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JOINT MASS SPECTROMETRY CENTRE

Lecture III:

Hands-on – gas chromatography atmospheric pressure photo ionisation Fourier transform ion-cyclotron resonance mass spectrometry GC APPI FT-ICR MS

Dr. Christopher P. Rüger
Joint Mass Spectrometry Centre – University of Rostock and Helmholtz Zentrum München

1st EU_FT-ICR_MS network short course, Rostock 03/2018

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Outline

1) Revision GC-APPI theory
2) Hardware GC-APPI at Univ. Rostock
3) Data analysis
4) Summary

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Revision GC-APPI theory 1

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Revision GC-APPI theory

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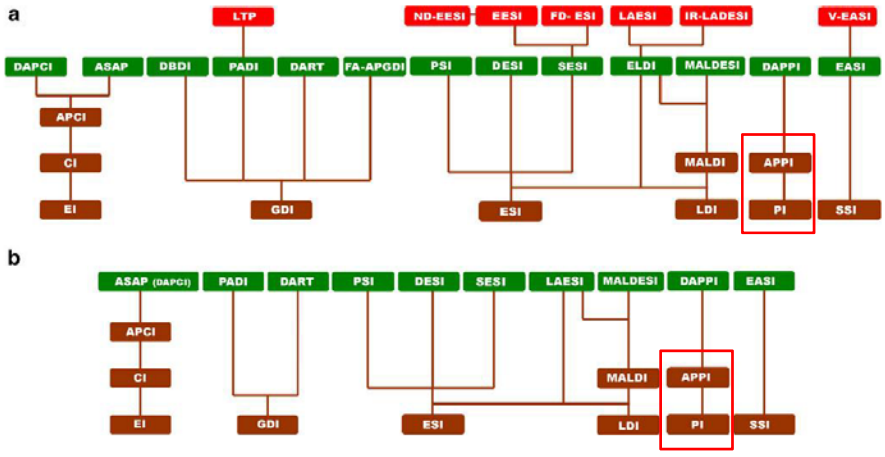
Overview mass spectrometric ionisation techniques



R. Alberici, R. Simas, V. de Souza, *Analytica Chimica Acta,* (2010) 659, 15 – 22

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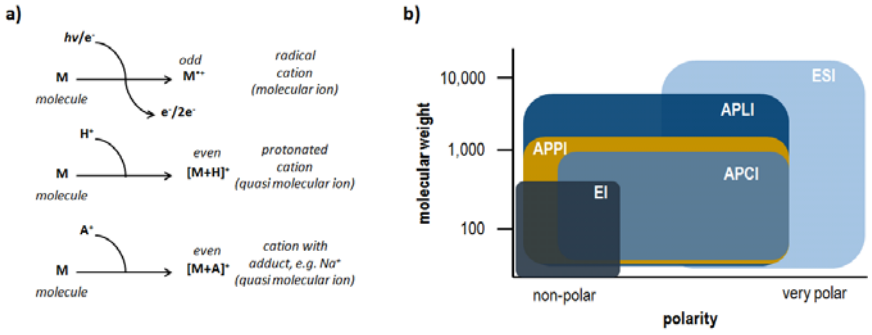
Overview mass spectrometric ionisation techniques



Doctorate Thesis, Christopher P. Rüger, University of Rostock, 2018

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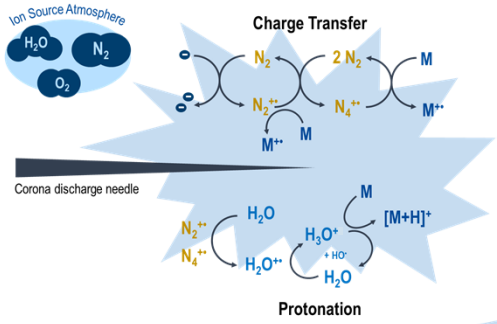
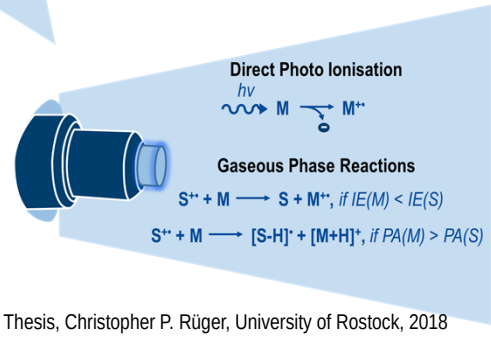


Ionisation scheme of atmospheric pressure chemical ionisation (APCI)

Ionisation scheme of atmospheric pressure photo ionisation (APPI)



Horning et al., Anal. Chem., 1973, 45 (6), 936-943
Robb et al., Anal. Chem., 2000, 72 (15), 3653-3659

Doctorate Thesis, Christopher P. Rüger, University of Rostock, 2018

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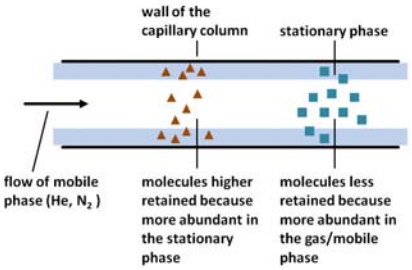
Gas chromatographic pre-separation

Advantages:

- chromatographic information (retention index)
- minimisation of matrix effects
- no solvent effects
- low sample mass needed
- …

Drawbacks:

- limited in volatility range
- complex data analysis for non-targeted approach
- time-consuming
- …



Doctorate Thesis, Christopher P. Rüger, University of Rostock, 2018

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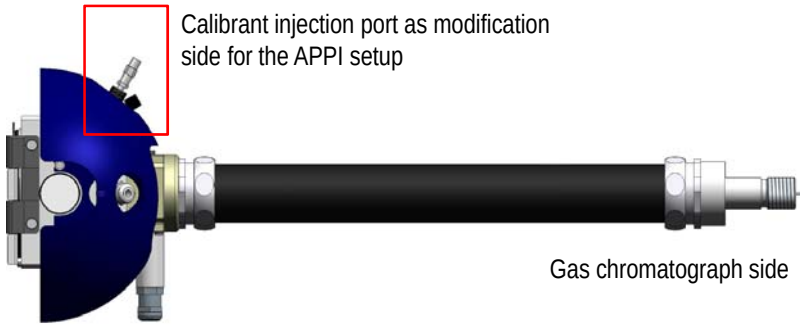
Hardware 2

Hardware overview (GC-APCI II Bruker source)



GC-APCI II Source, User Manual, Revision 1, June 2014, Bruker, p.1

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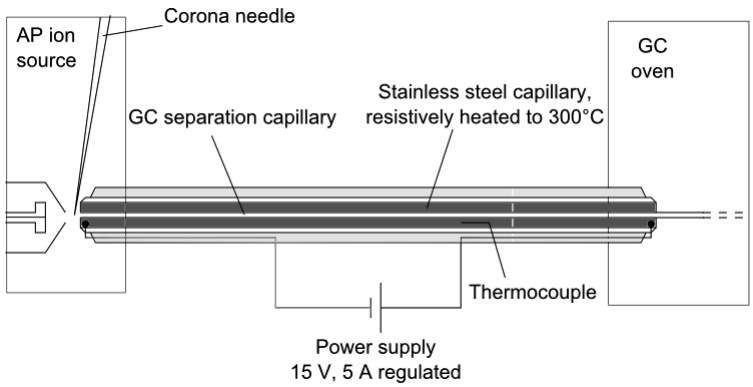
Hardware overview (GC-APCI II Bruker source)

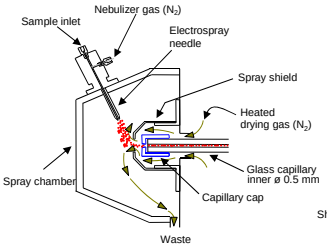


GC-APCI II Source, User Manual, Revision 1, June 2014, Bruker, p.18

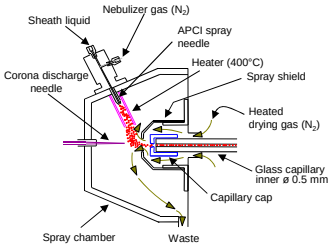
Hardware

Hardware comparison (Bruker) to other API techniques

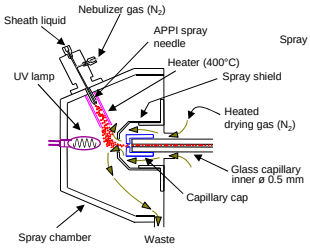
ESI



APCI



APPI



Complex mixture analysis by FT-ICR mass spectrometry, Matthias Witt, Bruker Daltonik

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Hardware – some pictures from the lab

GC-APCI II Source, User Manual, Revision 1, June 2014, Bruker, p. 23/25

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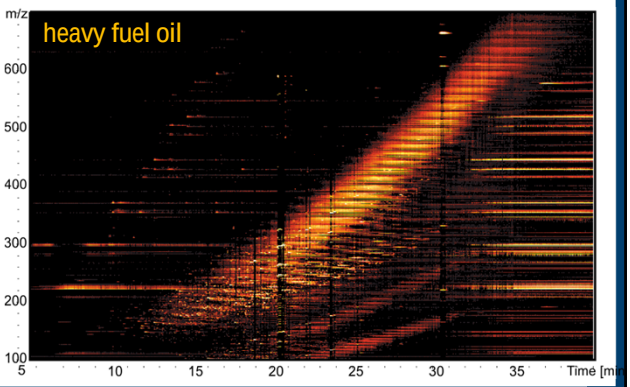
Basic data architecture



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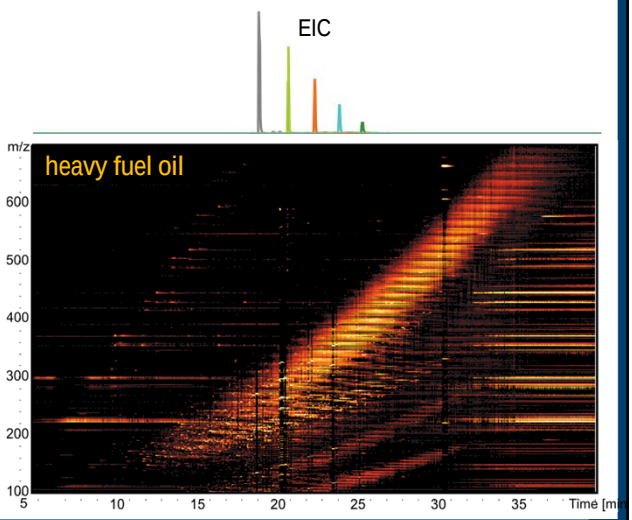
Basic data architecture



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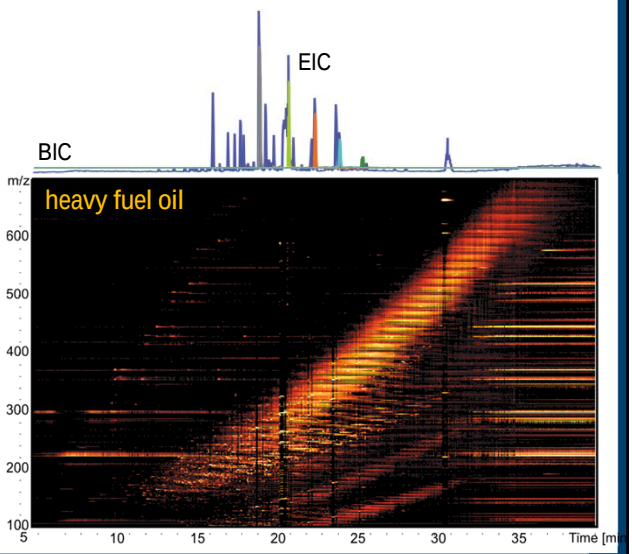
Basic data architecture



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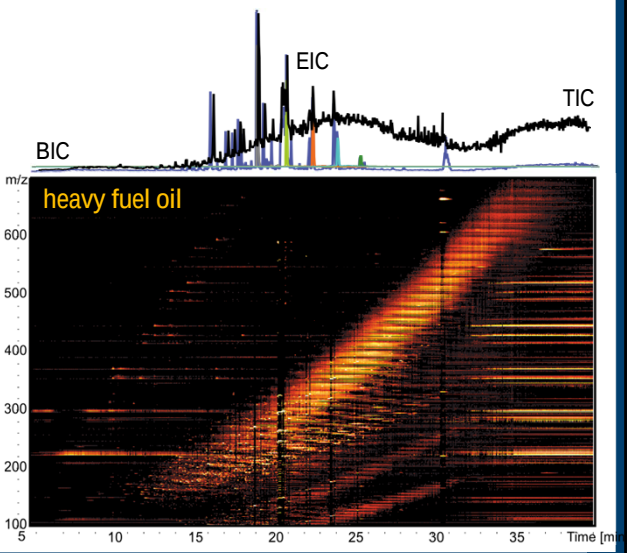

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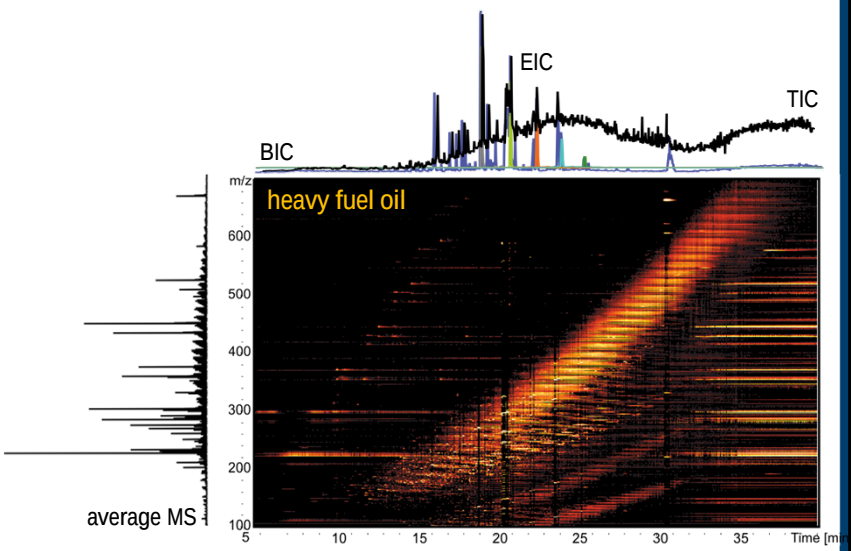

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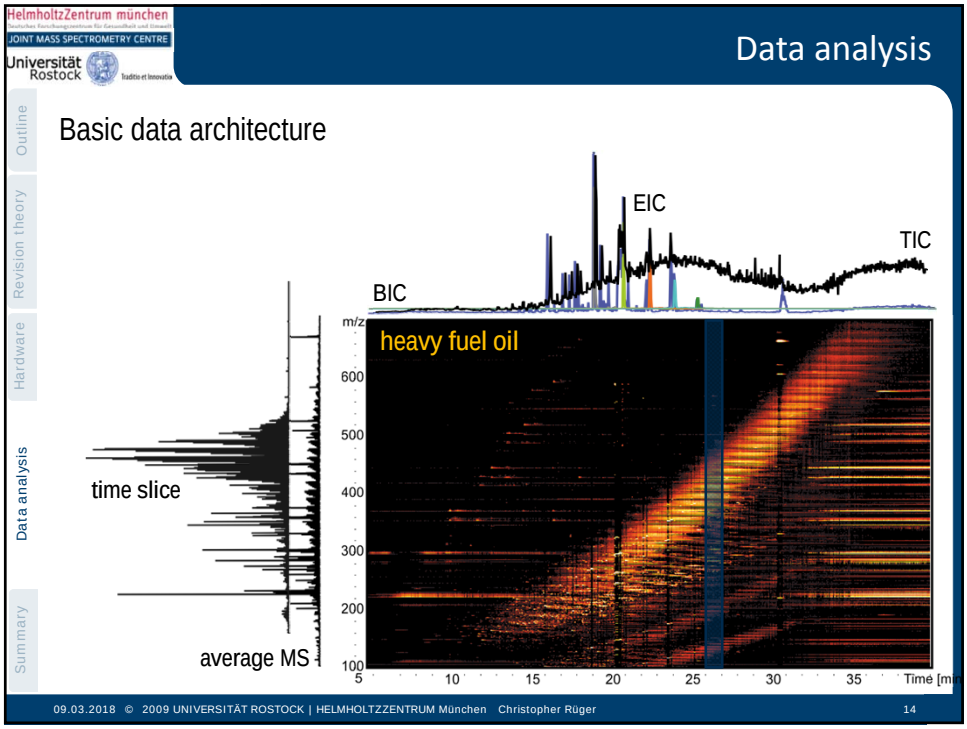
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Basic data architecture
EIC
TIC
BIC
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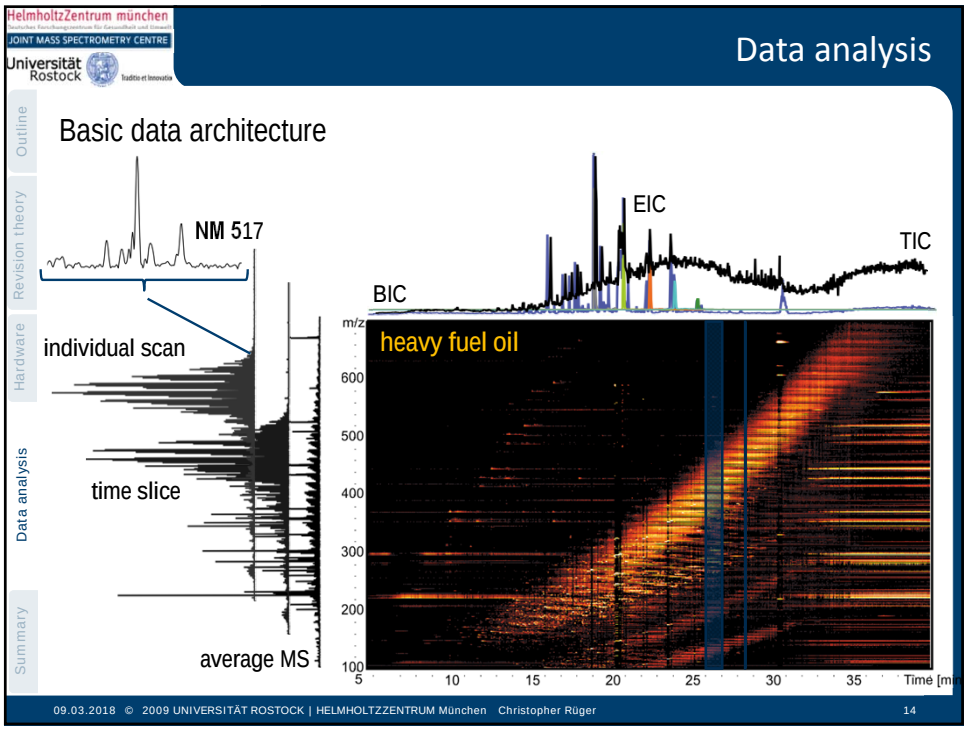
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NM 517
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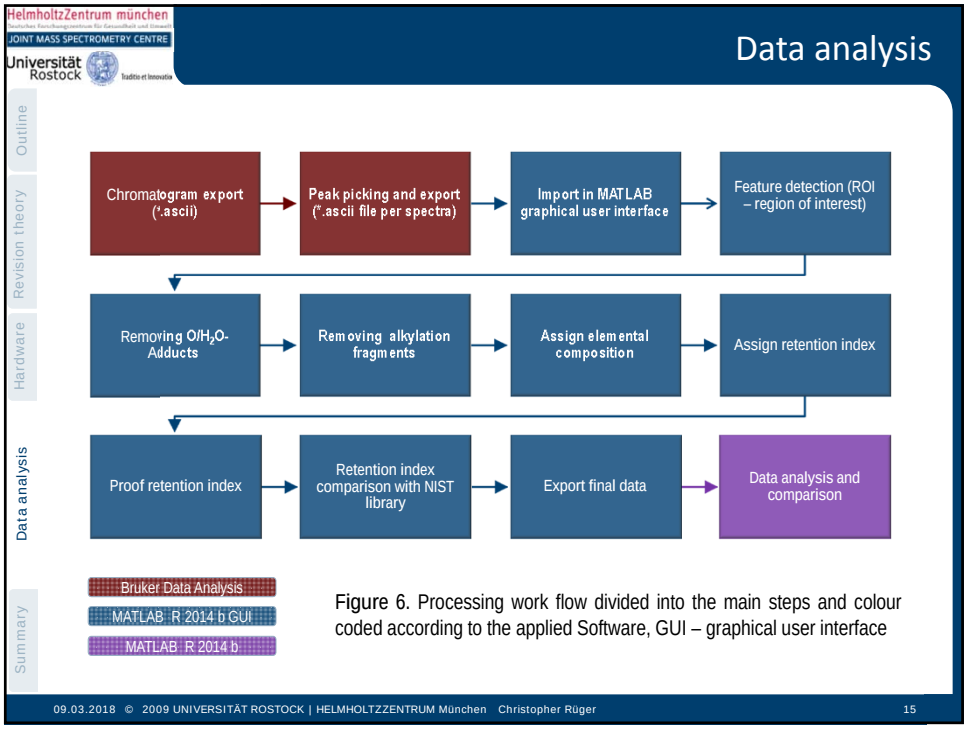
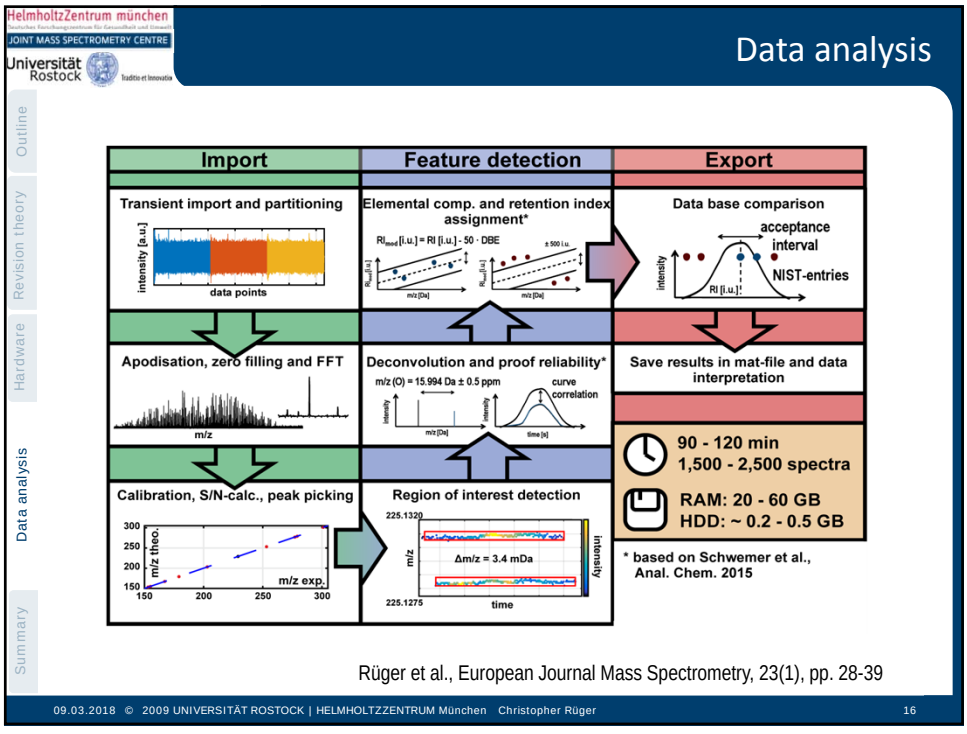


Figure 6. Processing work flow divided into the main steps and colour coded according to the applied Software, GUI – graphical user interface



Rüger et al., European Journal Mass Spectrometry, 23(1), pp. 28-39

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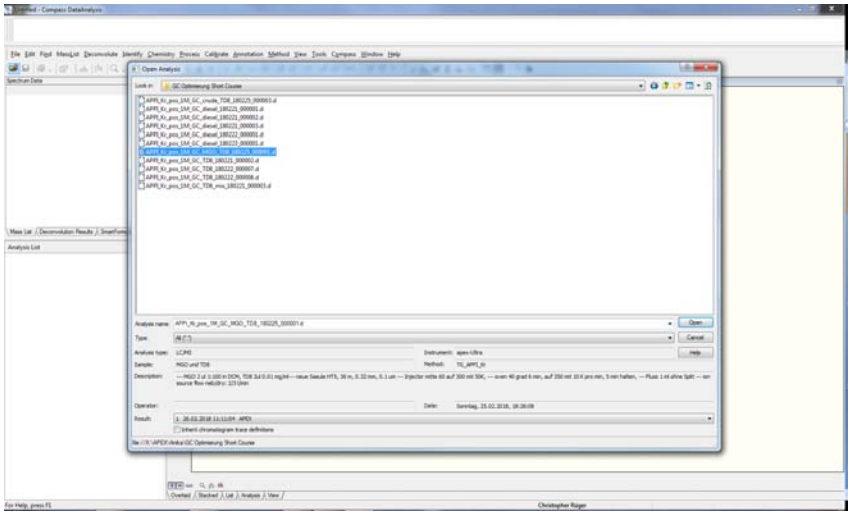
Loading *.baf-file – open measurement



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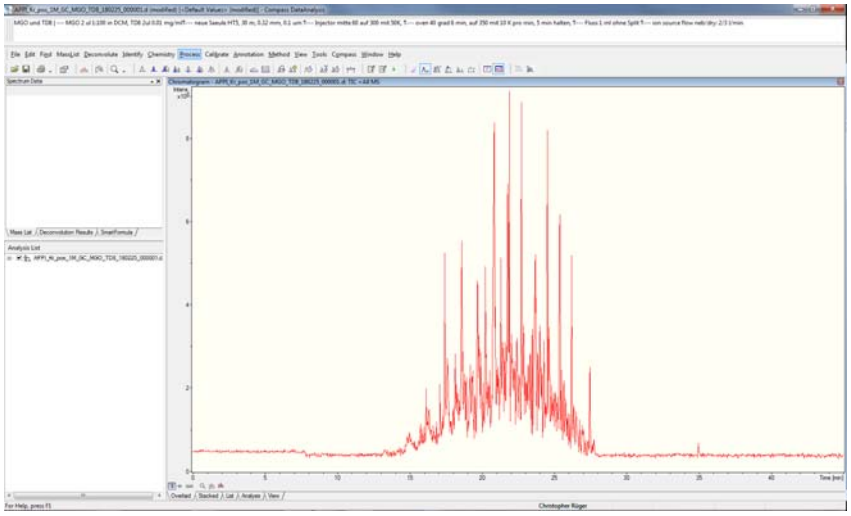

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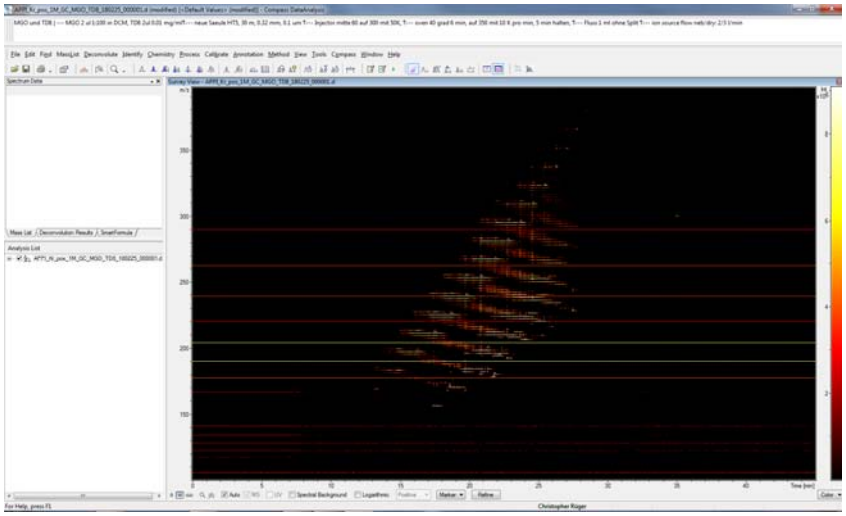
Survey view as first sample check



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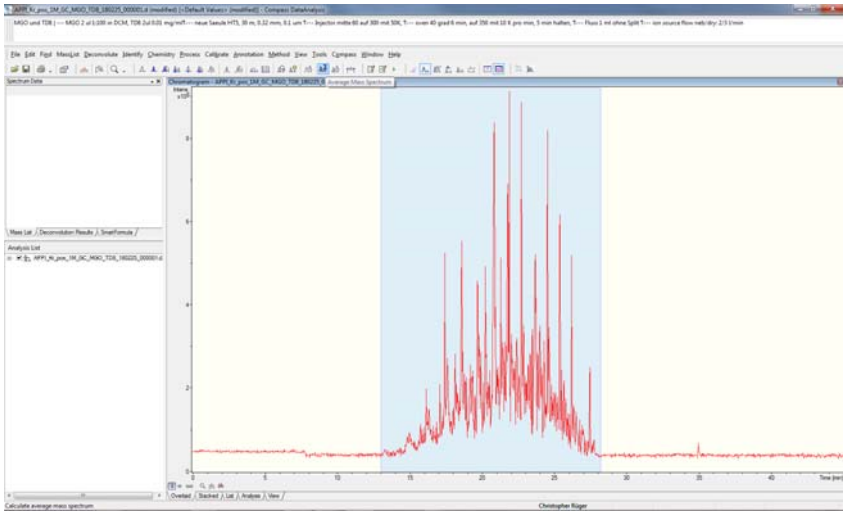
Average of the main response region (can take 1-2 min)



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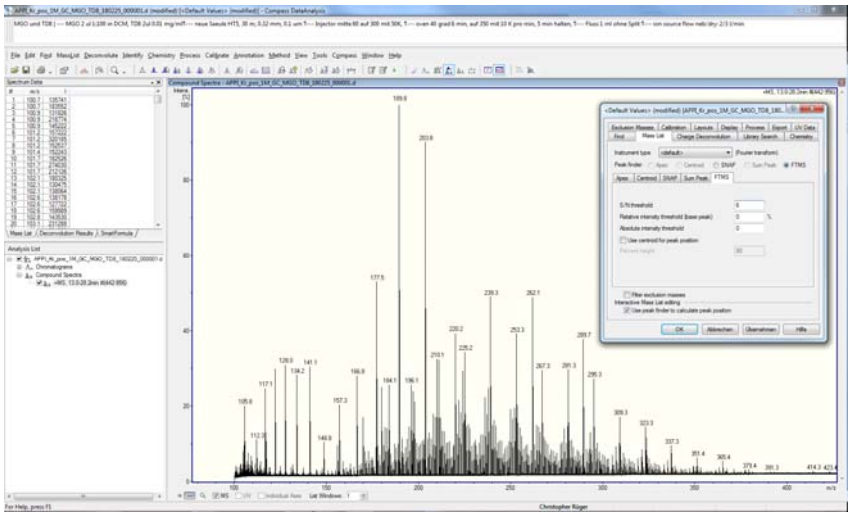
Copy to compound spectra and peak-picking (here 2600 signals > S/N 6)



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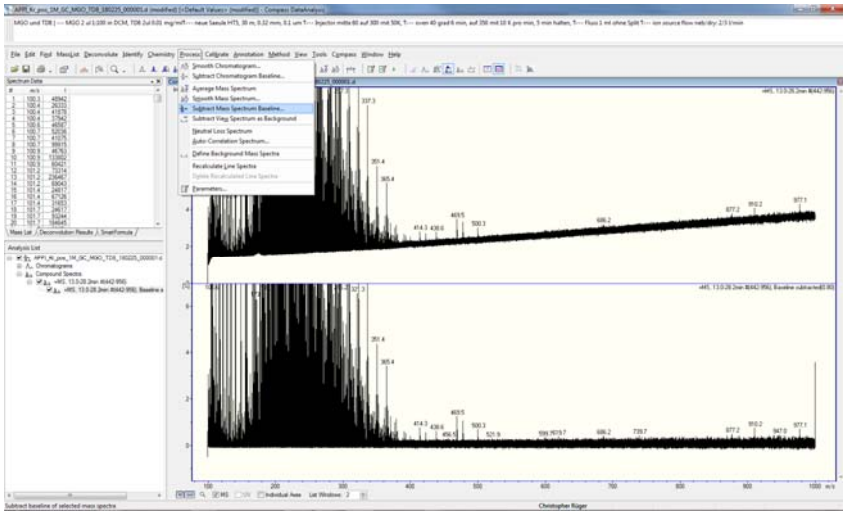
Baseline subtraction



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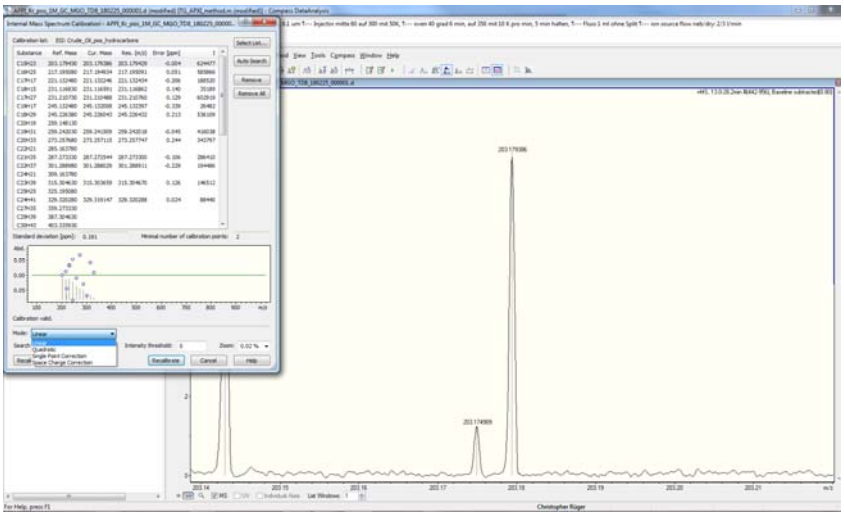
m/z-calibration (internal using standards, internal on homologous series)



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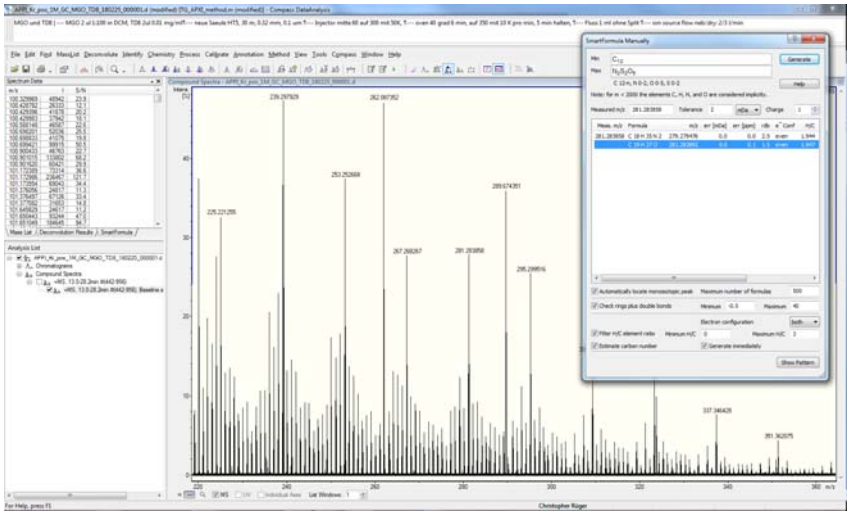
Manual check of the calibration by assigning elemental compositions



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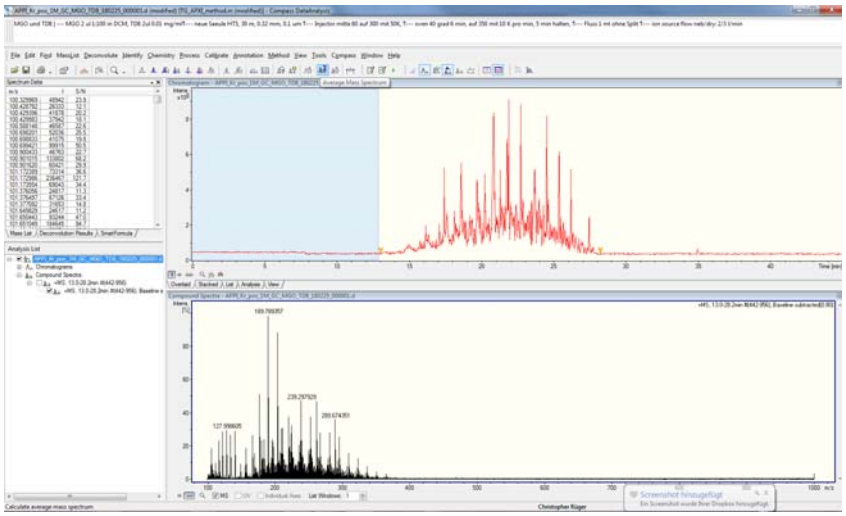
Average of the background noise and removing of the noise



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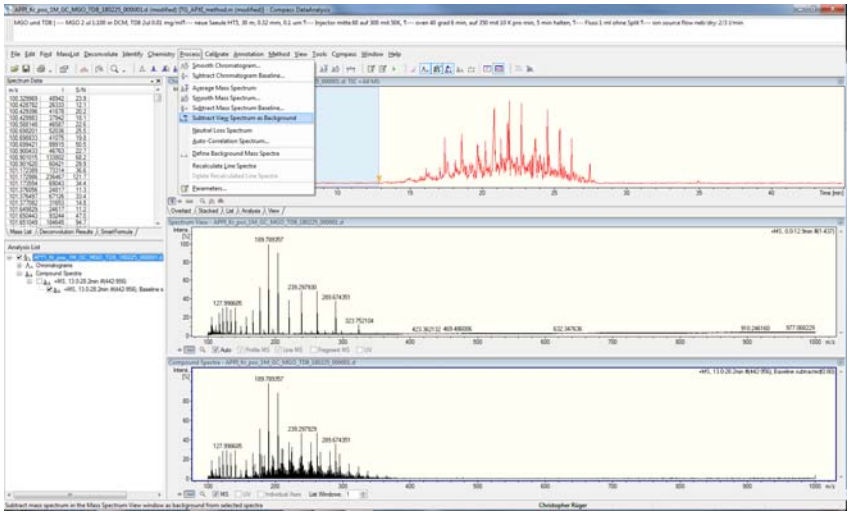

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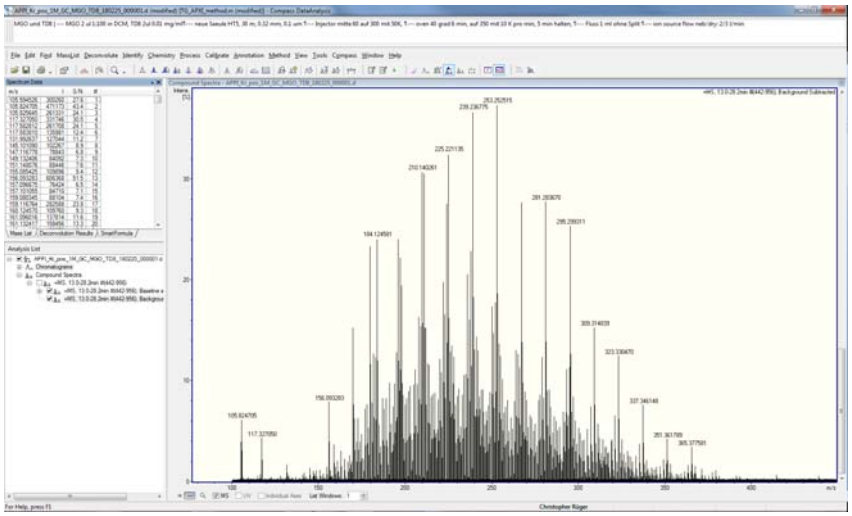
Final average spectra for assignment and export



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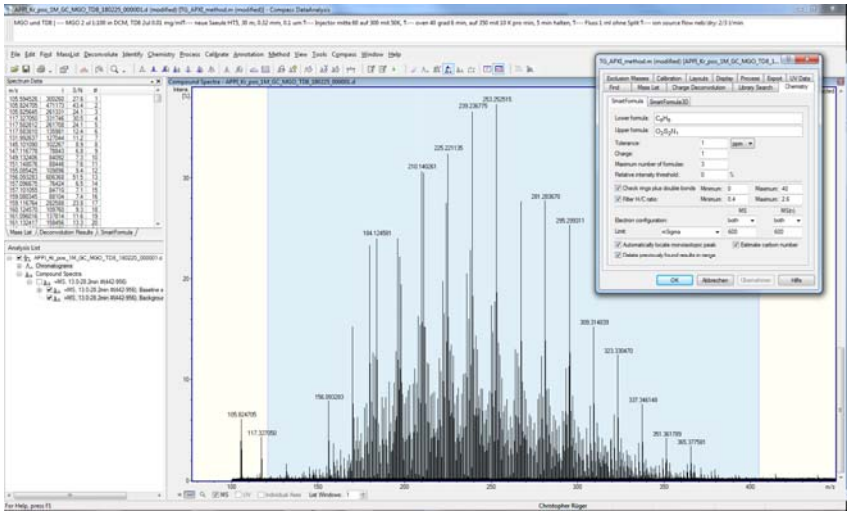
Assignment via Bruker Smart Formula and export as csv-file



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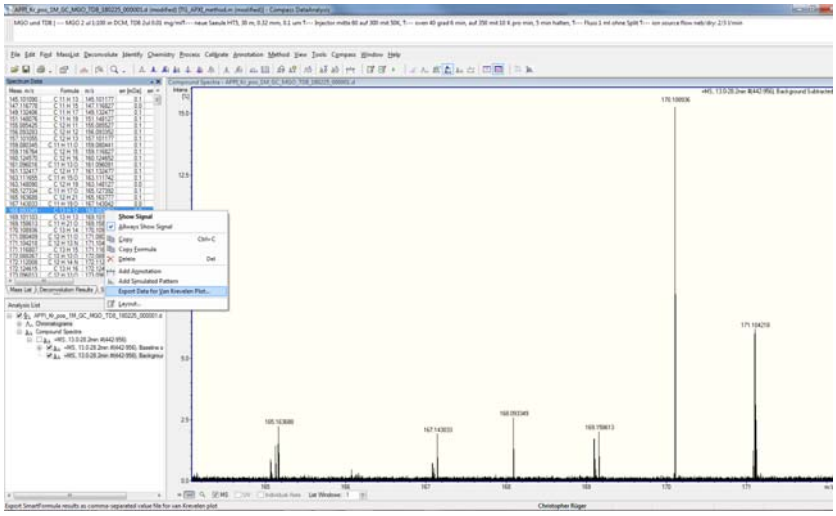
Assignment via Bruker Smart Formula and export as csv-file



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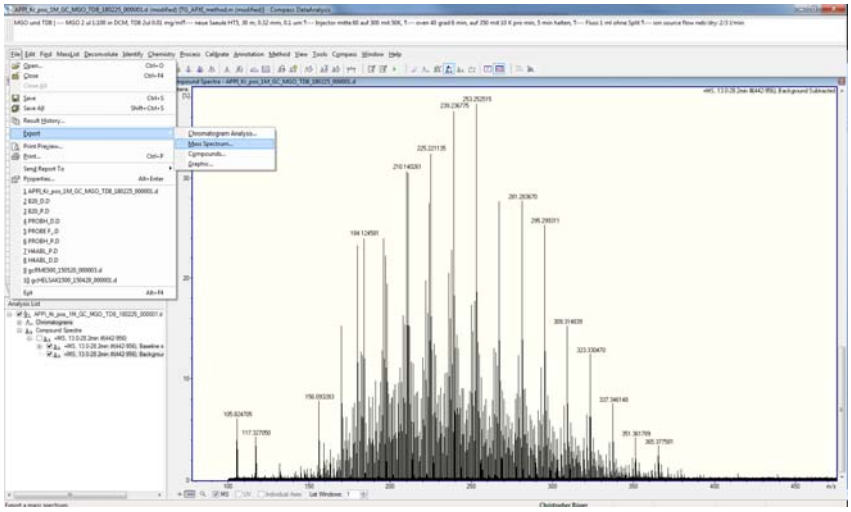
Export of mass list (e.g. *.asc) and assignment in external software



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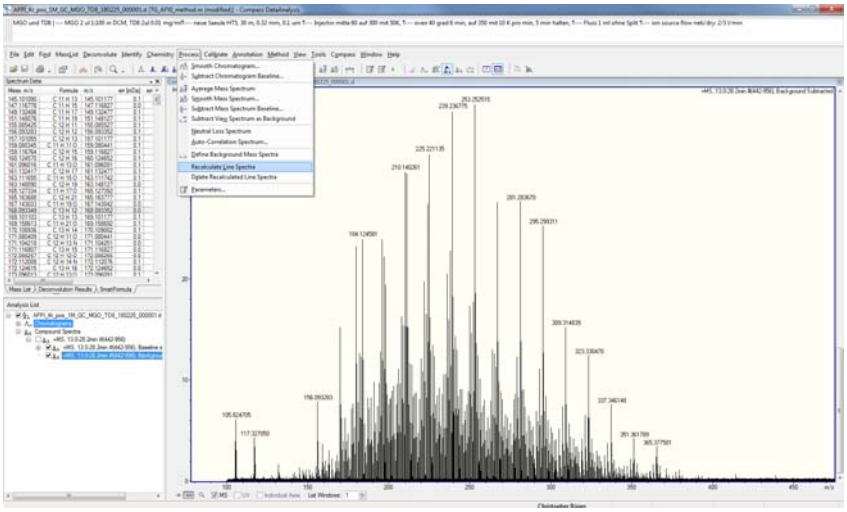
Recalculation of the line spectra – can tack very long (> 1-2 h)



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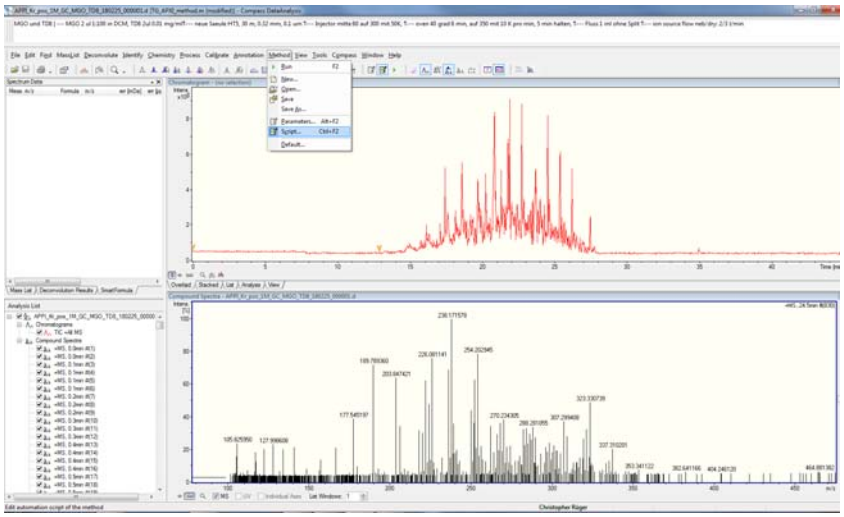
VisualBasic scripting for creation all individual scans and export as ascii-file



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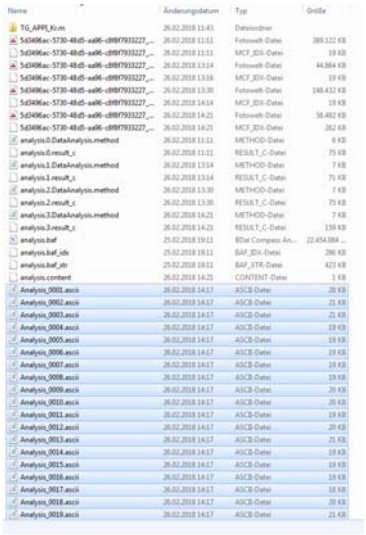

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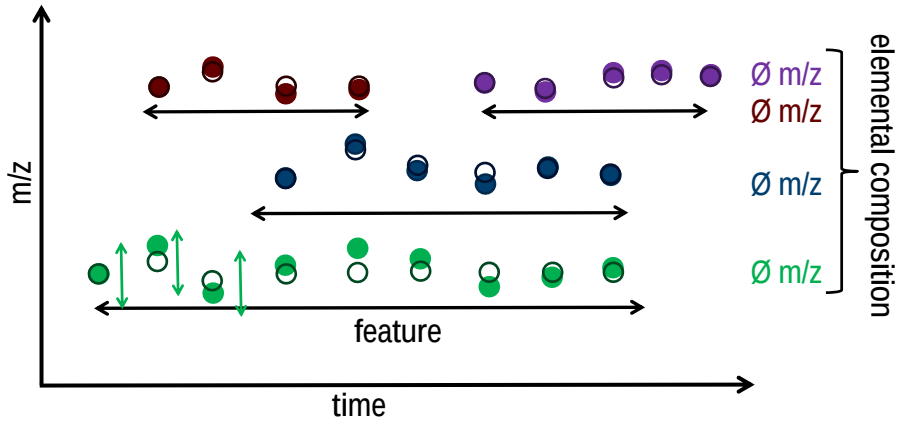
Feature detection / region of interest (ROI):

- feature detection based on time trace and moving mass window
- automatic discarding of non-chromatographic, to low intense and to short features and deconvolution



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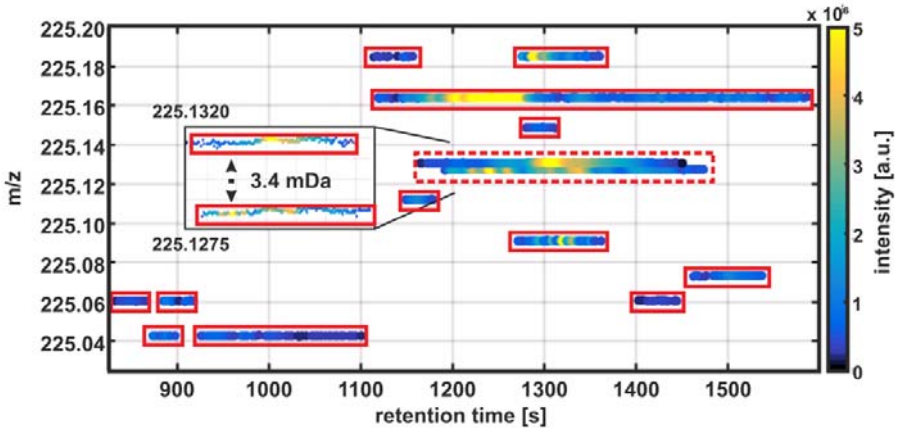
Feature detection – region of interest approach



Rüger et al., European Journal Mass Spectrometry, 23(1), pp. 28-39

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Data analysis

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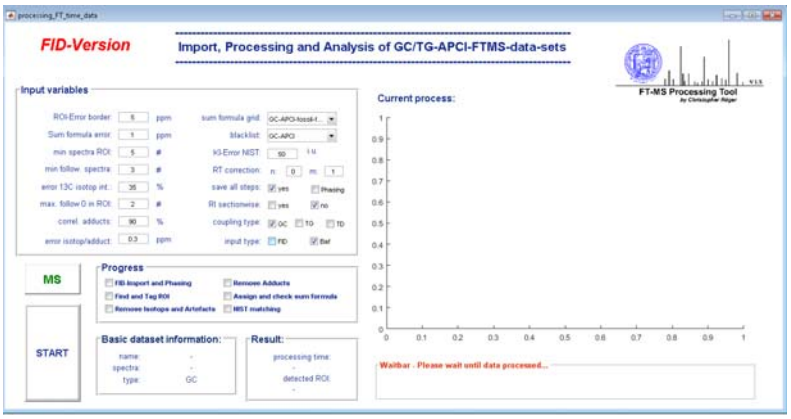
MATLAB graphical user interface for time-resolved processing



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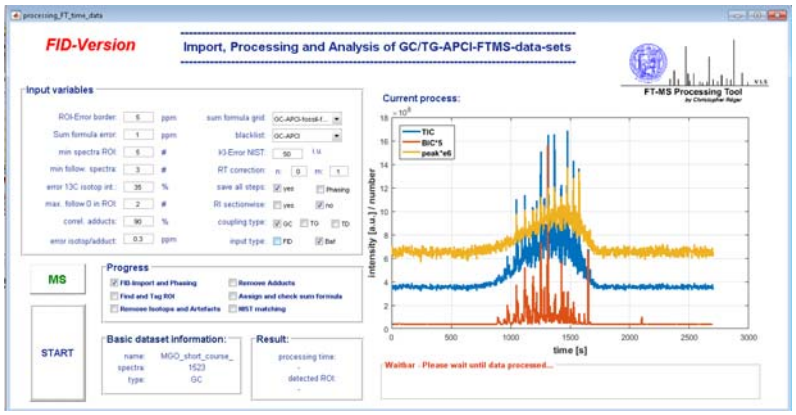

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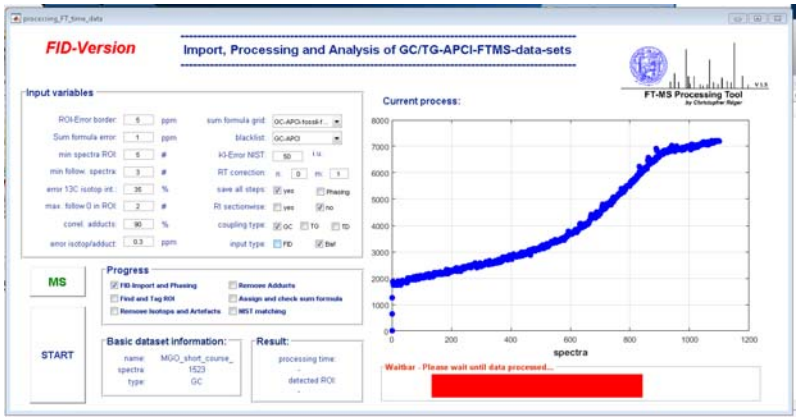

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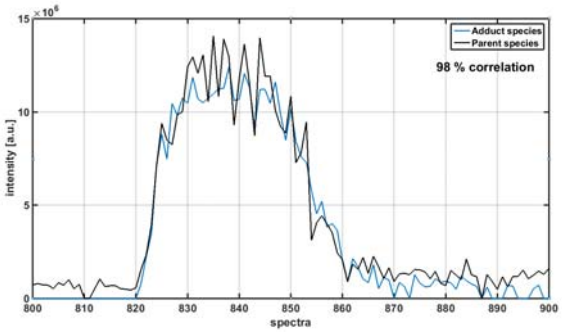
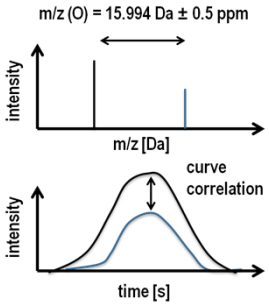
Filtering of artefacts and adducts:

- adducts, e.g. oxygen, filtered using shape correlation, exact mass difference and intensity ratio



Oxygen-Adduct-Artefact occurring in a light fuel oil sample



- removing adducts from the ionisation process via exact mass difference and curve correlation

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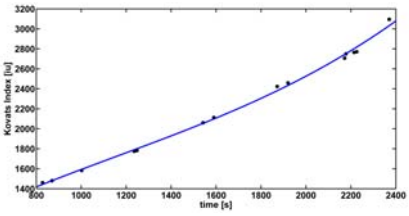
Validation using data base:

- calibration of the retention index (Kovats index) using external calibration with PAH mixture
- limit NIST 2011 data base using column polarity, elemental composition restrictions etc.

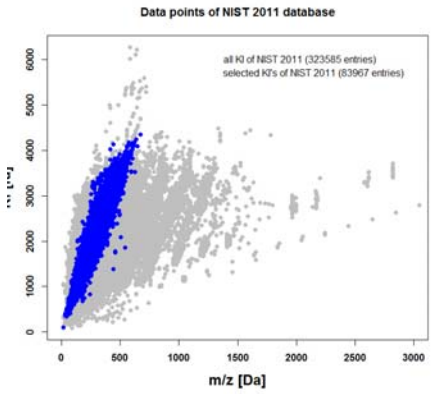


Calibration of the retention index

Gas Chromatography Coupled to Atmospheric Pressure Chemical Ionization FT-ICR Mass Spectrometry for Improvement of Data Reliability

Theo Schwemer,[1,2] Christopher P. Rüger,[1] Martin Sklorz,[1-3] and Ralf Zimmermann[1,2,3]

[1]Joint Mass Spectrometry Centre/Chair of Analytical Chemistry, University of Rostock, 18051 Rostock, Germany
[2]HICE – Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosols and Health, 85764 Neuherberg, Germany, www.hice-vi.eu
[3]Joint Mass Spectrometry Centre/Cooperation Group Comprehensive Molecular Analytics, Helmholtz Zentrum München, 85764 Neuherberg, Germany



Correlation of m/z and retention index (Kovats Index) of NIST database

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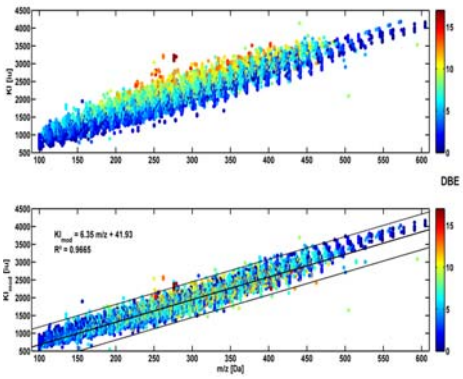
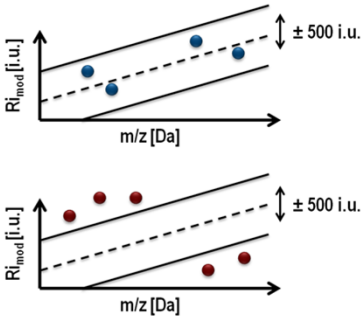
Validation using data base:



RI_{mod} [i.u.] = RI [i.u.] - 50 · DBE



RI_{mod} = RI – (50 x DBE) = 6.35 m/z + 41.93

- removing elemental composition assignments via the DBE and data base entries

Schwemer, Rüger et al., Analytical Chemistry, 87(24), pp. 11957-11961

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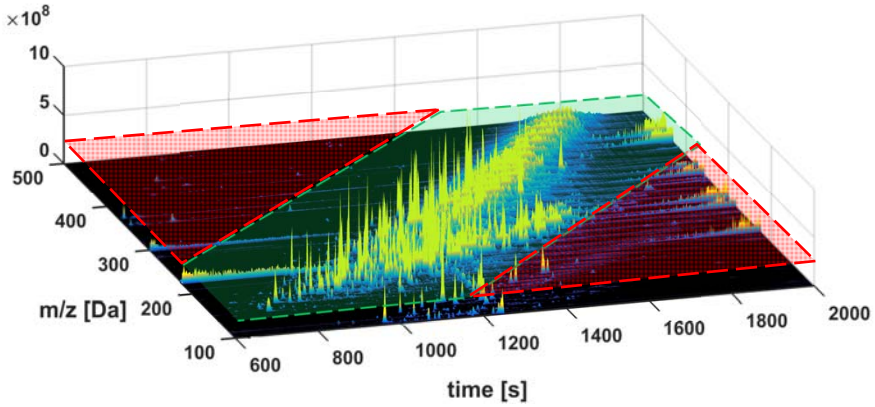
Data complexity:



Simplified view of the approach using a chromatogram of a heavy fuel oil sample with color coded filter areas

Schwemer, Rüger et al., Analytical Chemistry, 87(24), pp. 11957-11961

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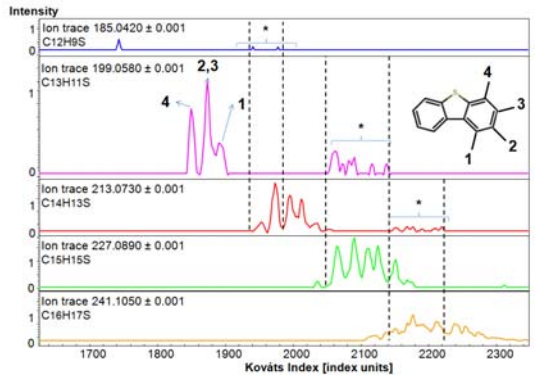
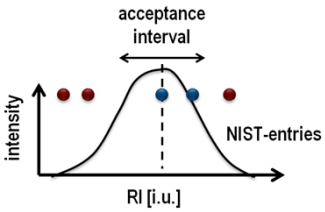
Structural elucidation:

• old approach: manually via data analysis and the results from the MATLAB processing for known species of interest, e.g. PAHs, Thiophens etc.(targeted approach)





• automatically adding structural hints via a direct comparison between NIST entries and acceptance interval

Manual data mining for structural elucidation of selected targets

Schwemer, Rüger et al., Analytical Chemistry, 87(24), pp. 11957-11961

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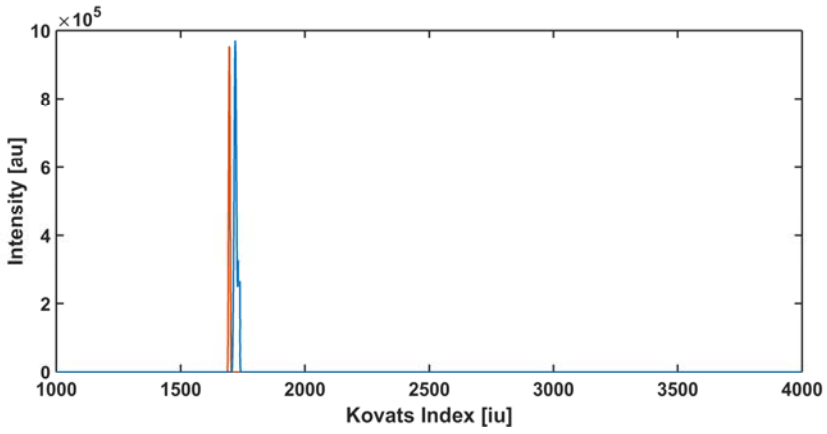
Example for structural elucidation utilizing Kovats index



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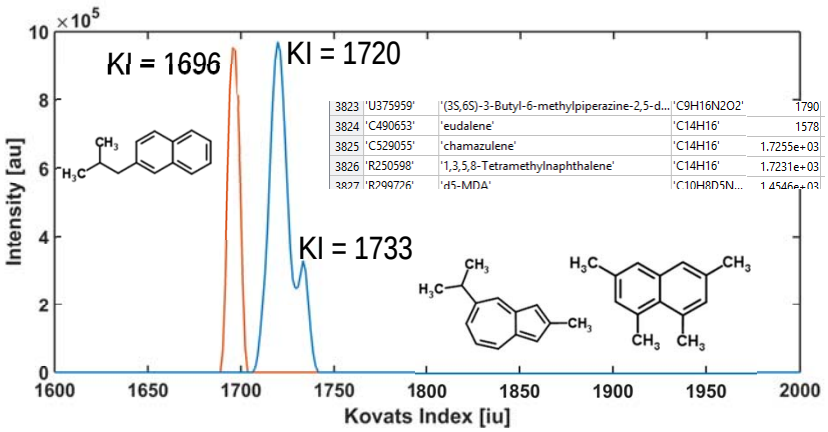
Example for structural elucidation utilizing Kovats index



3823	'U375959'	'(3S,6S)-3-Butyl-6-methylpiperazine-2,5-d...	'C9H16N2O2'	1790
3824	'C490653'	'eudalene'	'C14H16'	1578
3825	'C529055'	'chamazulene'	'C14H16'	1.7255e+03
3826	'R250598'	'1,3,5,8-Tetramethylnaphthalene'	'C14H16'	1.7231e+03
3827	'R299726'	'd5-MDA'	'C10H8D5N...	1.4546e+03

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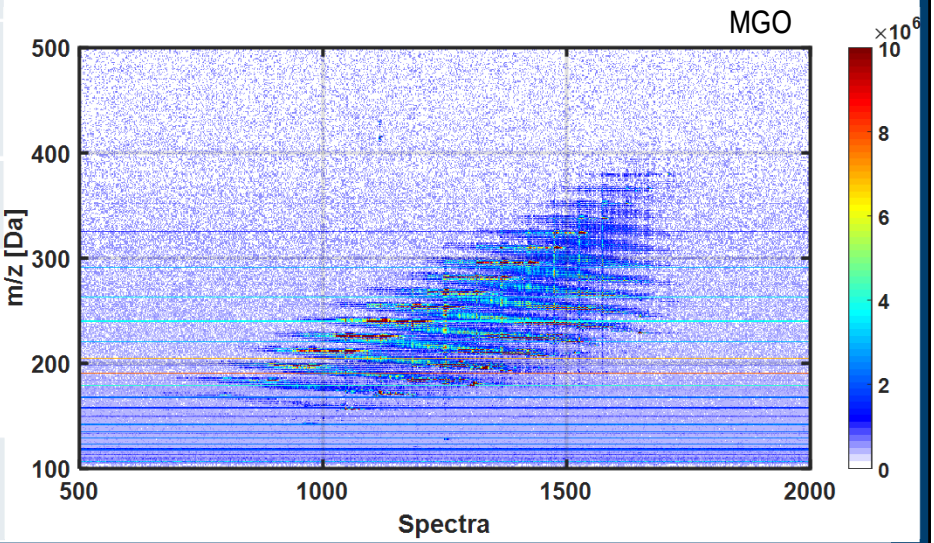
Visualisation of HR-MS data – Raw data survey



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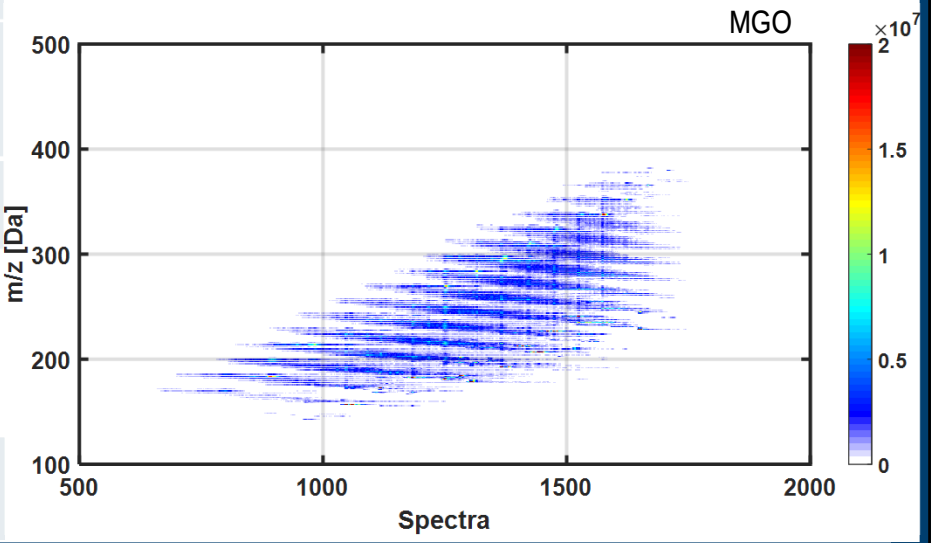
Visualisation of HR-MS data – Processed data survey



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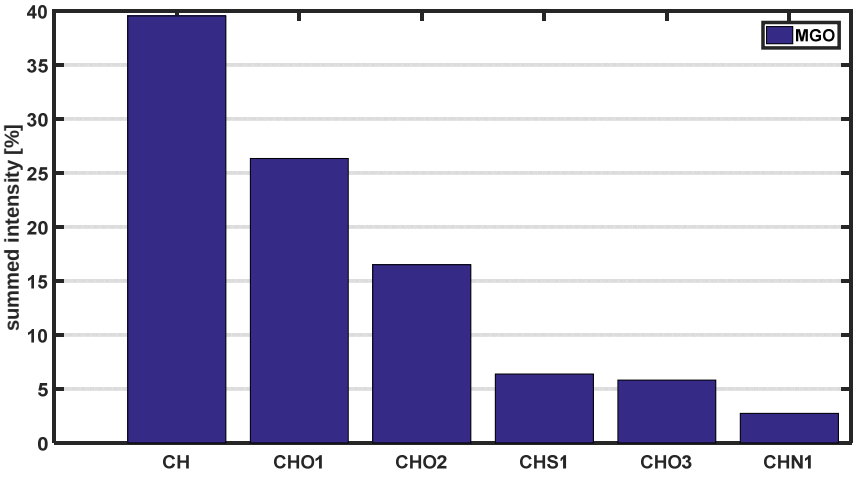
Visualisation of HR-MS data – I. Compound classes



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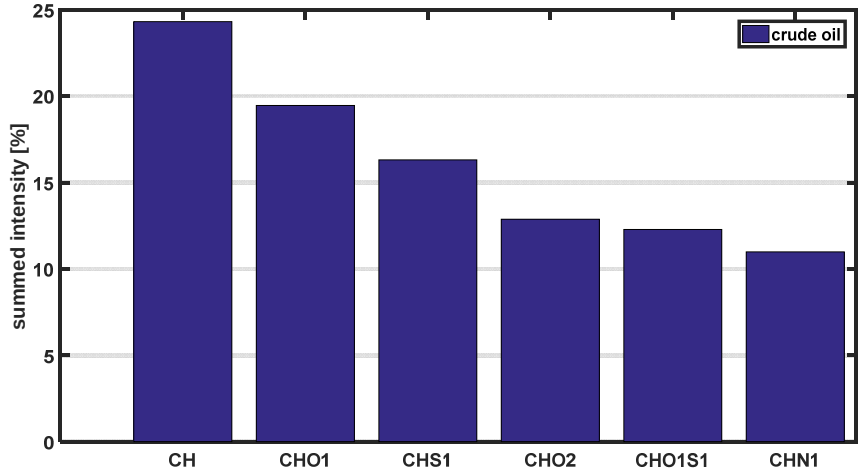
Visualisation of HR-MS data – I. Compound classes



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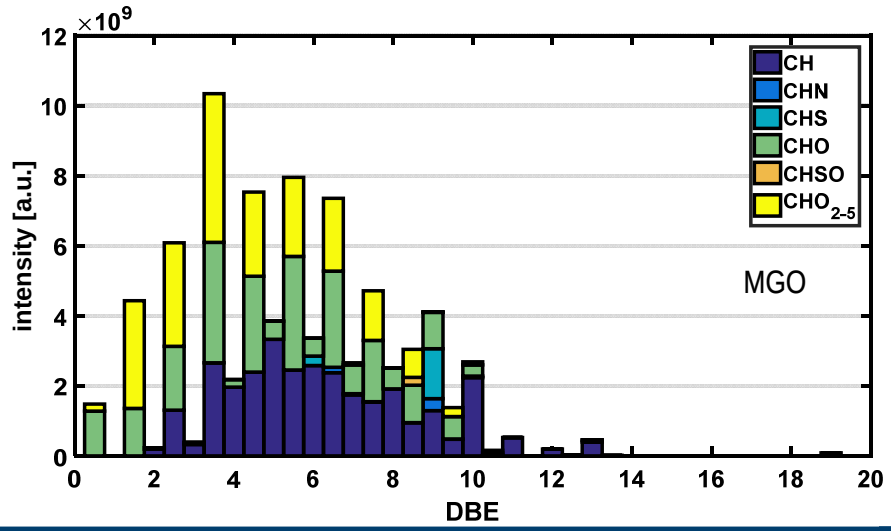
Visualisation of HR-MS data – II. Classes versus aromaticity (DBE)



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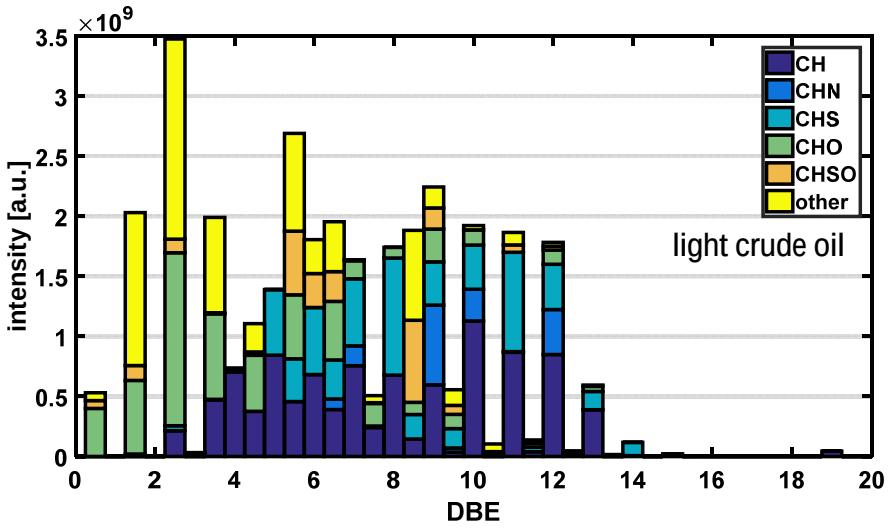
Visualisation of HR-MS data – II. Classes versus aromaticity (DBE)



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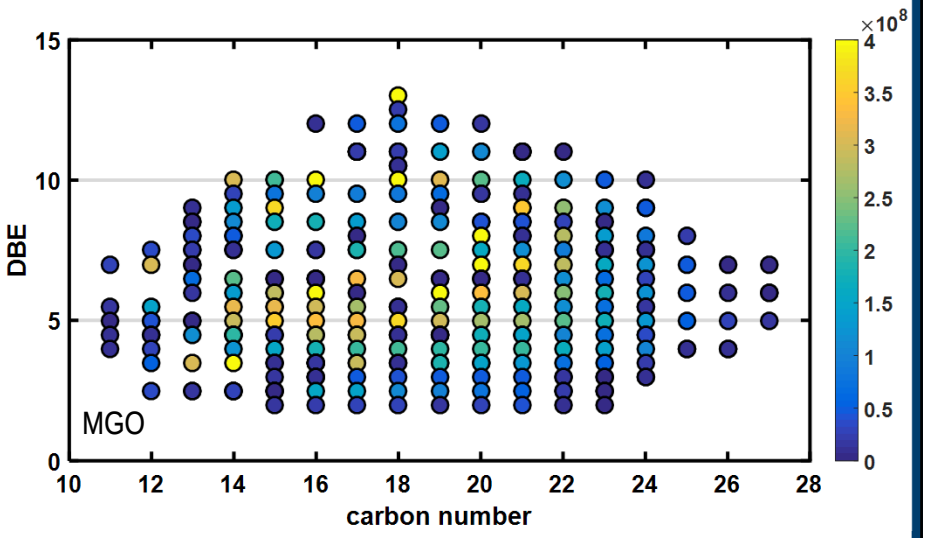
Visualisation of HR-MS data – III. Aromaticity (DBE) versus carbon number



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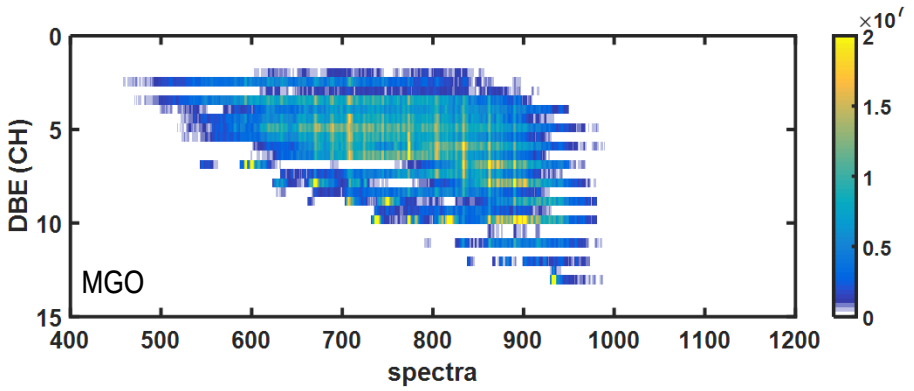
Visualisation of HR-MS data – IV. Classes versus time (spectra number)



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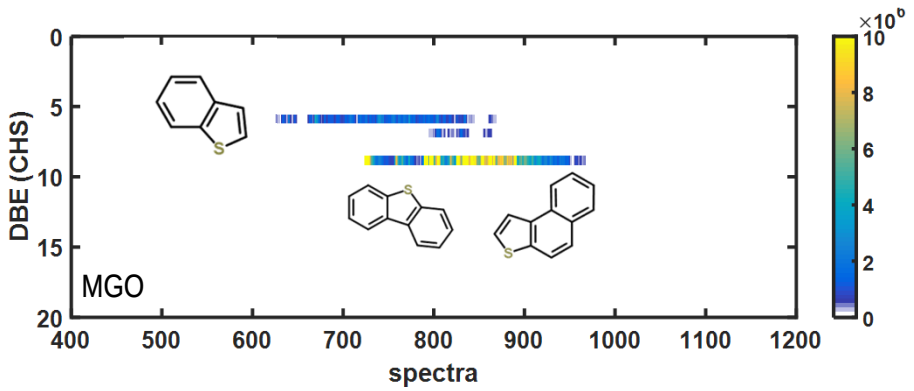

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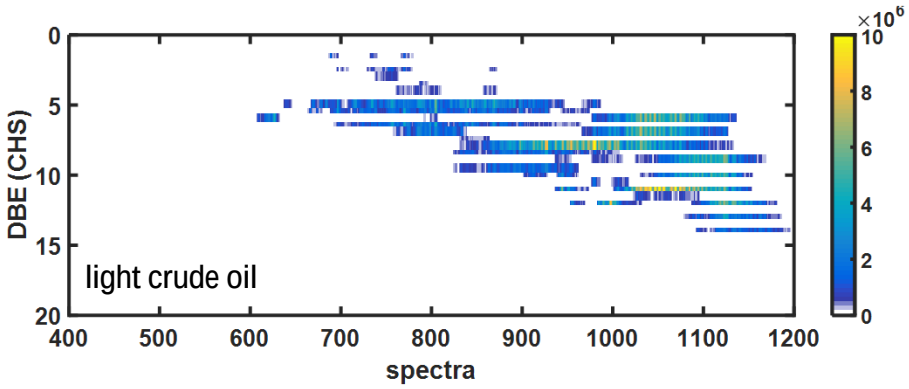
Visualisation of HR-MS data – IV. Classes versus time (spectra number)



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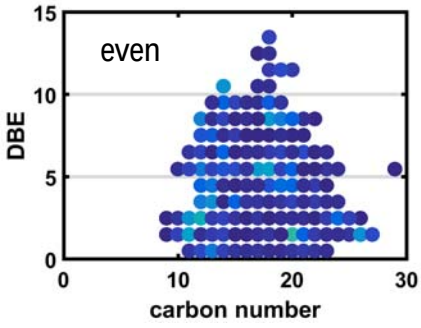
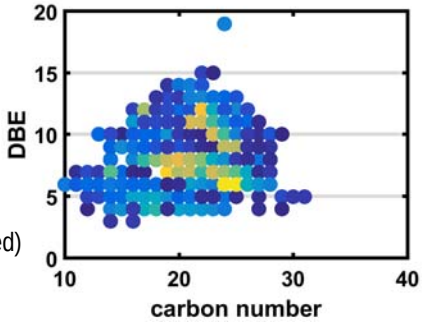
Visualisation of HR-MS data – Radical cation versus protonated ion



- odd species start at certain DBE cut-off
- odd species range to higher DBE values
- even ion intensity is far lower



- even ion species reveal lower carbon numbers
- ratio of odd/even (radical cations/protonated) as performance test (should be roughly 3)

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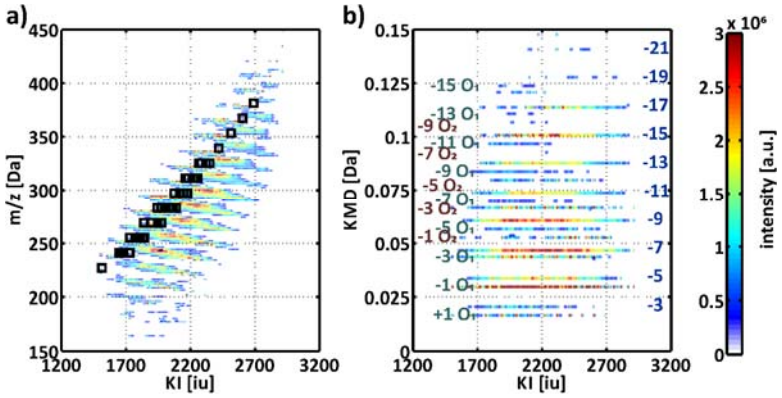
Example for data visualisation – adapted Kendrick mass defect plot



Smit, Rüger et al., Energy and Fuels, 29(9), pp. 5554-5562

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Hardware aspects
- coupling to LC can be done with common ESI, APCI and APPI sources
- GC hyphenation requires optimized cell design (flow aspects)

Data acquisition aspects
- GC hyphenation minimized matrix/solvents effects
- separation method have to carefully optimized on to the analytical problem, e.g. column, flow (not done within this course)

Data analysis aspects
- data processing requires sophisticated software tools to mine the information
- batch processing is more difficult compared to direct infusion
- high requirements on the processing side, in particular RAM

Conclusion
- APPI is a powerful technique studying non-polar and low-polar constituents
- aside from protonated species radical cations are more readily formed
- higher information depth - but have to be accessed via specialized processing solutions

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Thank you for your kind attention!