

report

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Analysis of N-, O-, and S- heterocyclics in petroleum products using GCxGC with specific detection



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Analysis of N-, O-, and S- heterocyclics in petroleum products using GCxGC with specific detection

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ABSTRACT

REACH dossiers on all petroleum product categories were compiled and submitted by Concawe in 2010. ECHA subsequently raised concerns regarding the technical justification of the assumptions and tools used to generate the current PNECs for petroleum substance components. One of these issues regarded the lack of 'oxygen and nitrogen containing petroleum substances' from the Concawe library of structures in the PETROTOX/PETRORISK IT tool. The uncertainty linked to this omission had not been addressed by the Registrant in the registration dossier in the context of assessment factor selection.

To address this specific issue, Concawe subsequently agreed to

- Perform a literature review of the presence on nitrogen, oxygen and sulphur heterocyclics (NOSHs) and their structures in petroleum products
- Carry out analysis of NOSHs in petroleum products using GCxGC with specific N- and S-detectors and GC-AED with O-detection

Literature review confirmed the relative abundance of C, H, N, O and S in petroleum was 83-87%, 10-14%, 0.1-2%, 0.05-1.5% and 0.05-6%, respectively with a relatively large number of (>150) of NOSH structures identified from previous analysis of petroleum products. Petroleum products ($n = 44$) ranging from low boiling naphthas to asphalts were analysed using GCxGC with selective N- and S-chemoluminescence Detectors (NCD and SCD, respectively) and GC-AED (Gas Chromatography Atomic Emission Detector, used for O-containing components, since there is currently no existing O-specific detector for GCxGC analysis). Eleven different compound classes, each of varying carbon number, could be differentiated based on polarity for N- and S-heterocyclics. Total S-heterocyclics ranged from <0.01-3.24% (mean = 0.58%), whereas total N-heterocyclics, ranging from <0.01-0.08% (mean = 0.02%), were less abundant. No O-containing components could be detected (i.e. <0.1%).

Based on the analytical data generated, it is concluded that NOSH compounds only occur in low concentrations within petroleum products.

KEYWORDS

N-heterocyclics, S-heterocyclics, O-heterocyclics, petroleum products, GCxGC, REACH

INTERNET

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	Page
SUMMARY	IV
1. INTRODUCTION	1
2. PETROLEUM PRODUCTS ANALYSED	2
3. TEST METHODS	4
3.1. LITERATURE SEARCH	4
3.2. PETROLEUM SAMPLE ANALYSIS	4
4. RESULTS	6
4.1. LITERATURE DATA	6
4.2. PETROLEUM SAMPLE ANALYSIS	6
5. DISCUSSION	17
6. GLOSSARY	18
7. REFERENCES	20

APPENDICES 1 - 3

SUMMARY

Following the concerns of ECHA regarding the lack of 'oxygen and nitrogen containing hydrocarbons' in the Concawe library of components of petroleum products that are used in the PETROTOX and PETRORISK models (to generate the current PNECs for petroleum substance components), Concawe agreed to generate analytical data on nitrogen, oxygen and sulphur heterocyclic compounds (NOSHs) in petroleum substances.

An initial literature review of the presence and structures of NOSHs in petroleum products was conducted [1] which identified a large number (>150) of NOSH structures from previous analyses of petroleum products. The relative abundances of carbon, hydrogen, sulphur, nitrogen and oxygen in petroleum were identified as 83-87%, 10-14%, 0.05-6%, 0.1-2% and 0.05-1.5%, respectively [2].

Analysis of a number of petroleum products (n=44) with varying boiling point ranges, from low boiling naphthas to asphalts, for NOSHs was subsequently performed using two-dimensional chromatography (GCxGC) with specific N- and S-detectors and GC-AED (Gas Chromatography Atomic Emission Detector, used for O-containing components, since there is currently no existing O-specific detector for GCxGC analysis). Analysis of petroleum products was able to differentiate 11 different sulphur and nitrogen compound classes in test samples based on polarity. The levels of total S-heterocyclics ranged from <0.01-3.24% (mean = 0.58%), whereas total N-heterocyclics were less abundant, ranging from <0.01-0.08% (mean = 0.02%). No O-containing components were detected (i.e. <0.1%).

Based on the analytical data generated, it is concluded that NOSH compounds only occur in low concentrations within petroleum products.

1. INTRODUCTION

In 2010, Concawe compiled and submitted REACH Dossiers on all petroleum product categories. The European Chemicals Agency (ECHA) has since raised concerns in draft decision letters to lead registrants regarding the technical justification of the assumptions and tools used to generate PNECs for petroleum substance components. One issue related to the lack of 'oxygen and nitrogen containing hydrocarbons' in the Concawe library of components of petroleum products that are used in the PETROTOX and PETRORISK models to fill the hydrocarbon blocks. In order to meet the regulatory compliance of REACH, ECHA requested that additional data on Nitrogen, Oxygen, and Sulphur Heterocyclic compounds (NOSHs) within petroleum substances be generated, allowing the Concawe registration dossiers to be revised and updated accordingly.

NOSHs are found in polar and asphaltic fractions of crude petroleum, produced waters, oil field tars and sludges, shale oils, coal synthetic fuels, and pyrogenic products [3-12]. Low and intermediate molecular weight NOSHs are generally found to be more water soluble in sediment-water systems than analogous PAHs and more resistant to chemical, photochemical and microbial degradation [9, 13-16].

An initial literature review of the presence and structure of NOSHs in petroleum products was undertaken [1]. Quantitative analysis of NOSHs in a number ($n=44$) of petroleum products with varying boiling point ranges was subsequently carried out at Shell Technology Centre Amsterdam, using two-dimensional chromatography (GC_xGC) with specific N- and S-detectors for nitrogen and sulphur heterocyclics, respectively and using GC-AED with O-detection [17-18]. This report summarises the % of NOSHs found in a wide range of representative petroleum products.

2. PETROLEUM PRODUCTS ANALYSED

A wide range of petroleum product samples were selected from a variety of petroleum substance categories for quantitative NOSH analysis (as summarised below). Samples were selected from a recent collection of products which was coordinated by the Concawe SIG (Substance Identification Group) in 2014. Information on these petroleum substance categories can be found in Concawe report no. 10/14 [19].

Table 1 Petroleum product samples analysed

Sample name	CAS No.	Category
Naphtha (Petroleum), Hydrodesulfurized light	64742-73-0	LBPN
Naphtha (petroleum), full-range coker	68513-02-0	LBPN
Gasoline	86290-81-5	LBPN
Kerosine (Petroleum)	8008-20-6	Kerosine
Kerosine (petroleum), Hydrodesulfurized	64742-81-0	Kerosine
Kerosine (petroleum), sweetened	91770-15-9	Kerosine
Residues (petroleum), atm. tower	64741-45-3	HFO component
Distillates (petroleum), vacuum	70592-78-8	HFO component
Fuel oil, residual	68476-33-5	HFO component
Distillates (petroleum), petroleum residues vacuum	68955-27-1	HFO component
MK1 diesel fuel	None	MK1 diesel fuel
Distillates (Petroleum), Full-range straight run middle	68814-87-9	SRGO
Distillates (Petroleum), Heavy straight run	68915-96-8	SRGO
Gas oils (petroleum), straight-run	64741-43-1	SRGO
Distillates (Petroleum), Straight-run middle	64741-44-2	SRGO
Gas oils (Petroleum), Light vacuum	64741-58-8	VHGO
Fuels, Diesel	68334-30-5	VHGO
Fuels, Diesel, NO. 2	68476-34-6	VHGO
Condensates (petroleum), vacuum tower	64741-49-7	VHGO
Distillates (petroleum), light catalytic cracked	64741-59-9	CGO
Distillates (petroleum), hydrodesulfurized middle coker	101316-59-0	CGO
Distillates (Petroleum), Hydrodesulfurized middle	64742-80-9	OGO
Distillates (Petroleum), Hydrodesulfurized middle	64742-80-9	OGO
White mineral oil (petroleum)	8042-47-5	HRBO
Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalting	68814-89-1	TDAE
Extracts (petroleum), solvent-refined heavy paraffinic distillate solvent	68783-04-0	TDAE
Extracts (petroleum), heavy paraffinic distillate solvent	64742-04-7	DAE
Distillates (petroleum), light paraffinic	64741-50-0	UATO
Distillates (petroleum), heavy paraffinic	64741-51-1	UATO
Foots oil (petroleum)	64742-67-2	Foots oil
Foots oil (petroleum), Hydrotreated	92045-12-0	Foots oil
Extracts (Petroleum), Residual oil solvent	64742-10-5	RAE
Extracts (Petroleum), Deasphalted Vac residue solvent	91995-70-9	RAE
Paraffin waxes and Hydrocarbon waxes	8002-74-2	P&H wax
Paraffin waxes (petroleum), Hydrotreated	64742-51-4	P&H wax
Petrolatum	8009-03-8	Petrolatum
Petrolatum (petroleum), Hydrotreated	92045-77-7	Petrolatum
Slack wax (petroleum)	64742-61-6	Slack wax

Sample name	CAS No.	Category
Paraffin oils (petroleum), catalytic dewaxed light	64742-71-8	OLBO
Distillates (petroleum), solvent-refined light naphthenic	64741-97-5	OLBO
Distillates (petroleum), solvent-dewaxed heavy paraffinic	64742-65-0	OLBO
Distillates (petroleum), Hydrotreated heavy paraffinic	64742-54-7	OLBO
Asphalt, oxidized	64742-93-4	Oxidized asphalt
Asphalt	8052-42-4	Bitumen

LBPN: low boiling point naphtha (gasoline); HFO: heavy fuel oils; SRGO: straight run gas oils; VHGO: vacuum gas oils, hydrocracked gas oils and distillate fuels; CGO: cracked gas oils; OGO: other gas oils; HRBO: Highly refined base oils; TDAE: treated distillate aromatic extracts; DAE: untreated distillate aromatic extracts; UATO: unrefined/acid treated oils; RAE: residual aromatic extracts; P&H wax: Paraffin and hydrocarbon wax; OLBO: other lubricant base oils

3. TEST METHODS

3.1. LITERATURE SEARCH

A literature search was initially carried out to identify names and typical chemical structures of NOSH compounds identified from previous petroleum product analyses as well as the relative abundance of carbon, hydrogen, sulphur, nitrogen and oxygen in petroleum [1].

The ECHA 'Registered Substances' database was searched for reliable (Klimisch score 1 or 2) experimental ecotoxicity data on the identified NOSH compounds, however experimental data were shown to be limited. The Action Plan that CONCAWE presented to ECHA addressed the availability of ecotoxicity data for NOSH compounds and whether such data for heterocyclic PAHs can be described by the Target Lipid Model (TLM). The work was subsequently undertaken by HydroQual and reported separately [20].

3.2. PETROLEUM SAMPLE ANALYSIS

A number of representative petroleum product samples ($n = 44$) with varying boiling point ranges, spanning 20 different categories (**Table 1**), were selected for quantitative GCxGC analysis of various N-, O- and S-compound classes based on polarity, using highly sensitive and selective N- and S-chemo-luminescence detectors (NCD and SCD, respectively) and GC-AED (Gas Chromatography Atomic Emission Detector, used for O-containing components, since there is currently no existing O-specific detector for GCxGC analysis). Current NCD, SCD and AED cover a boiling range of 40-450°C. Analysis was conducted at Shell Technology Centre Amsterdam.

The GCxGC-system used was based on an 7890 Gas Chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with an CIS4 PTV injector (Agilent) and an NCD or SCD (Sievers/Ionics, Boulder, CO, USA). The AED model used for O-compound analysis was an Agilent G2350A (Agilent, Avondale, PA, USA). The GCxGC modulation assembly was a KT2004 cryogenic loop modulator (Zoex Corp., Pasadena, TX, USA). A separate heating oven was used for independent temperature programming of the second dimension column. Columns were coupled using glass press-fits. The first dimension column used contained a non-polar stationary phase, which minimises the effect of the activity coefficient, meaning that retention is solely based on volatility (boiling-point separation). The second dimension column used was coated with a medium polarity stationary phase, and had an internal diameter of 100 µm I.D allowing for high-speed separations. Since volatility based separation has already occurred in the first dimension, the separation in the second dimension is solely based on polarity and/or based on additional interactions between the solutes and the stationary phase. Samples were injected pure or diluted dependent on the viscosity of the samples and the concentrations of components were calculated by means of an external standard for nitrogen and internal standard for sulphur.

Samples were run in split mode. Injection volumes were 1.0 µl for NCD and 0.5 µl for SCD, with helium as the carrier gas at a flow rate of 20 ml/min. Initial temperature was set at 50°C. The first dimension column (10 m, 0.25 mm I.D., 0.25 µm dimethylpolysiloxane (DB-1)) temperature profile was 40°C (5 min isothermal) then 2°C/min to 320°C (20 min isothermal). The second dimension column (2 m, 0.10 mm I.D., 0.05 µm polysilphenylene-siloxane (VF-17ms)) temperature profile was 50°C (offset from first-dimension 90°C (5 min isothermal)) then 2°C/min to 350°C (30 min isothermal). The cryogenic single jet loop type modulator used was set to a

modulation time of 7.5 to 12 s and pulse width of 500 ms. The modulation column was 2 m, 0.10 mm I.D. deactivated fused silica (1 m in loop). The transfer line from the second dimension column to the NCD/SCD was 0.3 m, 0.10 mm I.D. deactivated fused silica. Chemo-luminescence detector temperatures were 950°C for NCD and 800°C for SCD, with make-up gas of air and hydrogen. Resulting data was processed and visualized with in-house developed software.

For N-components, it was not technically possible to adequately distinguish between certain compound groups (e.g. indoles and quinolones and also carbazoles and acridines), since even with GCxGC these groups overlap. Detection limits for these analytical techniques were SCD = 50 ppb as S per component, and NCD = 1 ppm as N per component. Detection limits for O-component analysis was 20 ppm per component.

Comparison of a limited number of test samples against a reference diesel (known to be free from oxygen) was carried out to check whether any of these test samples contained any O-heterocyclics. Further analysis of six test samples (sample id numbers 023, 043, 130, 168, 188 and 096A, **Table 3**) was performed against a set of alcohol standards (methanol, ethanol, butanol and octanol) to confirm the absence of O-heterocyclics (<0.1%).

Further detailed analysis of the GCxGC chromatograms was carried out for seven of the samples analysed for S-heterocyclics (sample id number 73, 82, 135, 168, 188, 154541 and 154545, **Tables 2 and 3**) and one of the samples analysed for N-heterocyclics (sample id number 154554, Table 3) in order to identify the carbon chain lengths of the components from the various S-heterocyclic and N-heterocyclic classes.

4. RESULTS

4.1. LITERATURE DATA

The initial literature search identified names and chemical structures of a number (>150) of NOSH compounds (e.g. 112 N-heterocyclics, 26 O-heterocyclics, and 23 S-heterocyclics) identified from previous petroleum product analyses [1]. The search also established the relative abundance of carbon, hydrogen, sulphur, nitrogen and oxygen in petroleum is 83-87%, 10-14%, 0.05-6%, 0.1-2% and 0.05-1.5%, respectively [2].

4.2. PETROLEUM SAMPLE ANALYSIS

Analysis showed that total N-heterocyclics abundance out of the total mass of test samples ranged from <0.01-0.08% (mean = 0.02%) (**Table 2**), whereas total S-heterocyclics abundance ranged from <0.01-3.24% (mean = 0.58%) (**Table 3**). S-heterocyclics abundance was shown to be highest in TDAE, DAE, UATO and HFO component samples, and lowest in MK1 Diesel, OGO, HRBO and slack wax samples (**Figure 1**).

Comparison of a limited number of test samples against a reference diesel (known to be free from oxygen) indicated that those test samples were also most likely to be free of oxygen. Further analysis of six test samples (sample id numbers 023, 043, 130, 168, 188 and 096A, **Table 3**) against a set of alcohol standards (methanol, ethanol, butanol and octanol) confirmed the absence of any O-heterocyclics (<0.1%) in any of the samples.

Further detailed analysis of GCxGC chromatograms of seven samples analysed for S-heterocyclics (sample id number 73, 82, 135, 168, 188, 154541 and 154545, **Tables 2 and 3**) and one of the samples analysed for N-heterocyclics (sample id number 154554, **Table 2**) confirmed the carbon chain lengths of the components from the various S-heterocyclic and N-heterocyclic classes (**Tables 4 and 5**).

Table 2 Nitrogen group-type GCxGC analysis

Sample	Sample ID	Compound class amounts (ppmw N)*										% of total sample mass
		A, Pyr, P	Aryl-N	Ind, Q	N(Ind, Q)	Carb, Acr	N-(Carb, Acr)	B(Carb, Acr)	N-(Carb, Acr)	DB(Carb, Acr)	NDB(Carb, Acr)	
Distillates (Petroleum), Full-range straight run middle	154541	5.9 (5.48%)	6.9 (6.41%)	31.0 (28.81%)	11.9 (11.06%)	51.1 (47.49%)	0.8 (0.74%)	<0.1	<0.1	<0.1	<0.1	<0.1
Distillates (Petroleum), Heavy straight run samples	154545	4.1 (1.5%)	10.4 (3.81%)	38.7 (14.16%)	27.6 (10.1%)	171.6 (62.79%)	14.7 (5.38%)	6.2 (2.27%)	<0.1	<0.1	<0.1	107.6 0.01%
Distillates (Petroleum), Hydrodesulfurized middle	154937	<0.1	<0.1	<0.1	<0.1	0.8 (100%)	<0.1	<0.1	<0.1	<0.1	<0.1	273.3 0.03%
Distillates (Petroleum), Hydrodesulfurized middle	154549	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Gas oils (Petroleum), Light vacuum	154554	11.6 (1.37%)	34.8 (4.10%)	113.9 (13.41%)	76.9 (9.06%)	375.2 (44.18%)	94.1 (11.08%)	142.7 (16.8%)	<0.1	<0.1	<0.1	<0.1
Fuels, Diesel	154567	<0.1 (7.07%)	5.1 (11.23%)	8.1 (7.35%)	5.3 (67.55%)	48.7 (6.8%)	4.9 (0.01%)	<0.1	<0.1	<0.1	<0.1	18.1 0.00%
Fuels, Diesel, NO ₂	154579	36.1 (7.12%)	23.7 (4.68%)	101.4 (20.0%)	25.5 (5.03%)	298.5 (58.89%)	<0.1	<0.1	<0.1	<0.1	<0.1	849.2 0.08%
Extracts (Petroleum), Residual oil solvent**	154594	<0.1	<0.1	2.1 (3.06%)	3.8 (5.53%)	10.2 (14.85%)	9.5 (13.83%)	26.4 (38.43%)	16.7 (24.31%)	<0.1	<0.1	506.9 0.05%
Extracts (Petroleum), Deasphalted Vac residue solvent**	154598	<0.1	<0.1	2.2 (2.46%)	3.9 (4.36%)	10.7 (11.97%)	10.9 (12.19%)	33.6 (37.58%)	28.1 (31.43%)	<0.1	<0.1	68.7 0.01%
Naphtha (Petroleum), Hydrodesulfurized light	1174585	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	89.4 0.01%
Kerosine (Petroleum)	1174587	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
MK1 diesel fuel	1174588	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	<0.1 0.00%

Sample	Sample ID	Compound class amounts (ppmw N)*										% of total sample mass	
		A, Pyr, P	Aryl-N	Ind, Q	N-(Ind, Q)	Carb, Acr	N-(Carb, Acr)	B(Carb, Acr)	N-B(Carb, Acr)	DB(Ca rb, Acr)	NDB(Ca arb, Acr)	Rest	
Naphtha (petroleum), full-range coker	1174594	63.3 (43.24%)	27.6 (18.85%)	39.6 (27.05%)	6.8 (4.64%)	9.1 (6.22%)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	146.4 0.01%
Kerosine (petroleum), Hydrodesulfurized	1174601	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.00%
Distillates (petroleum), light catalytic cracked	1174609	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Distillates (petroleum), light catalytic cracked	1174584	24.7 (5.11%)	26.2 (5.42%)	75.0 (15.52%)	40.0 (8.28%)	283.5 (58.68%)	28.6 (5.92%)	4.9 (1.01%)	<0.1	<0.1	<0.1	<0.1	483.1 0.05%
Kerosine (petroleum), sweetened	1174608	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.00%
Gasoline	1174612	0.3 (27.27%)	0.8 (72.73%)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.1 0.00%
Gas oils (petroleum), straight-run	1174617	7.0 (2.48%)	10.1 (3.58%)	47.4 (16.78%)	35.7 (12.64%)	179.4 (63.50%)	2.9 (1.03%)	<0.1	<0.1	<0.1	<0.1	<0.1	282.5 0.03%
Condensate (petroleum), vacuum tower	1174619	16.8 (7.27%)	12.0 (5.19%)	48.8 (21.11%)	28.2 (12.20%)	106.9 (46.24%)	9.1 (3.94%)	9.4 (4.07%)	<0.1	<0.1	<0.1	<0.1	231.2 0.02%
Distillates (Petroleum), Straight-run middle	1174620	3.0 (2.82%)	4.5 (4.23%)	21.4 (20.13%)	12.1 (11.38%)	62.6 (58.89%)	2.7 (2.54%)	<0.1	<0.1	<0.1	<0.1	<0.1	106.3 0.01%
Paraffin oils (petroleum), catalytic dewaxed light	1174616	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.00%
Distillates (petroleum), solvent-refined light naphthenic	1174593	5.1 (54.84%)	1.9 (20.43%)	2.3 (24.73%)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	9.3 0.00%
Distillates (petroleum), light paraffinic	1174596	1.8 (0.95%)	4.3 (2.27%)	15.2 (8.01%)	20.8 (10.96%)	105.3 (55.51%)	22.3 (11.76%)	20.1 (10.6%)	<0.1	<0.1	<0.1	<0.1	189.7 0.02%
Distillate (petroleum), solvent-dewaxed heavy paraffinic	1174597	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.00%
White mineral oil (petroleum)	1174613	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.00%

Sample	Sample ID	Compound class amounts (ppmw N)*										% of total sample mass	
		A, Pyr, P	Aryl-N	Ind, Q	N-(Ind, Q)	Carb, Acr	N-(Carb, Acr)	B(Carb, Acr)	N-B(Carb, Acr)	DB(Carb, Acr)	NDB(Carb, Acr)	Rest	
Distillate (petroleum), Hydrotreated heavy paraffinic Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalting	1174614 (0.95%)	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Distillates (petroleum), heavy paraffinic	1174611 0.00%	7.4 0.00%	14.3 (1.83%)	55.4 (7.10%)	65.9 (8.44%)	330.9 (42.40%)	120.1 (15.39%)	179.0 (22.94%)	7.4 (0.95%)	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Extracts (petroleum), heavy paraffinic distillate solvent	1174590 0.00%	<0.1 0.00%	<0.1 0.00%	0.01% 0.00%	0.01% 0.00%	0.03% 0.00%	0.01% 0.00%	0.02% 0.00%	0.02% 0.00%	0.00% 0.00%	0.00% 0.00%	0.00% 0.00%	0.00% 0.00%
Extracts (petroleum), heavy paraffinic distillate solvent	1174604* *	<0.1 0.00%	10.6 (1.31%)	43.0 (5.30%)	60.5 (7.45%)	315.5 (38.86%)	146.1 (18.00%)	226.3 (27.88%)	9.8 (1.21%)	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Extracts (petroleum), solvent-refined heavy paraffinic distillate solvent	1174592* *	<0.1 0.00%	<0.1 0.00%	1.8 (4.04%)	2.0 (4.48%)	7.3 (16.37%)	6.6 (14.80%)	16.5 (37.00%)	10.4 (23.32%)	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Residues (petroleum), atm. tower	1174583* *	<0.1 0.00%	<0.1 0.00%	14.1 (4.68%)	14.7 (4.87%)	69.9 (23.18%)	42.9 (14.22%)	92.1 (30.54%)	67.8 (22.48%)	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Distillates (petroleum), vacuum	1174586* *	<0.1 0.00%	<0.1 0.00%	16.6 (2.95%)	20.3 (3.61%)	128.8 (22.91%)	70.8 (12.60%)	188.9 (33.61%)	102.8 (18.29%)	26.9 (4.79%)	7.1 (1.23%)	<0.1 0.00%	562.1 0.06%
Paraffin waxes and Hydrocarbon waxes	1174589 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Paraffin waxes (petroleum), Hydrotreated	1174591 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Fuel oil, residual	1174595* *	<0.1 0.00%	<0.1 0.00%	9.7 (3.48%)	10.3 (3.70%)	85.6 (30.75%)	32.0 (11.49%)	76.8 (27.59%)	48.5 (17.42%)	12.5 (4.49%)	3.0 (1.08%)	<0.1 0.00%	278.4 0.03%
Foots oil (petroleum)	1174602* *	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Petrolatum	1174603* *	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Foots oil (petroleum), Hydrotreated	1174606* *	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%
Petrolatum (petroleum), Hydrotreated	1174607* *	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%	<0.1 0.00%

Sample	Sample ID	Compound class amounts (ppmw N)*										% of total sample mass
		A, Pyr, P	Aryl-N	Ind, Q	N-(Ind, Q)	Carb, Acr	N-(Carb, Acr)	B(Carb, Acr)	N-(Carb, Acr)	DB(Carb, Acr)	NDB(Carb, Acr)	
Distillates (petroleum), petroleum residues vacuum	1174610*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Slack wax (petroleum)	1174615*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Asphalt	1174621*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Asphalt, oxidized	1174622*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

A, Pyr, P: Amines, Pyridines, Aryl-N: Aryl-N (e.g. Anilines, Nitrobenzenes); Ind, Q: Indoles, Quinolines; N-(Ind, Q): Naphthenic-Indoles, Quindolines; Carb, Acr: Carbazoles, Acridines; N-(Carb, Acr): Naphthenic-Carbazoles, Acridines; N-B(Carb, Acr): Benzo(Carbazoles, Acridines); DB(Carb, Acr): Naphthenic-Benzocarbazoles, Acridines); DB(Carb, Acr): Dibenzocarbazoles, Acridines; Rest: Unknown.

*The concentrations in ppmw N are calculated by means of an external standard. Results are based on the assumption that the (averaged) response factors for all nitrogen compounds is 1.

** Sample is too heavy, FBP out of the scope of this method.

Table 3 Sulphur group-type GCxGC analysis

Sample	Sample ID	Compound class amounts (ppmw S)*								% of total sample mass				
		S, Th, DS, T	Ar-S	BT	NBT	DIBT	NDiBT	BNaph thoT	NBNap thoT	DiNaph thoT	Rest	ES	Total	
Distillates (Petroleum), Full-range straight run middle	154541	1653.46 (17.43%)	1611.33 (16.98%)	3974.32 (41.89%)	859.80 (9.06%)	1307.47 (13.78%)	73.93 (0.78%)	7.55 (0.08%)	<0.01	<0.01	<0.01	<0.01	9487.9	0.95%
Distillates (Petroleum), Heavy straight run samples	154545	1881.72 (11.49%)	1486.20 (9.08%)	4939.93 (30.18%)	2398.67 (14.65%)	4721.25 (28.8%)	717.04 (4.38%)	225.04 (1.37%)	<0.01	<0.01	<0.01	<0.01	16369.9	1.64%
Distillates (Petroleum), Hydrodesulfurized middle	154937	<0.01	<0.01	0.13 (4.81%)	0.09 (3.33%)	2.44 (90.37%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	2.7	0.00%
Distillates (Petroleum), Hydrodesulfurized middle	154549	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	5.4	0.00%
Gas oils (Petroleum), Light vacuum	154554	193.99 (3.88%)	376.38 (7.52%)	902.88 (18.05%)	738.46 (14.76%)	1612.50 (32.23%)	615.24 (12.30%)	452.49 (9.05%)	86.27 (1.72%)	24.43 (0.49%)	<0.01	<0.01	5002.6	0.50%
Fuels, Diesel	154567	275.52 (44.77%)	85.04 (13.82%)	127.15 (20.66%)	23.50 (3.82%)	95.13 (15.46%)	7.09 (1.15%)	0.31 (0.05%)	0.05% (0.01%)	0.00% (0.01%)	0.00% (0.01%)	0.00% (0.01%)	615.4	0.06%
Fuels, Diesel, NO. 2	154579	6.72 (0.77%)	6.67 (45.08%)	391.34 (45.08%)	43.29 (4.99%)	404.75 (46.62%)	13.12 (1.51%)	2.17 (0.25%)	<0.01	<0.01	<0.01	<0.01	868.1	0.09%
Extracts (Petroleum), Residual oil solvent	154594*	228.35 (3.45%)	272.57 (4.12%)	1096.93 (16.58%)	708.85 (10.71%)	1260.39 (19.05%)	1039.05 (15.70%)	999.33 (15.10%)	679.25 (10.26%)	332.89 (5.03%)	<0.01	<0.01	6117.6	0.66%
Extracts (Petroleum), Deasphalted Vac residue solvent	154598*	196.10 (1.75%)	386.11 (3.44%)	1917.44 (17.07%)	1123.37 (10.00%)	2094.36 (18.65%)	1681.28 (14.97%)	1906.67 (16.98%)	1227.27 (10.93%)	699.40 (6.23%)	<0.01	<0.01	11232.0	1.12%
Naphtha (petroleum), hydrodesulfurized light	023	1.17 (97.50%)	0.04% (0.03%)	0.19% (0.11%)	0.11% (0.07%)	0.21% (0.13%)	0.17% (0.10%)	0.19% (0.10%)	0.12% (0.07%)	0.07% (0.03%)	0.00% (0.00%)	0.00% (0.00%)	1.2	0.00%
Kerosine (petroleum)	043	532.71 (91.37%)	34.23 (5.87%)	15.32 (2.63%)	<0.01 (0.01)	0.57 (0.10%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	0.22 (0.04%)	0.06% (0.00%)	583.0	0.06%

Sample	Sample ID	Compound class amounts (ppmw S)*										% of total sample mass	
		S, Th, DS, T	Ar-S	BT	NBT	DiBT	NDIBT	BNaphthoT	NBNaphthoT	Rest	ES		
MK1 diesel fuel	059	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.00%	
Naphtha (petroleum), full-range coker	1508.53 (82.12%)	0.00% (4.06%)	0.00% (11.37%)	0.00% (1.20%)	0.00% (1.04%)	0.00% (0.02%)	0.00% (0.02%)	0.00% (1.19%)	0.00% (0.01%)	0.00% (0.01%)	(100%)	0.04	0.00%
Kerosine (petroleum), hydrodesulfurized	086	2.17 (23.09%)	4.61 (49.04%)	0.66 (7.02%)	0.04 (0.43%)	1.89 (20.11%)	<0.01	<0.01	<0.01	<0.01	<0.01	1836.9	0.18%
Distillates (petroleum), light catalytic cracked	130	25.33 (0.89%)	7.57 (0.27%)	1591.07 (55.76%)	101.93 (3.57%)	1112.39 (38.99%)	14.44 (0.51%)	0.57 (0.02%)	<0.01	<0.01	<0.01	2853.3	0.29%
Distillates (petroleum), hydrodesulfurized middle coker	012	<0.01 (1.87%)	1.13 (3.42%)	2.07 (4.46%)	2.70 (84.98%)	51.41 (5.16%)	3.12 (0.17%)	0.10	<0.01	<0.01	<0.01	60.5	0.01
Kerosine (petroleum), sweetened	128	624.45 (72.22%)	101.59 (11.75%)	134.18 (15.52%)	1.35 (0.16%)	1.55 (0.18%)	1.45 (0.17%)	<0.01	<0.01	<0.01	<0.01	0.15 (0.02%)	864.7 0.09%
Gasoline	144	7.58 (99.74%)	<0.01 (0.01%)	<0.01 (0.01%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	7.6 (0.79%)	0.00%
Gas oils (petroleum), straight-run	168	2119.79 (19.23%)	1456.51 (13.21%)	3881.69 (35.21%)	1241.58 (11.26%)	2197.17 (19.93%)	116.19 (1.05%)	10.11 (0.09%)	<0.01 (0.09%)	<0.01 (0.09%)	<0.01 (0.09%)	11023.0	1.10%
Condensate (petroleum), vacuum tower	175	791.40 (17.06%)	684.86 (14.76%)	1654.70 (35.67%)	414.30 (8.93%)	987.59 (21.29%)	78.93 (1.70%)	26.69 (0.58%)	<0.01 (0.01%)	<0.01 (0.01%)	<0.01 (0.01%)	4638.7	0.46%
Distillates (petroleum), straight-run middle	188	1683.26 (17.39%)	1434.28 (14.82%)	3958.46 (40.90%)	648.58 (6.70%)	1774.39 (18.33%)	145.37 (1.50%)	32.28 (0.33%)	<0.01 (0.33%)	<0.01 (0.03%)	<0.01 (0.03%)	9679.5	0.97%
Paraffin oils (petroleum), catalytic dewaxed light	154	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)	<0.01 (0.00%)
Distillates (petroleum), solvent-refined light naphtenic	073	1435.93 (23.02%)	2519.67 (40.39%)	1727.89 (27.70%)	420.52 (6.74%)	133.71 (2.14%)	<0.01 (0.01%)	<0.01 (0.01%)	<0.01 (0.01%)	<0.01 (0.01%)	<0.01 (0.01%)	6237.7	0.62%

Sample	Sample ID	Compound class amounts (ppmw S)*										% of total sample mass		
		S, Th, DS, T	Ar-S	BT	NBT	NDIBT	BNaph thoT	NBNap thhoT	DiNaph thoT	Rest	ES			
Distillates (petroleum), light paraffinic	082	677.90 (10.08%)	569.51 (8.47%)	1649.60 (24.53%)	904.89 (13.46%)	1925.11 (28.63%)	644.26 (9.58%)	349.70 (5.20%)	3.50 (0.05%)	<0.01	<0.01	6724.5	0.67%	
Distillate (petroleum), solvent-dewaxed heavy paraffinic (A)	386.13 (18.08%)	521.48 (24.41%)	701.51 (32.84%)	227.36 (10.64%)	246.17 (11.52%)	50.01 (2.34%)	3.50 (0.16%)	<0.01	<0.01	<0.01	<0.01	2136.2	0.21%	
White mineral oil (petroleum)	145	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.00%	
Distillates (petroleum), hydrotreated heavy paraffinic	150	23.38 (7.63%)	34.43 (11.24%)	88.98 (29.04%)	47.53 (15.51%)	68.85 (22.47%)	33.30 (10.87%)	9.93 (3.24%)	<0.01	<0.01	<0.01	<0.01	306.4	0.03%
Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalted	2887.49 (8.92%)	1999.30 (6.17%)	7631.53 (23.56%)	4133.45 (12.76%)	7995.20 (24.69%)	4576.32 (14.13%)	2927.70 (9.04%)	229.97 (0.71%)	7.88 (0.02%)	<0.01	<0.01	32388.8	3.24%	
Distillates (petroleum), heavy paraffinic	064	761.16 (2.91%)	606.38 (2.32%)	5635.75 (21.54%)	2025.81 (7.74%)	5651.56 (21.60%)	4011.57 (15.33%)	6588.32 (25.18%)	800.32 (3.06%)	82.02 (0.31%)	<0.01	<0.01	26162.9	2.62%
Extracts (petroleum), heavy paraffinic distillate solvent	096A	2148.75 (7.19%)	1091.14 (3.65%)	7057.33 (23.62%)	3395.57 (11.36%)	7818.51 (26.17%)	4620.98 (15.47%)	3473.34 (11.62%)	262.60 (0.88%)	11.76 (0.04%)	<0.01	<0.01	29880.0	2.99%
Extracts (petroleum), solvent-refined heavy paraffinic distillate solvent	069**	1047.61 (4.36%)	1060.75 (4.42%)	5493.64 (22.88%)	2230.53 (9.29%)	5110.64 (21.29%)	2890.46 (12.04%)	3172.52 (13.21%)	1812.76 (7.55%)	1189.4 (4.95%)	<0.01	<0.01	24008.3	2.40%
Residues (petroleum), atm. Tower	006**	86.94 (4.56%)	80.71 (4.23%)	339.53 (17.81%)	177.16 (9.29%)	431.70 (22.64%)	265.47 (13.92%)	310.21 (16.27%)	145.08 (7.61%)	69.87 (3.66%)	<0.01	<0.01	1906.7	0.19%
Distillates (petroleum), vacuum	031**	668.92 (3.15%)	601.61 (2.83%)	4214.74 (19.85%)	1805.41 (8.50%)	4304.96 (20.28%)	2958.58 (13.94%)	3981.05 (18.75%)	1733.75 (8.17%)	961.79 (4.53%)	<0.01	<0.01	21230.8	2.12%

Sample	Sample ID	Compound class amounts (ppmw S)*										% of total sample mass		
		S, Th, DS, T	Ar-S	BT	NBT	DiBT	NDiBT	BNaphthoT	NBNaphthoT	DiNaphthoT	Rest	ES	Total	
Paraffin waxes and Hydrocarbon waxes	062	157.17 (28.05%)	61.39 (10.96%)	255.0 (45.51%)	44.78 (7.99%)	41.93 (7.48%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	560.3	0.06%
Paraffin waxes (petroleum), hydrotreated	065	<0.01 0.00%	0.01% 0.00%	0.03% (22.13%)	0.00% (9.31%)	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01	0.00%
Fuel oil, residual	078	777.57 (7.58%)	589.82 (5.75%)	2271.04 (19.66%)	955.67 (11.50%)	2018.22 (13.45%)	1180.47 (13.45%)	1380.95 (6.73%)	690.79 (3.89%)	398.96 (3.89%)	<0.01 0.04%	<0.01 0.00%	10263.5	1.03%
Foots oil (petroleum)	090**	609.42 (32.02%)	142.58 (7.49%)	718.85 (37.77%)	148.10 (7.78%)	197.85 (10.39%)	68.23 (3.58%)	18.40 (0.97%)	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	1903.4	0.19%
Petrolatum	093**	338.79 (54.81%)	36.29 (5.87%)	200.93 (32.51%)	22.47 (3.64%)	19.62 (3.17%)	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	618.1	0.06%
Foots oil (petroleum), hydrotreated	109**	5.74 (8.08%)	8.83 (12.44%)	24.40 (34.37%)	11.01 (15.51%)	16.53 (23.28%)	4.48 (6.31%)	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	71.0	0.01%
Petrolatum (petroleum), hydrotreated	111**	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01	0.00%
Distillates (petroleum), petroleum residues vacuum	131**	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01	0.00%
Slack wax (petroleum)	152	141.81 (51.18%)	27.50 (9.92%)	92.78 (33.48%)	14.99 (5.41%)	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	<0.01 0.00%	277.1	0.00%
Asphalt	189**	21.33 (1.32%)	20.43 (1.27%)	183.74 (11.39%)	63.39 (3.93%)	198.77 (12.32%)	169.82 (10.52%)	292.34 (18.12%)	281.27 (17.43%)	342.34 (21.21%)	40.27 (2.50%)	<0.01 0.03%	1613.7	0.16%
Asphalt, oxidized	193**	252.62 (4.34%)	268.97 (4.62%)	908.21 (15.59%)	619.04 (10.63%)	1046.74 (17.97%)	867.61 (14.89%)	1066.07 (18.30%)	486.24 (8.35%)	309.44 (5.31%)	<0.01 0.03%	<0.01 0.00%	5824.9	0.58%

S, Th, DS, T: Sulphides, Thiols, Disulphides, Thiophenes; Ar-S, ArVl-sulphides; BT: Benzo-thiophenes; NBT: Naphthenic-Benzothiophenes; DiBT: Di-Benzothiophenes; NDiBT: Naphthenic-di-Benzothiophenes; BNaphthoT: Benzo-Naphthothiophenes; DiNaphthoT: Naphthenic-Benzo-Naphthothiophenes; Rest: Highly polar sulphur species; ES: Elementary Sulphur.

*The concentrations in ppmw S are calculated by means of an internal standard. Results are based on the assumption that the (averaged) response factors for all sulphur compounds is 1.
** Sample is too heavy, FBP out of the scope of this method.

Table 4

Carbon chain lengths of S-heterocyclics

Sample ID	Range of carbon chain lengths for components identified in the following S-heterocyclic classes										
	S, Th, DS, T	Ar-S	BT	NBT	DiBT	NDiBT	BNaphthoT	NBNaphthoT	DiNaphthoT	Rest	ES
73, 82, 135, 168, 188, 154541, 154545	<6-20	8-17	8-18	11-16	12-18	14-18	15-19	nd	nd	nd	nd

S, Th, DS and T = Sulphides, Thiols, DiSulphides and Thiophenes

Ar-S = Aryl-Sulphides

BT= Benzothiophenes

NBT = Naphthenic-Benzothiophenes

DiBT = Di-Benzothiophenes

NDiBT = Naphthenic-Di-Benzothiophenes

BNaphthoT = Benzo-Naphthothiophenes

NBNaphthoT = Naphthenic-Benzo-Naphthothiophenes

DiNaphthoT = DiNaphthothiophenes

ES = Elementary Sulphur

Table 5

Carbon chain lengths of N-heterocyclics

Sample ID	Range of carbon chain lengths for components identified in the following N-heterocyclic classes										
	A, Pyr, P	Aryl-N	Ind, Q	N-(Ind, Q)	Carb, Acr	N-(Carb, Acr)	B(Carb, Acr)	N-B(Carb, Acr)	DB(Carb, Acr)	NDB(Carb, Acr)	Rest
154554	nd	nd	nd	nd	13-17	nd	17-20	nd	nd	nd	nd

A, Pyr, P = Amines, Pyrroles, Pyridines

Aryl-N = Aryl-N (e.g. Anilines, Nitrobenzenes)

Ind, Q= Indoles, Quinolines

N-(Ind, Q) = Naphthenic-(Indoles, Quinolines)

Carb, Acr = Carbazoles, Acridines

N-Carb, Acr = Naphthenic-(Carbazoles, Acridines)

B(Carb, Acr) = Benzo(Carbazoles, Acridines)

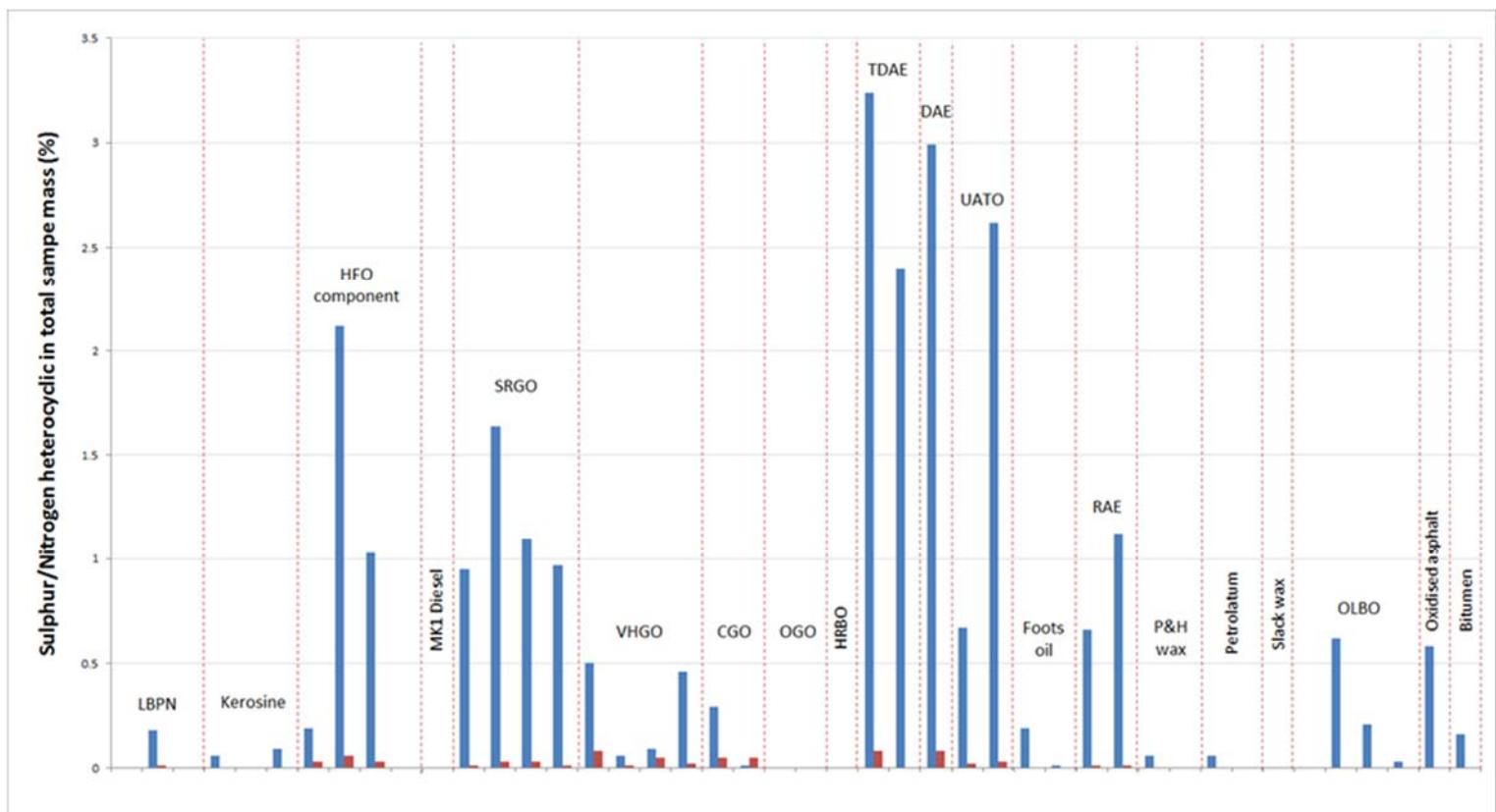
N-B(Carb, Acr) = Naphthenic-Benzo(Carbazoles, Acridines)

DB(Carb, Acr) = Dibenzo(Carbazoles, Acridines)

NDB(Carb, Acr) = Naphthenic Dibenzo(Carbazoles, Acridines)

Figure 1

Comparison of total sulphur and total nitrogen compound amounts present in 44 petroleum product samples analysed using sulphur and nitrogen specific GCxGC. Blue bars indicate sulphur compound amounts, red bars indicate nitrogen compound amounts. LBPN: low boiling point naphtha (gasoline); HFO: heavy fuel oils; SRGO: straight run gas oils; VHGO: vacuum gas oils, hydrocracked gas oils and distillate fuels; CGO: cracked gas oils; OGO: other gas oils; HRBO: Highly refined base oils; TDAE: treated distillate aromatic extracts; DAE: untreated distillate aromatic extracts; UATO: unrefined/acid treated oils; RAE: residual aromatic extracts; P&H wax: Paraffin and hydrocarbon wax; OLBO: other lubricant base oils



5. DISCUSSION

Concawe compiled and submitted REACH Dossiers on all petroleum product categories in 2010. The European Chemicals Agency (ECHA) subsequently raised concerns in draft decision letters to lead registrants regarding the technical justification of the assumptions and tools used to generate PNECs for petroleum substance components. One issue related to the lack of 'oxygen and nitrogen containing hydrocarbons' in the Concawe library of components of petroleum products that are used in the PETROTOX and PETRORISK models to fill the hydrocarbon blocks. In order to meet the regulatory compliance of REACH, ECHA requested that additional data on Nitrogen, Oxygen, and Sulphur Heterocyclic compounds (NOSHS) within petroleum substances be generated, allowing the Concawe registration dossiers to be revised and updated accordingly.

A review of the literature confirmed the presence of these compounds in petroleum products and identified >150 different NOSH structures. Quantitative analysis of a number ($n=44$) of representative petroleum product samples for N- and S-heterocyclics using GCxGC with specific N- and S-detectors showed that S-heterocyclics were more abundant in test samples than N-heterocyclics, showing total sample amounts ranging from <0.01-3.24% (mean = 0.58%) and <0.01-0.08% (mean = 0.02%) respectively (**Figure 1**). This result was consistent with previously reported relative abundances in petroleum, which stated ranges of 0.05-6% and 0.1-2% of sulphur and nitrogen, respectively [2]. Further analysis of a limited number ($n=6$) of petroleum product samples confirmed the absence of any O-heterocyclics (<0.1%) in any of the samples.

Further detailed analysis of GCxGC chromatograms of seven samples analysed for S-heterocyclics and one of the samples analysed for N-heterocyclics confirmed the carbon chain lengths of the components from the various S-heterocyclic and N-heterocyclic classes, where confirmed, covered the range <6-20 and 13-20, respectively.

Based on the analytical data generated, it is concluded that NOSH compounds only occur in low concentrations within petroleum products. The PETRORISK library of representative structures will be extended to reflect these findings.

6. GLOSSARY

A, Pyr, P	Amines, Pyrroles, Pyridines
Ar-S	Aryl-sulphides
Aryl-N	Aryl-N (e.g. Anilines, Nitrobenzenes)
B(Carb, Acr)	Benzo(Carbazoles, Acridines)
BNaphthoT	Benzo-Naphthothiophenes;
BT	Benzothiophenes
Carb, Acr	Carbazoles, Acridines
CAS no.	Chemical Abstracts Service (Registry) Number
CGO	Cracked Gas Oils
DAE	Untreated Distillate Aromatic Extracts
DB(Carb, Acr)	Dibenzo(Carbazoles, Acridines)
DiBT	Di-Benzothiophenes
DiNaphthoT	DiNaphthothiophenes
ECHA	European CHemicals Agency
ES	Elementary Sulphur
GC-AED	Gas Chromatography - Atomic Emission Detector
GCxGC	Two-Dimensional Gas Chromatography
GCxGC-FID	Two-Dimensional Gas Chromatography – Flame Ionisation Detection
HFO	Heavy Fuel Oils
HRBO	Highly Refined Base Oils
Ind, Q	Indoles, Quinolines
LBPN	Low Boiling Point Naphtha (gasoline)
L(E)C50	50% Lethal (Effective) Concentration
mg/L	Milligram per litre
N-(Carb, Acr)	Naphthenic-(Carbazoles, Acridines)

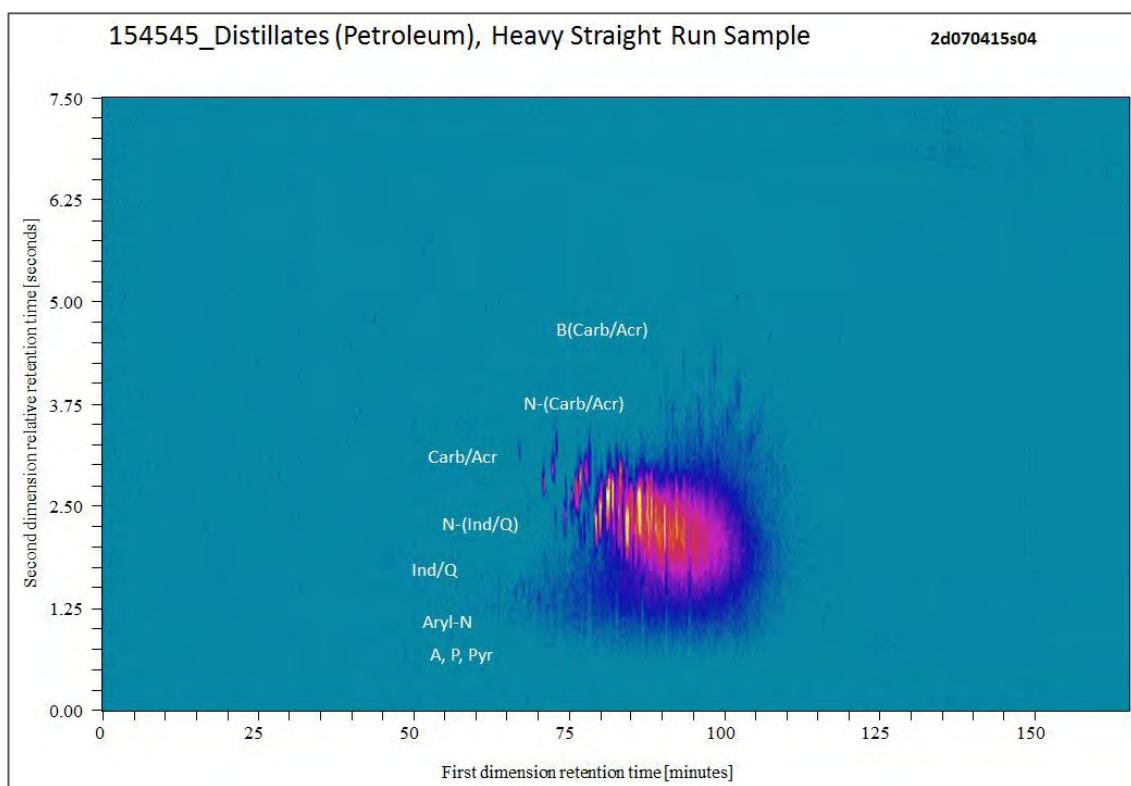
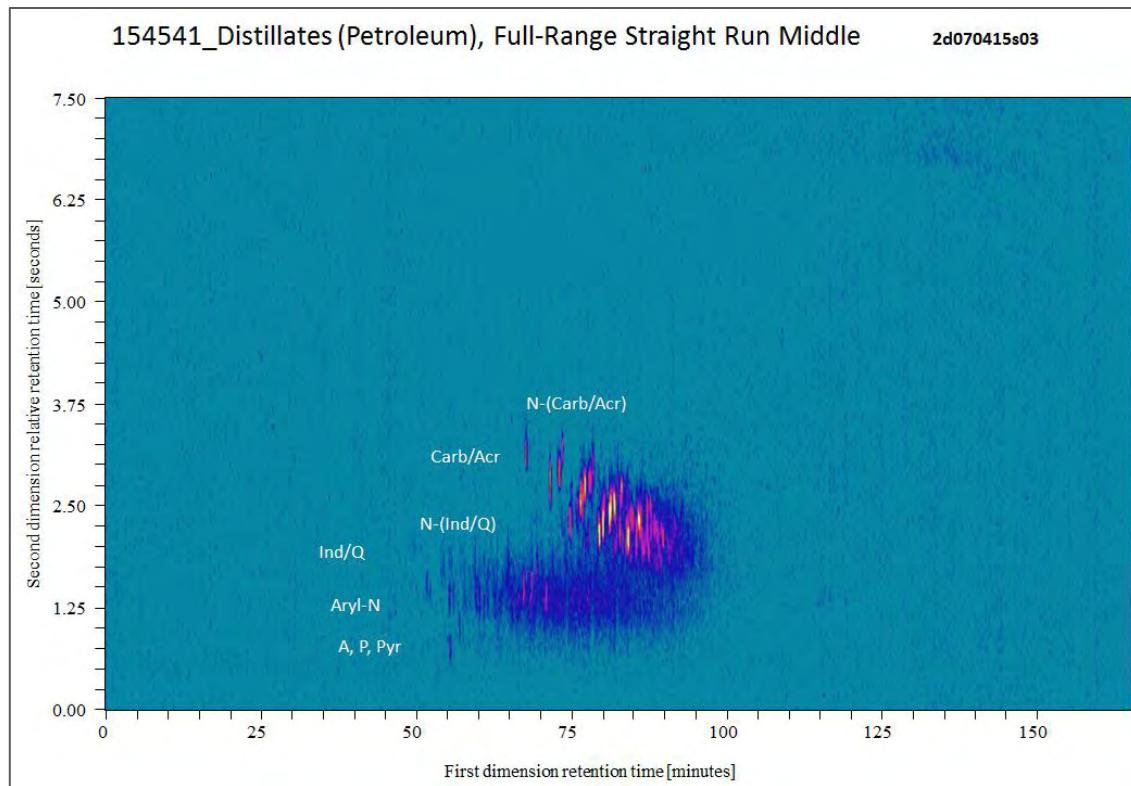
N-(Ind, Q)	Naphthenic-(Indoles, Quinolines)
N-B(Carb, Acr)	Naphthenic-Benzo(Carbazoles, Acridines)
NBNaphthoT	Naphthenic-Benzo-Naphthothiophenes
NBT	Naphthenic-Benzothiophenes
NDB(Carb, Acr)	Naphthenic-Dibenzo(Carbazoles, Acridines)
NDiBT	Naphthenic-di-Benzothiophenes
NCD	Nitrogen Chemiluminescence Detector
NOSH	Nitrogen, Oxygen, and Sulphur Heterocyclics
OGO	Other Gas Oils
OLBO	Other Lubricant Base Oils
P&H wax	Paraffin and Hydrocarbon wax
RAE	Residual Aromatic Extracts
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals
S, Th, DS, T	Sulphides, Thiols, DiSulphides, Thiophenes;
SCD	Sulphur Chemiluminescence Detector
SMILES	Simplified Molecular Input Line Entry System
SRGO	Straight Run Gas Oils
TDAE	Treated Distillate Aromatic Extracts
UATO	Unrefined/Acid Treated Oils
VHGO	Vacuum gas oils, Hydrocracked Gas Oils and distillate fuels

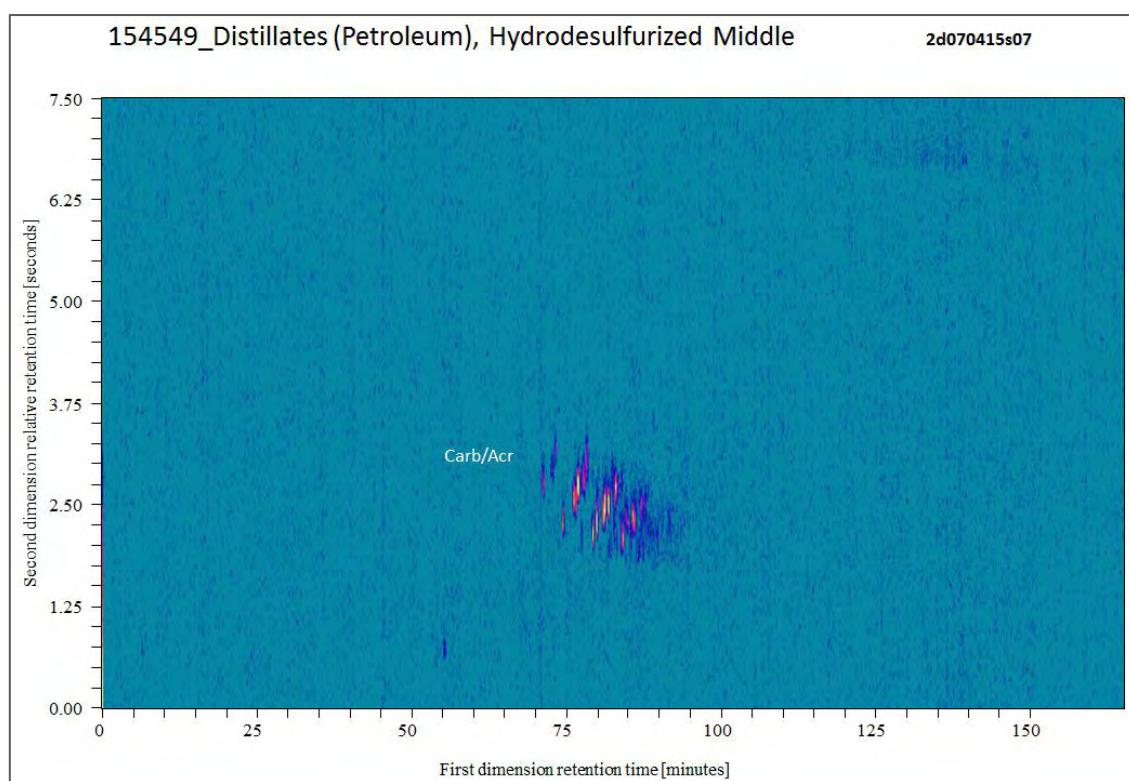
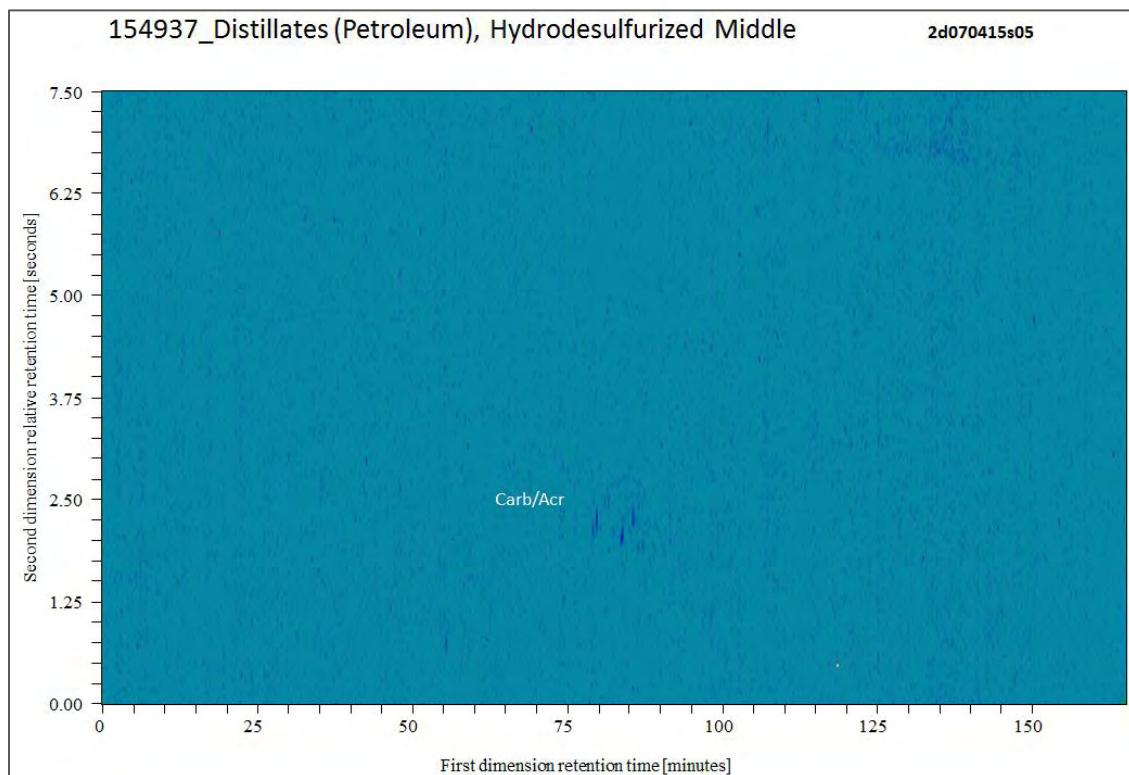
7. REFERENCES

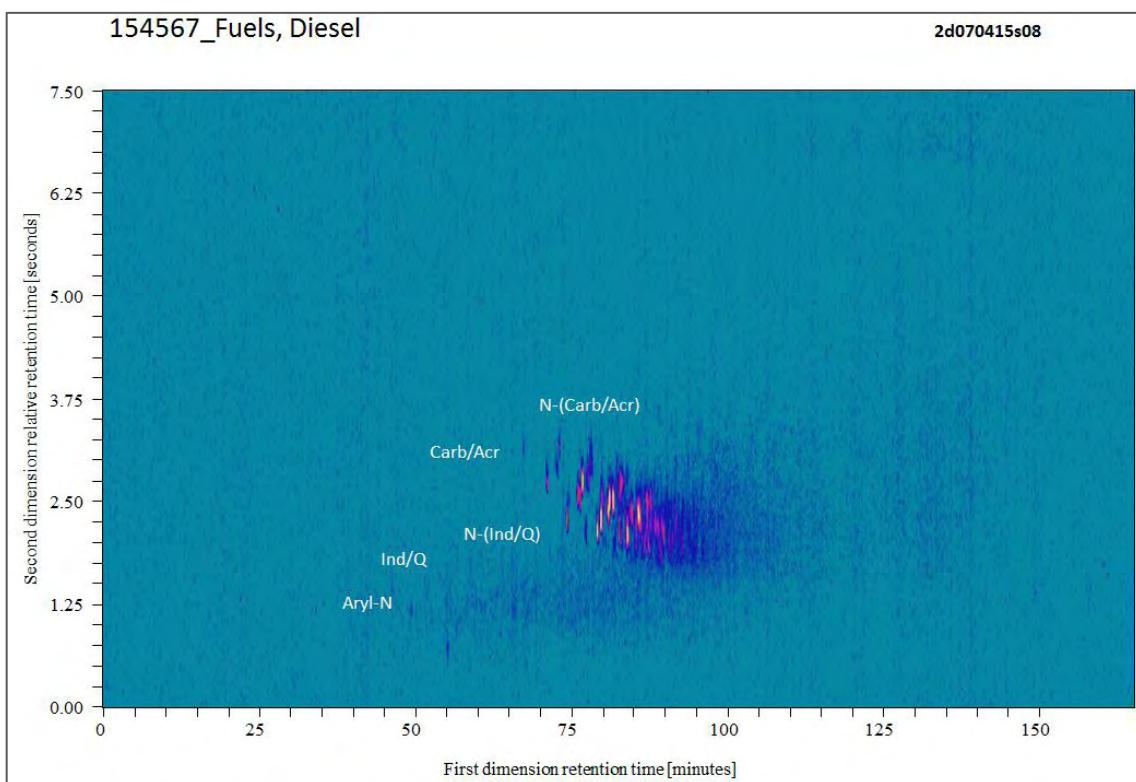
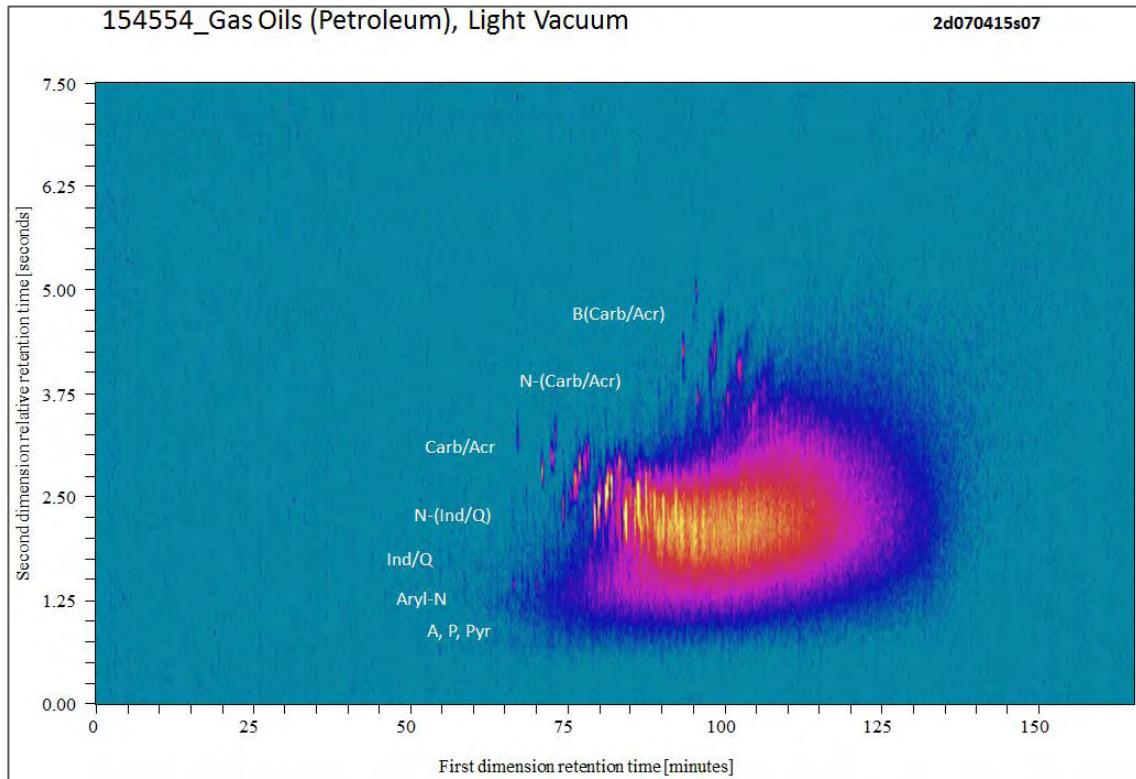
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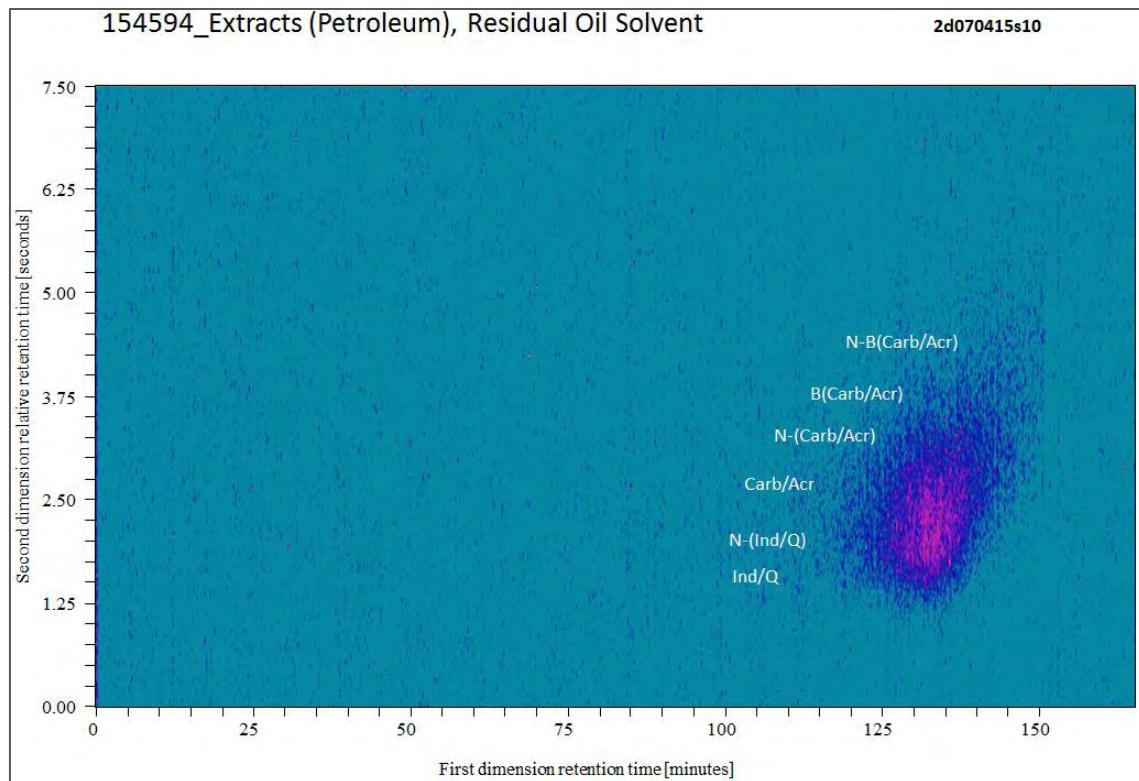
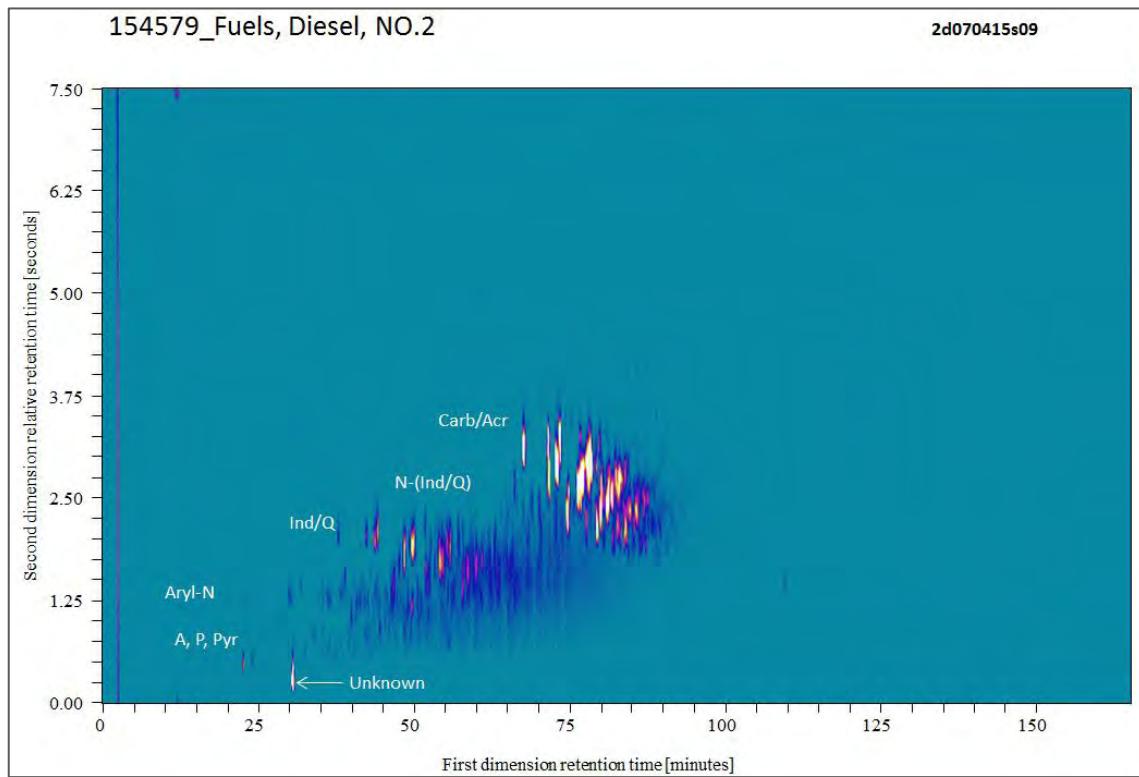
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APPENDIX 1: NITROGEN GROUP TYPE GC_xGC CHROMATOGRAMS



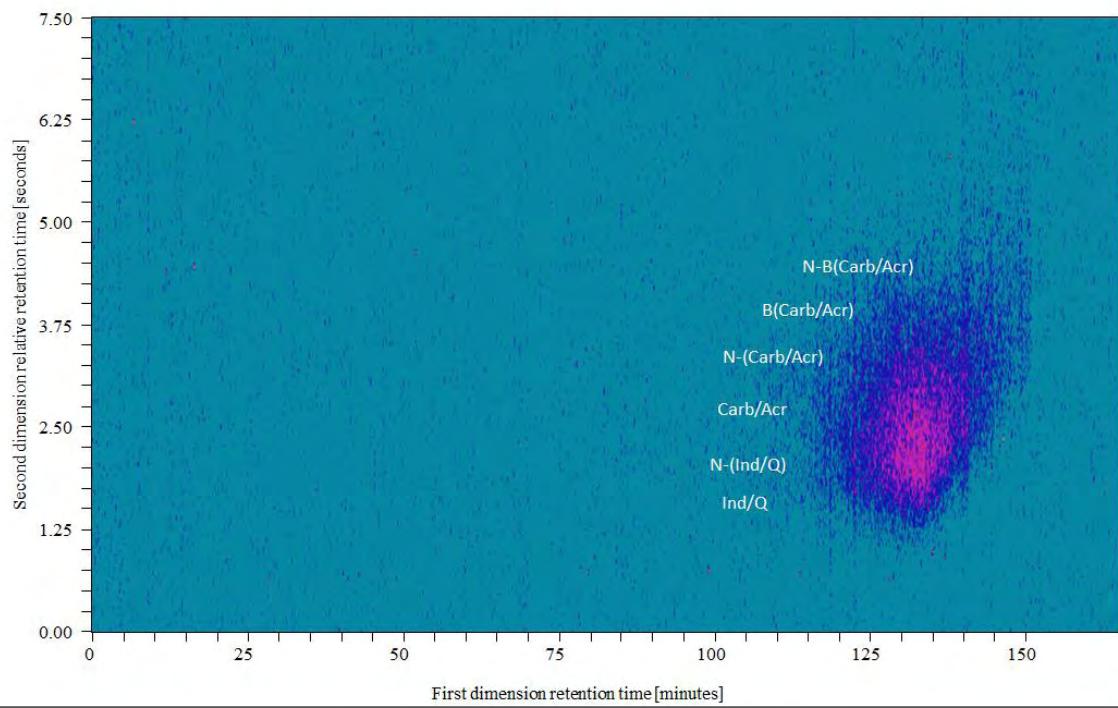






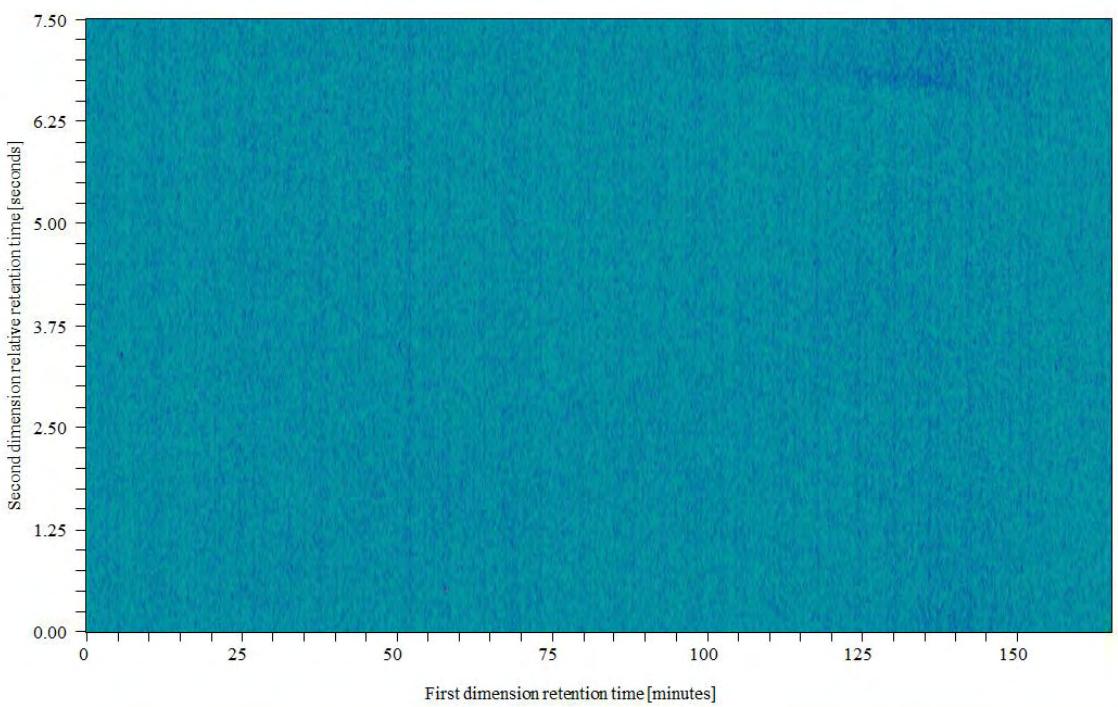
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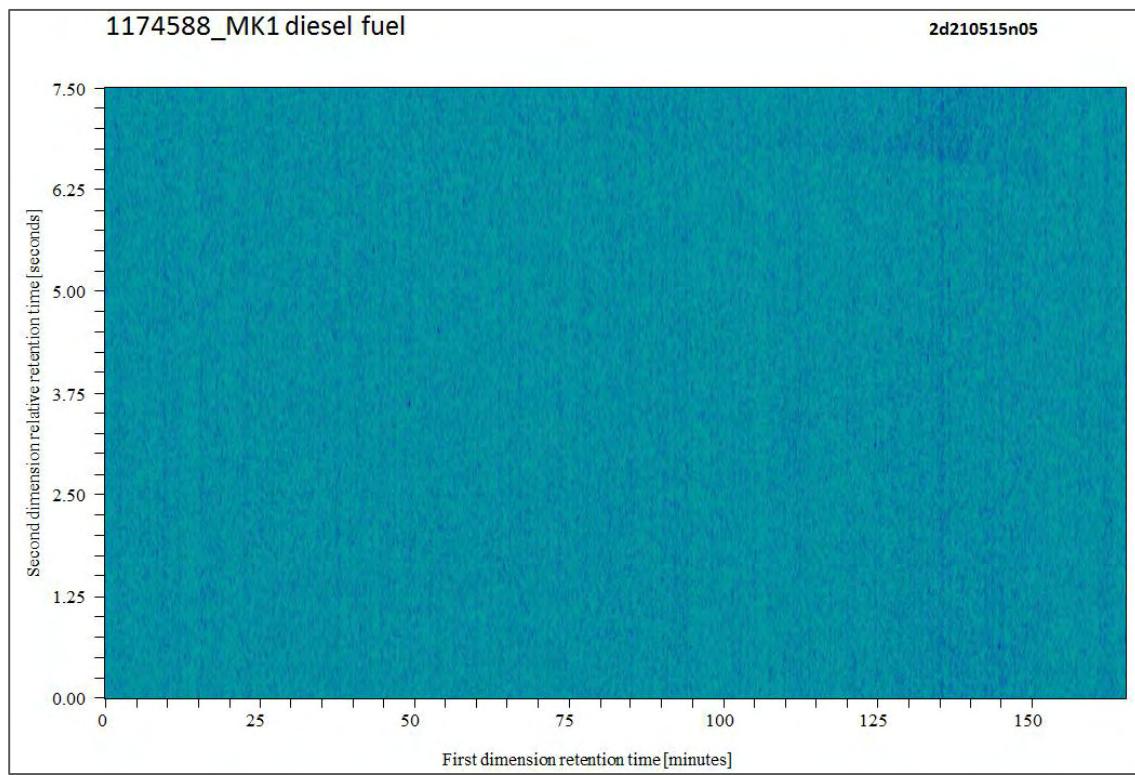
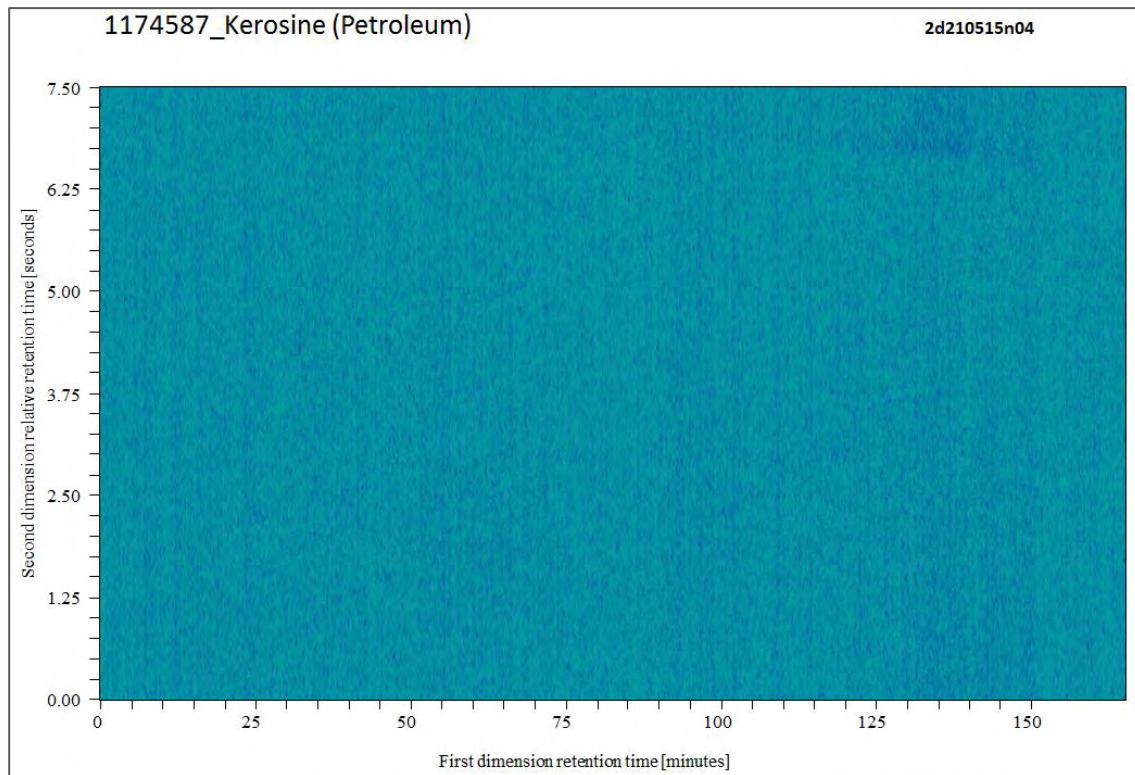
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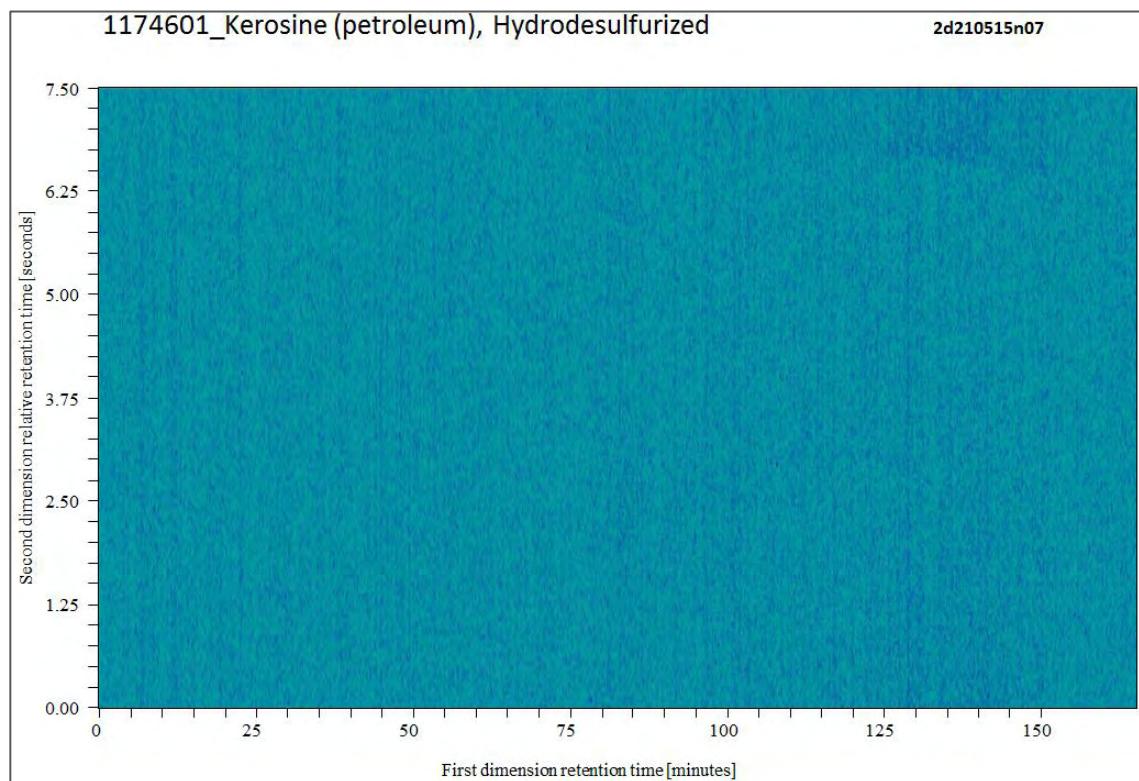
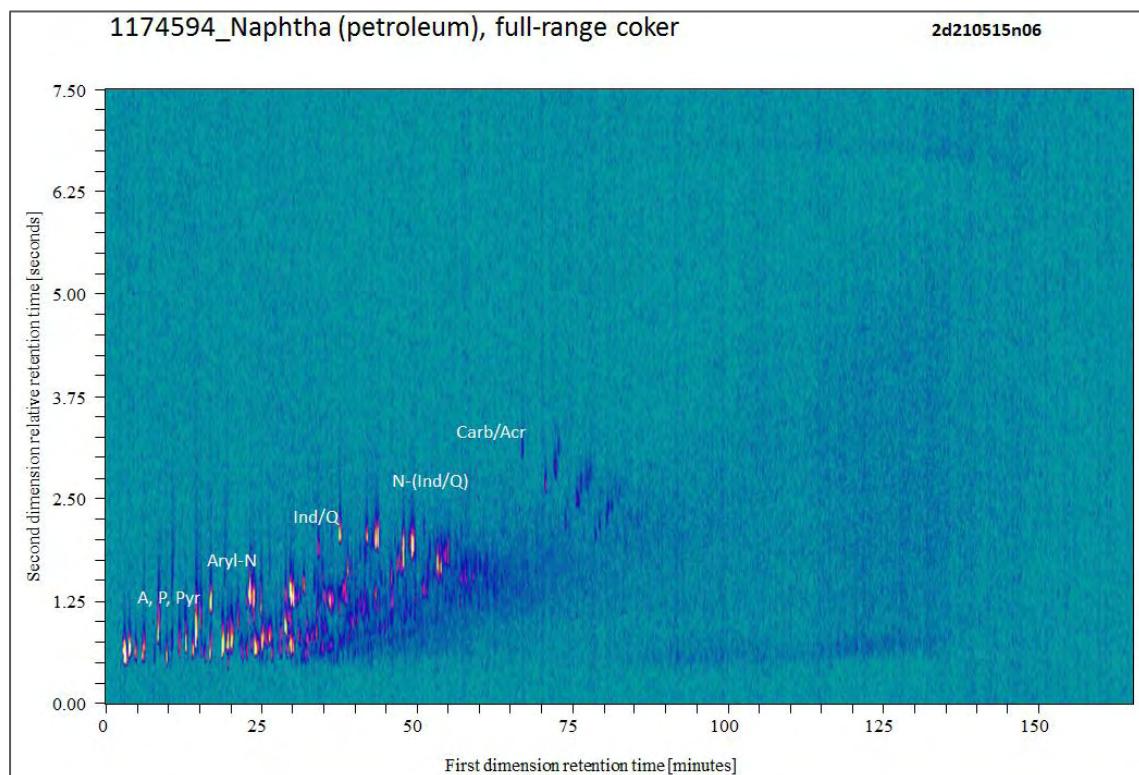


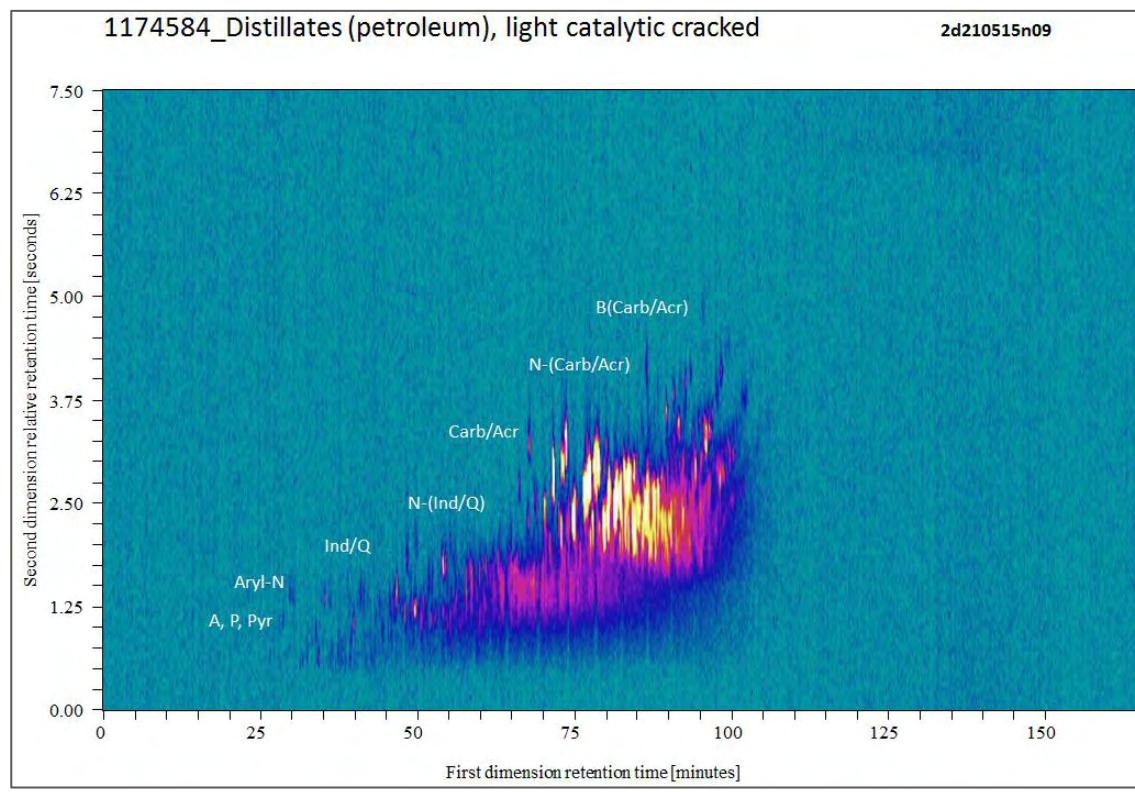
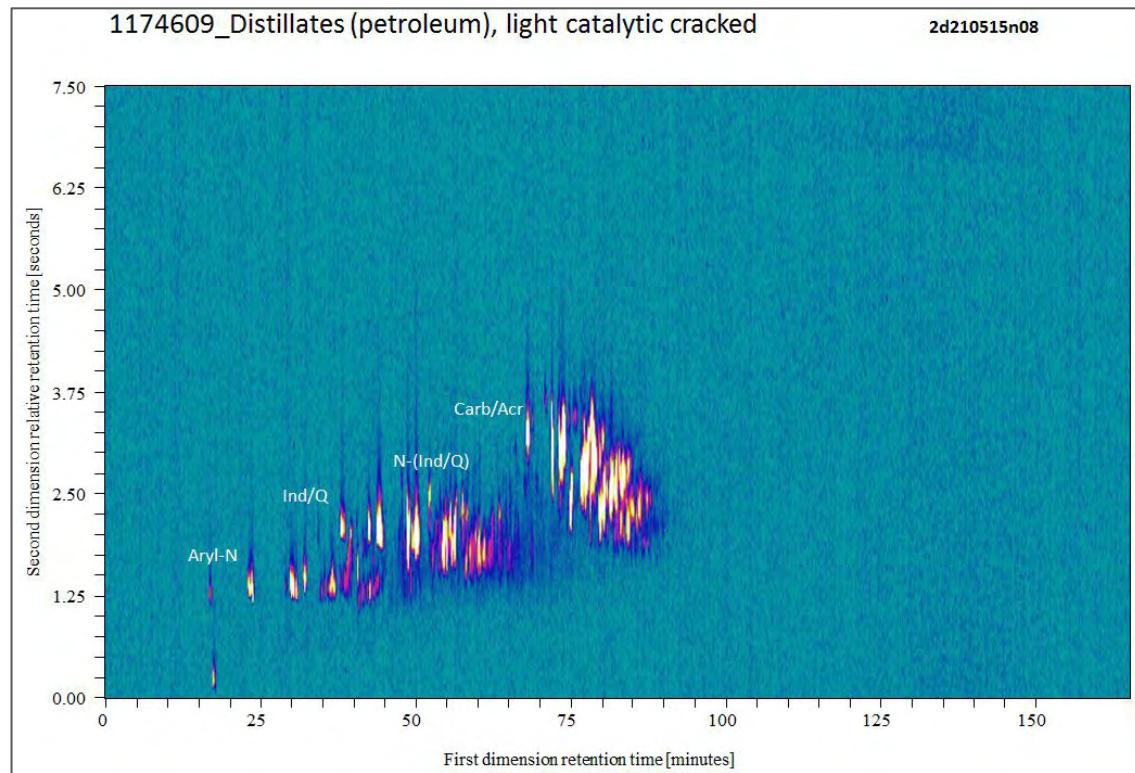
1174585_Naphtha (Petroleum), Hydrodesulfurized light

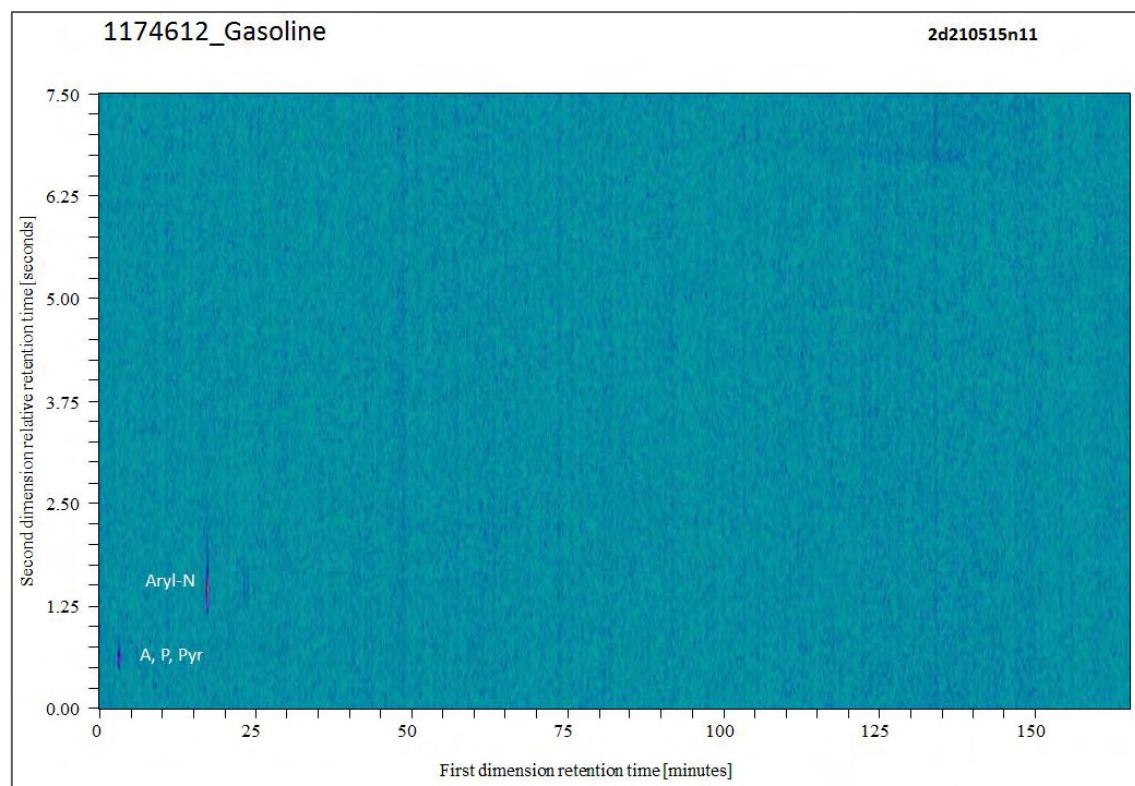
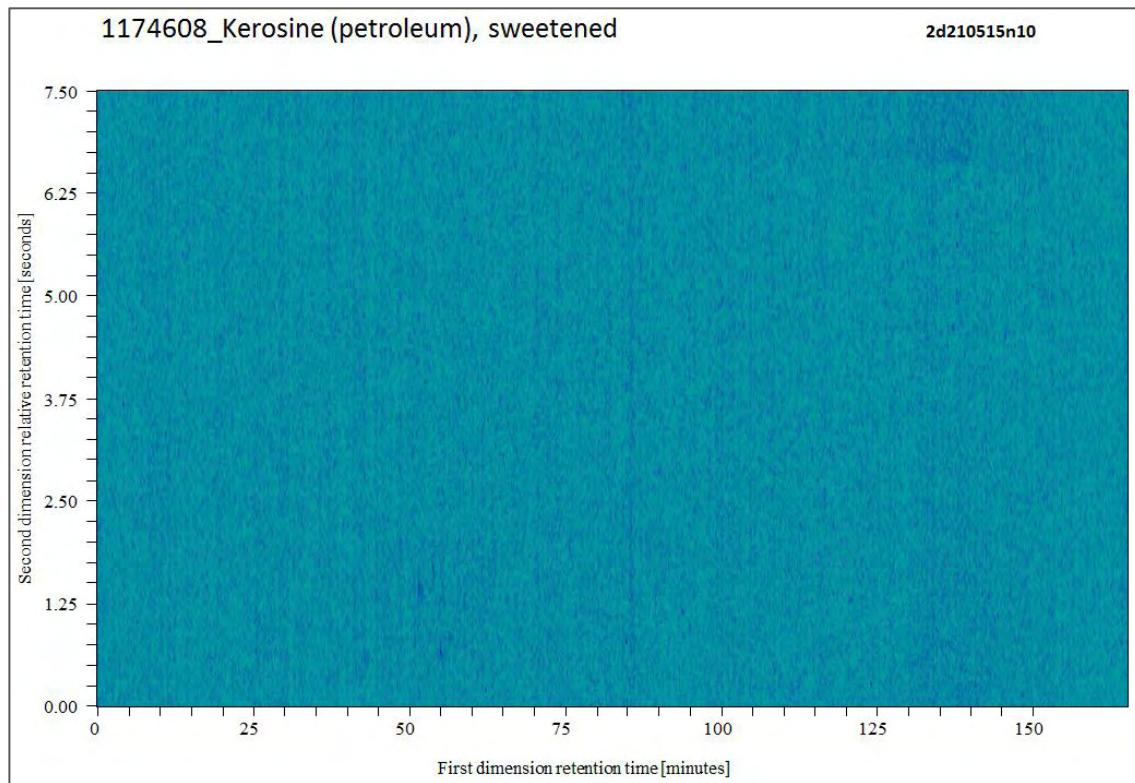
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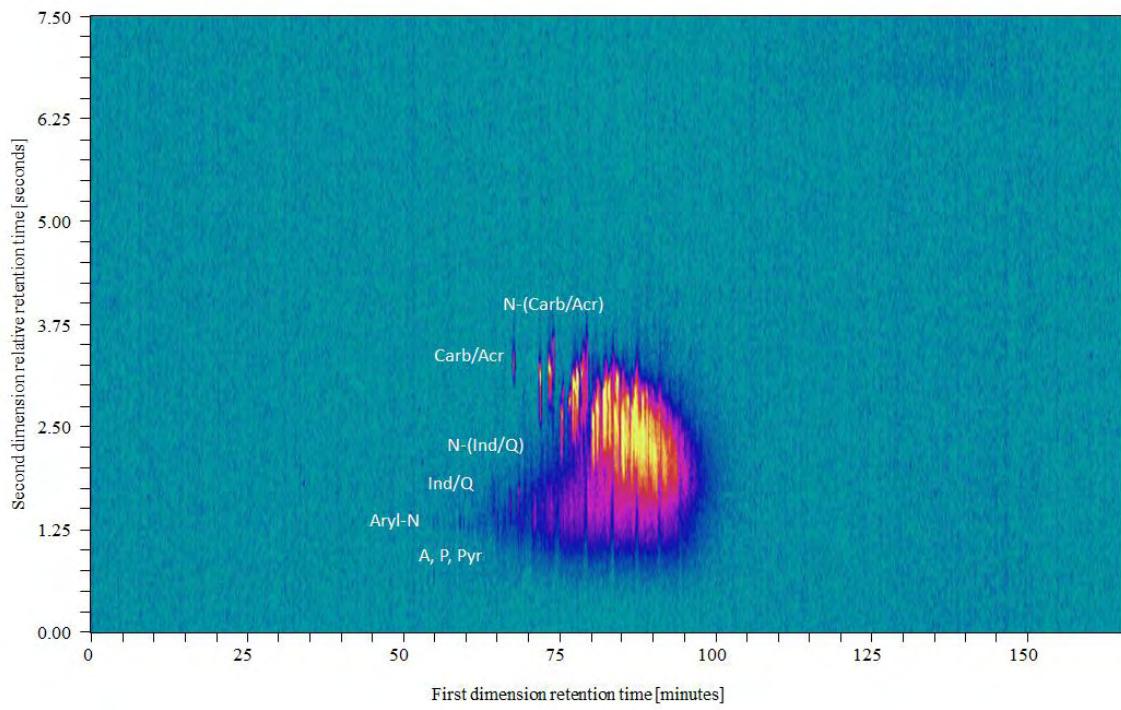






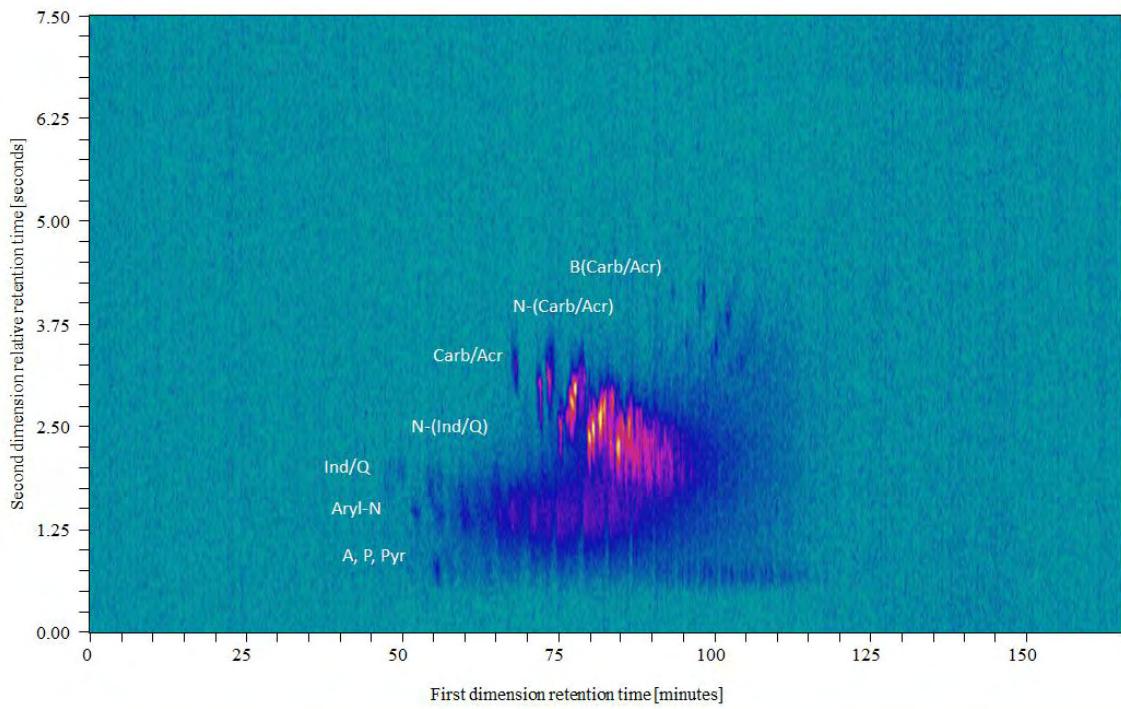
1174617_Gas oils (petroleum), straight-run

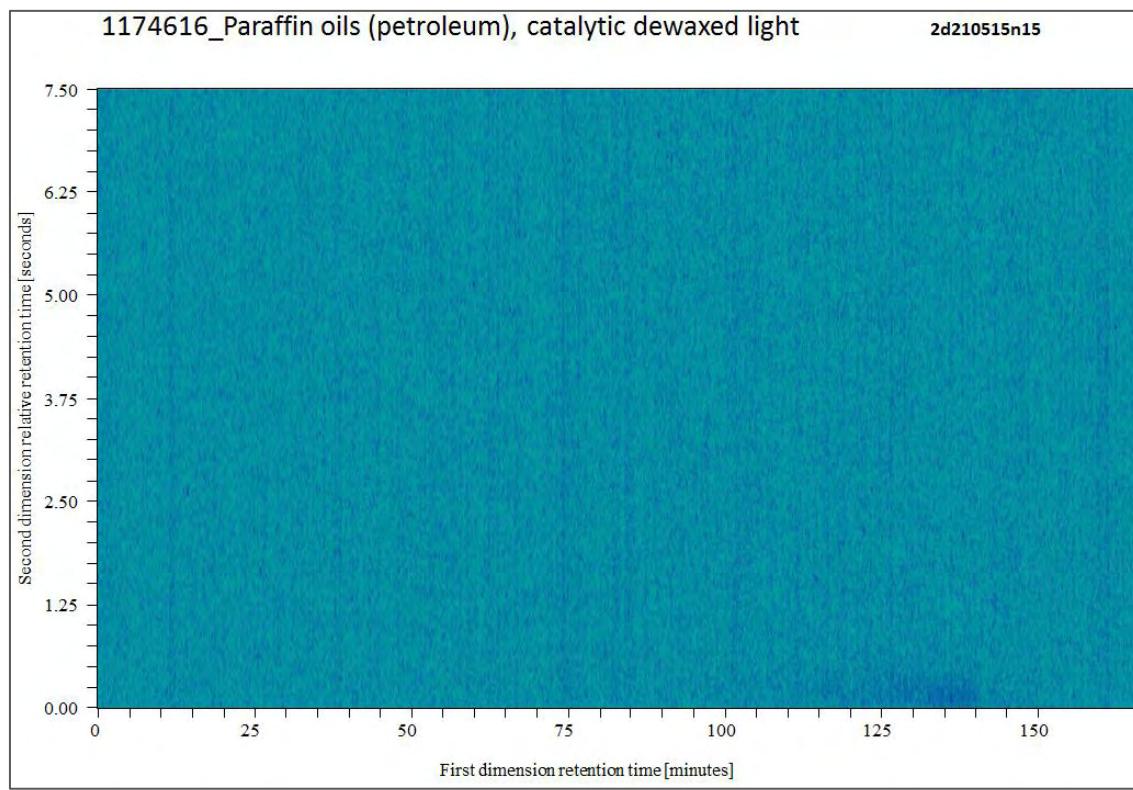
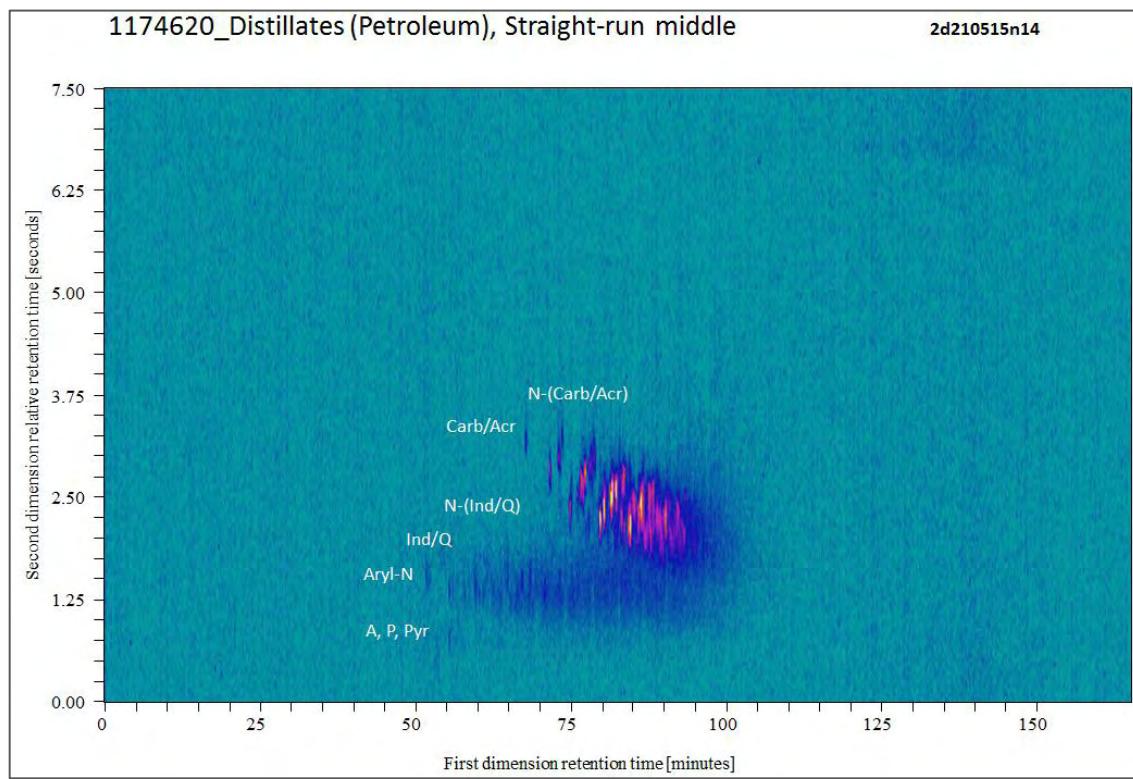
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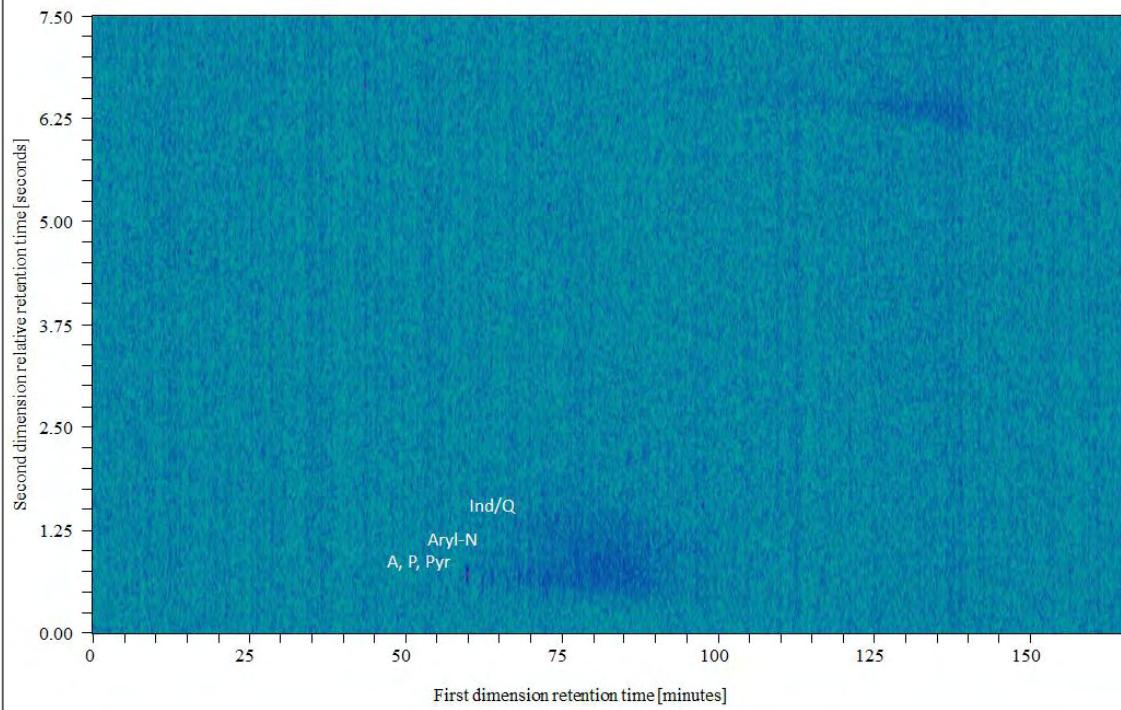
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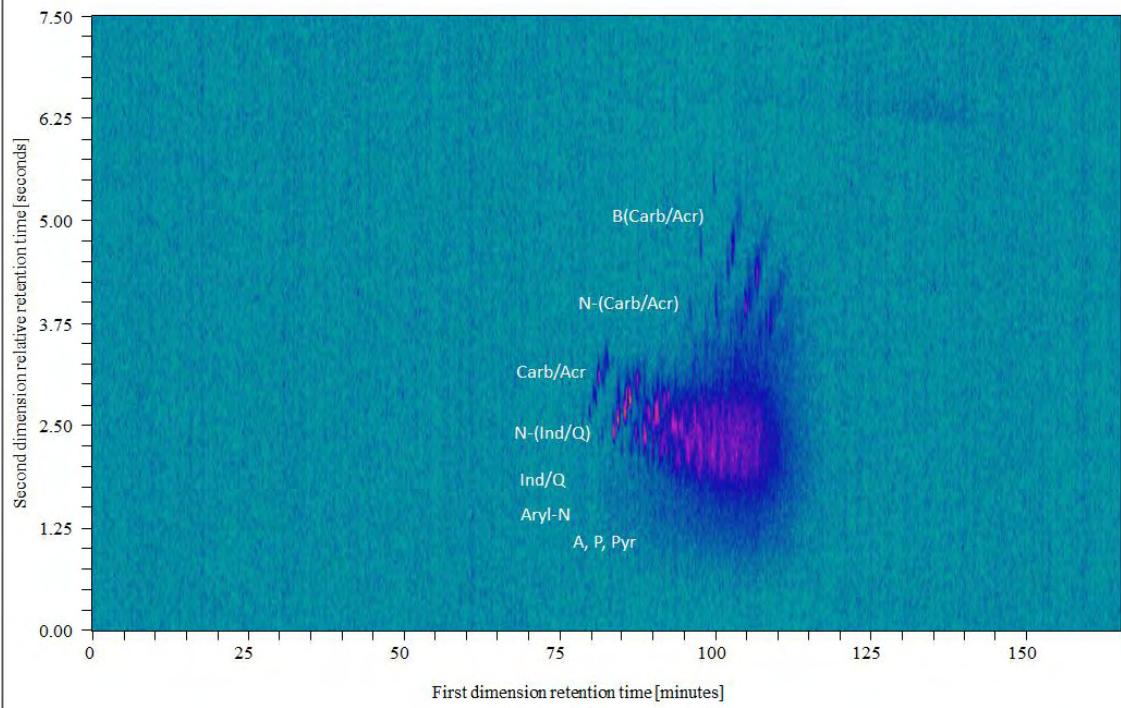




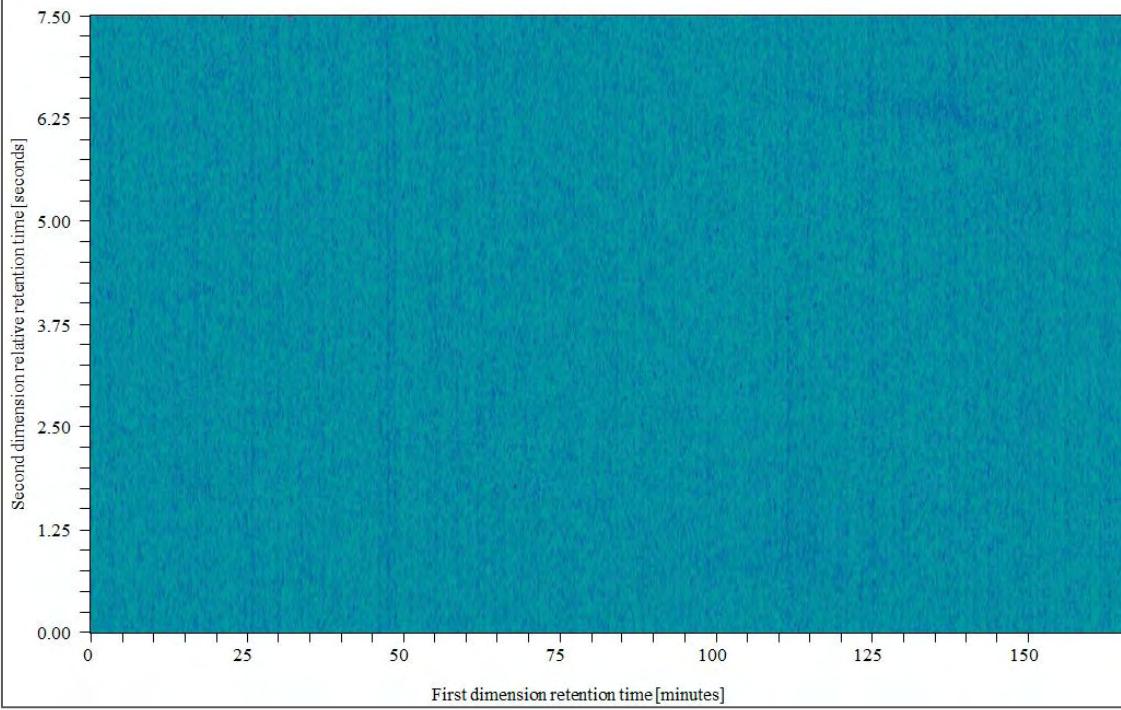
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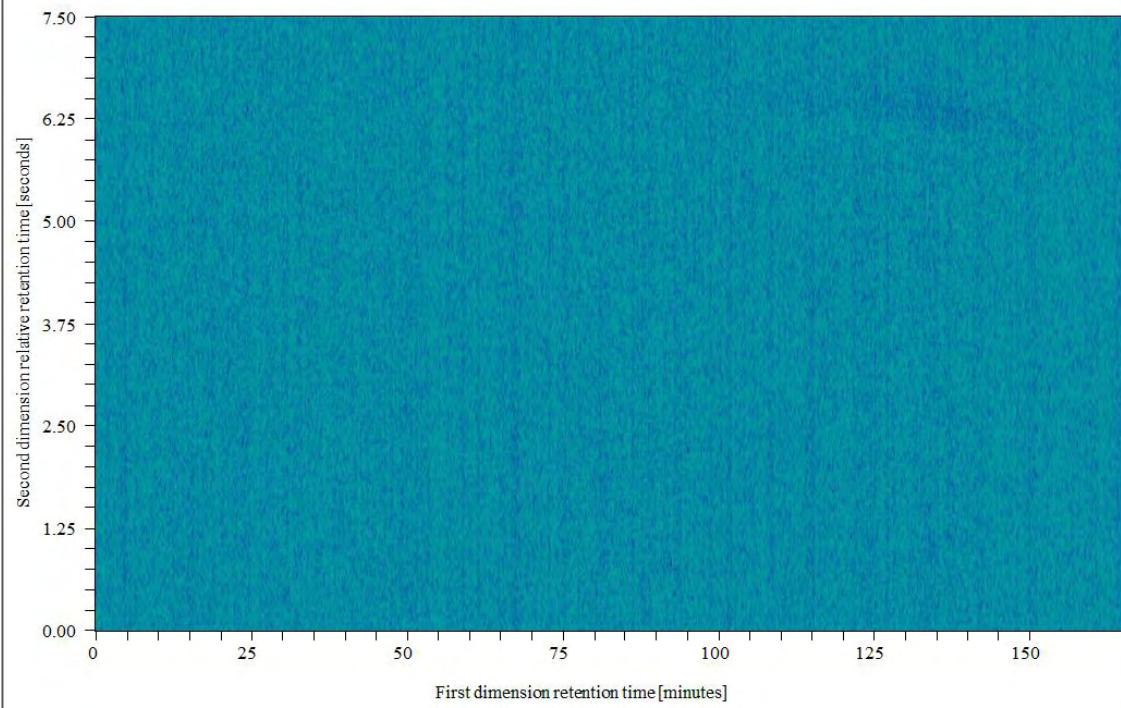
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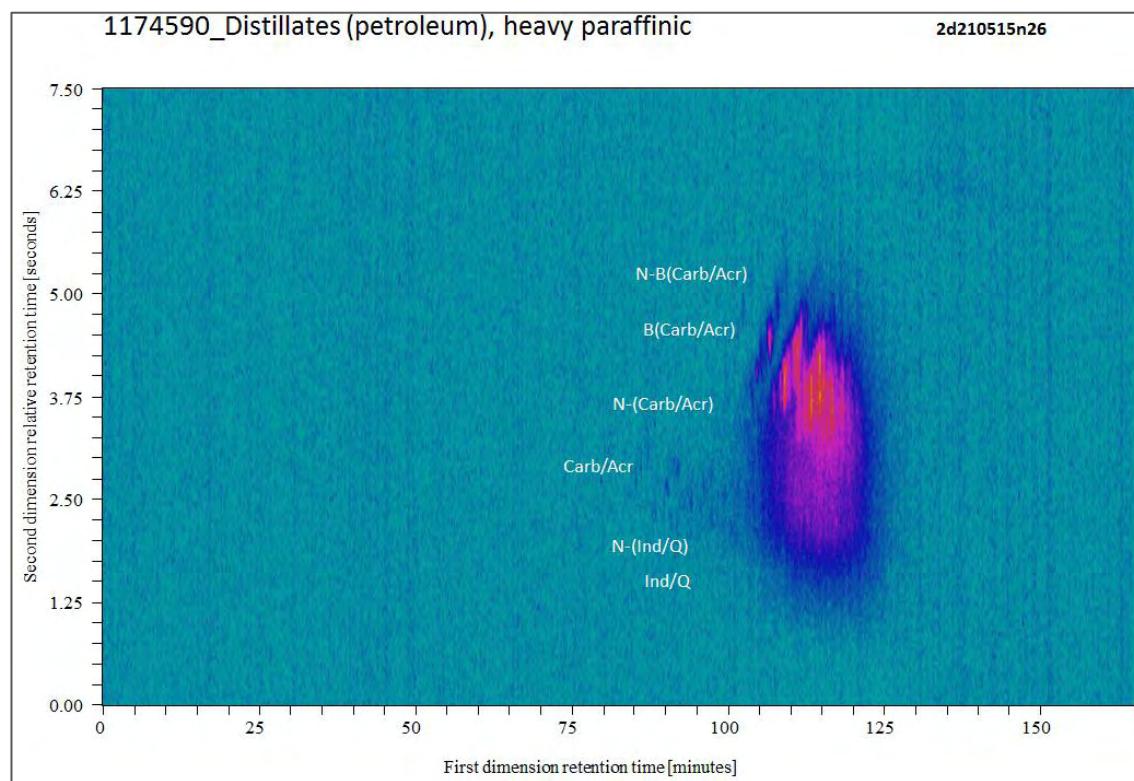
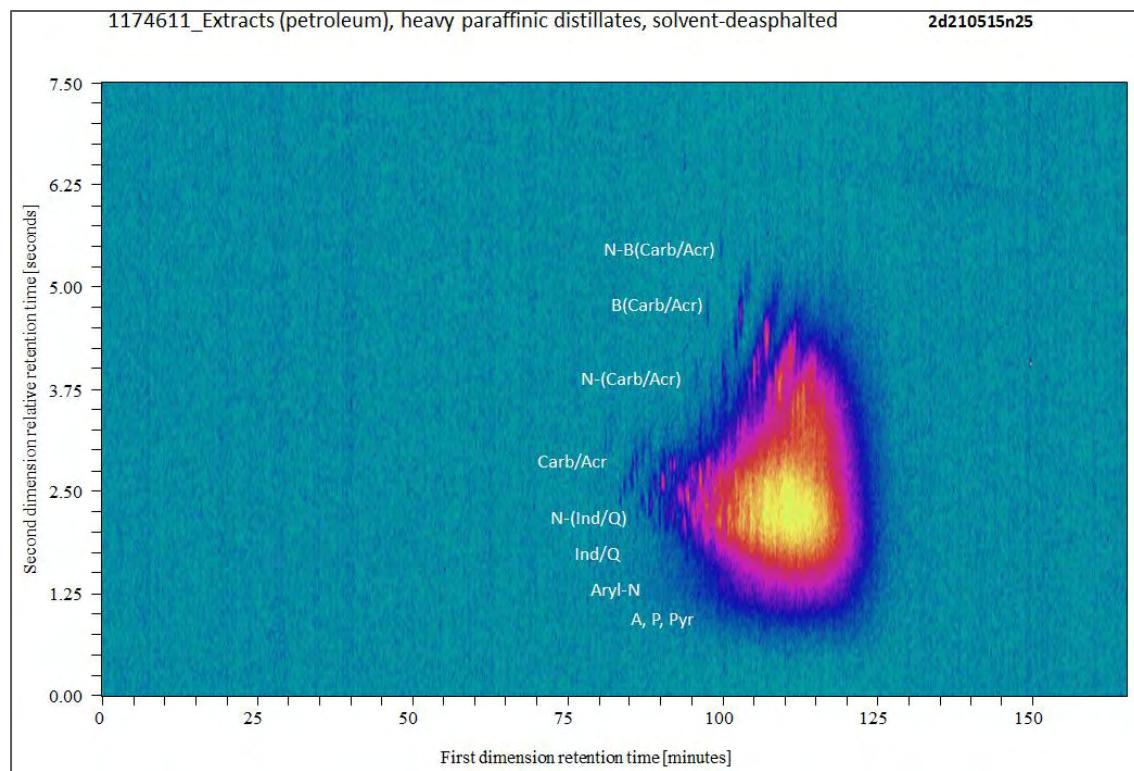


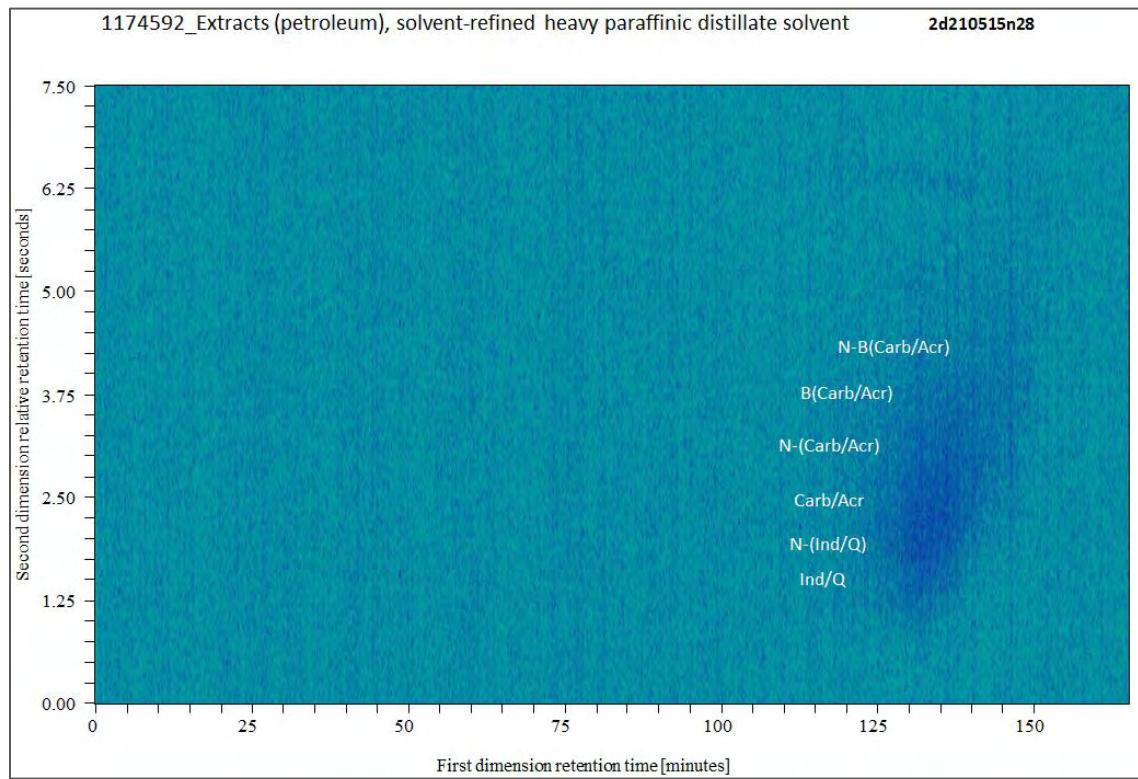
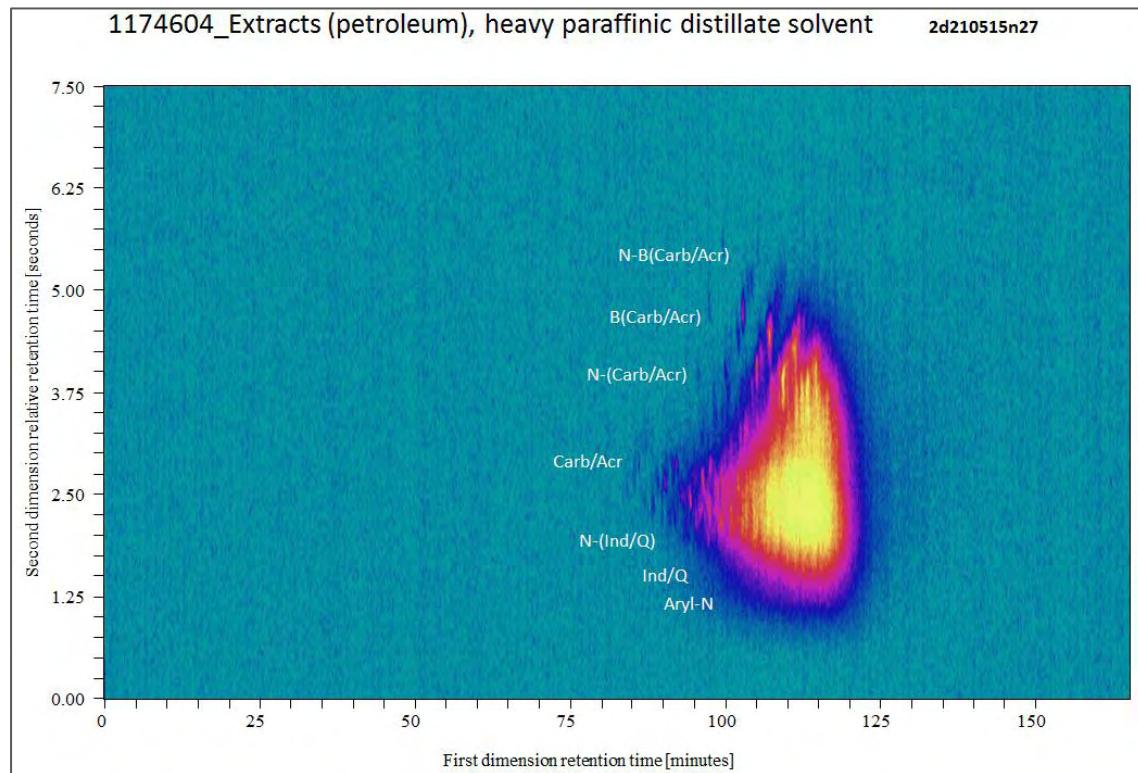
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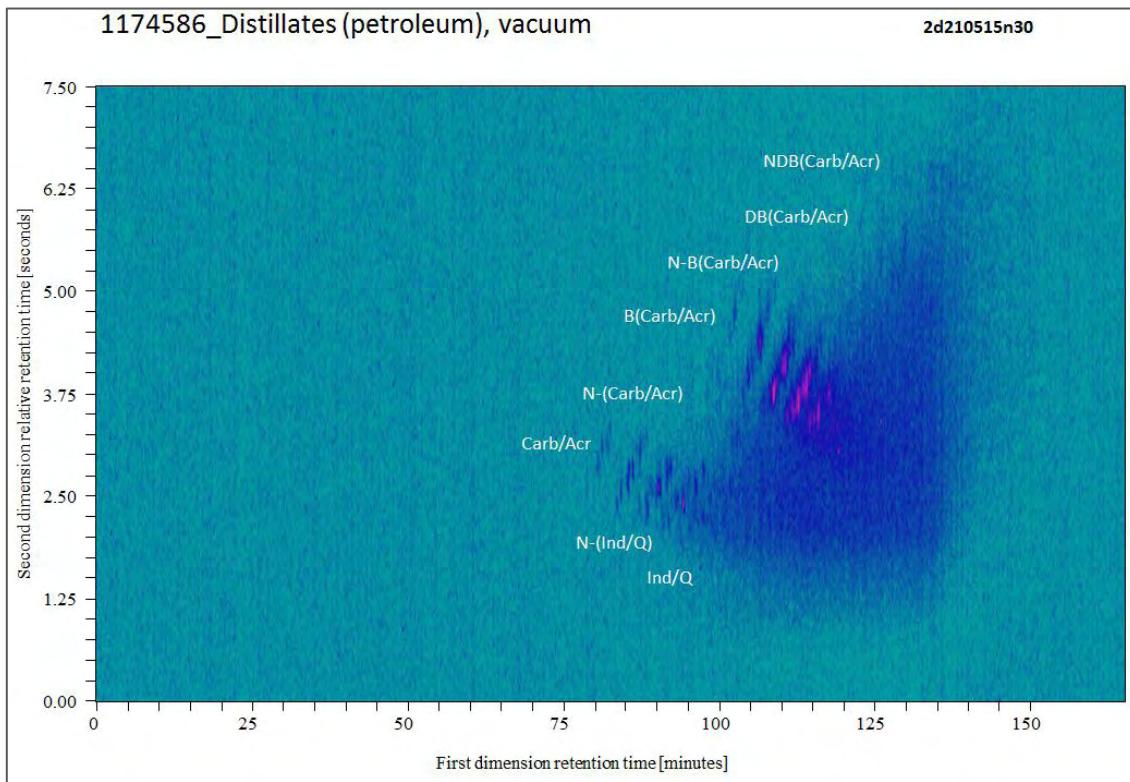
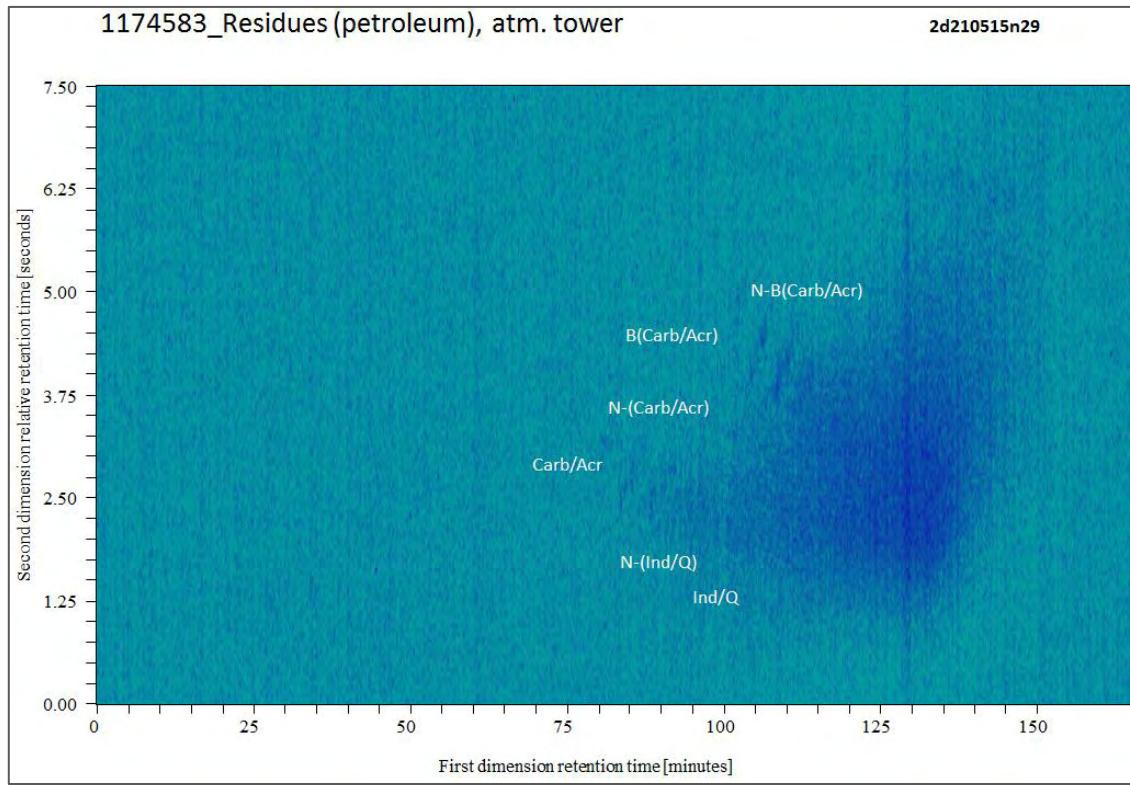


1174613_White mineral oil (petroleum) 2d210515n22



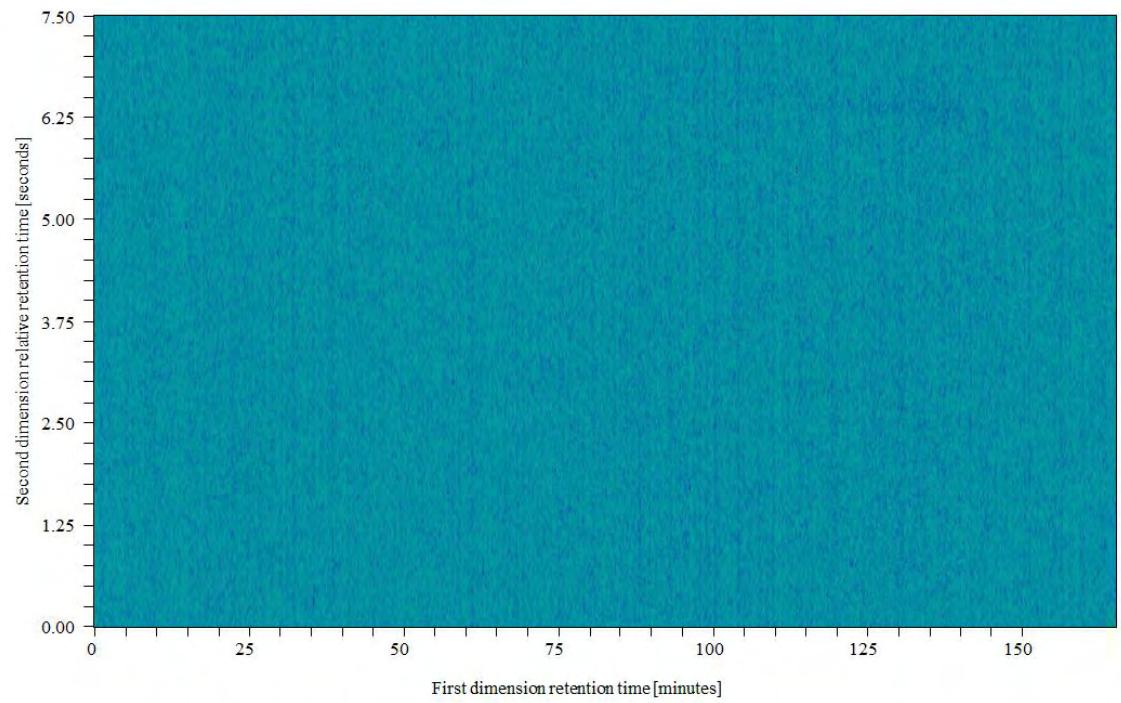




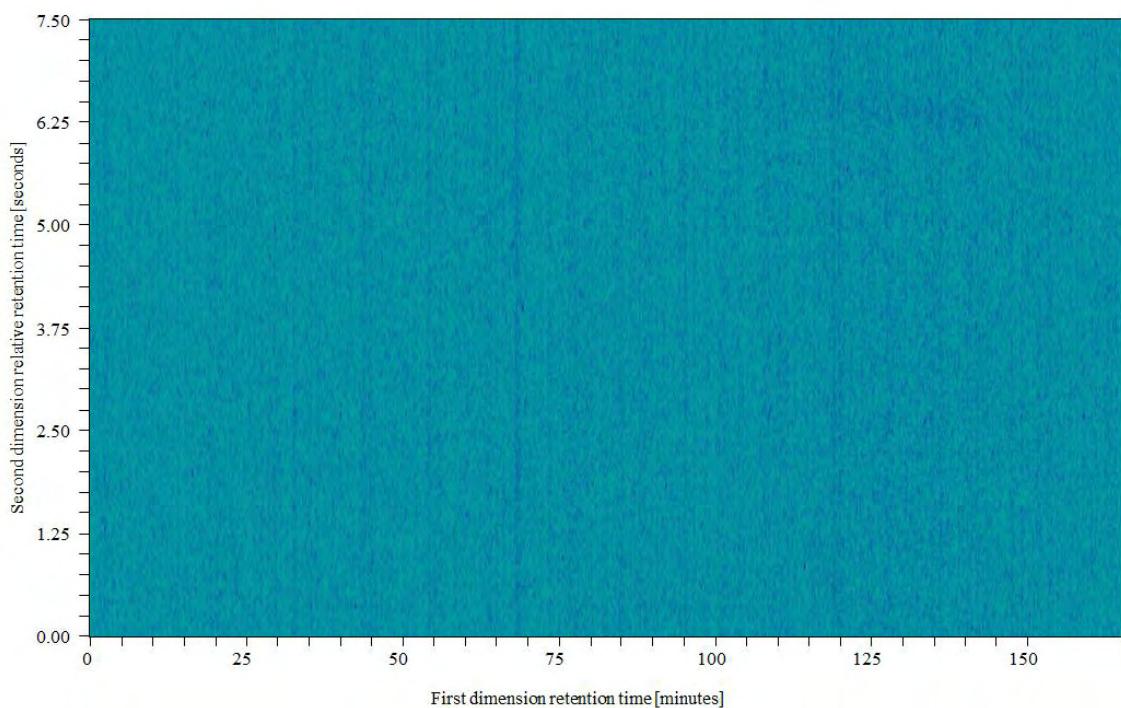


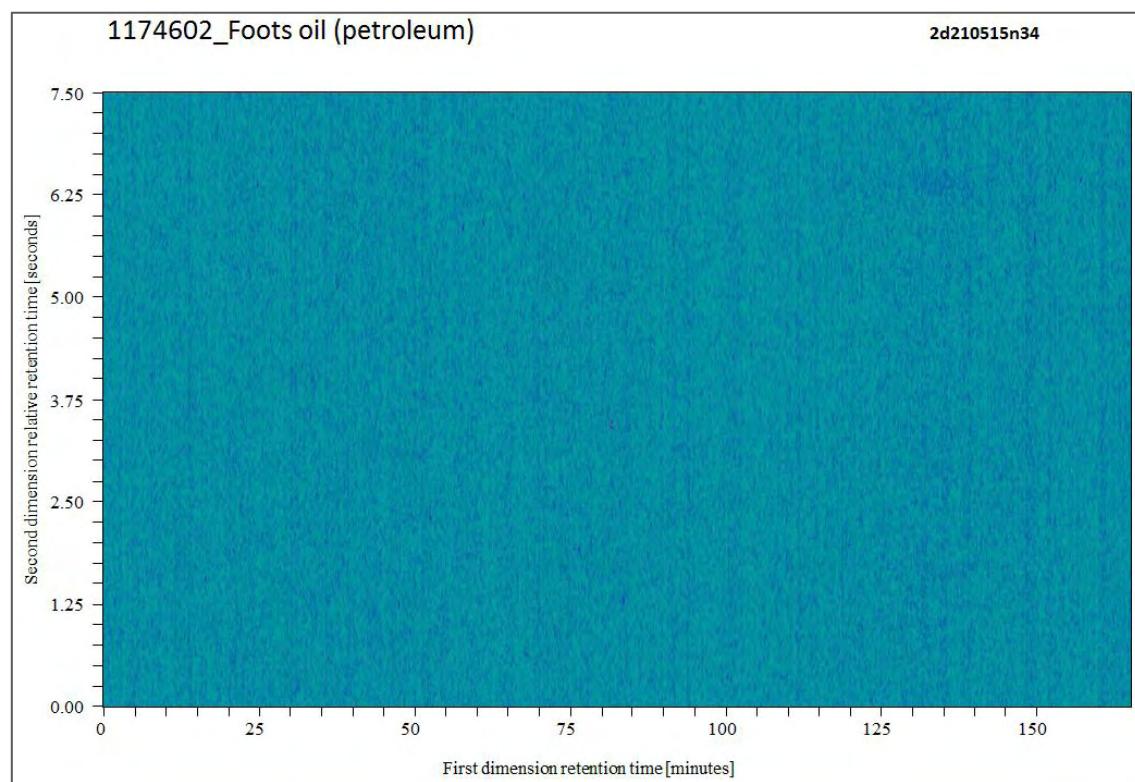
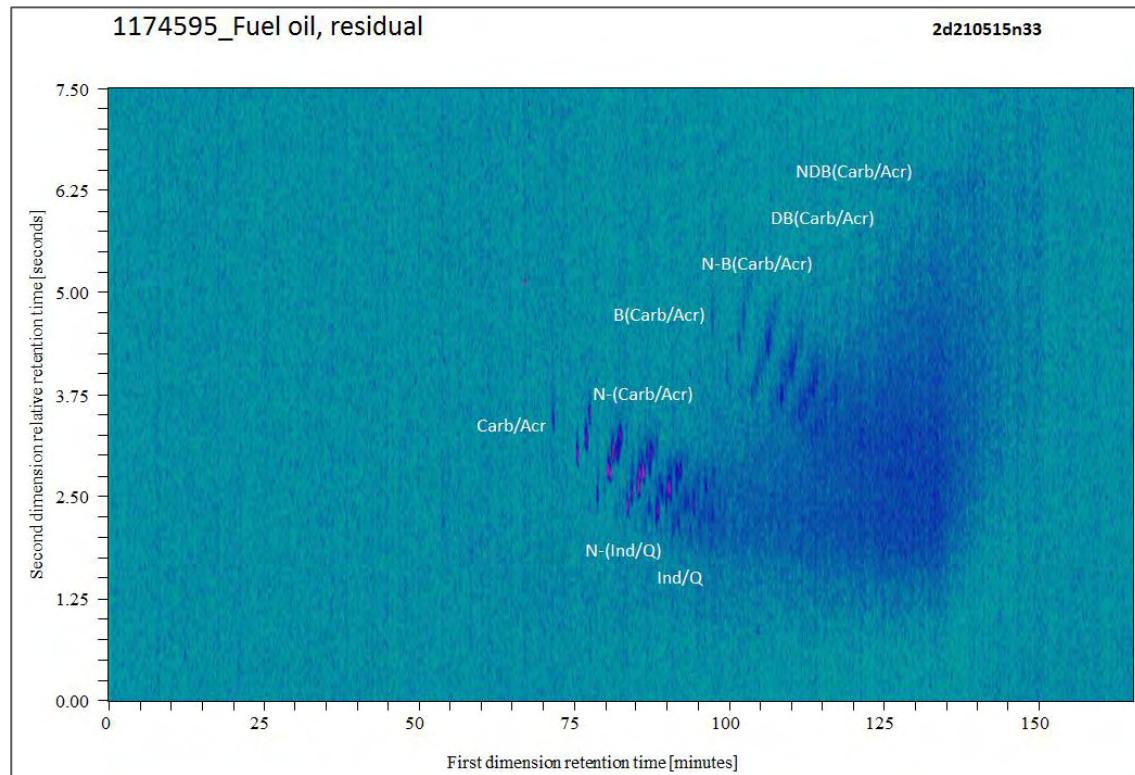
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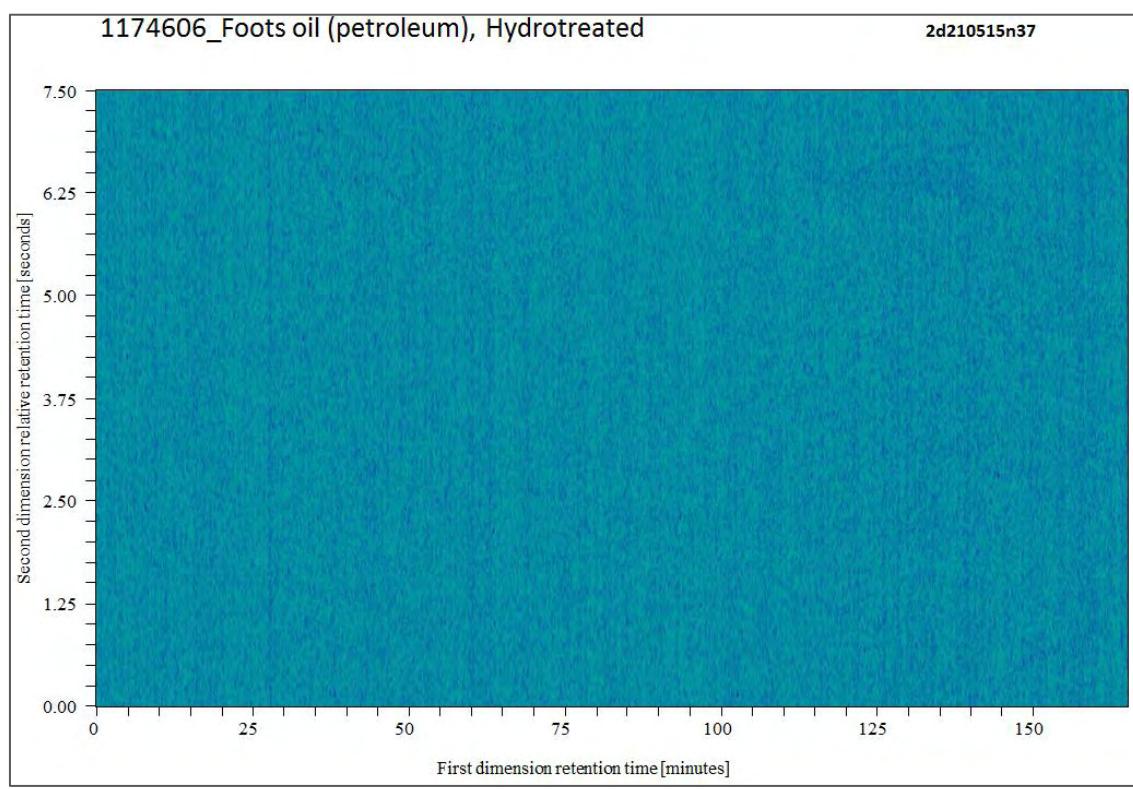
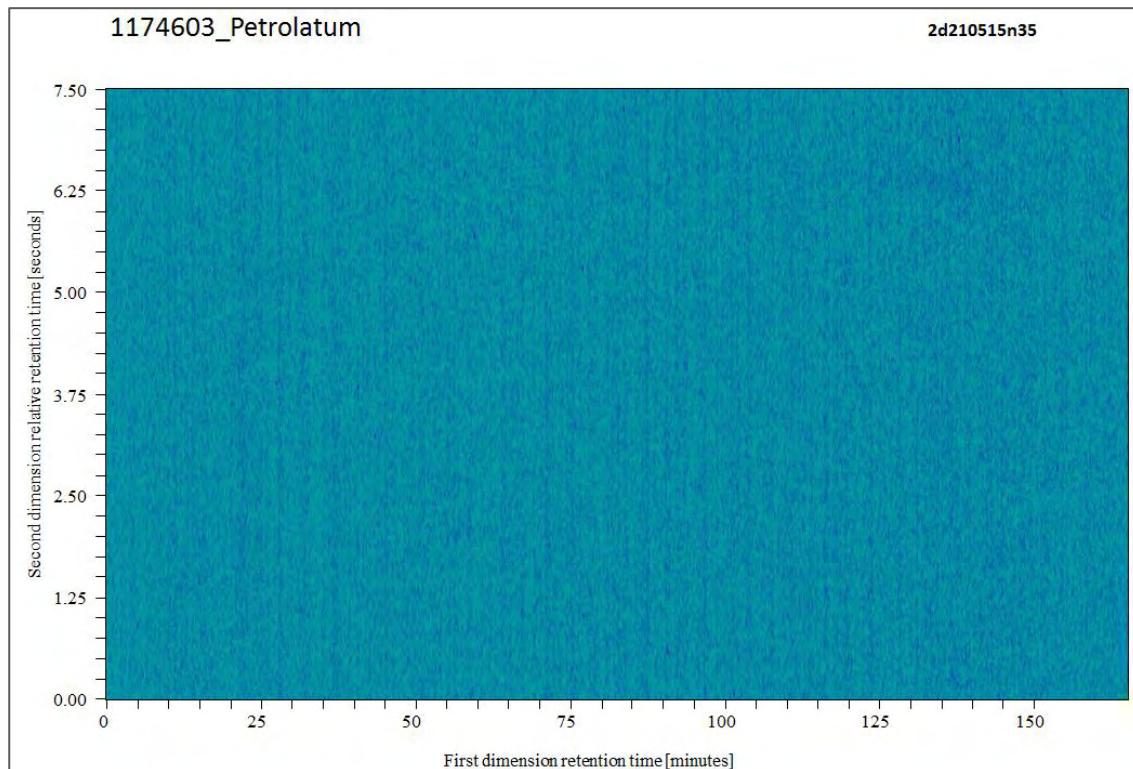
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**1174591_Paraffin waxes (petroleum), Hydrotreated**

2d210515n32

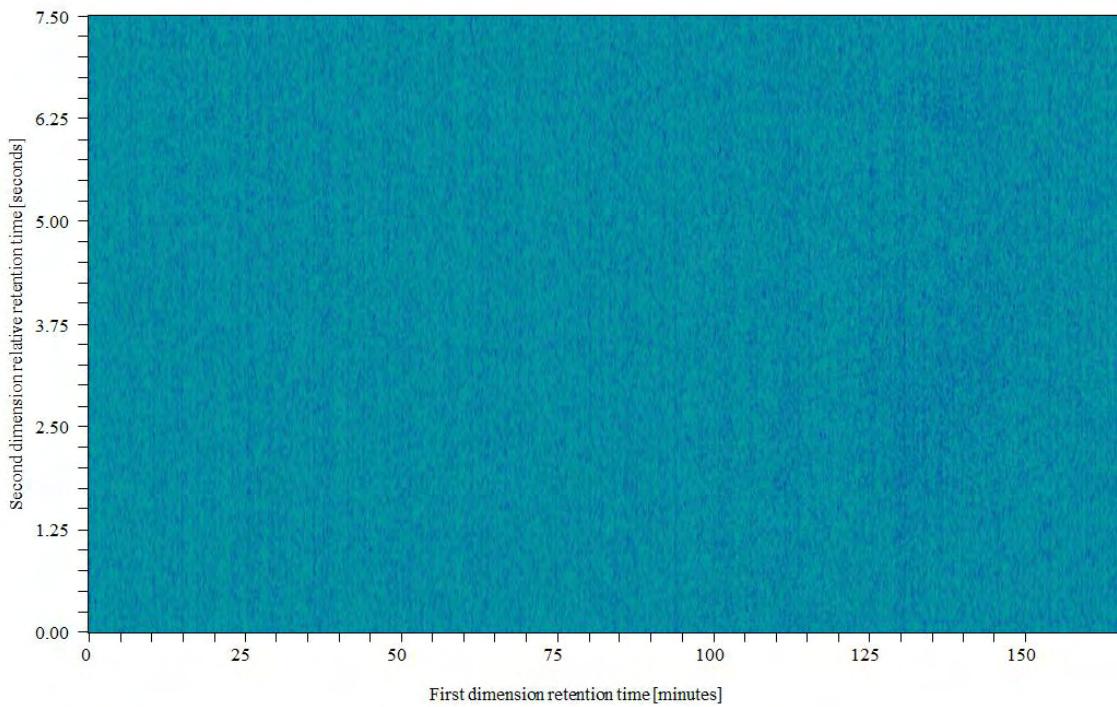






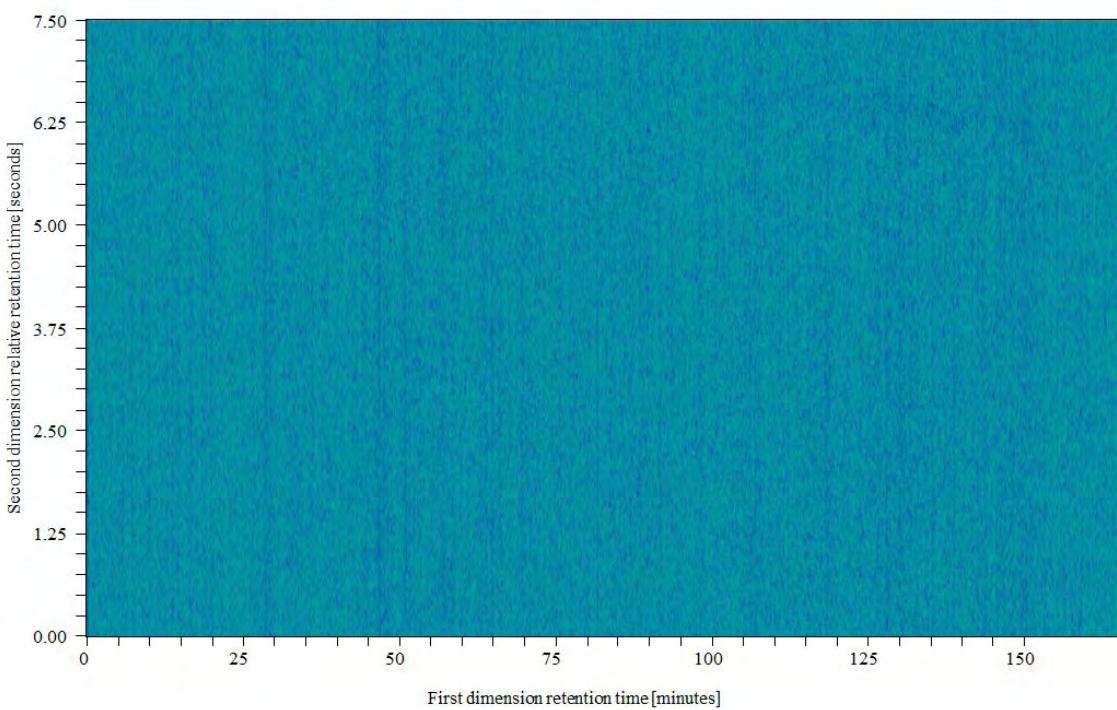
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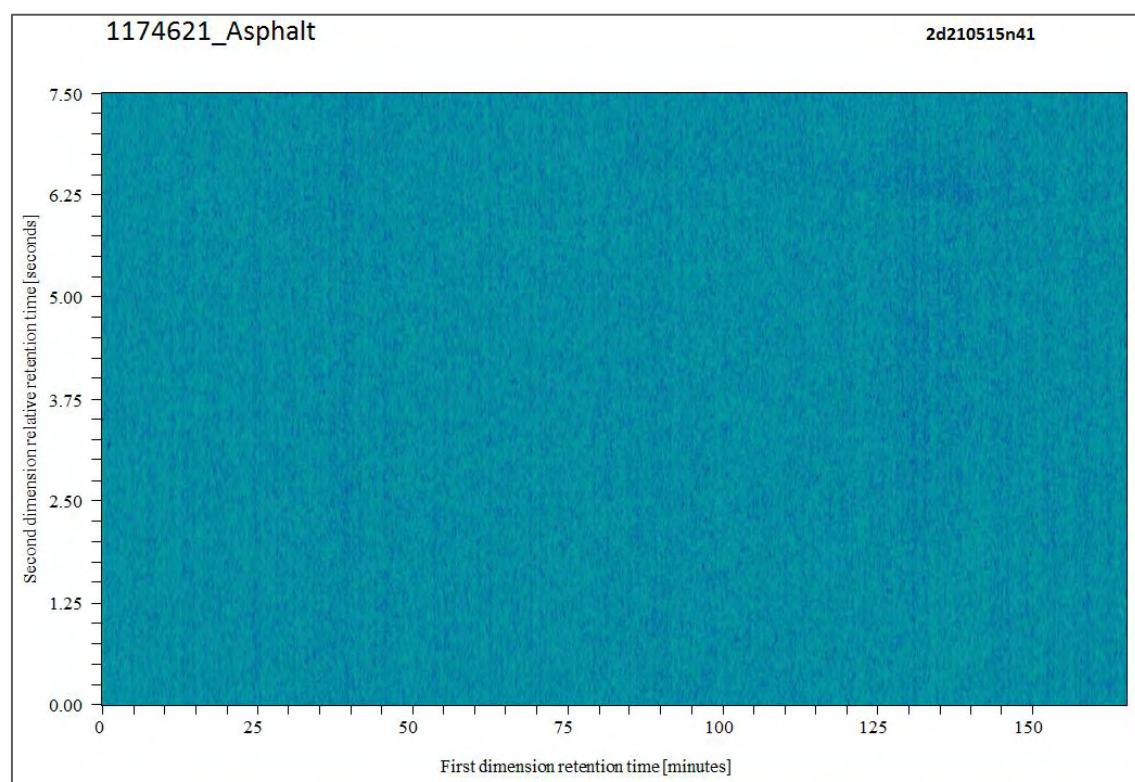
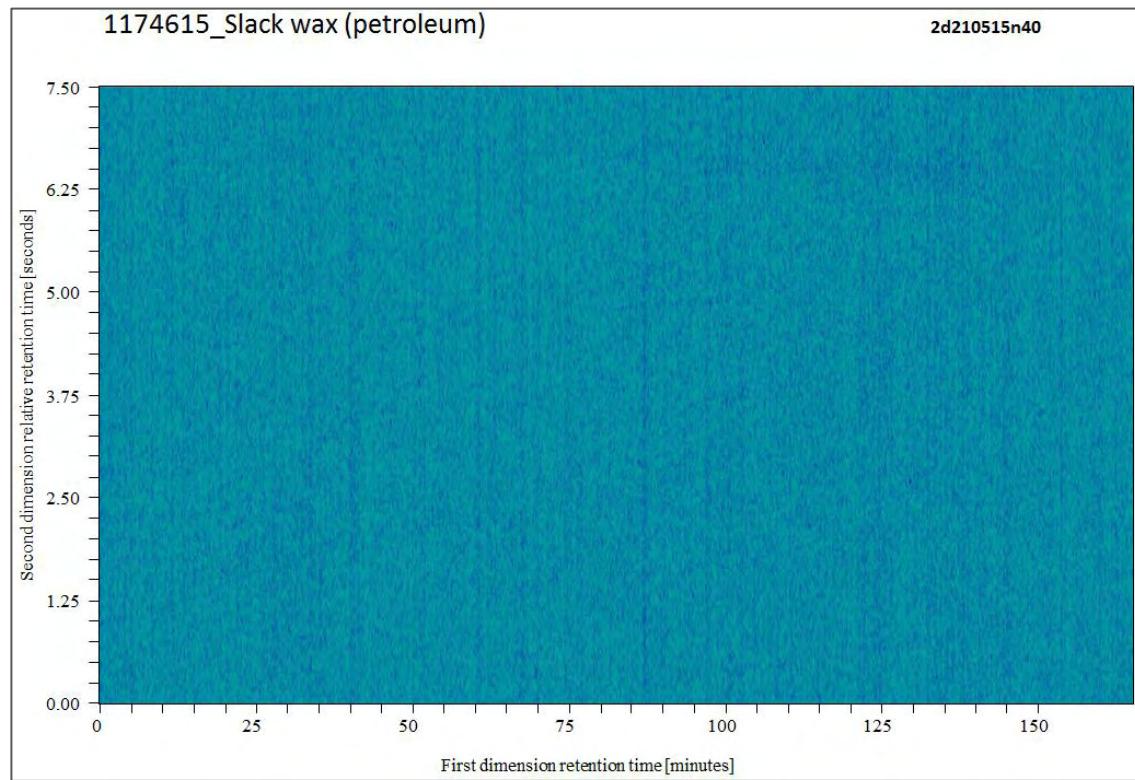
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1174610_Distillates (petroleum), petroleum residues vacuum

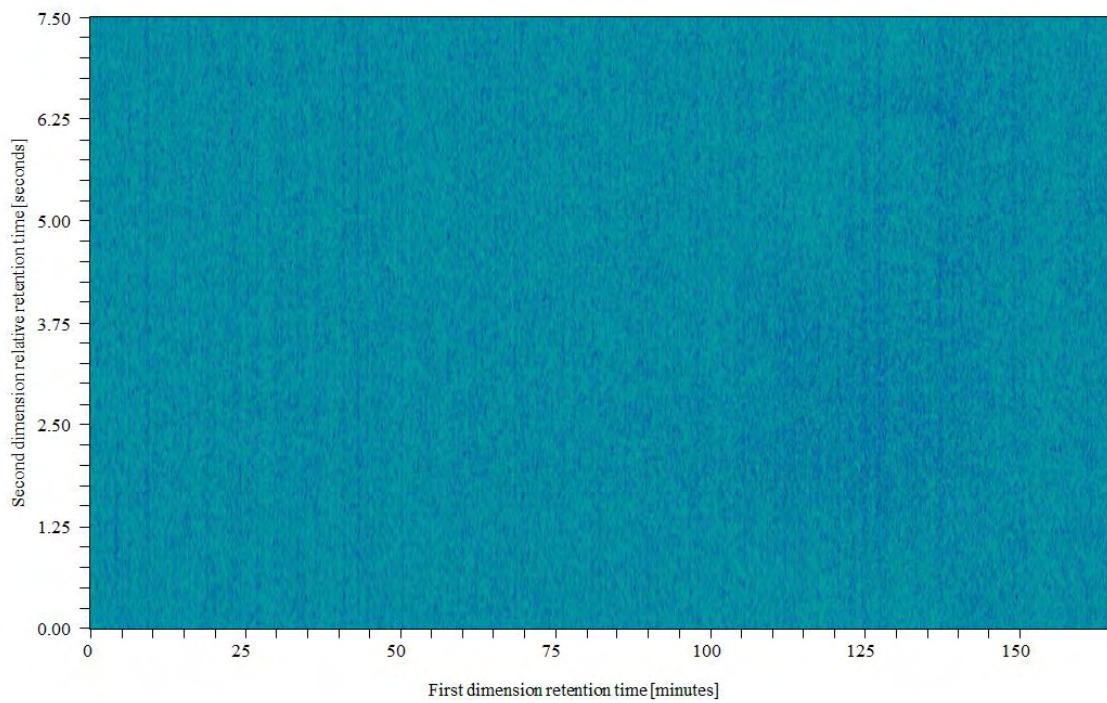
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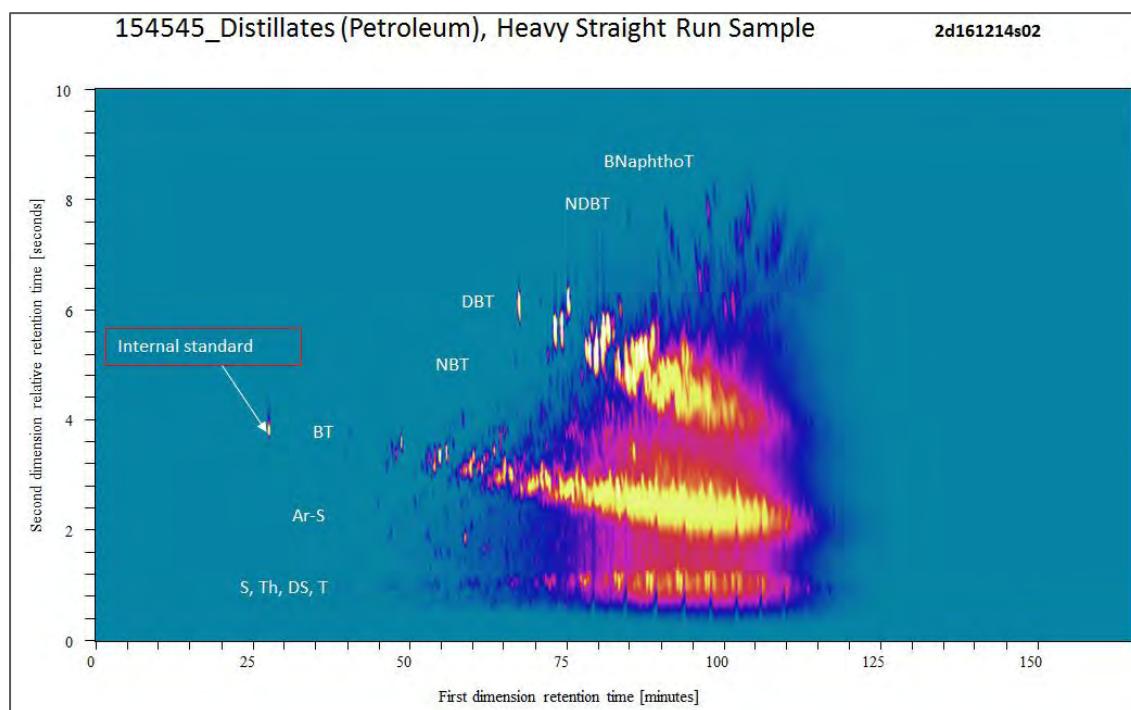
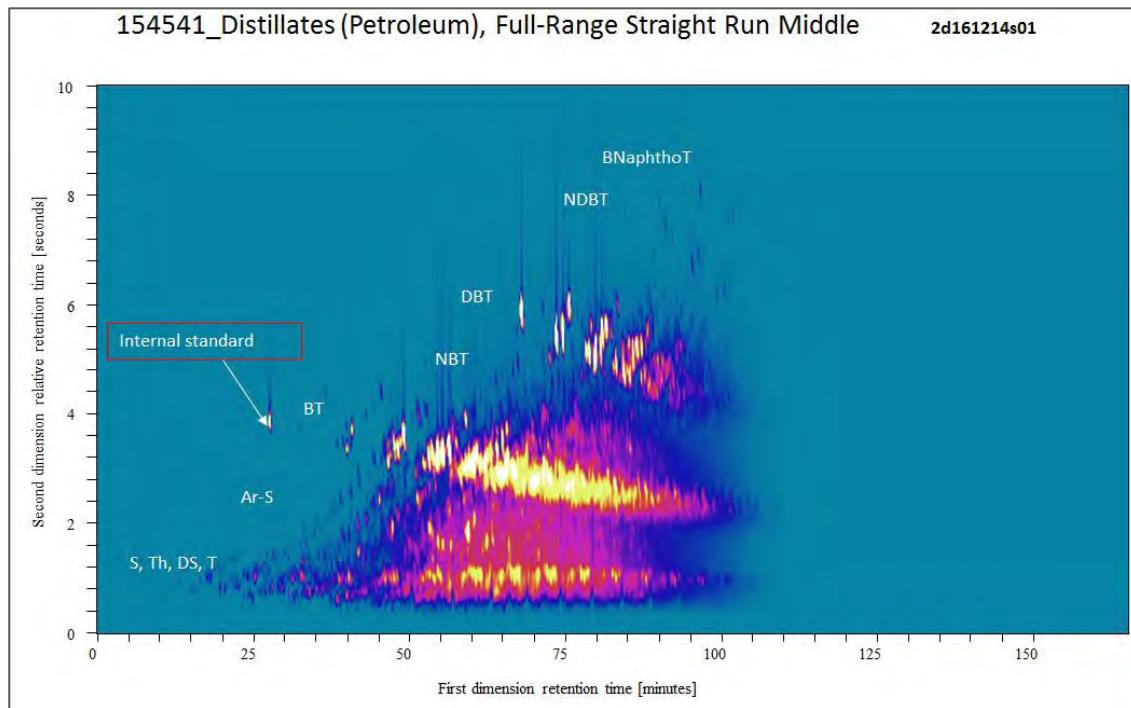


1174622_AspHALT, oxidized

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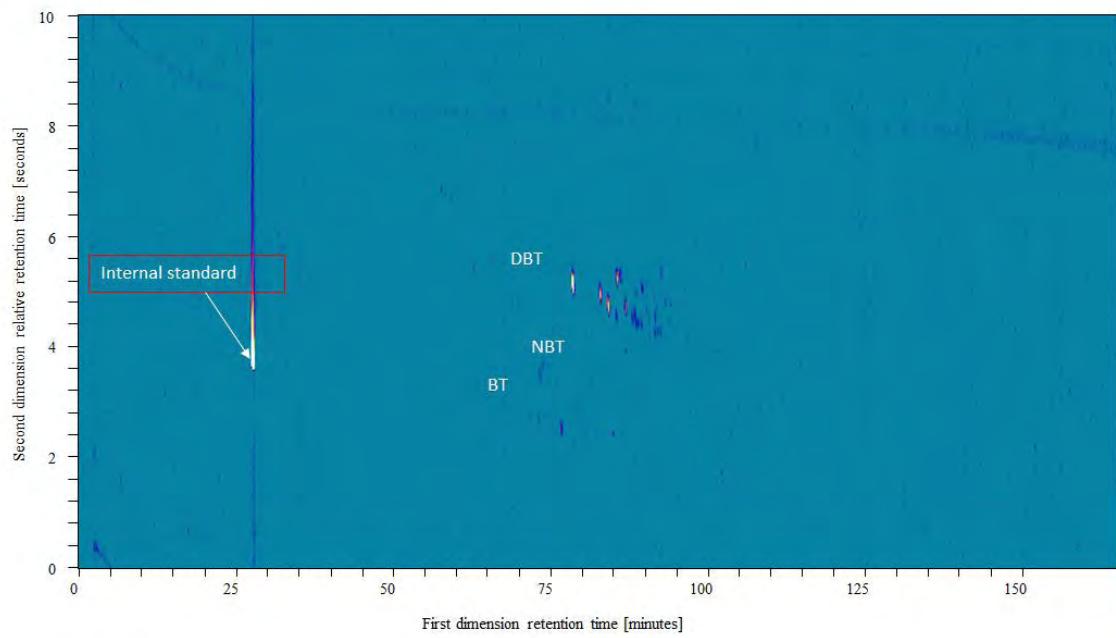


APPENDIX 2: SULPHUR GROUP TYPE GCxGC CHROMATOGRAMS



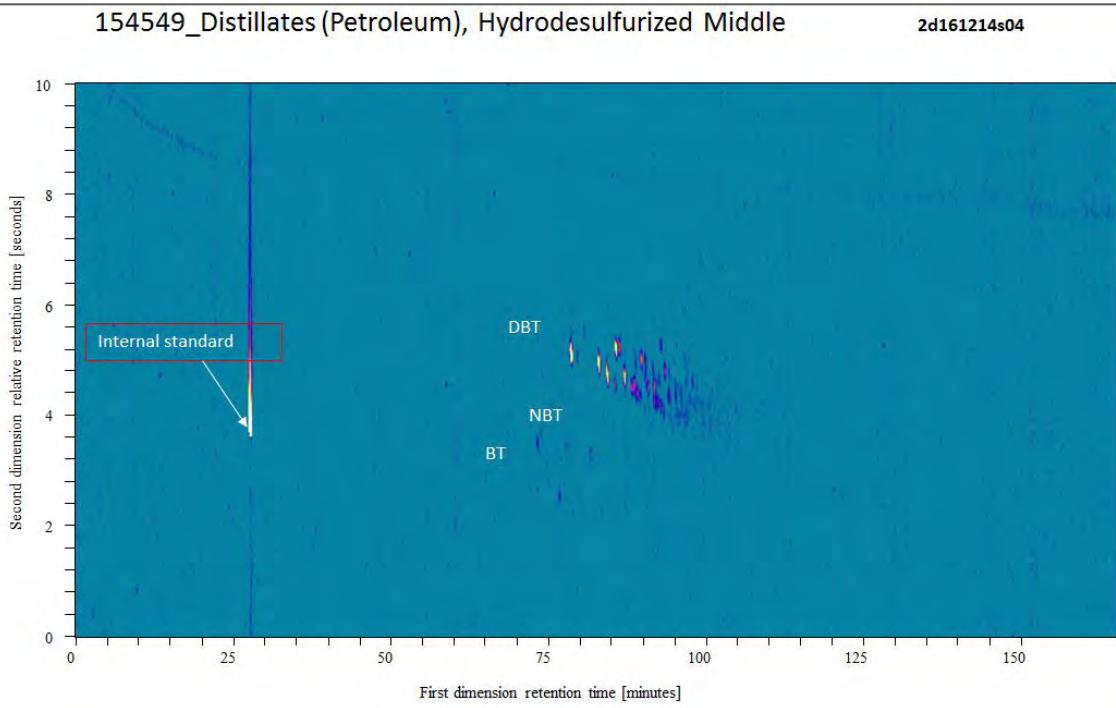
154937_Distillates (Petroleum), Hydrodesulfurized Middle

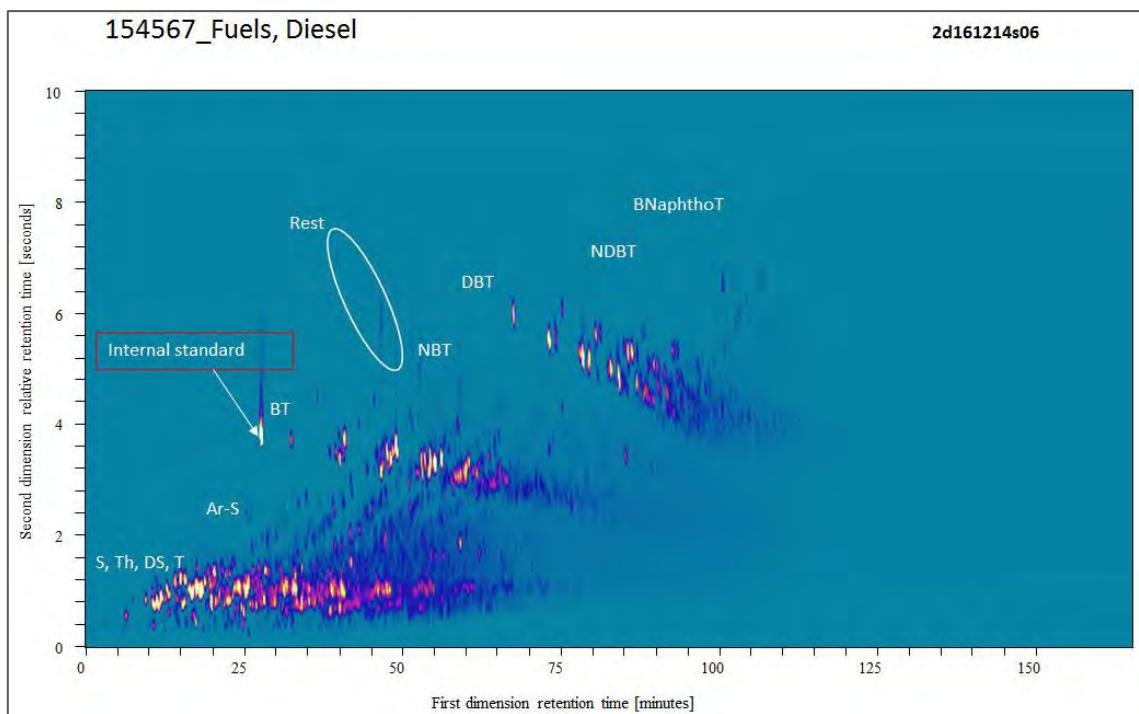
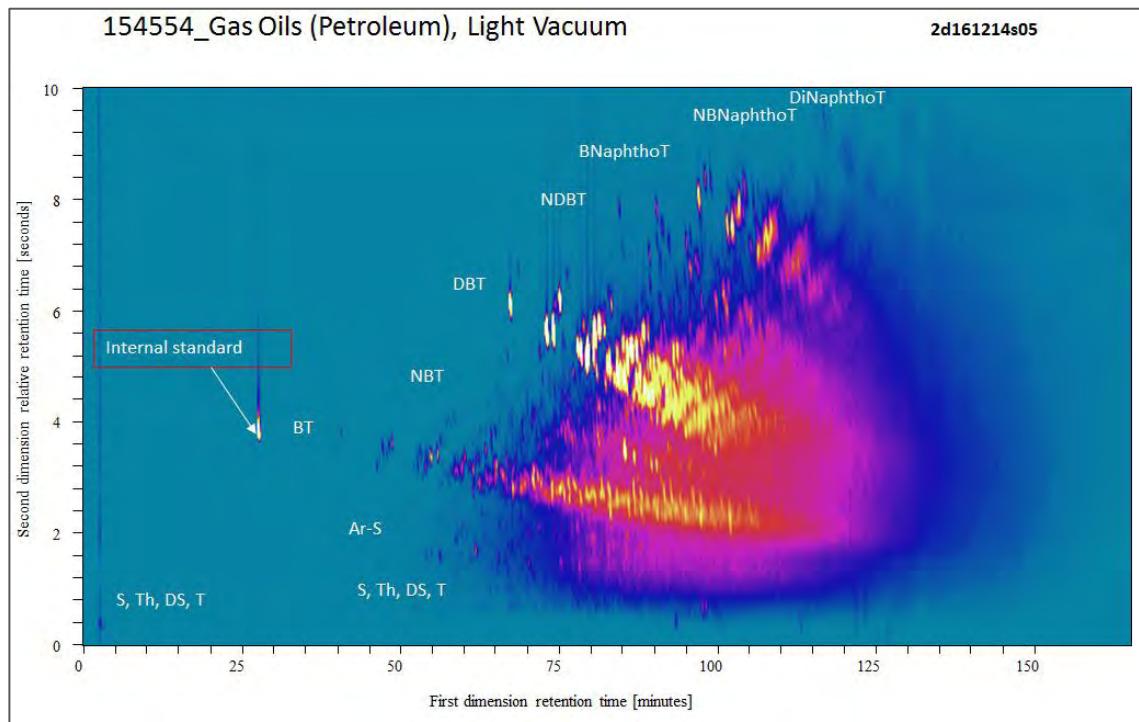
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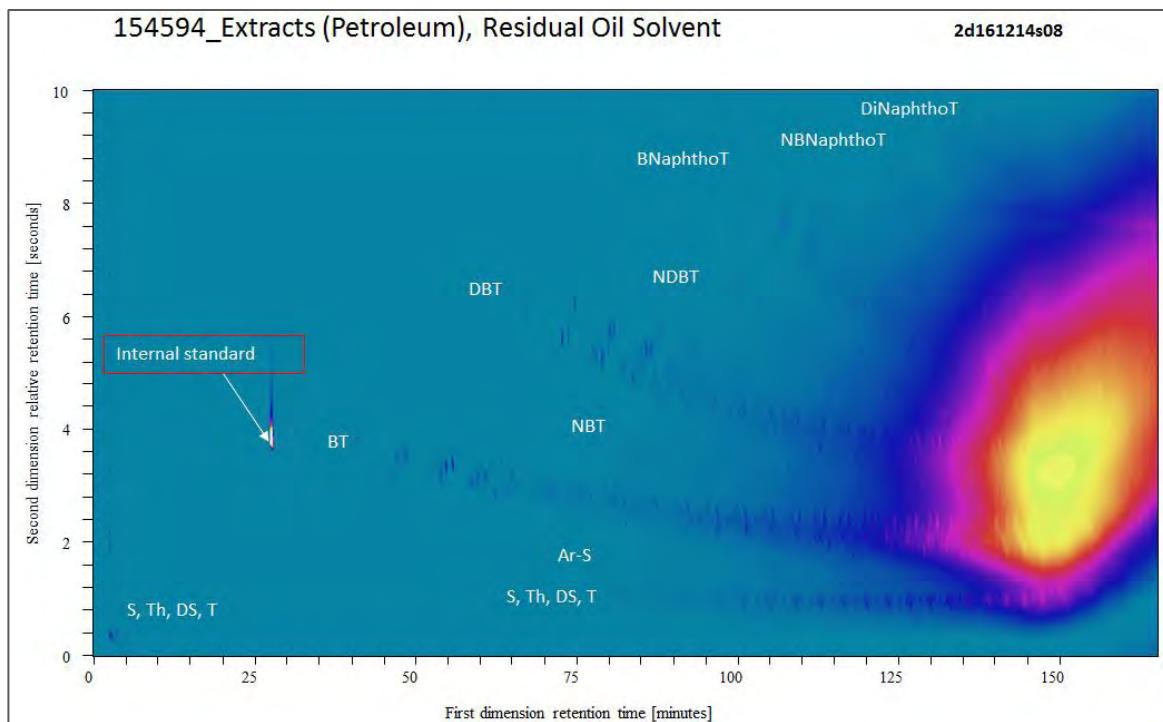
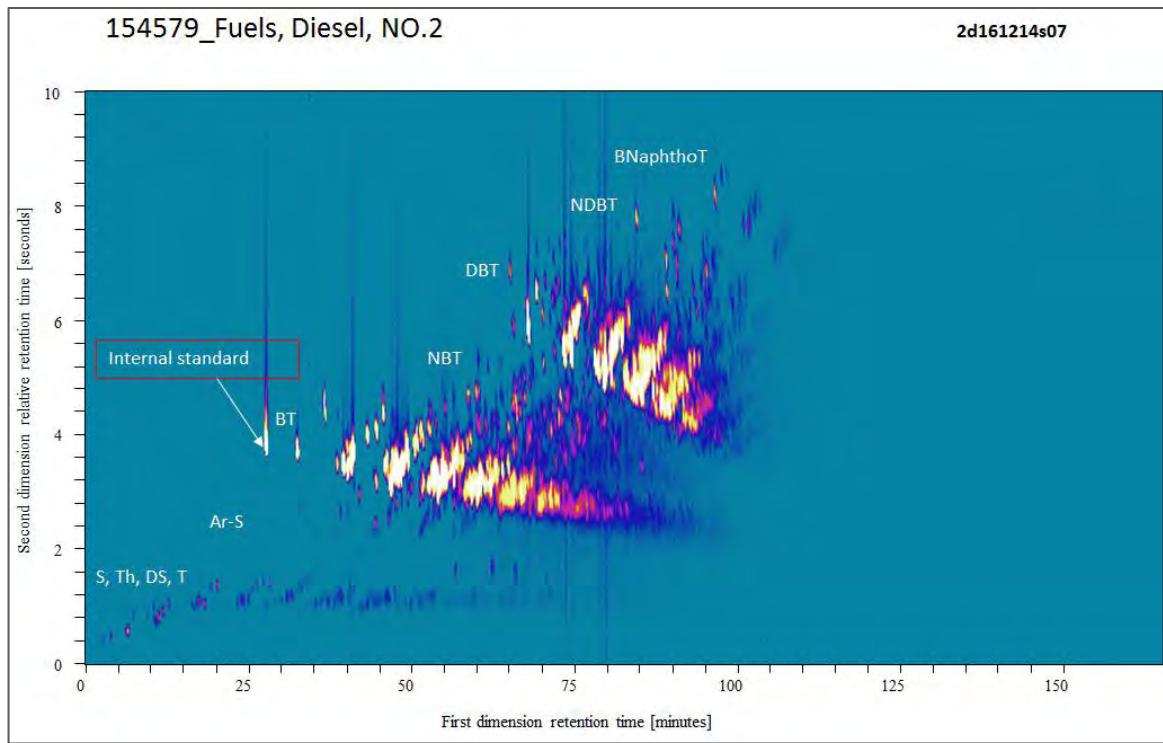


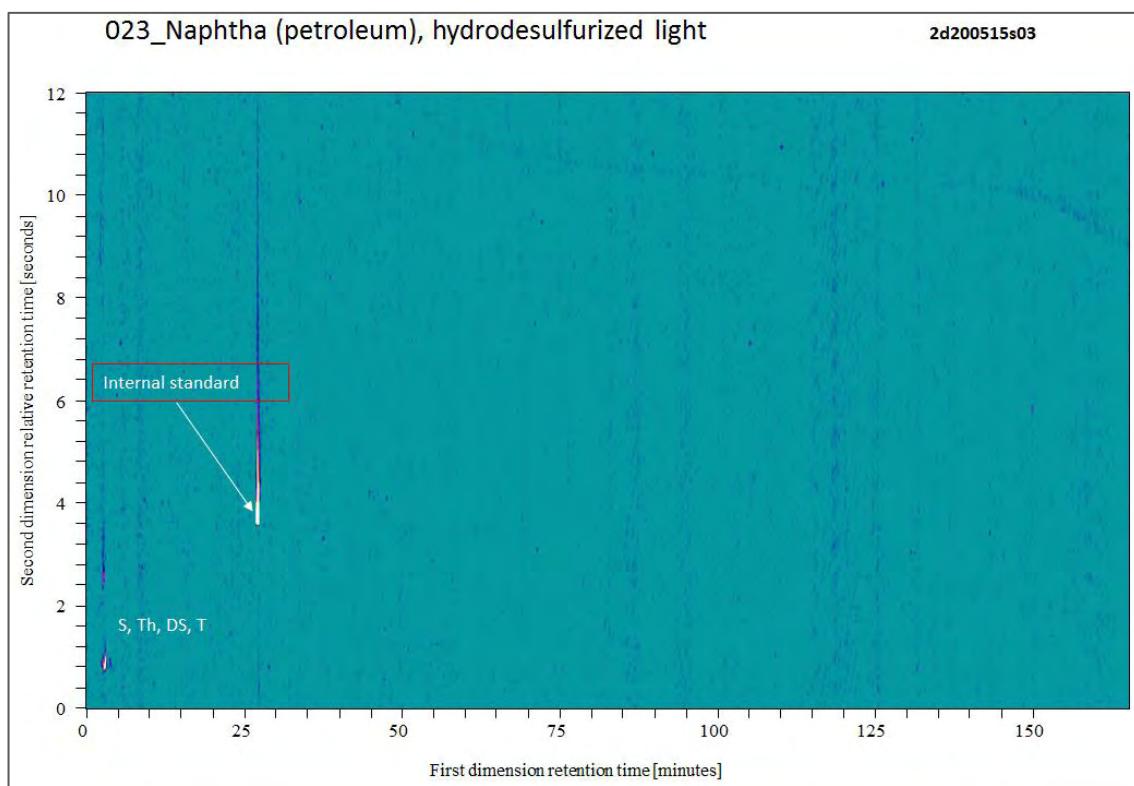
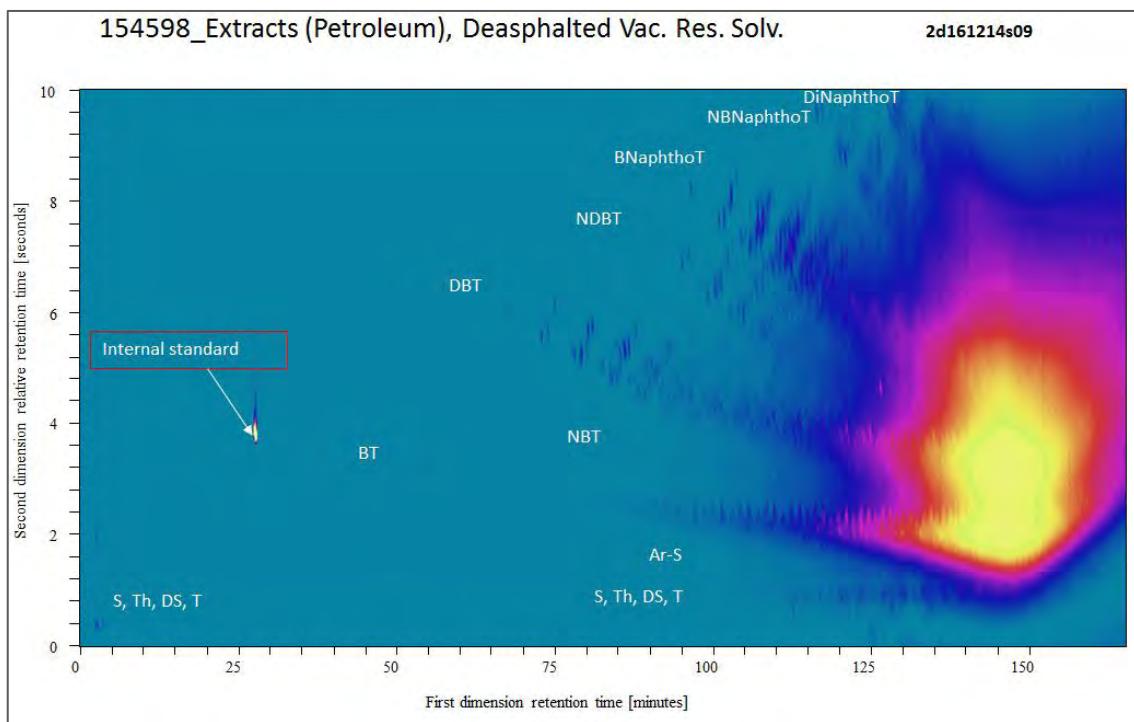
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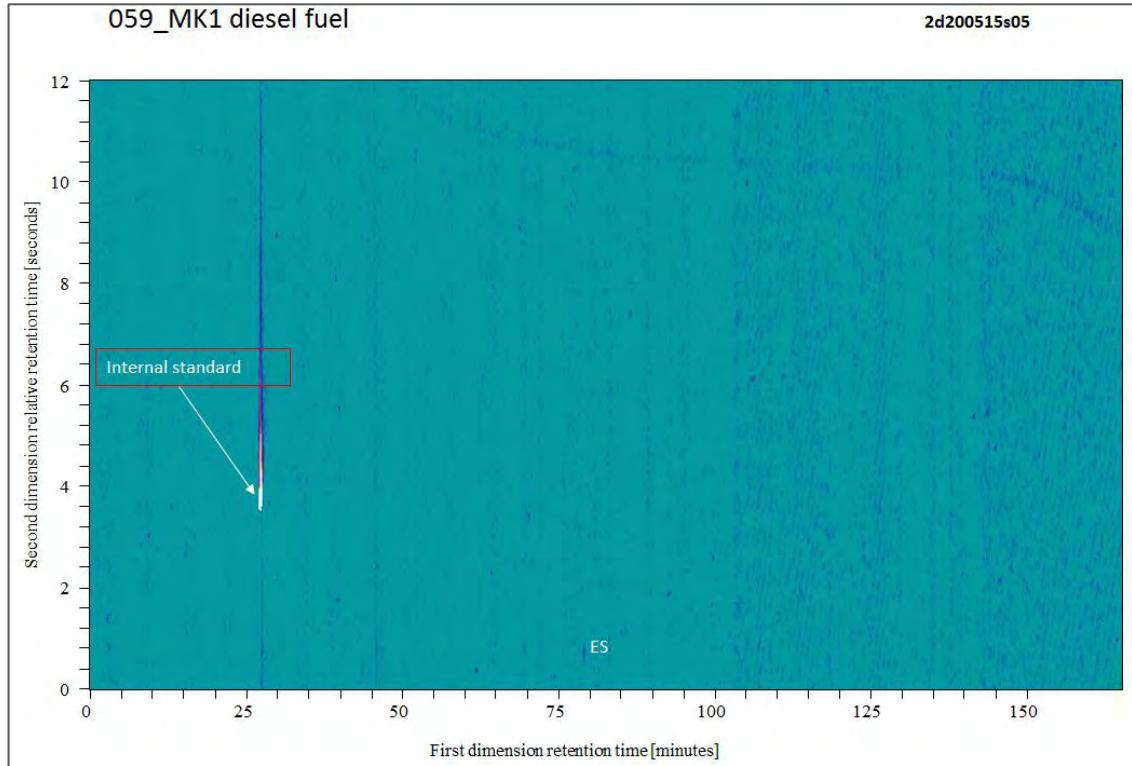
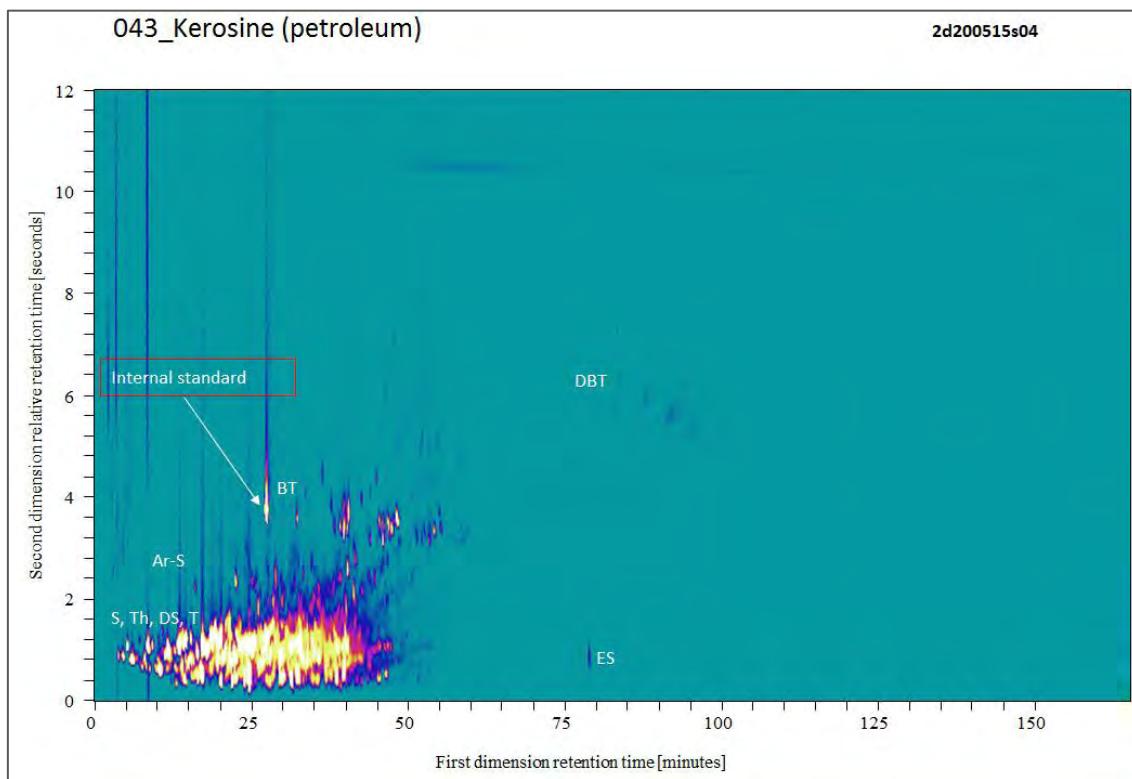
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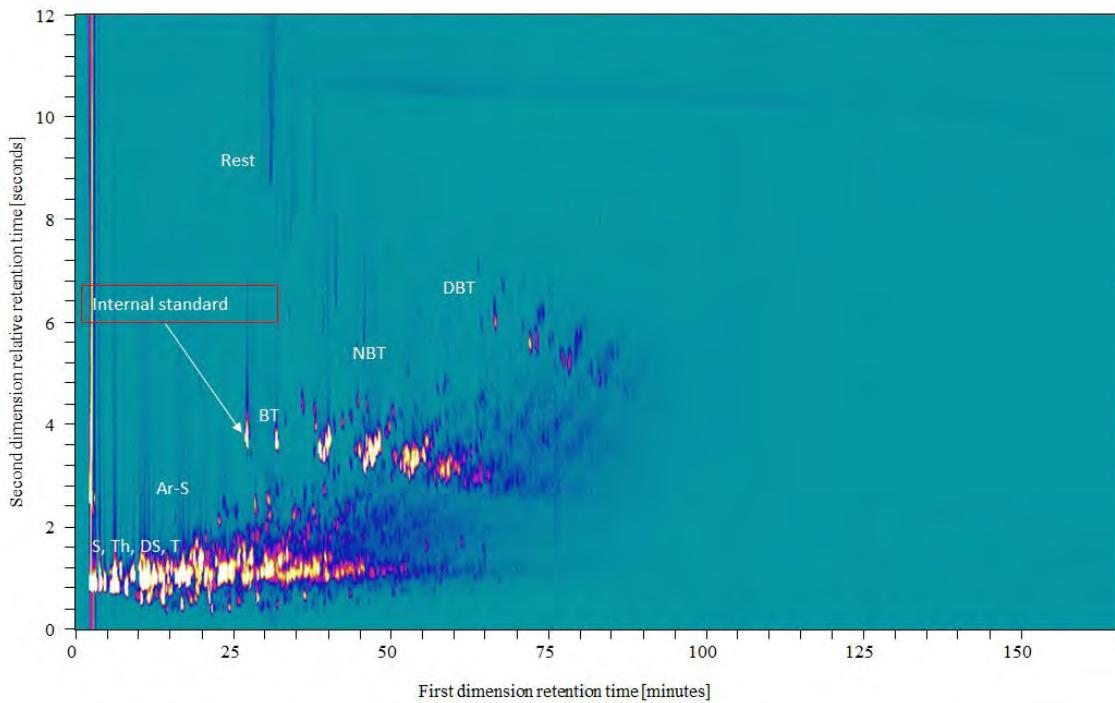






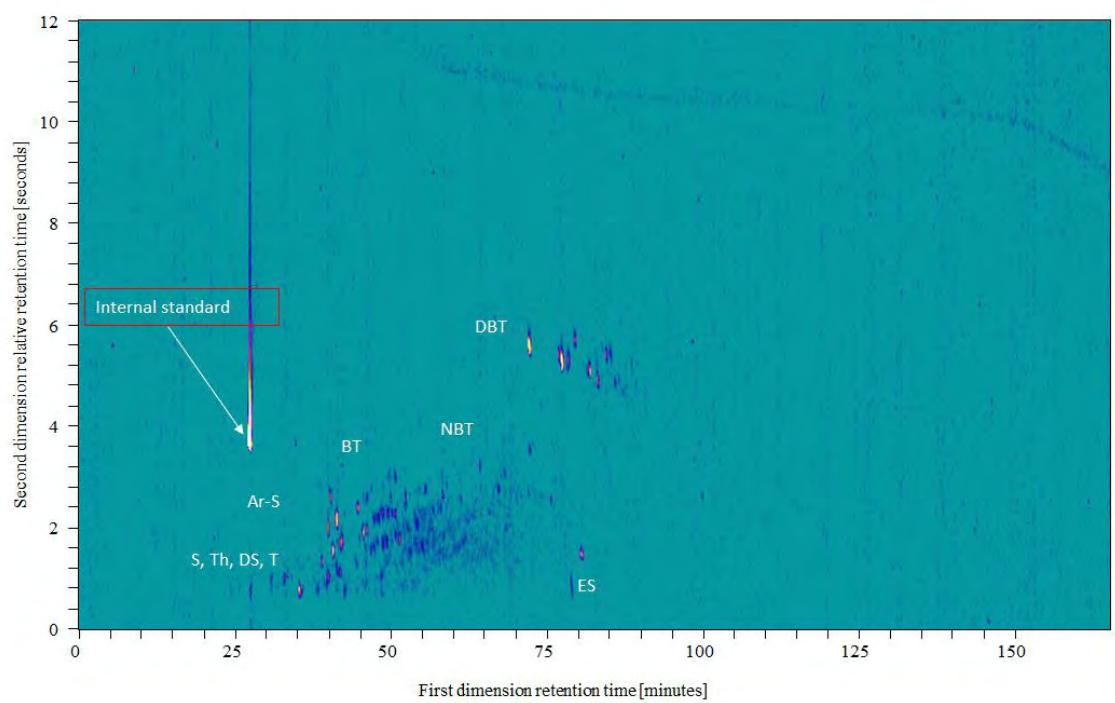
076_Naphtha (petroleum), full-range coker

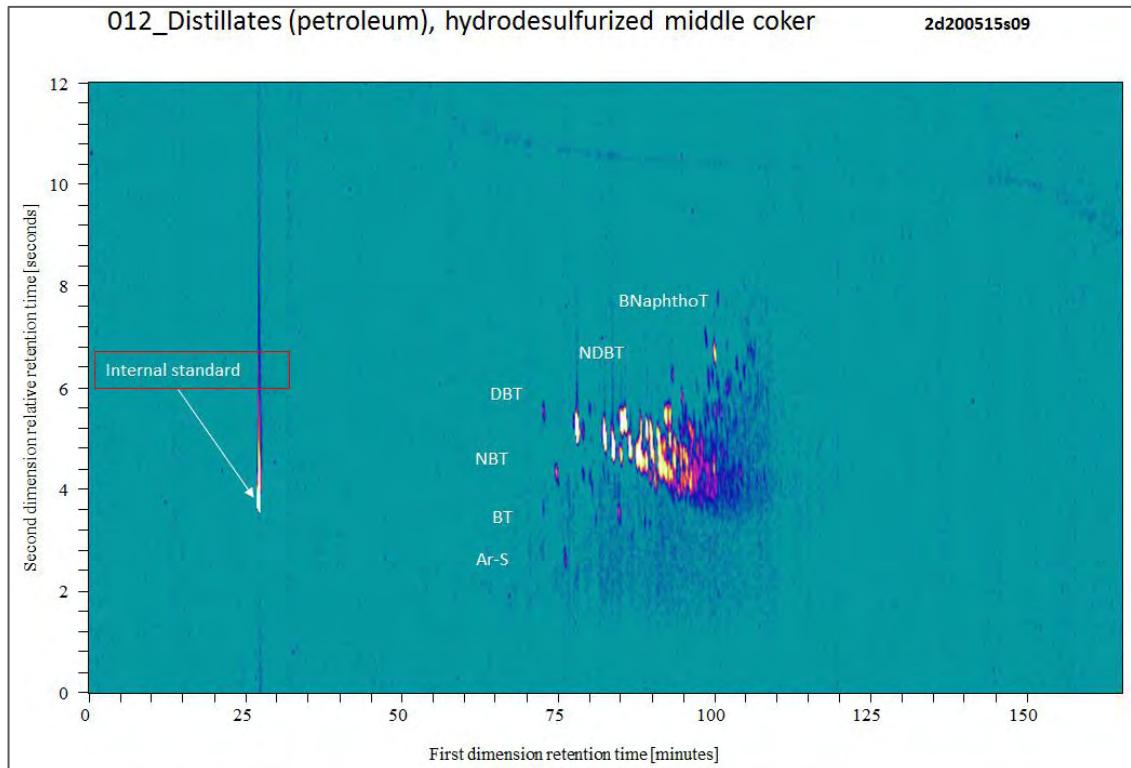
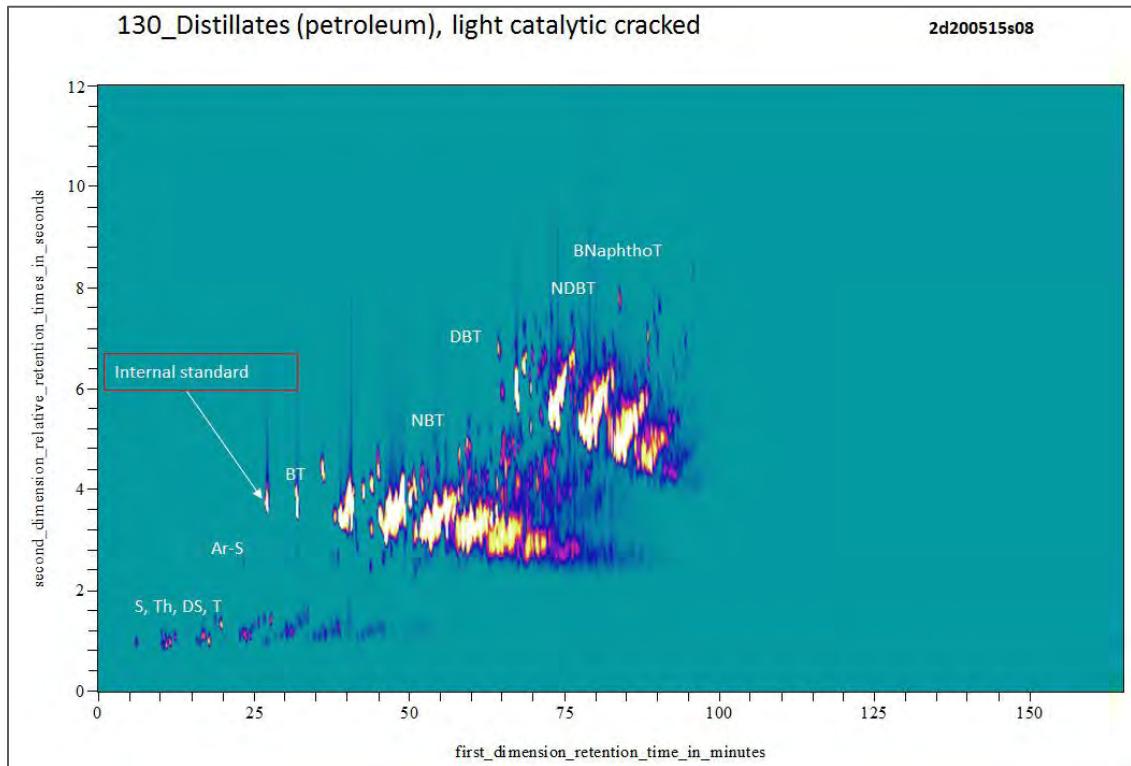
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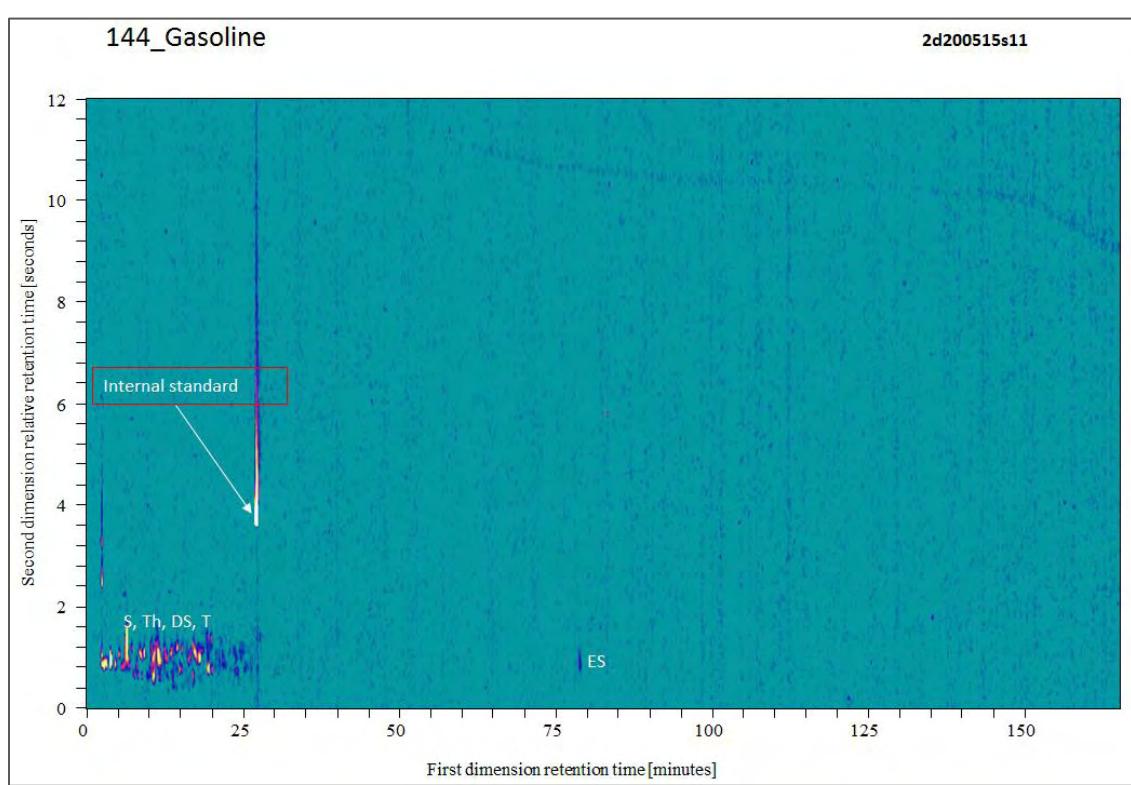
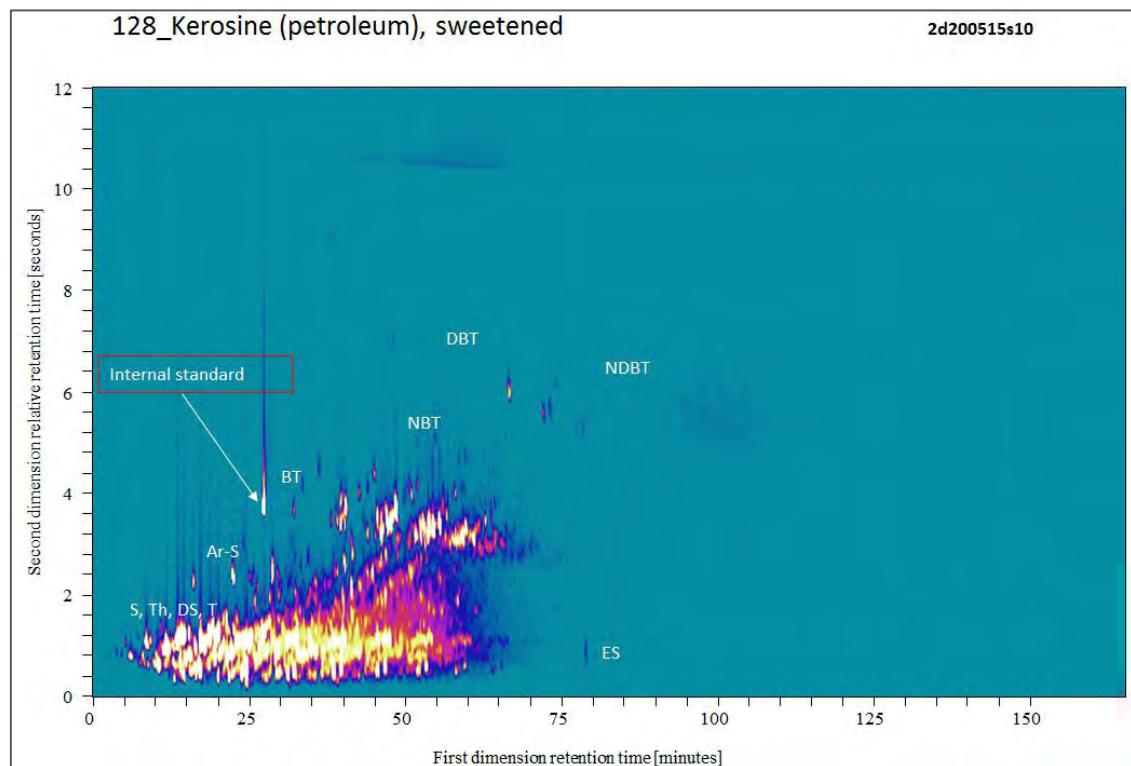


086_Kerosine (petroleum), hydrodesulfurized

2d200515s07

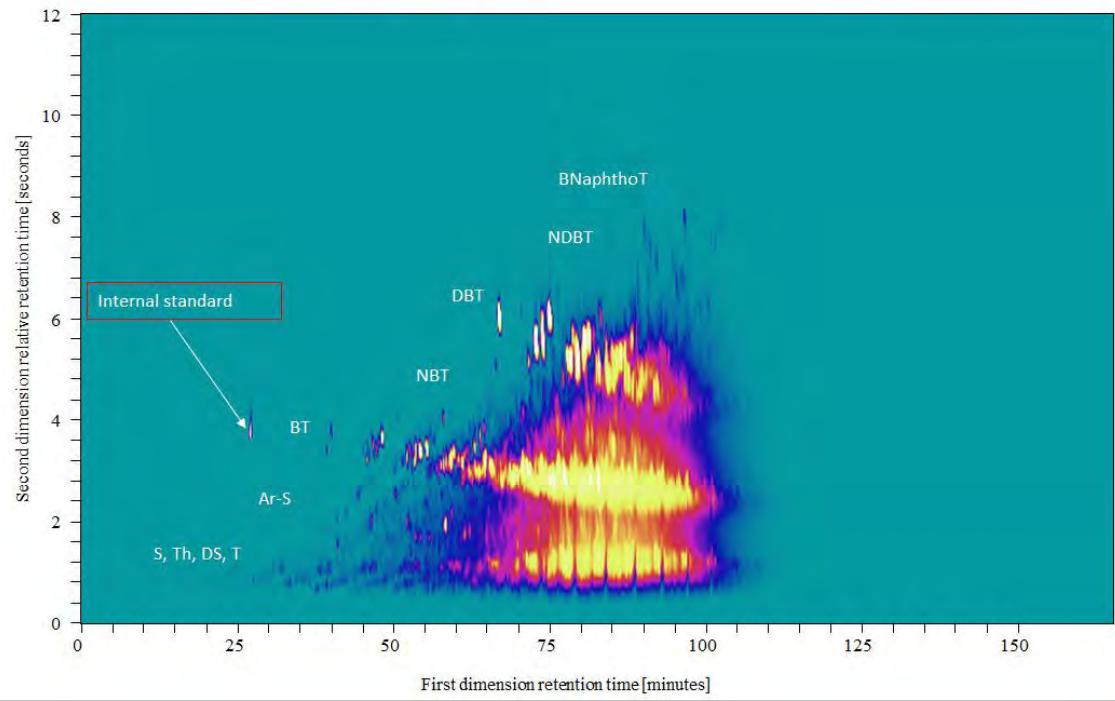






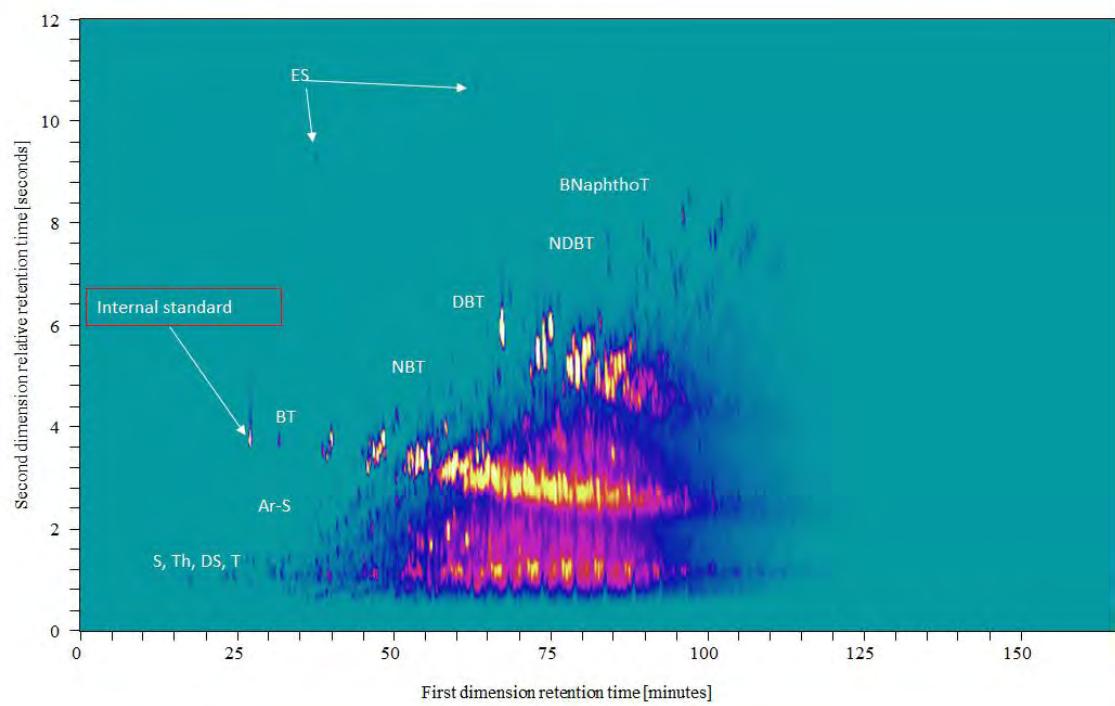
168_Gas oils (petroleum), straight-run

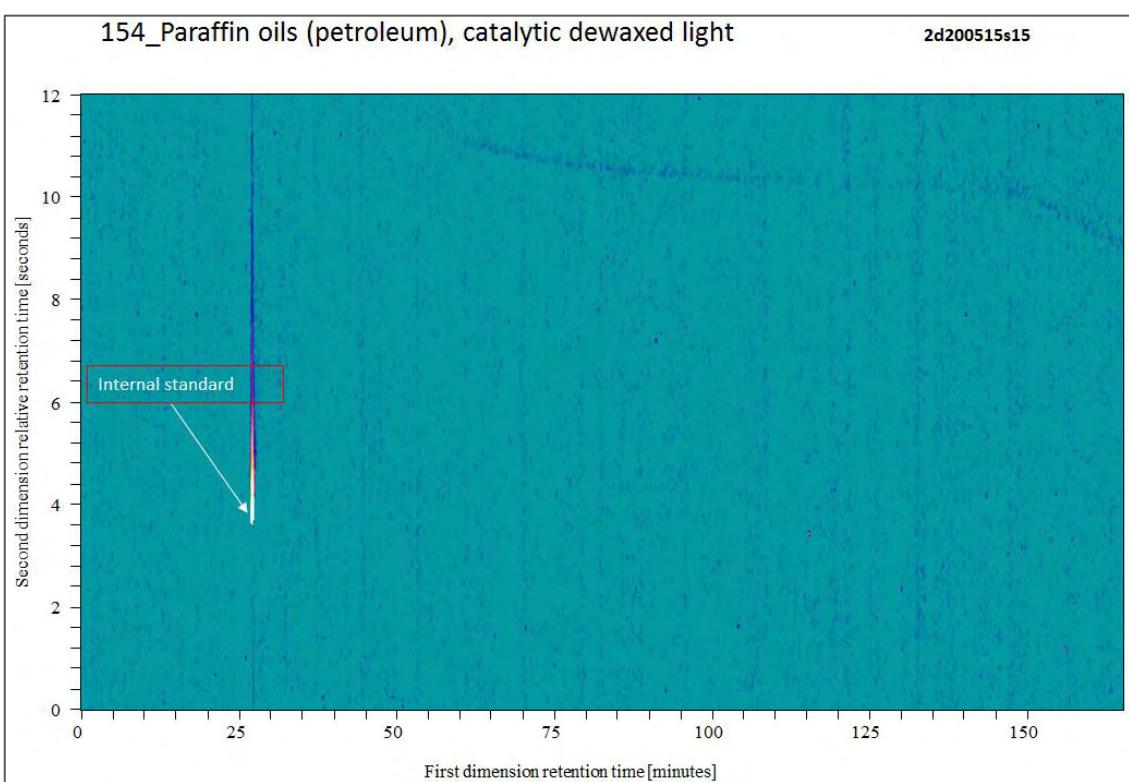
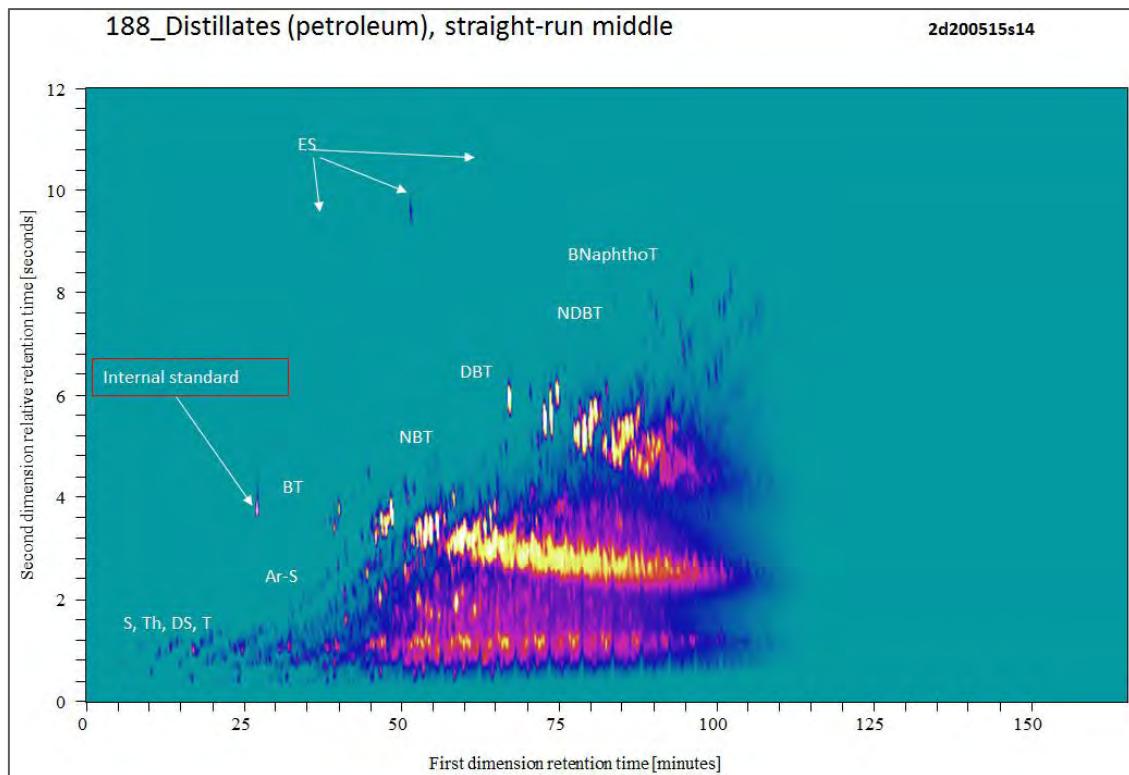
2d200515s12

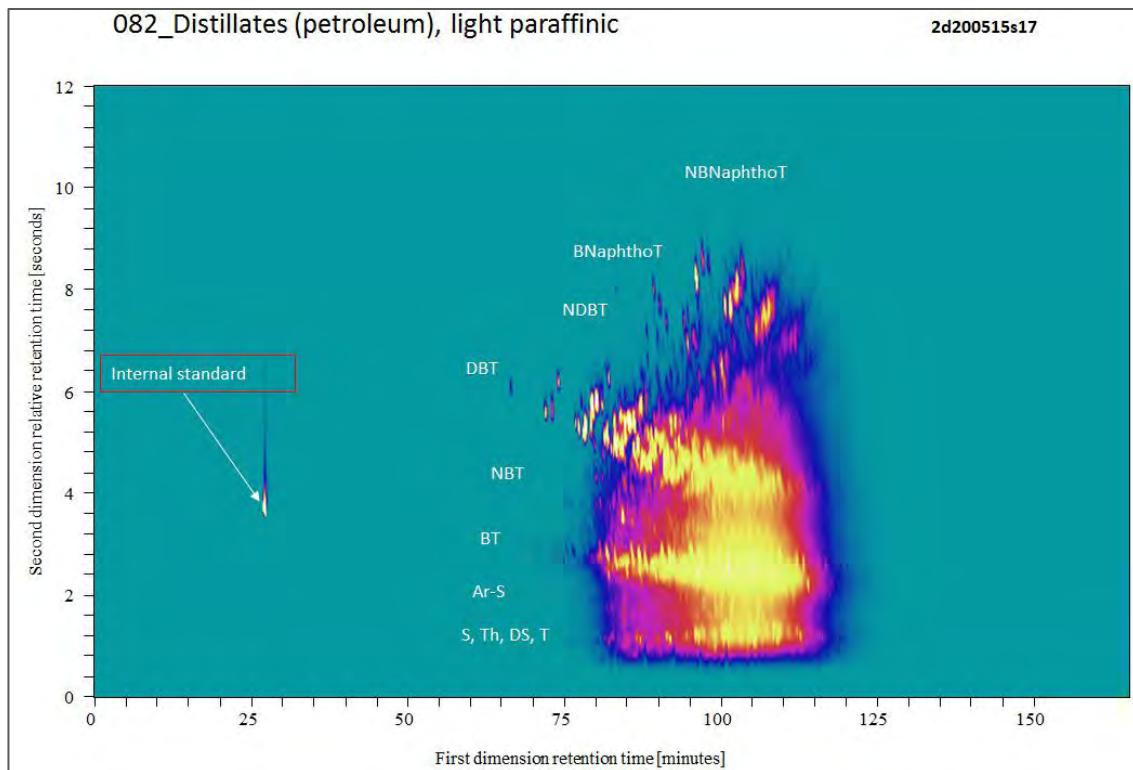
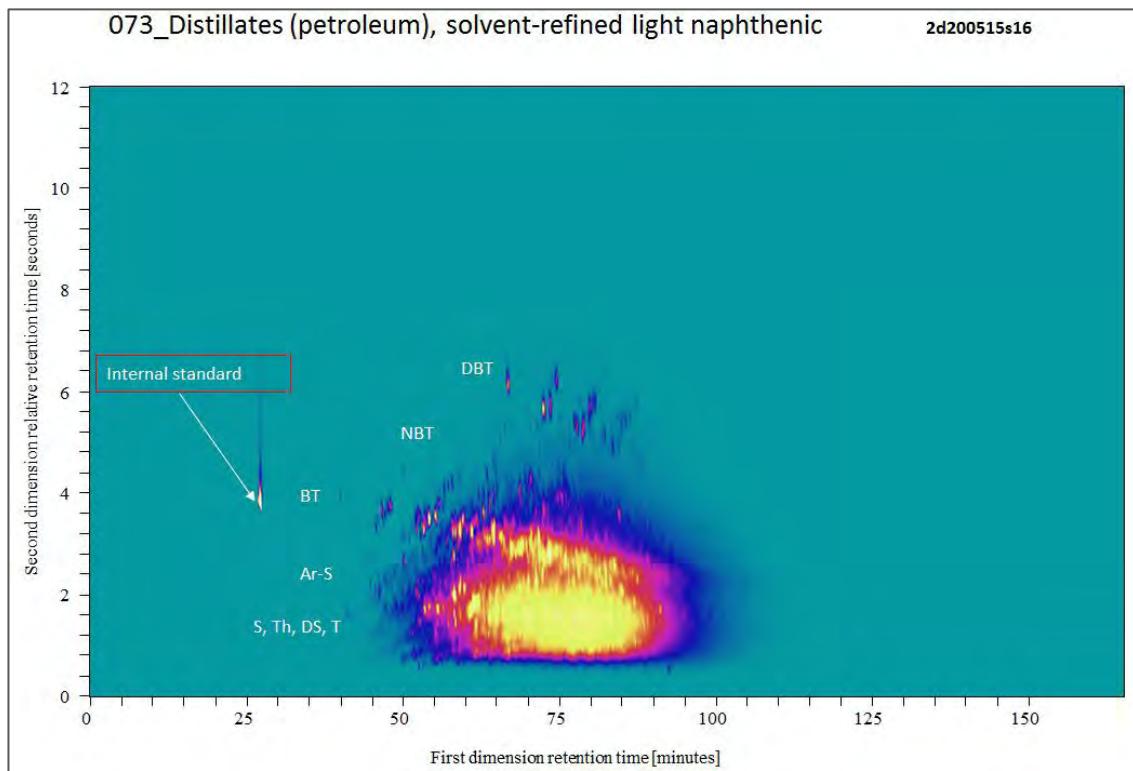


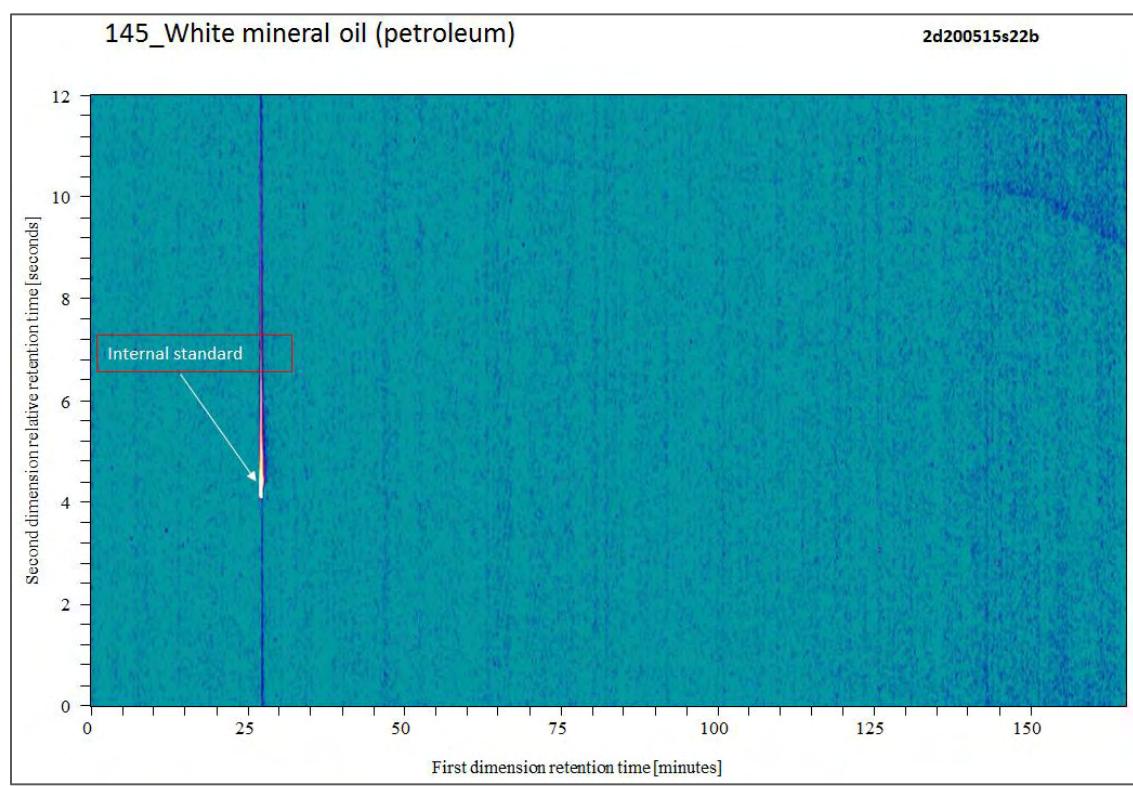
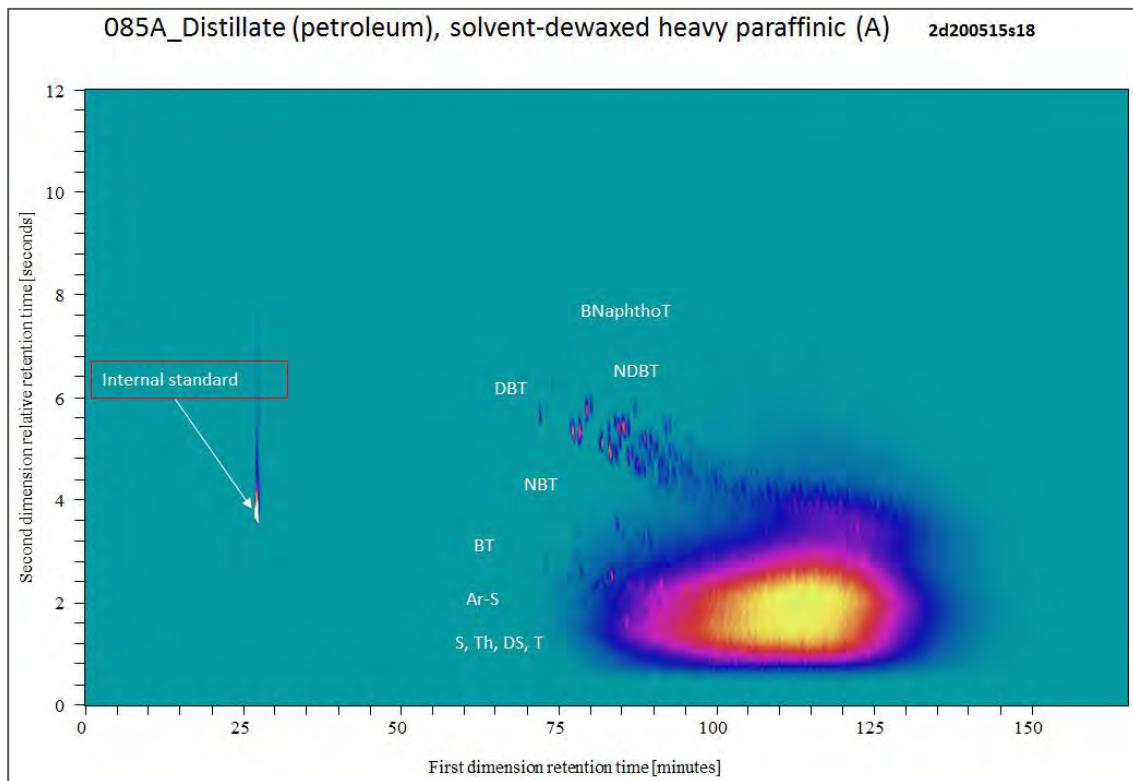
175_Condensate (petroleum), vacuum tower

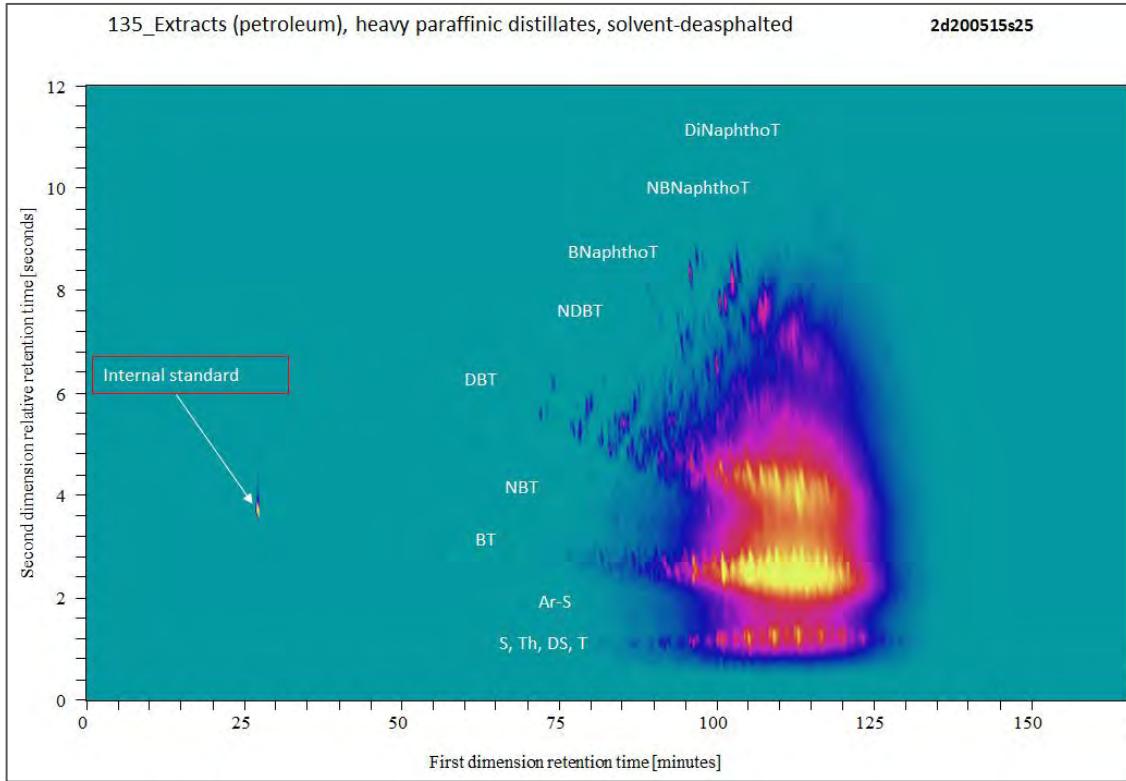
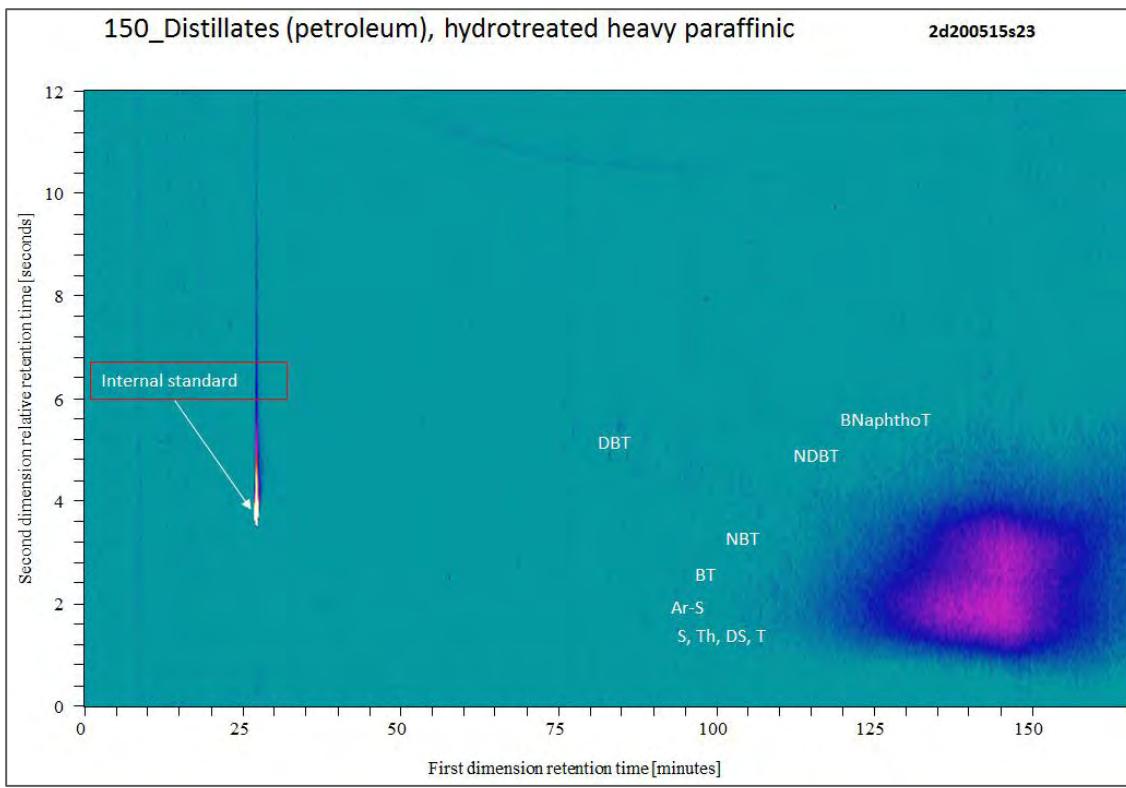
2d200515s13

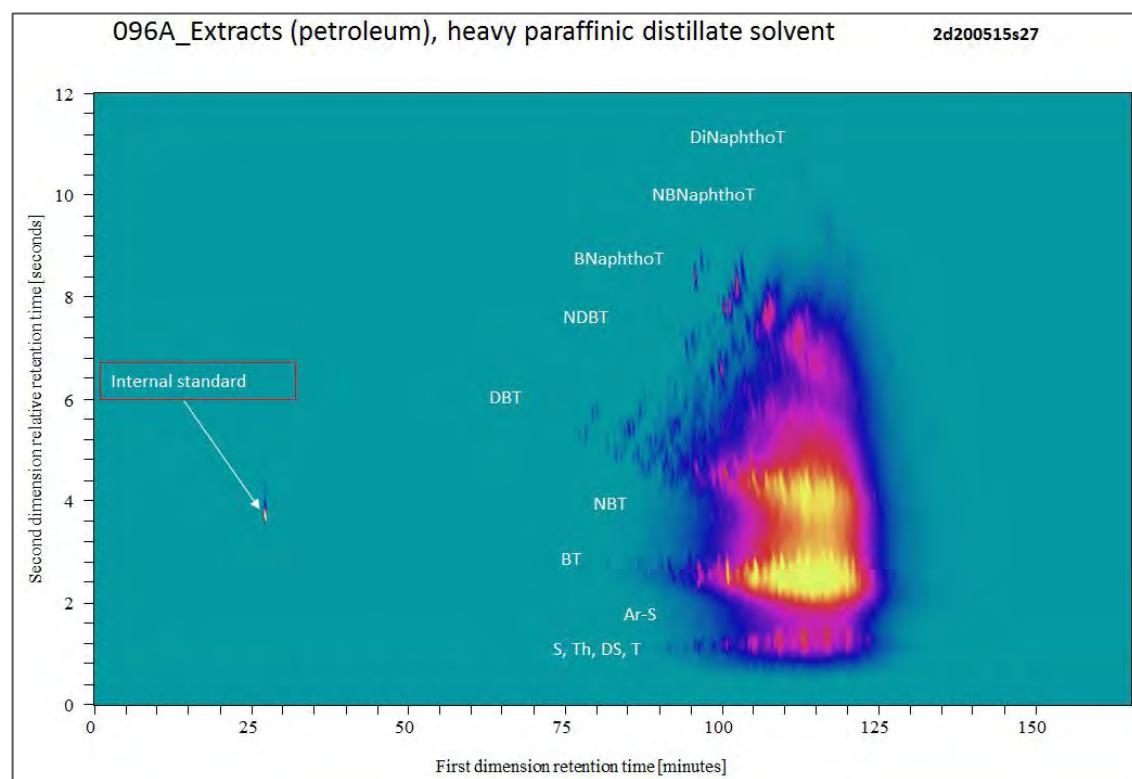
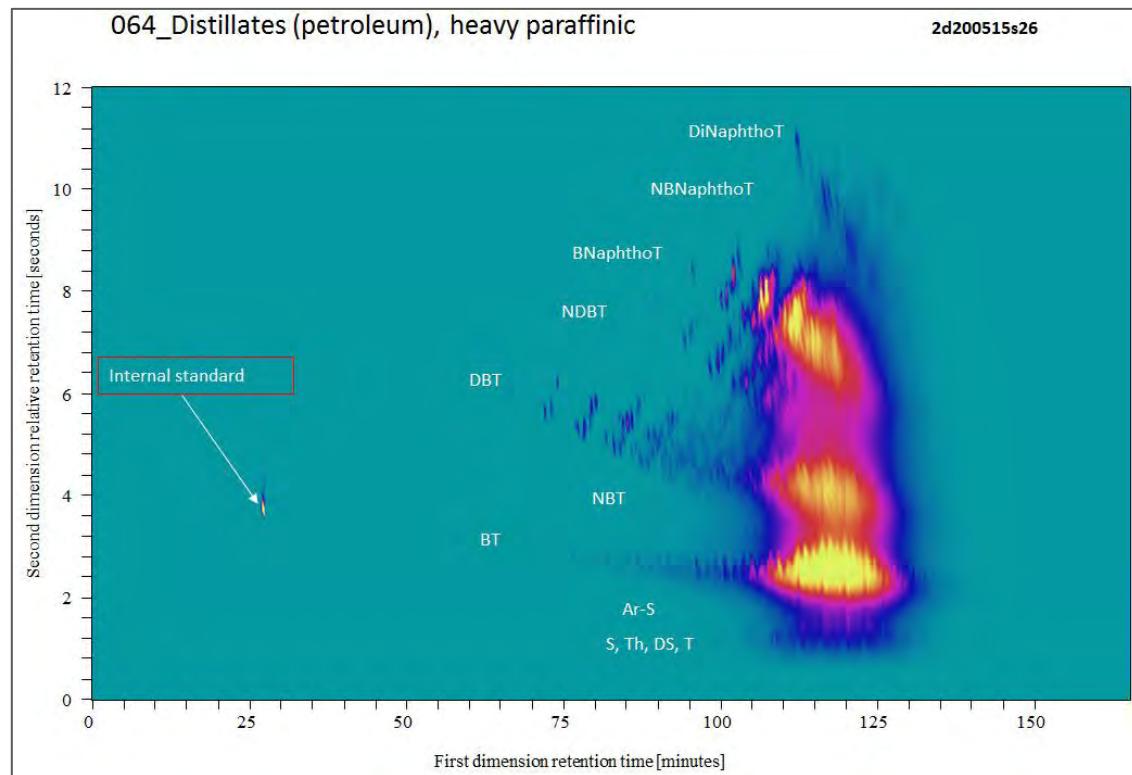


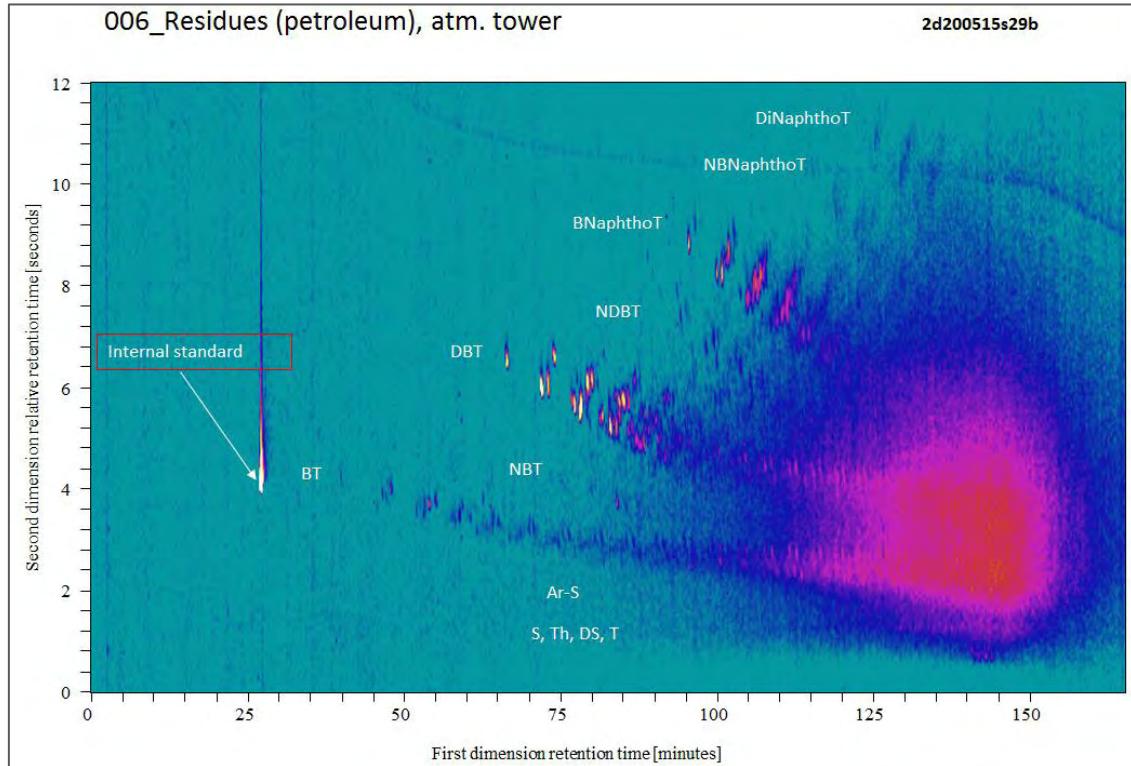
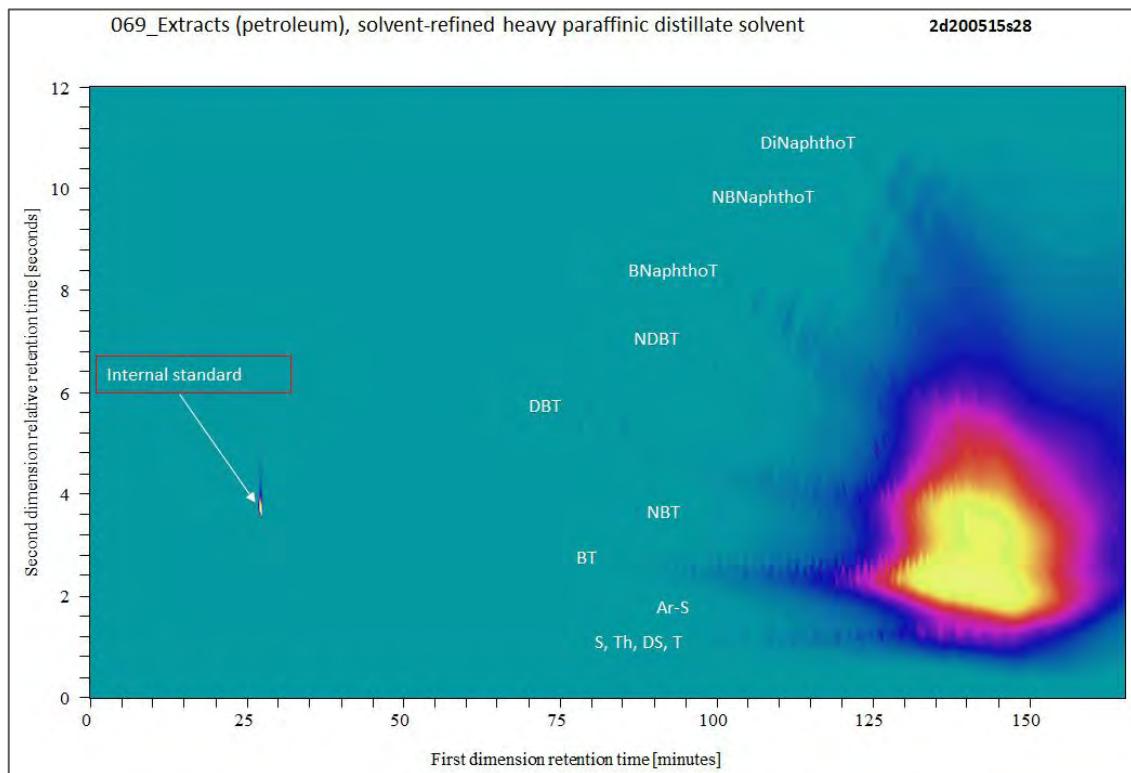


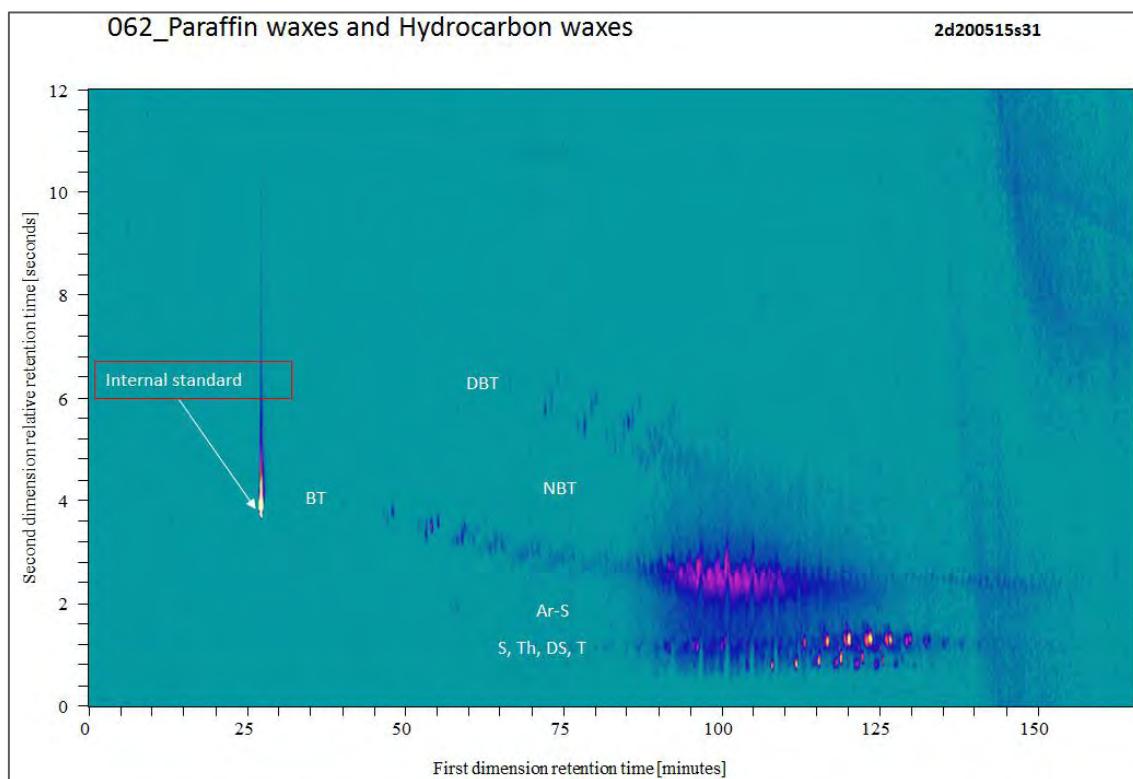
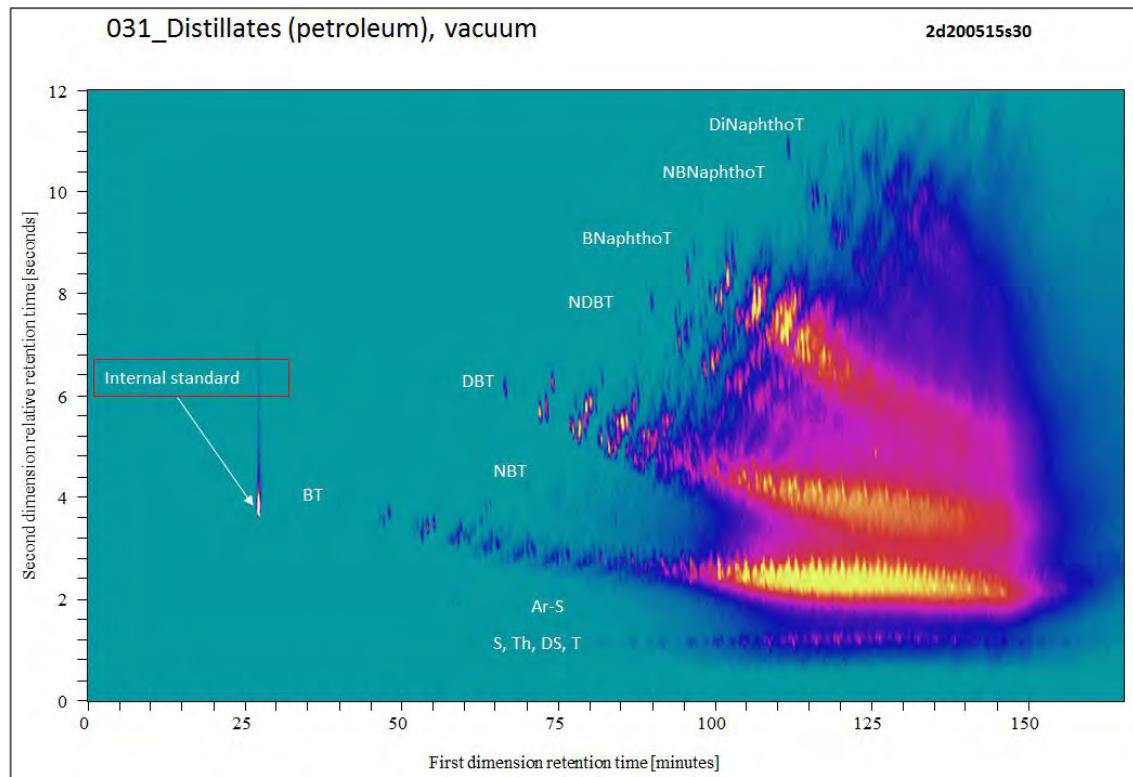


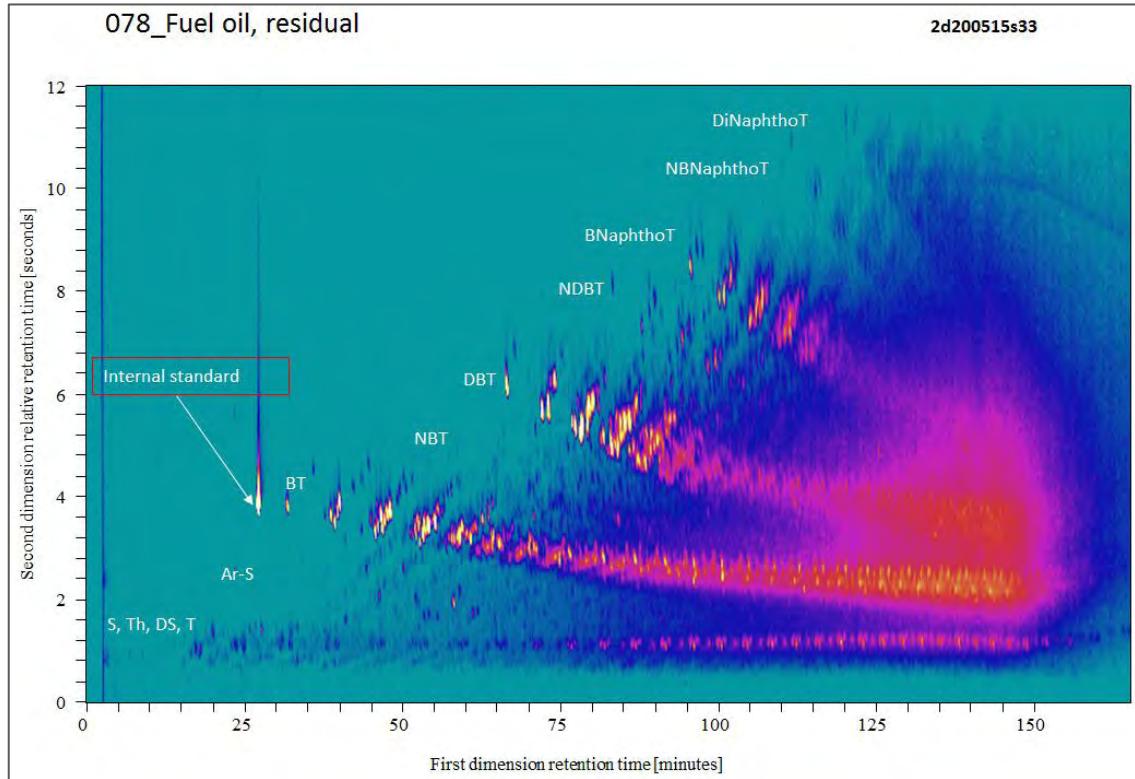
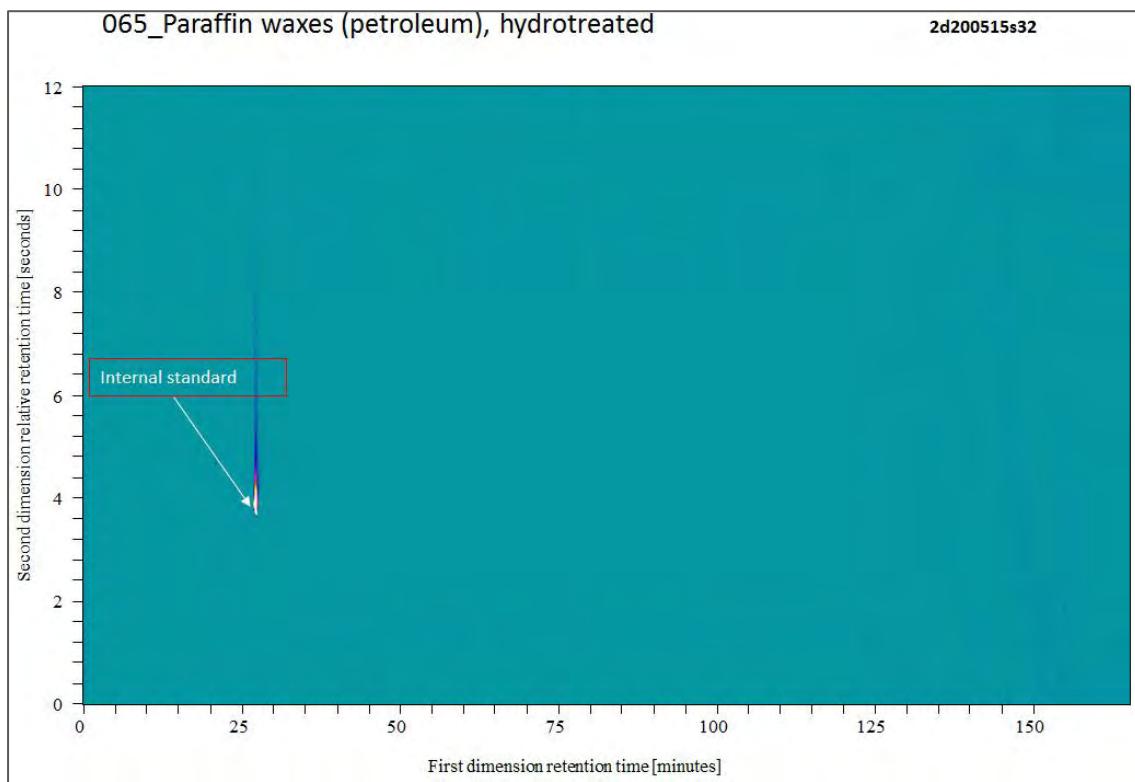


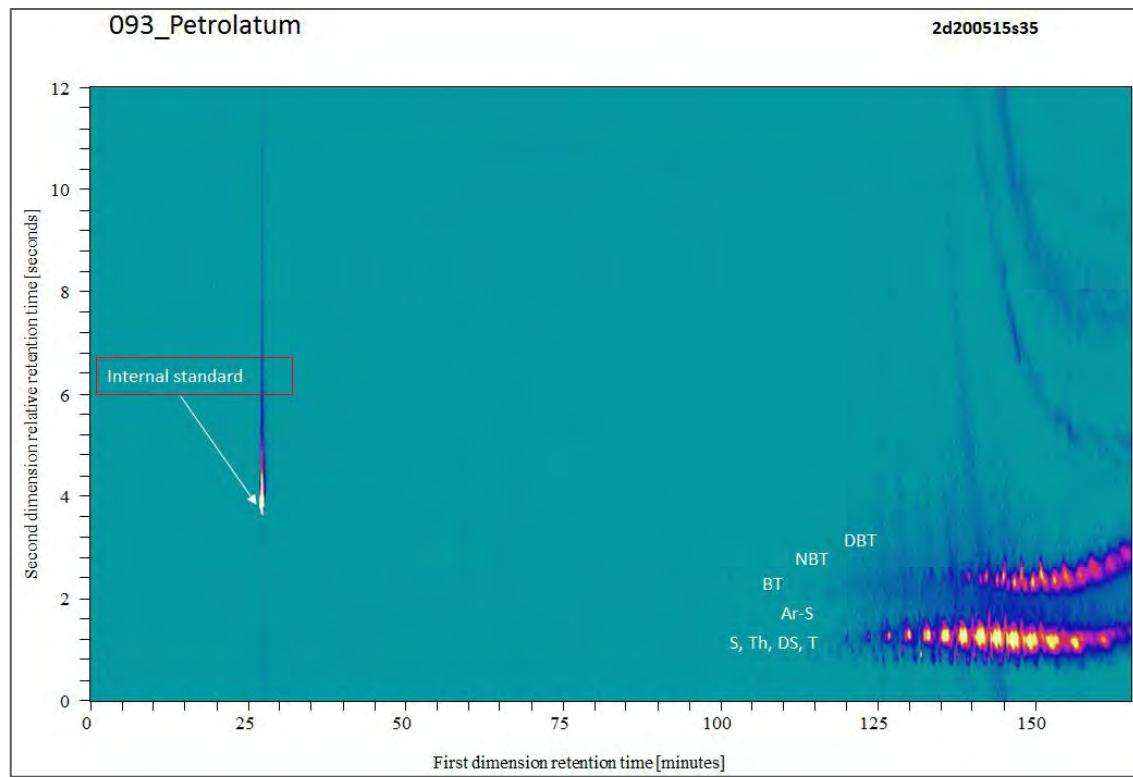
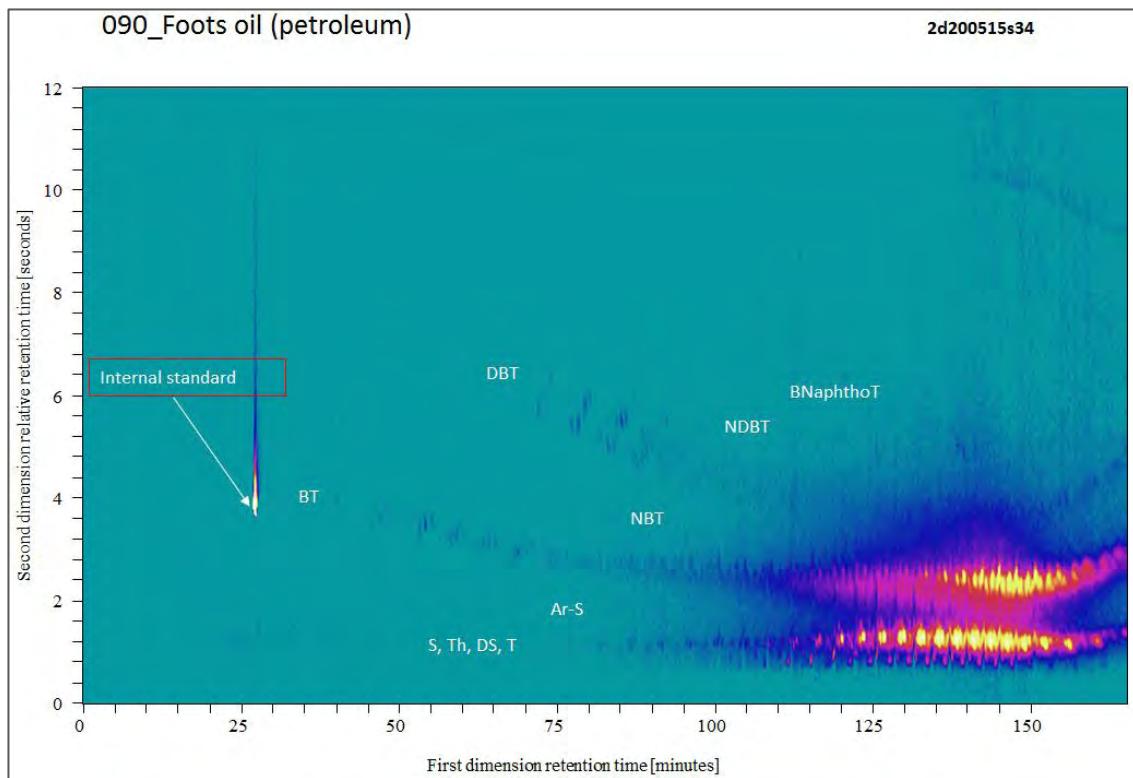






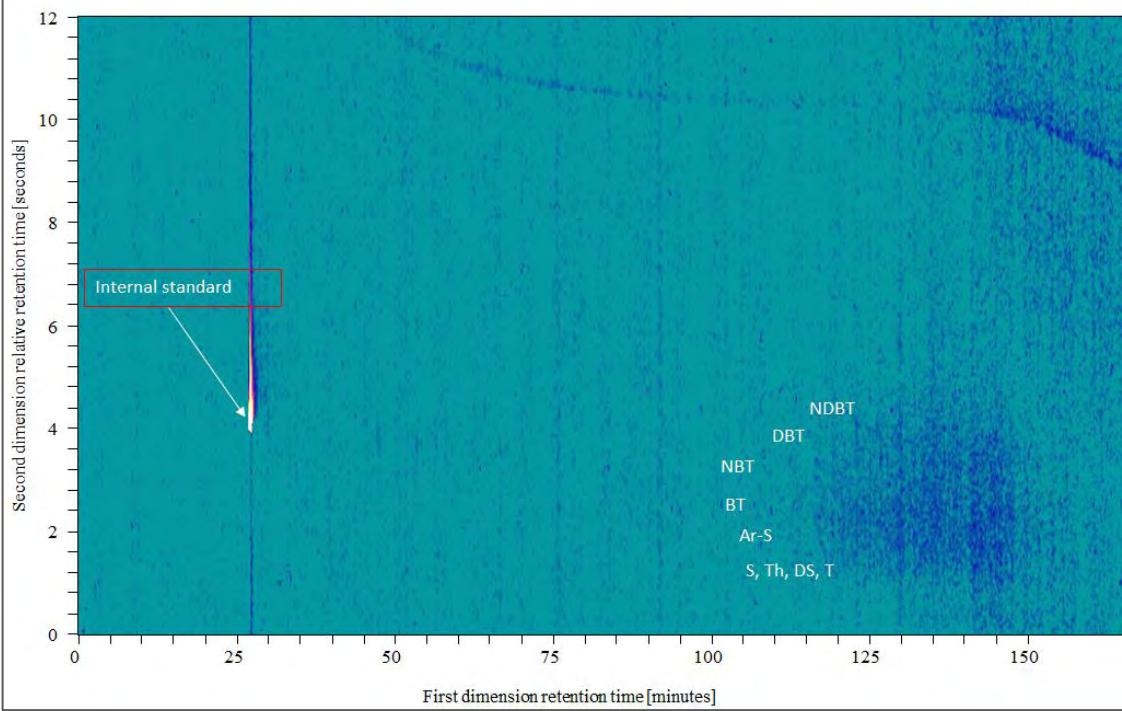






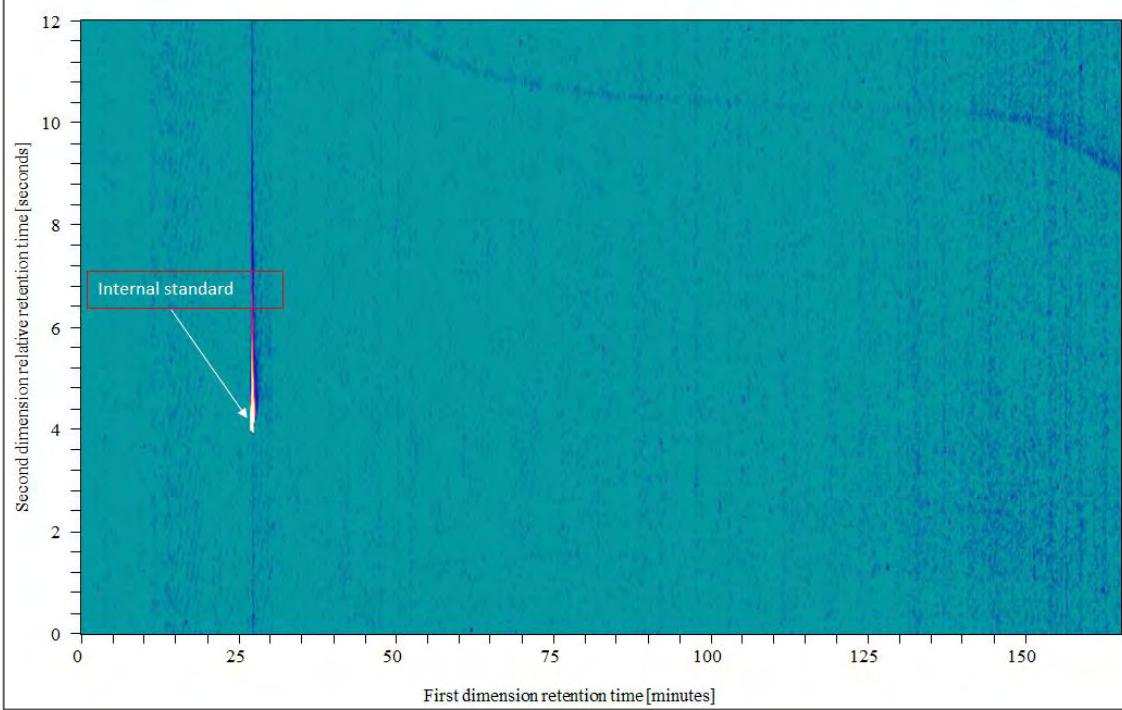
109_Foots oil (petroleum), hydrotreated

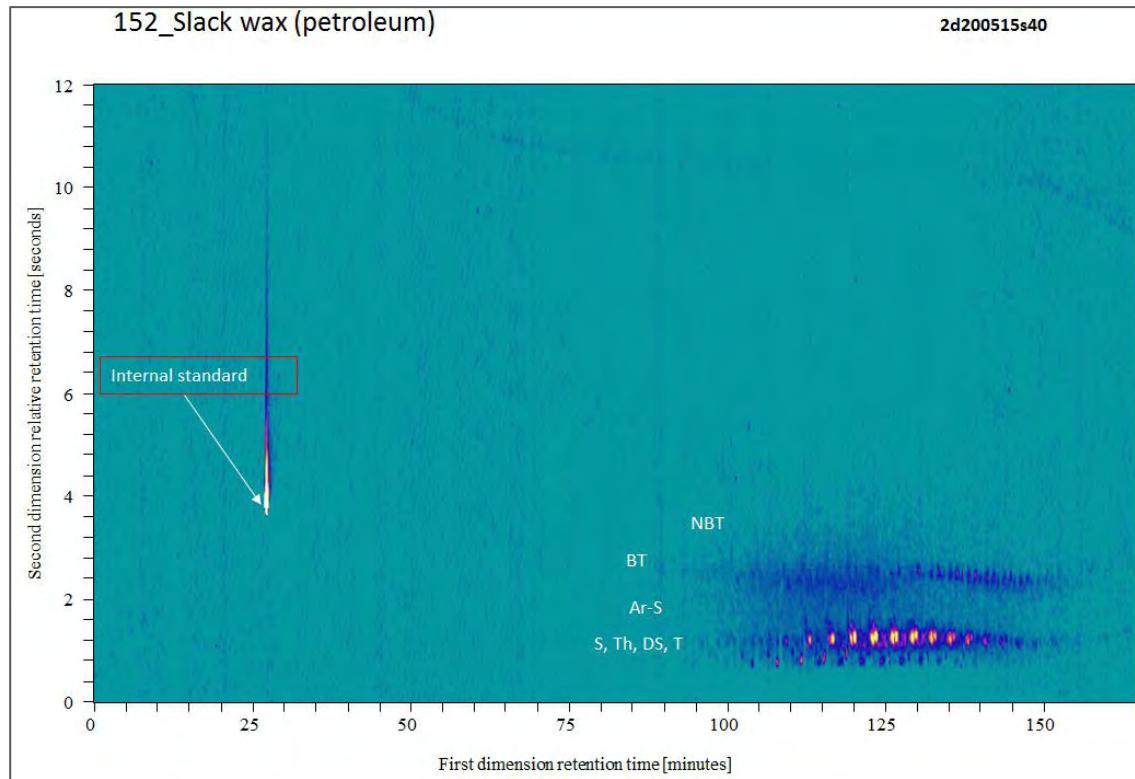
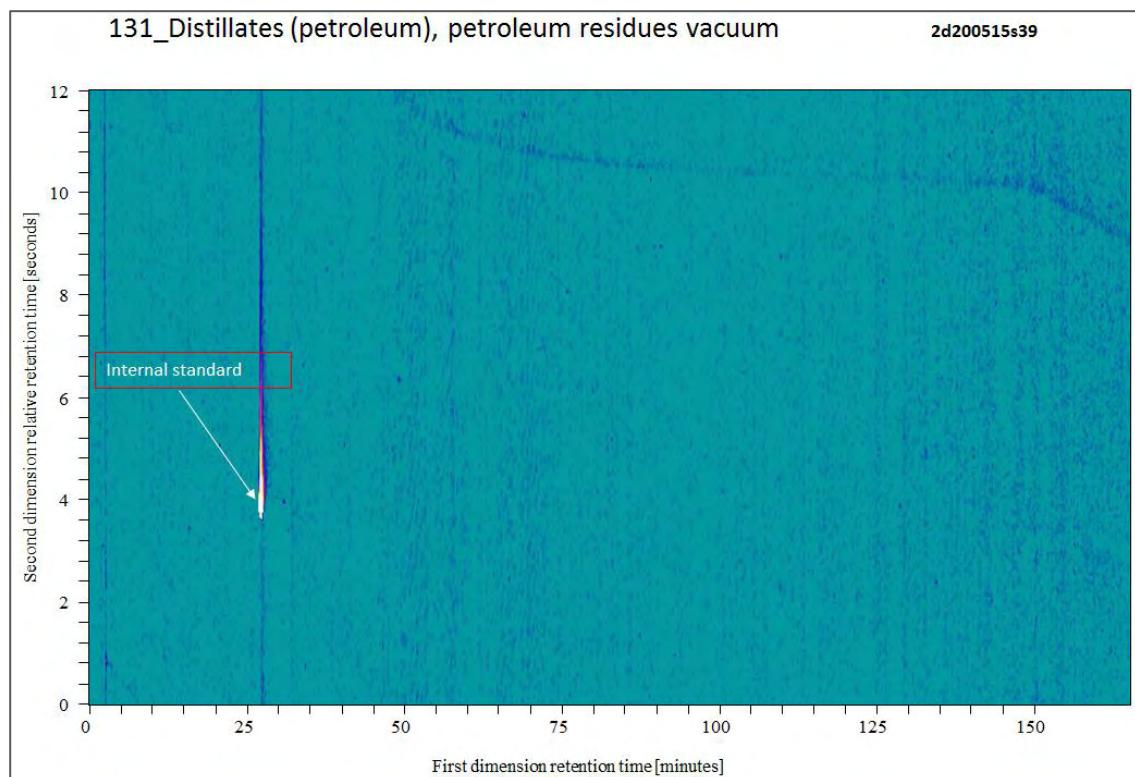
2d200515s37b

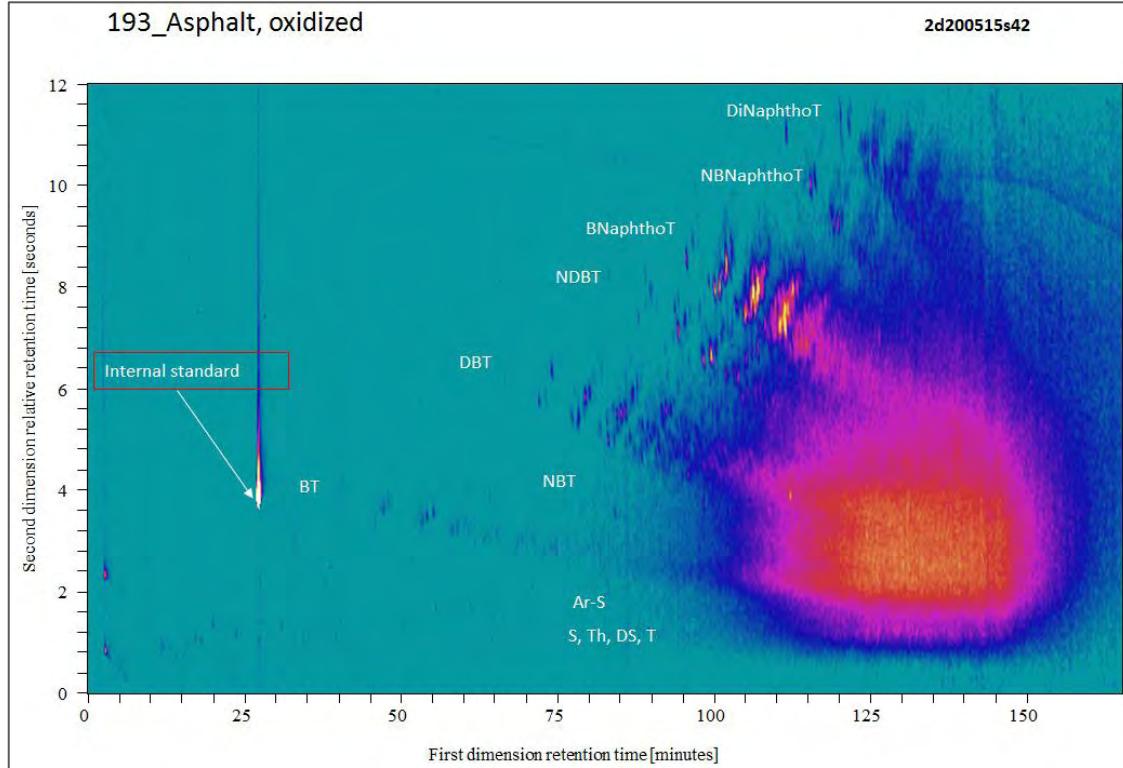
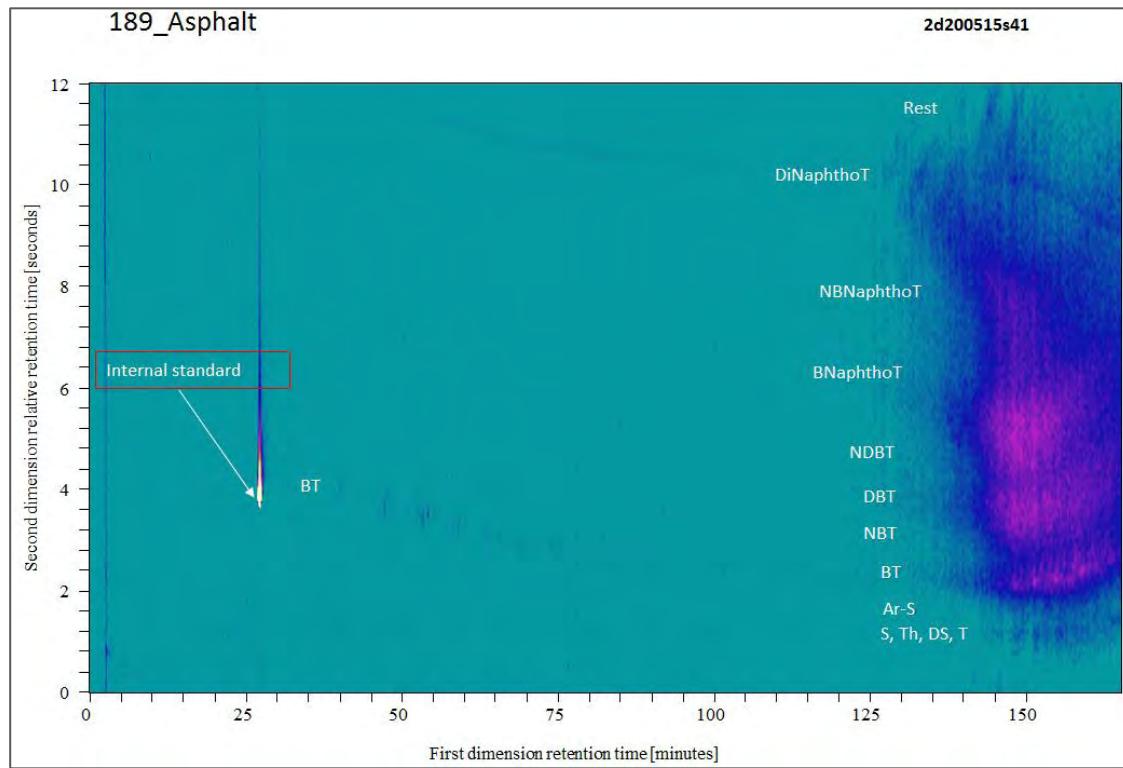


111_Petrolatum (petroleum), hydrotreated

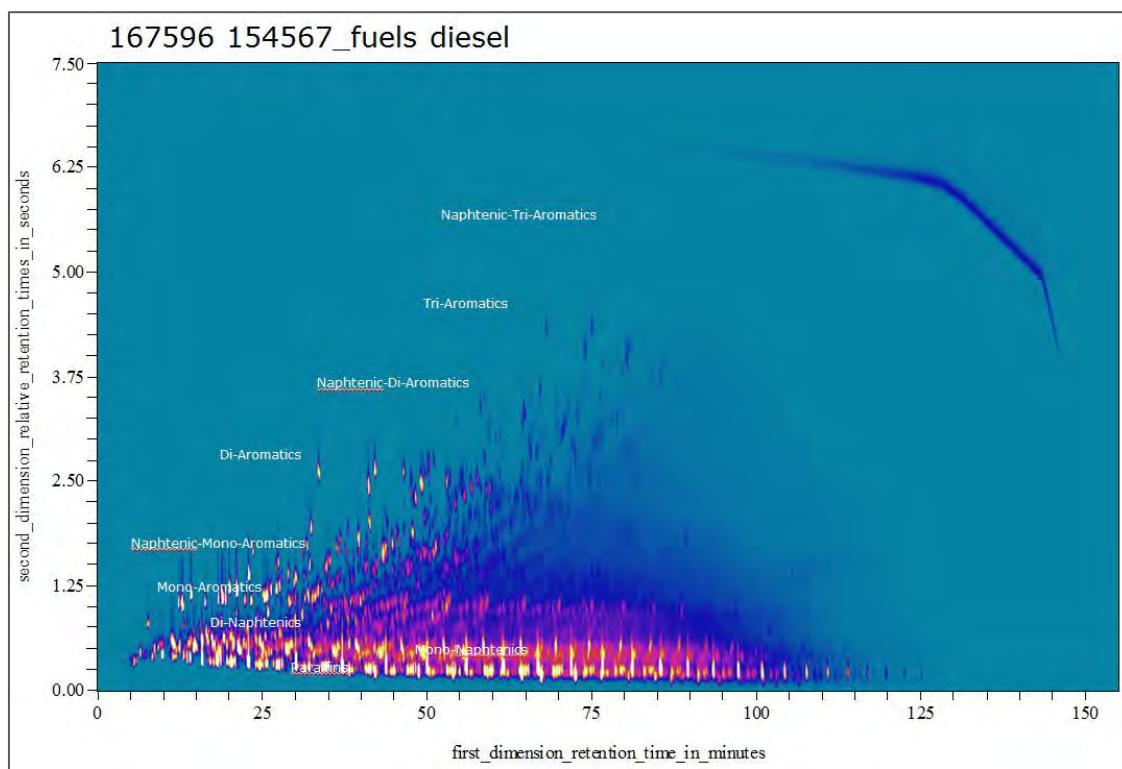
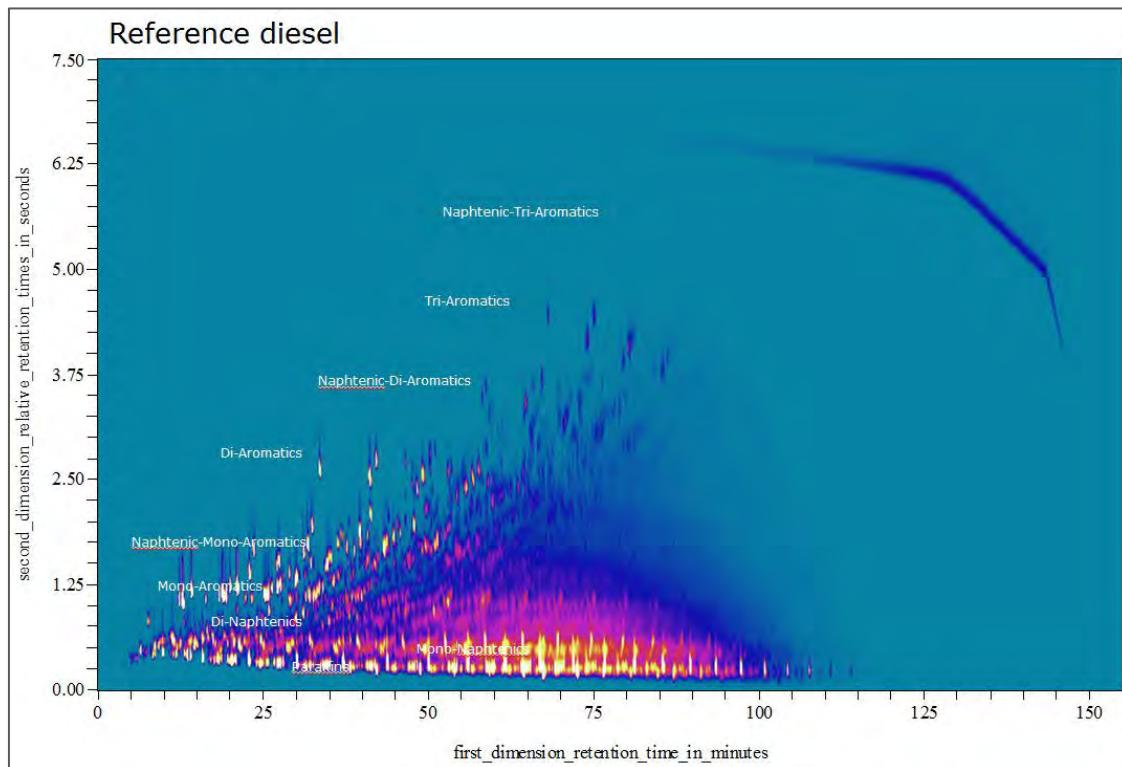
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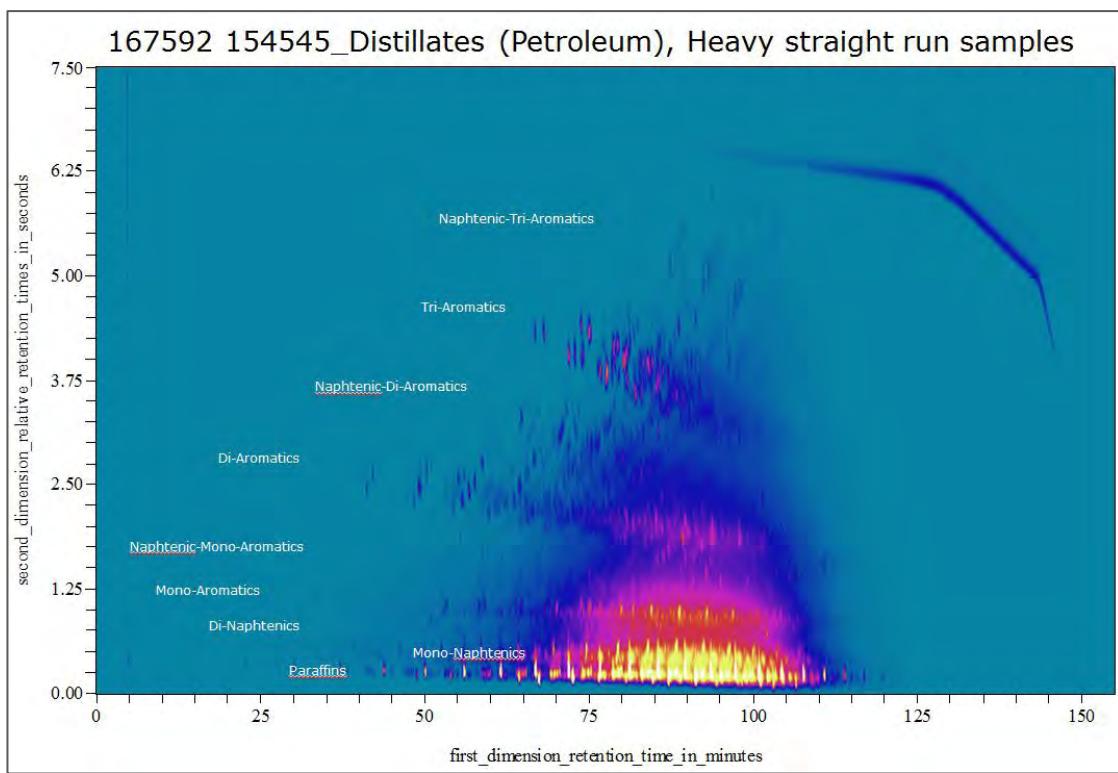
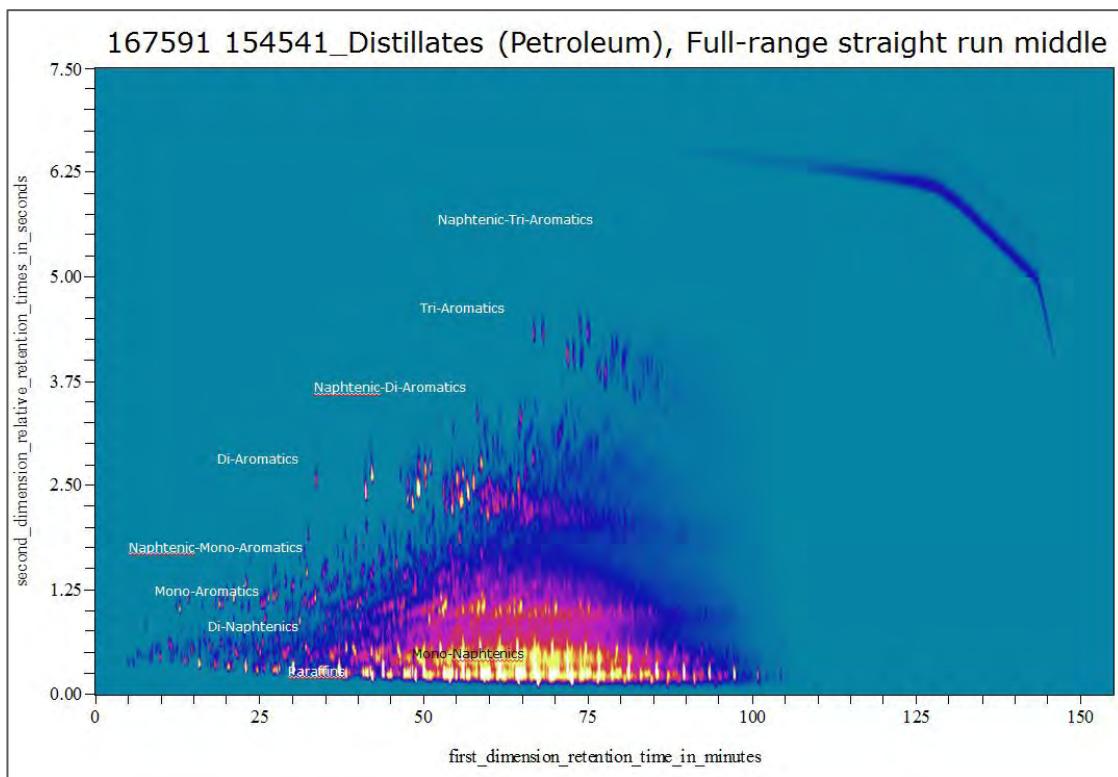


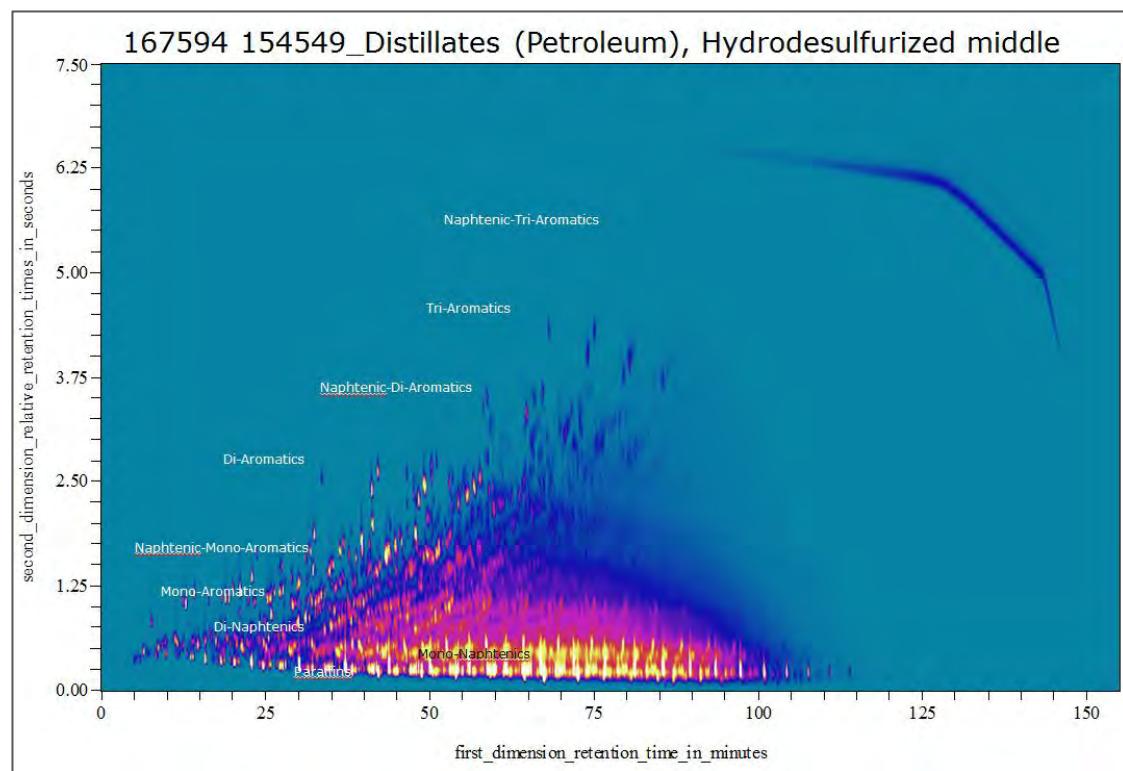
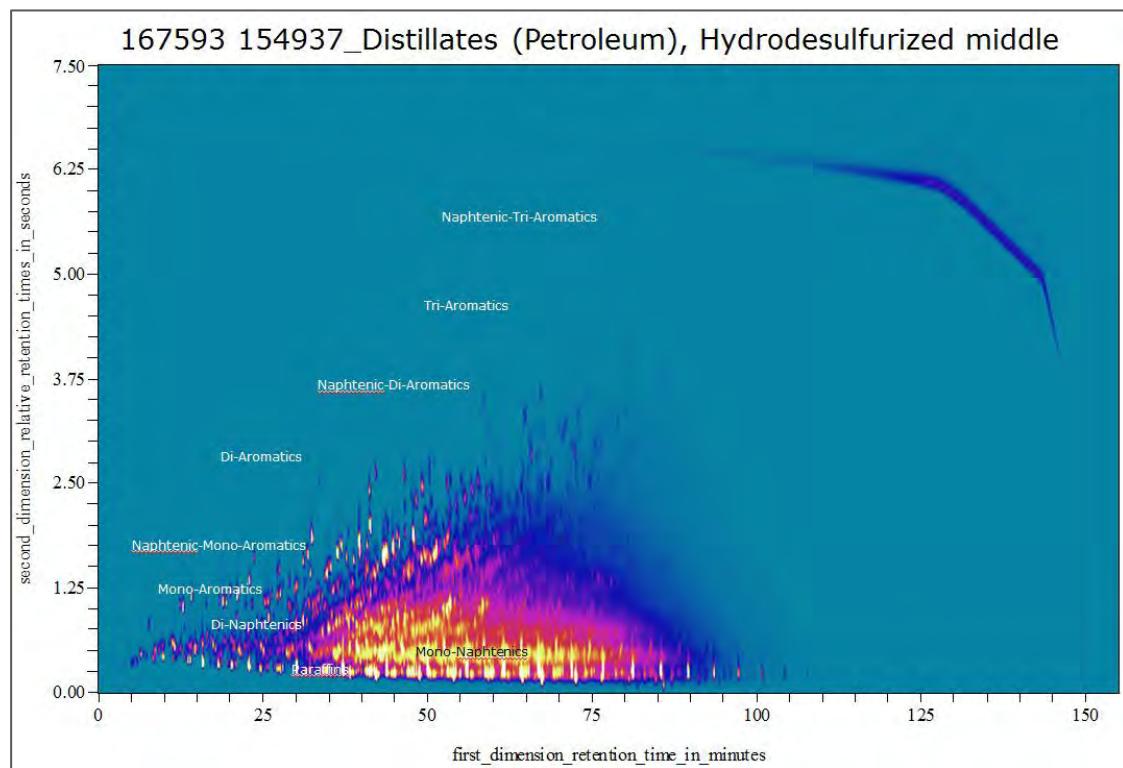




APPENDIX 3: OXYGEN GROUP TYPE GCxGC-FID CHROMATOGRAMS







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