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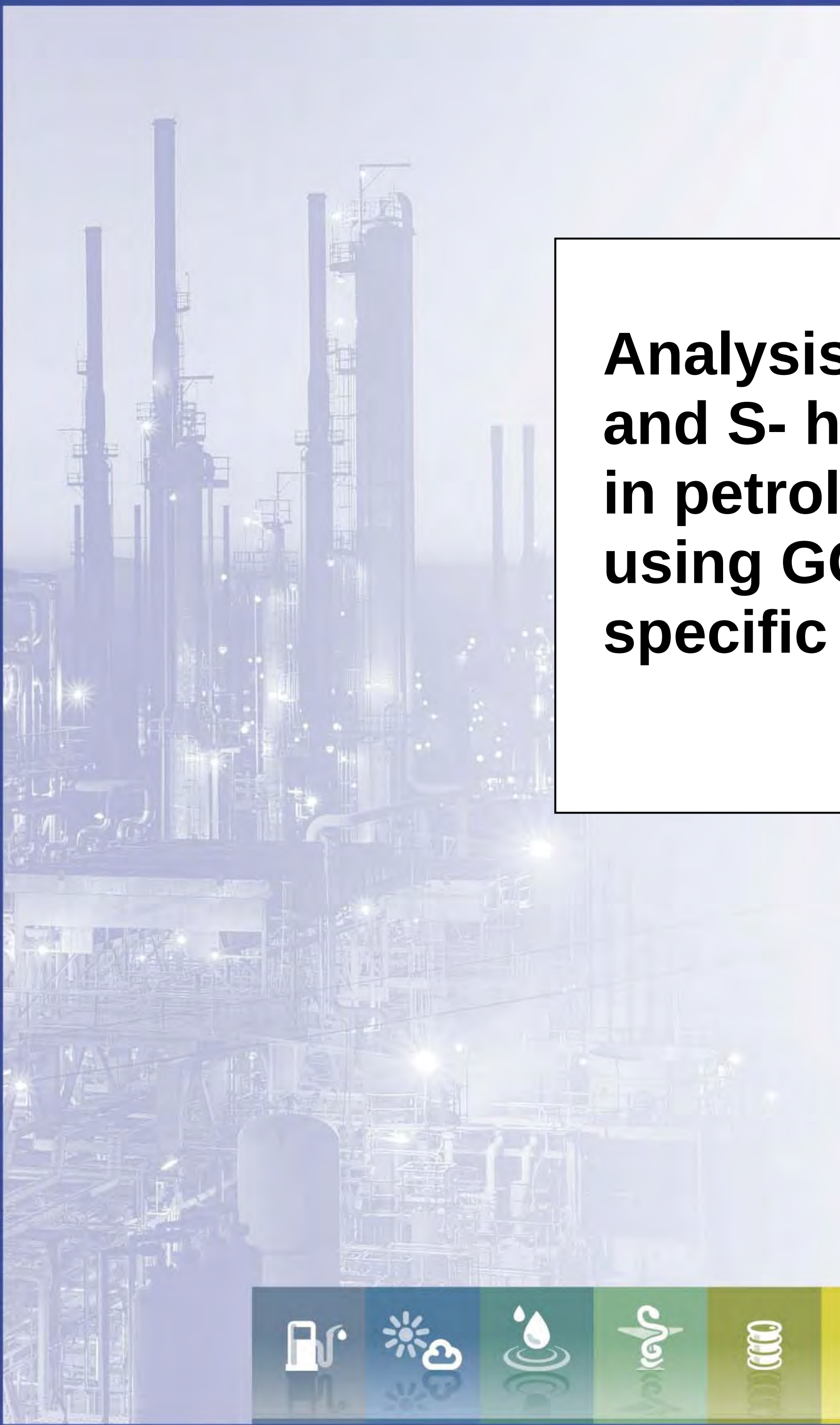

Analysis of N-, O-, and S- heterocyclics in petroleum products using GCxGC with specific detection

Environmental science for the European refining industry

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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-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). 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

This report is available as an Adobe pdf file on the Concawe website (www.concawe.org).

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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 (GCxGC) 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 NOS H 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 8629	0-81-5	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-deasphalted	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	UDAE
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 9204	5-12-0	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; UDAE: 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, UDAE, 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-B(Carb, Acr)	DB(Carb, Acr)	NDB(Carb, Acr)	Rest	**Total**	
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	**107.6**	0.01%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	<0.1	**273.3**	0.03%
		0.00%	0.00%	0.00%	0.00%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	<0.1	**0.8**	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), Hydrodesulfurized middle	154549	<0.1	<0.1	<0.1	<0.1	18.1 (100%)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**18.1**	0.00%
		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	**849.2**	0.08%
		0.00%	0.00%	0.01%	0.01%	0.04%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%		
Fuels, Diesel	154567	<0.1	5.1 (7.07%)	8.1 (11.23%)	5.3 (7.35%)	48.7 (67.55%)	4.9 (6.8%)	<0.1	<0.1	<0.1	<0.1	<0.1	**72.1**	0.01%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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	21.8 (4.3%)	**506.9**	0.05%
		0.00%	0.00%	0.01%	0.00%	0.03%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	<0.1	**68.7**	0.01%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	<0.1	**89.4**	0.01%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Naphtha (Petroleum), Hydrodesulfurized light	1174585	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
MK1 diesel fuel	1174588	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		

Sample	Sample ID	Compound class amounts (ppmw N)*											Total	% 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		
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%
		0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	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	1174609	<0.1	36.5 (7.70%)	138.9 (29.29 %)	8.4 (1.77%)	290.5 (61.25 %)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**474.3**	0.05%
		0.00%	0.00%	0.01%	0.00%	0.03%	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%
		0.00%	0.00%	0.01%	0.00%	0.03%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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%
		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), 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%
		0.00%	0.00%	0.00%	0.00%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	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), 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%
		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 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%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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	Total	
Distillate (petroleum), Hydrotreated heavy paraffinic	1174614	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalted	1174611	7.4 (0.95%)	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	<0.1	<0.1	**780.4**	0.08%
		0.00%	0.00%	0.01%	0.01%	0.03%	0.01%	0.02%	0.00%	0.00%	0.00%	0.00%		
Distillates (petroleum), heavy paraffinic	1174590	<0.1	<0.1	7.3 (2.46%)	8.9 (3.00%)	63.3 (21.37%)	46.7 (15.77%)	154.8 (52.26%)	15.2 (5.13%)	<0.1	<0.1	<0.1	**296.2**	0.03%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.02%	0.00%	0.00%	0.00%	0.00%		
Extracts (petroleum), heavy paraffinic distillate solvent	1174604**	<0.1	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	<0.1	<0.1	**811.8**	0.08%
		0.00%	0.00%	0.00%	0.01%	0.03%	0.01%	0.02%	0.00%	0.00%	0.00%	0.00%		
Extracts (petroleum), solvent-refined heavy paraffinic distillate solvent	1174592**	<0.1	<0.1	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	<0.1	<0.1	**44.6**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Residues (petroleum), atm. tower	1174583**	<0.1	<0.1	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	<0.1	<0.1	**301.6**	0.03%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.01%	0.01%	0.00%	0.00%	0.00%		
Distillates (petroleum), vacuum	1174586**	<0.1	<0.1	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	**562.1**	0.06%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.01%	0.02%	0.01%	0.00%	0.00%	0.00%		
Paraffin waxes and Hydrocarbon waxes	1174589	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Paraffin waxes (petroleum), Hydrotreated	1174591	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Fuel oil, residual	1174595**	<0.1	<0.1	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	**278.4**	0.03%
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%		
Foots oil (petroleum)	1174602**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Petrolatum	1174603**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Foots oil (petroleum), Hydrotreated	1174606**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Petrolatum (petroleum), Hydrotreated	1174607**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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	**Total**	
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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Asphalt	1174621**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.1**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		

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); 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	BNaphthoT	NBNaphthoT	DiNaphthoT	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%
		0.17%	0.16%	0.40%	0.09%	0.13%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%		
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%
		0.19%	0.15%	0.49%	0.24%	0.47%	0.07%	0.02%	0.00%	0.00%	0.00%	0.00%		
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%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Distillates (Petroleum), Hydrodesulfurized middle	154549	<0.01	<0.01	0.07 (1.30%)	0.11 (2.04%)	5.24 (97.04%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**5.4**	0.00%
		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	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%
		0.02%	0.04%	0.09%	0.07%	0.16%	0.06%	0.05%	0.01%	0.00%	0.00%	0.00%		
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 (1.115%)	0.31 (0.05%)	<0.01	<0.01	1.68 (0.27%)	<0.01	**615.4**	0.06%
		0.03%	0.01%	0.01%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Fuels, Diesel, NO. 2	154579	6.72 (0.77%)	6.67 (0.77%)	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%
		0.00%	0.00%	0.04%	0.00%	0.04%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**6617.6**	0.66%
		0.02%	0.03%	0.11%	0.07%	0.13%	0.10%	0.10%	0.07%	0.03%	0.00%	0.00%		
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%
		0.02%	0.04%	0.19%	0.11%	0.21%	0.17%	0.19%	0.12%	0.07%	0.00%	0.00%		
Naphtha (petroleum), hydrodesulfurized light	023	1.17 (97.50%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**1.2**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Kerosine (petroleum)	043	532.71 (91.37%)	34.23 (5.87%)	15.32 (2.63%)	<0.01	0.57 (0.10%)	<0.01	<0.01	<0.01	<0.01	<0.01	0.22 (0.04%)	**583.0**	0.06%
		0.05%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		

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	
MK1 diesel fuel	059	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04 (100%)	**0.04**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Naphtha (petroleum), full-range coker	076	1508.53 (82.12%)	74.54 (4.06%)	208.84 (11.37%)	22.13 (1.20%)	19.19 (1.04%)	<0.01	<0.01	<0.01	<0.01	3.67 (0.20%)	<0.01	**1836.9**	0.18%
		0.15%	0.01%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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	<0.01	**9.4**	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	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	<0.01	**2853.3**	0.29%
		0.00%	0.00%	0.16%	0.01%	0.11%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Distillates (petroleum), hydrodesulfurized middle coker	012	<0.01	1.13 (1.87%)	2.07 (3.42%)	2.70 (4.46%)	51.41 (84.98%)	3.12 (5.16%)	0.10 (0.17%)	<0.01	<0.01	<0.01	<0.01	**60.5**	0.01
		0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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%
		0.06%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Gasoline	144	7.58 (99.74%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 (0.79%)	**7.6**	0.00%
		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), 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	<0.01	<0.01	<0.01	**11023.0**	1.10%
		0.21%	0.15%	0.39%	0.12%	0.22%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	0.27 (0.01%)	**4638.7**	0.46%
		0.08%	0.07%	0.17%	0.04%	0.10%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	<0.01	<0.01	2.91 (0.03%)	**9679.5**	0.97%
		0.17%	0.14%	0.40%	0.06%	0.18%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%		
Paraffin oils (petroleum), catalytic dewaxed light	154	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**<0.01**	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), solvent-refined light naphthenic	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	**6237.7**	0.62%
		0.14%	0.25%	0.17%	0.04%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		

Sample	Sample ID	Compound class amounts (ppmw S)*											Total	% of total sample mass
		S, Th, DS, T	Ar-S	BT	NBT	DiBT	NDiBT	BNaphthoT	NBNaphthoT	DiNaphthoT	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	<0.01	**6724.5**	0.67%
		0.07%	0.06%	0.16%	0.09%	0.19%	0.06%	0.03%	0.00%	0.00%	0.00%	0.00%		
Distillate (petroleum), solvent-dewaxed heavy paraffinic (A)	085A	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%
		0.04%	0.05%	0.07%	0.02%	0.02%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	**<0.01**	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), 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%
		0.00%	0.00%	0.01%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalted	135	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%
		0.29%	0.20%	0.76%	0.41%	0.80%	0.46%	0.29%	0.02%	0.00%	0.00%	0.00%		
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%
		0.08%	0.06%	0.56%	0.20%	0.57%	0.40%	0.66%	0.08%	0.01%	0.00%	0.00%		
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%
		0.21%	0.11%	0.71%	0.34%	0.78%	0.46%	0.35%	0.03%	0.00%	0.00%	0.00%		
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%
		0.10%	0.11%	0.55%	0.22%	0.51%	0.29%	0.32%	0.18%	0.12%	0.00%	0.00%		
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%
		0.01%	0.01%	0.03%	0.02%	0.04%	0.03%	0.03%	0.01%	0.01%	0.00%	0.00%		
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%
		0.07%	0.06%	0.42%	0.18%	0.43%	0.30%	0.40%	0.17%	0.10%	0.00%	0.00%		

Sample	Sample ID	Compound class amounts (ppmw S)*											Total	% of total sample mass
		S, Th, DS, T	Ar-S	BT	NBT	DiBT	NDiBT	BNaphthoT	NBNaphthoT	DiNaphthoT	Rest	ES		
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%
		0.02%	0.01%	0.03%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Paraffin waxes (petroleum), hydrotreated	065	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**<0.01**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Fuel oil, residual	078	777.57 (7.58%)	589.82 (5.75%)	2271.04 (22.13%)	955.67 (9.31%)	2018.22 (19.66%)	1180.47 (11.50%)	1380.95 (13.45%)	690.79 (6.73%)	398.96 (3.89%)	<0.01	<0.01	**10263.5**	1.03%
		0.08%	0.06%	0.23%	0.10%	0.20%	0.12%	0.14%	0.07%	0.04%	0.00%	0.00%		
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	<0.01	<0.01	<0.01	**1903.4**	0.19%
		0.06%	0.01%	0.07%	0.01%	0.02%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%		
Petrolatum	093**	338.79 (54.81%)	36.29 (5.87%)	200.93 (32.51%)	22.47 (3.64%)	19.62 (3.17%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**618.1**	0.06%
		0.03%	0.00%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
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	<0.01	<0.01	<0.01	<0.01	**71.0**	0.01%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Petrolatum (petroleum), hydrotreated	111**	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**<0.01**	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), petroleum residues vacuum	131**	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**<0.01**	0.00%
		0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		
Slack wax (petroleum)	152	141.81 (51.18%)	27.50 (9.92%)	92.78 (33.48%)	14.99 (5.41%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**277.1**	0.00%
		0.01%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	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	**1613.7**	0.16%
		0.00%	0.00%	0.02%	0.01%	0.02%	0.02%	0.03%	0.03%	0.03%	0.00%	0.00%		
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	<0.01	**5824.9**	0.58%
		0.03%	0.03%	0.09%	0.06%	0.10%	0.09%	0.11%	0.05%	0.03%	0.00%	0.00%		

S,Th,DS,T: Sulphides, Thiols, DiSulphides, Thiophenes; Ar-S: Aryl-sulphides; BT: Benzothiophenes; NBT: Naphthenic-Benzothiophenes; DiBT: Di-Benzothiophenes; NDiBT: Naphtenic-di-Benzothiophenes; BNaphthoT: Benzo-Naphthothiophenes; NBNaphthoT: Naphthenic-Benzo-Naphthothiophenes; DiNaphthoT: DiNaphthothiophenes; 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

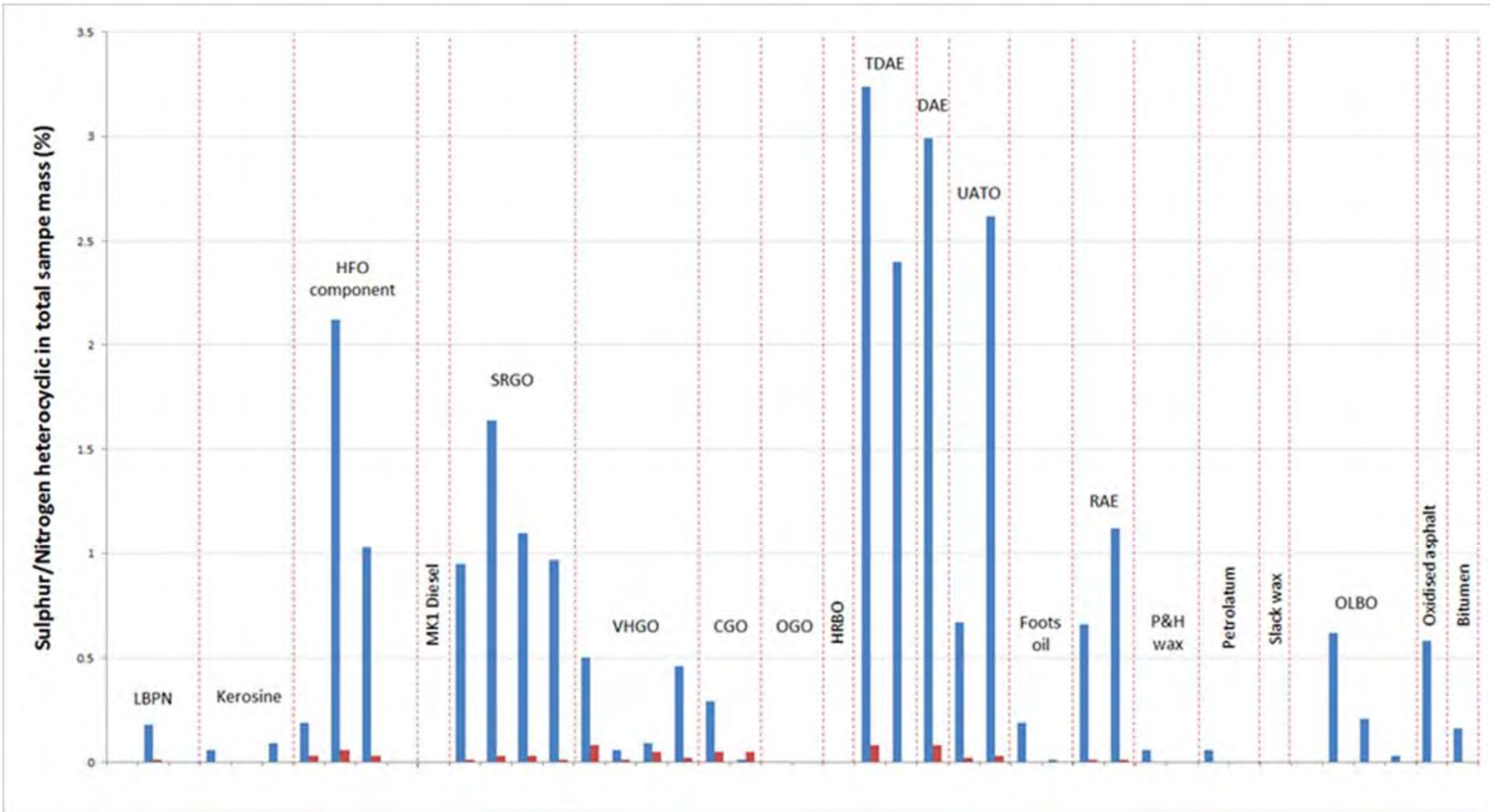
S, Th, DS and T = Sulphides, Thiols, DiSulphides and Thiophenes
Ar-S = Aryl-Sulphides
BT= Benzothiophenes
NBT = Naphthenic-Benzothiophenes
DiBT = Di-Benzothiophenes
NDiBT = Naphthenic-Di-Benzothiophenes
BNaphthoT = Benzo-Naphthothiophenes
NBNaphthoT = Naphthenic-Benzo-Naphthothiophenes
DiNaphthoT = DiNaphthothiophenes
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; UDAE: 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
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 Nap	hthenic-Benzo-Naphthothiophenes
NBT	Naphthenic-Benzothiophenes
NDB(Carb, Acr)	Naphthenic-Dibenzo(Carbazoles, Acridines)
NDiBT Nap	hthenic-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 Regi	stration, Evaluation, Authorisation and re striction 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
UDAE	Untreated Distillate Aromatic Extracts
VHGO	Vacuum gas oils, Hydrocracked Gas Oils and distillate fuels

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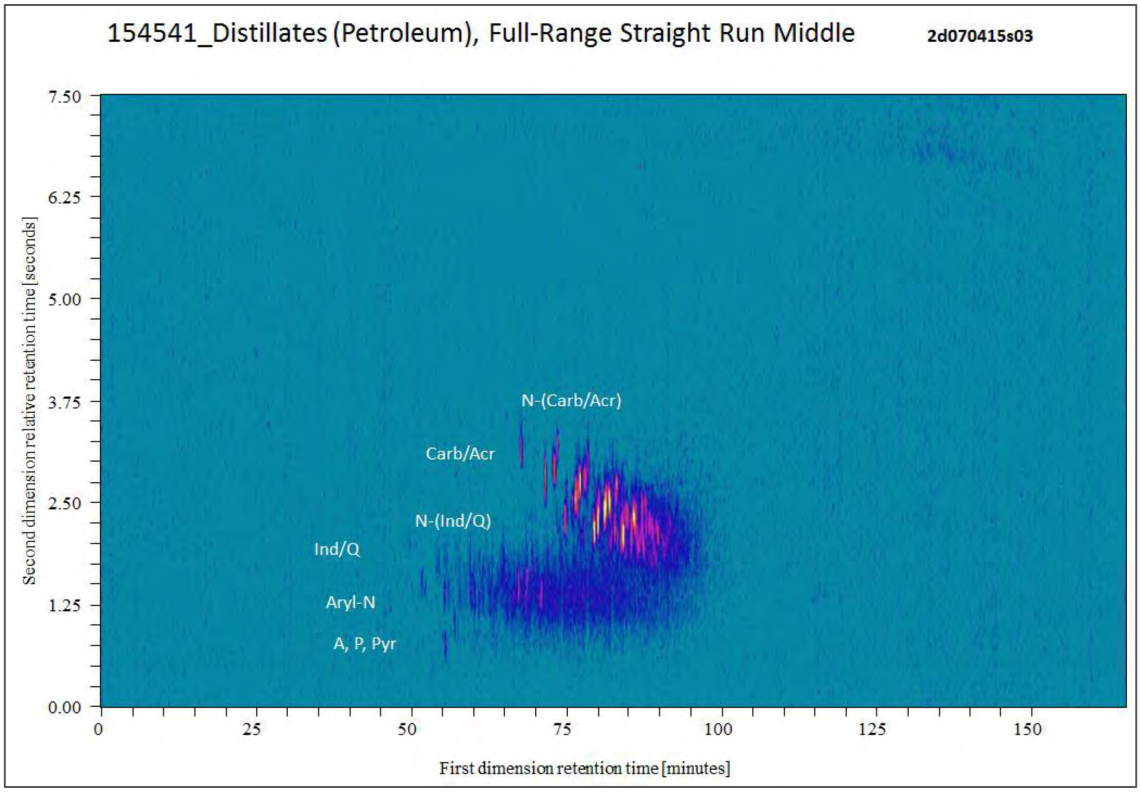
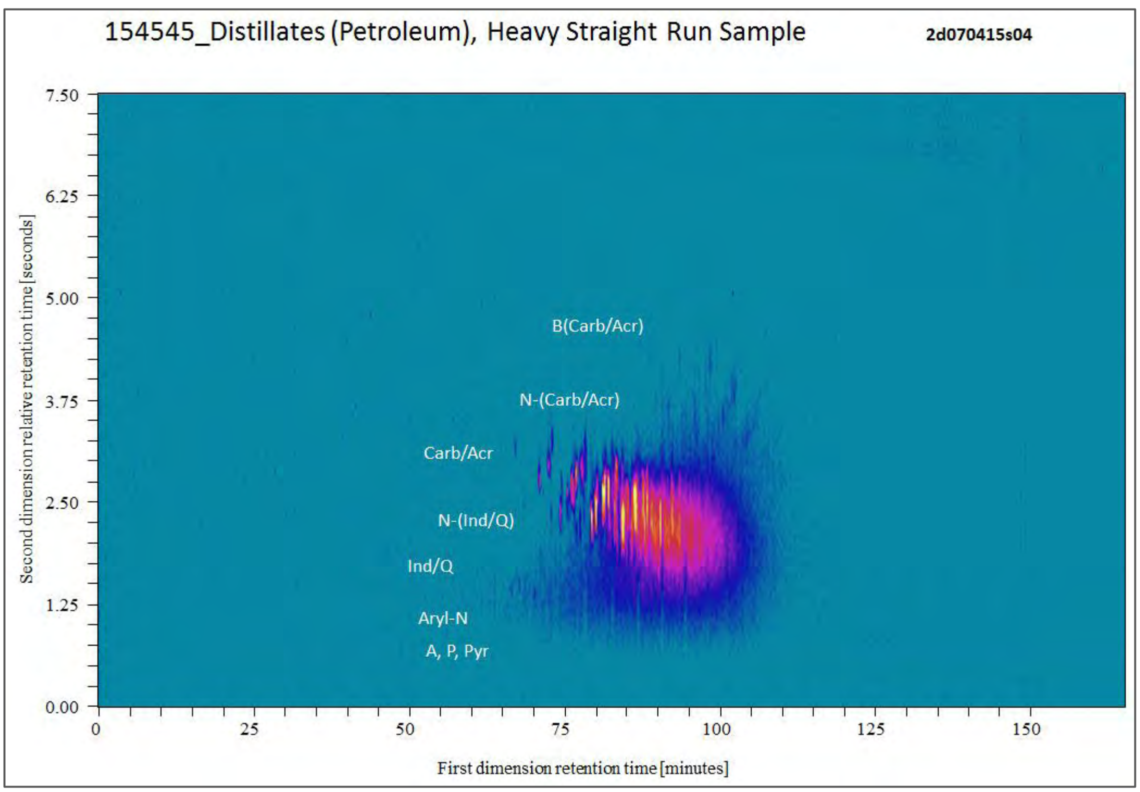
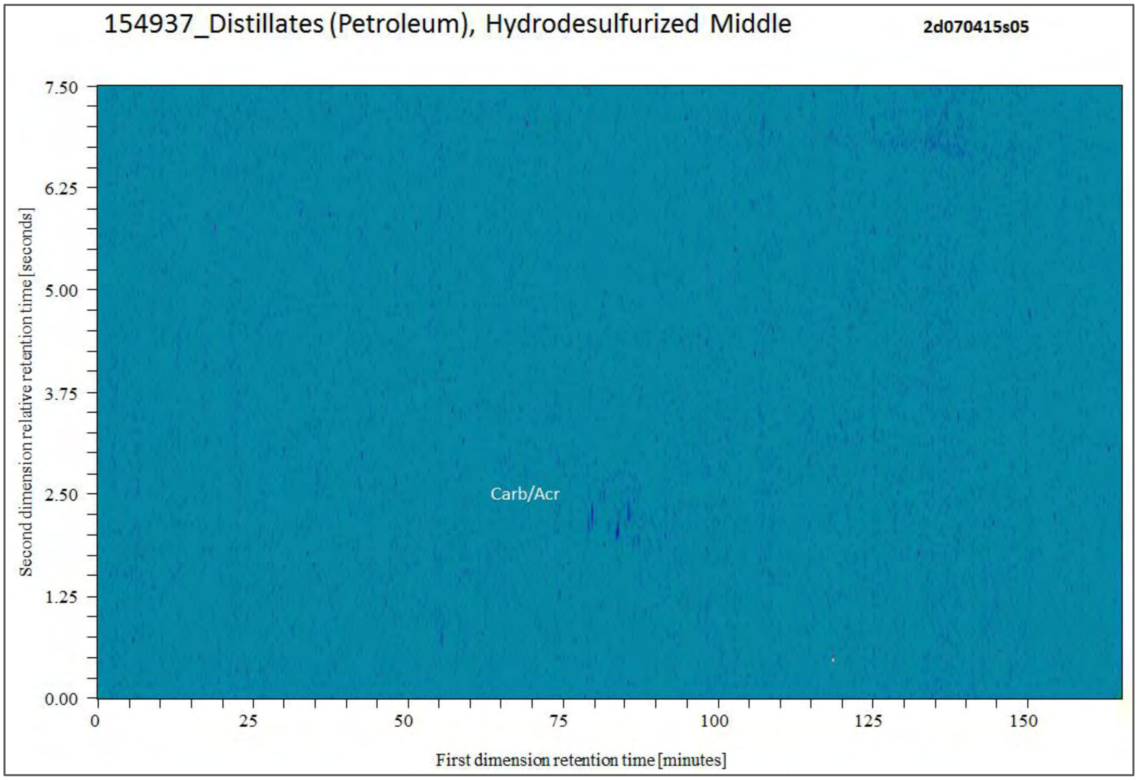
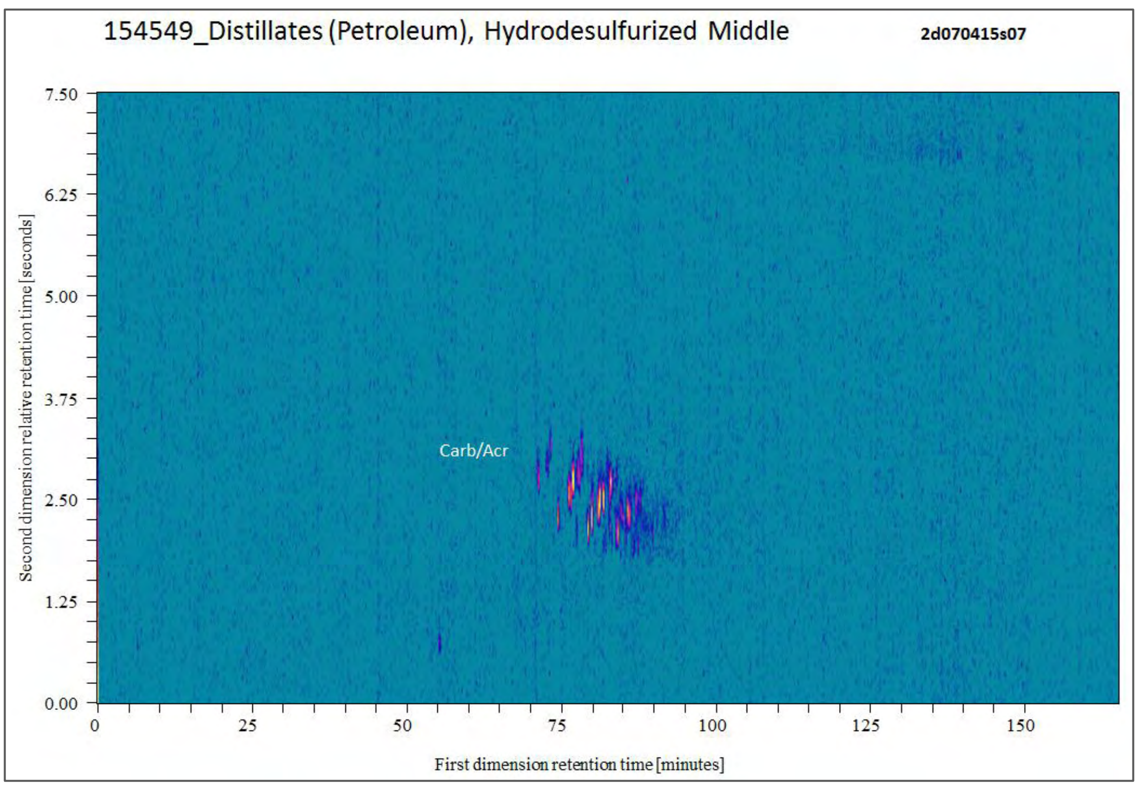
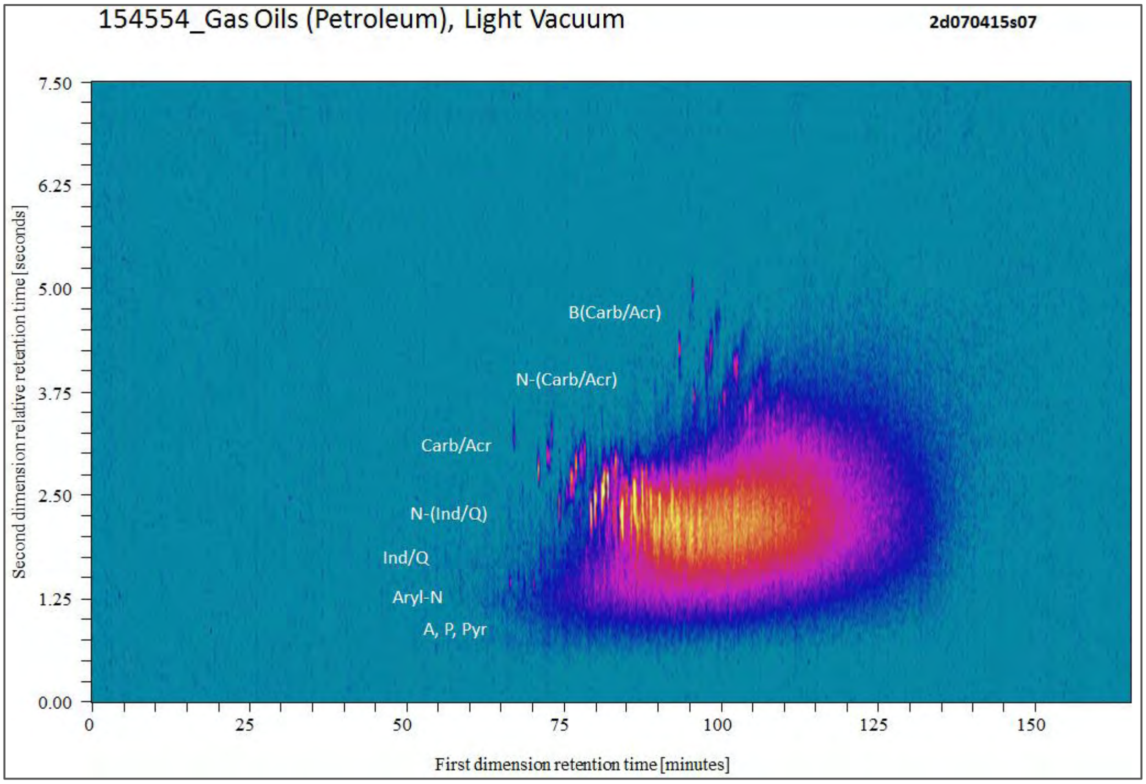
APPENDIX 1: NITROGEN GROUP TYPE GCxGC CHROMATOGRAMS

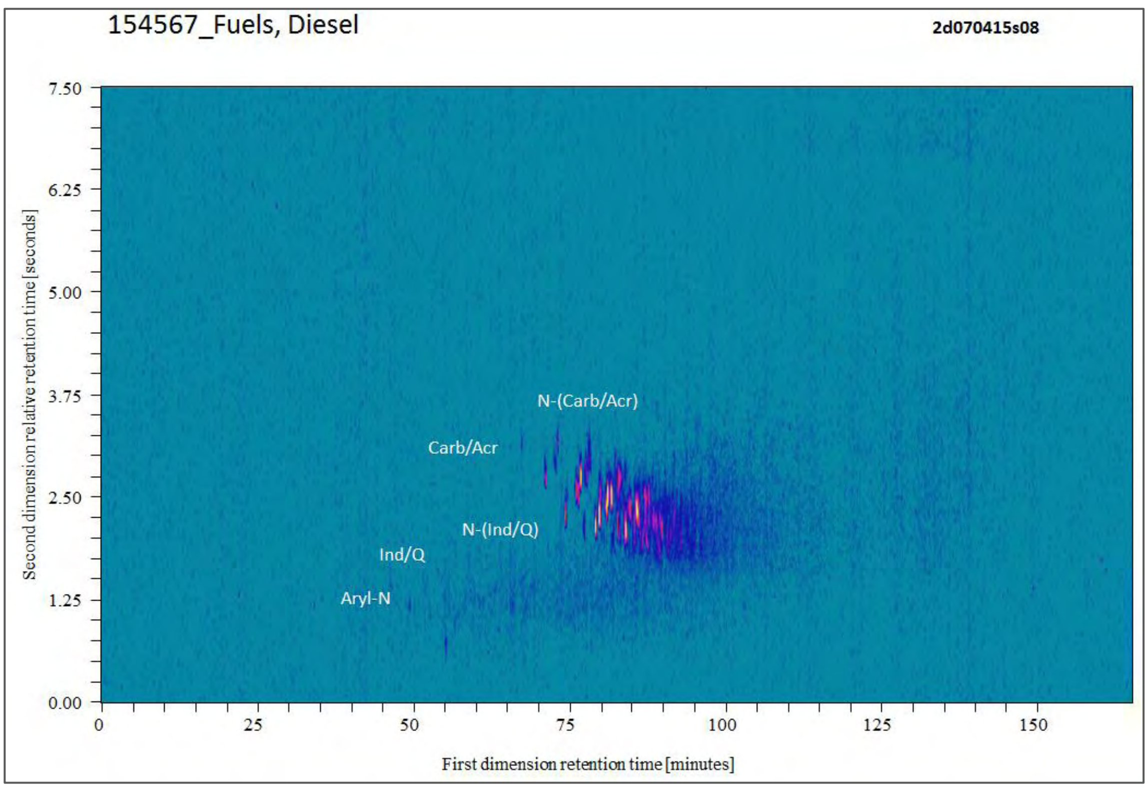


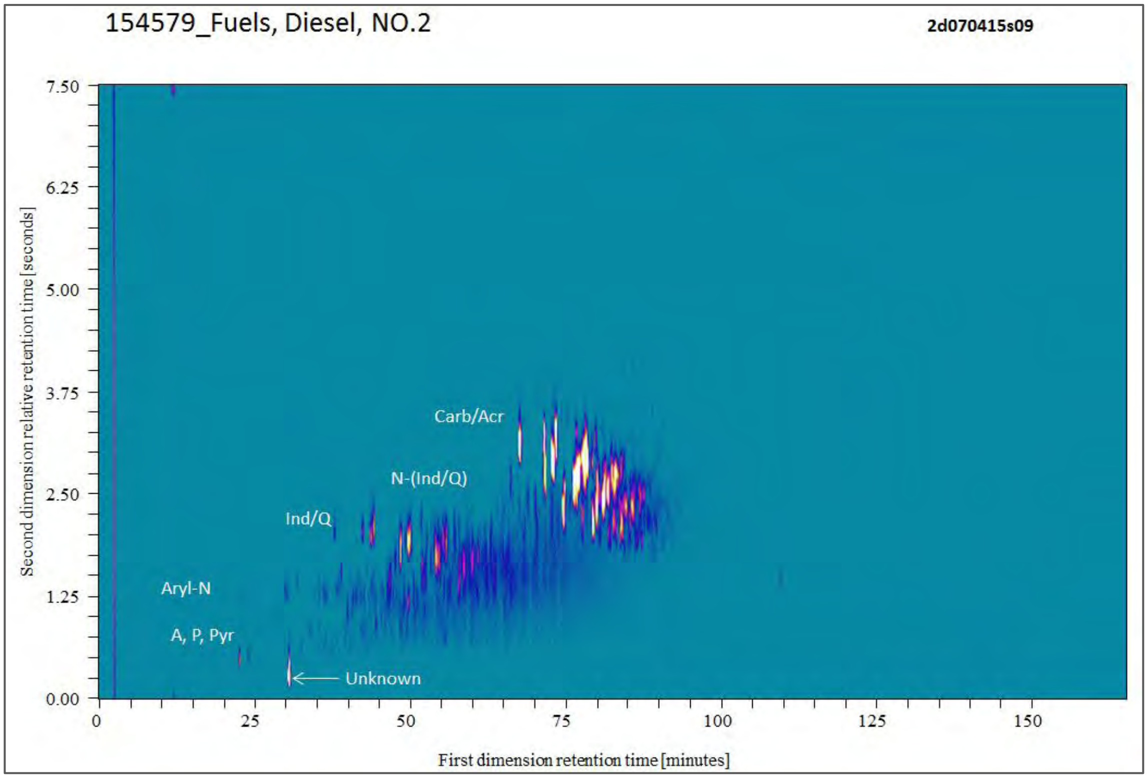


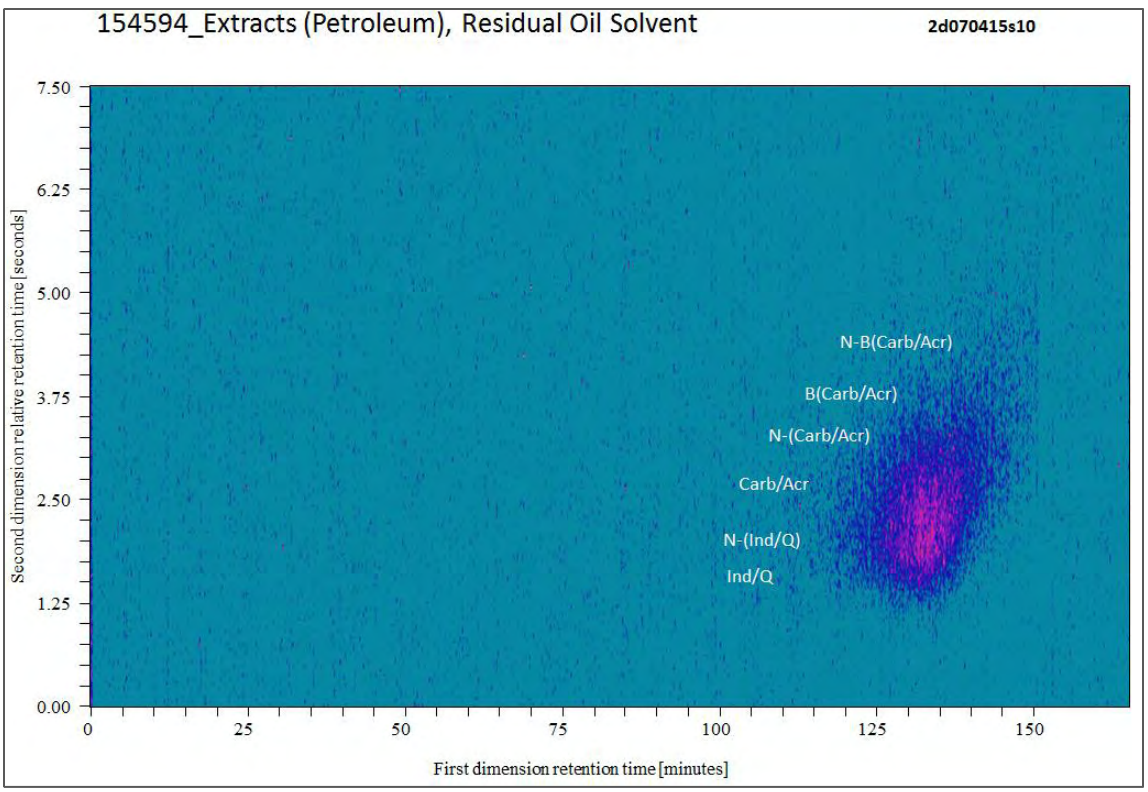

154937_Distillates (Petroleum), Hydrodesulfurized Middle
2d070415s05
Carb/Acr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

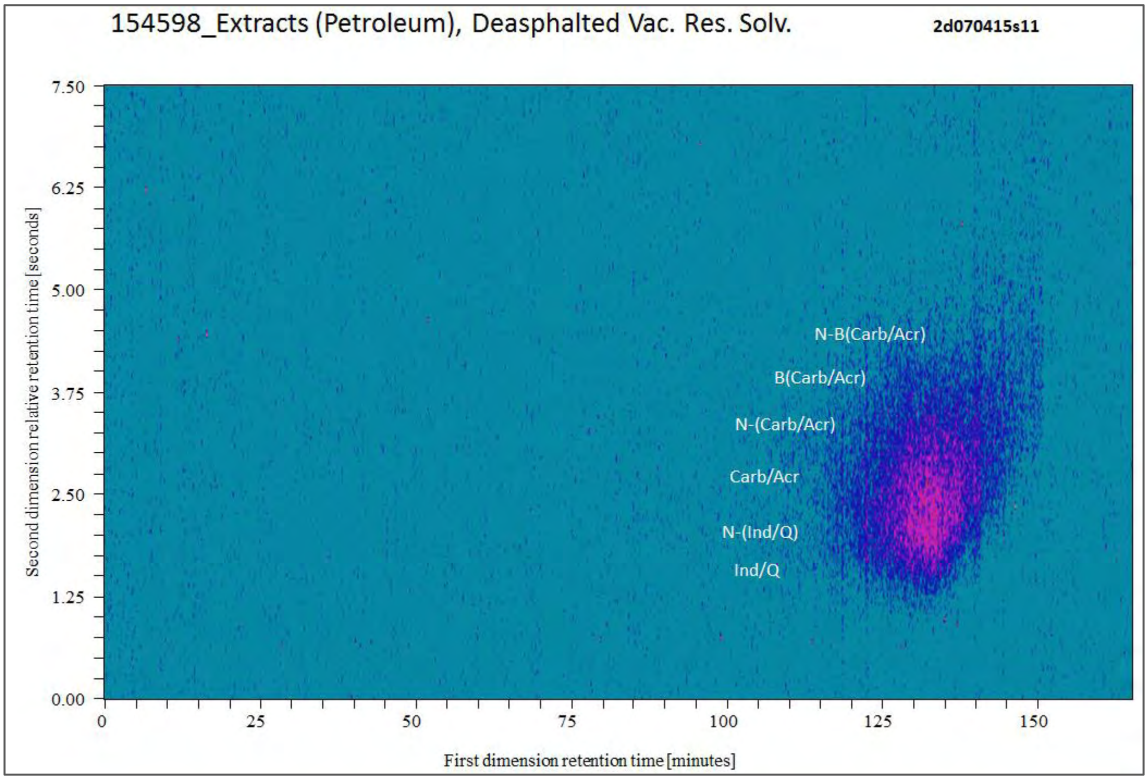

154549_Distillates (Petroleum), Hydrodesulfurized Middle
2d070415s07
Carb/Acr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

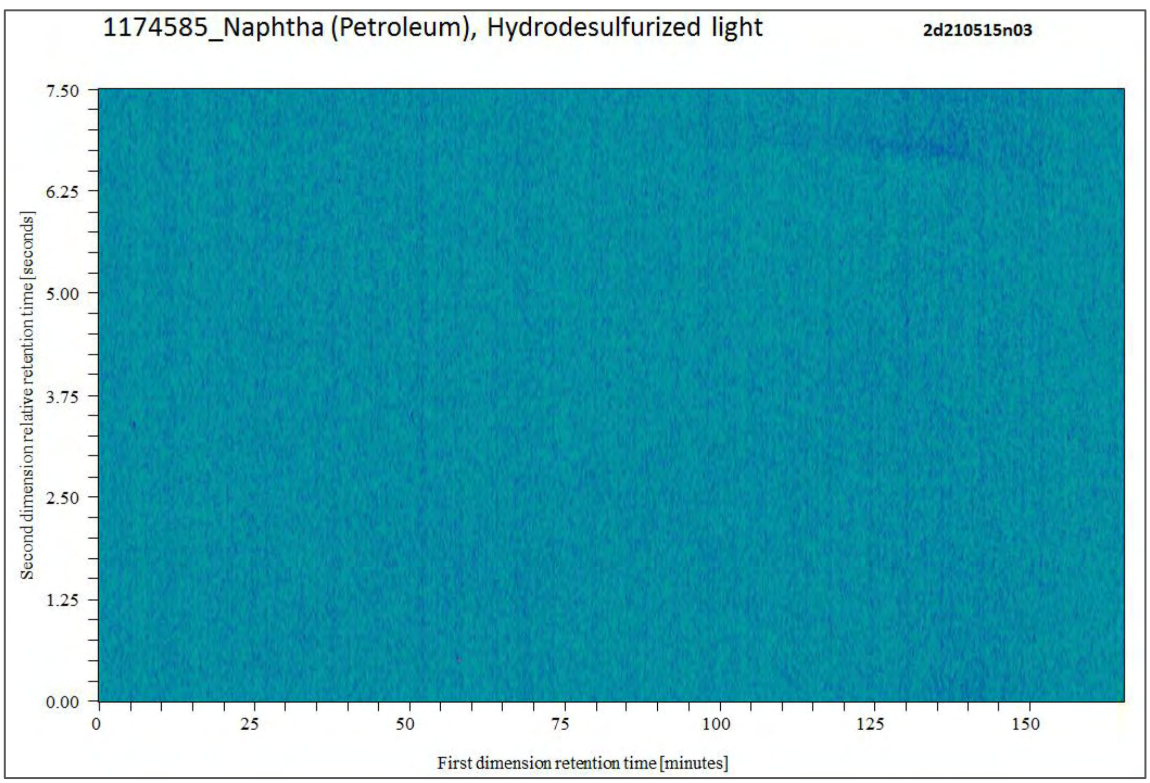

154554_Gas Oils (Petroleum), Light Vacuum
2d070415s07
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

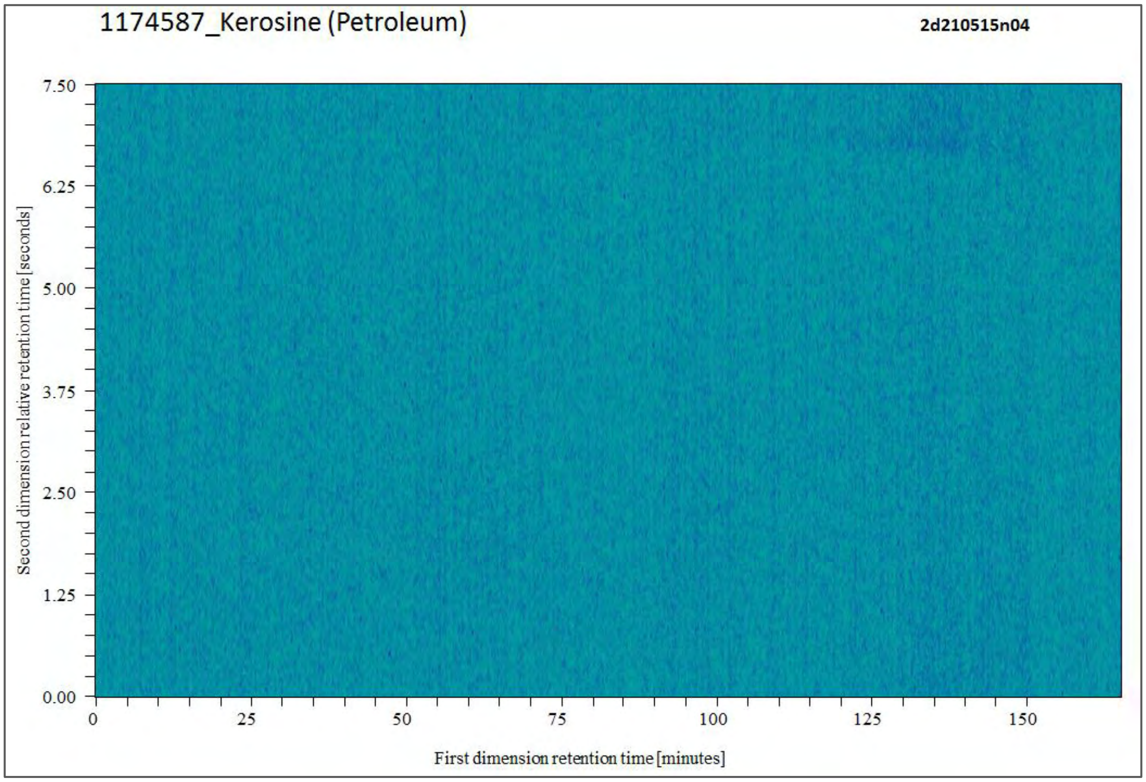

154567_Fuels, Diesel
2d070415s08
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

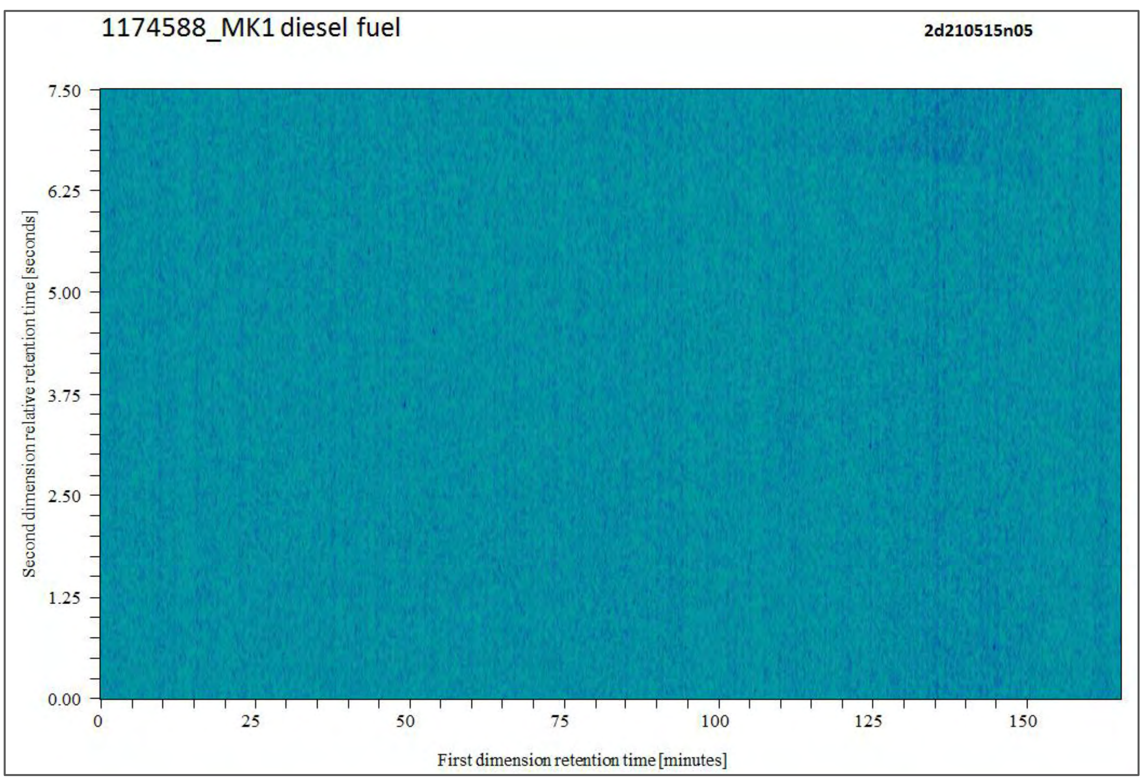

154579_Fuels, Diesel, NO.2
2d070415s09
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Unknown
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

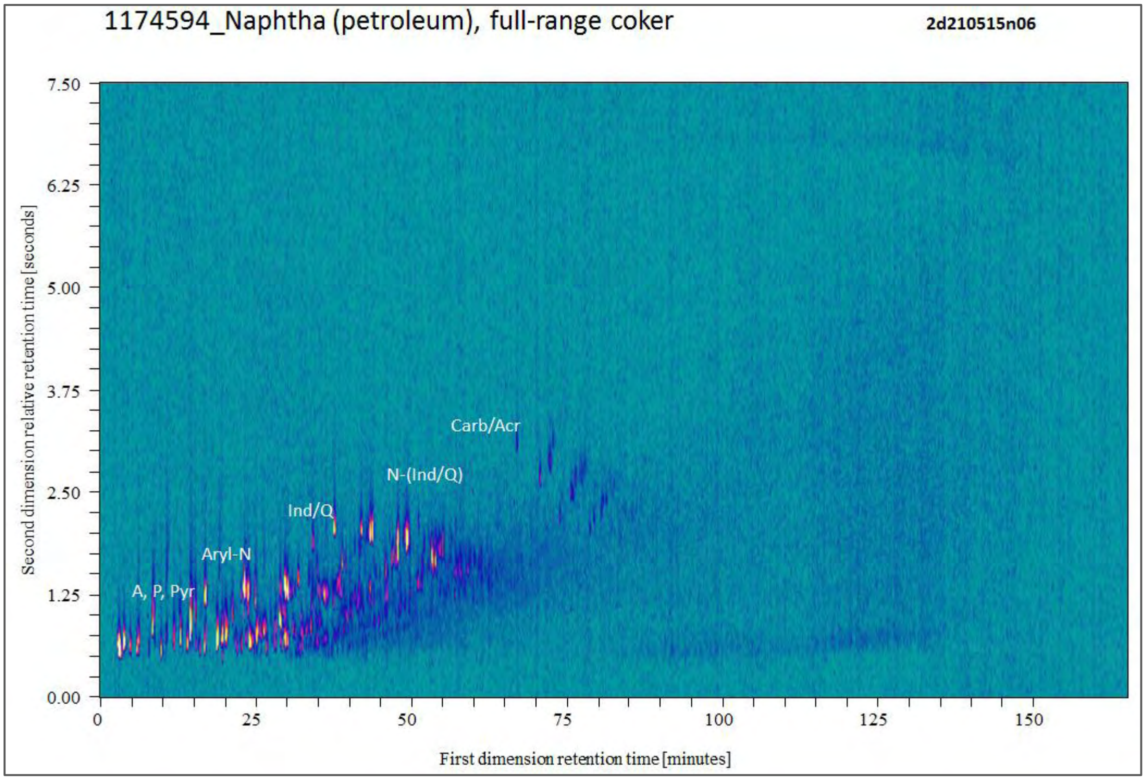

154594_Extracts (Petroleum), Residual Oil Solvent
2d070415s10
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

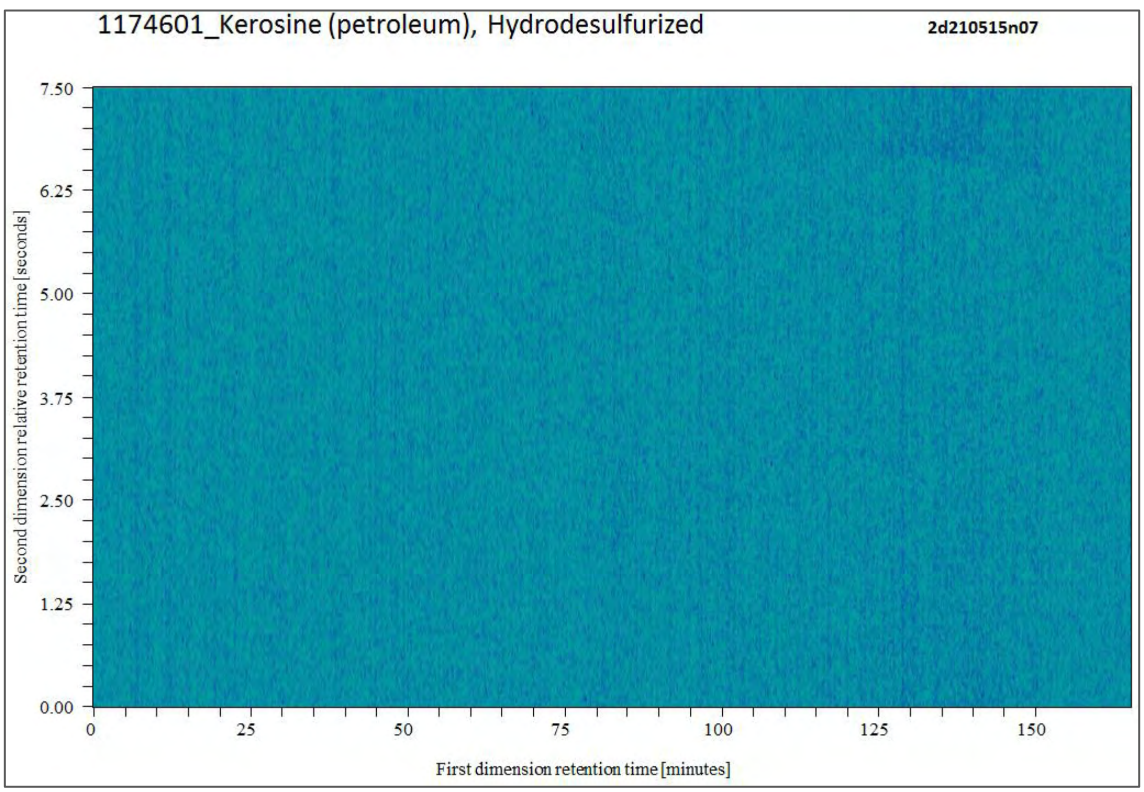

154598_Extracts (Petroleum), Deasphalted Vac. Res. Solv.
2d070415s11
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

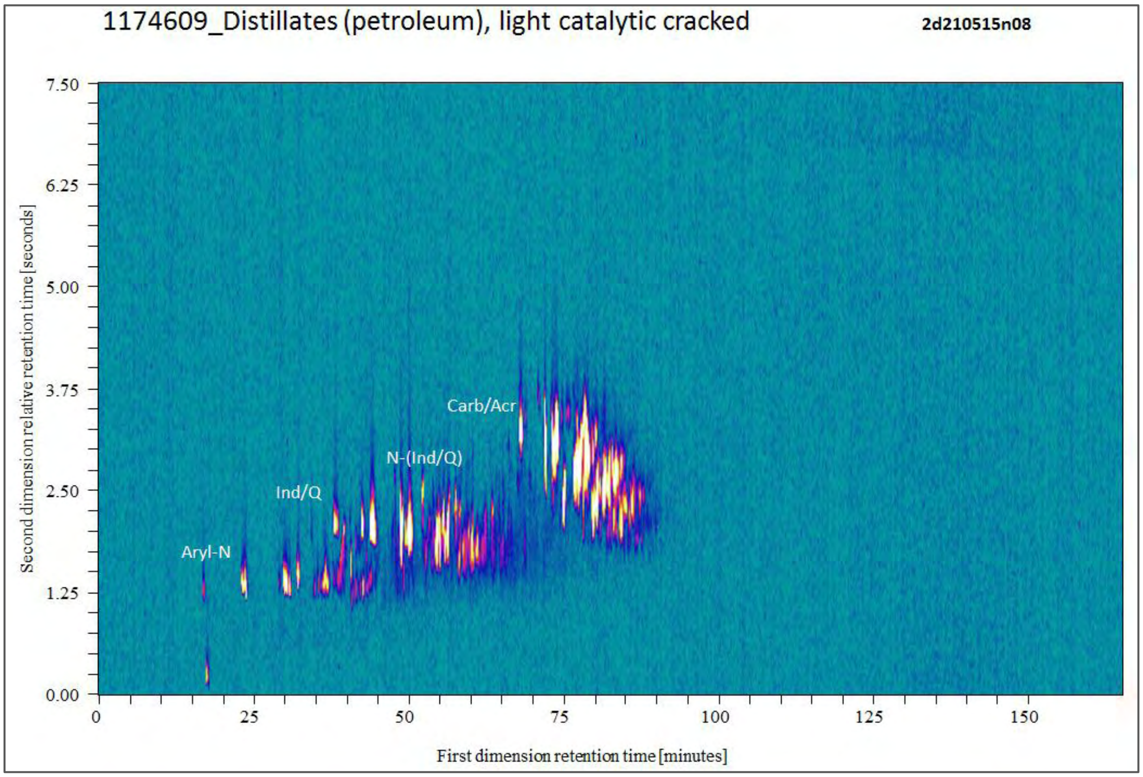

1174585_Naphtha (Petroleum), Hydrodesulfurized light
2d210515n03
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

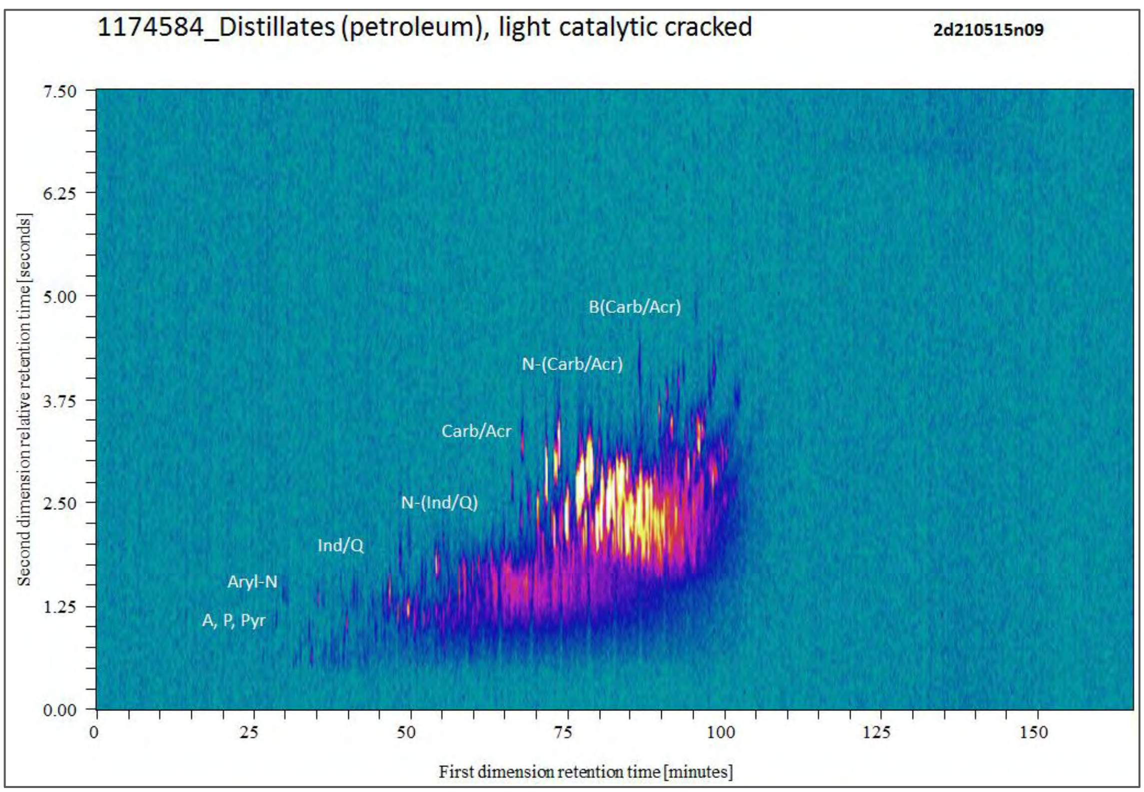

1174587_Kerosine (Petroleum)
2d210515n04
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]

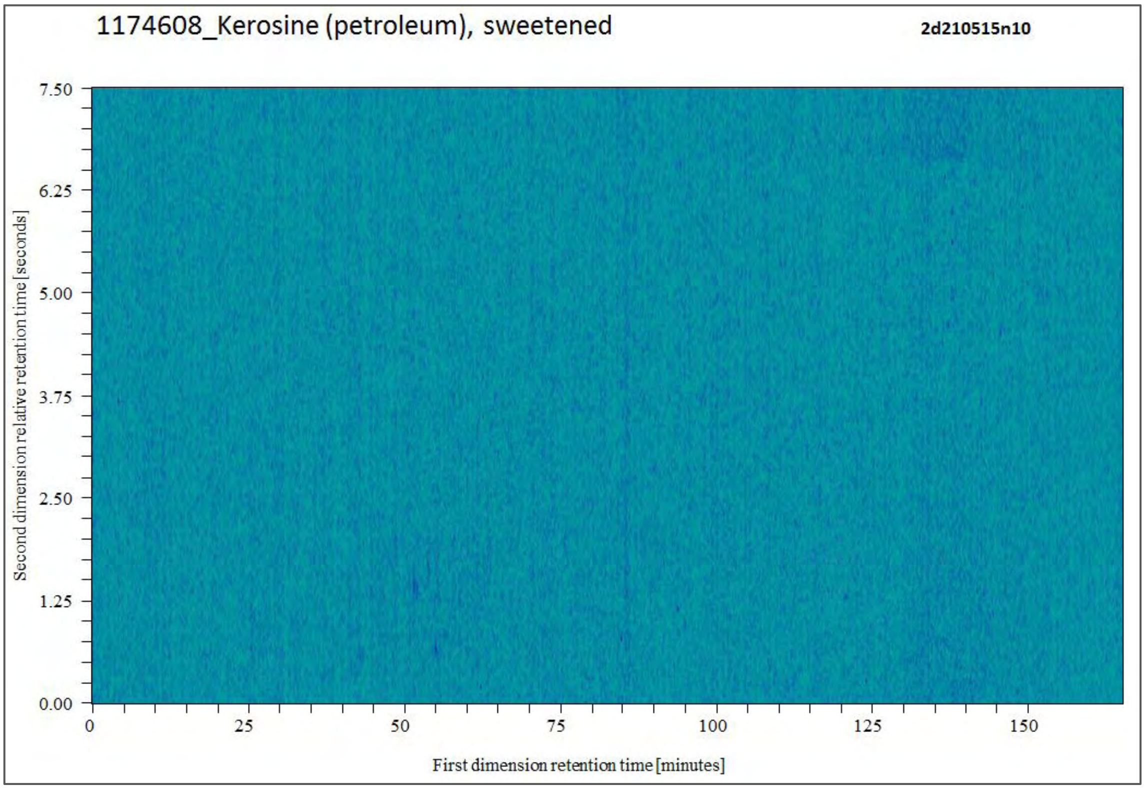

1174588_MK1 diesel fuel
2d210515n05
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]

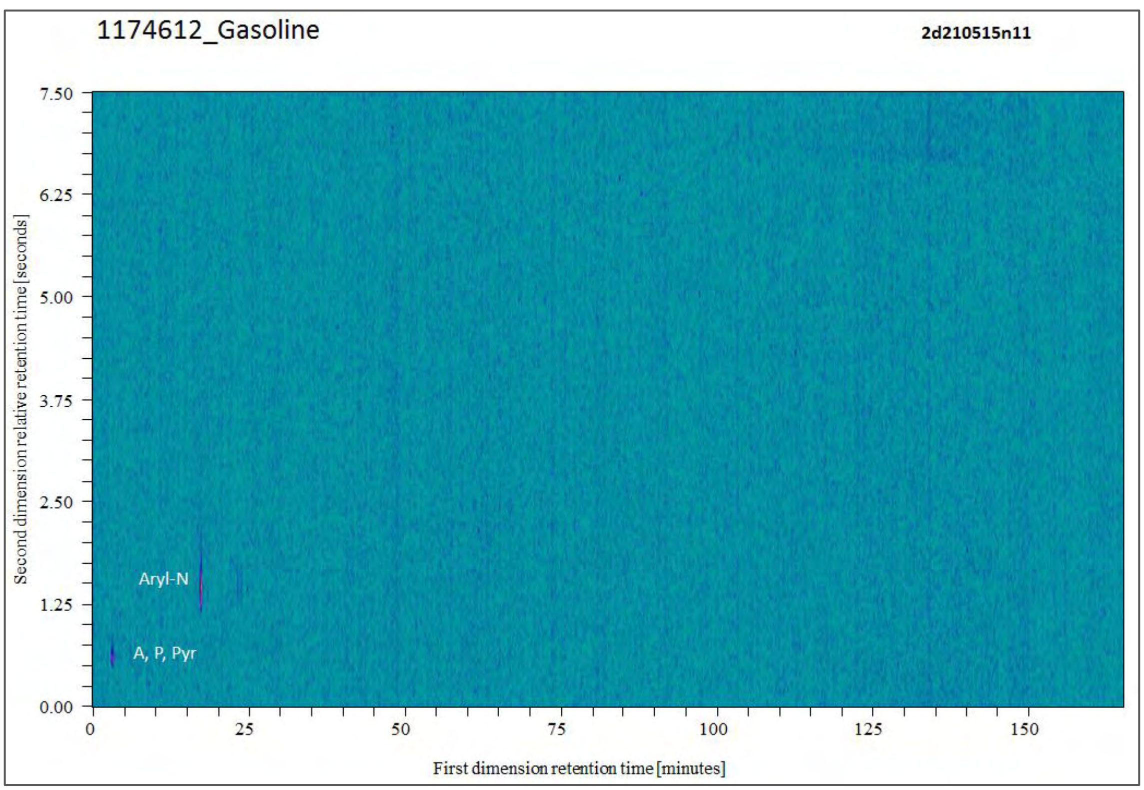

1174594_Naphtha (petroleum), full-range coker
2d210515n06
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
A, P, Pyr
Aryl-N
Ind/Q
N-(Ind/Q)
Carb/Acr

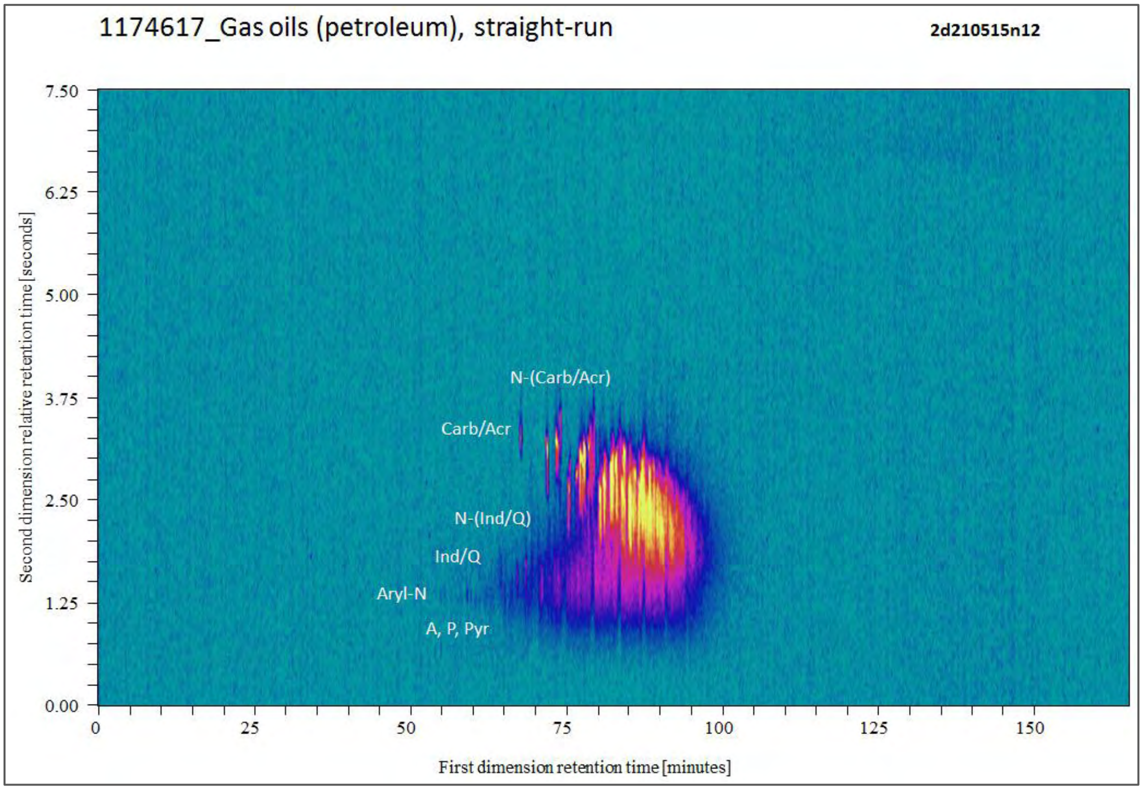

1174601_Kerosine (petroleum), Hydrodesulfurized
2d210515n07
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

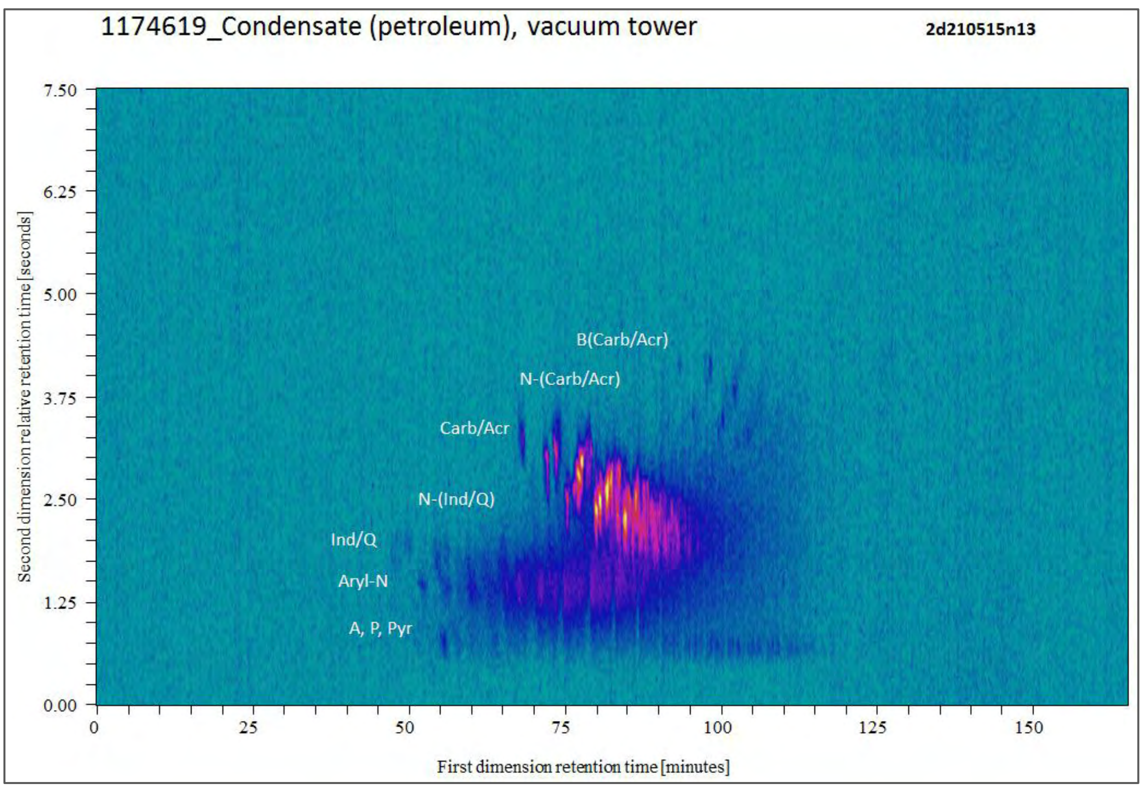

1174609_Distillates (petroleum), light catalytic cracked
2d210515n08
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

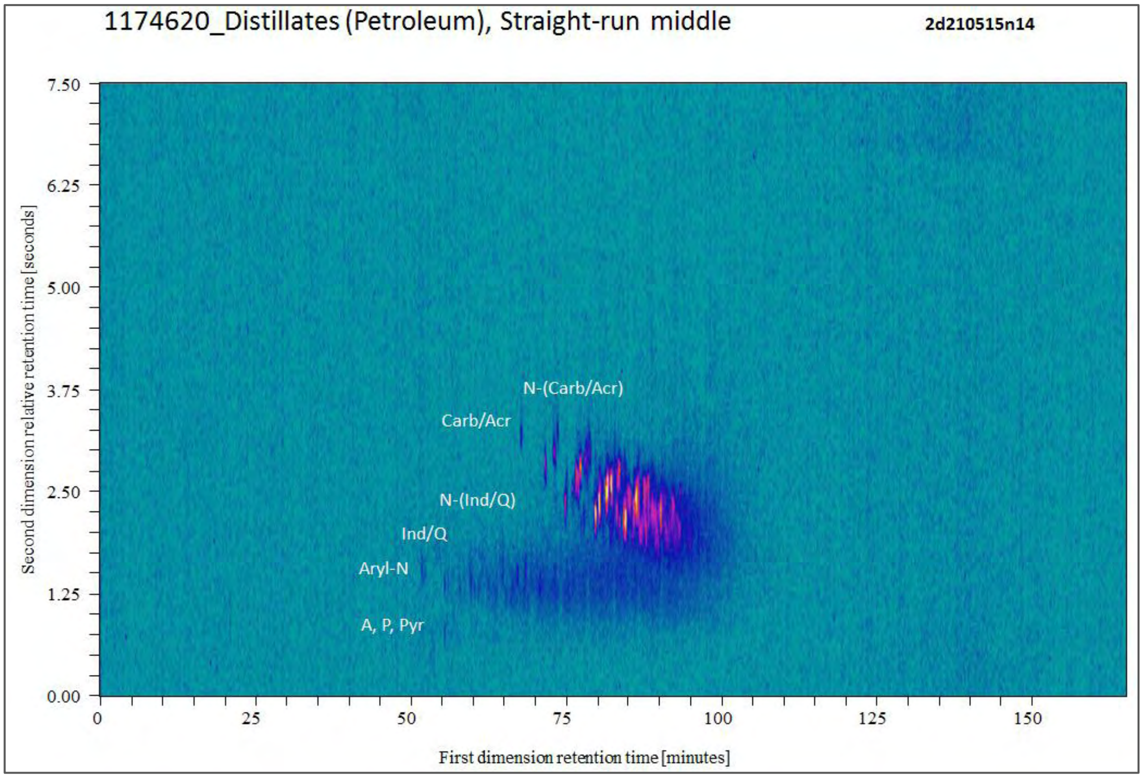

1174584_Distillates (petroleum), light catalytic cracked
2d210515n09
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

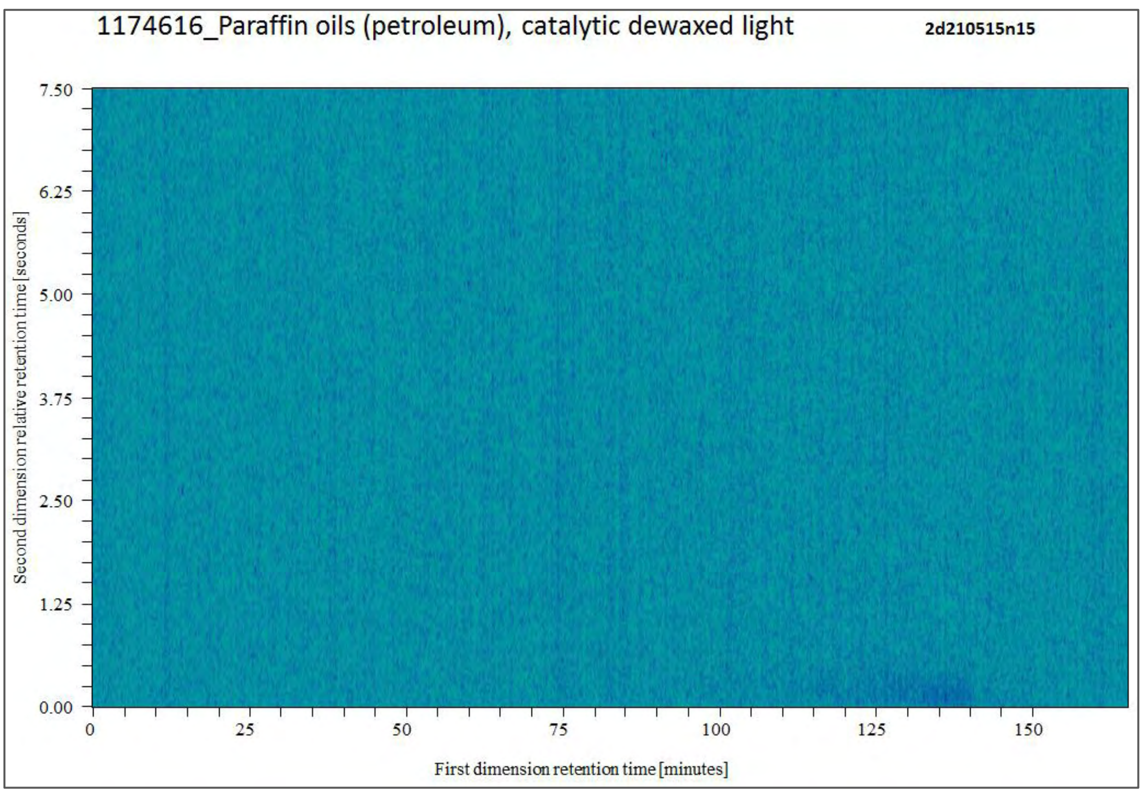

1174608_Kerosine (petroleum), sweetened
2d210515n10
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150
First dimension retention time [minutes]

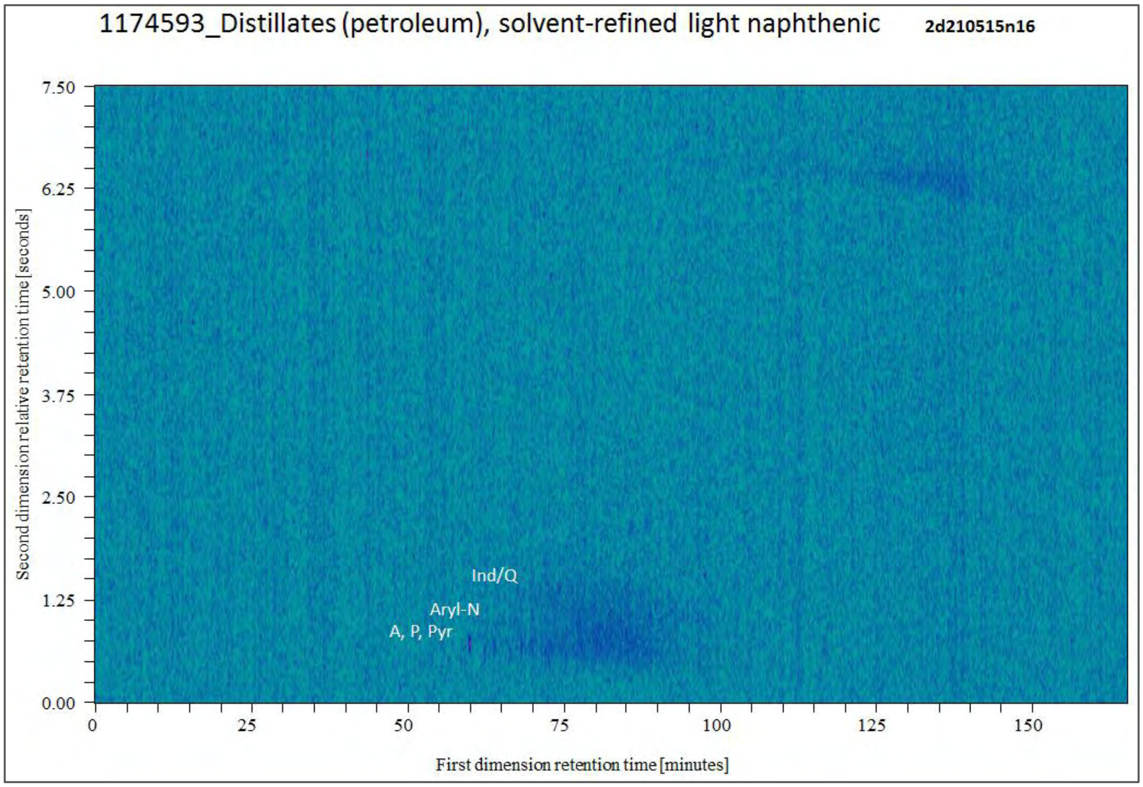

1174612_Gasoline
2d210515n11
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Aryl-N
A, P, Pyr
0
25
50
75
100
125
150
First dimension retention time [minutes]

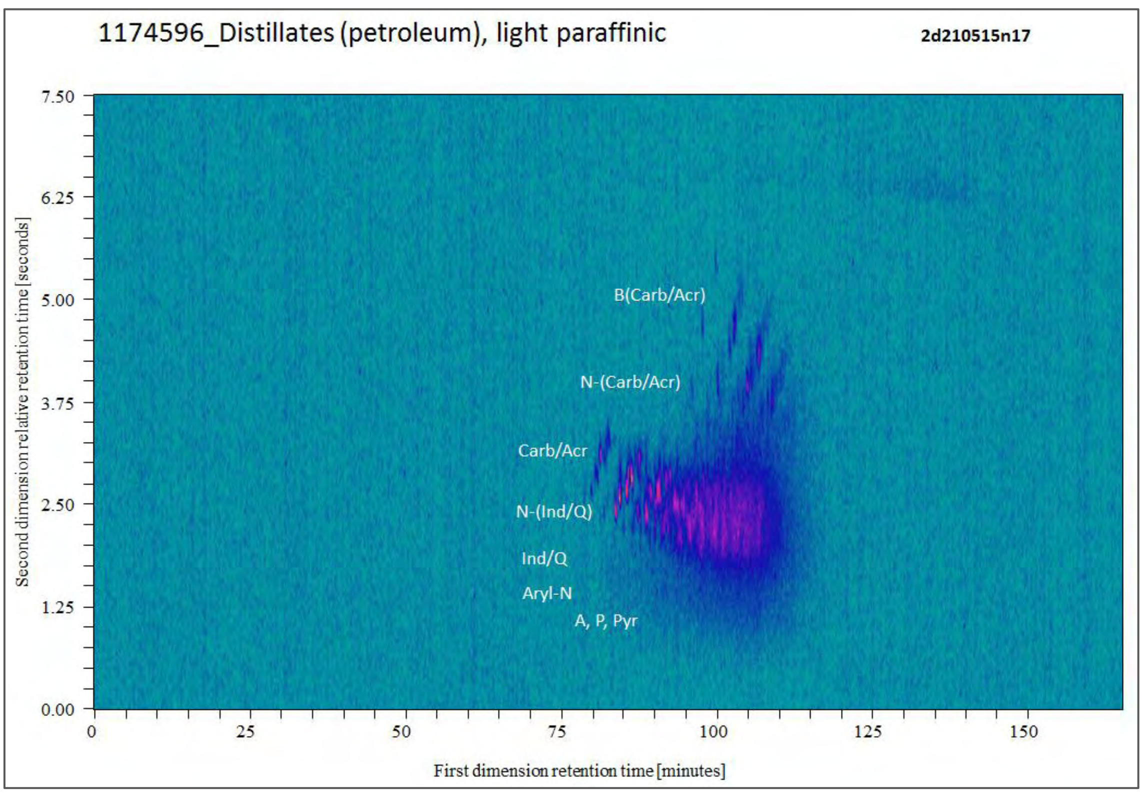

1174617_Gas oils (petroleum), straight-run
2d210515n12
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

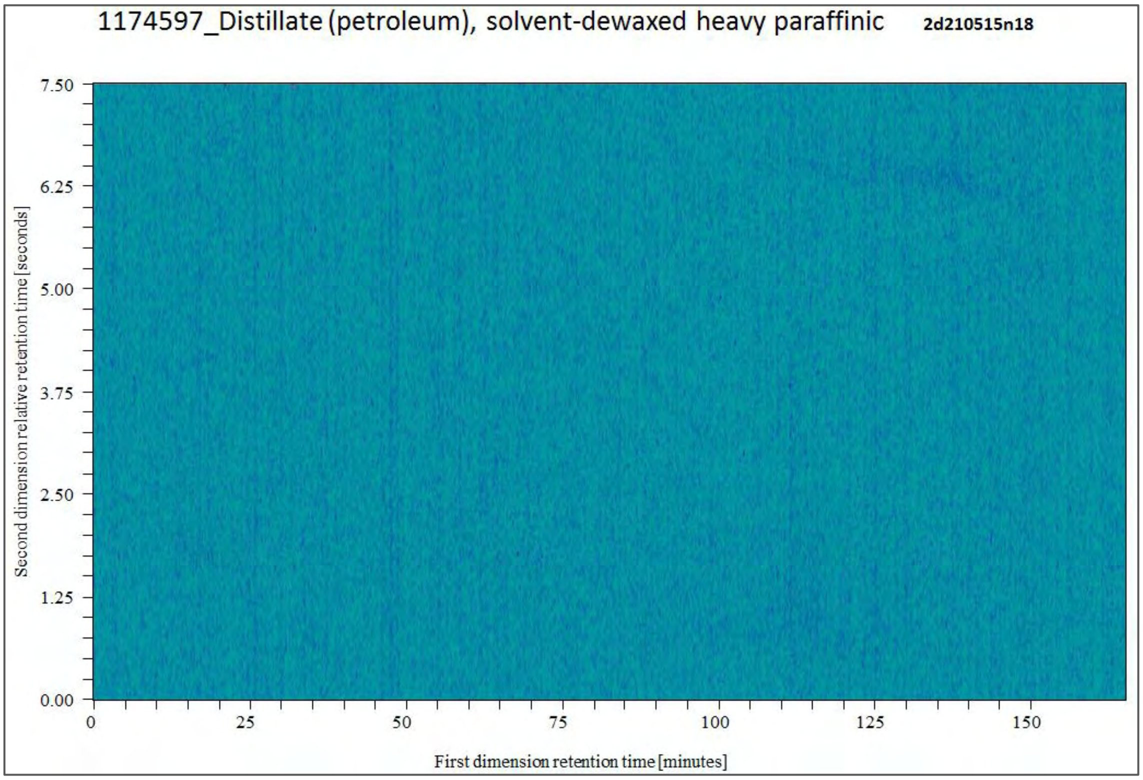

1174619_Condensate (petroleum), vacuum tower
2d210515n13
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

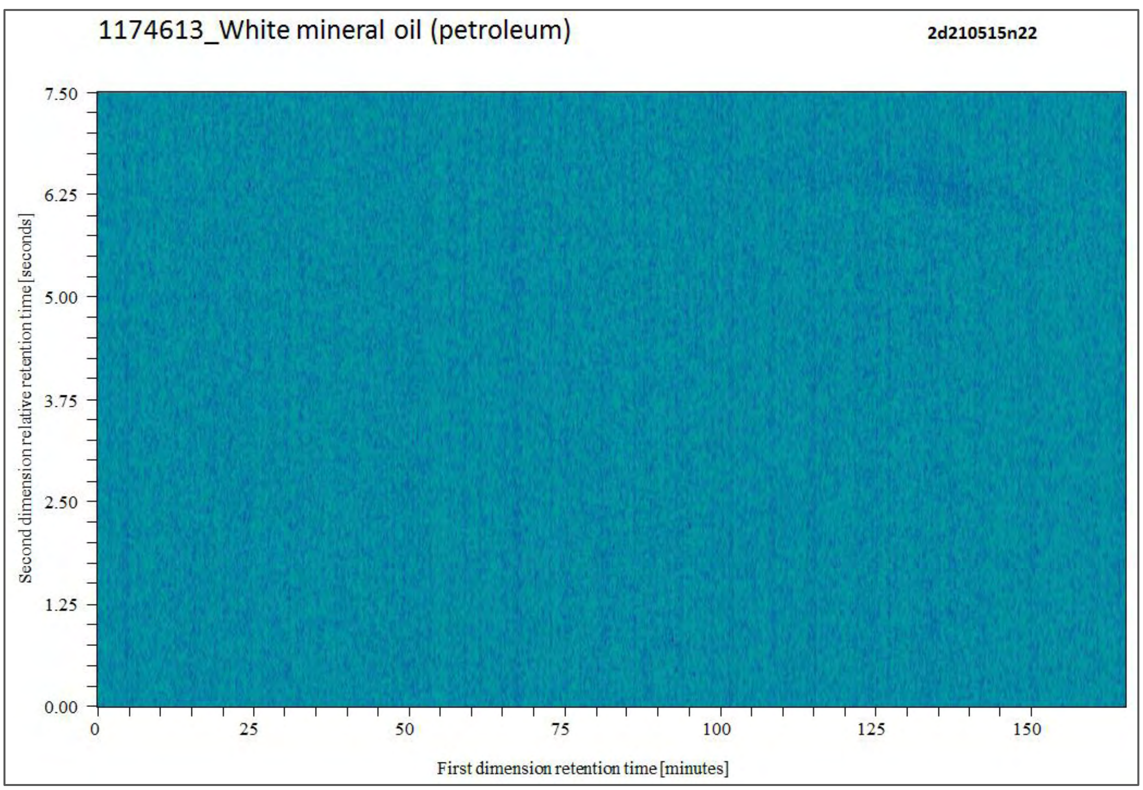

1174620_Distillates (Petroleum), Straight-run middle
2d210515n14
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

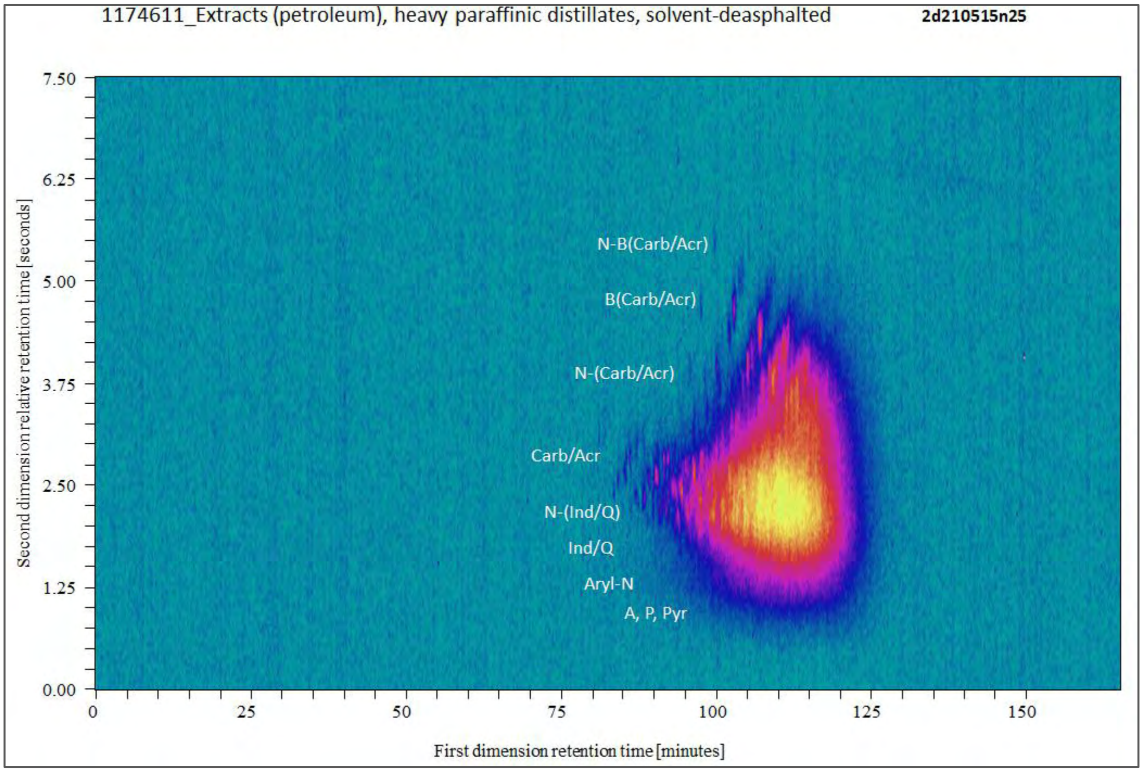

1174616_Paraffin oils (petroleum), catalytic dewaxed light
2d210515n15
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

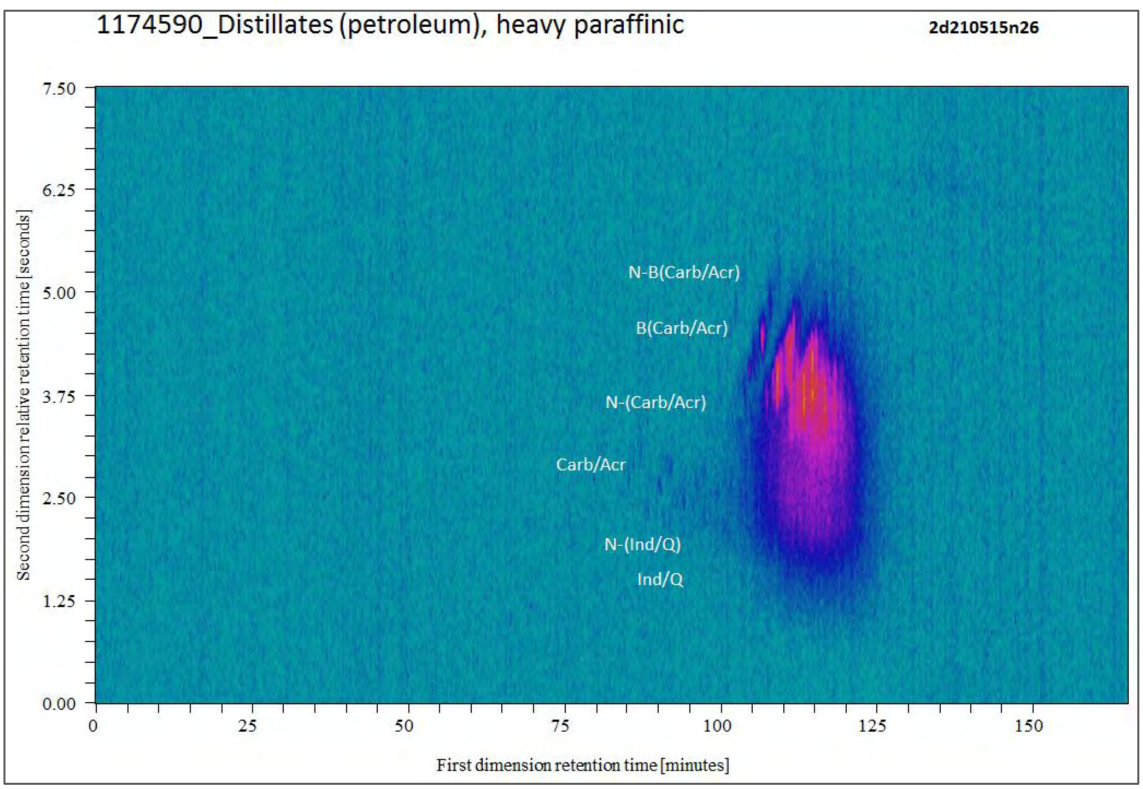

1174593_Distillates (petroleum), solvent-refined light naphthenic
2d210515n16
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

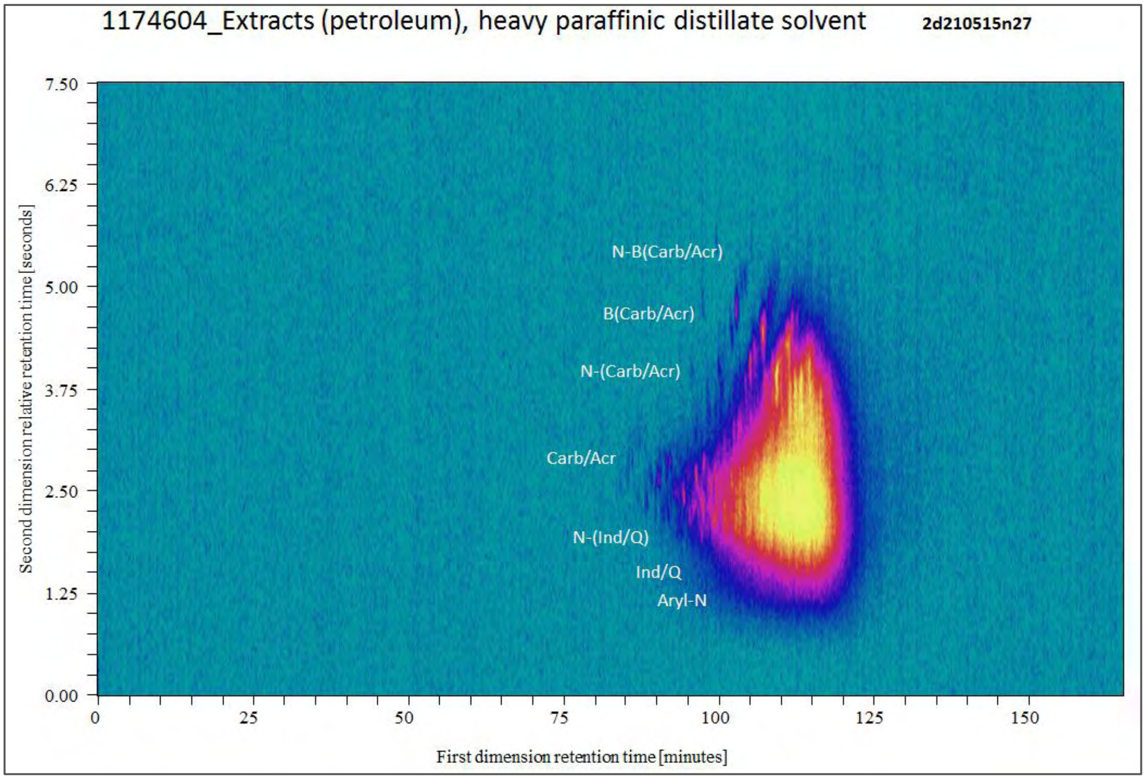

1174596_Distillates (petroleum), light paraffinic
2d210515n17
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

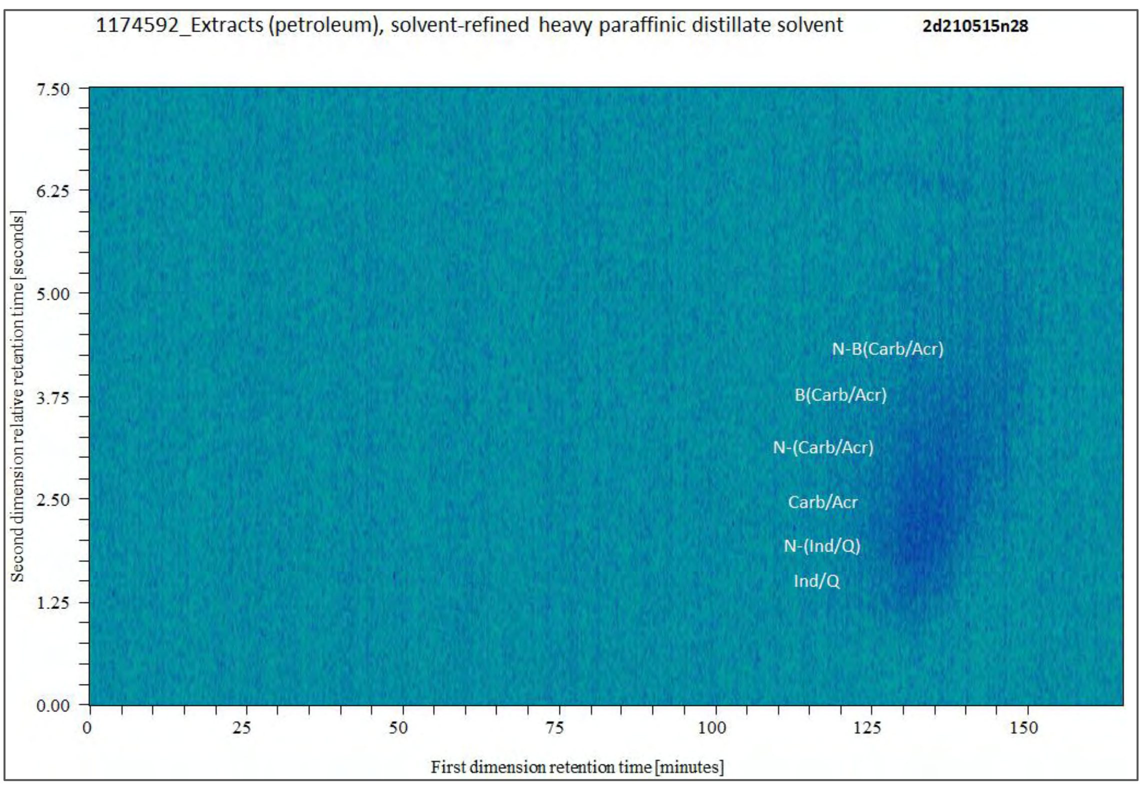

1174597_Distillate (petroleum), solvent-dewaxed heavy paraffinic
2d210515n18
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150
First dimension retention time [minutes]

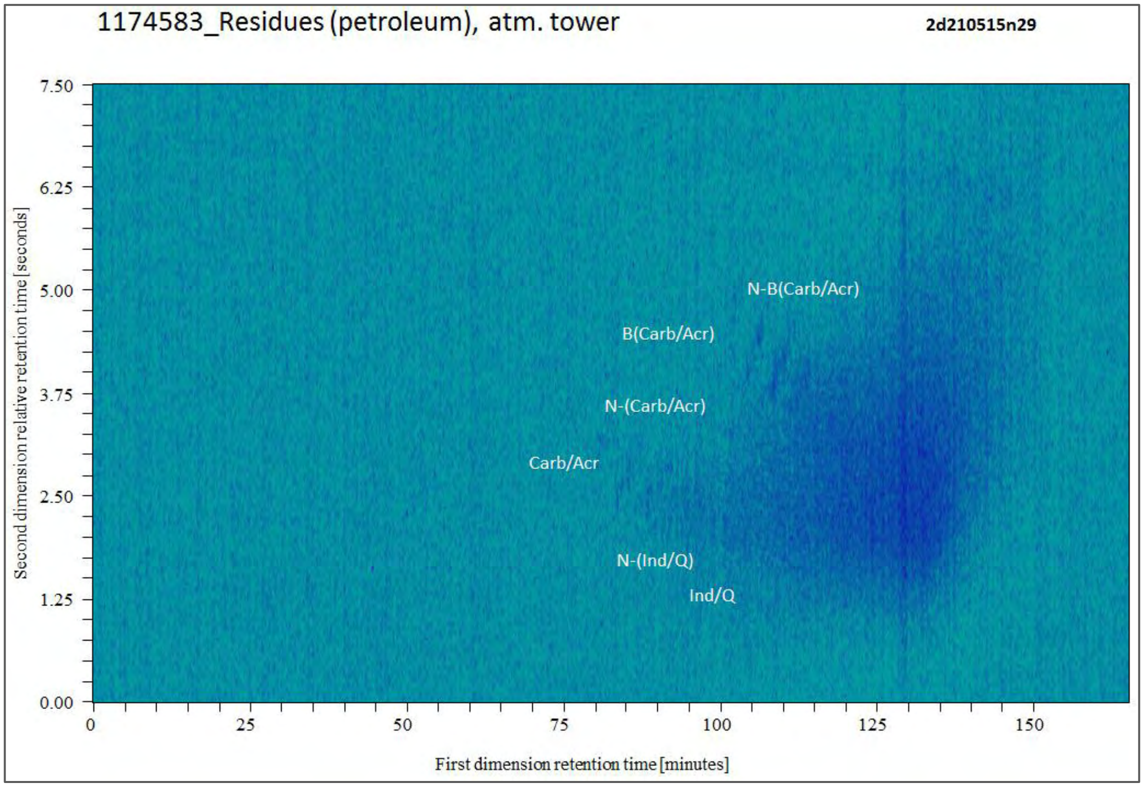

1174613_White mineral oil (petroleum)
2d210515n22
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150
First dimension retention time [minutes]

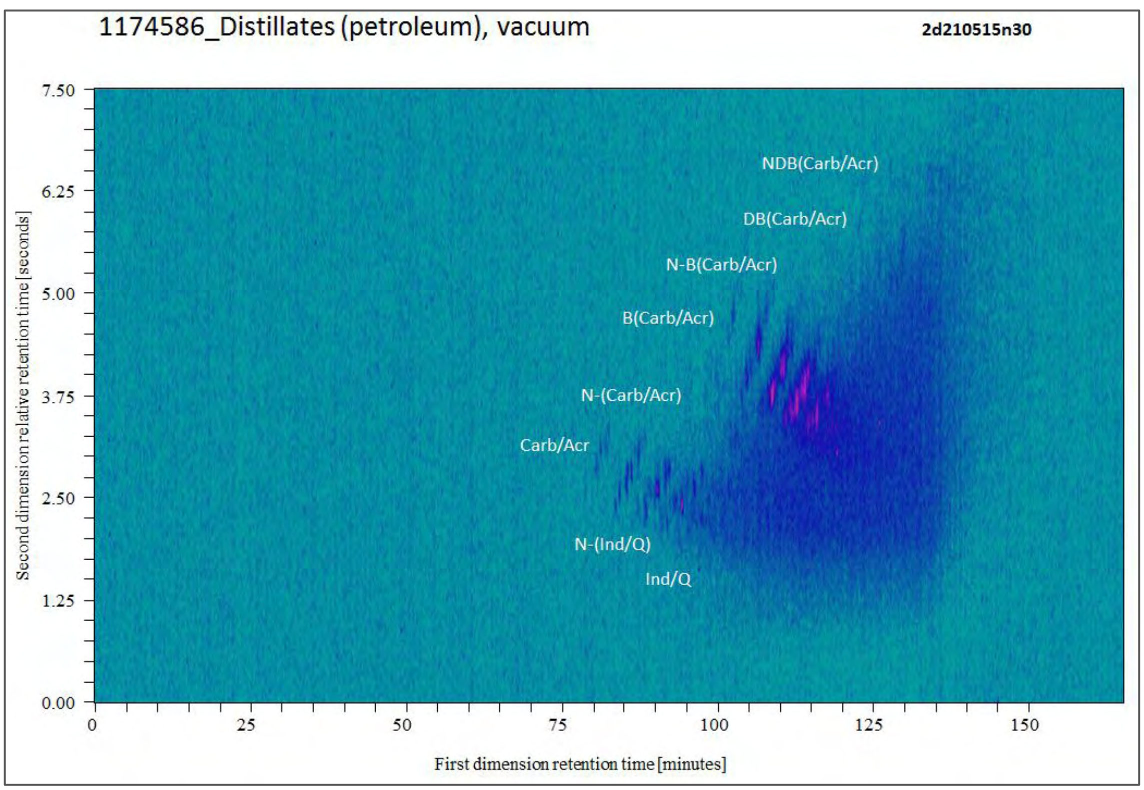

1174611_Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalted
2d210515n25
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
A, P, Pyr
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

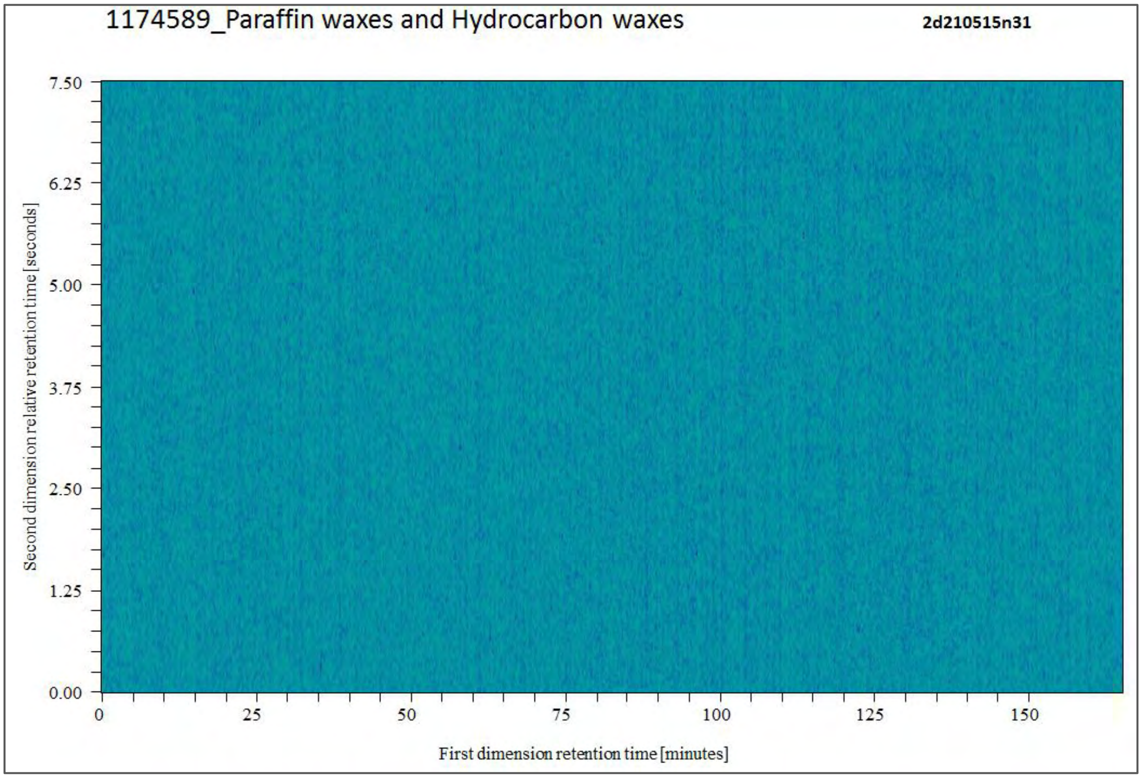

1174590_Distillates (petroleum), heavy paraffinic
2d210515n26
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

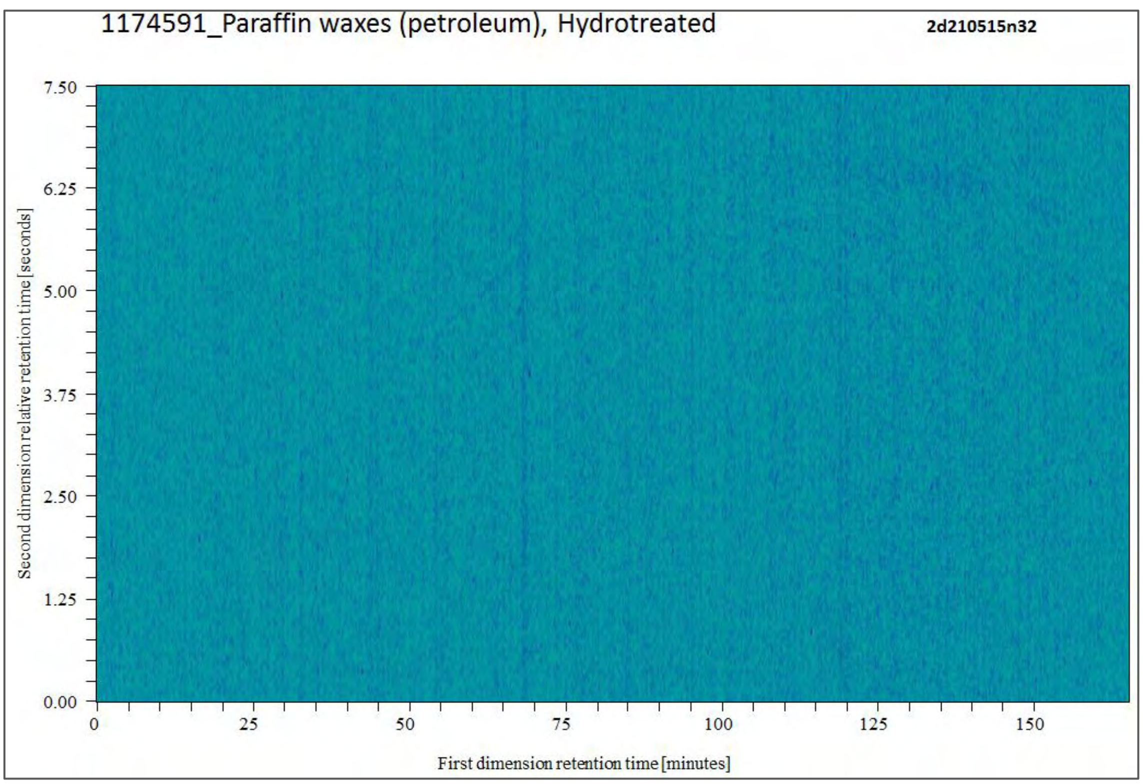

1174604_Extracts (petroleum), heavy paraffinic distillate solvent
2d210515n27
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Aryl-N
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

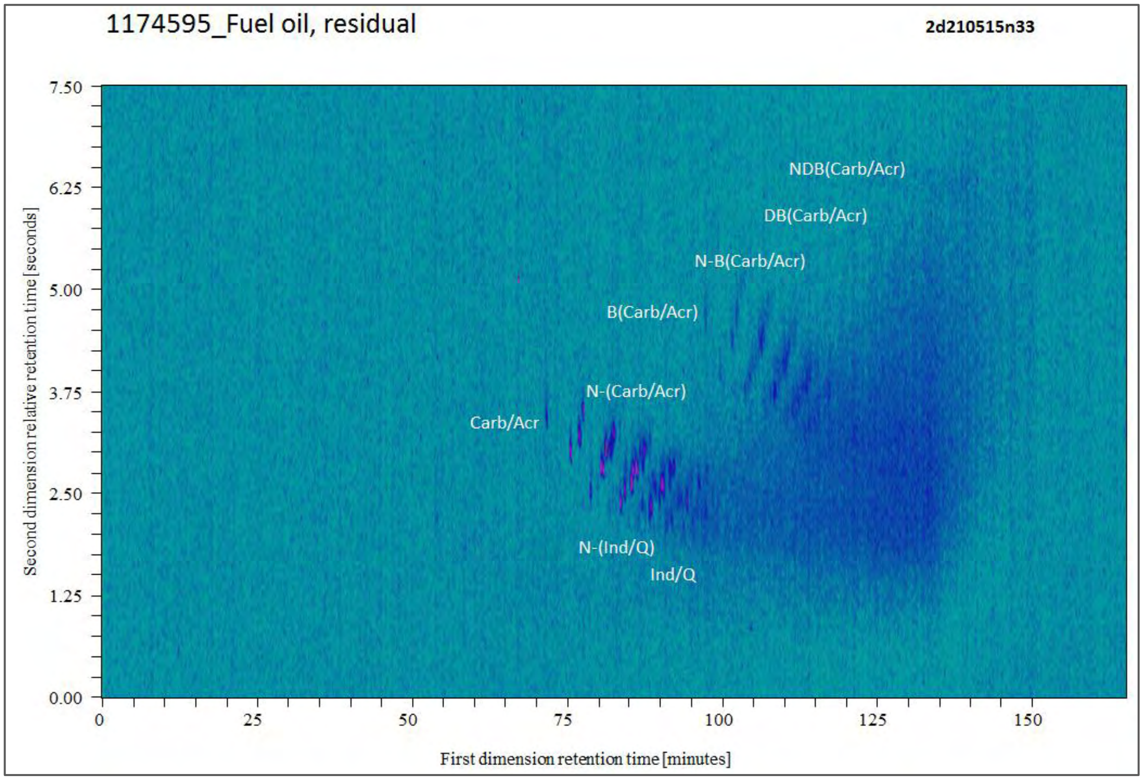

1174592_Extracts (petroleum), solvent-refined heavy paraffinic distillate solvent
2d210515n28
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

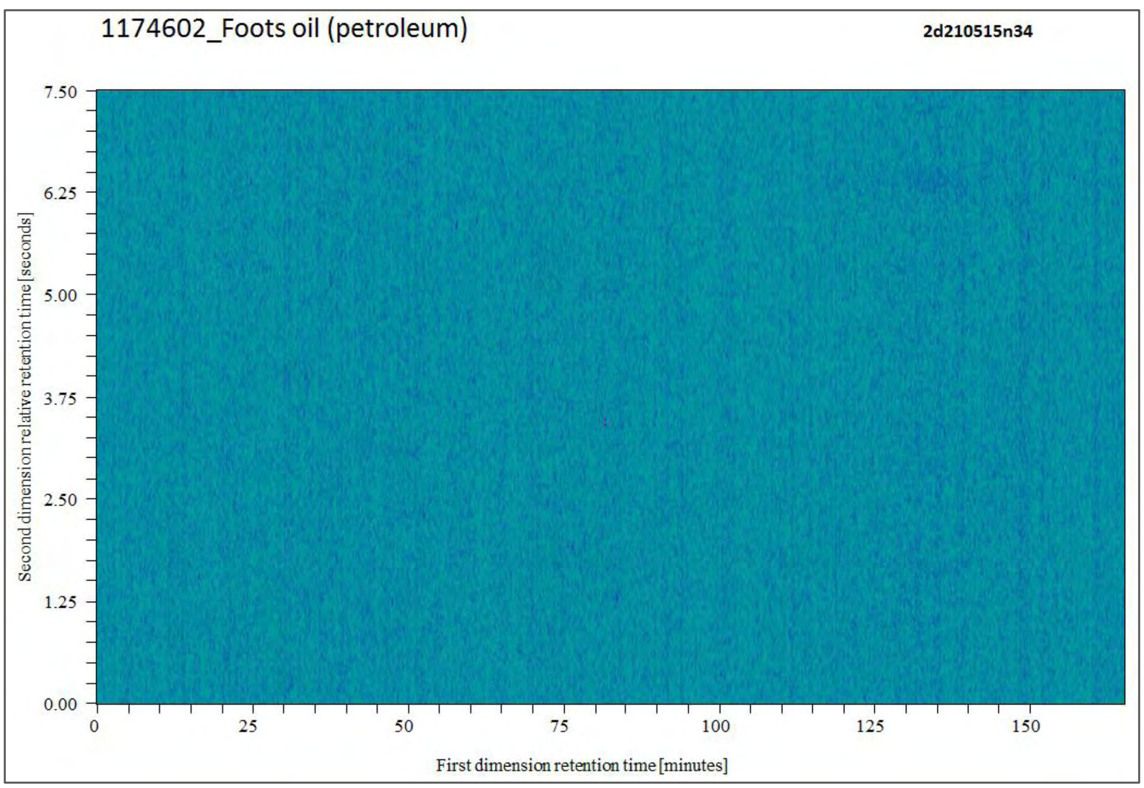

1174583_Residues (petroleum), atm. tower
2d210515n29
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

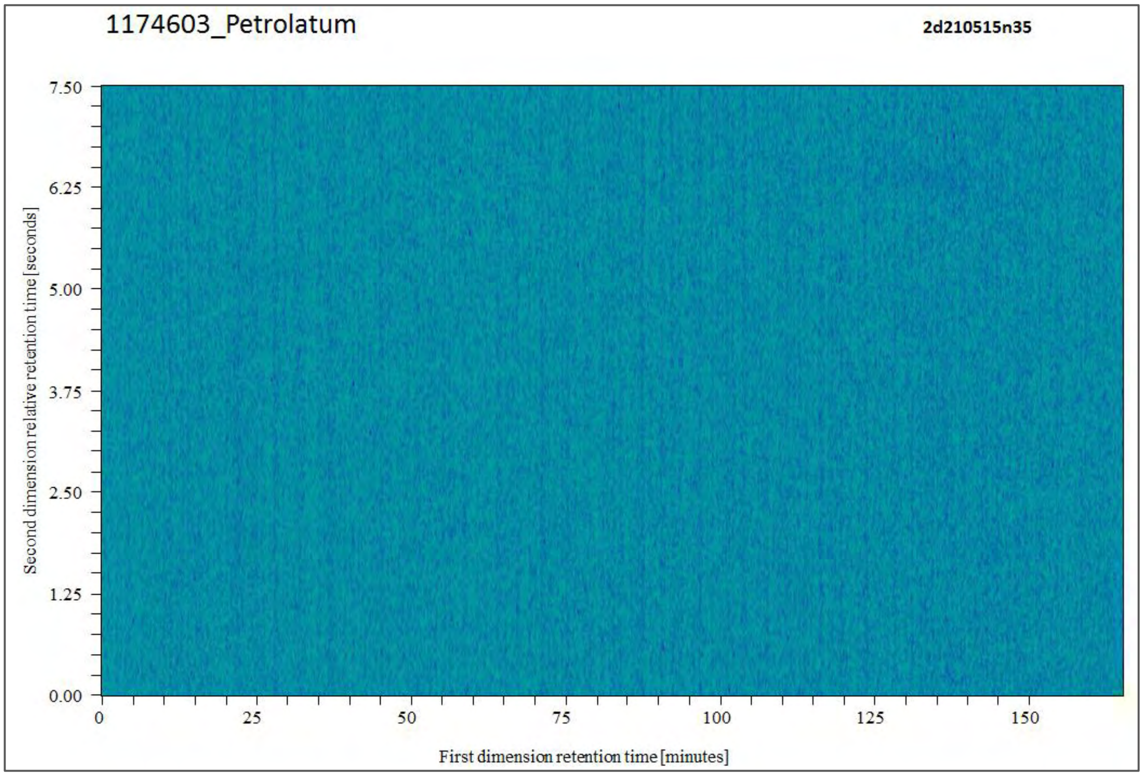

1174586_Distillates (petroleum), vacuum
2d210515n30
NDB(Carb/Acr)
DB(Carb/Acr)
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

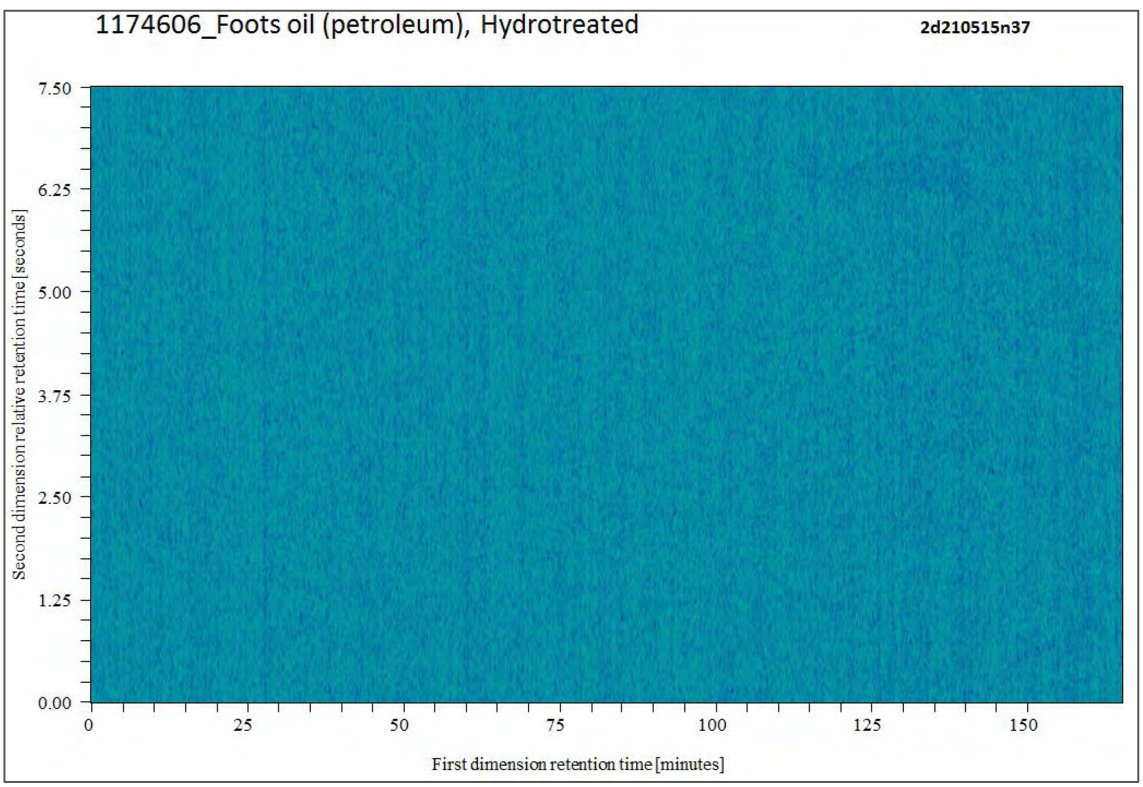

1174589_Paraffin waxes and Hydrocarbon waxes
2d210515n31
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150
First dimension retention time [minutes]

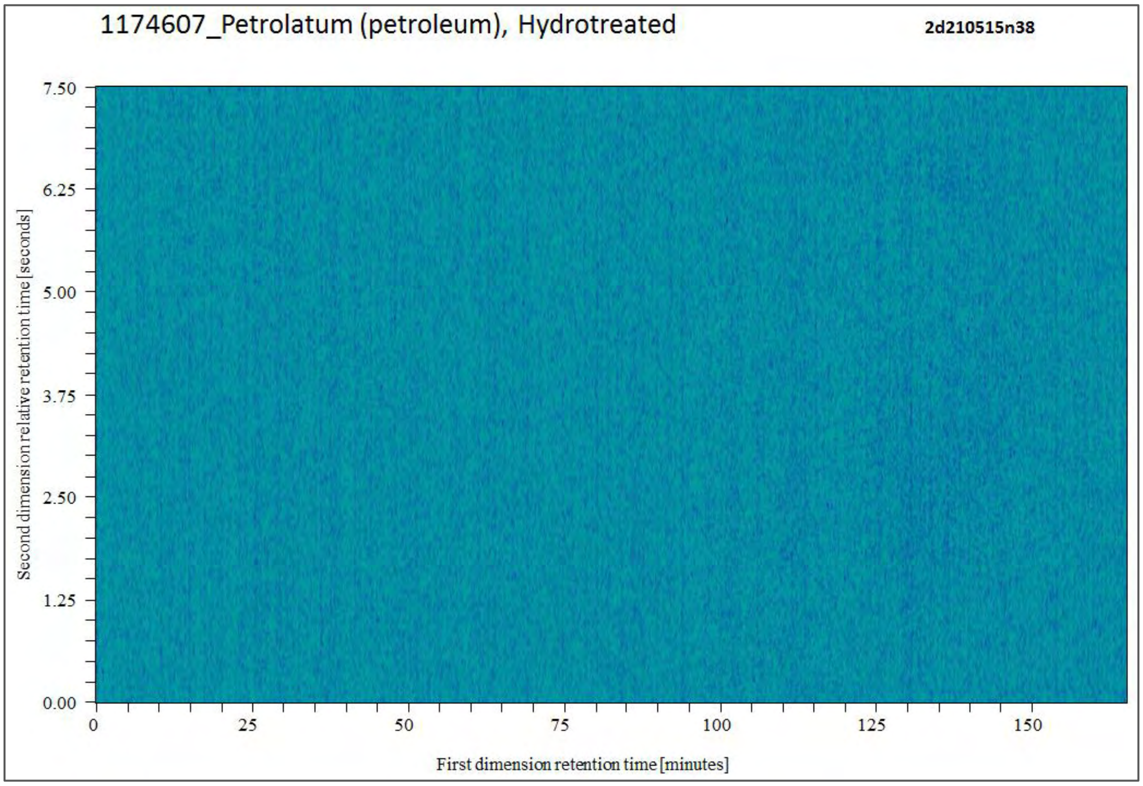

1174591_Paraffin waxes (petroleum), Hydrotreated
2d210515n32
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150
First dimension retention time [minutes]

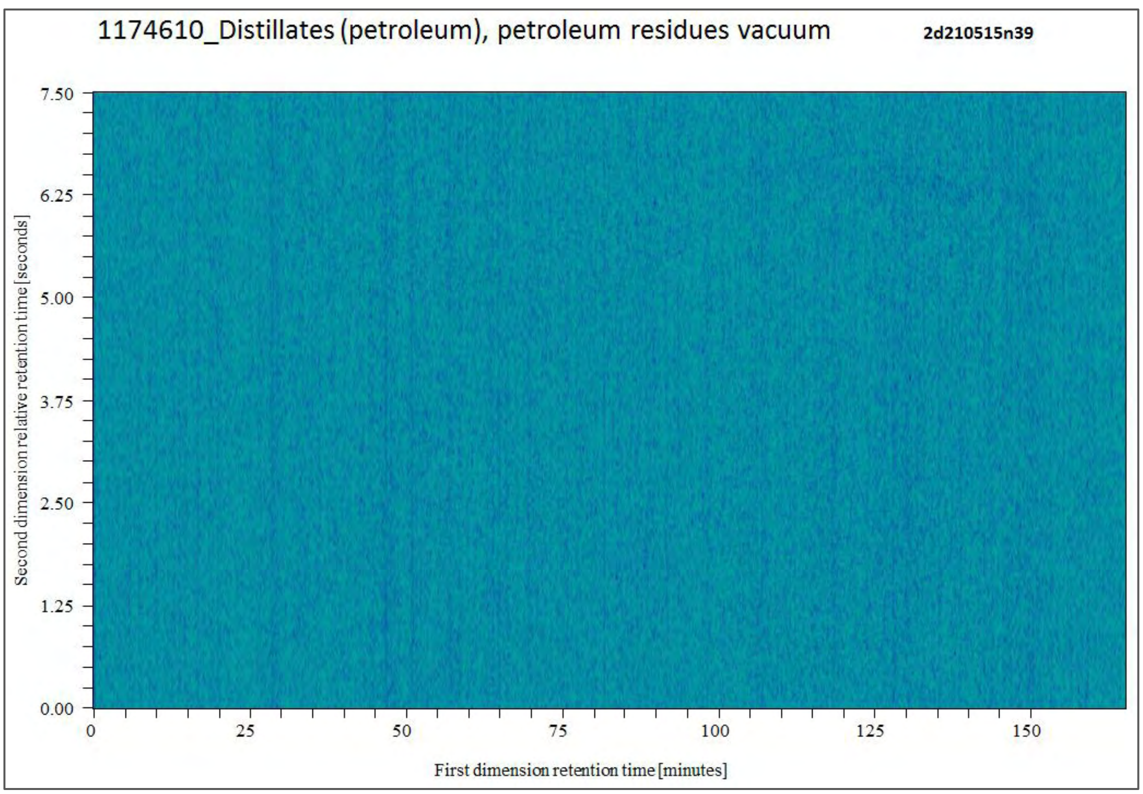

1174595_Fuel oil, residual
2d210515n33
NDB(Carb/Acr)
DB(Carb/Acr)
N-B(Carb/Acr)
B(Carb/Acr)
N-(Carb/Acr)
Carb/Acr
N-(Ind/Q)
Ind/Q
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

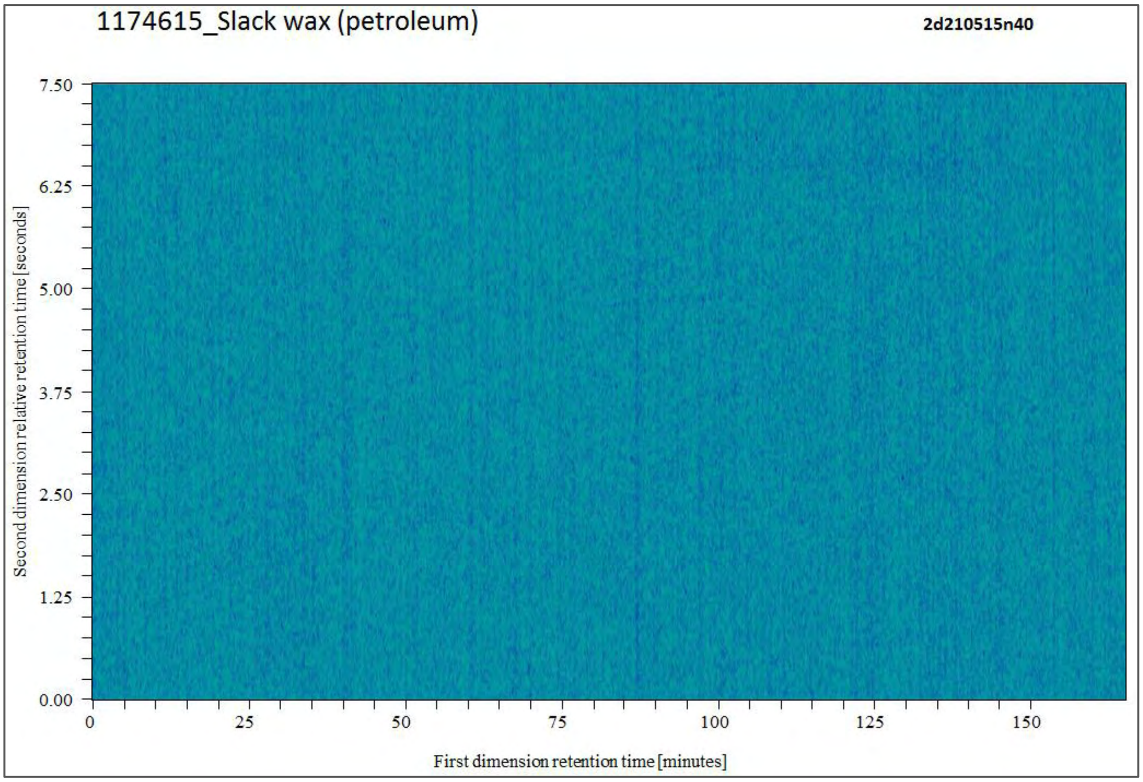

1174602_Foots oil (petroleum)
2d210515n34
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150

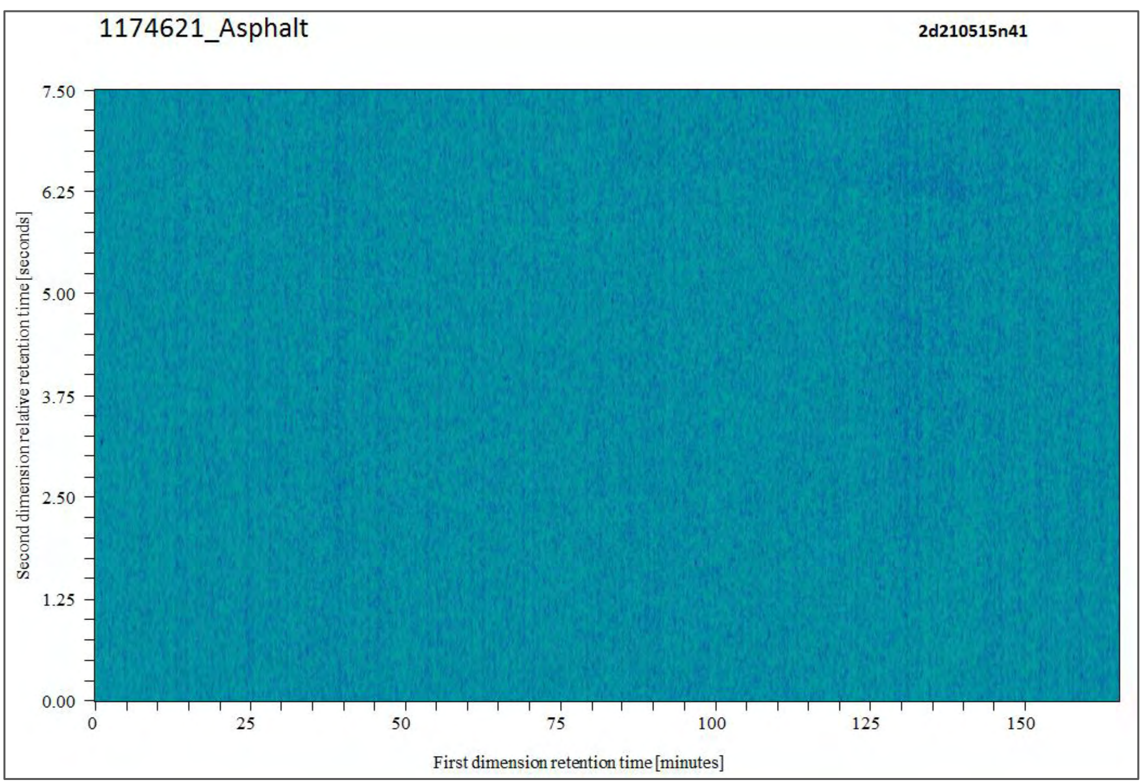

1174603_Petrolatum
2d210515n35
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]

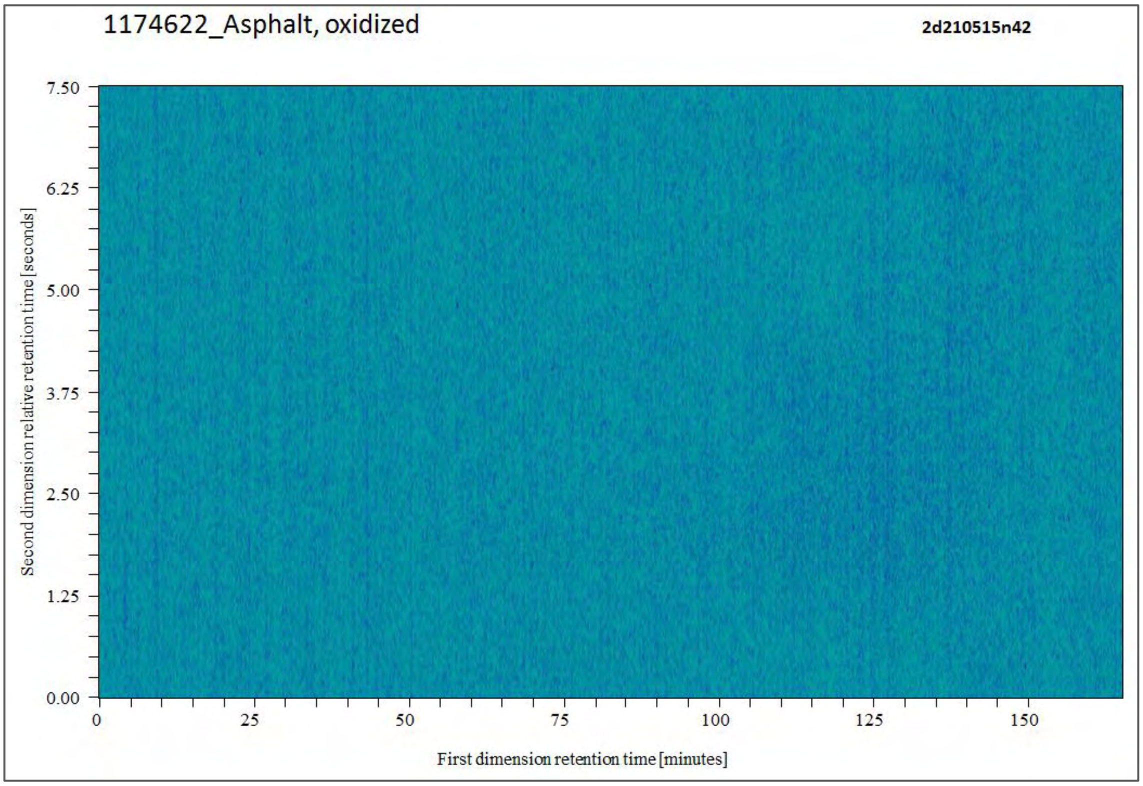

1174606_Foots oil (petroleum), Hydrotreated
2d210515n37
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]


1174607_Petrolatum (petroleum), Hydrotreated
2d210515n38
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]


1174610_Distillates (petroleum), petroleum residues vacuum
2d210515n39
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]

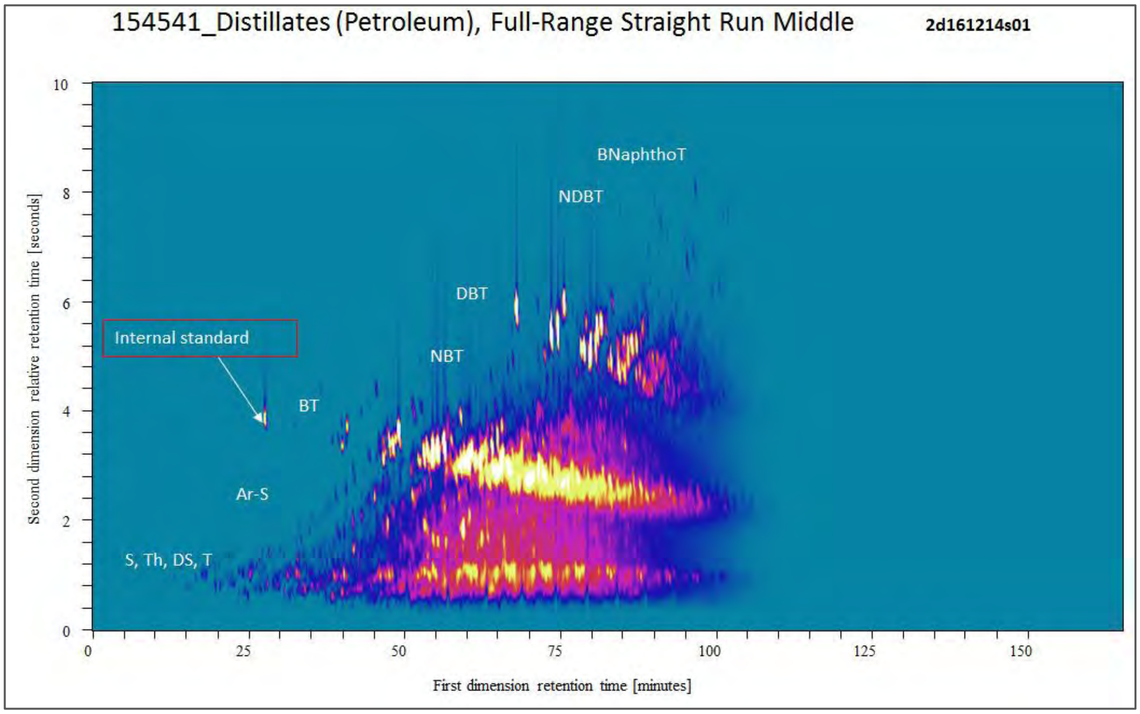

1174615_Slack wax (petroleum)
2d210515n40
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]

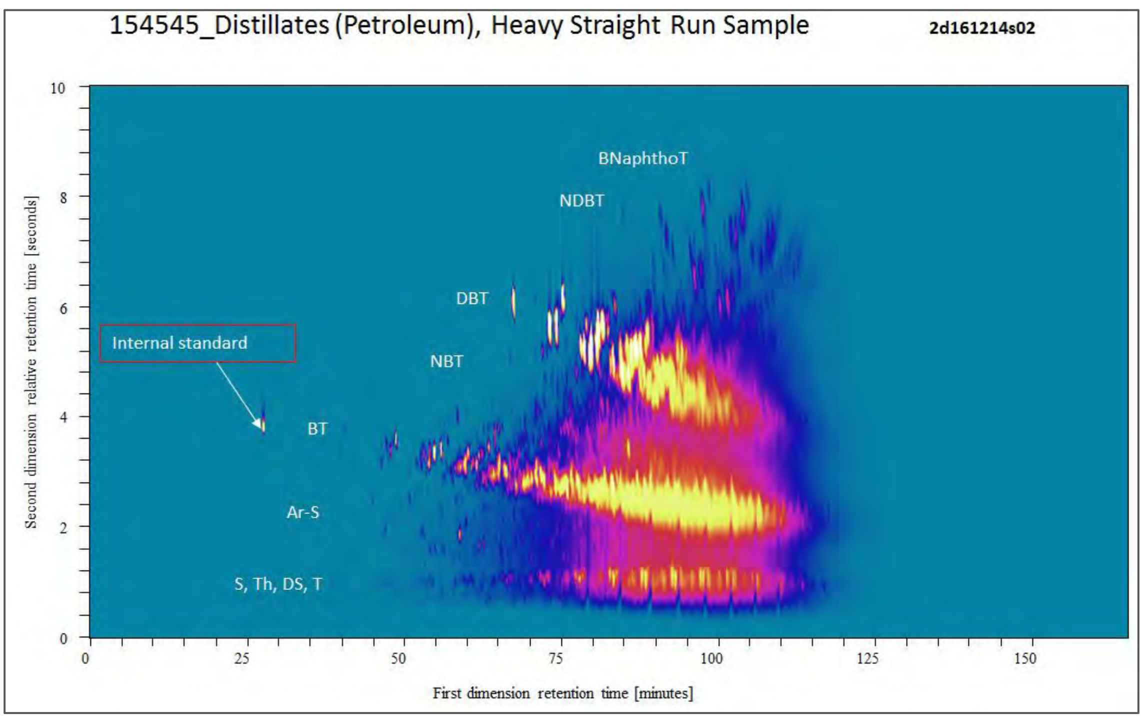

1174621_Asphalt
2d210515n41
7.50
6.25
5.00
3.75
2.50
1.25
0.00
Second dimension relative retention time [seconds]
0
25
50
75
100
125
150
First dimension retention time [minutes]

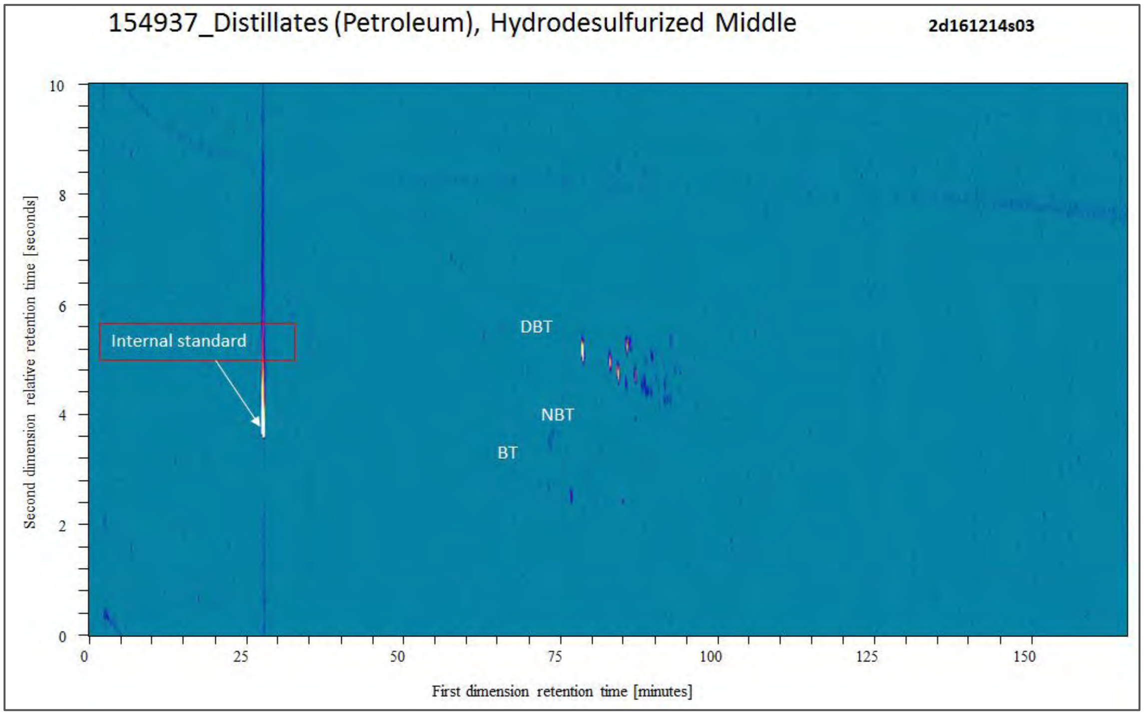


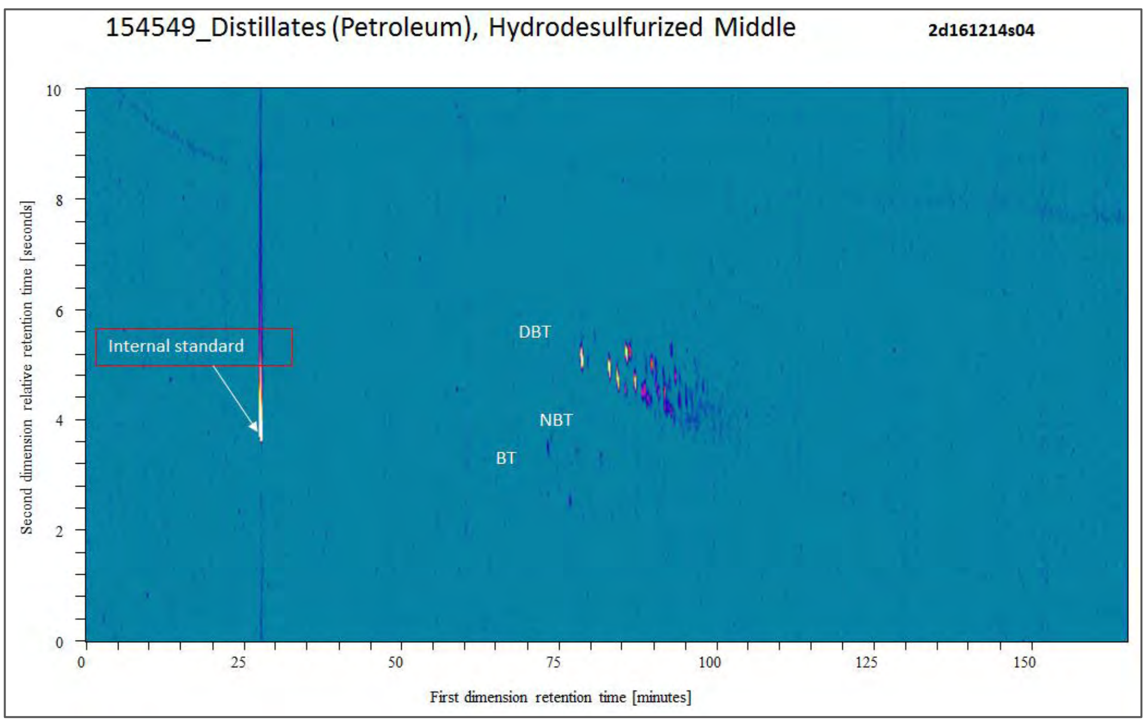
1174622_Asphalt, oxidized
2d210515n42
Second dimension relative retention time [seconds]
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150
First dimension retention time [minutes]

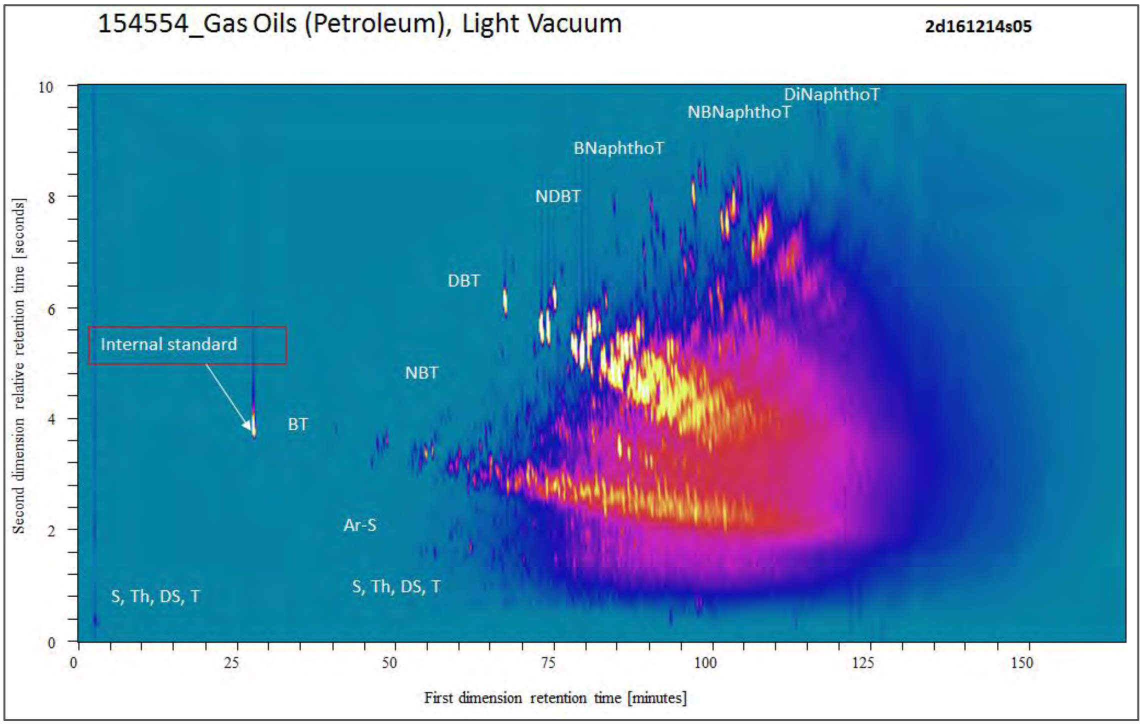
APPENDIX 2: SULPHUR GROUP TYPE GCxGC CHROMATOGRAMS

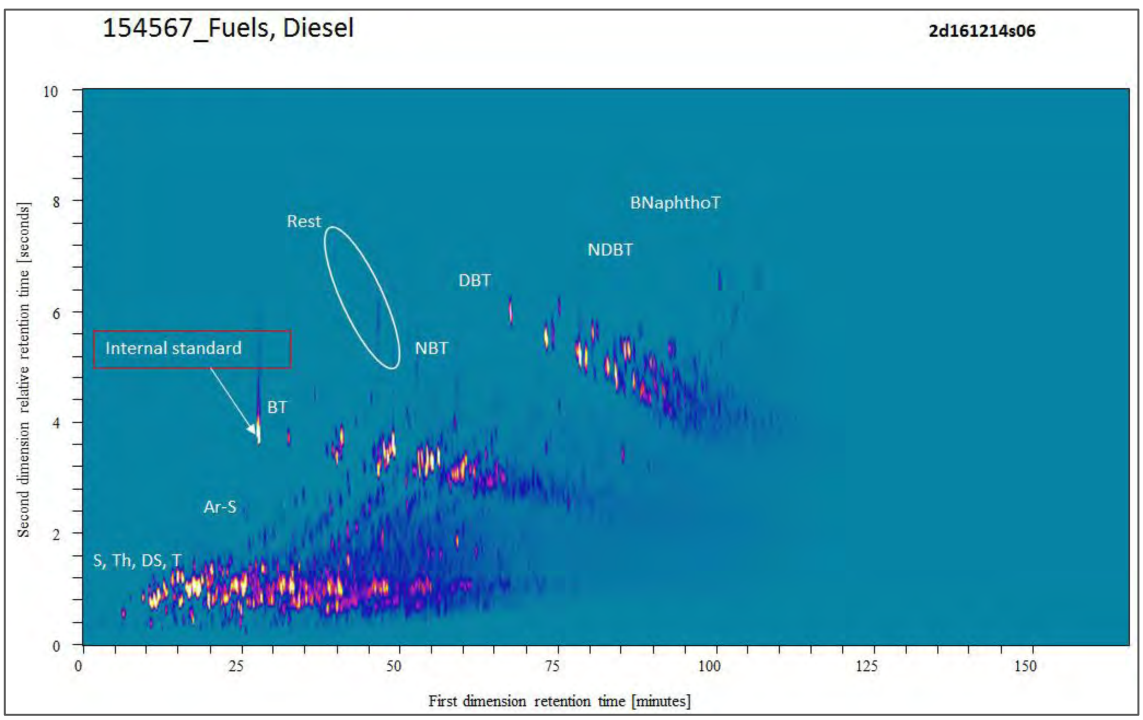


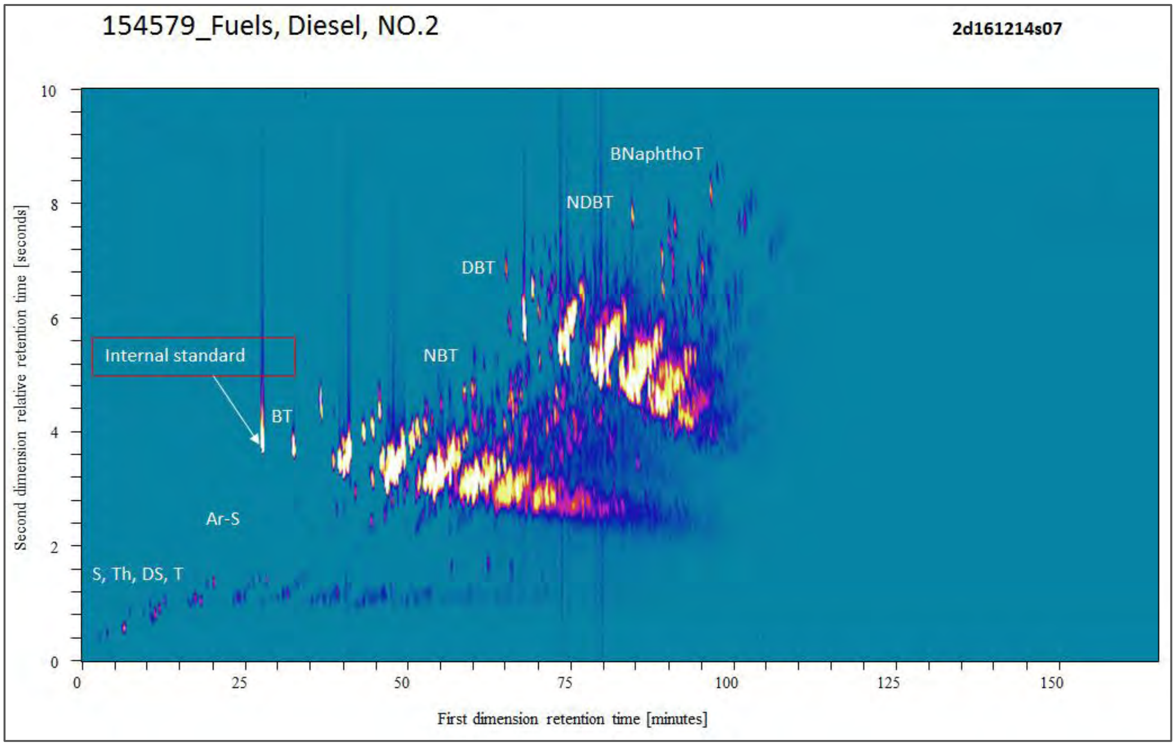


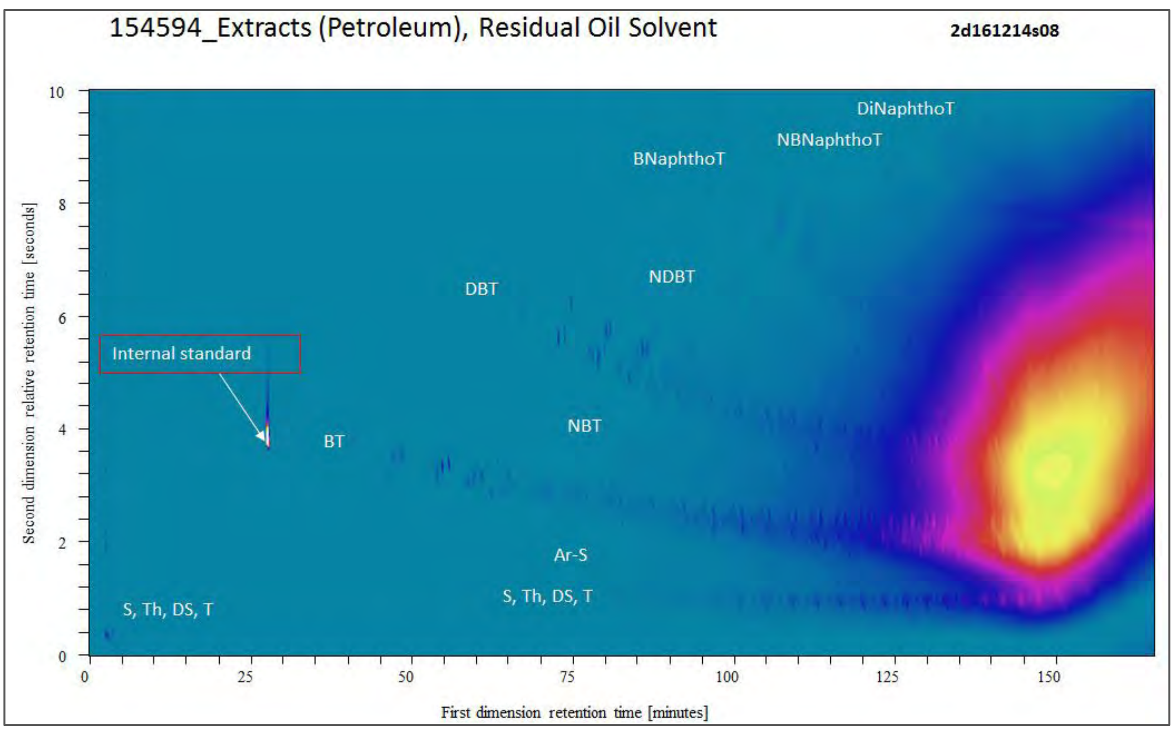

154937_Distillates (Petroleum), Hydrodesulfurized Middle
2d161214s03
Internal standard
DBT
NBT
BT
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
0
25
50
75
100
125
150

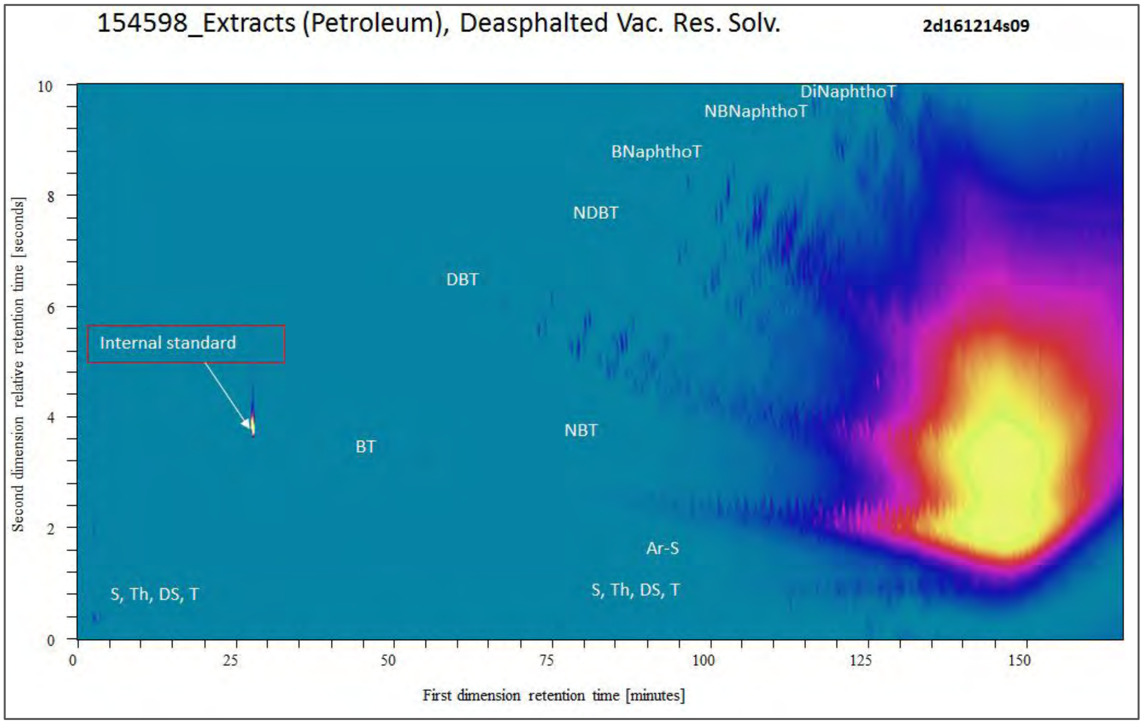

154549_Distillates (Petroleum), Hydrodesulfurized Middle
2d161214s04
Internal standard
DBT
NBT
BT
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
0
25
50
75
100
125
150

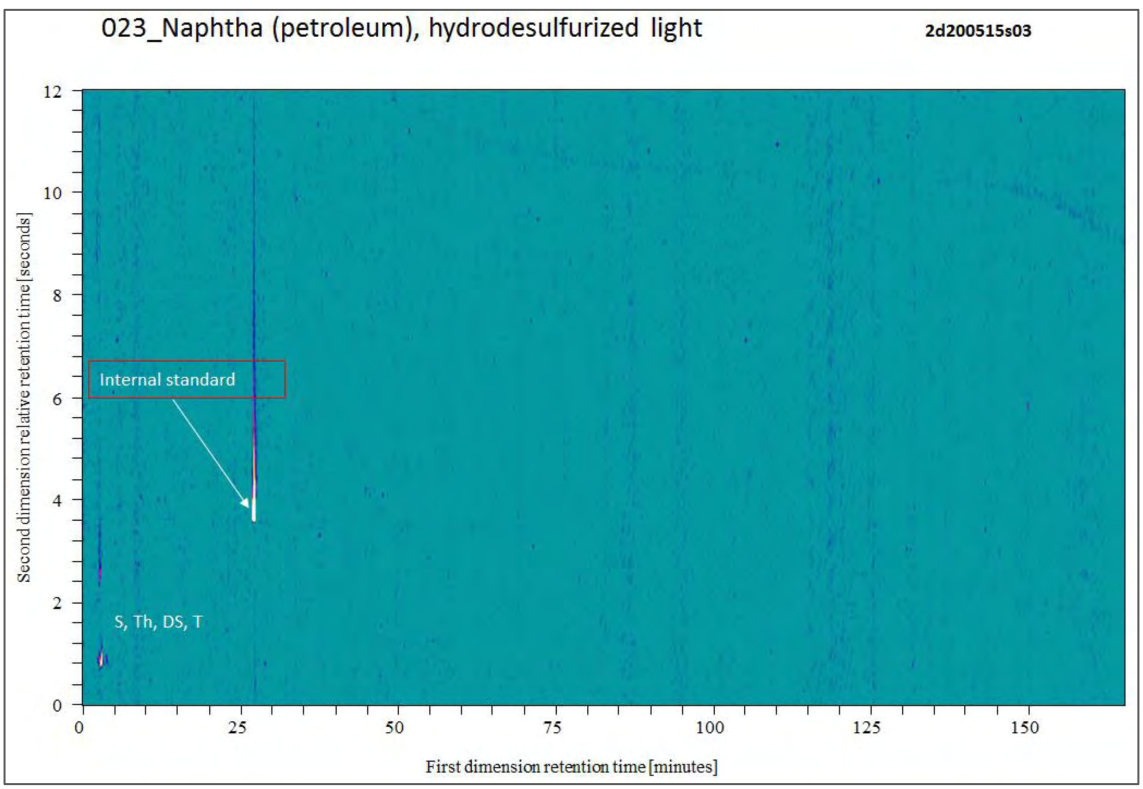

154554_Gas Oils (Petroleum), Light Vacuum
2d161214s05
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
DBT
Internal standard
NBT
BT
Ar-S
S, Th, DS, T
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
0
25
50
75
100
125
150

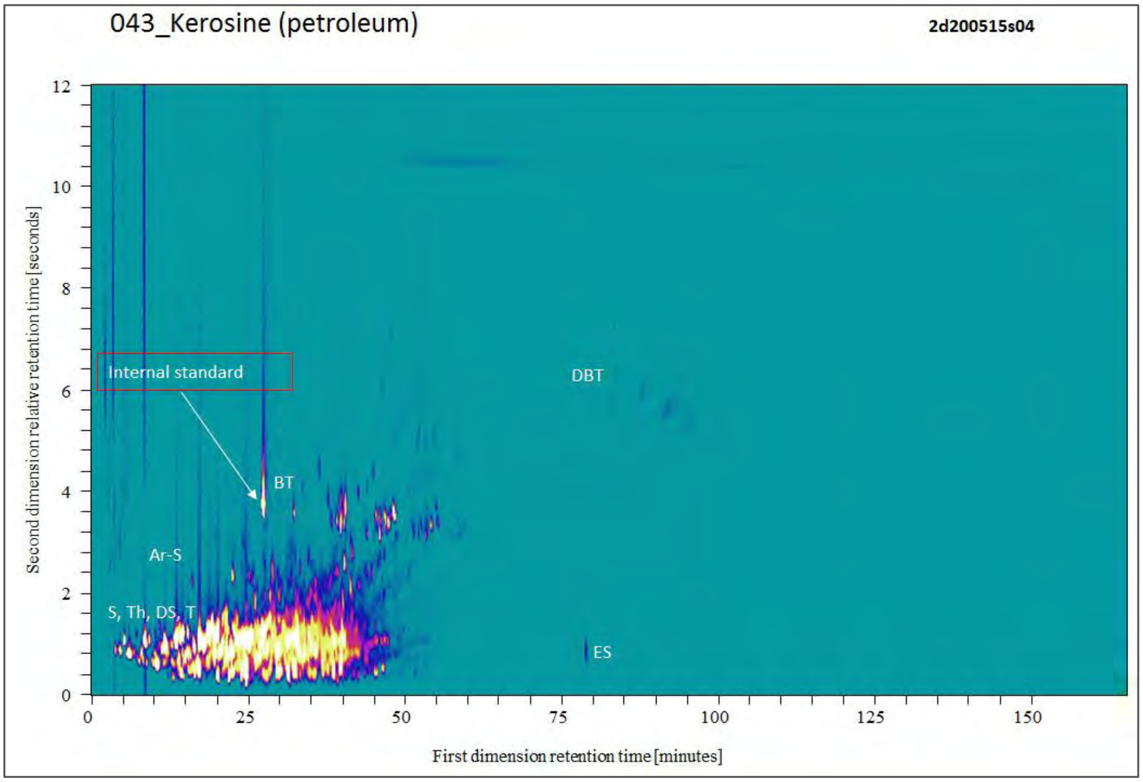

154567_Fuels, Diesel
2d161214s06
BNaphthoT
Rest
NDBT
DBT
Internal standard
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
0
25
50
75
100
125
150

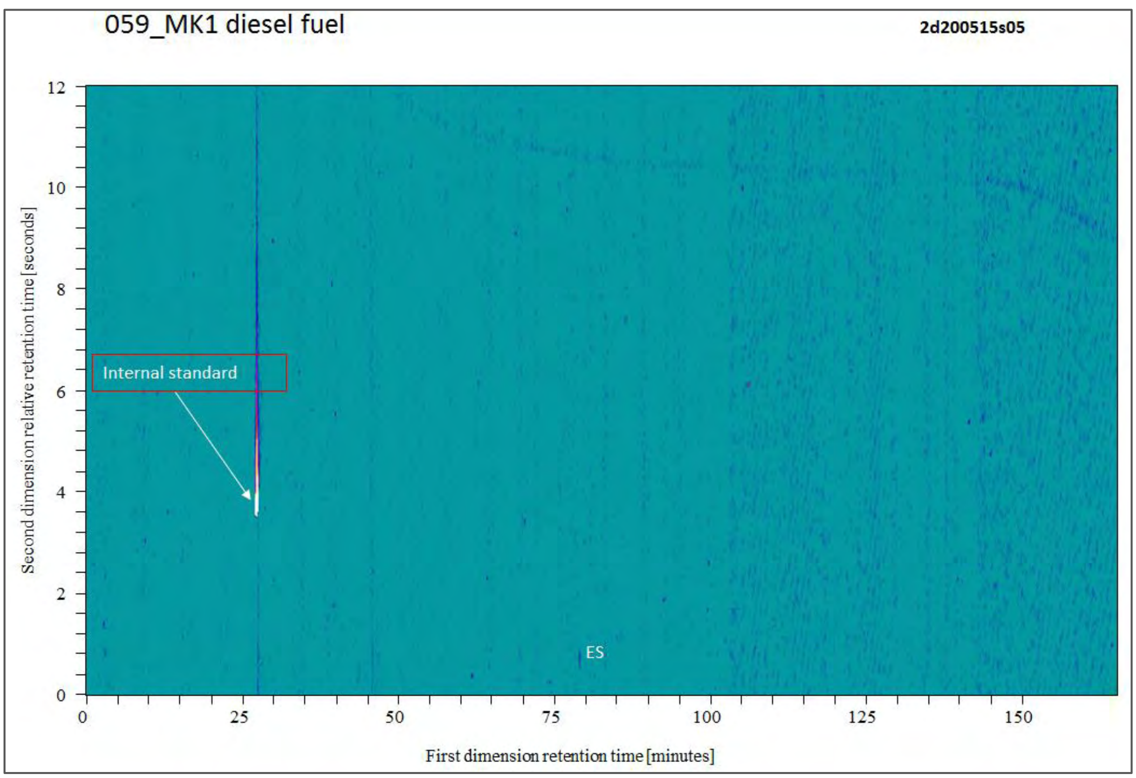

154579_Fuels, Diesel, NO.2
2d161214s07
Internal standard
BT
NBT
DBT
NDBT
BNaphthoT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
25
50
75
100
125
150

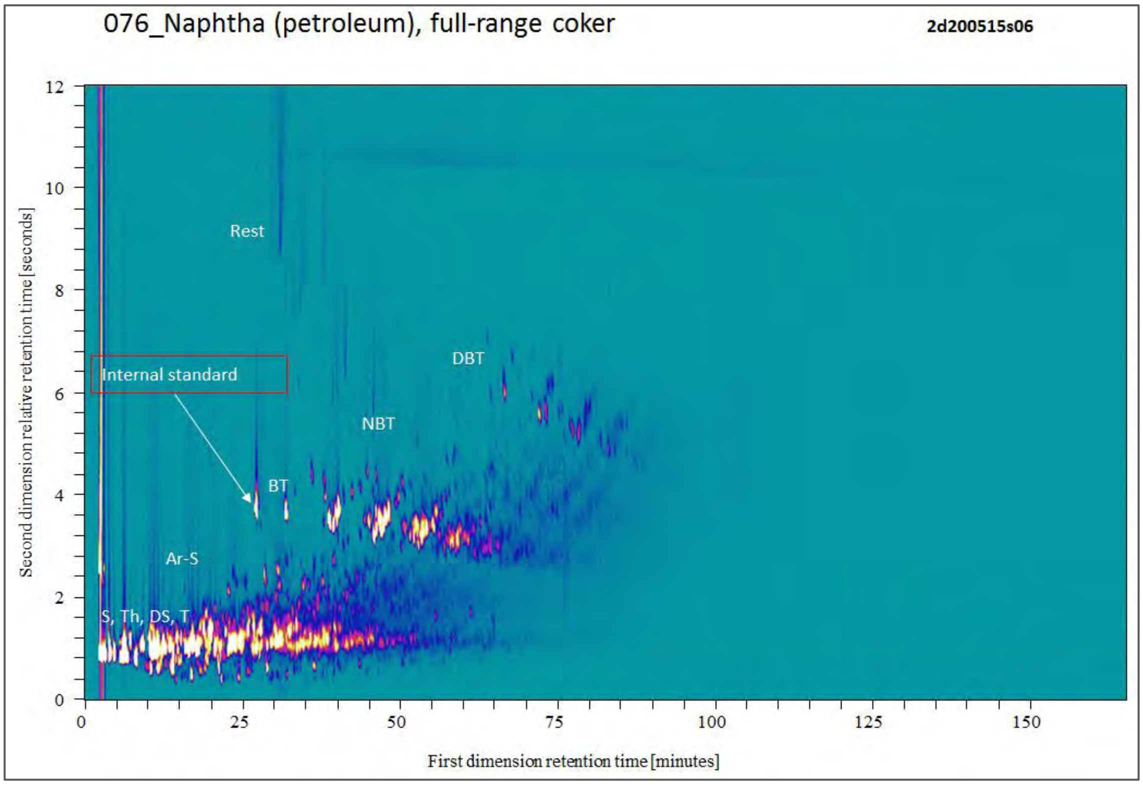

154594_Extracts (Petroleum), Residual Oil Solvent
2d161214s08
Internal standard
BT
NBT
DBT
NDBT
BNaphthoT
NBNaphthoT
DiNaphthoT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
25
50
75
100
125
150

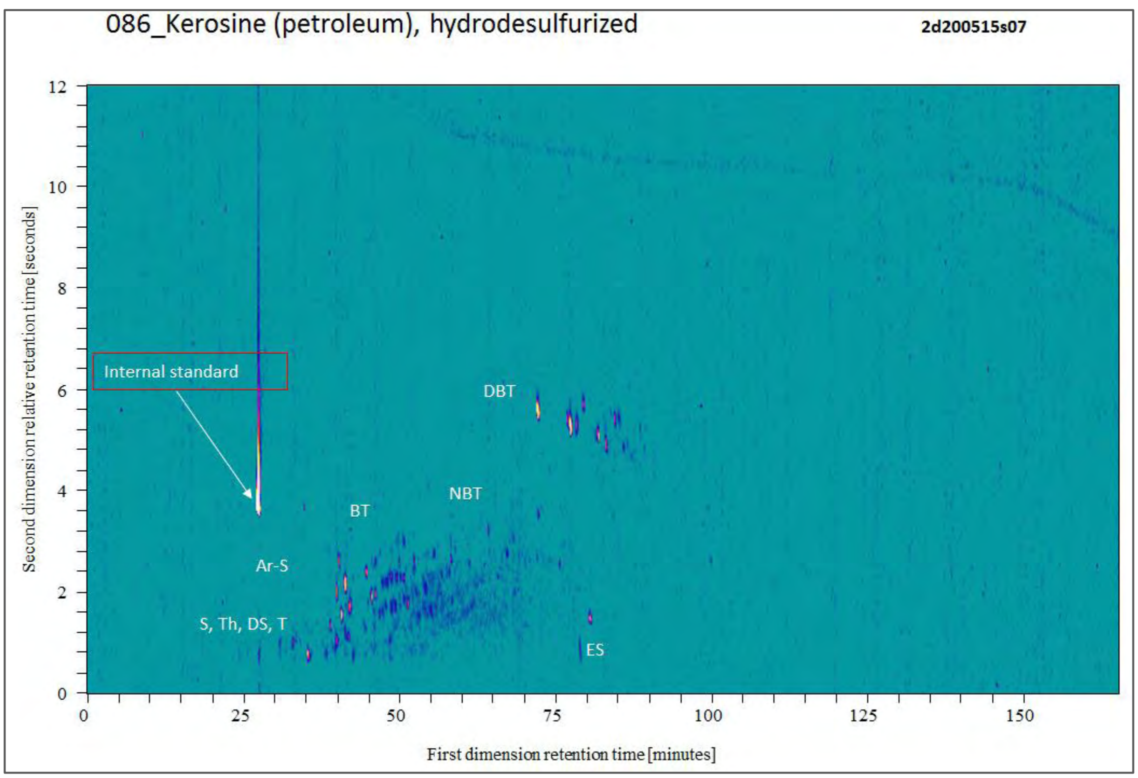

154598_Extracts (Petroleum), Deasphalted Vac. Res. Solv.
2d161214s09
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
DBT
Internal standard
BT
NBT
Ar-S
S, Th, DS, T
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

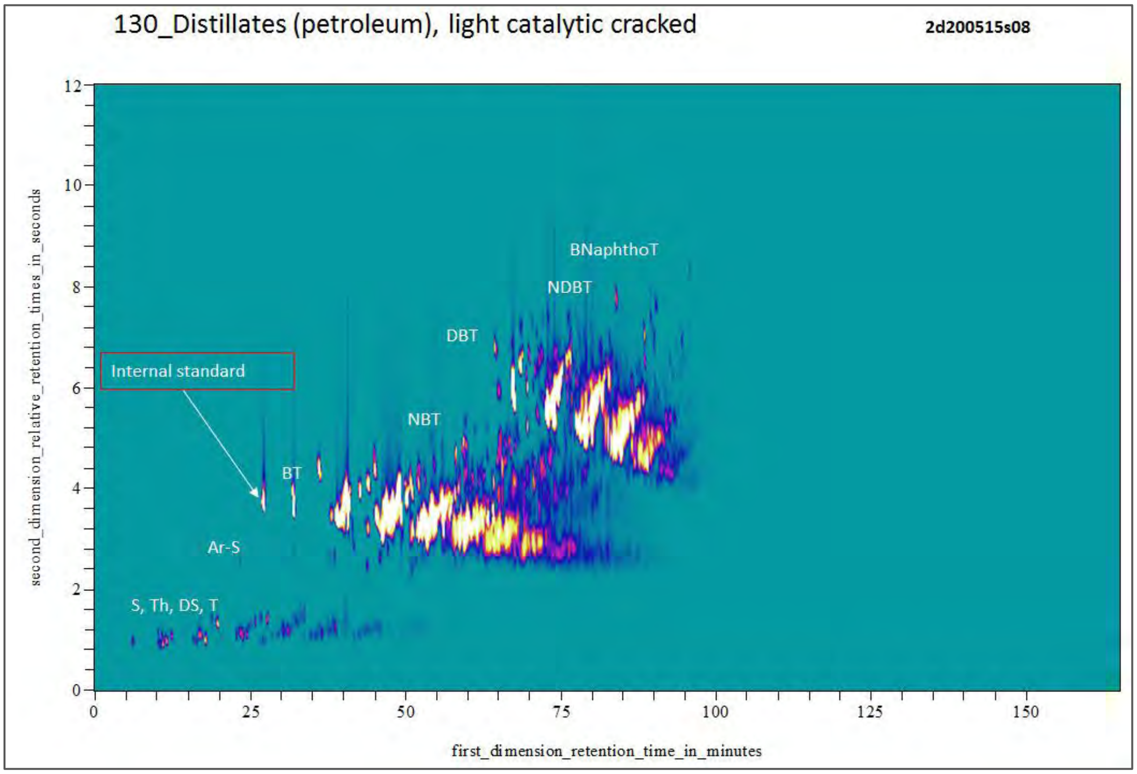

023_Naphtha (petroleum), hydrodesulfurized light
2d200515s03
Internal standard
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

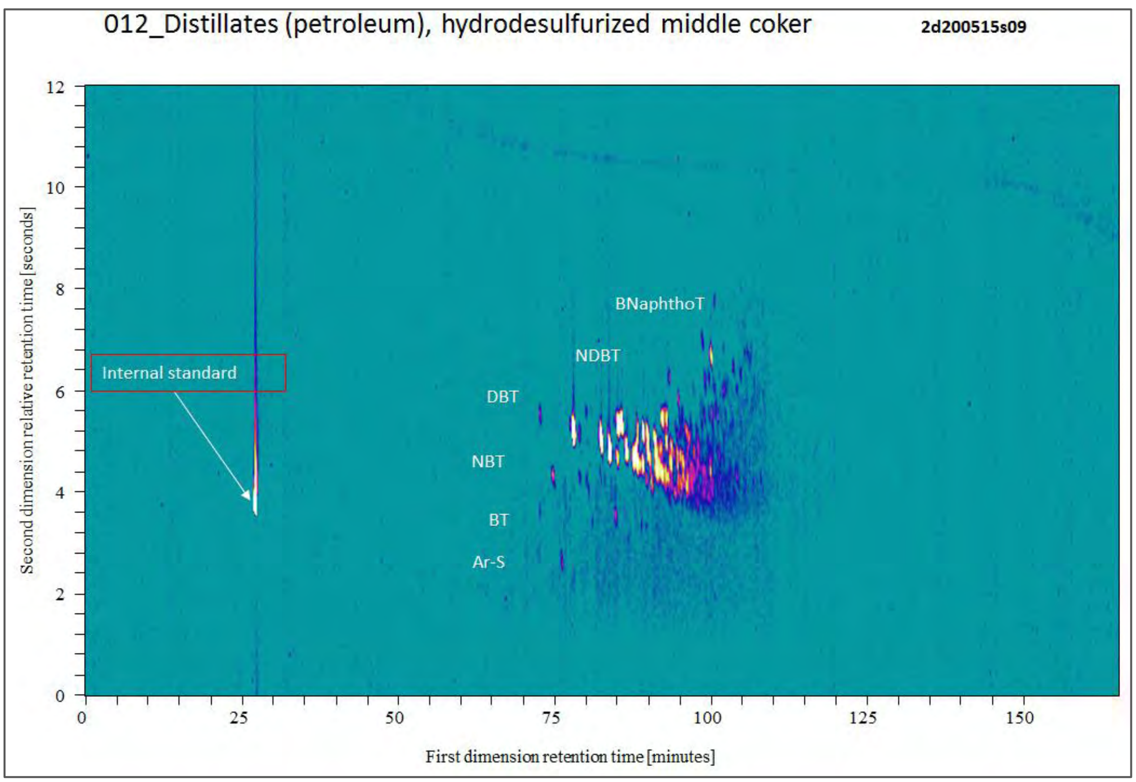

043_Kerosine (petroleum)
2d200515s04
Internal standard
DBT
BT
Ar-S
S, Th, DS, T
ES
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

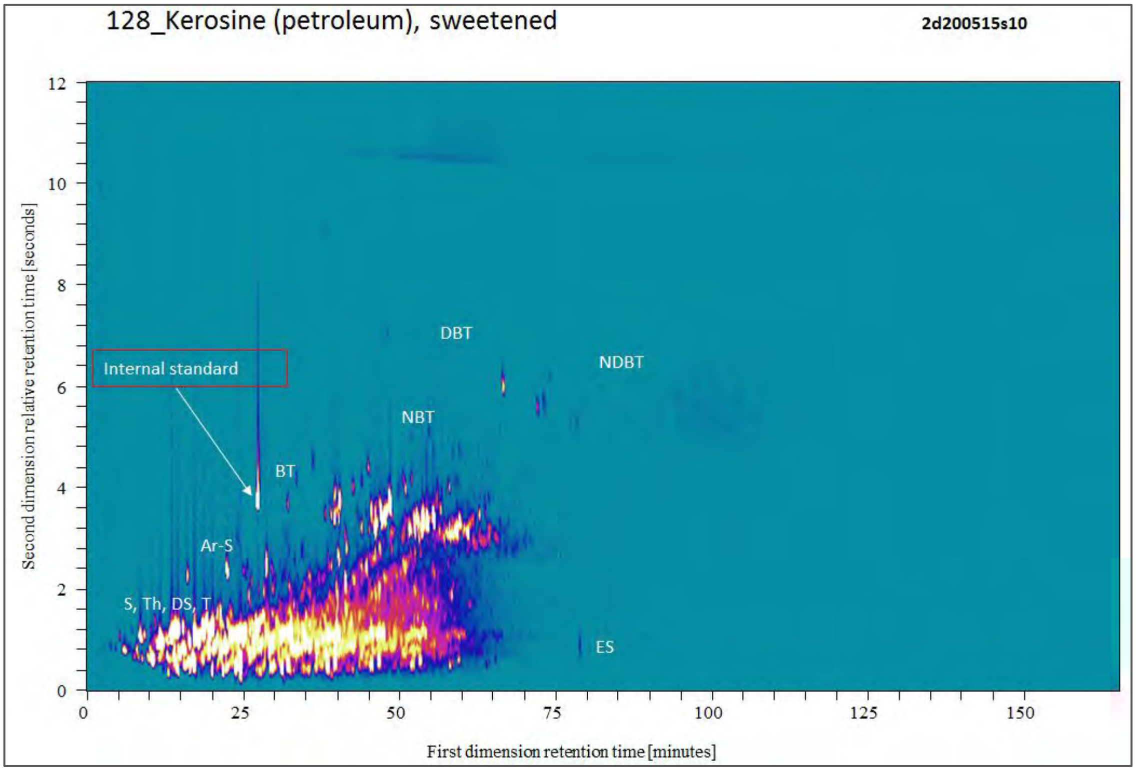

059_MK1 diesel fuel
2d200515s05
Internal standard
ES
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

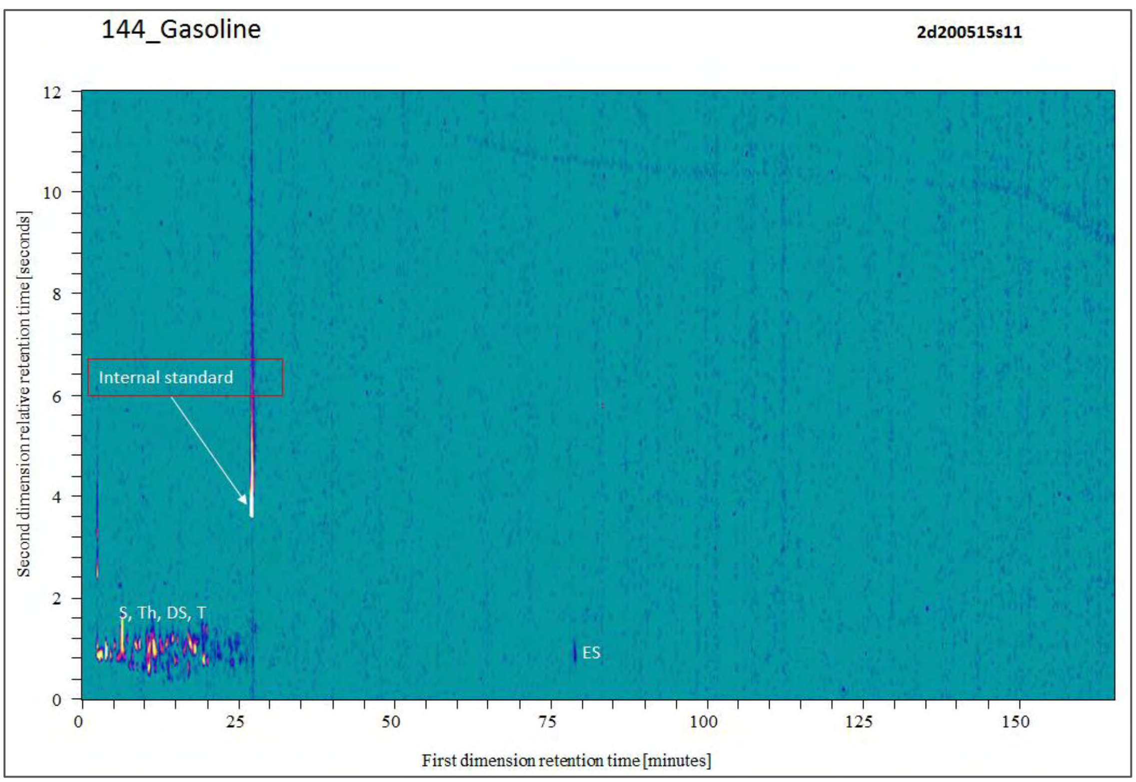

076_Naphtha (petroleum), full-range coker
2d200515s06
Rest
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
25
50
75
100
125
150

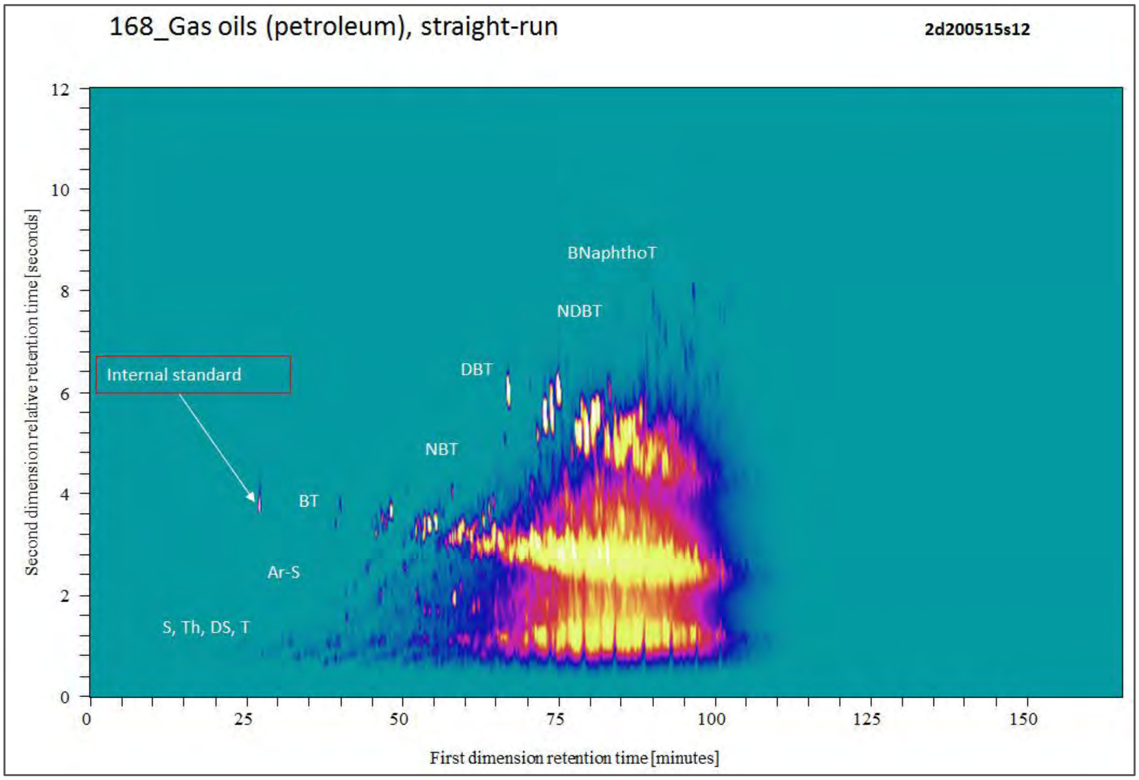

086_Kerosine (petroleum), hydrodesulfurized
2d200515s07
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
ES
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
25
50
75
100
125
150


130_Distillates (petroleum), light catalytic cracked
2d200515s08
BNaphthoT
NDBT
DBT
Internal standard
NBT
BT
Ar-S
S, Th, DS, T
second_dimension_relative_retention_times_in_seconds
first_dimension_retention_time_in_minutes
0
2
4
6
8
10
12
25
50
75
100
125
150

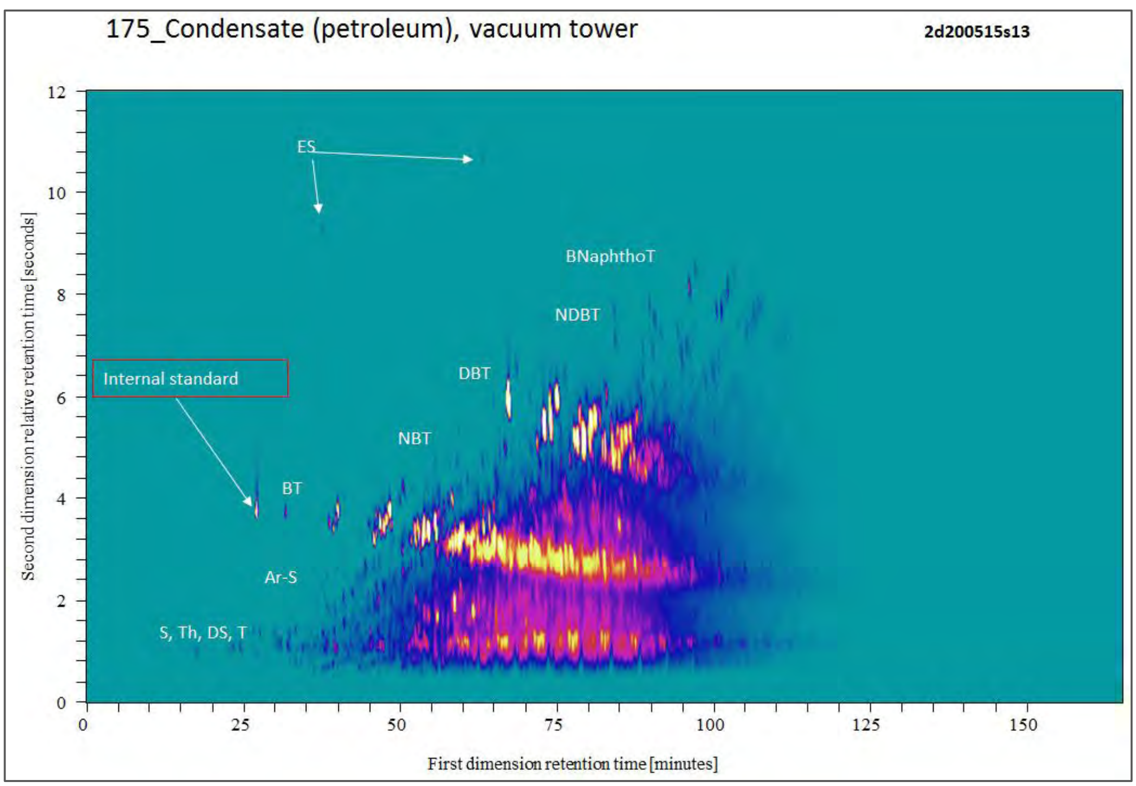

012_Distillates (petroleum), hydrodesulfurized middle coker
2d200515s09
BNaphthoT
NDBT
DBT
Internal standard
NBT
BT
Ar-S
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
25
50
75
100
125
150


128_Kerosine (petroleum), sweetened
2d200515s10
Internal standard
BT
Ar-S
S, Th, DS, T
NBT
DBT
NDBT
ES
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

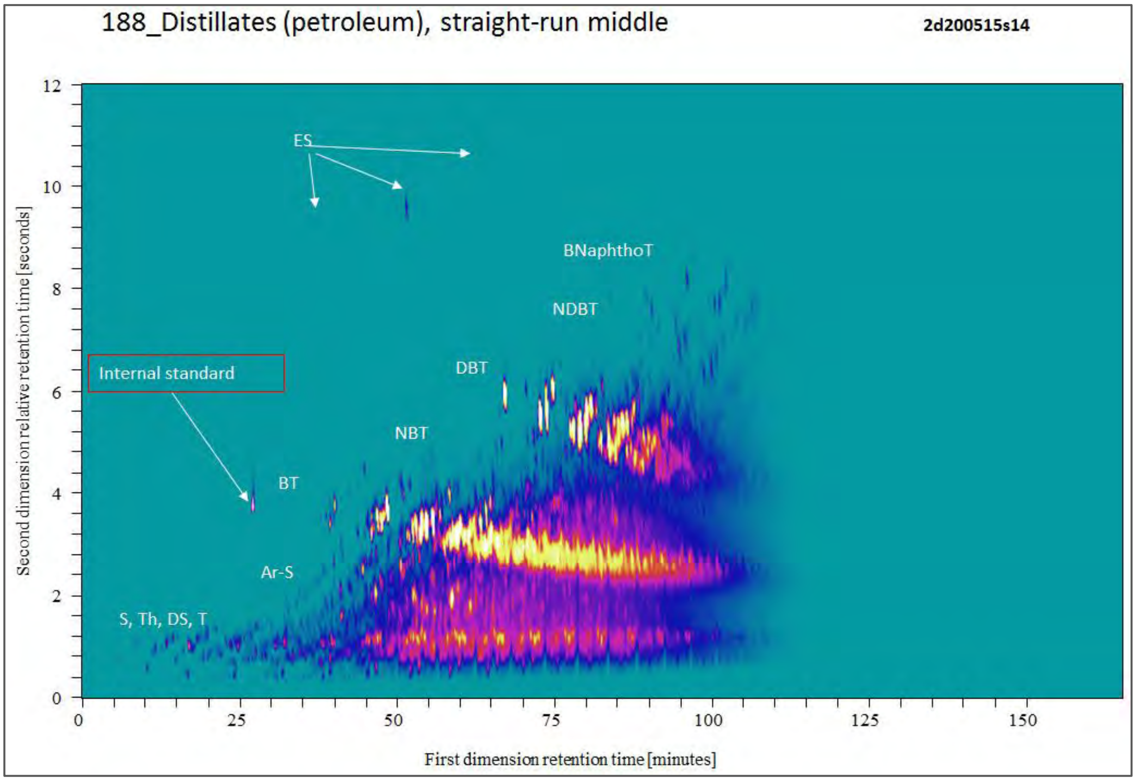

144_Gasoline
2d200515s11
Internal standard
S, Th, DS, T
ES
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

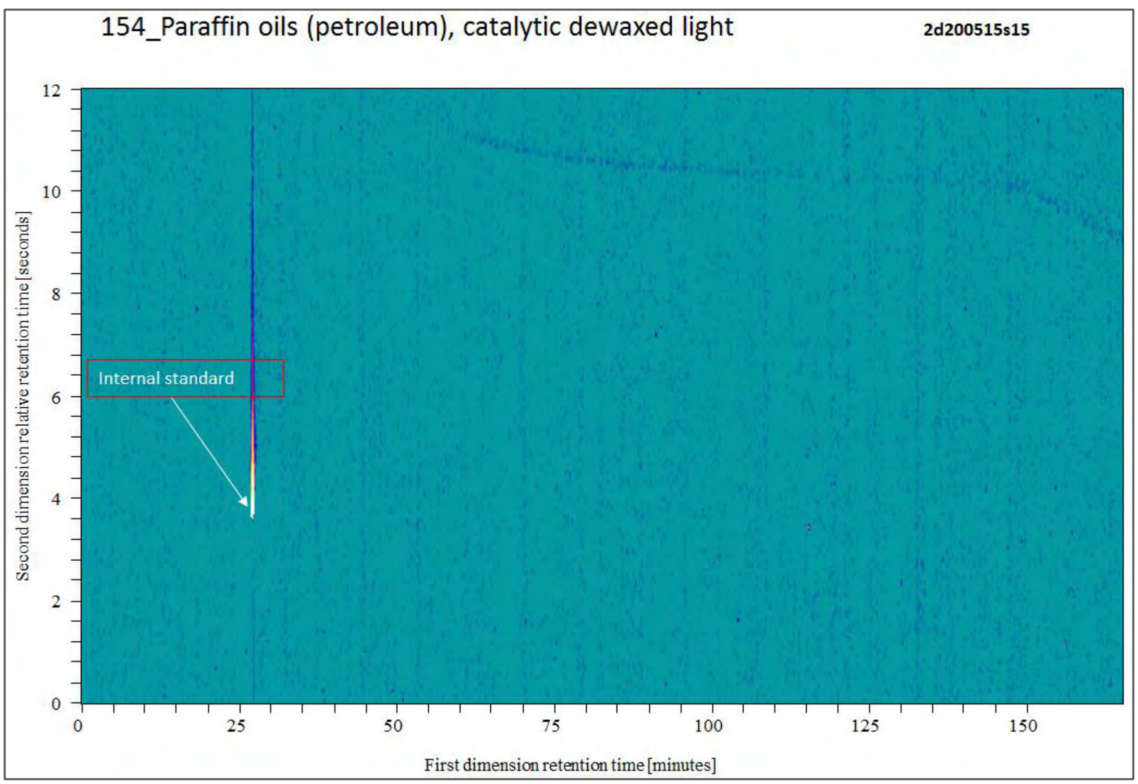


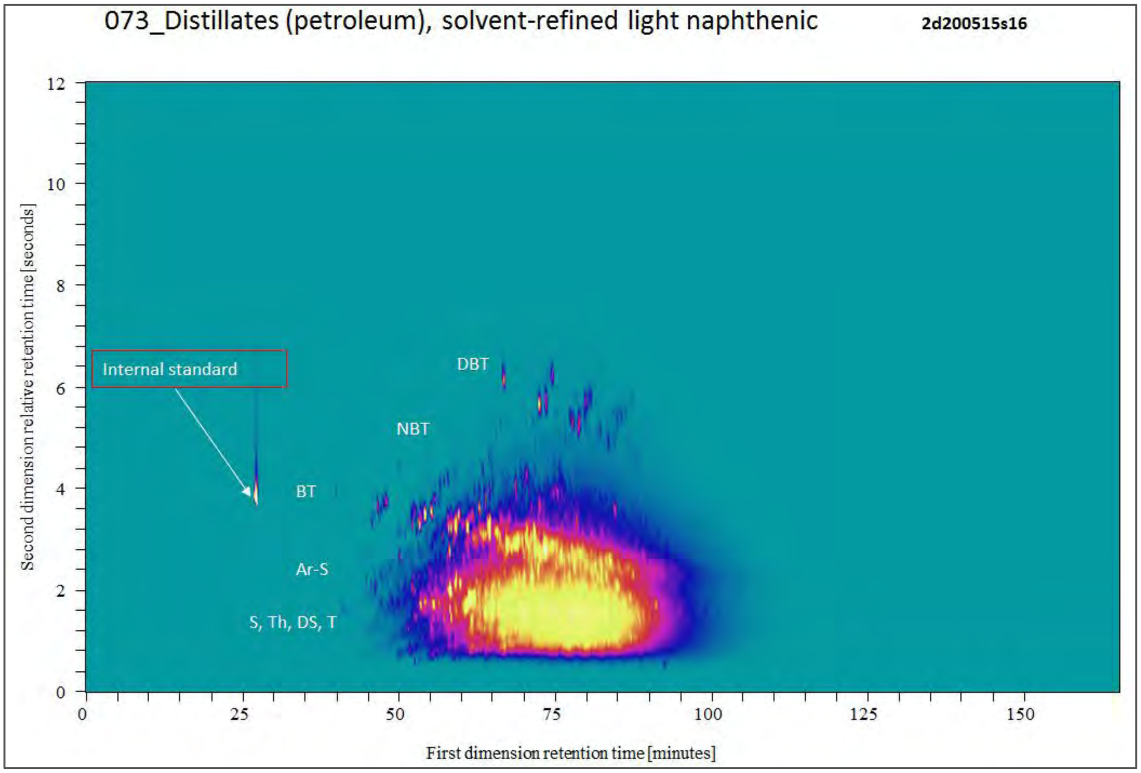
168_Gas oils (petroleum), straight-run
2d200515s12
Internal standard
BT
Ar-S
S, Th, DS, T
NBT
DBT
NDBT
BNaphthoT
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

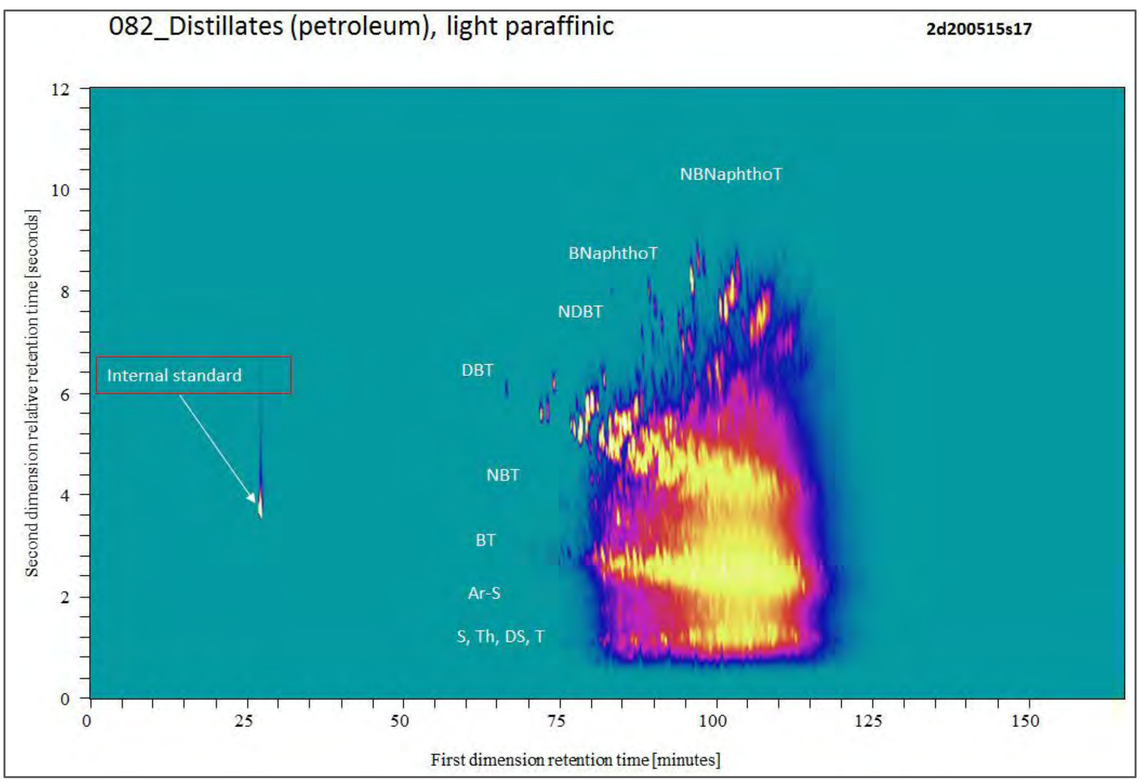


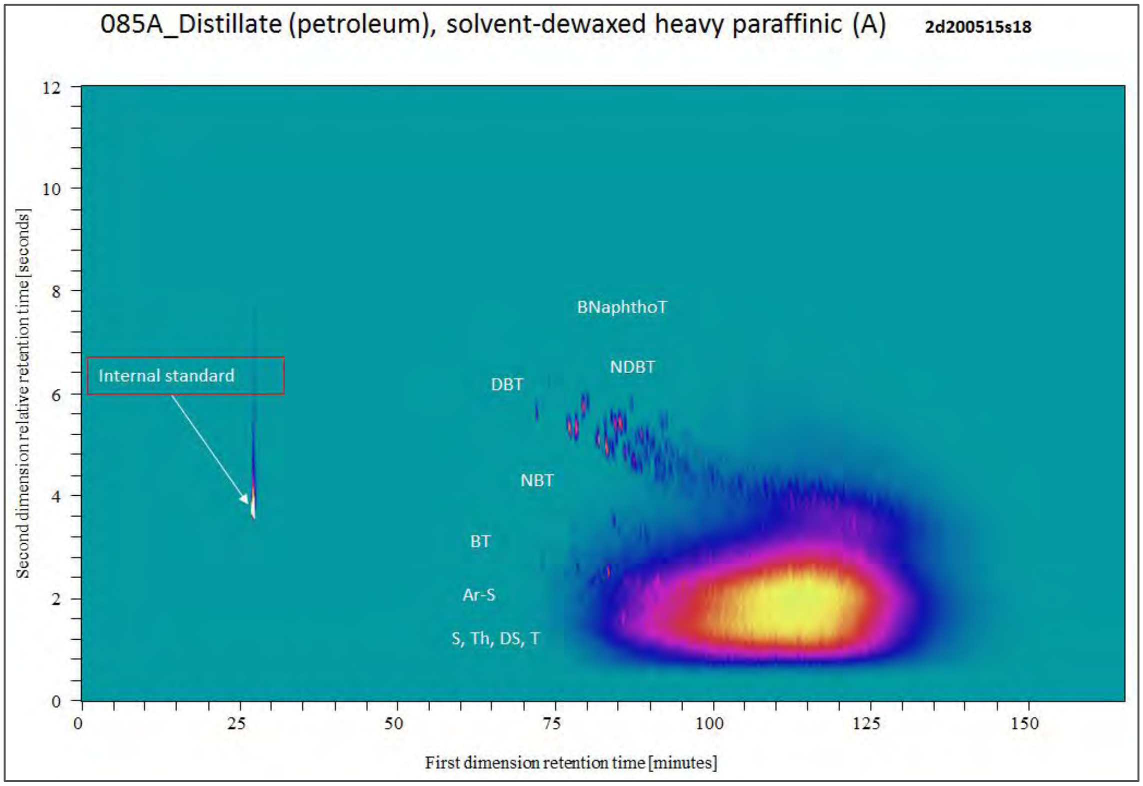
175_Condensate (petroleum), vacuum tower
2d200515s13
ES
Internal standard
BT
Ar-S
S, Th, DS, T
NBT
DBT
NDBT
BNaphthoT
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

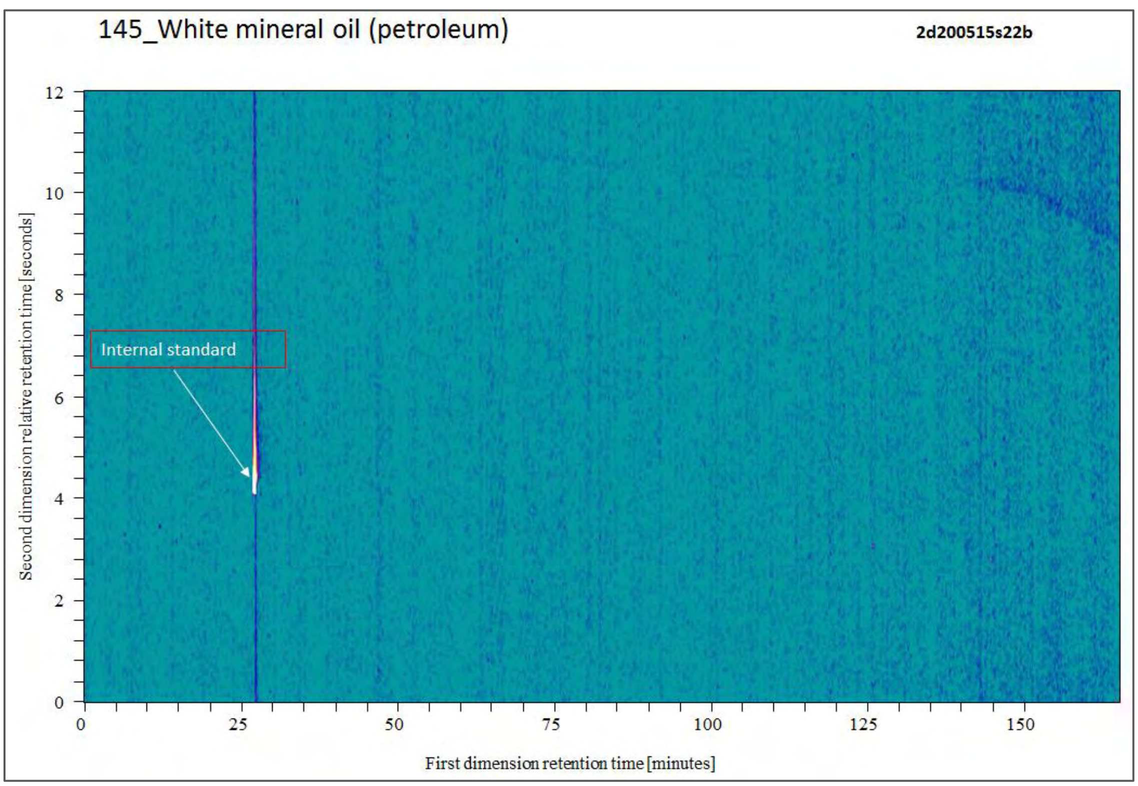

188_Distillates (petroleum), straight-run middle
2d200515s14
ES
BNaphthoT
NDBT
DBT
Internal standard
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

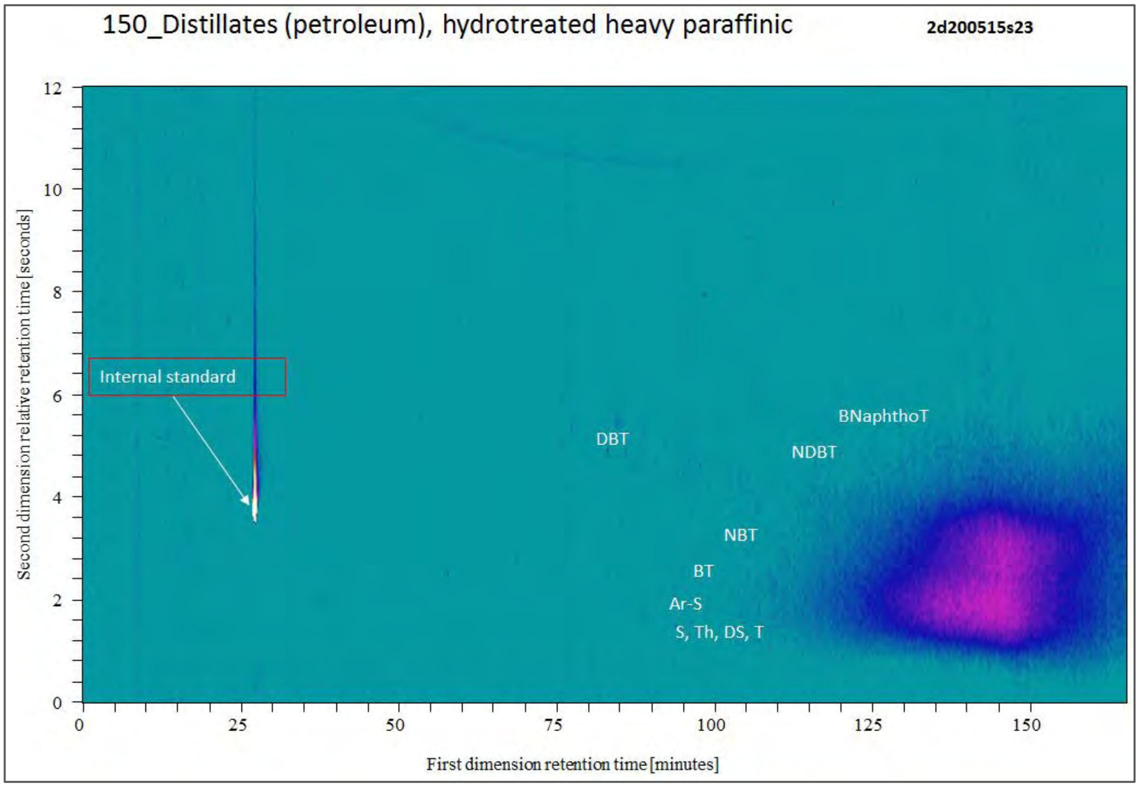

154_Paraffin oils (petroleum), catalytic dewaxed light
2d200515s15
Internal standard
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

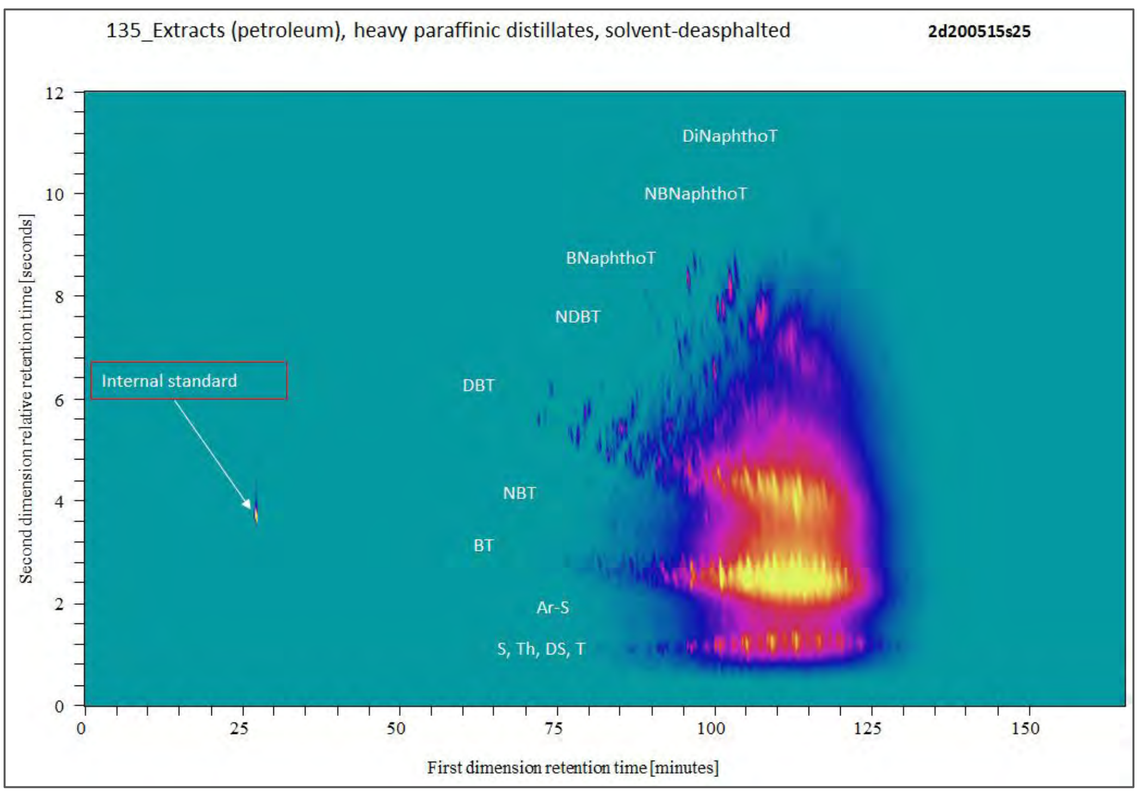

073_Distillates (petroleum), solvent-refined light naphthenic
2d200515s16
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

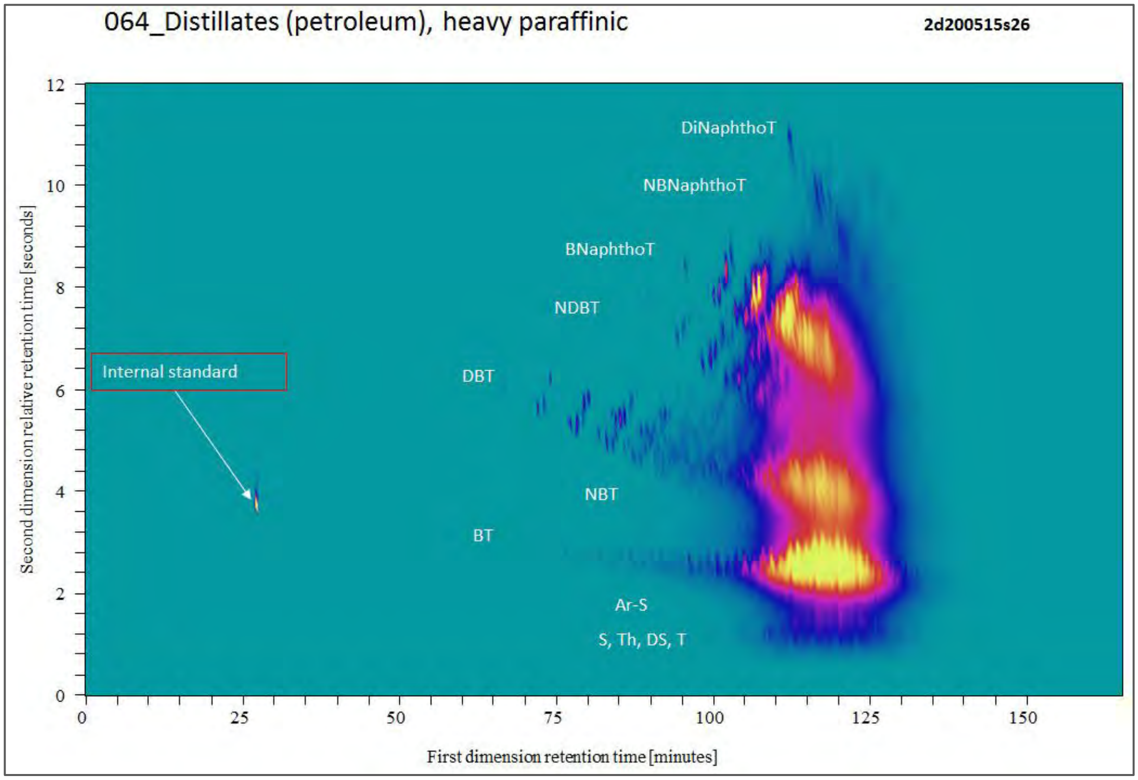

082_Distillates (petroleum), light paraffinic
2d200515s17
NBNaphthoT
BNaphthoT
NDBT
DBT
Internal standard
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

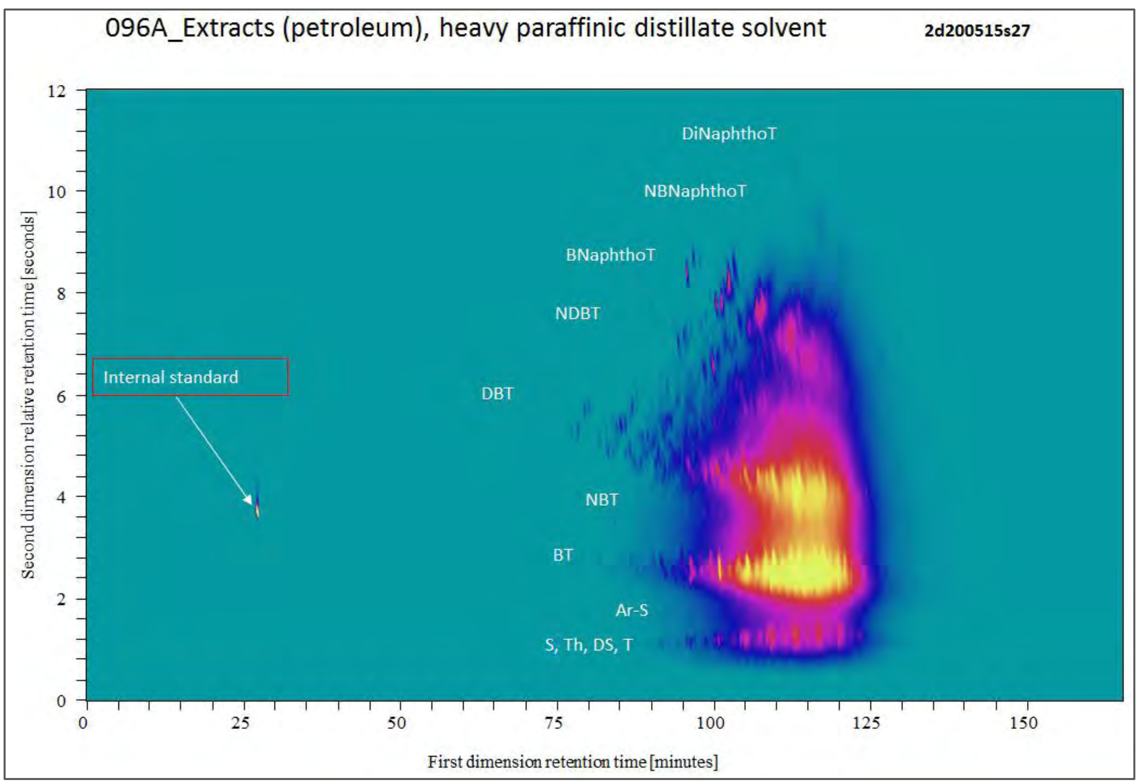

085A_Distillate (petroleum), solvent-dewaxed heavy paraffinic (A)
2d200515s18
Internal standard
BNaphthoT
NDBT
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

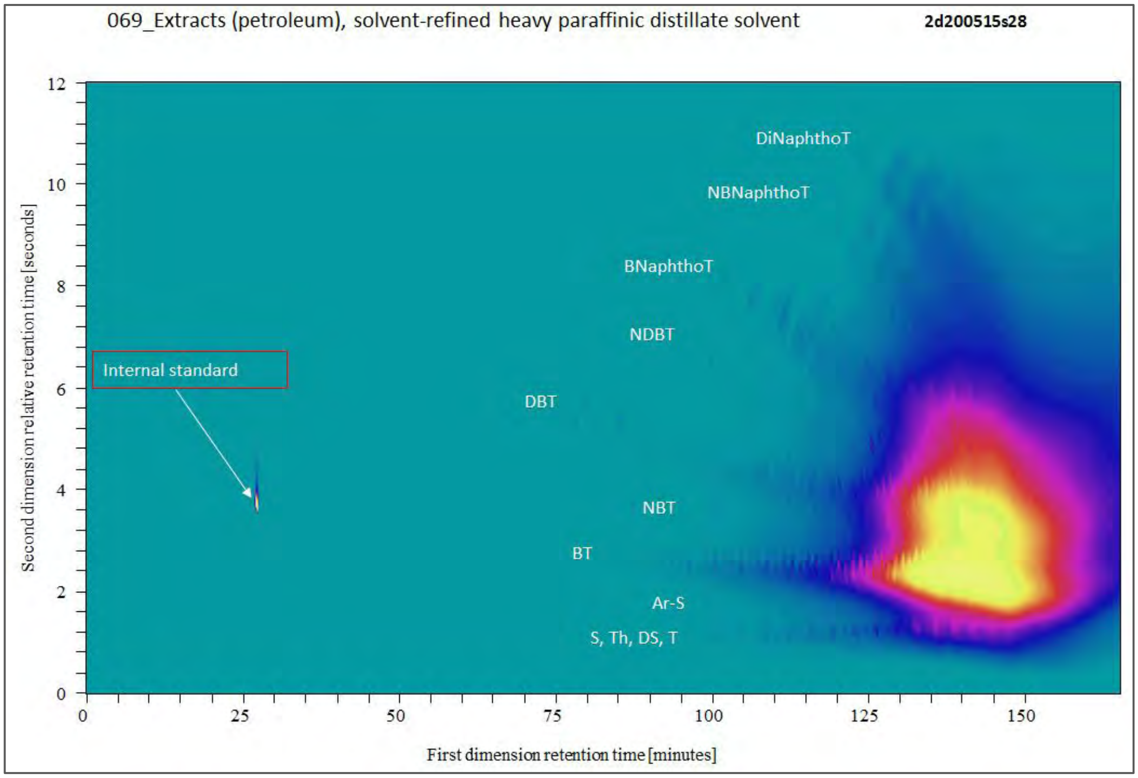

145_White mineral oil (petroleum)
2d200515s22b
Internal standard
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

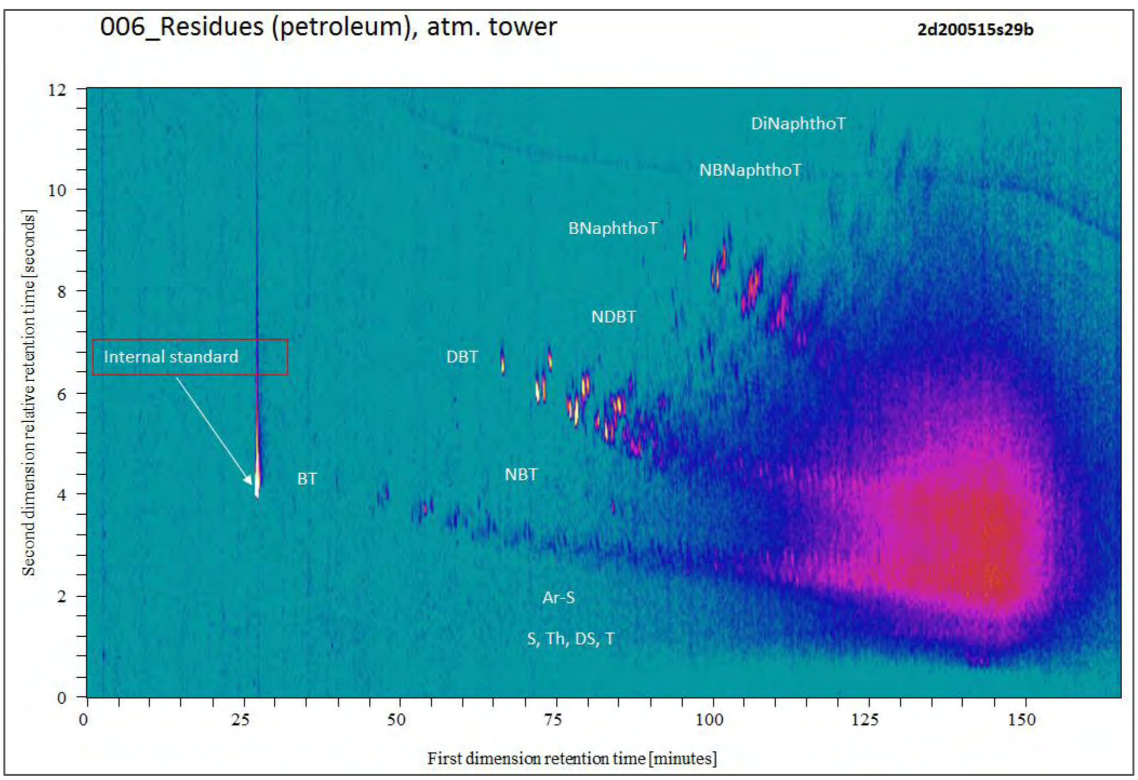

150_Distillates (petroleum), hydrotreated heavy paraffinic
2d200515s23
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
Internal standard
DBT
BNaphthoT
NDBT
NBT
BT
Ar-S
S, Th, DS, T

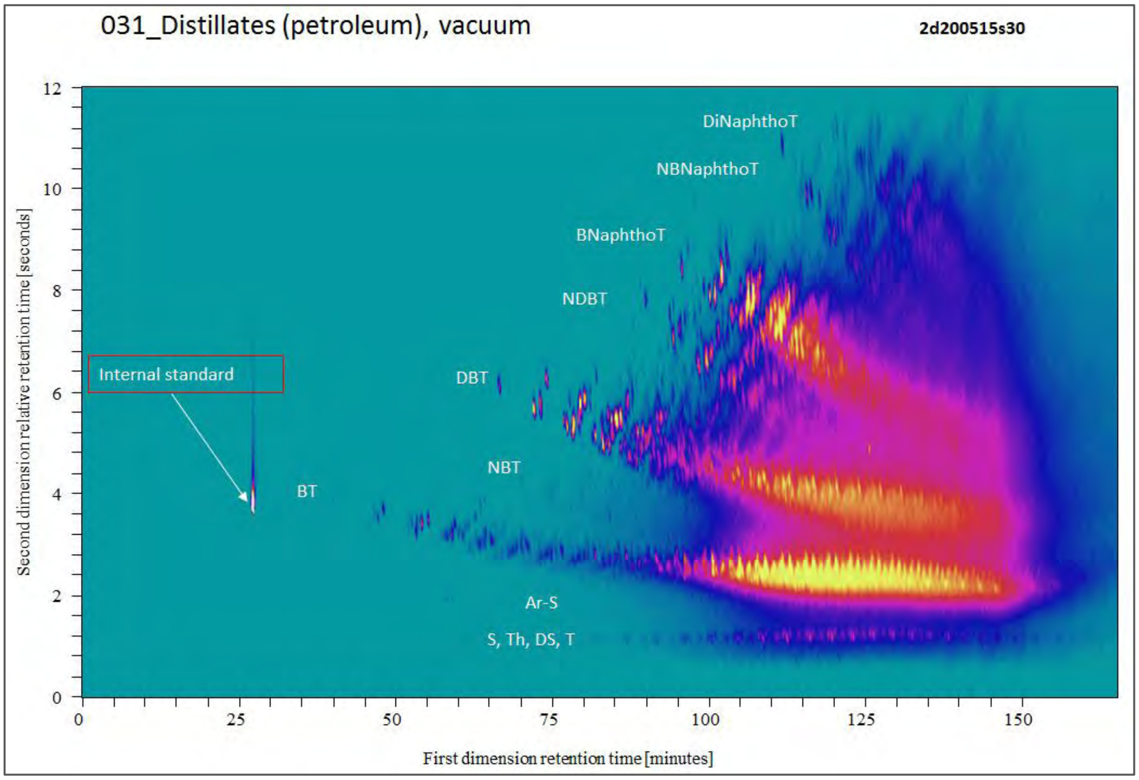

135_Extracts (petroleum), heavy paraffinic distillates, solvent-deasphalted
2d200515s25
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
Internal standard
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
DBT
NBT
BT
Ar-S
S, Th, DS, T


064_Distillates (petroleum), heavy paraffinic
2d200515s26
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

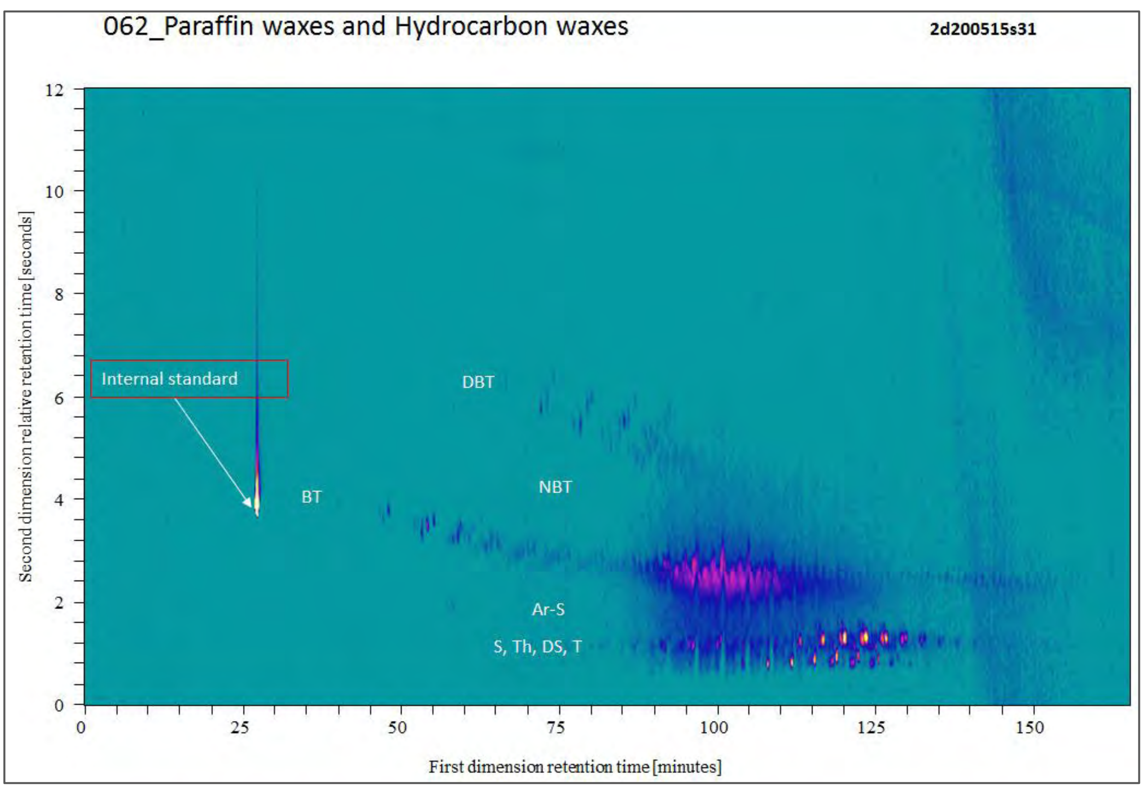

096A_Extracts (petroleum), heavy paraffinic distillate solvent
2d200515s27
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150


069_Extracts (petroleum), solvent-refined heavy paraffinic distillate solvent
2d200515s28
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

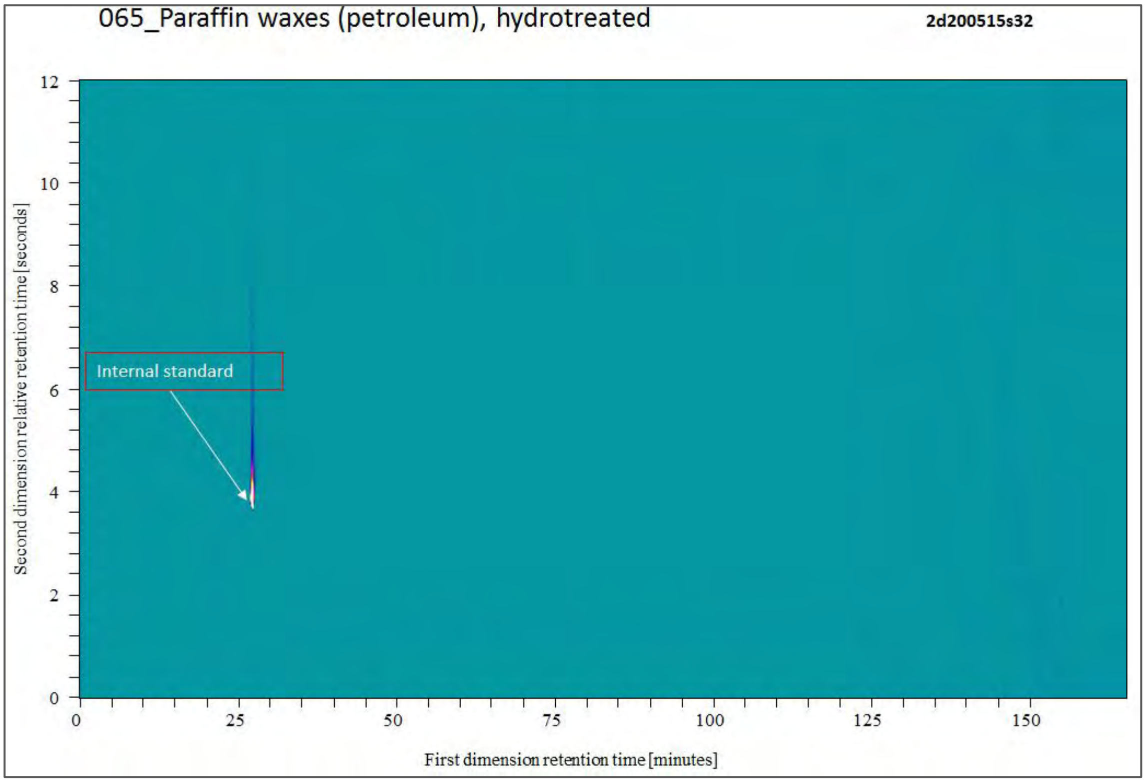

006_Residues (petroleum), atm. tower
2d200515s29b
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
Internal standard
DBT
BT
NBT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

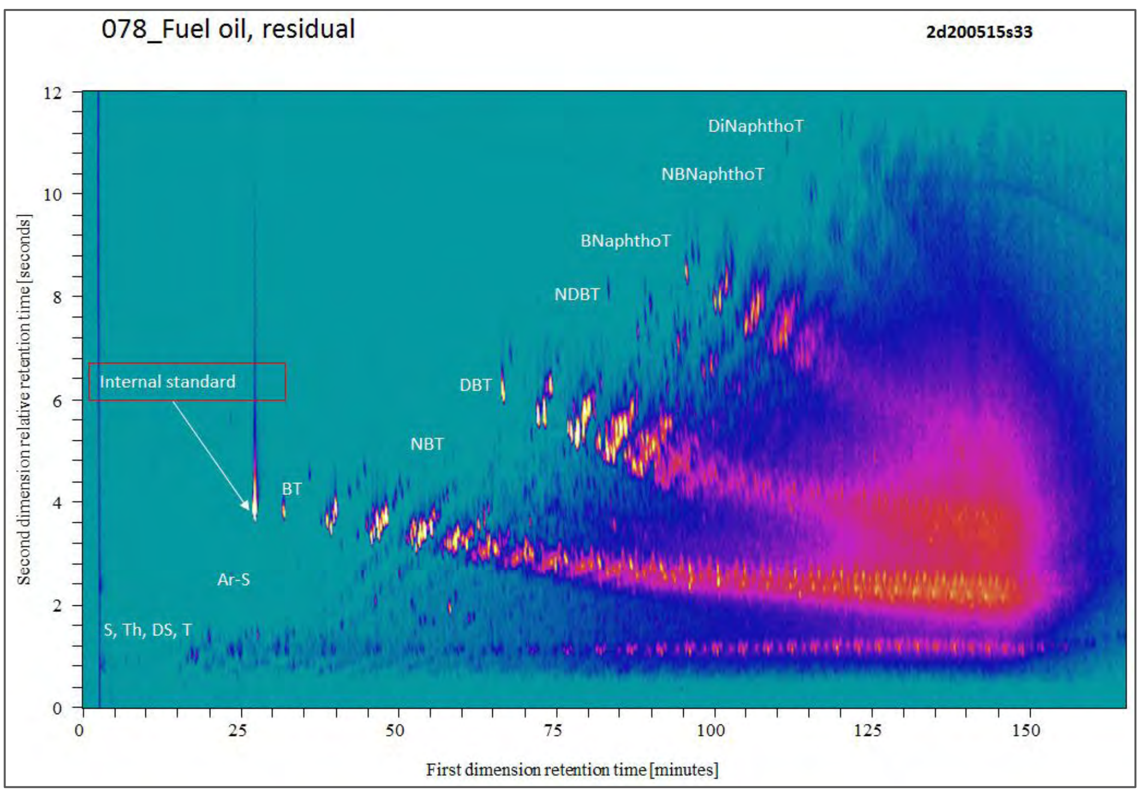


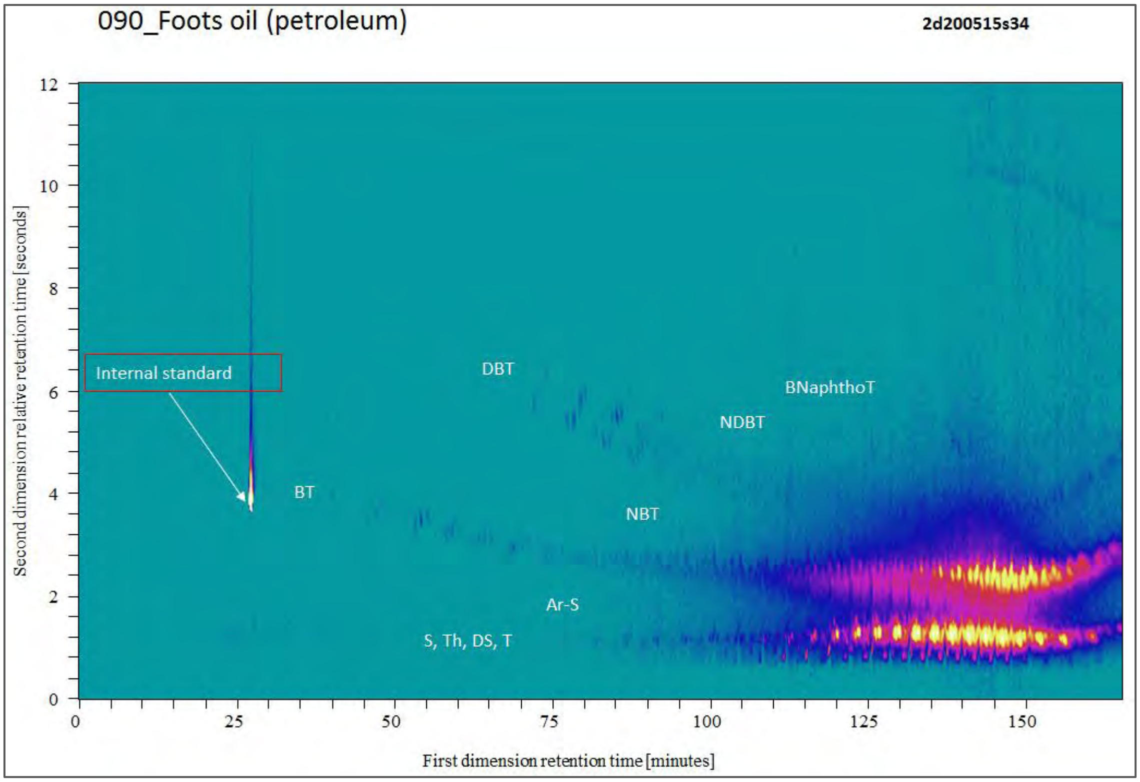
031_Distillates (petroleum), vacuum
2d200515s30
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

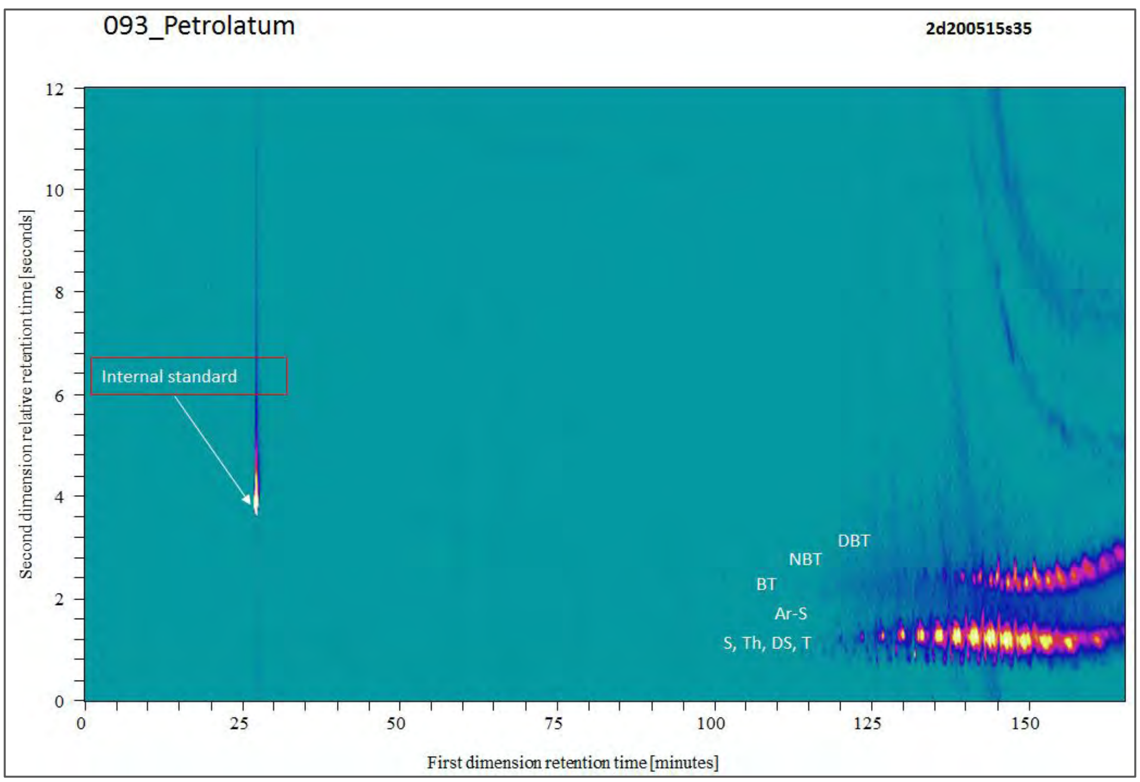


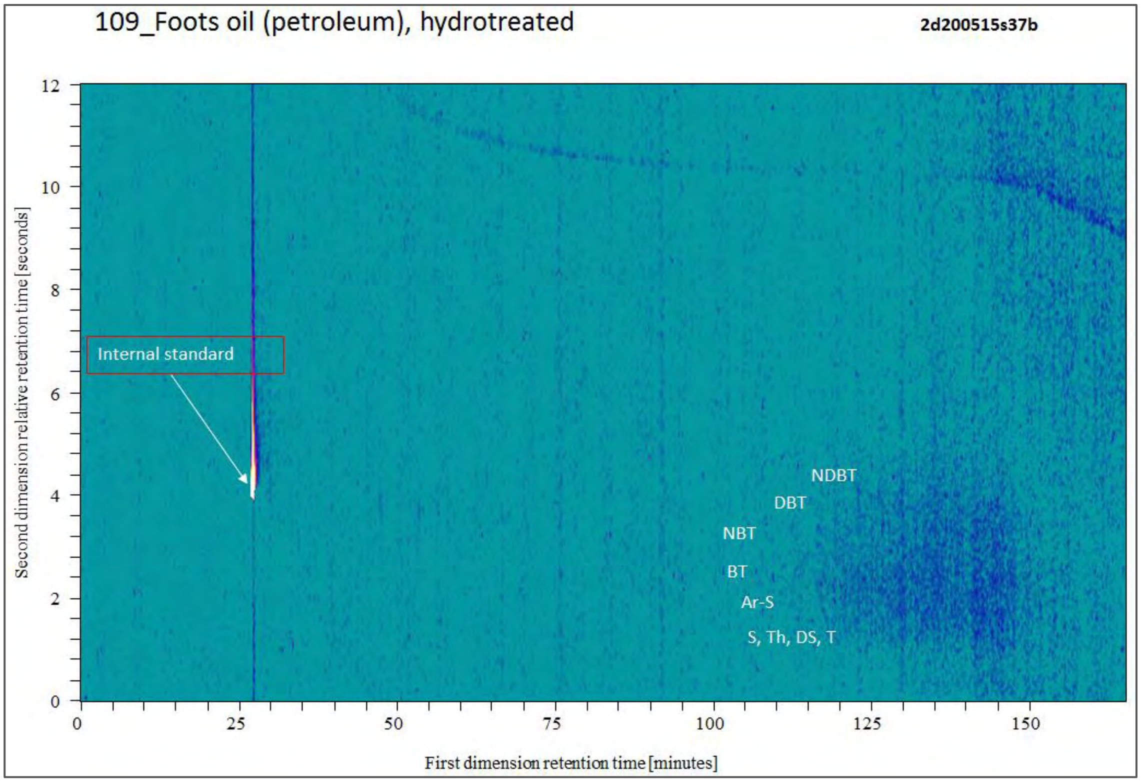
062_Paraffin waxes and Hydrocarbon waxes
2d200515s31
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

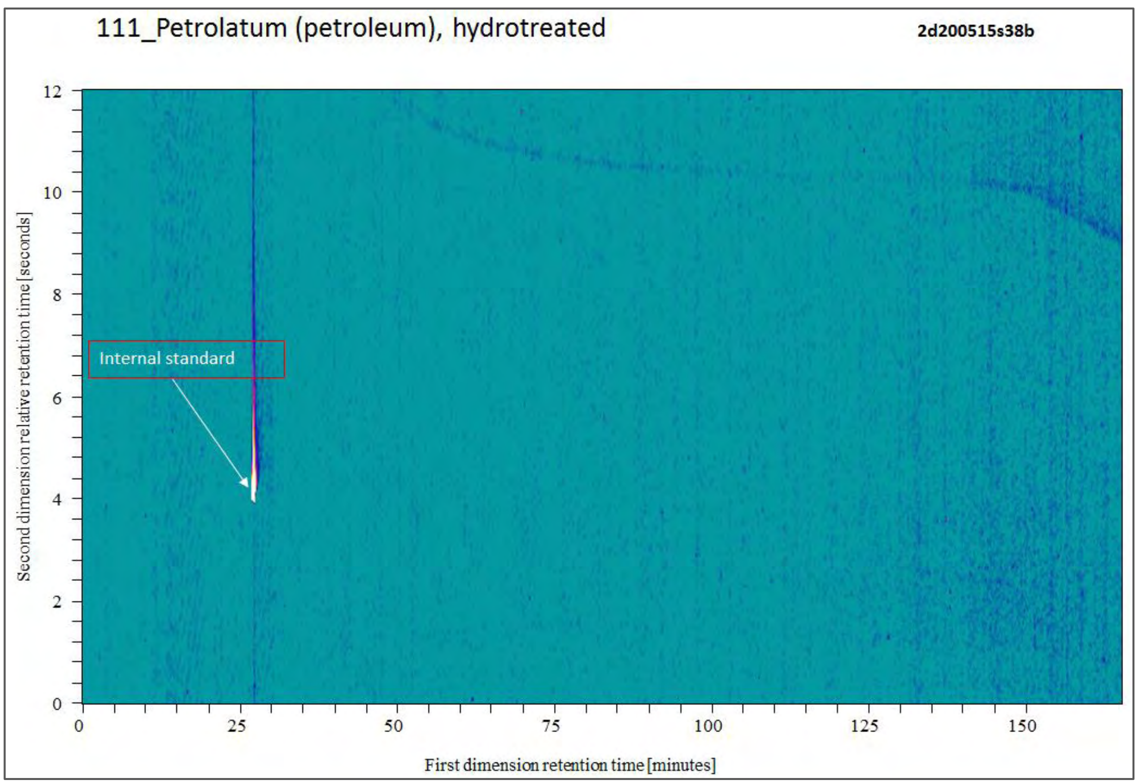

065_Paraffin waxes (petroleum), hydrotreated
2d200515s32
Internal standard
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

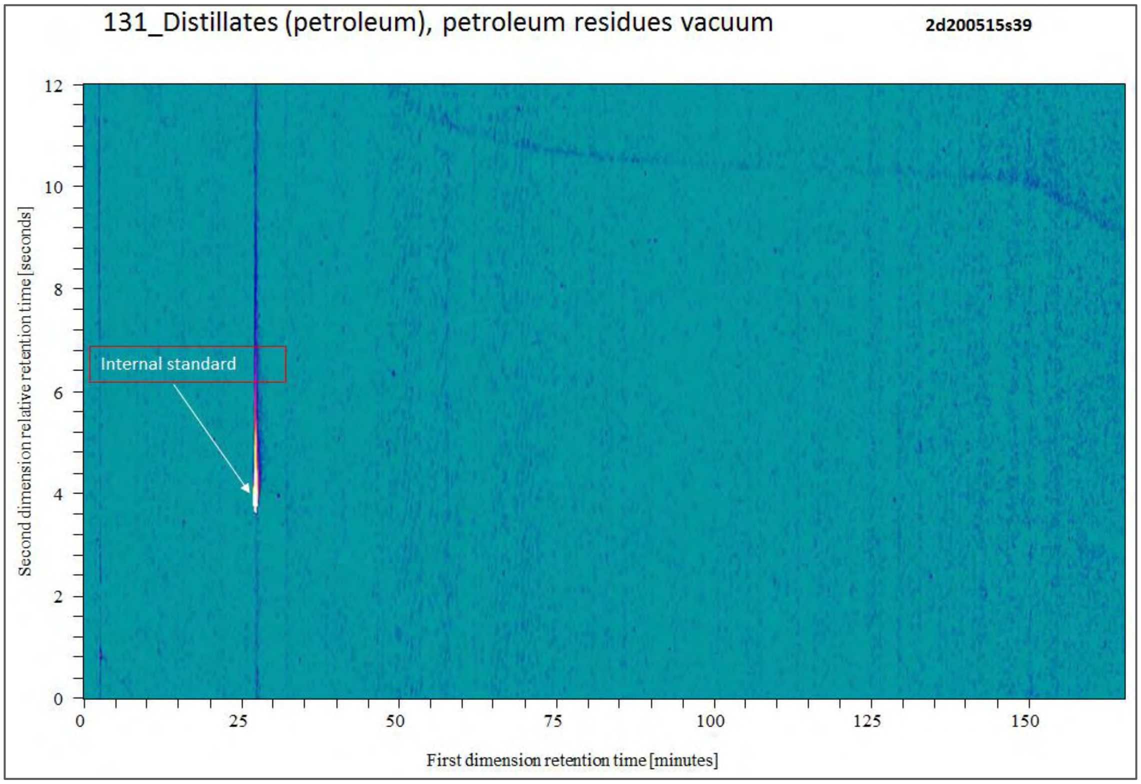

078_Fuel oil, residual
2d200515s33
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
DBT
NBT
BT
Internal standard
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150


090_Foots oil (petroleum)
2d200515s34
Internal standard
DBT
BNaphthoT
NDBT
BT
NBT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]

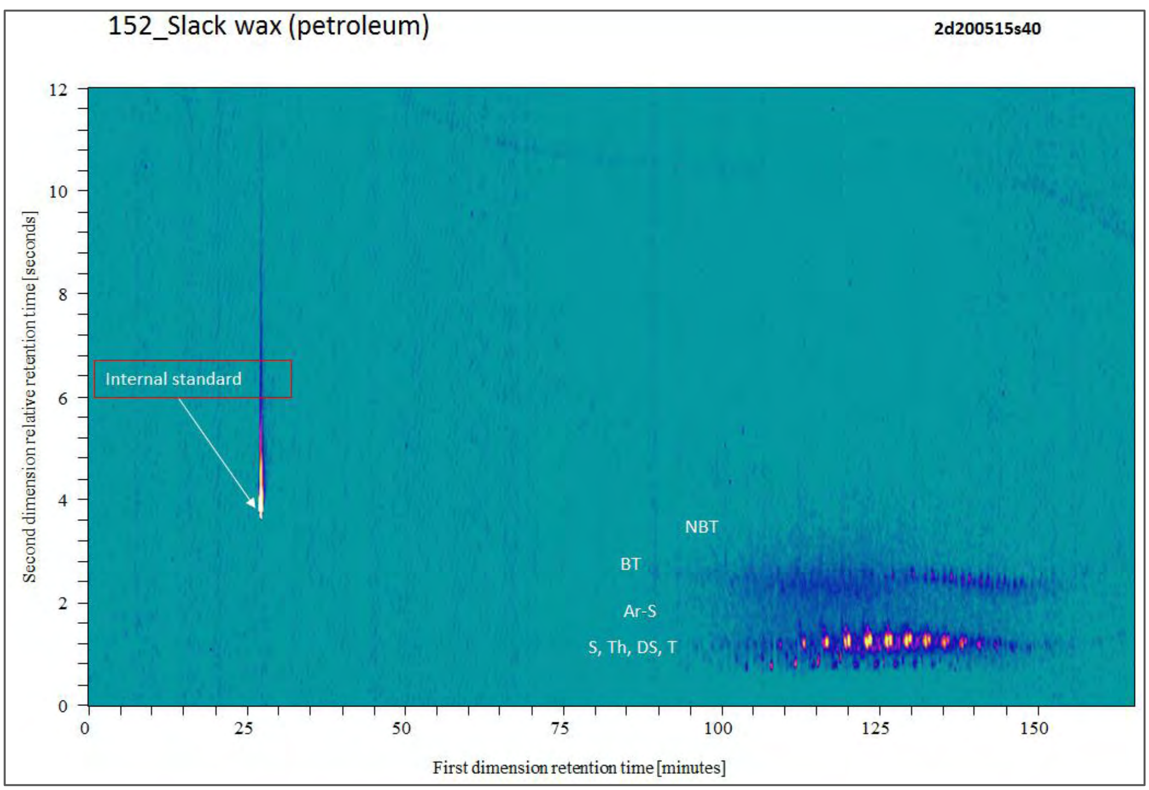

093_Petrolatum
2d200515s35
Internal standard
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]


109_Foots oil (petroleum), hydrotreated
2d200515s37b
Internal standard
NDBT
DBT
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

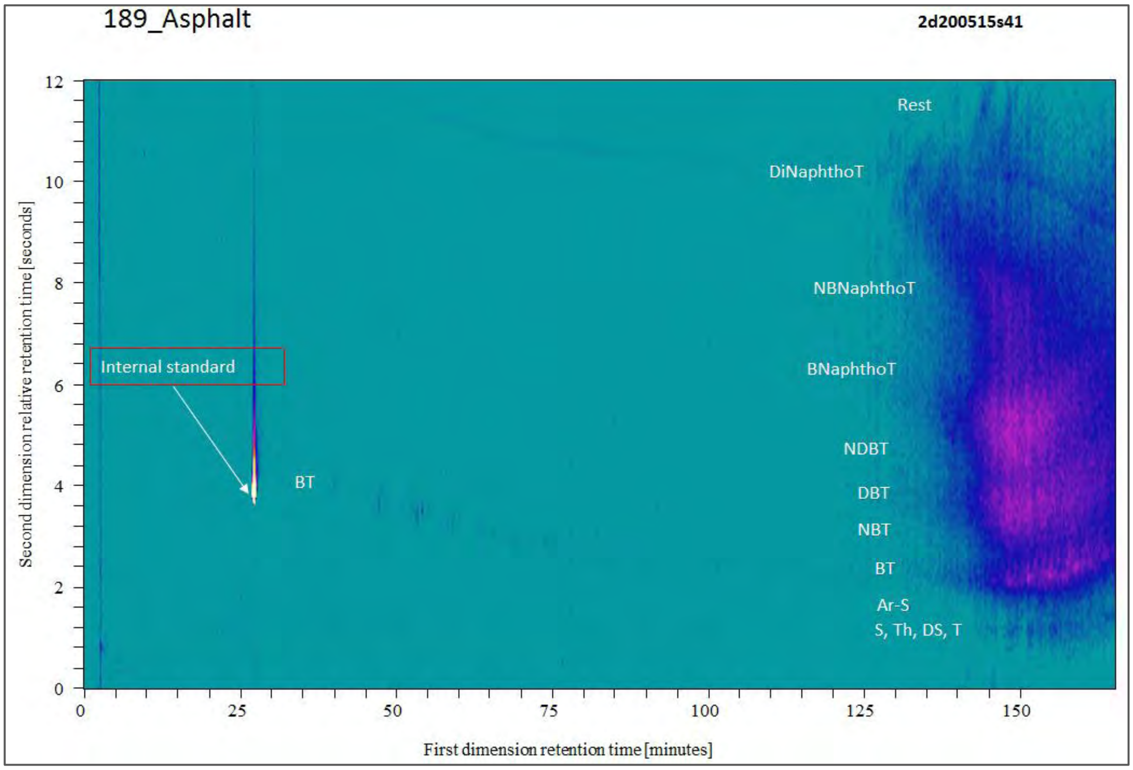

111_Petrolatum (petroleum), hydrotreated
2d200515s38b
Internal standard
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

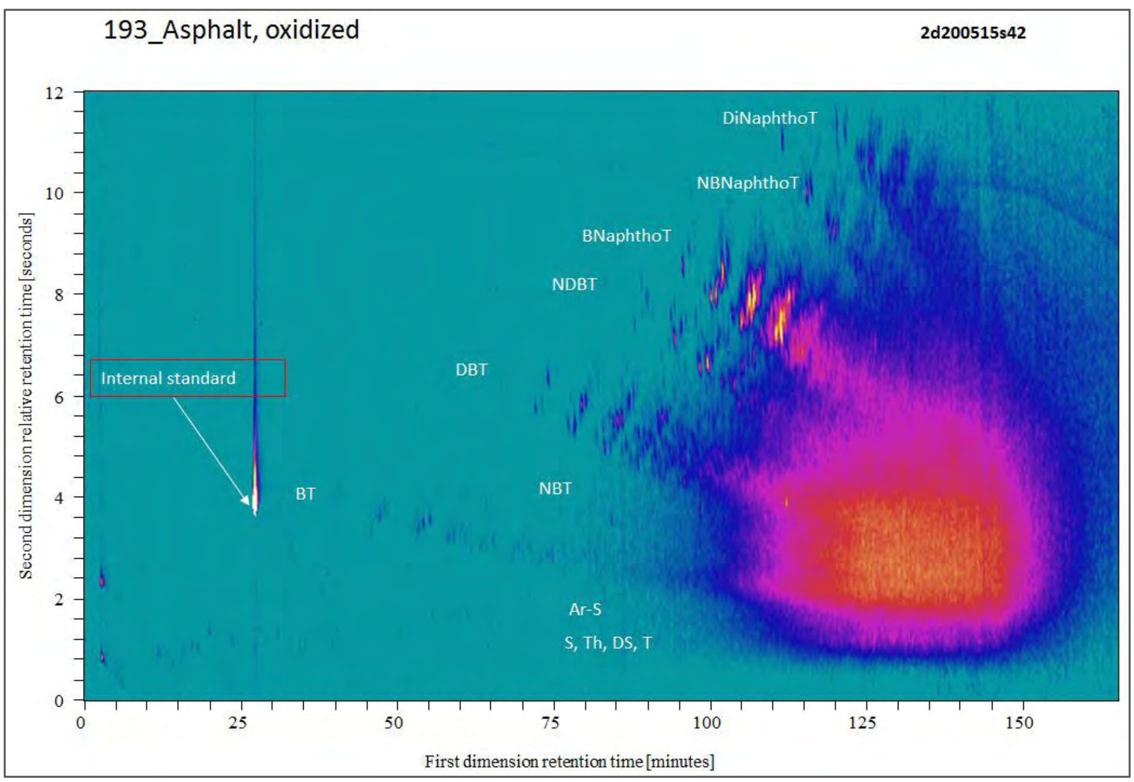


131_Distillates (petroleum), petroleum residues vacuum
2d200515s39
Internal standard
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
25
50
75
100
125
150

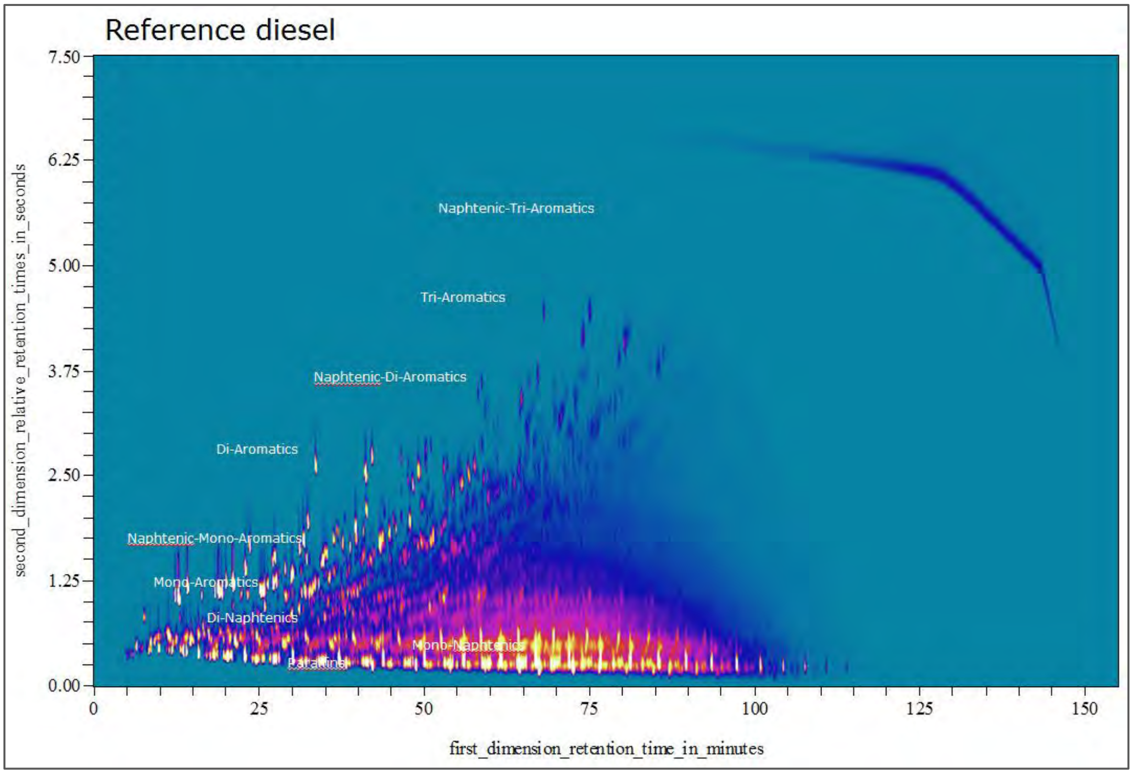


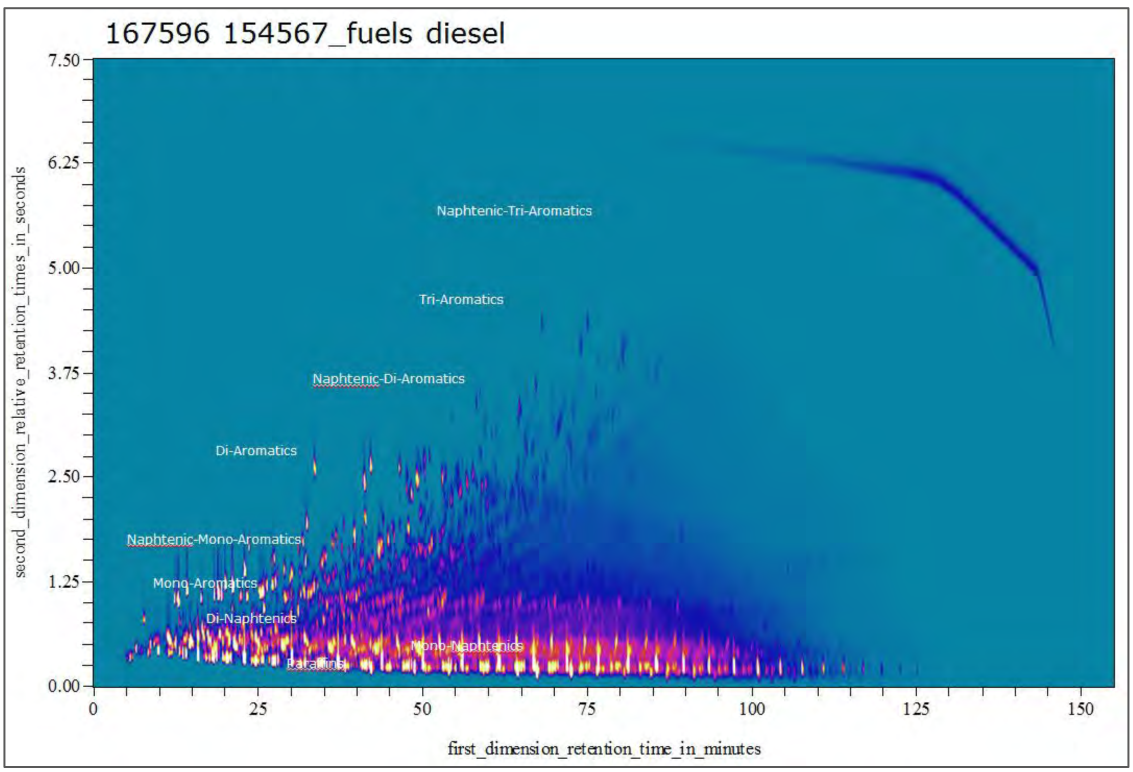
152_Slack wax (petroleum)
2d200515s40
Internal standard
NBT
BT
Ar-S
S, Th, DS, T
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
25
50
75
100
125
150

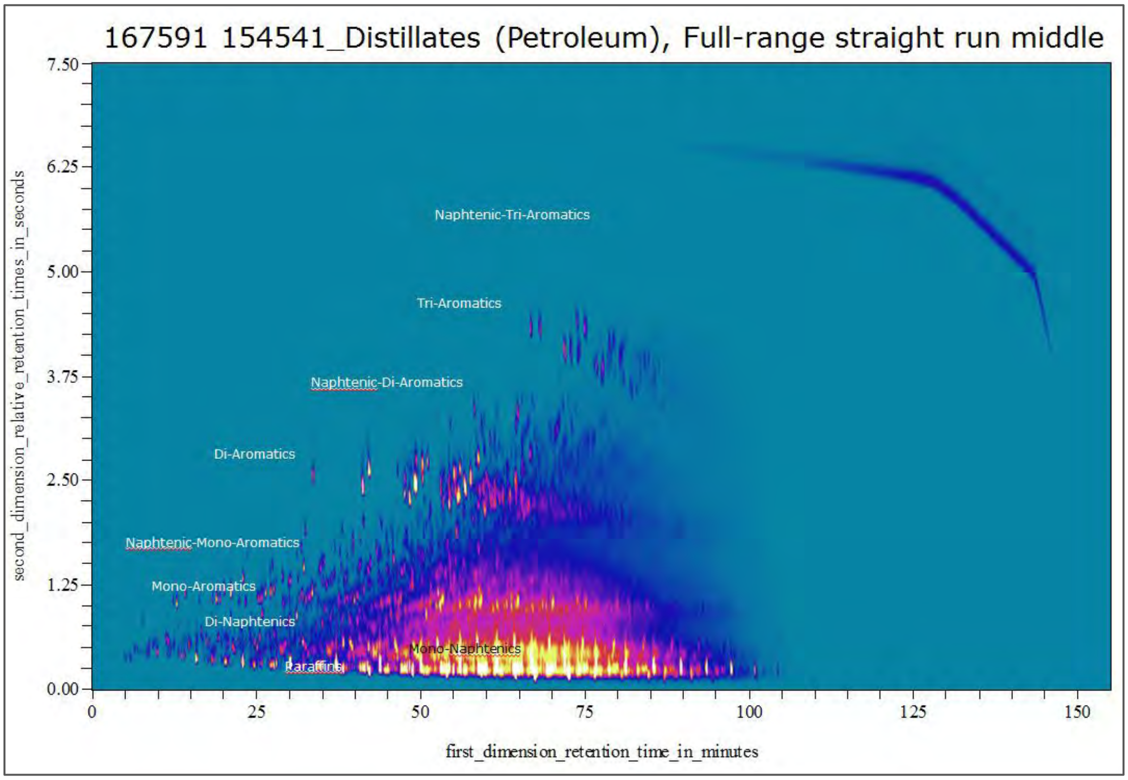

189_Asphalt
2d200515s41
Rest
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
DBT
NBT
BT
Ar-S
S, Th, DS, T
Internal standard
BT
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

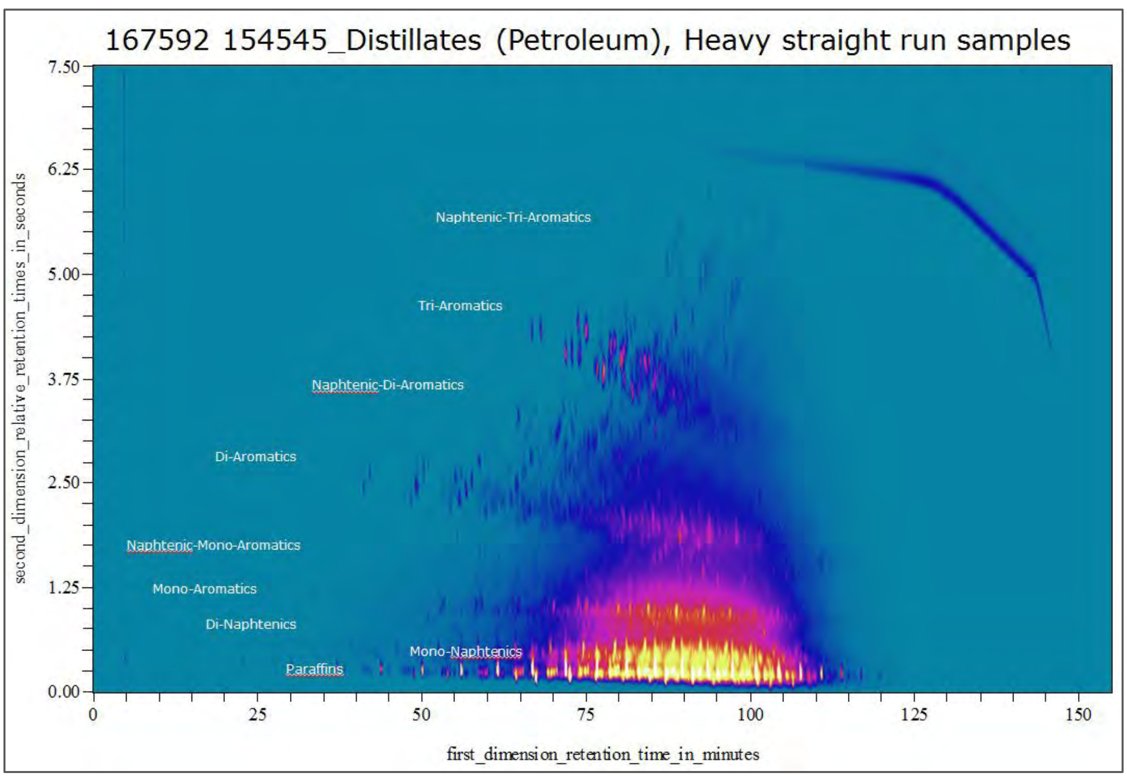

193_Asphalt, oxidized
2d200515s42
DiNaphthoT
NBNaphthoT
BNaphthoT
NDBT
DBT
NBT
Ar-S
S, Th, DS, T
Internal standard
BT
Second dimension relative retention time [seconds]
First dimension retention time [minutes]
0
2
4
6
8
10
12
0
25
50
75
100
125
150

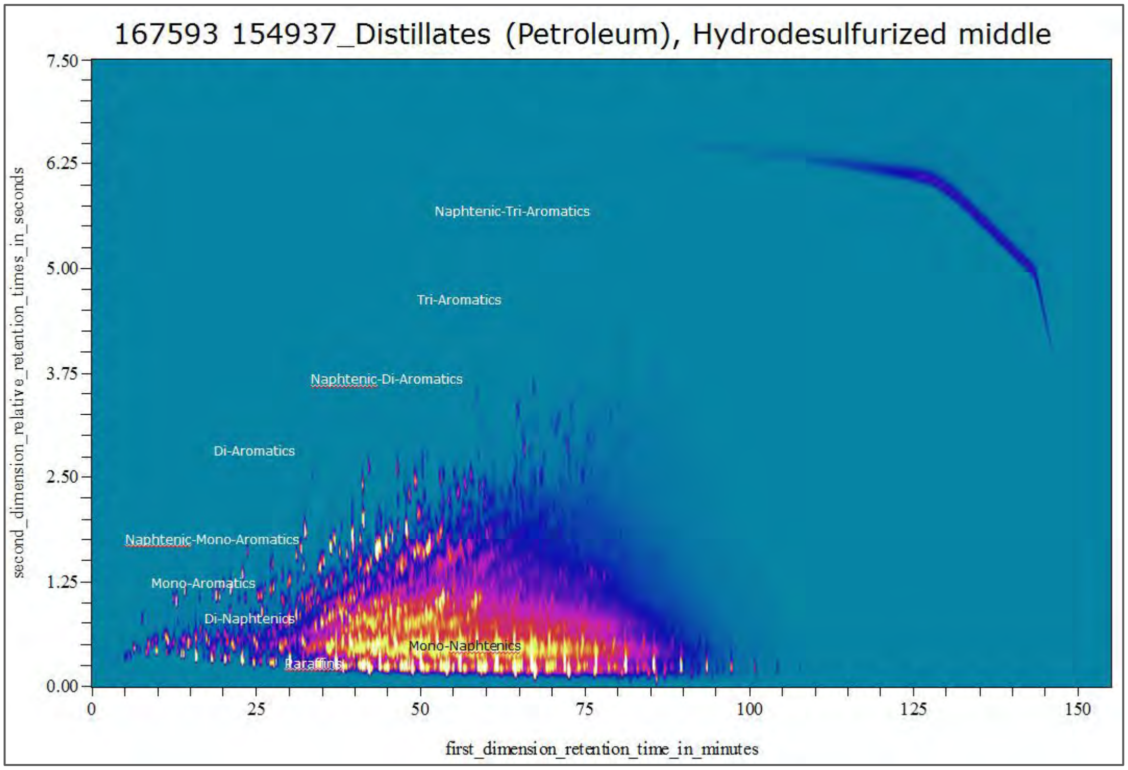
APPENDIX 3: OXYGEN GROUP TYPE GCxGC-FID CHROMATOGRAMS

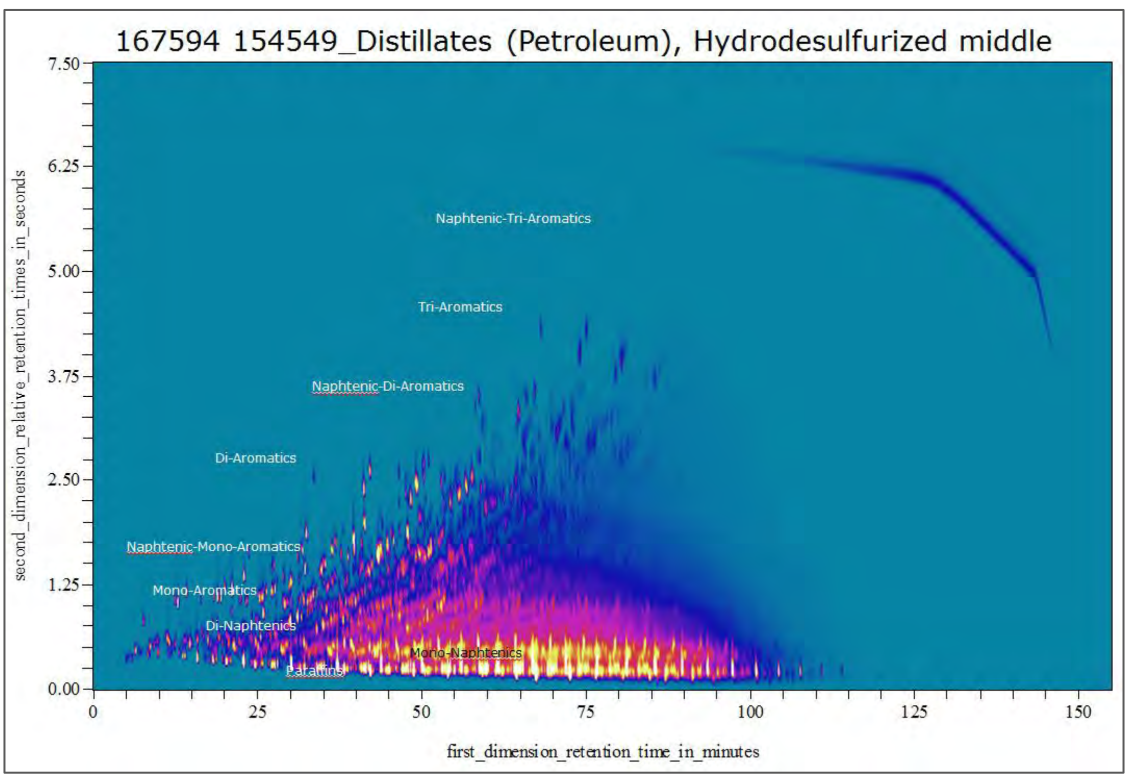





167591 154541_Distillates (Petroleum), Full-range straight run middle
Naphtenic-Tri-Aromatics
Tri-Aromatics
Naphtenic-Di-Aromatics
Di-Aromatics
Naphtenic-Mono-Aromatics
Mono-Aromatics
Di-Naphtenics
Mono-Naphtenics
Paraffins
second_dimension_relative_retention_times_in_seconds
first_dimension_retention_time_in_minutes
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150


167592 154545_Distillates (Petroleum), Heavy straight run samples
Naphtenic-Tri-Aromatics
Tri-Aromatics
Naphtenic-Di-Aromatics
Di-Aromatics
Naphtenic-Mono-Aromatics
Mono-Aromatics
Di-Naphtenics
Mono-Naphtenics
Paraffins
second_dimension_relative_retention_times_in_seconds
first_dimension_retention_time_in_minutes
7.50
6.25
5.00
3.75
2.50
1.25
0.00
0
25
50
75
100
125
150


167593 154937_Distillates (Petroleum), Hydrodesulfurized middle
Naphtenic-Tri-Aromatics
Tri-Aromatics
Naphtenic-Di-Aromatics
Di-Aromatics
Naphtenic-Mono-Aromatics
Mono-Aromatics
Di-Naphtenics
Mono-Naphtenics
Paraffins
second_dimension_relative_retention_times_in_seconds
first_dimension_retention_time_in_minutes


167594 154549_Distillates (Petroleum), Hydrodesulfurized middle
Naphtenic-Tri-Aromatics
Tri-Aromatics
Naphtenic-Di-Aromatics
Di-Aromatics
Naphtenic-Mono-Aromatics
Mono-Aromatics
Di-Naphtenics
Mono-Naphtenics
Paraffins
second_dimension_relative_retention_times_in_seconds
first_dimension_retention_time_in_minutes

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