LECO WEBINAR:

HIGH TEMP GC×GC OF LIGHT CRUDE OIL AND HIGH BOILERS USING NOMINAL AND HIGH RESOLUTION TOFMS

Hike to Zugspitze, JMSC Retreat Meeting 2016

HIGH TEMP GC×GC OF LIGHT CRUDE OIL AND HIGH BOILERS USING NOMINAL AND HIGH RESOLUTION TOFMS

Uwe Käfer, Maximilian Jennerwein, Benedikt Weggler, Markus Eschner, Ralf Zimmermann and Thomas Gröger

Joint Mass Spectrometry Centre (JMSC)
University of Rostock and Helmholtz Zentrum München
München, Germany

Universität Rostock Traditio et Innovatio
HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt
JOINT MASS SPECTROMETRY CENTRE

Photonion GmbH
Schwerin, Germany

ASG Analytik-Service Gesellschaft mbH
Neusäß, Germany

SIM GmbH
Oberhausen, Germany

LECO Instrumente GmbH
Mönchengladbach, Germany

JOINT MASS SPECTROMETRY CENTRE (JMSC)

of the Helmholtz Zentrum München and the University of Rostock

(Staff: about 50 people)

Universität Rostock Traditio et Innovatio

Chair for Analytical Chemistry

Thermal Analysis / Photionization mass spectrometry	Aerosol and Laser-Mass Spectrometry	Ultra-high Resolution Mass Spectrometry
		
Thorsten Streibel	Johannes Passig	Marin Sklorz

CMA Cooperation Group Comprehensive Molecular Analytics

Aerosol Chemistry	Aerosol Toxicology	Aerosol Physics	Bio-monitoring	Comprehensive Separation
				
Jürgen Schnelle-Kreis	Sebastian Öder	Thomas Adam	(Jutta Lintelmann)	Thomas Gröger

HelmholtzZentrum münchen
German Research Center for Environmental Health

der Bundeswehr Universität München

Chair for Chemistry, Environmental- & Energy process technology

photonion

Spin-off Company
Photoionization mass spectrometry and online process analytics

Ralf Zimmermann
University Rostock
Chair for Analytical Chemistry and Head of the Cooperation Group Complex molecular Analysis

HICE Aerosols and Health
Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health

Aerosol & Health

Enabling Technologies

WHO DID THE WORK...

Application and instrumental development on *GC×GC(-TOFMS)* since 2003 (PhD Thesis Werner Welthagen, now Sasol). >12 ongoing or accomplished **PhD Theses on comprehensive separations** including *GC×GC*

Uwe Käfer
PhD Student

"Characterization of Heavy Petroleum Products (tentative title, since 2016)"
DIP-HRT, TA-HRT, GCxGC-HRT

Maximilian Jennerwein
ASG mbH

"PhD Thesis: Application of comprehensive two-dimensional Gas Chromatography Time-of-Flight Mass Spectrometry and Visual Basic Script for detailed Analysis of fossil and biogenic Fuels, 2017"
GC×GC-TOFMS (Peg4D)

Benedikt Weggler
Postdoctoral Researcher at Penn State University

"PhD Thesis: Untargeted Analyses of the Semi-Volatile Organic Fraction in Anthropogenic Particulate Matter, 2016"
GCxGC-TOFMS (Peg4D and HRT)

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JOINT MASS SPECTROMETRY CENTRE

Thomas Gröger
Helmholtz Zentrum München
PI Comprehensive Separation and Enabling Technologies (2004)

Mohammad Saraji
(former PhD Student)
Photonion GmbH
R&D, TOF Systems, Ionization techniques, Thermal Analysis

Markus Eschner
(former PhD Student)
ASG mbH
Head of R&D, Team manager 'chromatography', Scope: Special analysis

INSTRUMENTATION

Pegasus GC-HRT 4D

(Actual: Pegasus GC-HRT+ 4D)

Installation: 2012 as 1D - System (pre-release, beta-state), Field upgrade to GC×GC and 6000er detection system

Key Features: Mass Accuracy 2ppm, Resolution up to 50.000, Acquisition Frequency 200 Hz, LN2 Modulation System, EI/CI (DIP and TG as alternative Frontend, SPI as alternative ionization technique)

Software: ChromaTOF 1.xx – 5.10 (… AMCA), MatLab, Decodon (*GasPedal)*

Applications: Environmental, Petro and Health

Pegasus 4D GC×GC-TOFMS

(Actual: Pegasus 4D-C)

Installation: 2003 (PEG III)

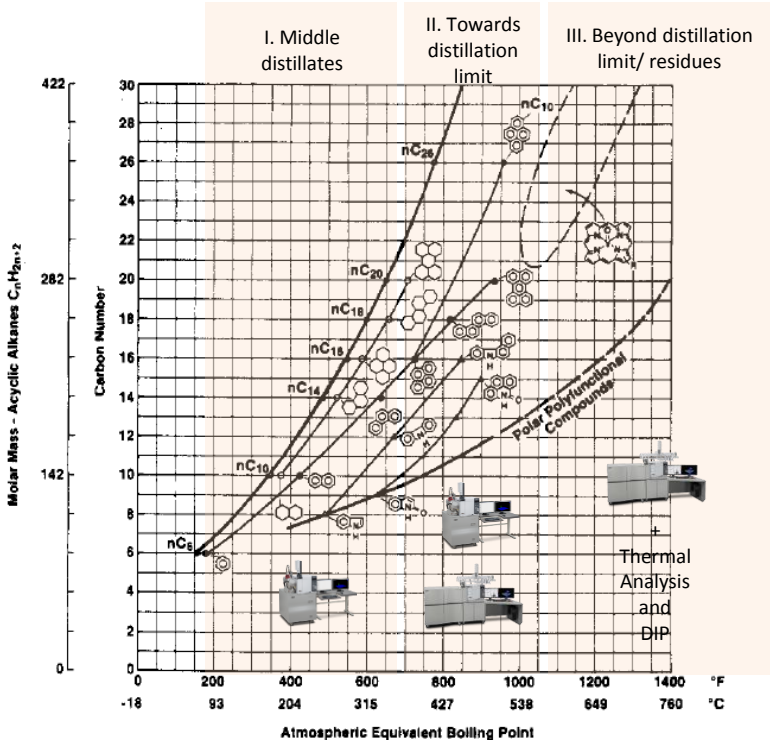
Key Features: unit mass resolution, robust EI source, high throughput analysis, LN2 Modulation System (ASG: Electric Chiller), (Automatic online-derivatization)

Software: ChromaTOF 2.xx – 4.51 (Statistical Compare, Scripting), MatLab (Eigenvector PLS toolbox), Decodon (GasPedal), Lablicate (OpenChrom)

Applications: Environmental, Forensics, Metabolomics, (Petro)

AGENDA

Application of…



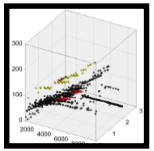
Boduszynski, Energy&Fuel, 1987, 1, 2

I

… GC×GC-TOFMS for an detailed PIONA analysis and complete quantification of middle distillates

II

… High temperature GC×GC-TOFMS for a two-dimensional simulated distillation



… GC×GC in combination with high resolution and accurate mass TOFMS for a better characterization of petroleum

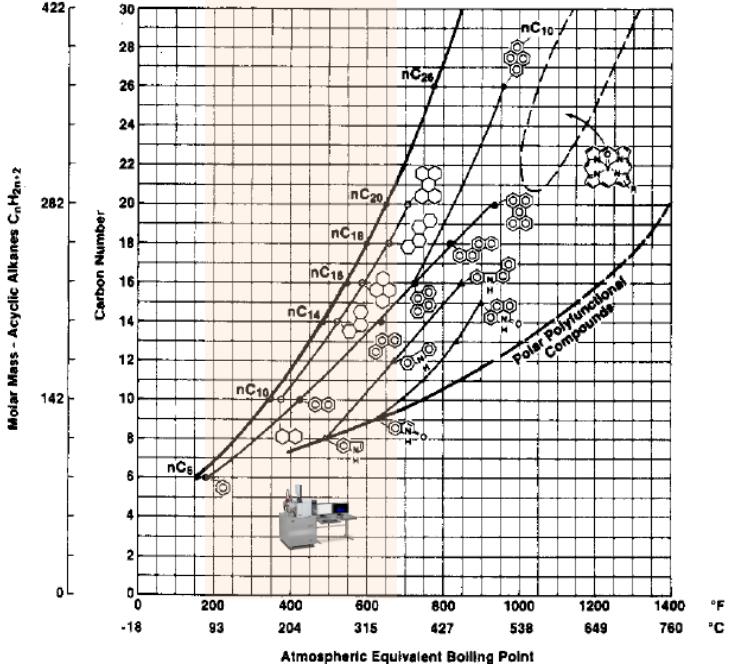
II

… Thermal methods as alternative front ends as alternative inlet systems for HRT to go beyond the boiling point limit

AGENDA

Application of…

I. Middle distillates



Boduszynski, Energy&Fuel, 1987, 1, 2

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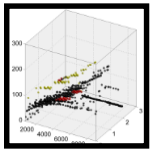

… GC×GC in combination with high resolution and accurate mass TOFMS for a better characterization of petroleum

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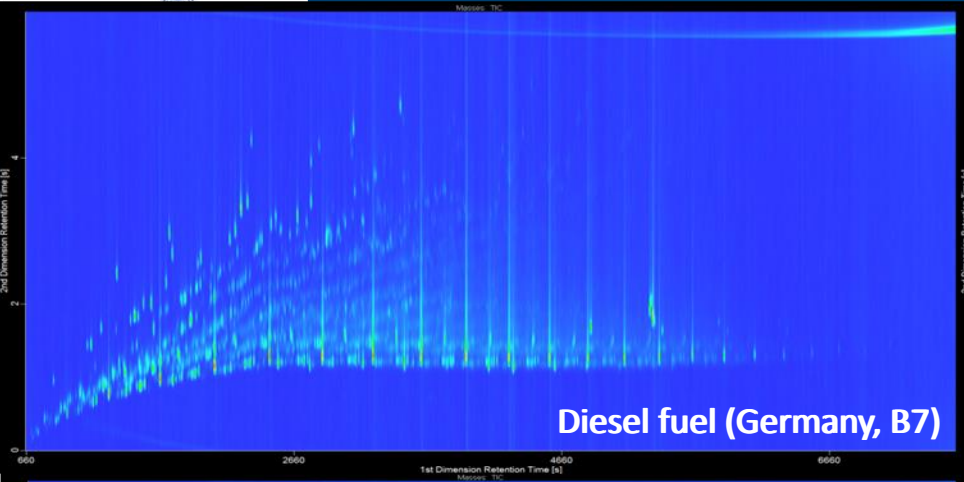
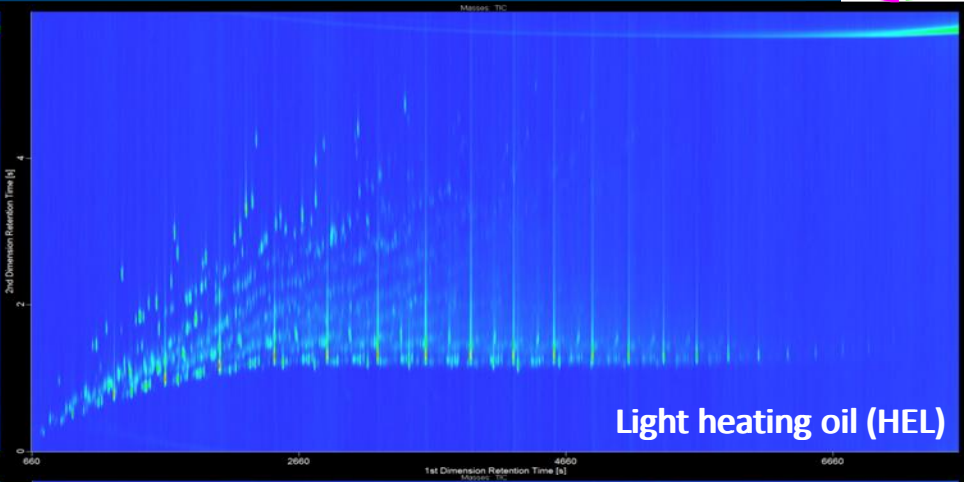
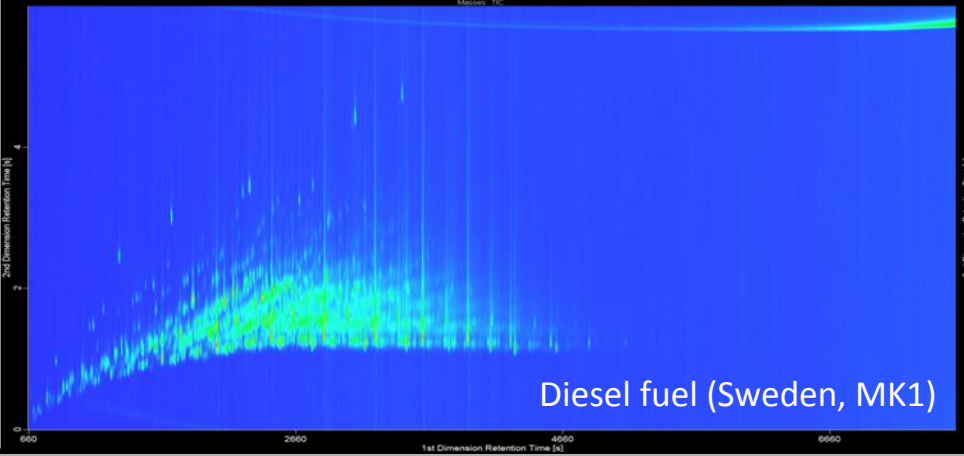
Analysis of Middle Distillates



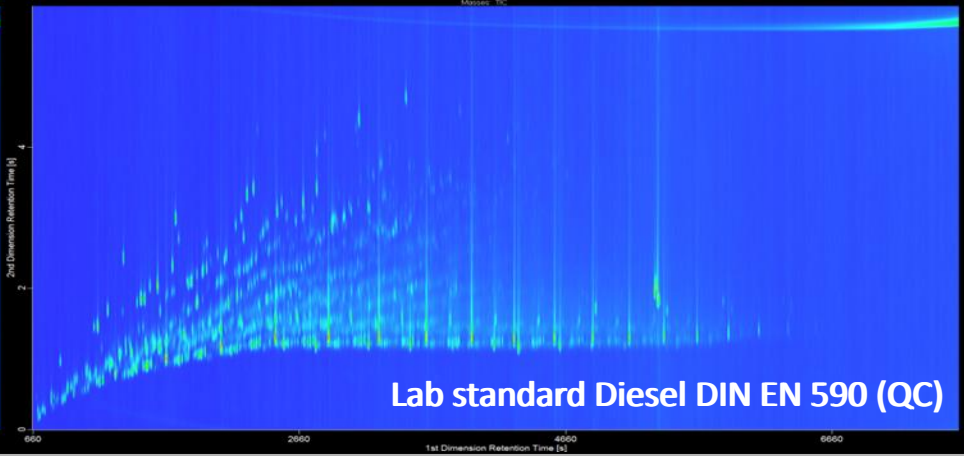
Diesel fuel (Germany, B7)



Light heating oil (HEL)

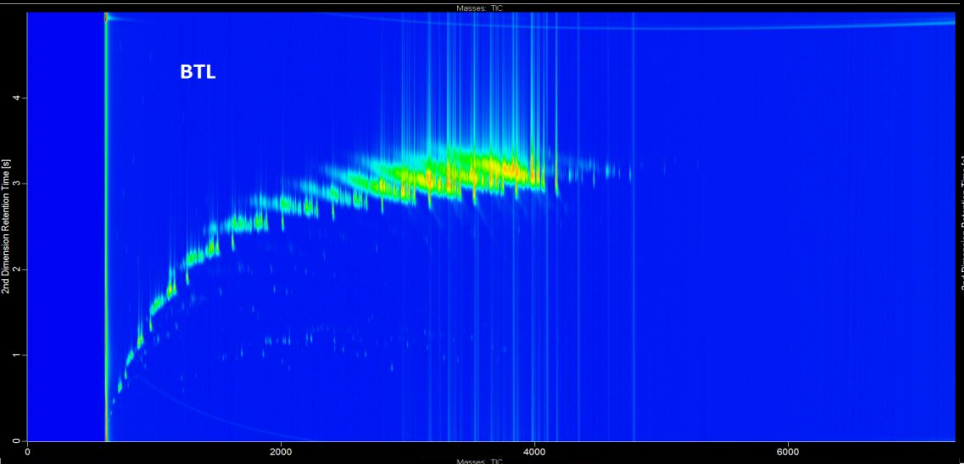


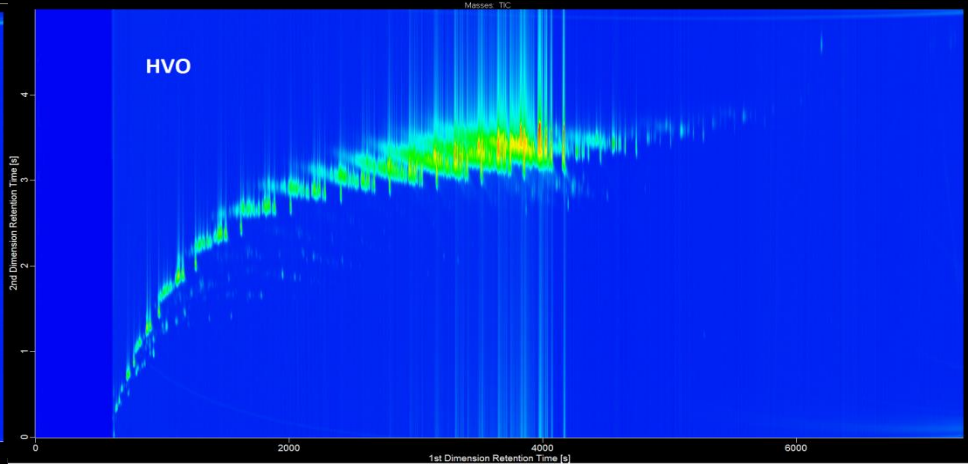
Diesel fuel (Sweden, MK1)

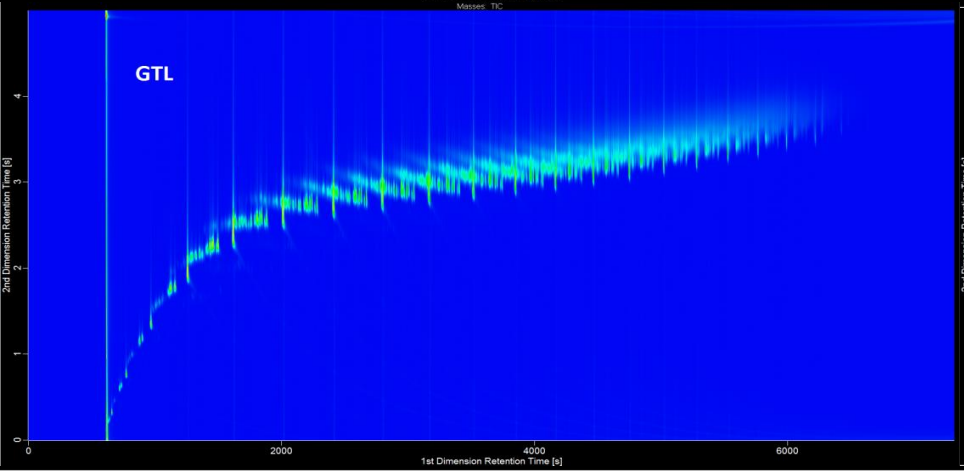


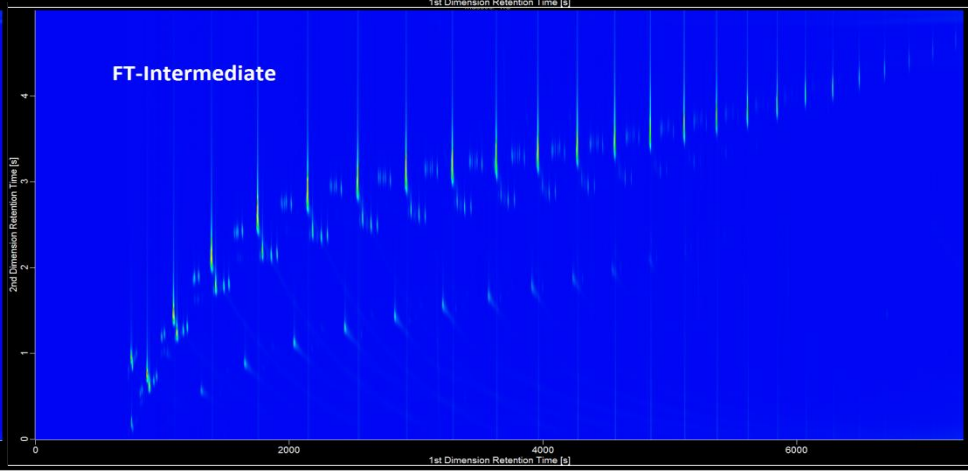
Lab standard Diesel DIN EN 590 (QC)

Analysis of Middle Distillates





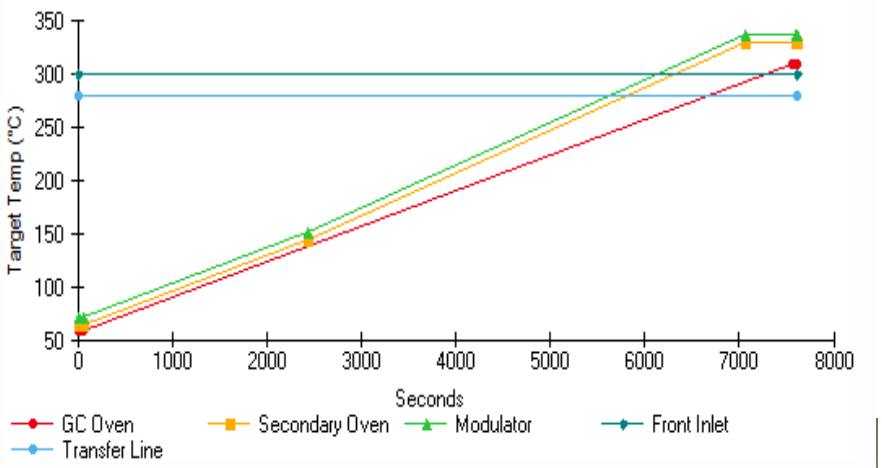




INSTRUMENTATION

Instrument
LECO Pegasus 4D GC×GC-TOFMS
consumable free modulation

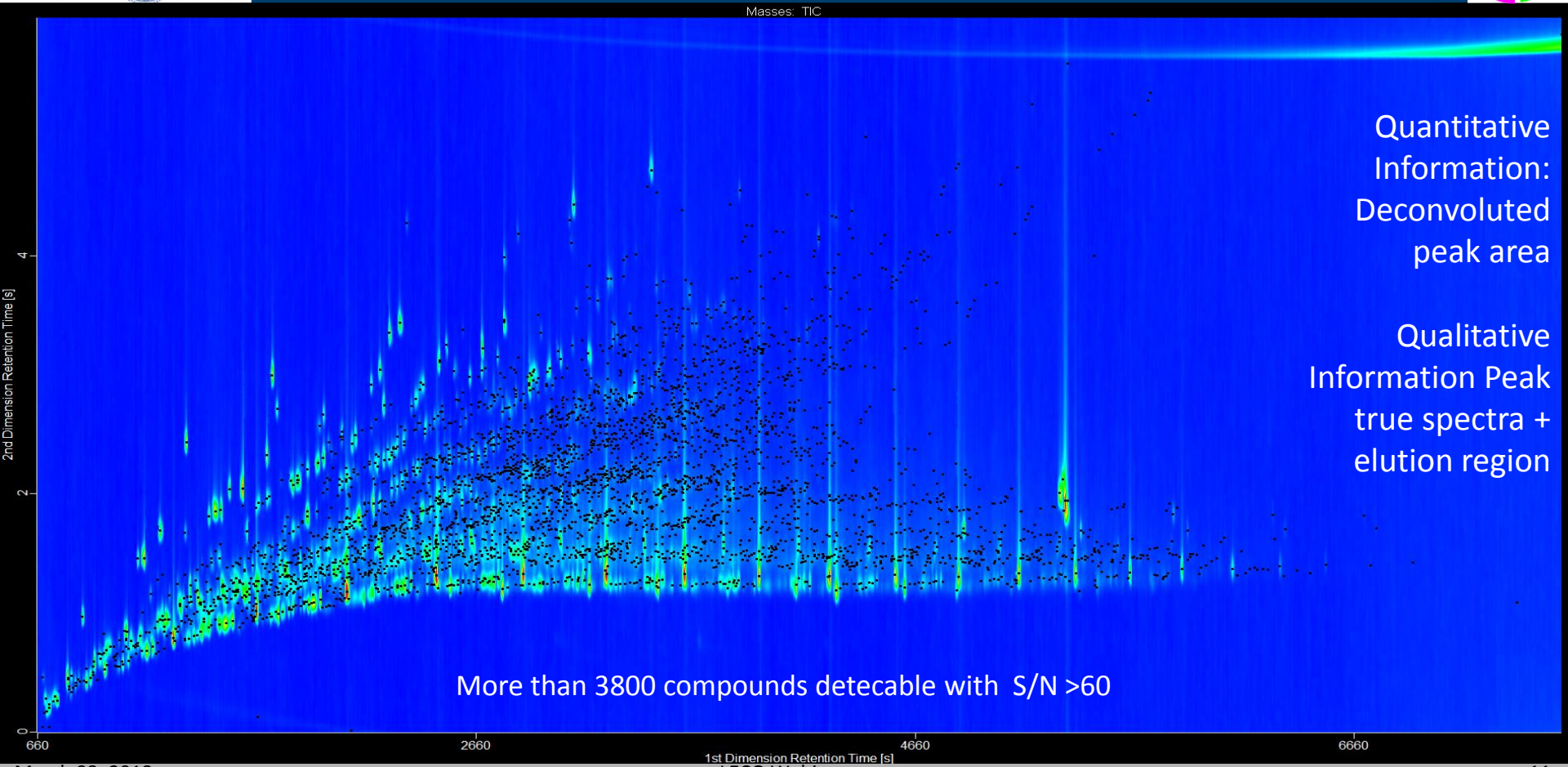
Columns (“normal phase” / ”reversed phase”)
1st Dim.: 60m × 0.25mm × 0.25µm BPX1/BPX50
Mod.: 0.2m × 0.1mm × 0.2µm Rtx1
2nd Dim.: 3.0m × 0.1mm × 0.1µm BPX50/BPX1
Xline: 0.2m × 0.1mm



MS Parameter
Mass range: m/z 35 – 400
Acquisition frequency: 200Hz
Ion Source Temp.: 200°C

GC×GC conditions
Injection: 280°C, 0.2µL, Split 1:400
Flow: 1mL/min const. flow.
Oven T.: 60°C (1min), 2°C/min, 300°C (1min)
6 s modulation, 0.6 s hot pulse time

Data Processing



Quantitative Information: Deconvoluted peak area

Qualitative Information Peak true spectra + elution region

More than 3800 compounds detecable with S/N >60

ASSIGNMENT TO COMPOUND CLASSES

Mass spectrometric scripting based on peak true spectra

Algorithm based on e.g. visual basic (VBS) which could be applied to deconvoluted mass spectra (MS). MS are analyzed for characteristic features. Regional information (classification criteria) could be introduced.

Structure of Scripts (VSB):

- Selection of characteristic fragments or patterns for each substance class

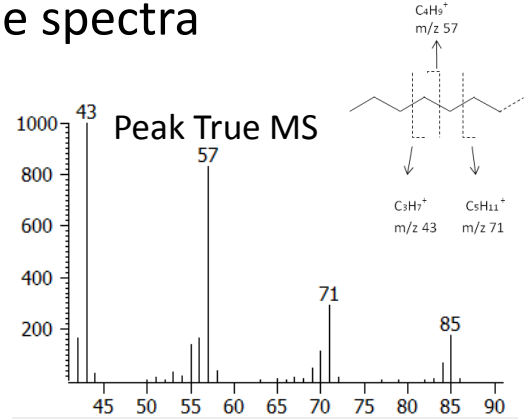
Class Mass (e.g. 43,57…) → Positive feedback → add to class → next spectra or algorithm

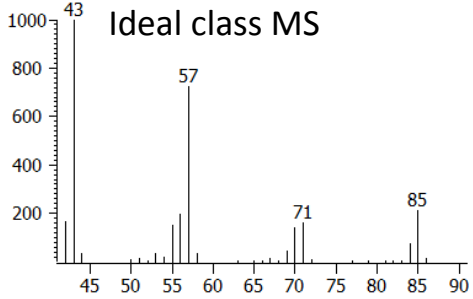
Class Mass (e.g. 43,57…) → negative feedback → next spectra or algorithm

- E.g. Hierarchical ranking of typical fragments according to intensity

Rank 1: mass(43) → Rank 2: mass(57) → Rank 3: mass(71) → Add to class → Next spectra

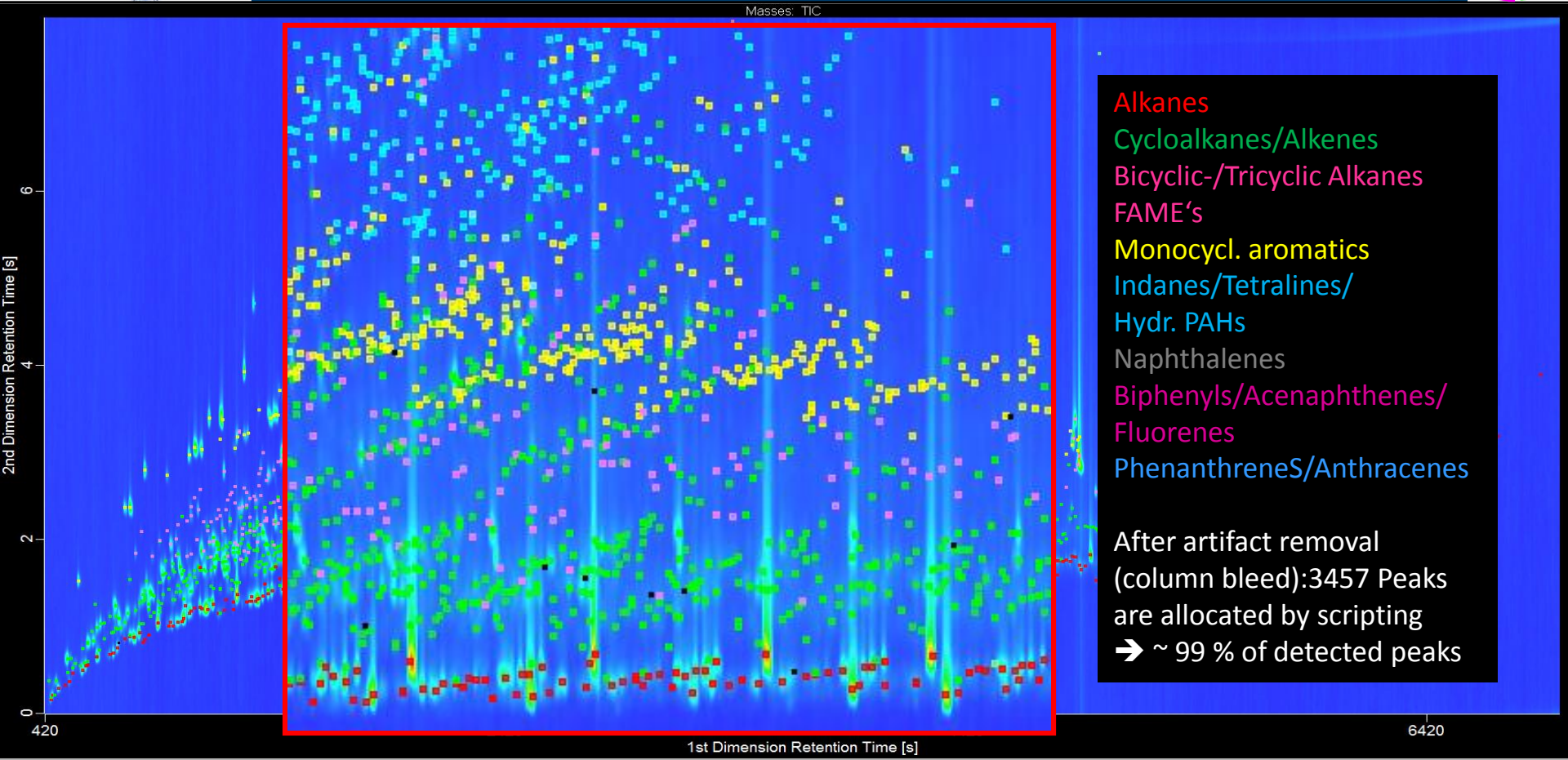
(Intensity ranking, neutral losses (differences), logical connections (if/or/and…))





Welthagen, J.Chrom A (2003), 1019, 233-249
Vogt, J. Chrom A (2007), 1150, 2-12
Weggler, J. Chrom A (2014), 1364, 241 - 248

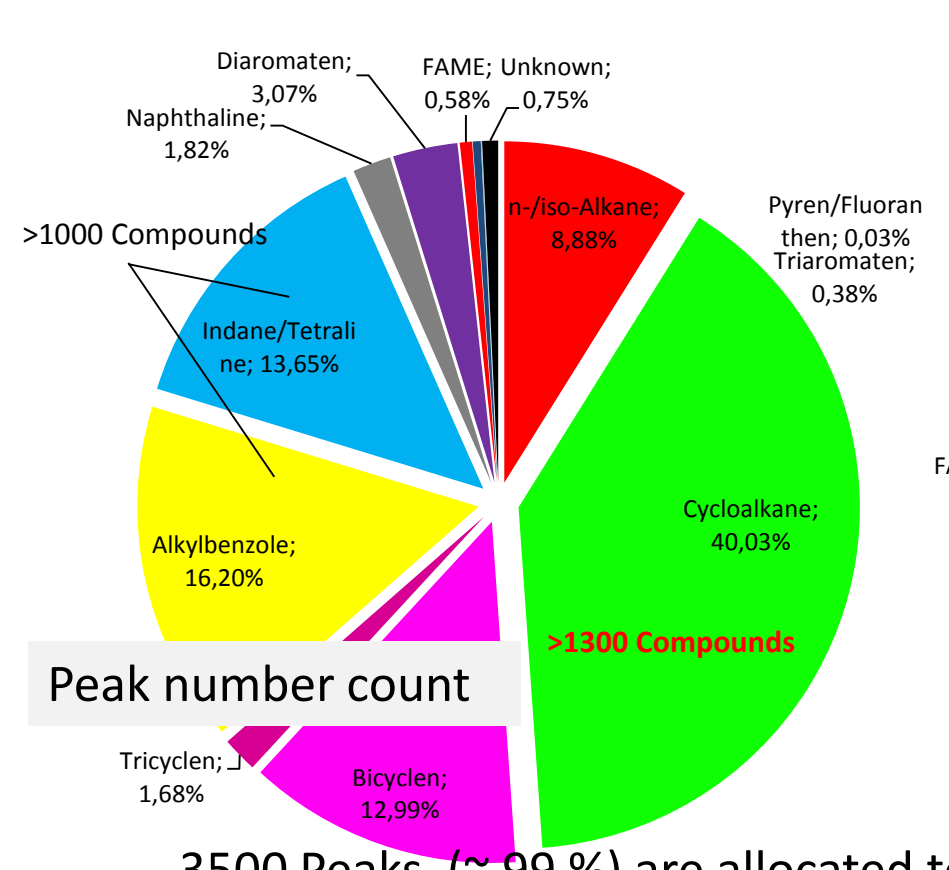
CLASSIFICATION



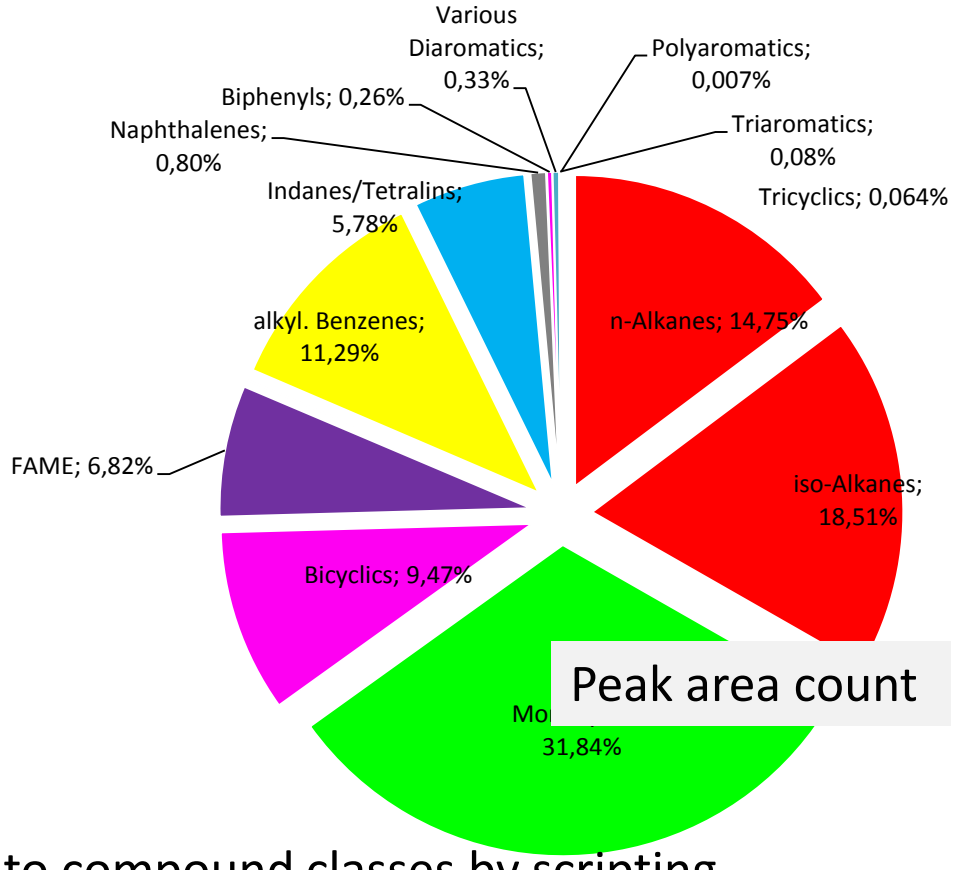
Alkanes
Cycloalkanes/Alkenes
Bicyclic-/Tricyclic Alkanes
FAME‘s
Monocycl. aromatics
Indanes/Tetralines/
Hydr. PAHs
Naphthalenes
Biphenyls/Acenaphthenes/
Fluorenes
PhenanthreneS/Anthracenes

After artifact removal (column bleed):3457 Peaks are allocated by scripting
➔ ~ 99 % of detected peaks

CLASSIFICATION



Peak number count



Peak area count

3500 Peaks (~ 99 %) are allocated to compound classes by scripting

Class and Carbon Number Specific Quantification

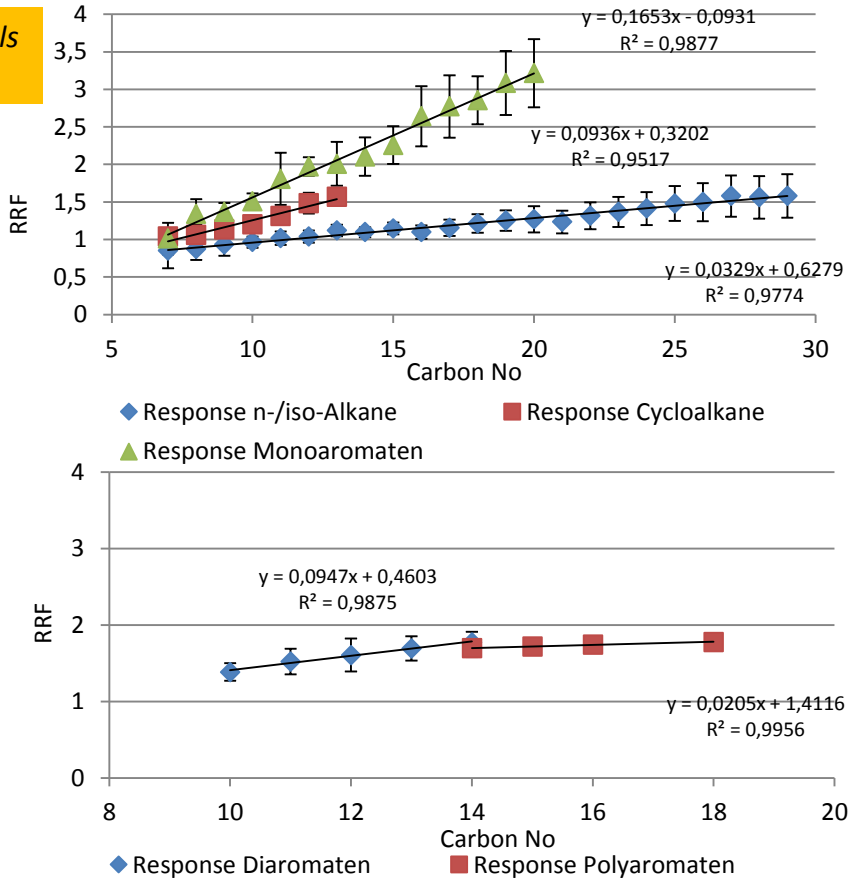
Step 1: Substance class determination:
MS - Scripting (+ GCxGC area)

Jennerwein et al., Energy Fuels 28 (2014) 5670–5681

Step 2: Relative **response function** for **chain length** via external standards

- ➔ for response measurements: Standard stock solution 8000 ppm, Dilution series 1:2, 1:4, 1:10, 1:20, 1:40, 1:100, 1:200, 1:400
- ➔ monoaromatics: 45 external standards, Range: C_7-$C_{20,}$ Int. Standards 1,2-dichlorbenzene, 1,2,4-trichlorbenz.
- ➔ diring-aromat.:31 external standards, Range C_{10}-$C_{16,}$ Internal Standard: 1-Bromonaphthalin
- ➔ triring-aromat.: 10 external standards, Range: C_{14}-$C_{18,}$ Internal Standard 9-Bromoanthracene

Step 3: Internal standard for quantification E.g.: Mono-, di- und tri-ring aromatics: Halogenated aromatic compounds



Class and Carbon Number Specific Quantification

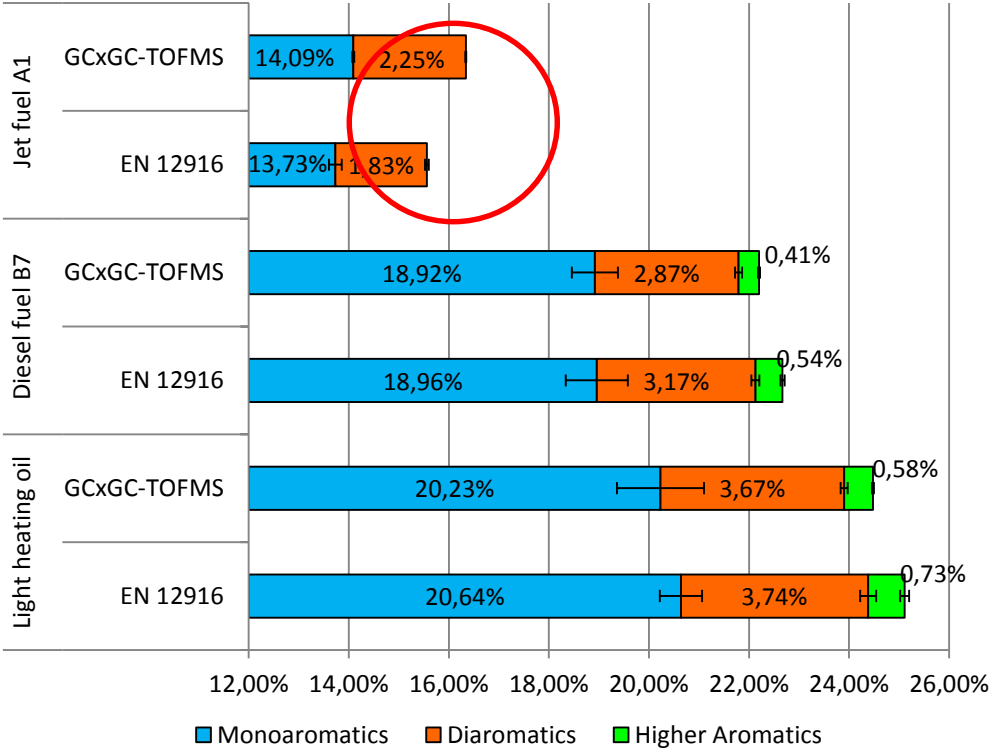
Carbon No.	n-Alkanes	iso-Alkanes	Monocyclics	Bicyclics	Tricyclics	alkyl. Benzenes	Indanes	Tetralines	Naphthalenes	Biphenyls	Fluorenes	Diphenyl methanes	Ace napthenes	Tri aromatics	Poly aromatics	FAME	Total
7	0,01%	-	0,03%		-	0,03%	-	-	-	-	-	-	-	-	-	-	0,07%
8	0,14%	0,07%	0,25%	0,01%	-	0,19%	-	-	-	-	-	-	-	-	-	-	0,65%
9	0,75%	0,30%	1,06%	0,09%	-	0,64%	0,16%	-	-	-	-	-	-	-	-	-	2,99%
10	1,32%	0,89%	2,61%	0,76%	0,00%	0,93%	0,60%	0,60%	0,07%	-	-	-	-	-	-	-	7,79%
11	1,58%	0,91%	1,85%	0,69%	0,01%	0,91%	1,77%		0,17%	-	-	-	-	-	-	-	7,89%
12	1,45%	0,56%	2,00%	0,86%	0,02%	0,77%	1,99%		0,31%	0,03%	-	-	0,01%	-	-	-	8,00%
13	1,56%	0,94%	2,85%	0,73%	0,02%	0,82%	2,59%		0,34%	0,16%	0,01%	0,01%	-	0,03%	-	-	10,08%
14	1,64%	0,92%	3,01%	0,71%	0,01%	0,81%	2,11%		0,34%	0,44%	0,06%	-	-	0,11%	-	0,15%	10,30%
15	2,12%	1,21%	2,99%	0,46%	-	0,58%	0,94%		0,28%	0,35%	0,08%	-	-	0,14%	-	1,35%	10,50%
16	2,12%	1,53%	3,40%	0,38%	-	0,37%	0,76%		0,09%	-	(				0,04%	0,04%	8,92%
17	1,79%	0,89%	3,22%	0,36%	-	0,29%	0,18%		-	-					0,01%	0,28%	7,01%
18	1,61%	1,46%	2,72%	0,67%	-	0,26%	0,13%		-	-					-	3,32%	10,17%
19	1,81%	1,54%	1,68%	0,47%	-	0,16%	-		-	-					-	0,96%	6,61%
20	1,16%	0,59%	1,13%	0,18%	-	0,21%	-		-	-					-	0,41%	3,68%
21	1,20%	0,59%	0,60%	0,01%	-	0,08%	-		-	-					-	0,05%	2,53%
22	0,58%	0,22%	0,25%	-	-	0,04%	-		-	-					-	0,07%	1,16%
23	0,35%	0,36%	0,01%	-	-	-	-		-	-					-	0,02%	0,73%
24	0,13%	0,18%	-	-	-	-	-		-	-					-	0,01%	0,32%
25	0,06%	0,09%	-	-	-	-	-		-	-					-	-	0,14%
26	0,03%	0,02%	-	-	-	-	-		-	-					-	-	0,06%
27	0,02%	0,01%	-	-	-	-	-		-	-					-	-	0,03%
28	0,01%	-	-	-	-	-	-		-	-					-	-	0,01%
29	0,01%	-	-	-	-	-	-		-	-					-	-	0,01%
Various	-	-	-	-	-	-	-		-	-	-	-	-	-	-	0,20%	0,20%
Total	21,45%	13,27%	29,66%	6,38%	0,06%	7,08%	11,82%		1,61%	0,99%	0,26%	0,01%	0,01%	0,36%	0,04%	6,86%	99,86%

	GCxGC-TOFMS	EN 14103
C14:0	0,35%	0,36%
C16:0	12,29%	12,06%
C16:1	0,55%	0,57%
C18:0	2,51%	2,36%
C18:1	54,27%	54,86%
C18:2	18,92%	18,99%
C18:3	7,79%	7,75%
C20:0	0,47%	0,54%
C20:1	1,02%	0,93%
C22:0	0,19%	0,22%
C22:1	0,12%	0,14%
Various	1,50%	1,18%

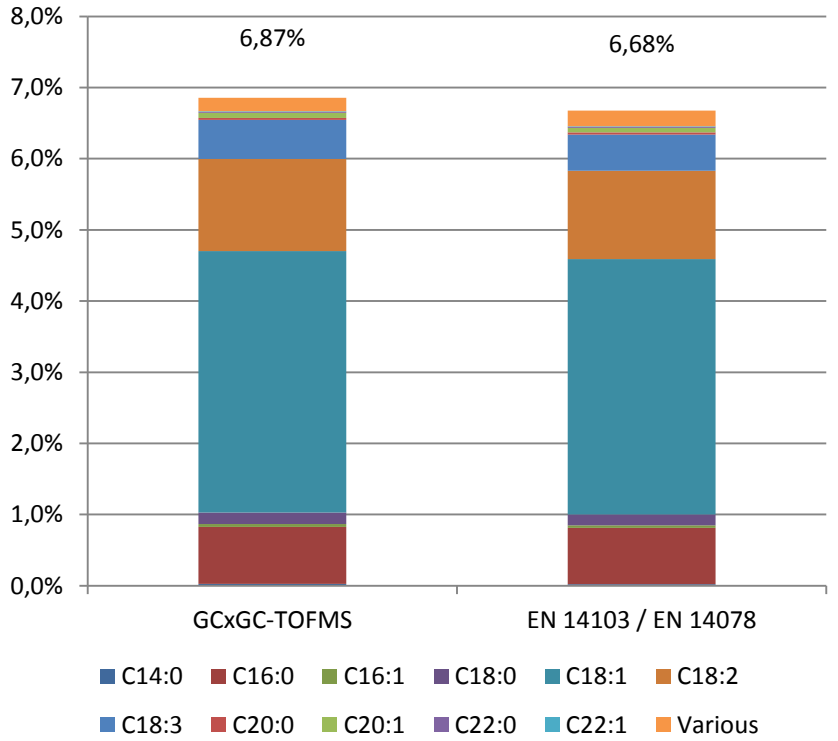
Jennerwein et al., Energy Fuels 28 (2014) 5670–5681

VALIDATION VS DIN EN

Comparison to DIN EN 12916 (Aromatics by LC Method):

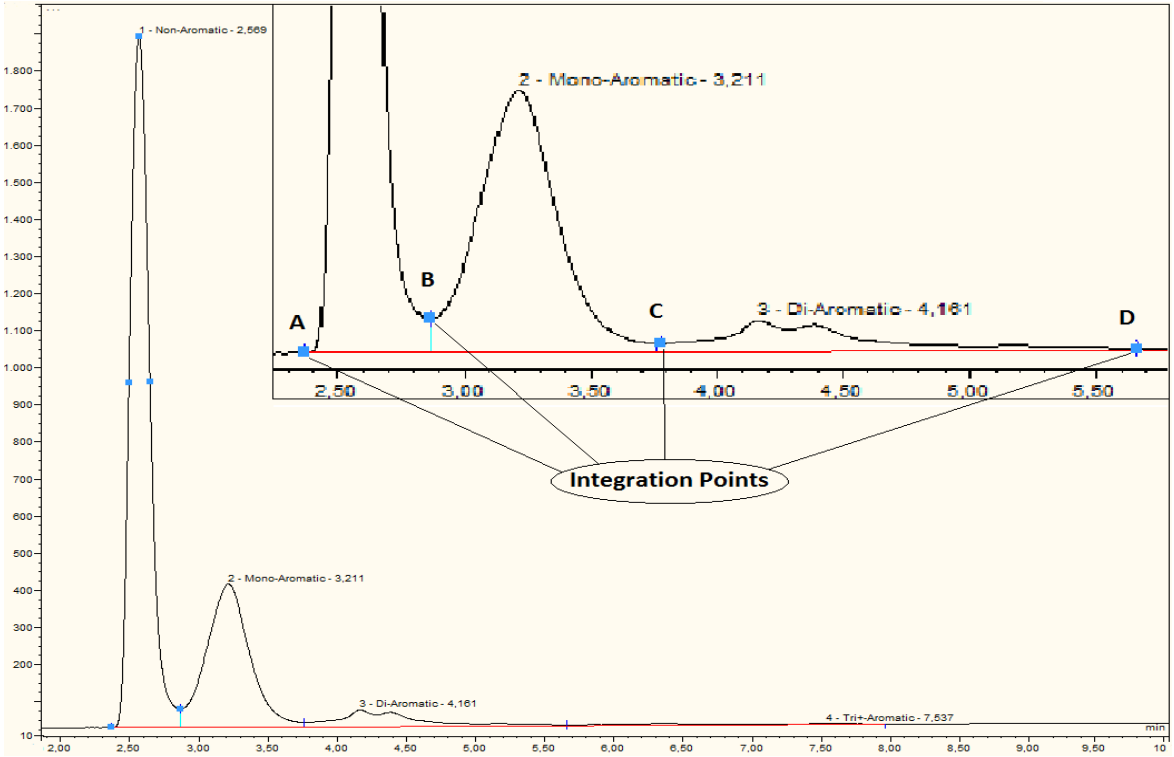


Comparison to DIN EN 14078 and 14103 (FAME, IR and GC):



GCxGC vs ASTM

HPLC – RID for the determination of the aromatic content in middle distillates



Specification of the method:

6 – 30% mono-aromatics

1 – 10% di-aromatics

0 – 2% tri+-aromatics

≤ 5% FAME

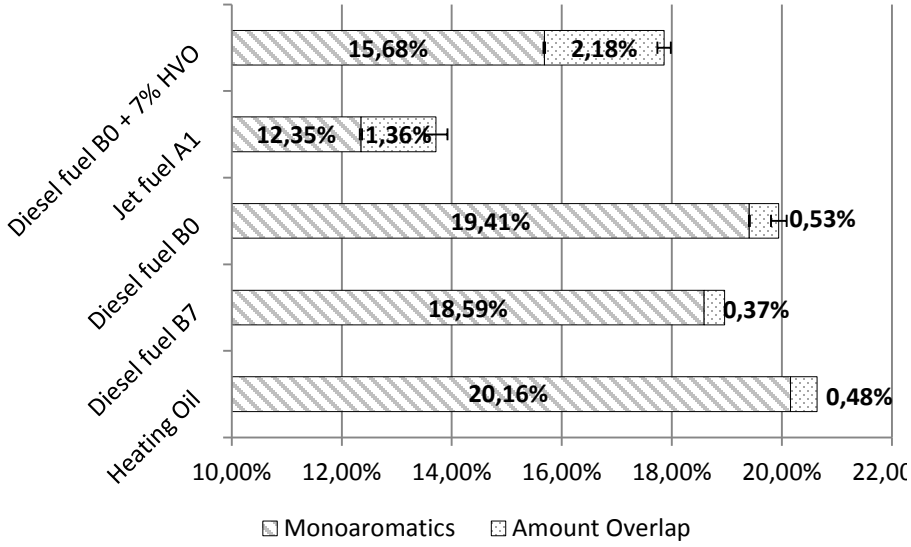
GCxGC vs ASTM

Masses: 40:400

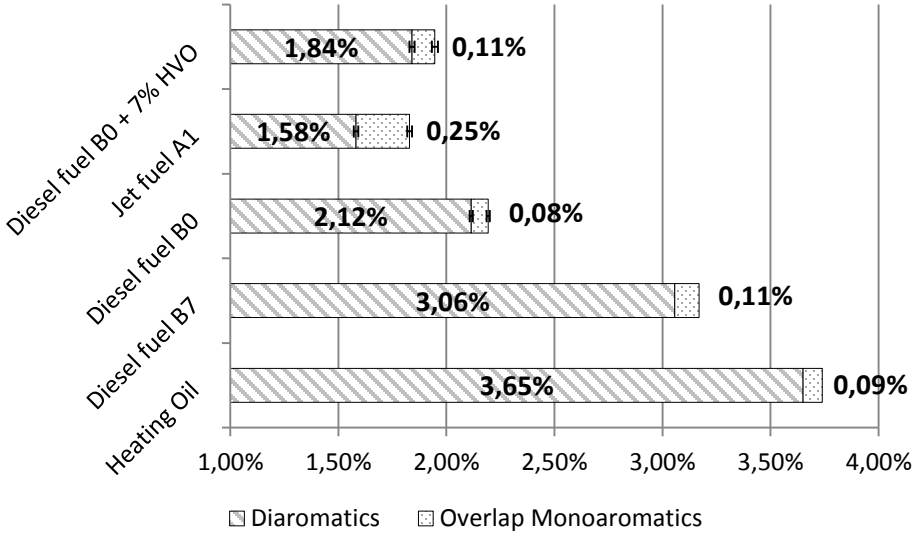
Heart-cut of monoaromatic fraction

n-/iso-Paraffins
Naphthenes
Monoaromatics

Amount overlap of saturated compounds within monoaromatic content



Amount Overlap monoaromatic compounds within diaromatic fraction

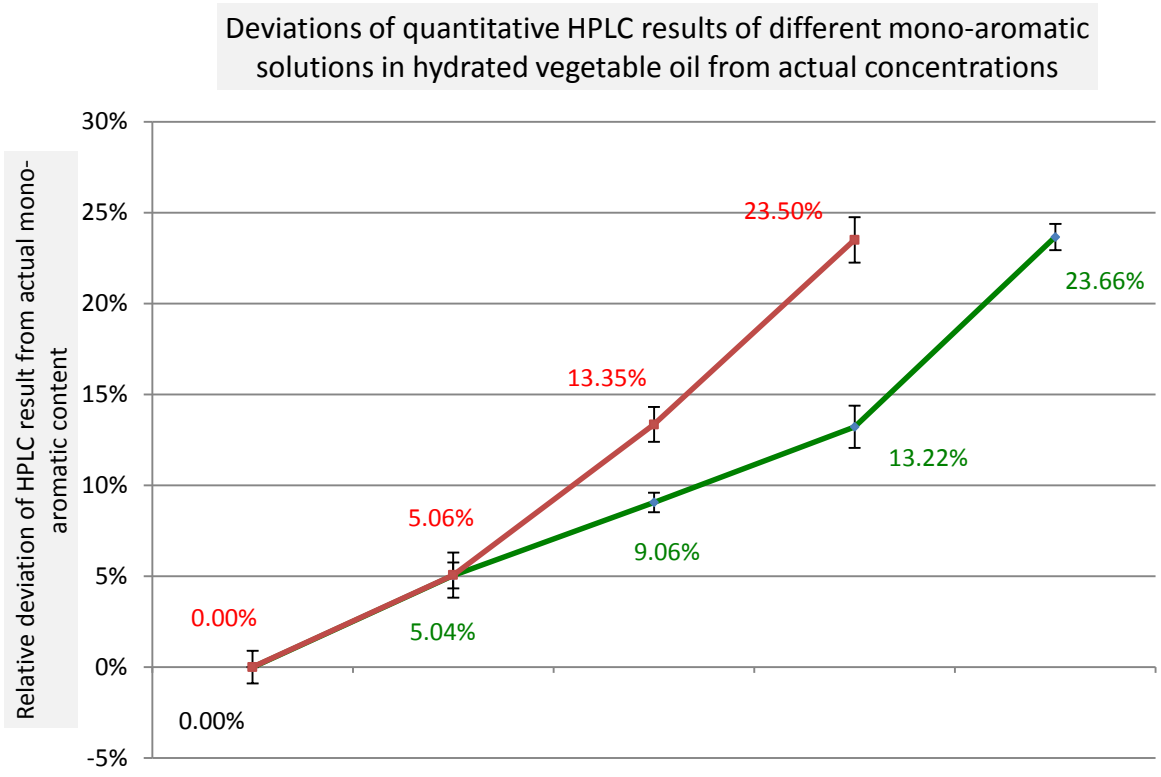


GCxGC vs ASTM

"Modern“ Fuels (e.g. artificial blend of aromatics in HVO)

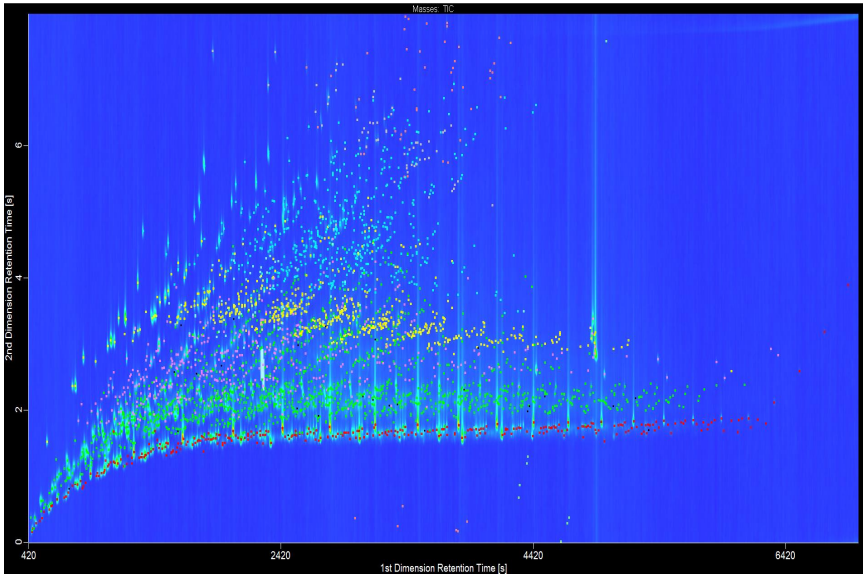
SET	#	o-Xylene	Indane/Tetralin	Total mono-aromatic content
A	1	30,04	0,00	30,04
	2	20,10	9,94	30,04
	3	10,18	20,03	30,22
	4	0,00	30,15	30,15
B	1	21,15	0,00	21,15
	2	16,18	5,51	21,68
	3	10,06	9,77	19,83
	4	5,97	15,88	21,84
	5	0,00	19,72	19,72

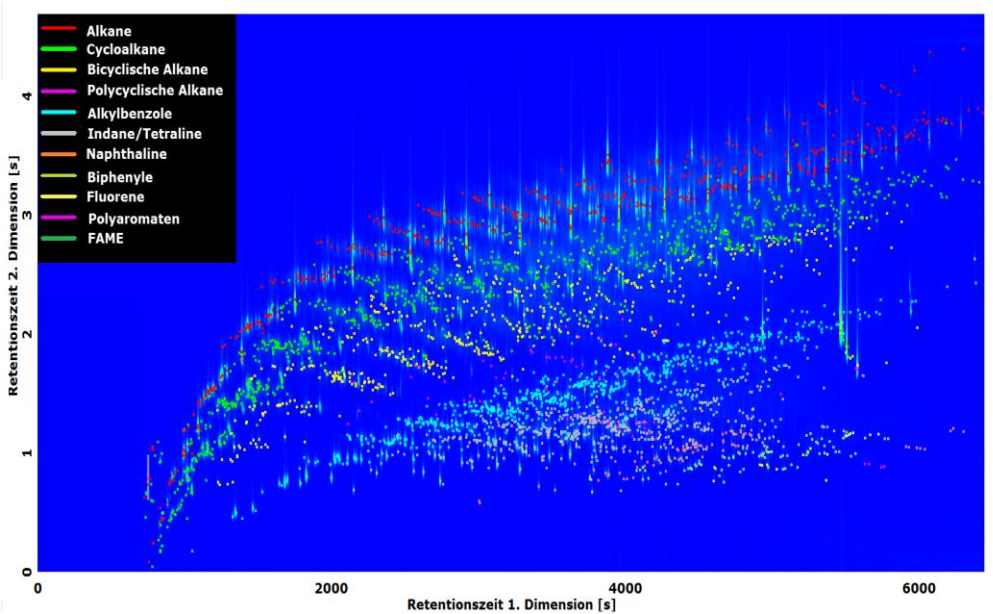
*% [m/m]



Further Improvement

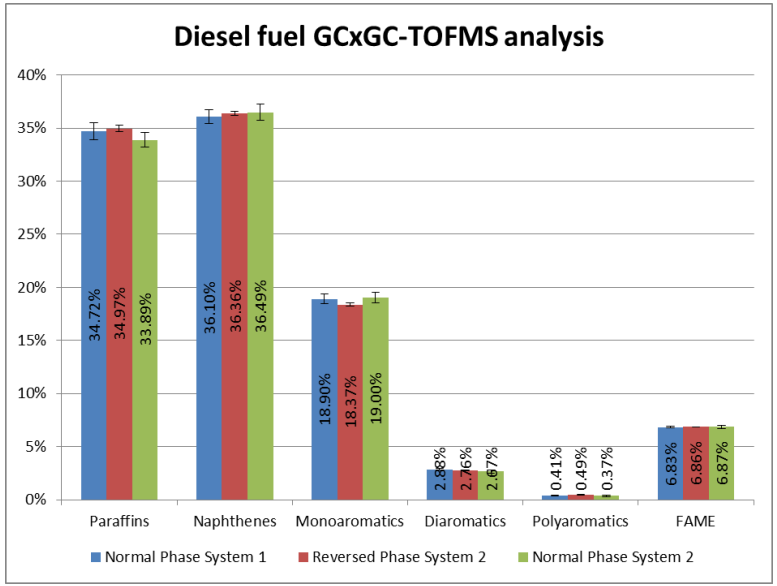
Phase Considerations





FURTHER IMPROVEMENT

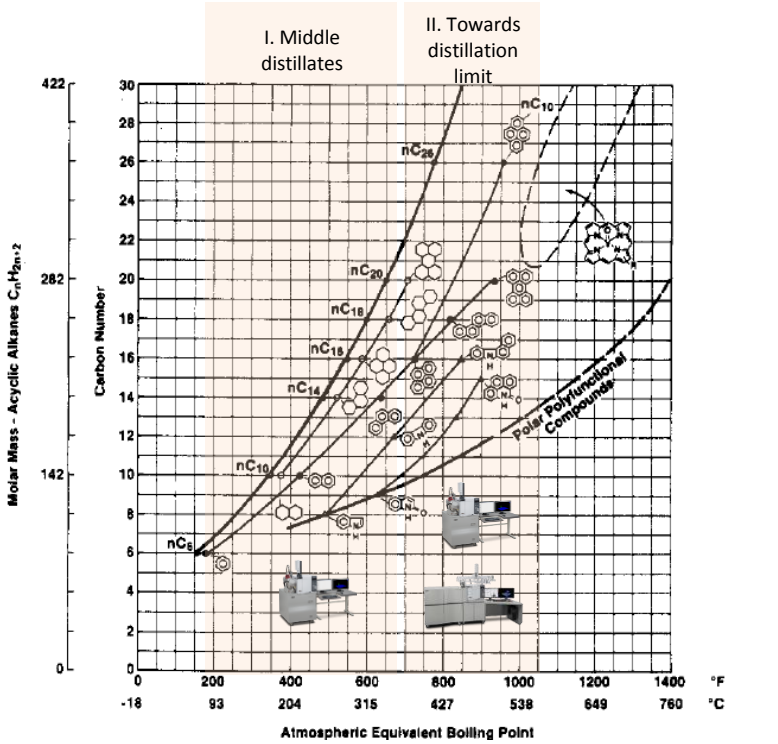
Phase Considerations



	Normal Phase System 1		Normal Phase System 2		Reversed Phase System 2	
	Amount	Std dev	Amount	Std dev	Amount	Std dev
Paraffins	34,72%	0,80%	33,89%	0,69%	34,97%	0,27%
Naphthenes	36,10%	0,66%	36,49%	0,75%	36,36%	0,21%
Monoaromatics	18,90%	0,46%	19,00%	0,49%	18,37%	0,14%
Diaromatics	2,88%	0,07%	2,67%	0,14%	2,76%	0,02%
Polyaromatics	0,41%	0,02%	0,37%	0,09%	0,49%	0,03%
FAME	6,83%	0,06%	6,87%	0,14%	6,86%	0,03%

High Temperature GC × GC

AGENDA



Boduszynski, Energy&Fuel, 1987, 1, 2

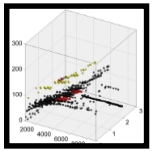
Application of…

I

… GC×GC-TOFMS for an detailed PIONA analysis and complete quantification of middle distillates

II

… high temperature GC×GC-TOFMS for a two-dimensional simulated distillation



… GC×GC in combination with high resolution and accurate mass TOFMS for a better characterization of petroleum

II

… Thermal methods as alternative front ends as alternative inlet systems for HRT to go beyond the boiling point limit

INSTRUMENTATION

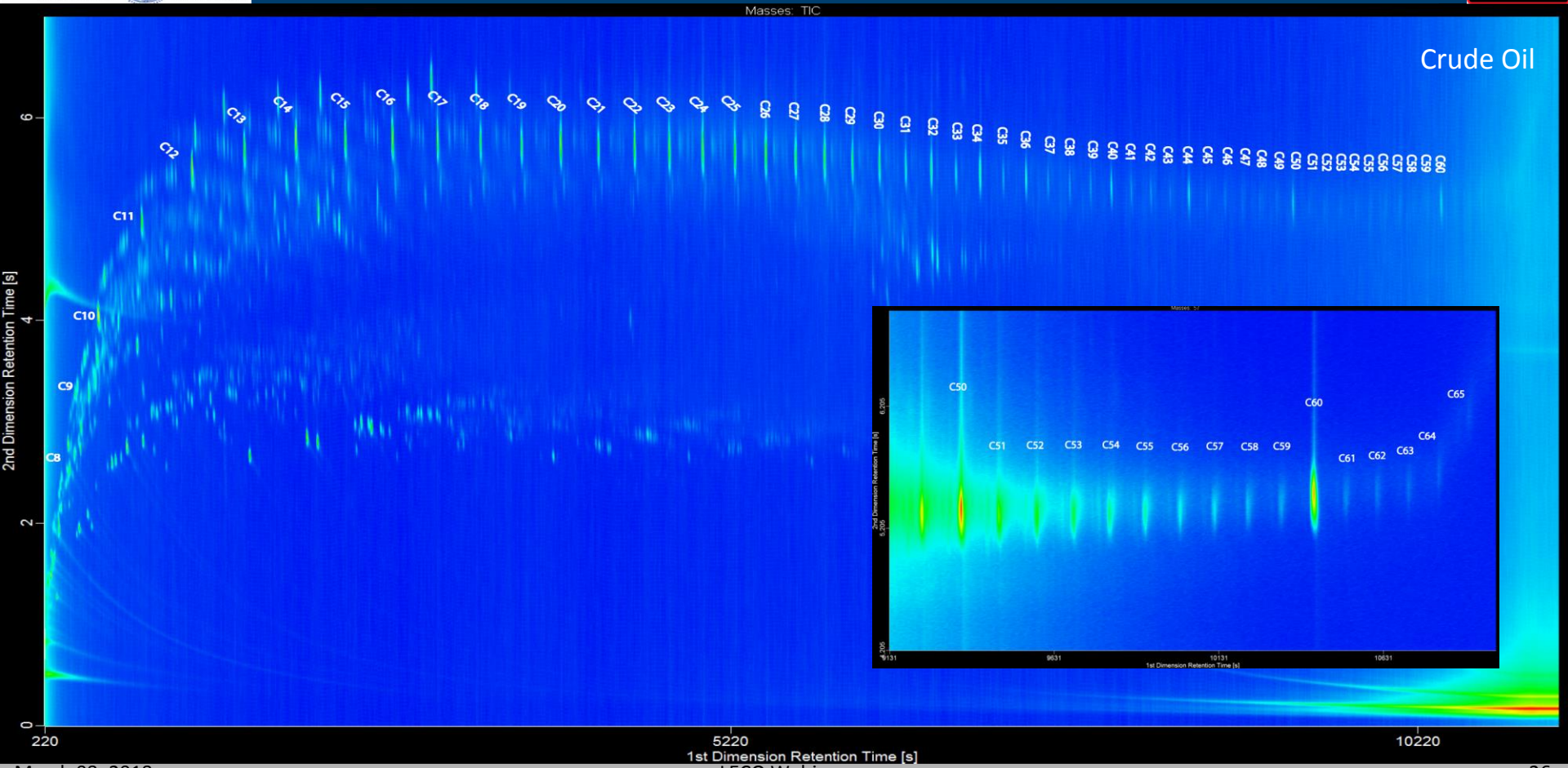
Instrument
LECO Pegasus 4D GC×GC-TOFMS
consumable free modulation

Columns ”reversed phase”
1st Dim.: 20m × 0.25mm × 0.1µm ZB-35HT
~~Mod.: 0.2m × 0.1mm × 0.2µm Rtx1~~
2nd Dim.: 0.8m × 0.1mm × 0.1µm BPX1
Xline: 0.2m × 0.1mm

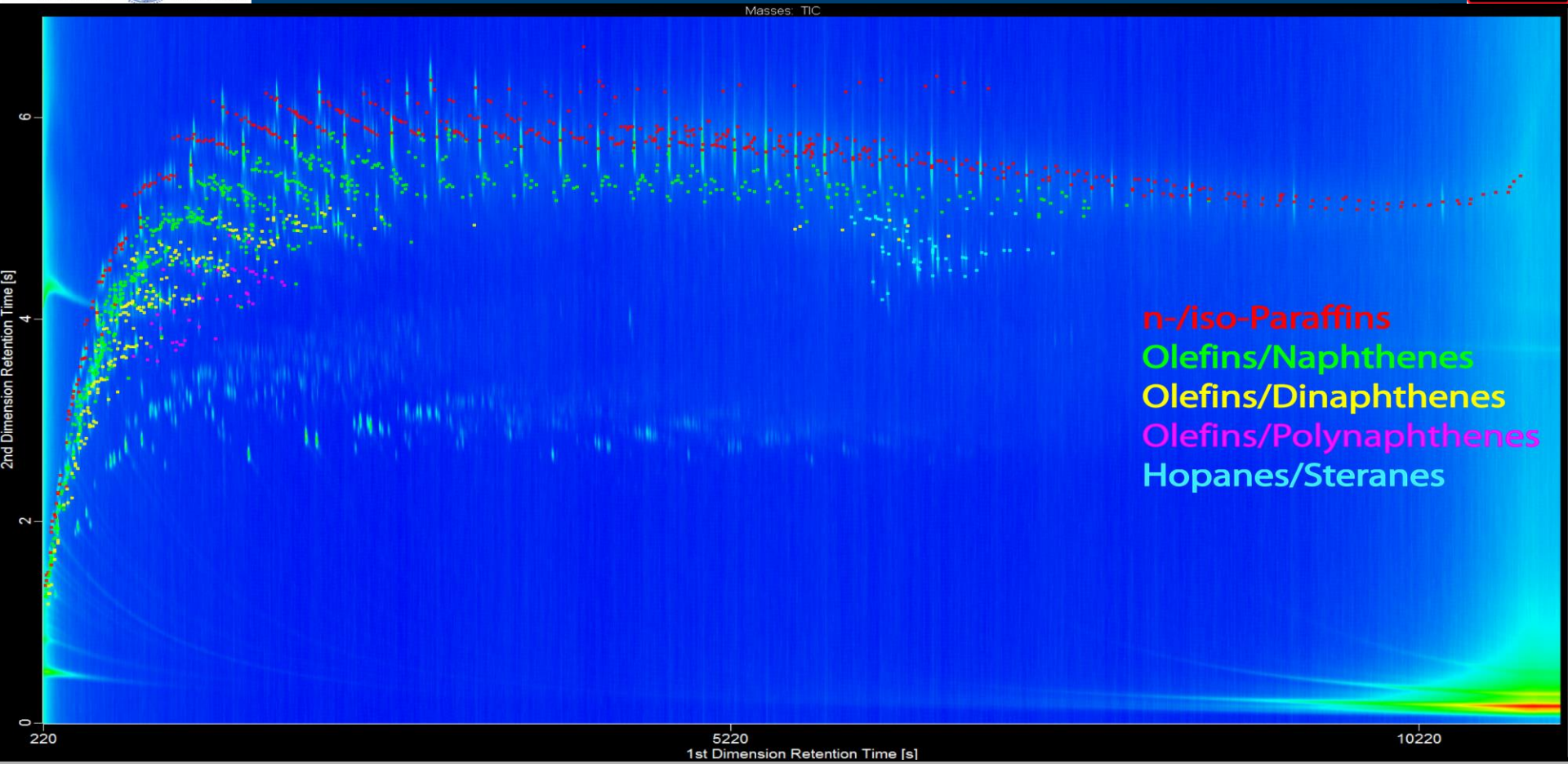
MS Parameter
Mass range: m/z 35 – 600
Acquisition frequency: 200Hz
Ion Source Temp.: 250°C
Xline Temp.: 350°C

GC×GC conditions
Injection: PTV 50 - 430°C, 1.0µL, split 1:50 / on-column
Flow: 1.2mL/min const.
Oven Temp.: 35°C (1min), 3°C/min, 400°C (1min)

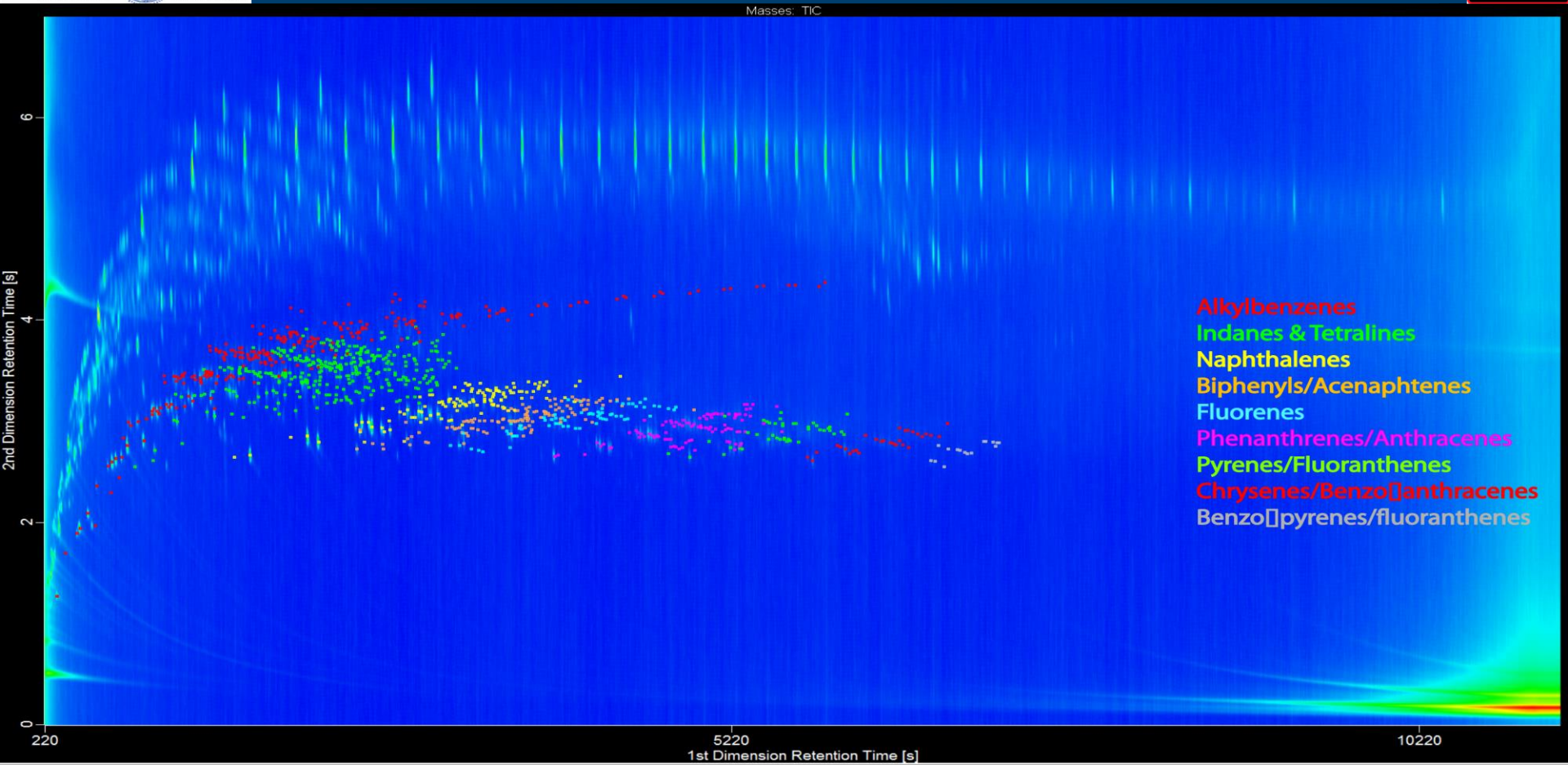
HIGH TEMPERATURE GC × GC



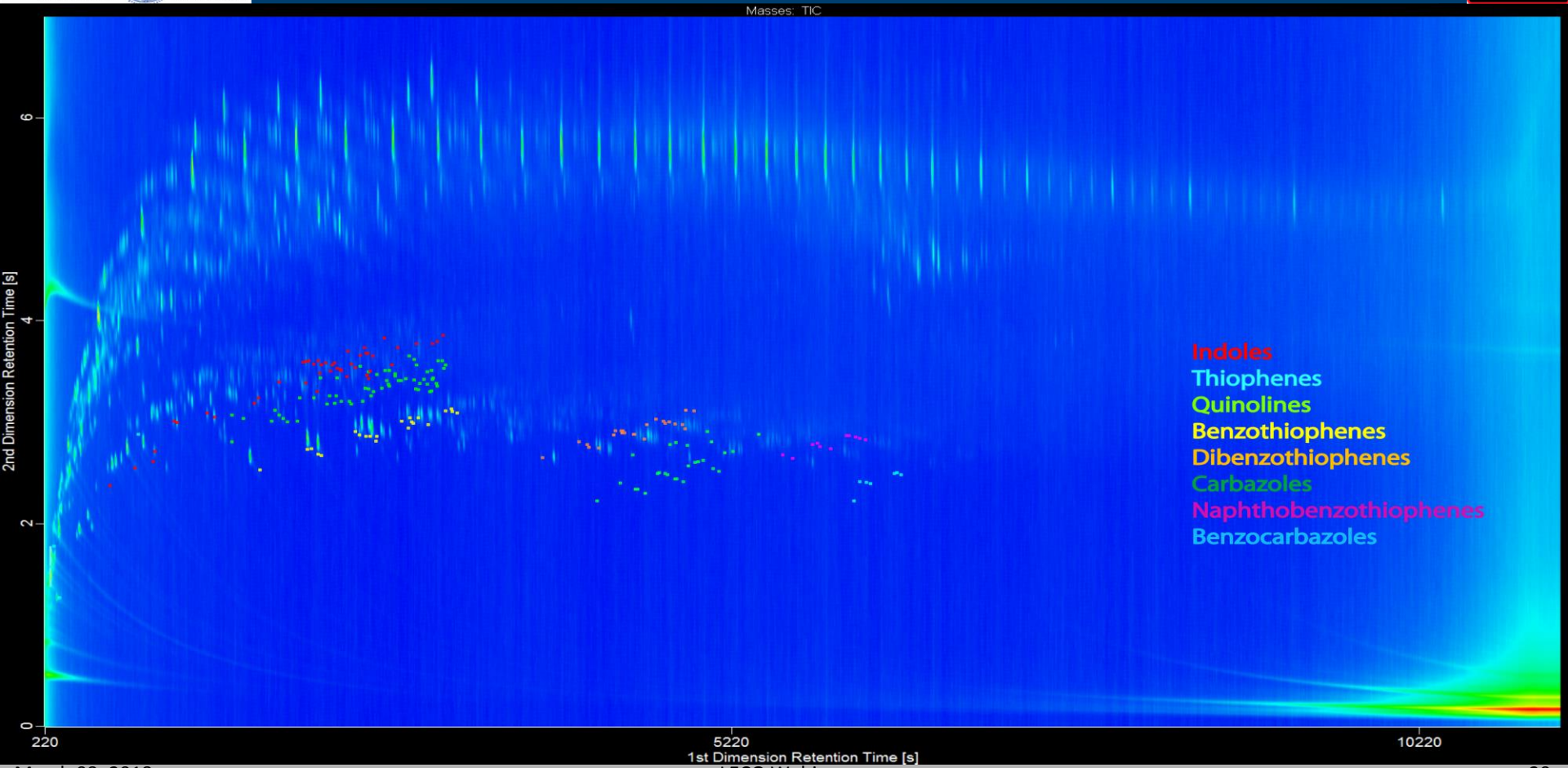
CLASSIFICATION & SCRIPTING



CLASSIFICATION & SCRIPTING



CLASSIFICATION & SCRIPTING

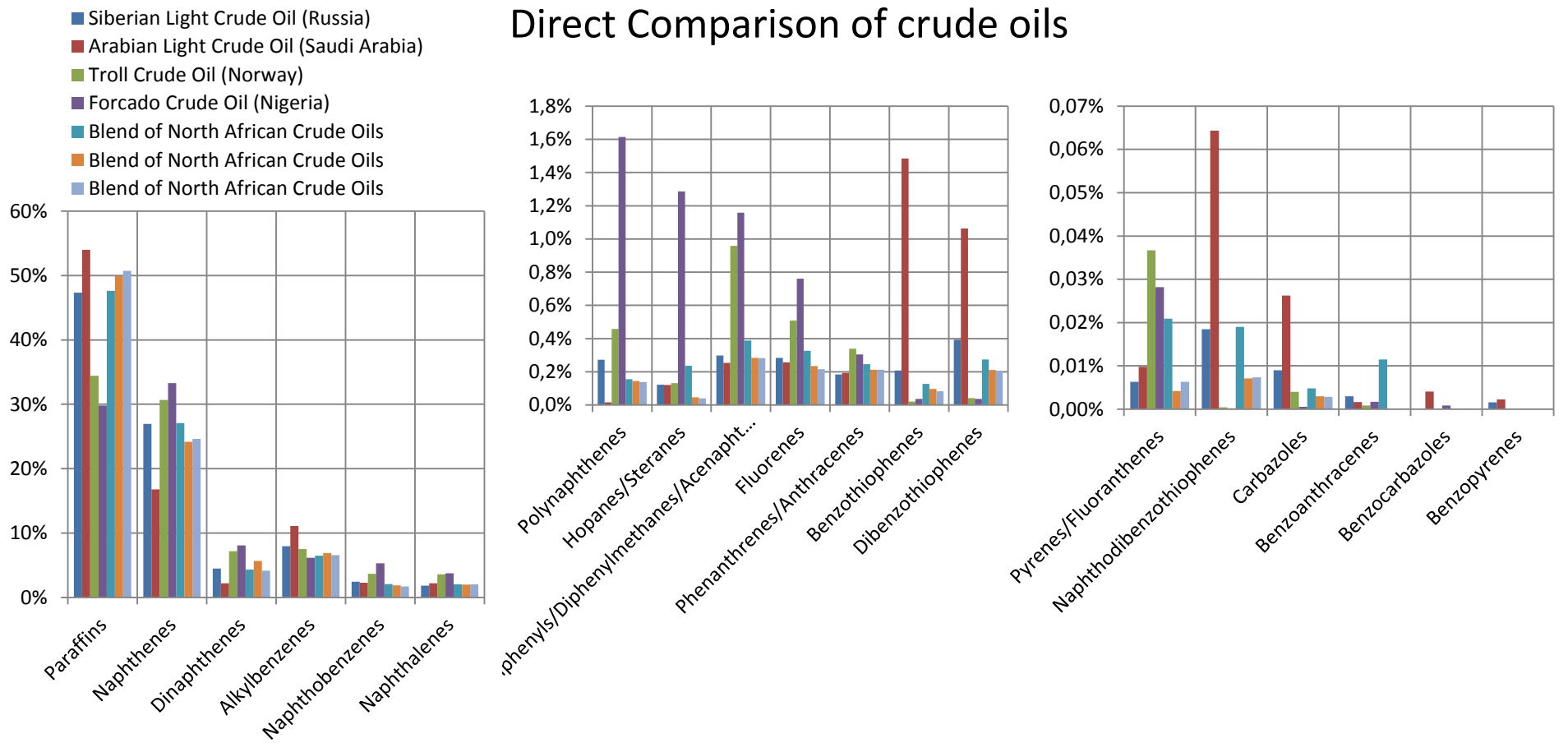


Crude Oils & Blends

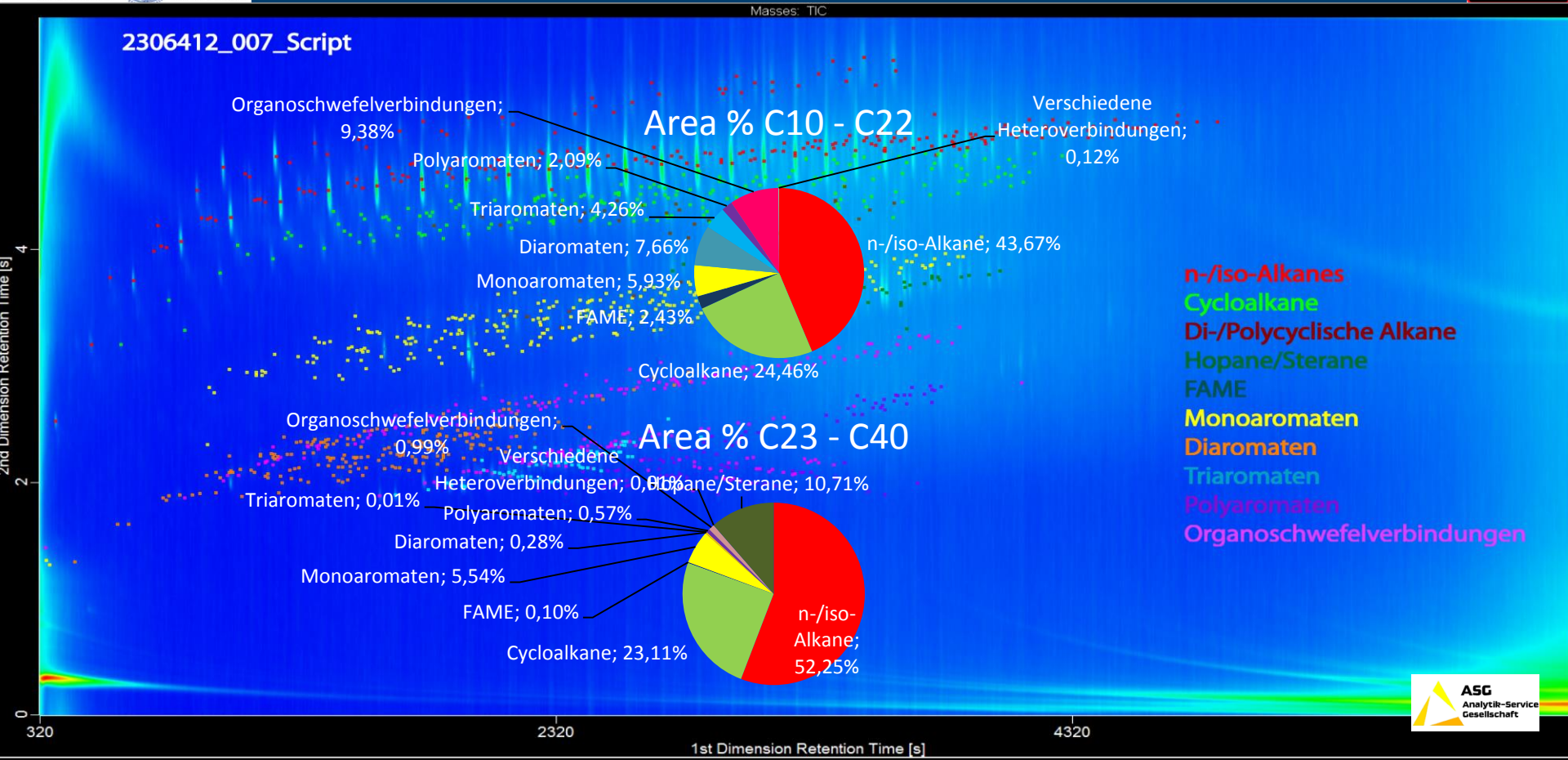
	Siberian Light Crude Oil	Arabian Light Crude Oil	Troll Crude Oil	Forcado Crude Oil	North African Crude Oil (Blend)	North African Crude Oil (Blend)	North African Crude Oil (Blend)
n-/iso-Paraffins	47,35%	53,98%	34,44%	29,83%	47,61%	49,89%	50,74%
Naphthenes	26,97%	16,77%	30,68%	33,29%	27,07%	24,17%	24,63%
Dinaphthenes	4,47%	2,21%	7,19%	8,07%	4,31%	5,66%	4,14%
Polynaphthenes	0,27%	0,02%	0,46%	1,61%	0,16%	0,14%	0,14%
Hopanes/Steranes	0,12%	0,12%	0,13%	1,29%	0,24%	0,05%	0,04%
Alkylbenzenes	7,96%	11,11%	7,52%	6,14%	6,49%	6,90%	6,56%
Indanes /Tetralins	2,46%	2,30%	3,66%	5,32%	2,08%	1,85%	1,72%
Naphthalenes	1,82%	2,21%	3,57%	3,77%	2,02%	1,99%	2,02%
Biphenyls	0,30%	0,25%	0,96%	1,16%	0,39%	0,28%	0,28%
Fluorenes	0,28%	0,26%	0,51%	0,76%	0,33%	0,23%	0,22%
Phenanthrenes/Anthracenes	0,18%	0,19%	0,34%	0,30%	0,25%	0,21%	0,21%
Pyrenes/ Fluoranthenes	0,01%	0,01%	0,04%	0,03%	0,02%	0,00%	0,01%
Benzothiophenes	0,21%	1,48%	0,02%	0,04%	0,13%	0,10%	0,08%
Dibenzothiophenes	0,39%	1,06%	0,04%	0,04%	0,27%	0,21%	0,21%
Naphthodibenzo-thiophenes	0,02%	0,06%	<0,01%	<0,01%	0,02%	0,01%	0,01%
Carbazoles	0,01%	0,03%	<0,01%	<0,01%	<0,01%	<0,01%	<0,01%
Benzoanthracenes	<0,01%	<0,01%	<0,01%	<0,01%	0,01%		
Benzocarbazoles		<0,01%		<0,01%			
Benzopyrenes	<0,01%	<0,01%					
Terphenyles		0,01%					
	92,84%	92,08%	89,57%	91,65%	91,39%	91,70%	91,01%

CRUDE OILS & BLENDS

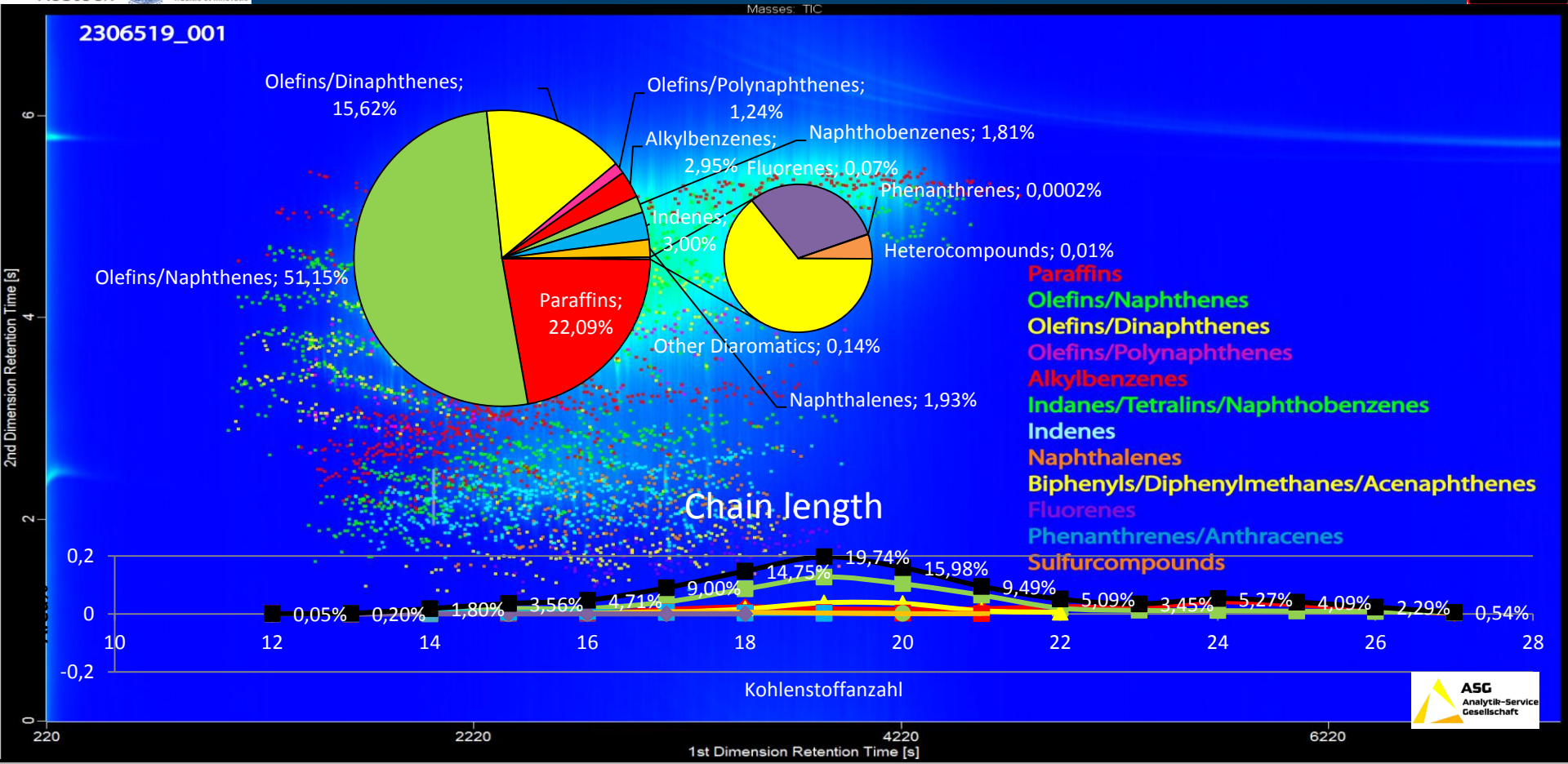
Direct Comparison of crude oils



Heavy Oil


Masses: TIC
2306412_007_Script
Area % C10 - C22
Organoschwefelverbindungen; 9,38%
Polyaromaten; 2,09%
Triaromaten; 4,26%
Diaromaten; 7,66%
Monoaromaten; 5,93%
FAME; 2,43%
Cycloalkane; 24,46%
n-/iso-Alkane; 43,67%
Verschiedene Heteroverbindungen; 0,12%
Area % C23 - C40
Organoschwefelverbindungen; 0,99%
Verschiedene Heteroverbindungen; 0,00%
Triaromaten; 0,01%
Polyaromaten; 0,57%
Diaromaten; 0,28%
Monoaromaten; 5,54%
FAME; 0,10%
Cycloalkane; 23,11%
Hopane/Sterane; 10,71%
n-/iso-Alkane; 52,25%
n-/iso-Alkanes
Cycloalkane
Di-/Polycyclische Alkane
Hopane/Sterane
FAME
Monoaromaten
Diaromaten
Triaromaten
Polyaromaten
Organoschwefelverbindungen
2nd Dimension Retention Time [s]
0
2
4
320
2320
4320
1st Dimension Retention Time [s]

SPINDLE OIL


Masses: TIC
2306519_001
Olefins/Dinaphthenes; 15,62%
Olefins/Polynaphthenes; 1,24%
Alkylbenzenes; 2,95%
Naphthobenzenes; 1,81%
Fluorenes; 0,07%
Phenanthrenes; 0,0002%
Indenes; 3,00%
Heterocompounds; 0,01%
Olefins/Naphthenes; 51,15%
Paraffins; 22,09%
Other Diaromatics; 0,14%
Naphthalenes; 1,93%
Paraffins
Olefins/Naphthenes
Olefins/Dinaphthenes
Olefins/Polynaphthenes
Alkylbenzenes
Indanes/Tetralins/Naphthobenzenes
Indenes
Naphthalenes
Biphenyls/Diphenylmethanes/Acenaphthenes
Fluorenes
Phenanthrenes/Anthracenes
Sulfurcompounds
Chain length
0,05%
0,20%
1,80%
3,56%
4,71%
9,00%
14,75%
19,74%
15,98%
9,49%
5,09%
3,45%
5,27%
4,09%
2,29%
0,54%
Kohlenstoffanzahl
2nd Dimension Retention Time [s]
1st Dimension Retention Time [s]
ASG Analytik-Service Gesellschaft

2D HT Simulated Distillation

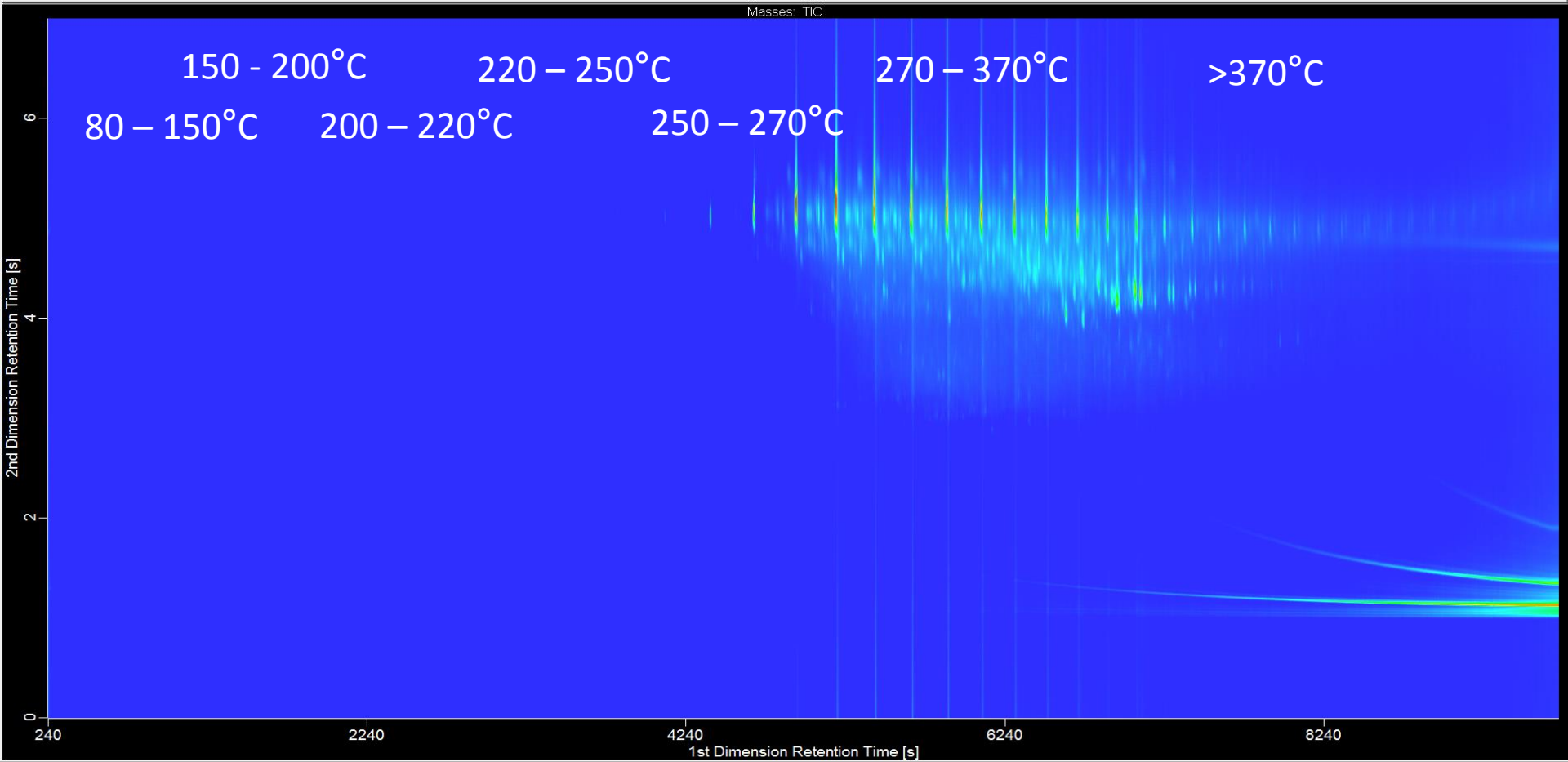
Pilodist® Petrodist ® 100 CC

- Distillation according to **ASTM D-2892**
- Including Debutanization
- Operating temperature up to 350°C (420°C AET)
- Operating pressure down to vaccum 1 Torr

- Distillation according to **ASTM D-5236**
- Operating temperature up to 400°C
- Final cut temperature 650°C AET
- Operating pressure down to vaccum 0.1 Torr

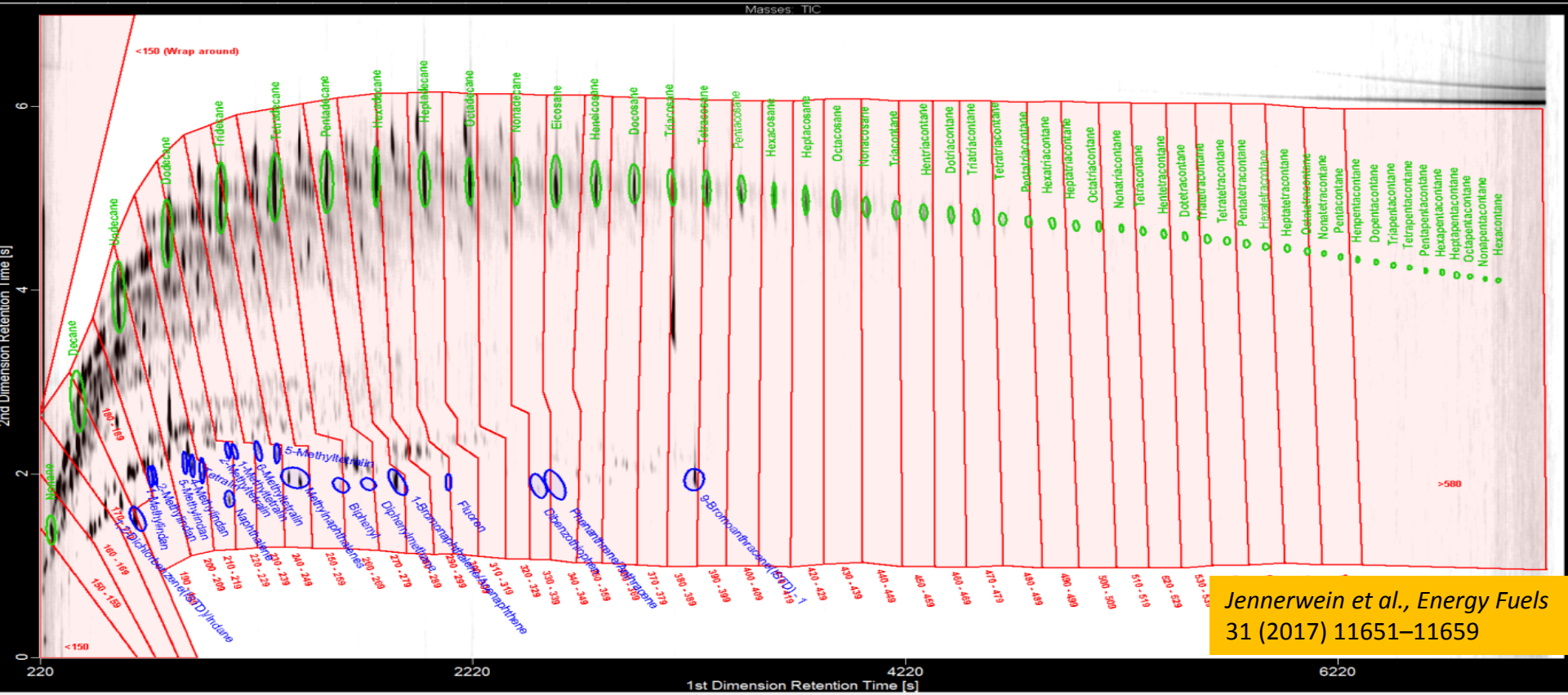
Pilodist® Petrodist ® 200 CC

2D HT Simulated Distillation



2D HT Simulated Distillation

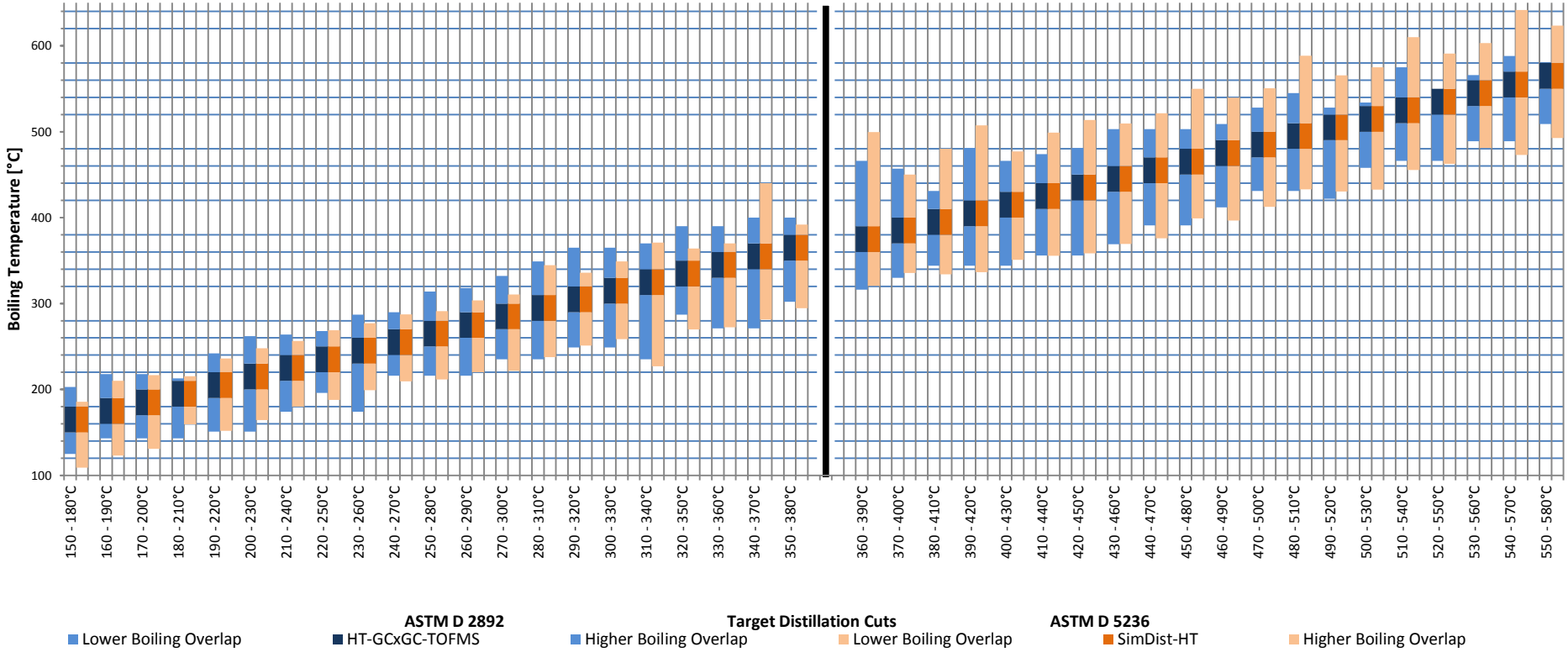
Qualitative AND Quantitative Analysis of Crude Oils



Jennerwein et al., Energy Fuels 31 (2017) 11651–11659

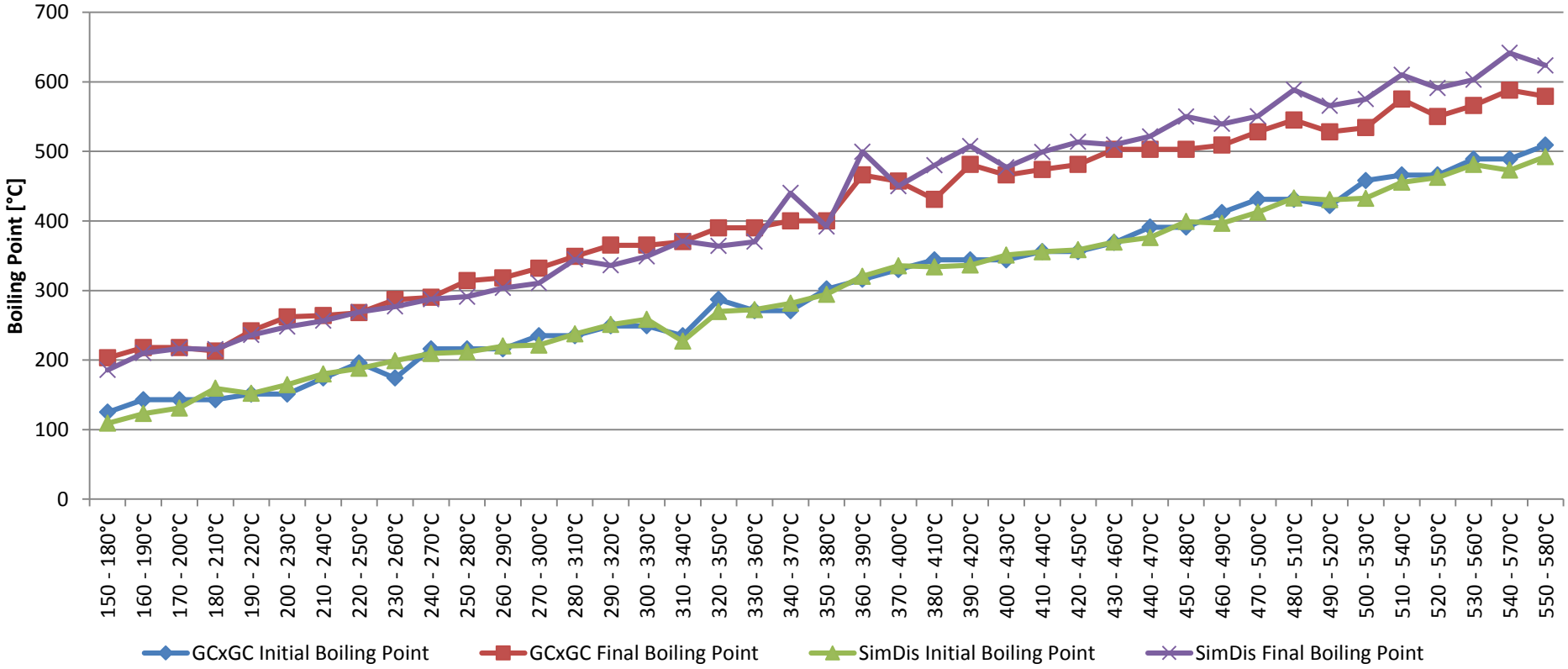
2D HT Simulated Distillation

2D HT SimDist vs 1D HT SimDist

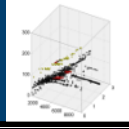


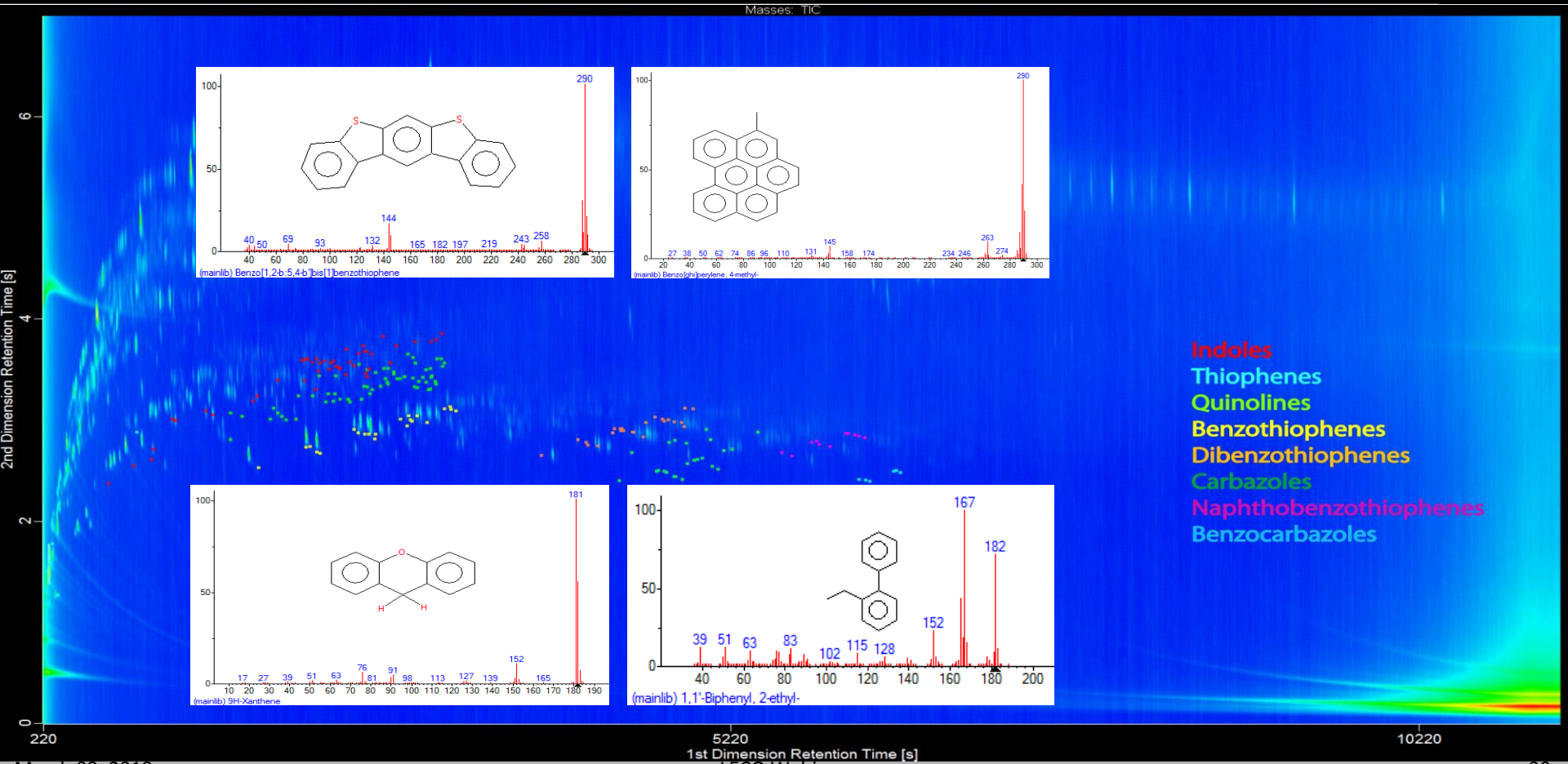
2D HT Simulated Distillation

Initial and Final Boiling Points



GC × GC - High Resolution TOFMS





INSTRUMENTATION

Instrument
LECO Pegasus GC×GC-HRT
liquid nitrogen modulation

Columns ”reversed phase”
1st Dim.: 20m × 0.25mm × 0.1µm ZB-35HT
2nd Dim.: 0.8m × 0.1mm × 0.1µm BPX1
Xline: 0.8m × 0.1mm

MS Parameter
Mass range: m/z 35 – 600
Acquisition frequency: 120 (200)Hz
Mass Resolution: 35.000
Mass Accuracy: < 2ppm
Ion Source Temp.: 300°C
Xline Temp.: 350°C

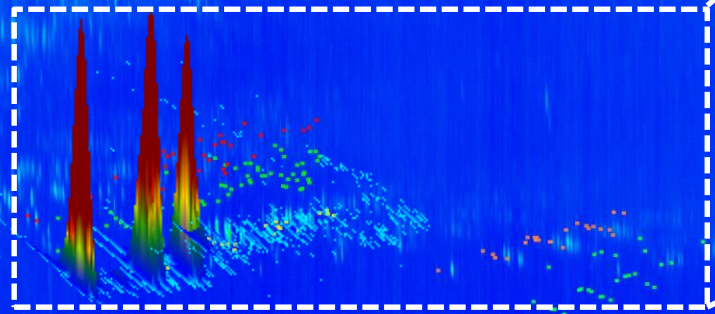
GC×GC conditions
Injection: PTV 50 - 430°C, 1.0µL, split 1:50 / on-column
Flow: 1.2mL/min const.
Oven Temp.: 35°C (1min), 3°C/min, 400°C (1min)

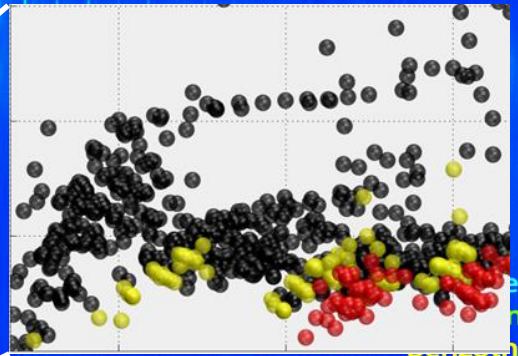
GC × GC - High Resolution TOFMS

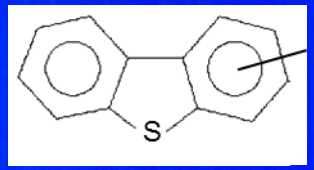
Masses: TIC

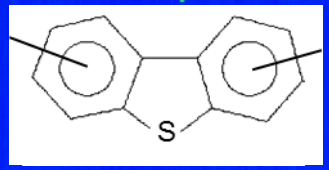
Application of GCxGC - high resolution time-of-flight mass spectrometry (HRT) with electron and/or single photon ionization for further confirmation of ambiguous compounds

Additional confirmation by accurate mass of the molecular ion and mass fragments → Calculation of elemental composition



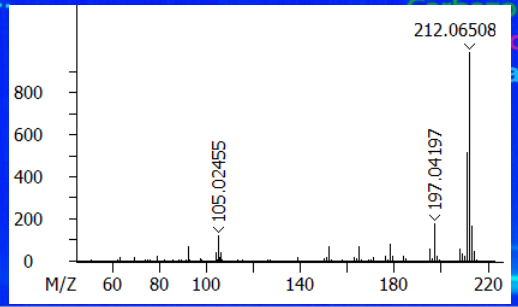






198.0498
± 2ppm

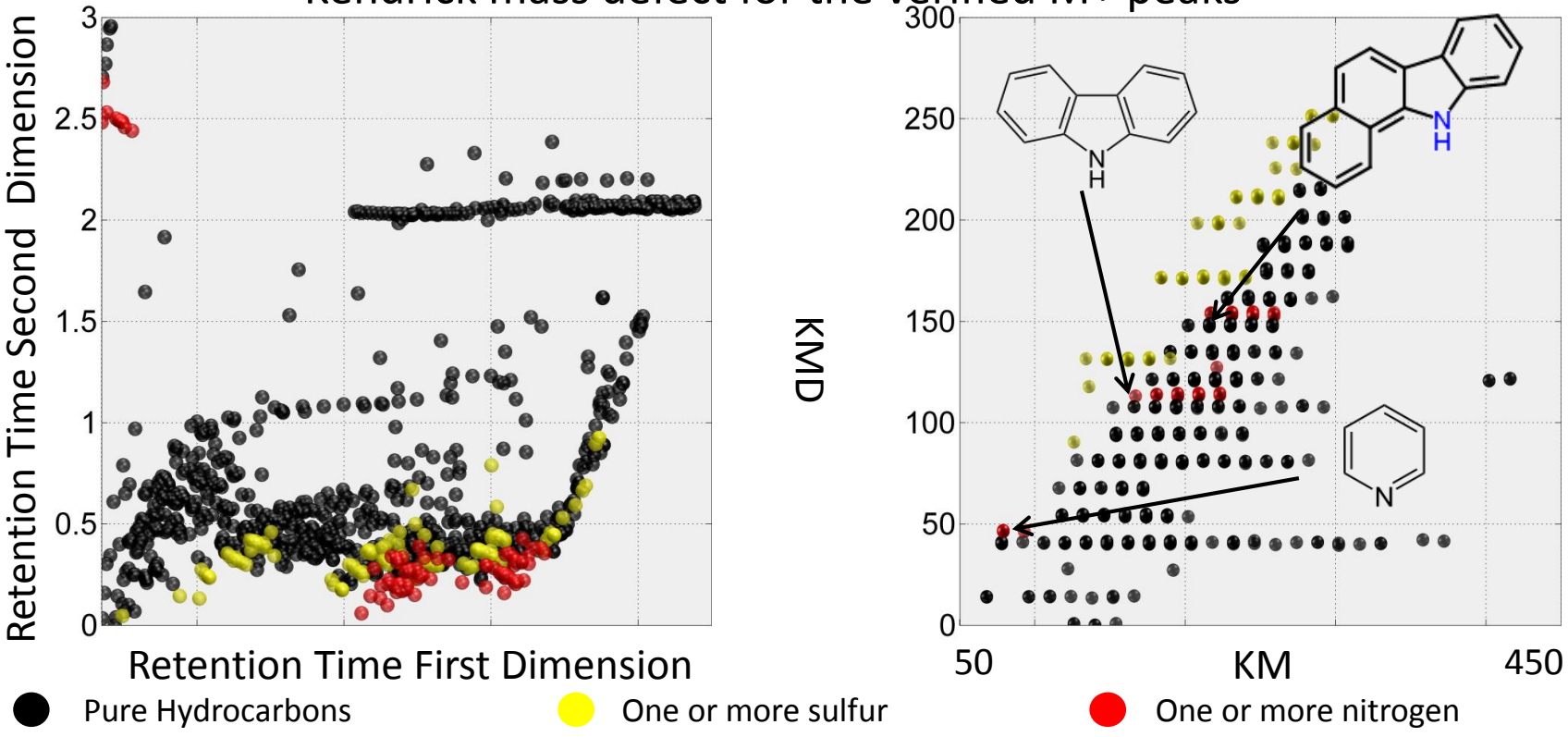
212.0654
± 2ppm



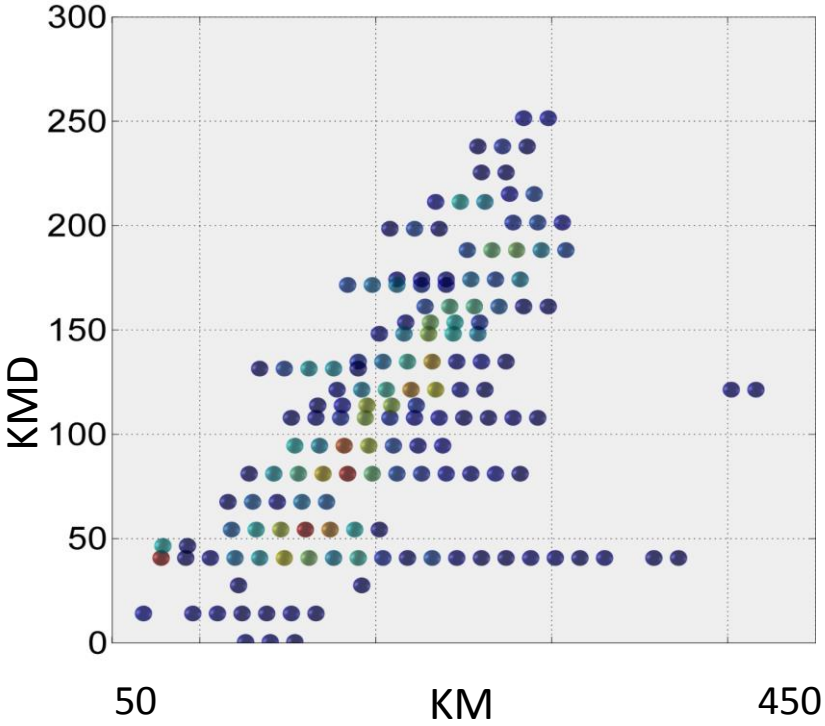
Dibenzothiophenes

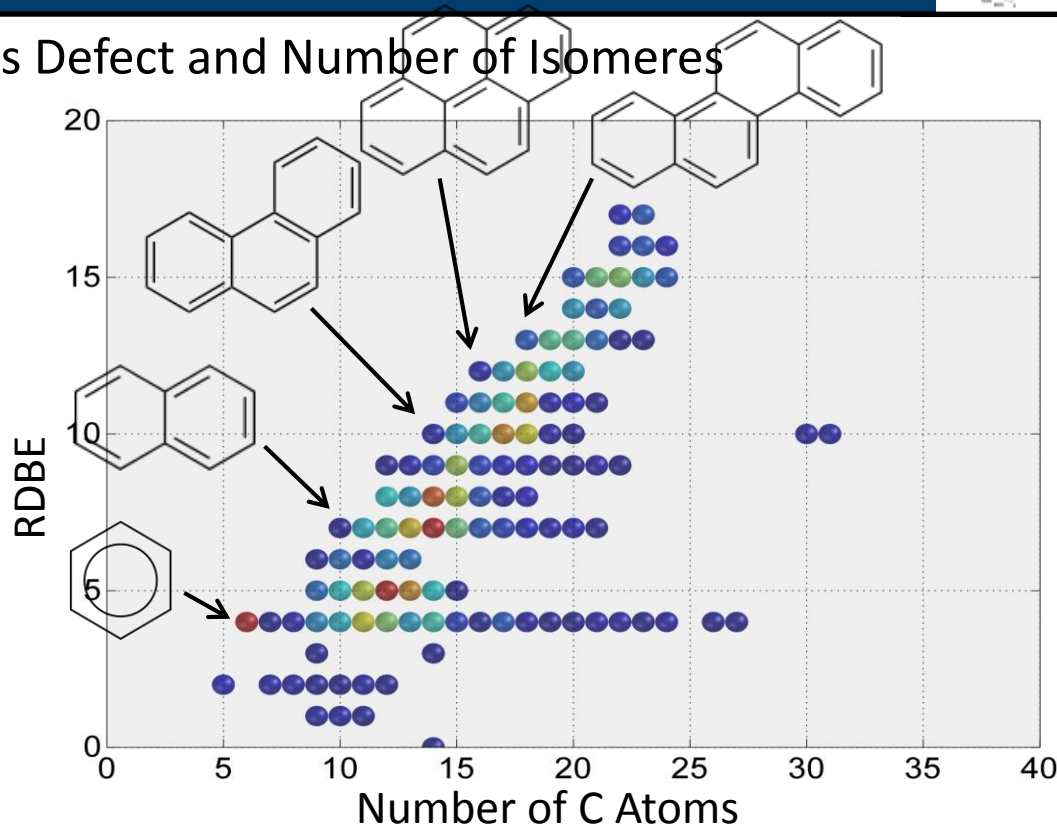
2nd Dimension Retention Time [s]
0
2
4
6
220
5220
10220
1st Dimension Retention Time [s]

Accurate mass information could be used to calculate elemental composition and Kendrick mass defect for the verified M+ peaks



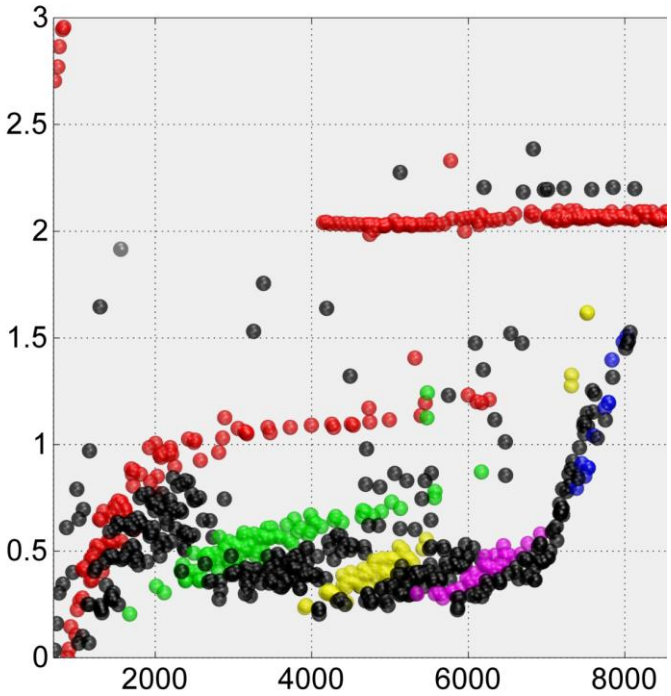
Direct link between Mass Defect and Number of Isomeres

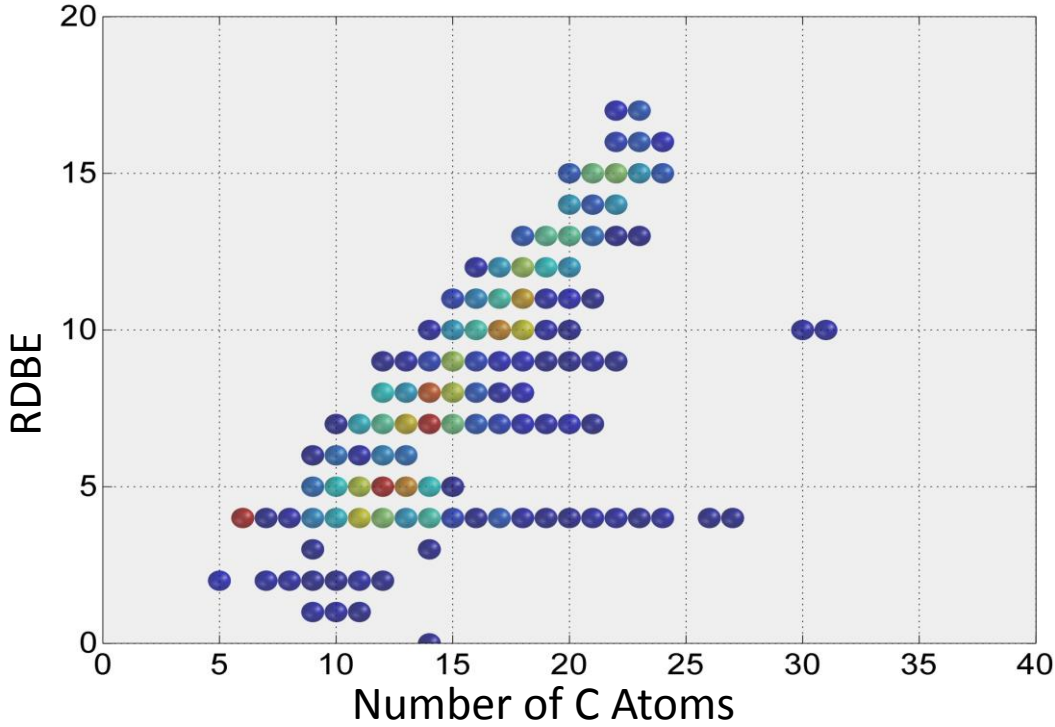




Number of isomers (CyHx Compounds)

Direct link between Mass Defect and Number of Isomeres



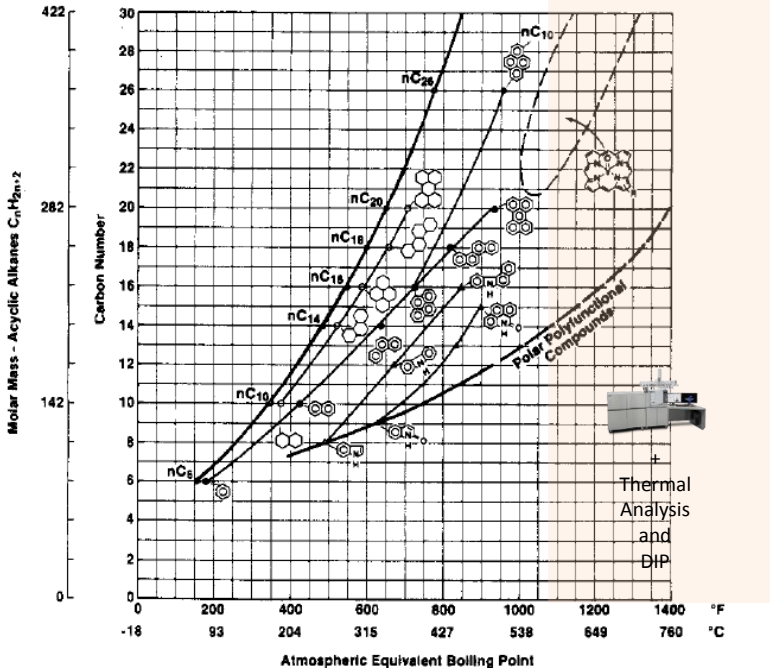


Number of isomers (CyHx Compounds)

AGENDA

Application of…

III. Beyond distillation limit/ residues



+ Thermal Analysis and DIP

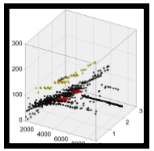
Boduszynski, Energy&Fuel, 1987, 1, 2

I

… GC×GC-TOFMS for an detailed PIONA analysis and complete quantification of middle distillates

II

… high temperature GC×GC-TOFMS for a two-dimensional simulated distillation

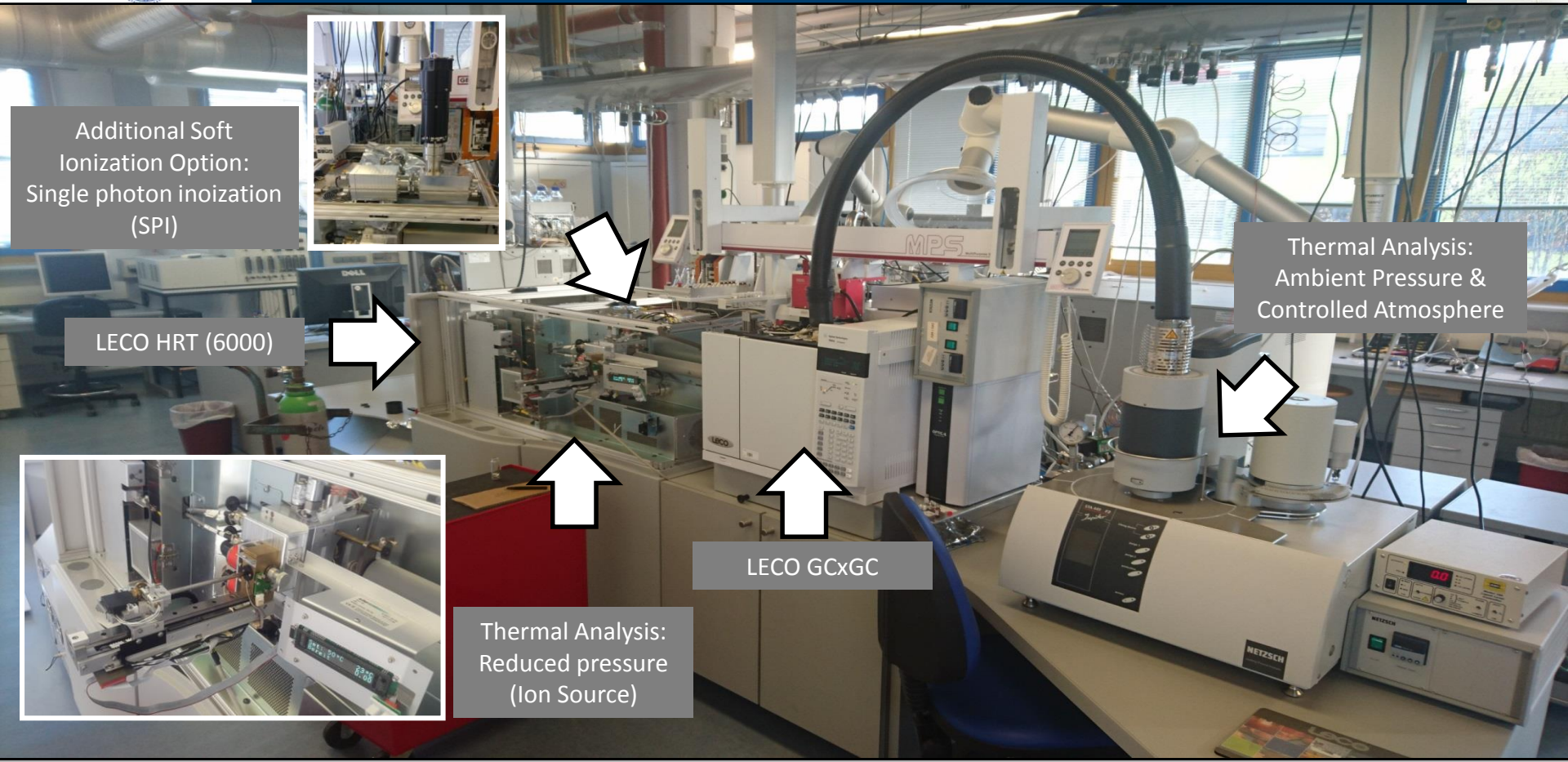


… GC×GC in combination with high resolution and accurate mass TOFMS for a better characterization of petroleum

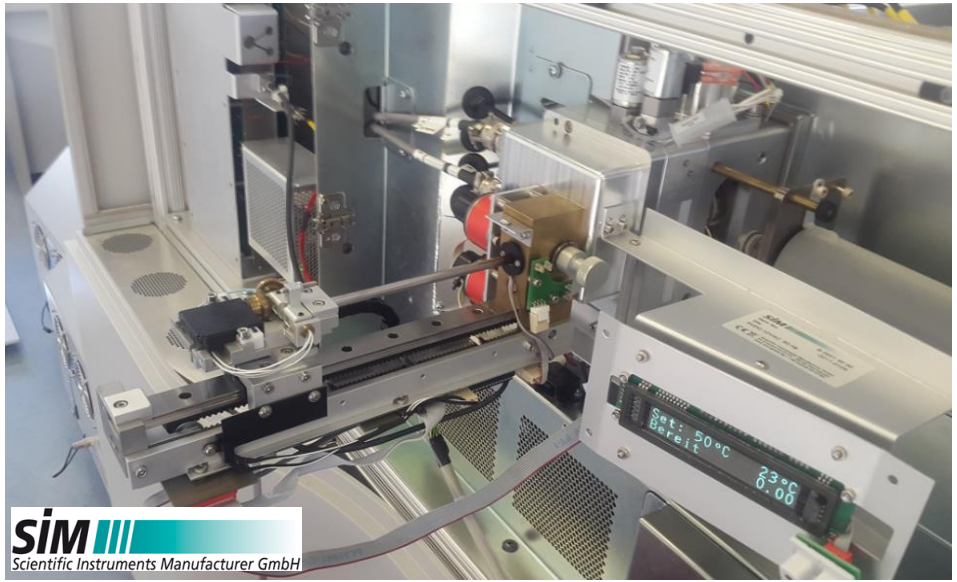
II

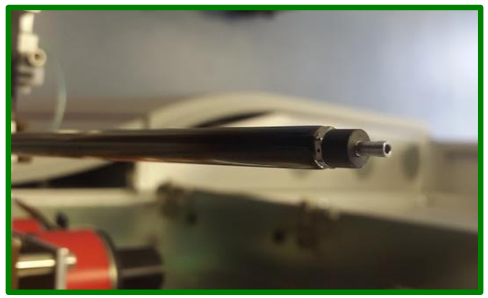
… Thermal methods as alternative frontends as alternative inlet systems for HRT to go beyond the boiling point limit

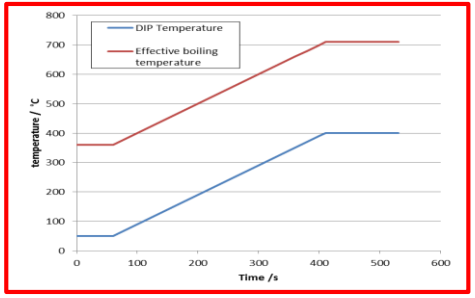
Direct Inseration Probe



Direct Inseration Probe (DIP)

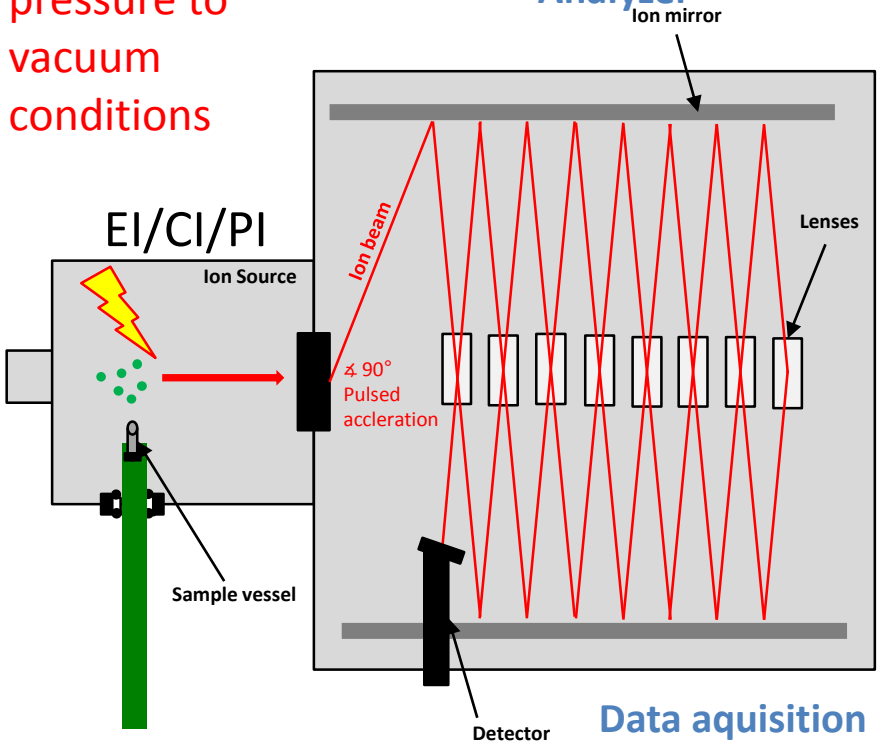






From ambient pressure to vacuum conditions

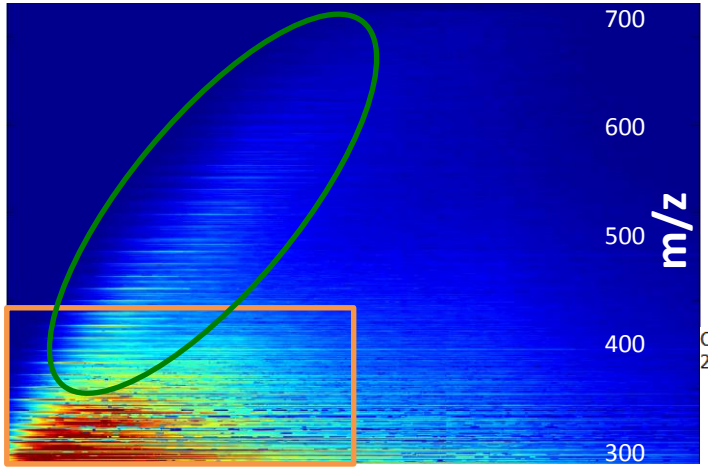
FFP - Time of Flight Mass Analyzer

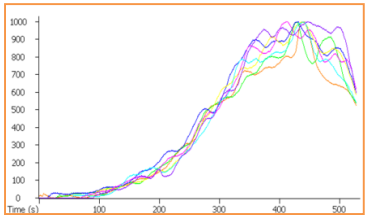


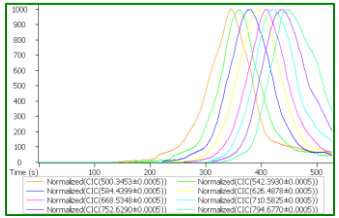
Data aquisition & processing

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

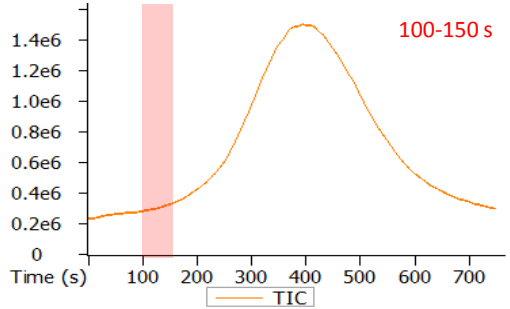


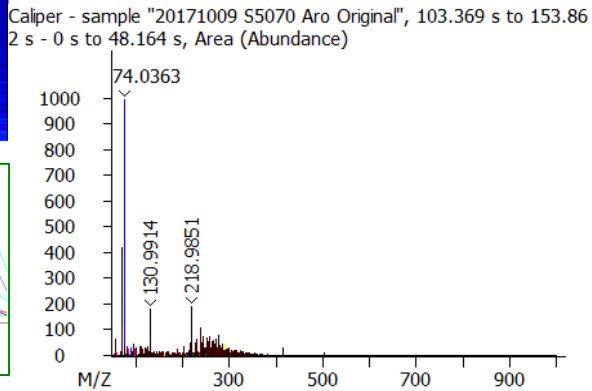




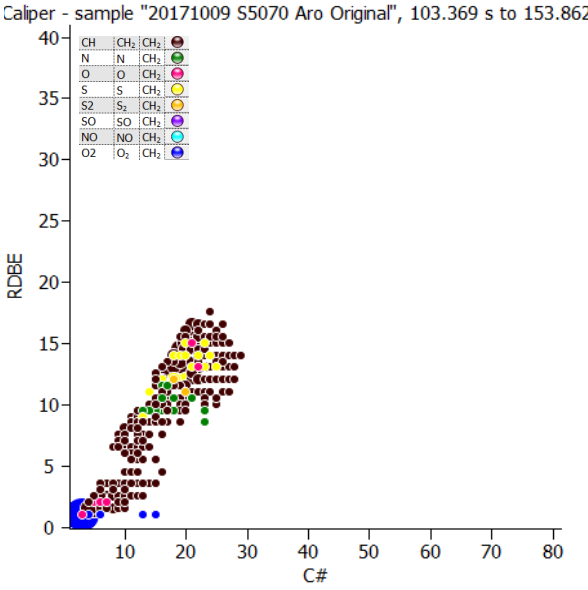
Non specific Fragmentation

Molecular Information





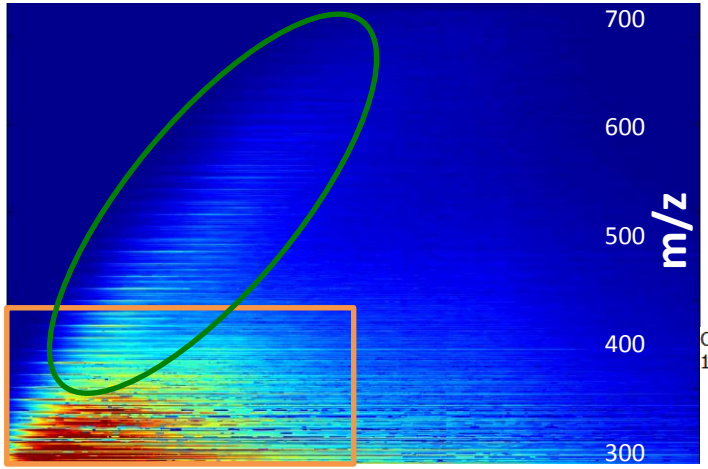
Boiling behavior

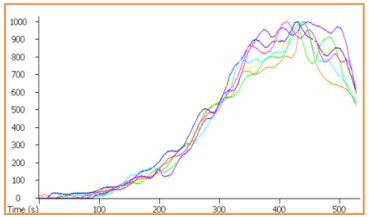


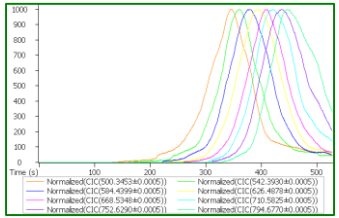
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

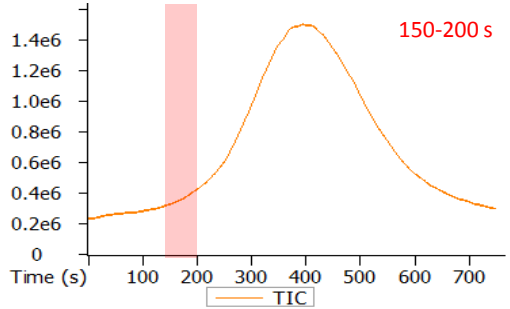


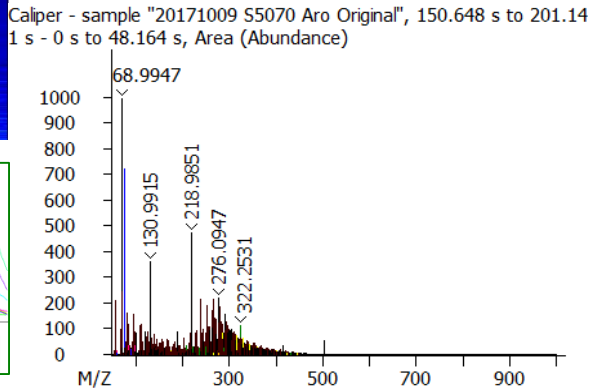




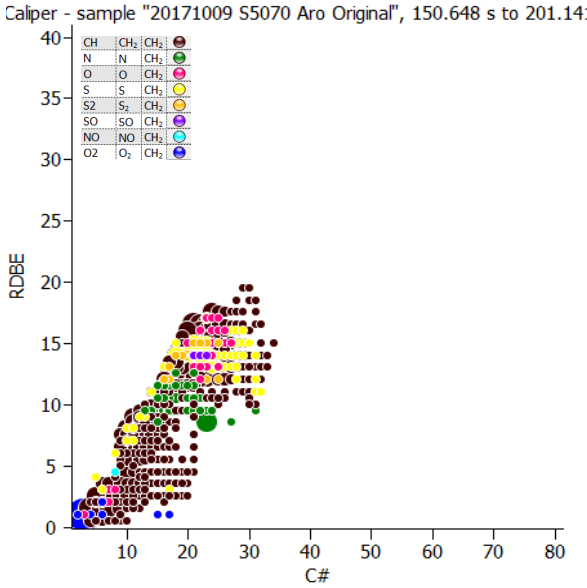
Non specific Fragmentation

Molecular Information





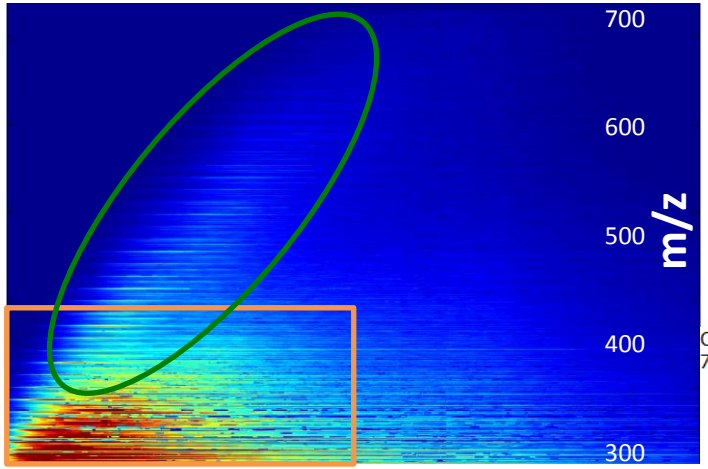
Boiling behavior

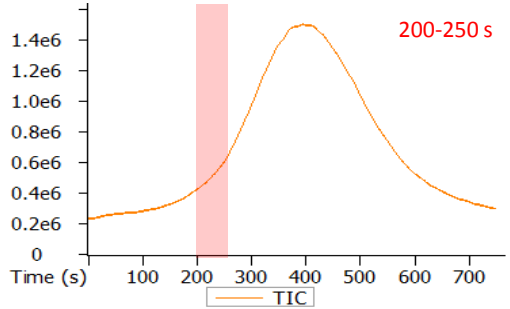


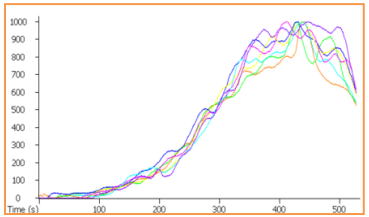
Class Information

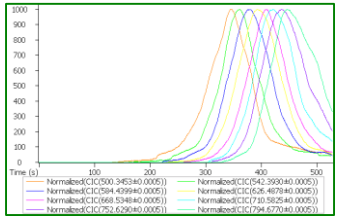
DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil



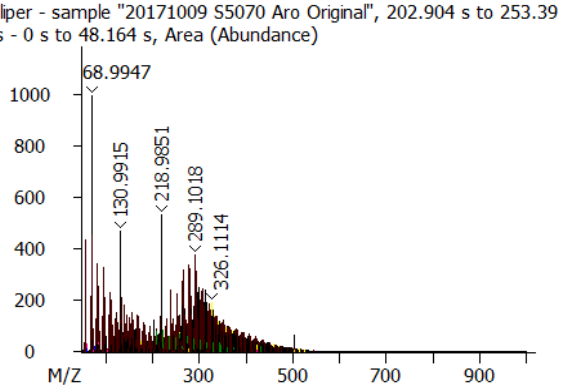




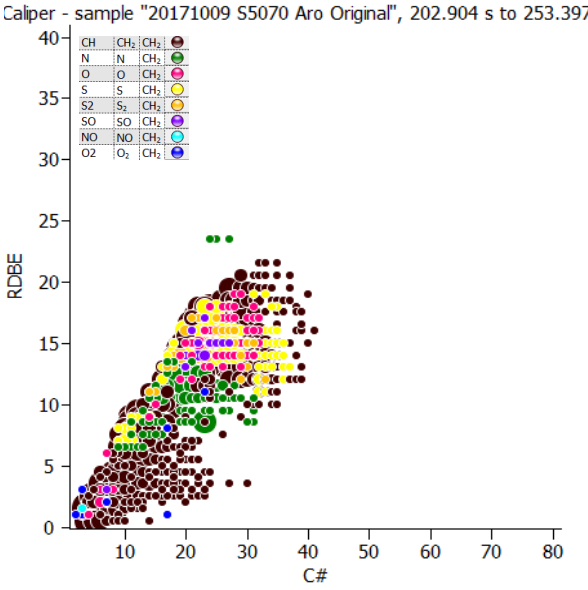


Non specific Fragmentation

Molecular Information



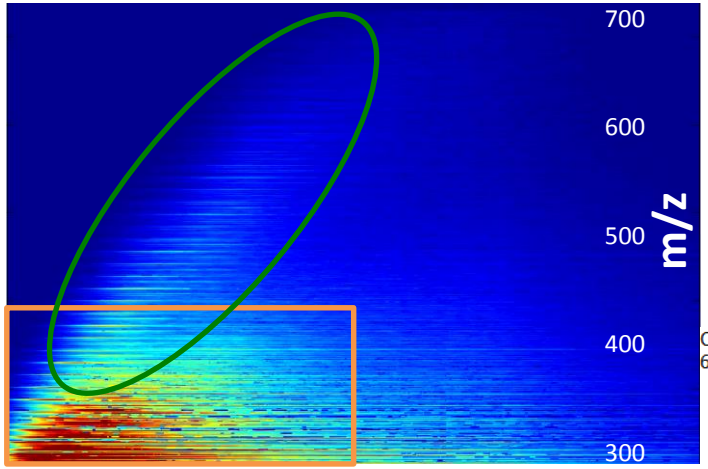
Boiling behavior

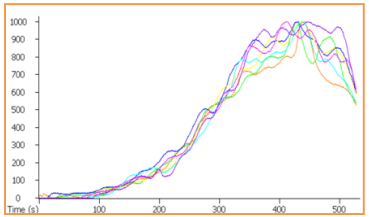


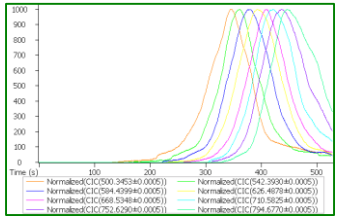
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

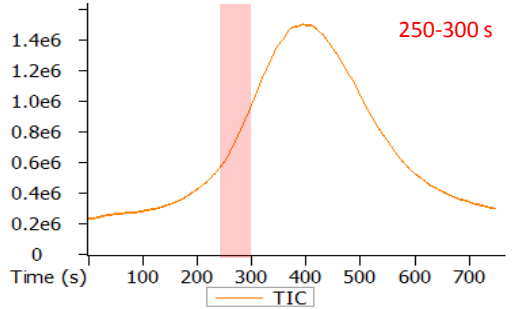


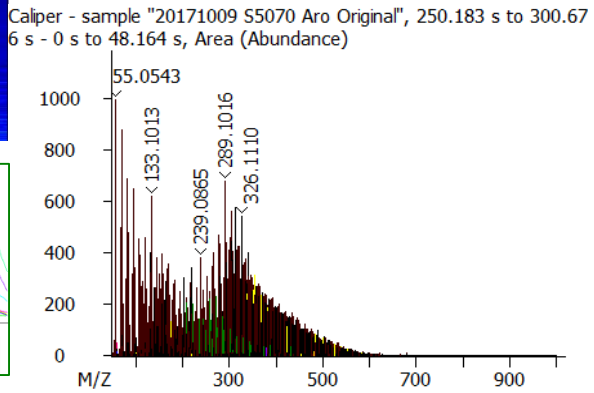




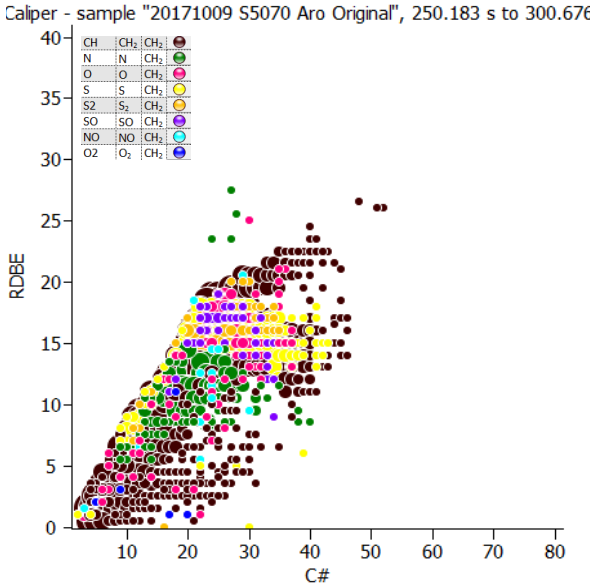
Non specific Fragmentation

Molecular Information





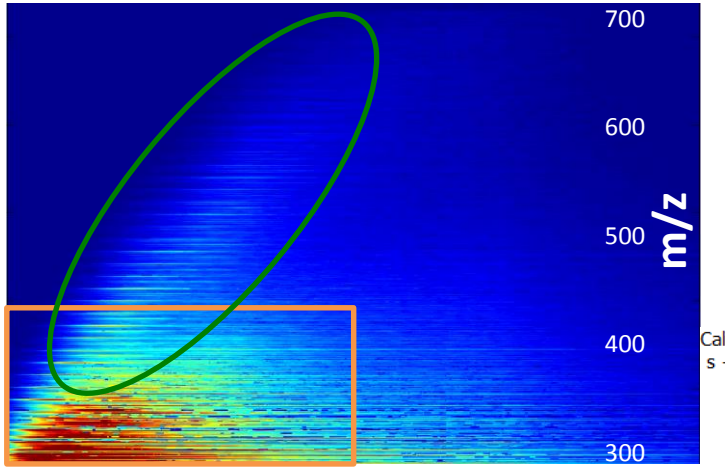
Boiling behavior

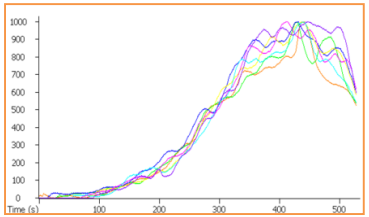


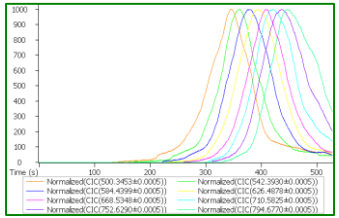
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

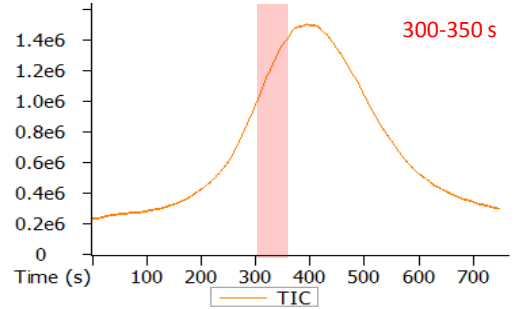


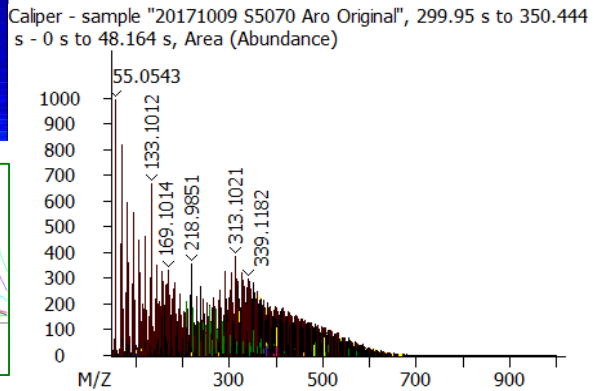




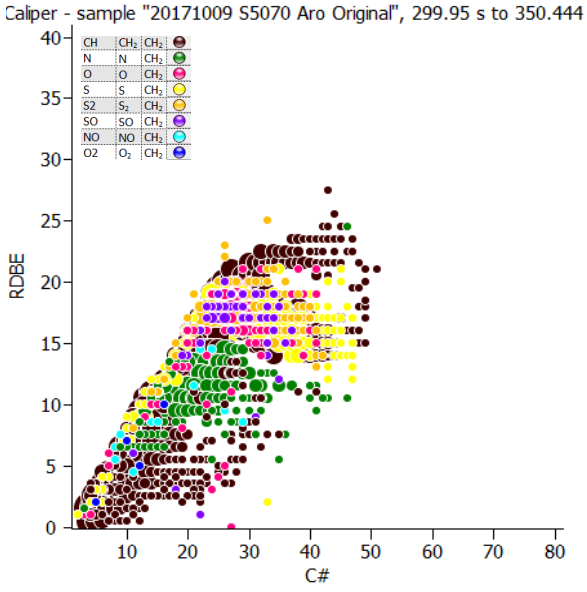
Non specific Fragmentation

Molecular Information





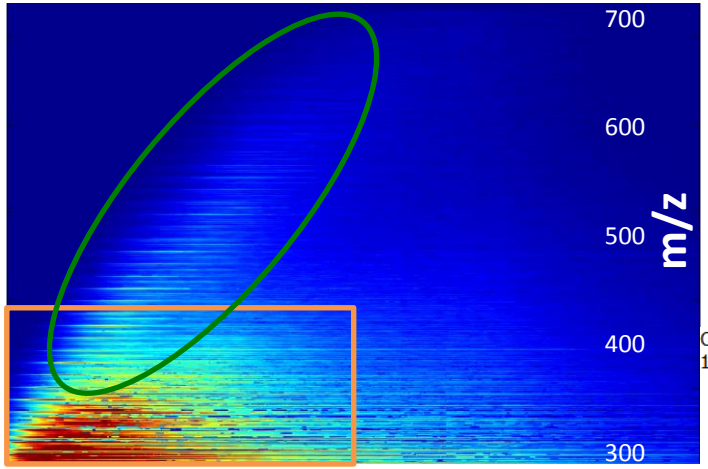
Boiling behavior

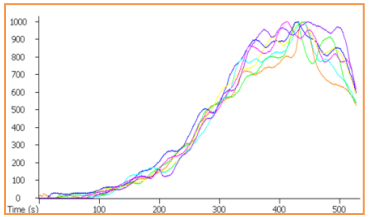


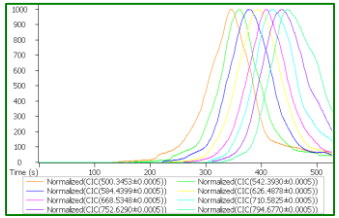
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

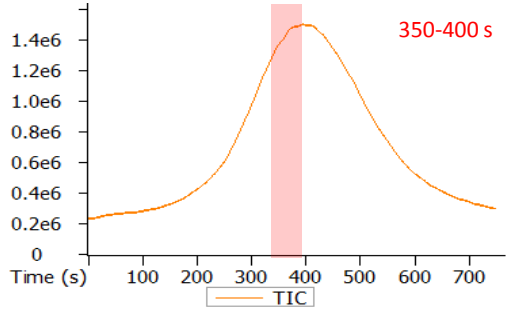


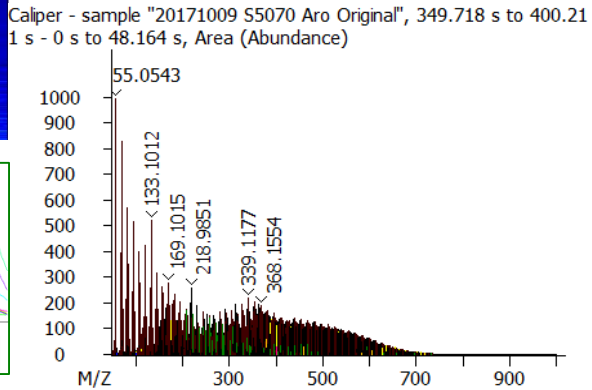




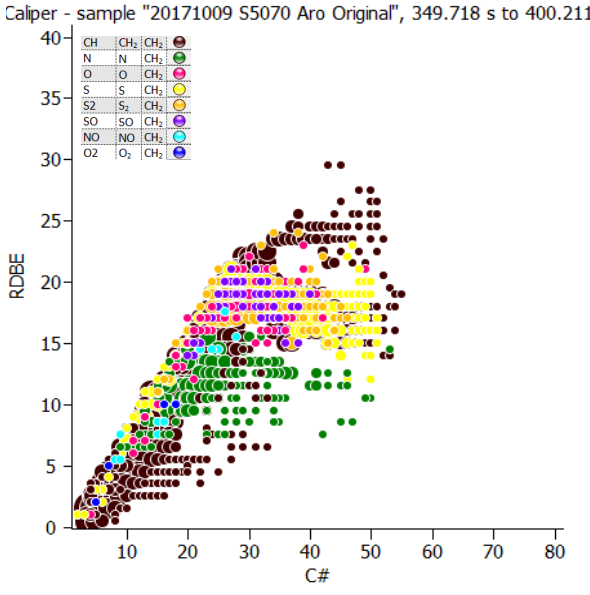
Non specific Fragmentation

Molecular Information





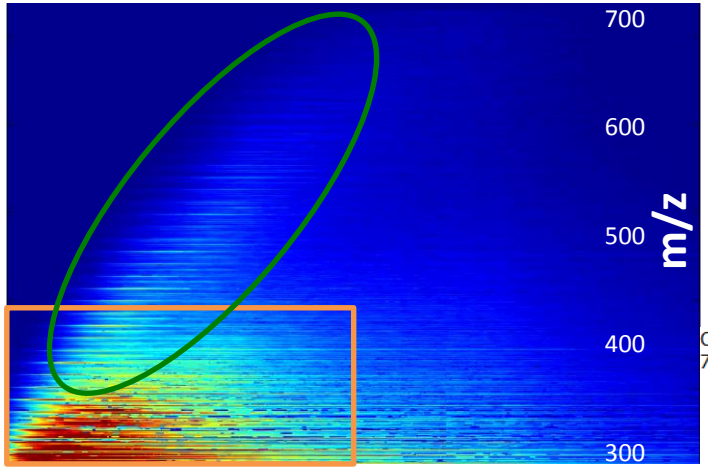
Boiling behavior

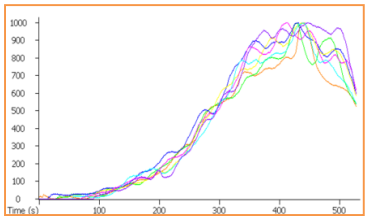


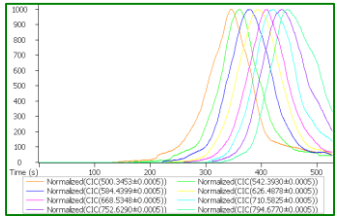
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

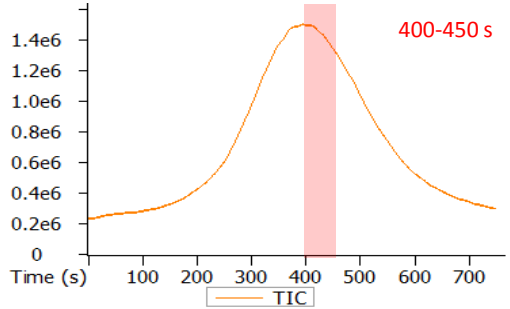


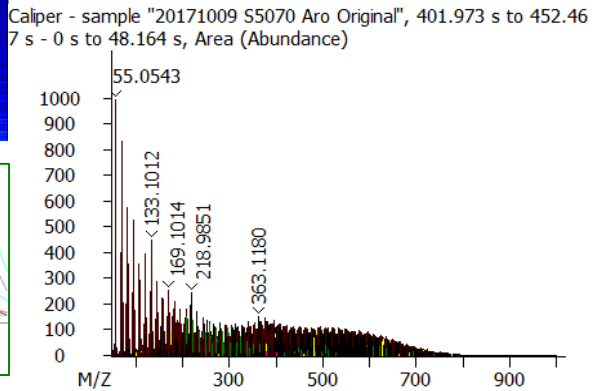




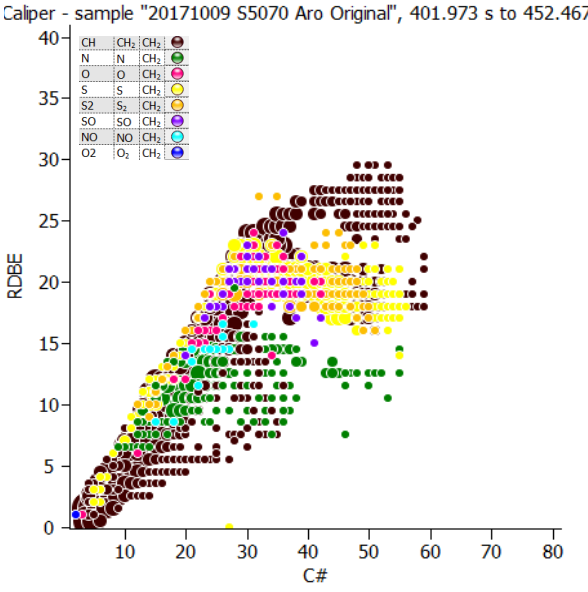
Non specific Fragmentation

Molecular Information





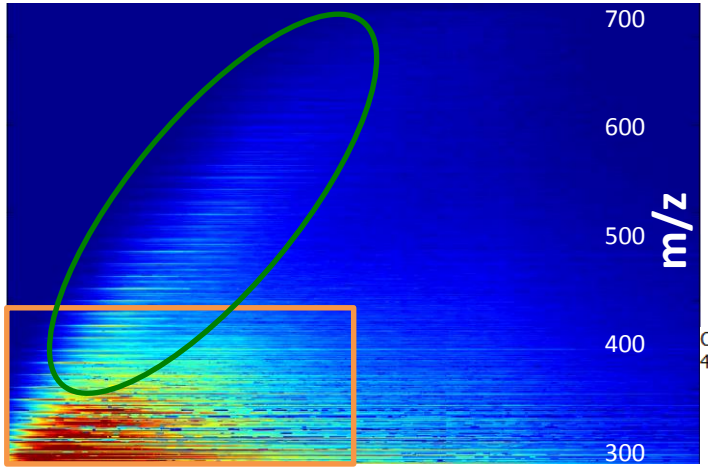
Boiling behavior

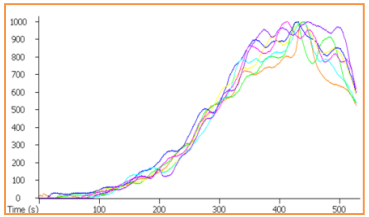


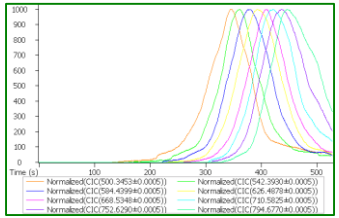
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

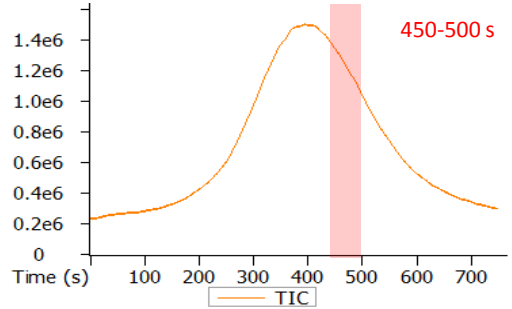


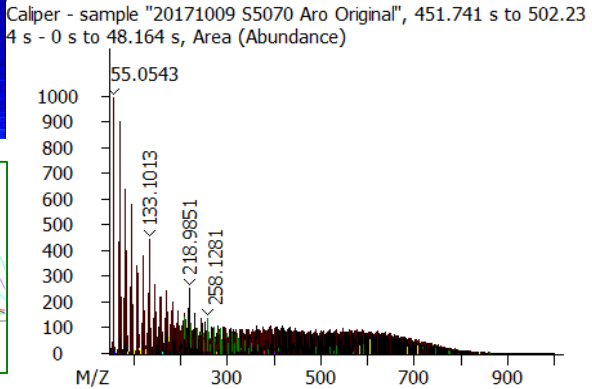




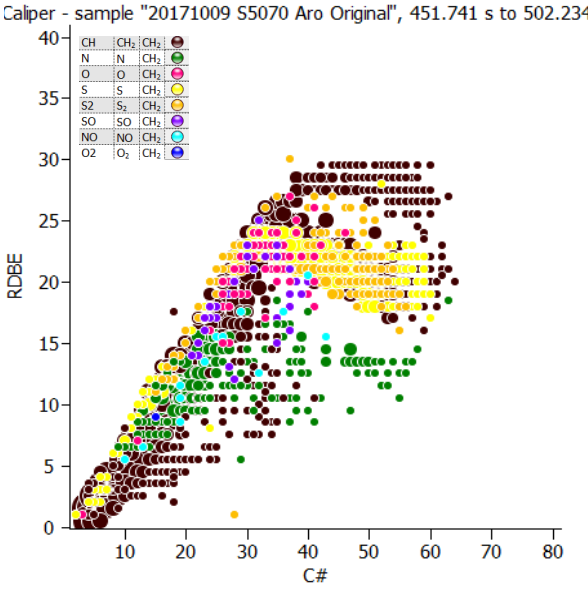
Non specific Fragmentation

Molecular Information





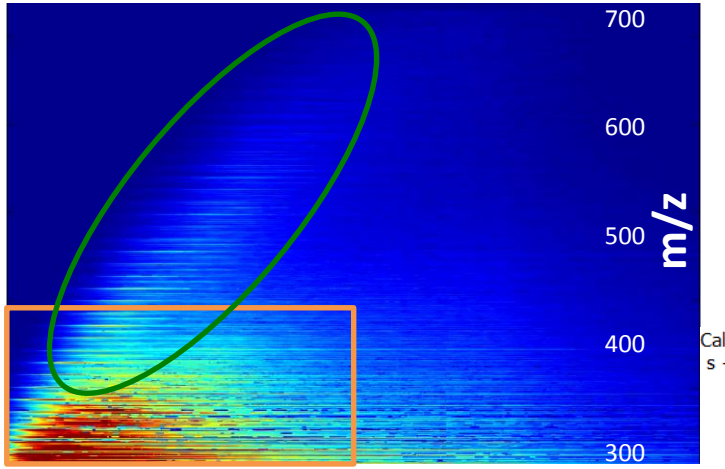
Boiling behavior

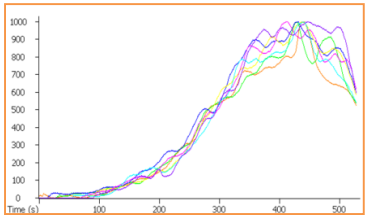


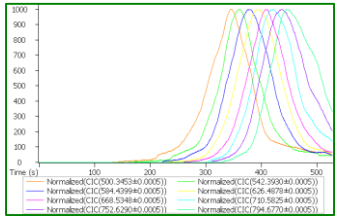
Class Information

DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil

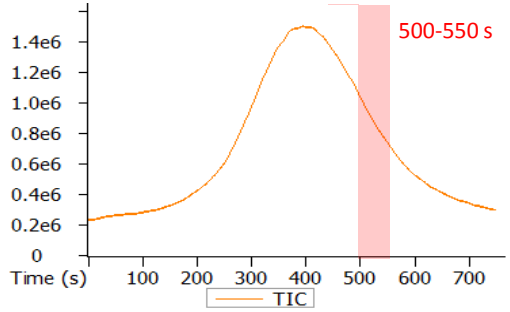


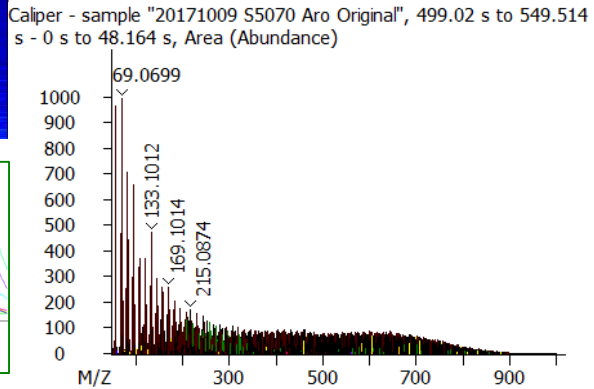




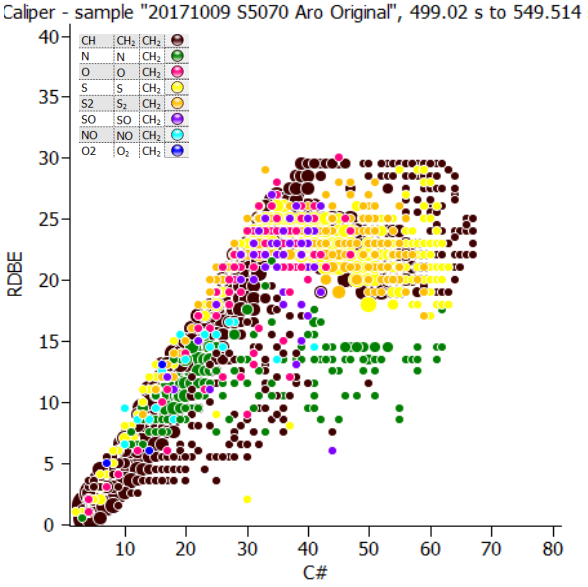
Non specific Fragmentation

Molecular Information





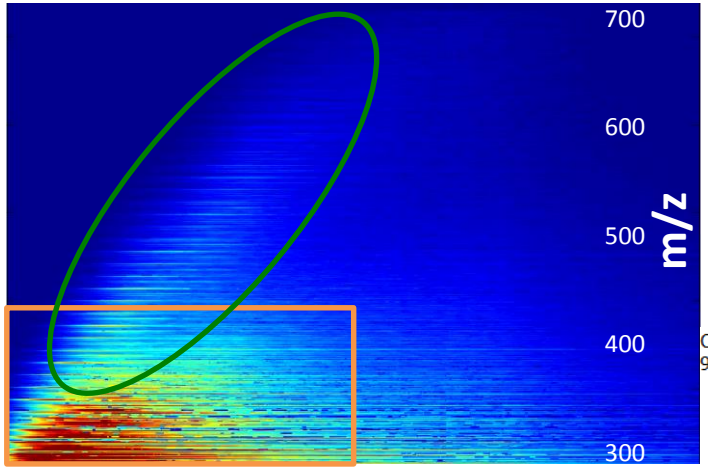
Boiling behavior

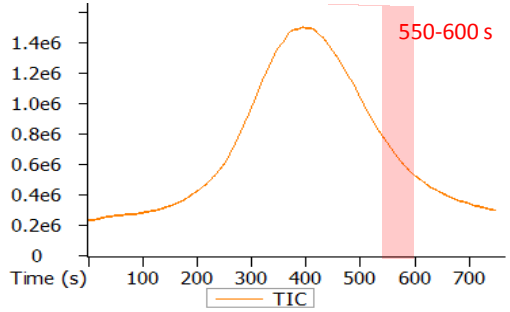


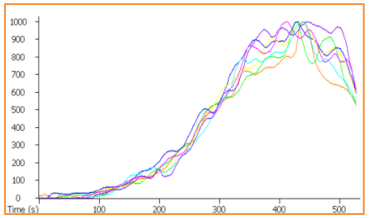
Class Information

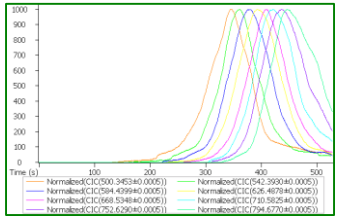
DIRECT INSERATION PROBE (DIP)

Vacuum Gas Oil



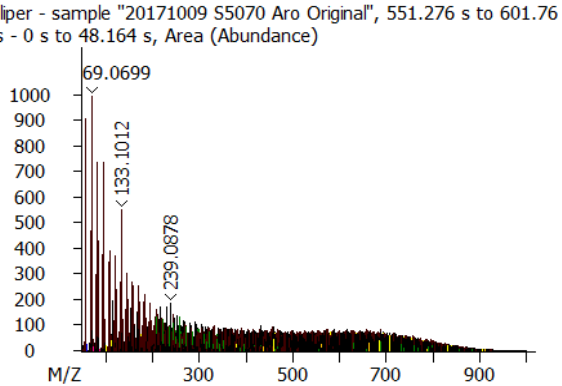




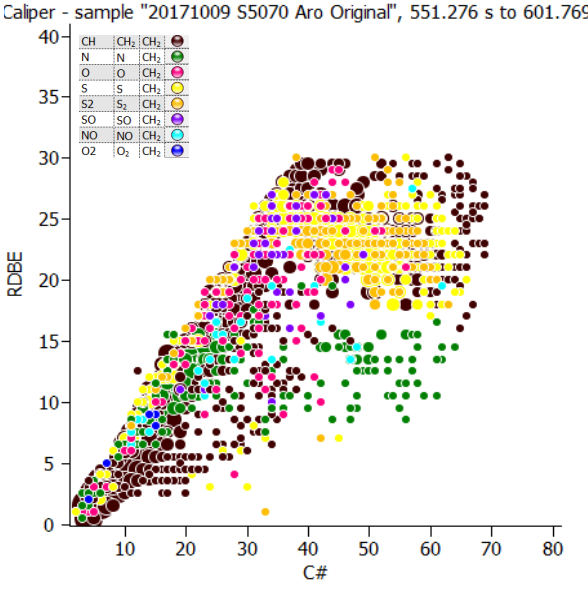


Non specific Fragmentation

Molecular Information



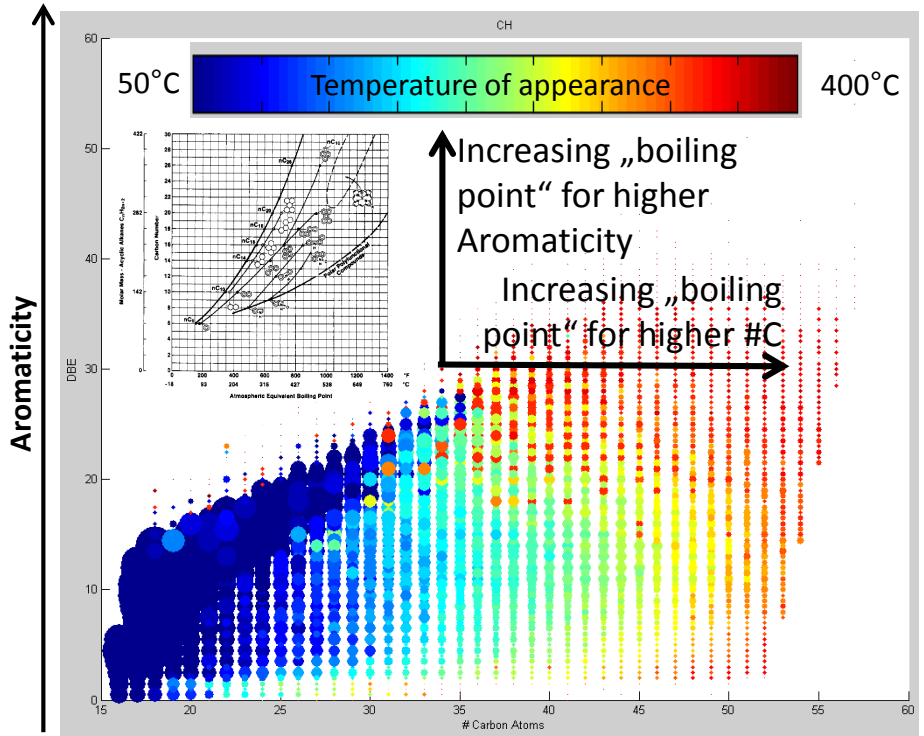
Boiling behavior

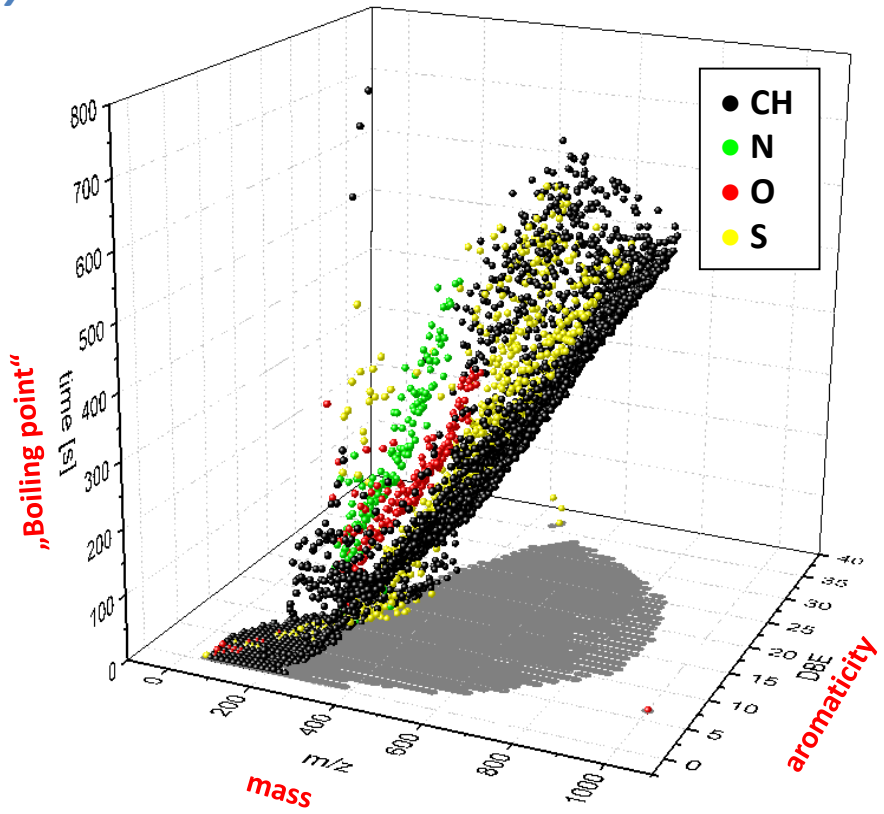


Class Information

DIRECT INSERATION PROBE (DIP)

Boduszynsky model

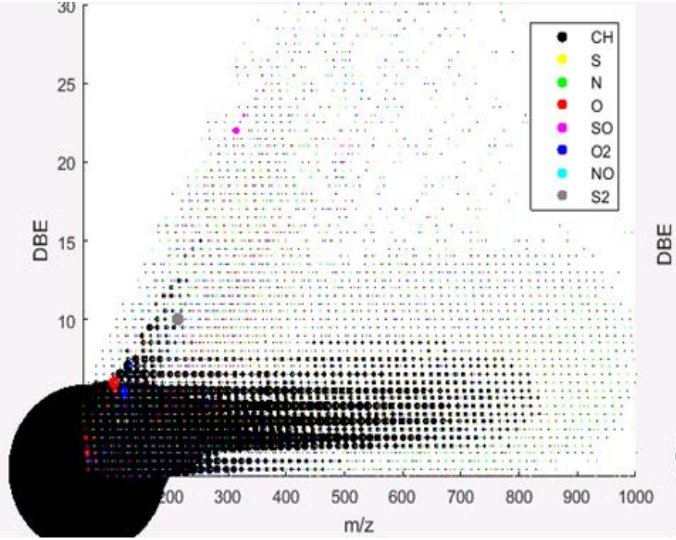




DIRECT INSERATION PROBE (DIP)

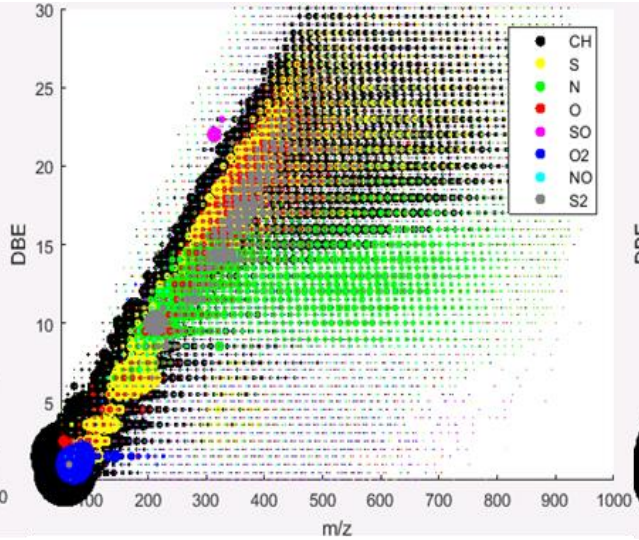
Bitumen SARA fractions:

Saturates



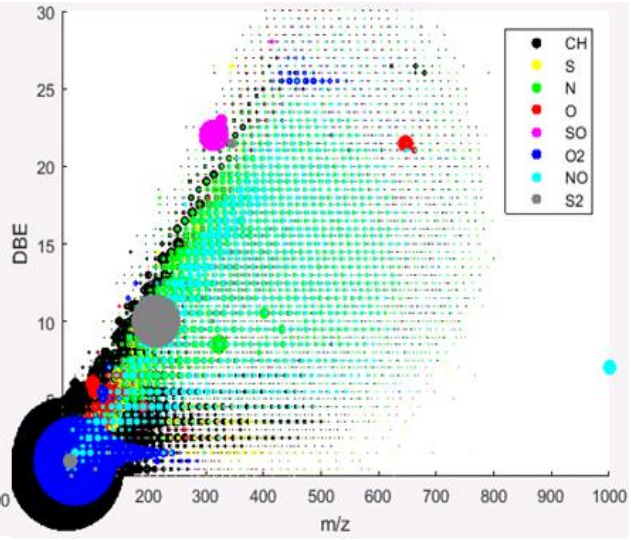
- Aliphatic structures (low DBE)
- Few heteroatoms

Aromatics



- Aromatic carbon- skeletons
- Aliphatic side chains
- N,O and S hetero-cycliclics

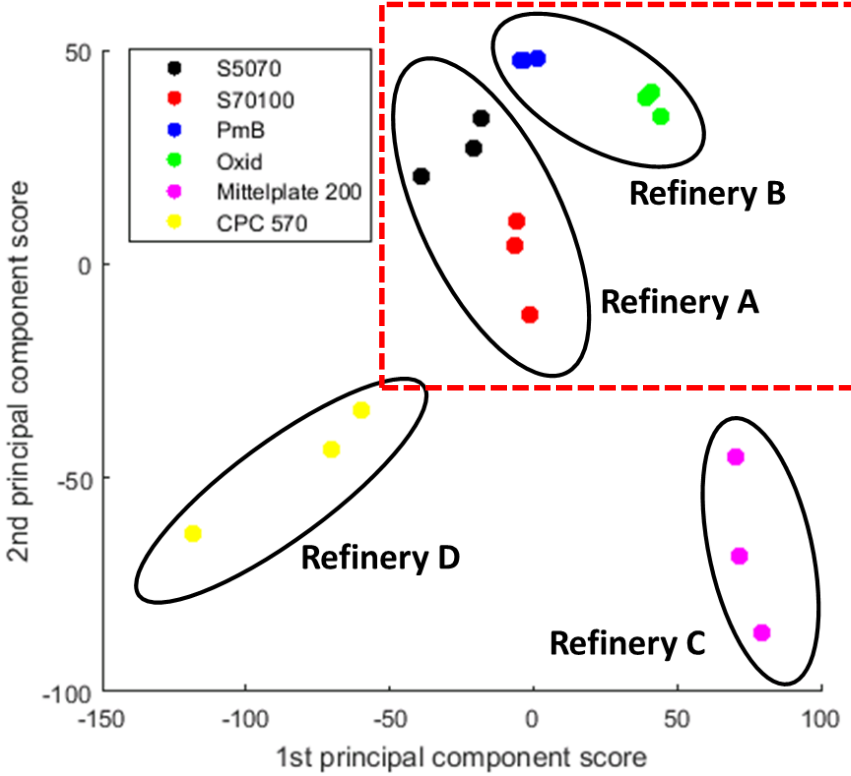
Resins

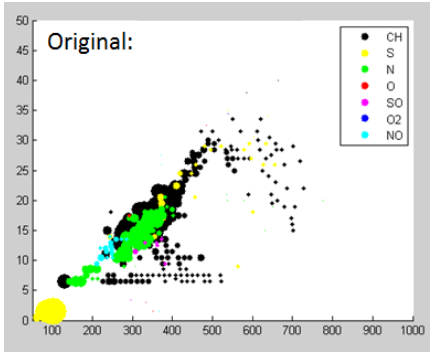


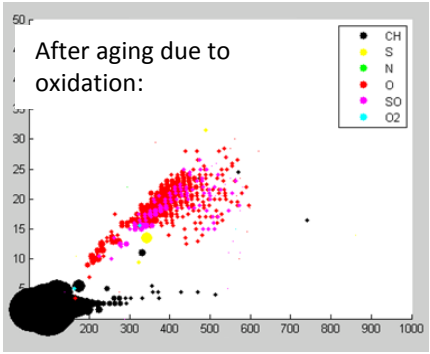
- Many heteroatoms (e.g. O_2-class)
- Fewer aromatic structures

DIRECT INSERATION PROBE (DIP)

Differentiation of Bitumen







Example above: Aged bitumen

- Original and aged sample each in triplicates
- Statistical evaluation (T-Test, confidence intervall: 90%)

Example left: Fingerprinting

- Principal component analysis with 6 bitumen samples (á 3 replicates) from 4 refineries
- ≈ 25.000 mass traces (variables) used for discrimination

LECO WEBINAR:

HIGH TEMP GC×GC OF LIGHT CRUDE OIL AND HIGH BOILERS USING NOMINAL AND HIGH RESOLUTION TOFMS

THANK YOU FOR YOUR ATTENTION!

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Contact: thomas.groeger@helmholtz-muenchen.de

Upcoming Conferences 2018 where we will present some of the shown topics:

European Mass Spectrometry Conference, Germany
Petromass, Slovenia
ASMS, USA
NATAS, USA
IMSC, Italy
Analytica, Germany
ISCC, Italy
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