot differentiate between molecules which have exactly the same molecular formula but different structures
- Muller *et al.* performed the quantitative characterization of sulfur containing compounds in gas oil (GO). GC×GC was used as the reference method. The comparison of FT-ICR MS results with GC×GC results showed good agreement for sulfur families as in most cases the deviation was within 5% and 15%.

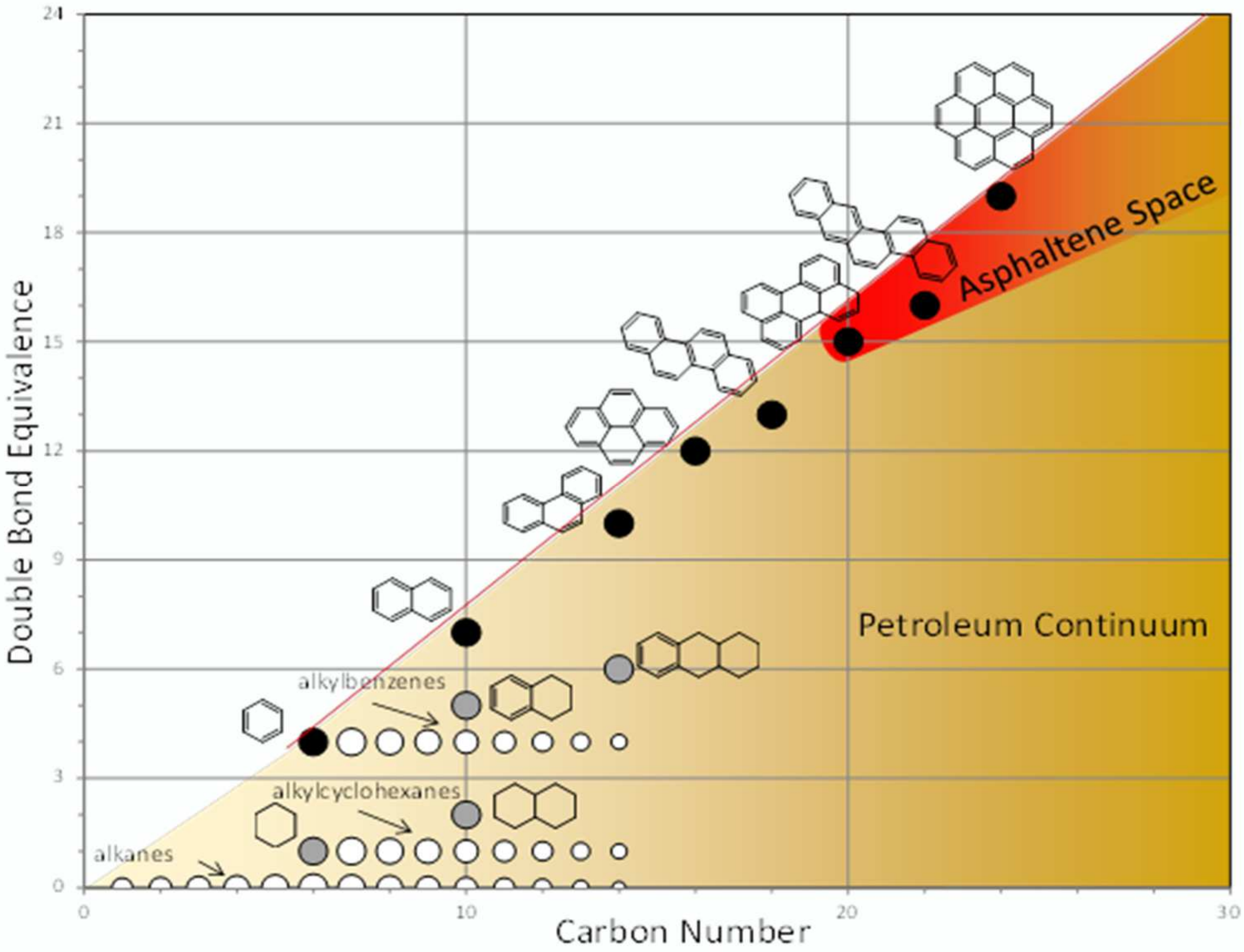
Working principle



- Ions are generated in the source and pass through a series of pumping stages to increasingly high vacuum
- Then ions enter the cell (ion trap)
- Cell is located inside high field magnet (typically 4.7 to 13 Tesla)

- The frequency of rotation of the ions is dependent on their *m/z* ratio
- Excitation of each individual *m/z* is achieved by a swept RF pulse across the excitation plates of the cell=>measurement of all the ions in one go
- producing a complex frequency vs. time spectrum (the convoluted frequency spectrum or FID) containing all the signals. Deconvolution of this signal by FT methods results in the deconvoluted frequency vs. intensity spectrum which is then converted to the mass vs. intensity spectrum

Schematic of Carbon number vs. DBE



Outline

- Molecule driven process optimization
- GC-FIMS
- Comprehensive 2D GC analysis using FID/SCD/NCD/TOF-MS
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Conclusions

Conclusions

- **Molecule driven process optimization** is the key driver for the oil and petrochemical industry to consider more advanced analytical techniques

- **GC×GC-SCD/NCD/FID/Tof-MS** setups enable quantitative analysis of PA(S)(N) H compounds and shale oil

- **GC×GC-NCD/SCD/Tof-MS/FID** successfully applied online

- **GC×GC, GC-FIMS and FT-ICMS** should join forces to resolve the challenges of the future

Acknowledgements

Thank you for
your attention!

Glossary

- GC×GC – comprehensive two-dimensional gas chromatography
- SCD – sulfur chemiluminescence detector