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

Marc Gibert - Ingenieria Anal’nitica 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)
Light crude oil A
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

<table>
<thead>
<tr>
<th>Nr</th>
<th>Name</th>
<th>RT1; RT2 (min)</th>
<th>b.p. °C</th>
<th>Polarity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-hexane</td>
<td>10.436; 0.715</td>
<td>69.0</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>benzene</td>
<td>12.536; 1.277</td>
<td>80.1</td>
<td>2.7</td>
</tr>
<tr>
<td>3</td>
<td>cyclohexane</td>
<td>12.536; 0.766</td>
<td>80.7</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>n-heptane</td>
<td>14.036; 0.817</td>
<td>98.4</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>cyclohexane, methyl</td>
<td>15.386; 0.868</td>
<td>101.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>toluene</td>
<td>18.086; 1.635</td>
<td>111.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>
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 simplify instrument use for routine analysis
- **One** GCxGC method is here described:
  - to optimise the separation among classes;
  - to discriminate among information the more interesting ones:
    - Hydrocarbons group type
    - S-containing compounds
    - N-containing compounds
Hydrocarbons in light crude oil A

Three ring-aromatics

Double ring-aromatics

Single-ring aromatics

HC Saturated and unsaturated
GCxGC analysis of light petroleum distillate

- Single-ring aromatics
- Double ring-aromatics
- Three ring-aromatics
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**

<table>
<thead>
<tr>
<th>Number</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dimethyldisulfide</td>
</tr>
<tr>
<td>2</td>
<td>ethyl-methylethyl disulfide</td>
</tr>
<tr>
<td>3</td>
<td>2-pentanethiol</td>
</tr>
<tr>
<td>4</td>
<td>1-pentanethiol</td>
</tr>
<tr>
<td>5</td>
<td>4-methyl, 2-pentanethiol</td>
</tr>
<tr>
<td>6</td>
<td>methyl ethyl disulfide</td>
</tr>
<tr>
<td>7</td>
<td>hexanethiol</td>
</tr>
<tr>
<td>8</td>
<td>tetrahydro thiopyran</td>
</tr>
<tr>
<td>9</td>
<td>hexanethiol</td>
</tr>
<tr>
<td>10</td>
<td>diethyl disulfide</td>
</tr>
<tr>
<td>11</td>
<td>methyl propyl disulfide</td>
</tr>
<tr>
<td>12</td>
<td>cyclohexanethiol</td>
</tr>
<tr>
<td>13</td>
<td>heptanethiol</td>
</tr>
<tr>
<td>14</td>
<td>dimethyl trisulfide</td>
</tr>
<tr>
<td>15</td>
<td>methyl cyclohexanethiol</td>
</tr>
</tbody>
</table>
S-compounds in light crude oil A
Benzothiophenes in light crude oil A

- 1 - benzothiophene
- 2 - benzothiophene, 2,3-dihydro
- 3 - benzothiophene, methyl
- 4 - benzothiophene, 2M
- 5 - benzothiophene, 3M
- 6 - benzothiophene, 4M
S-compounds in light crude oil A
Dibenzothiophenes in light crude oil A

1 – dibenzothiophene
2 – dibenzothiophene, methyl
3 – dibenzothiophene, 2M
4 – dibenzothiophene, 3M

64 identified compounds
S-compounds in light crude oil C
Thiophenes in light crude oil C

- thiophene
- methyl-thiophene
- tetrahydro-thiophene
- dimethyl-thiophene
- methyl-tetrahydrothiophene
- dimethyl-thiophane
- tetra-hydro-thiopirane
- dimethyl-tetrahydrothiophene
- dimethyl-thiophene
- dimethyl-thiophane
- cis-2,3-dimethyl-thiophane
- trans-2,3-dimethyl-thiophane
- dimethyl-thiophene
- methyl-tetrahydrothiophane
- dimethyl-tetrahydrothiophene
- ethyl-tetrahydrothiophene
- ethyl-methyl-thiophane
- trimethyl-thiophene

Benzene
3D-view: Thiophenones in light crude oil C
GCxGC S-compound map of light petroleum distillate (527 ppm S)

36 identified S-compounds
Benzothiophenes 3D-view

- Benzothiophene, dimethyl
- Benzothiophene, 2,3-dihydro
- Benzothiophene
- Naphthalene, dimethyl
- Naphthalene, methyl
- Naphthalene
S-compound identification: comparison with GC-AED data

36 S-compounds peaks
GC-MS analysis

Benzothiophene
Benzothiophene GC-MS

Benzothiophene NIST MS spectrum

Benzothiophene GCxGC-MS spectrum
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

- Pyrrole, methyl
- Pyrrole, ethyl
- Pyrrole, dimethyl
- Pyrrole, trimethyl
- Pyridine, methyl
- Pyridine, dimethyl
- Pyridine, trimethyl
- Benzenamine, methyl
- Benzenamine, dimethyl
- Benzenamine, methyl ethyl
- Hexanenitrile
- Heptanenitrile

N-compounds in Petroleum fraction
N-compounds in Petroleum fraction
N-compounds in Petroleum fraction

57 identified compounds
GC-MS analysis

Carbazole 42.123 min

Rt Carbazole 42.123 min
Carbazole MS Spectra

GC-MS spectrum

Carbazole NIST MS spectrum

Carbazole GCxGC-MS spectrum

167 m/z

139 m/z
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
- ZOEX Dual Stage Thermal Modulator
- GC 6890 Agilent Technologies
- LN2 Zoex Auto-Fill Unit
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 length)
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 length?
- 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

Modulation period : 6 sec.
1 meter DB-1701

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

Modulation period : 9 sec.
1 meter HP-17
Secondary column 2 m x 0.1 mmID x 0.1 um WAX
Oven: 40°Cx0.5min, incr. 0.5°C/min to 260°C for 40 min
Secondary Oven: 30°C above main oven

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

Modulation period : 9 sec.

2 meters WAX

byphenyl

Naphtalene

Wrap-around

Three ring aromatics

Modulation period : 9 sec.

0.7 meter WAX

byphenyl

Naphtalene

Three ring aromatics
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

Naphtalene

byphenyl

Three ring aromatics
## Modulation period

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**Diagram:**

1. Benzene
2. Ciclohexane
Modulation period

Benzene
Ciclohexane
1st modulation
2nd modulation
3rd modulation
4th modulation
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.
Thank you for your attention