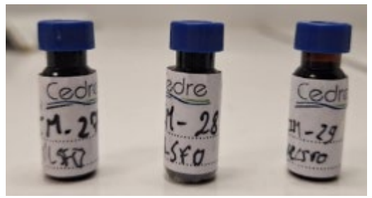
WP3 Characterizations and impacts

Oil Fingerprinting analysis

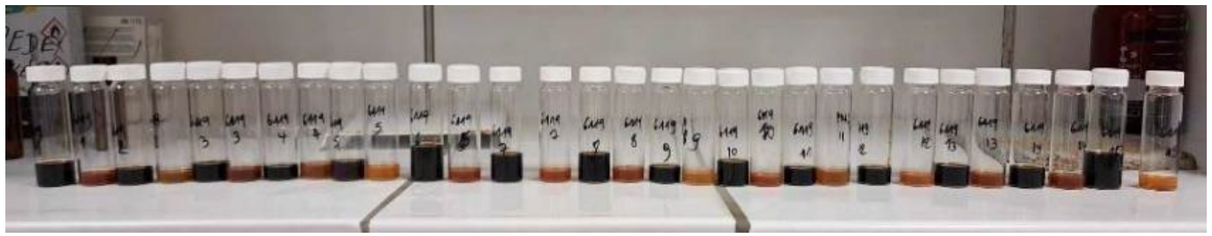
Marijke Neyts

natural sciences .be

Samples and Sample treatment



Samples diluted to 8 +/- 1mg/ml.
Clean-up with 0.5 g Silica gel.

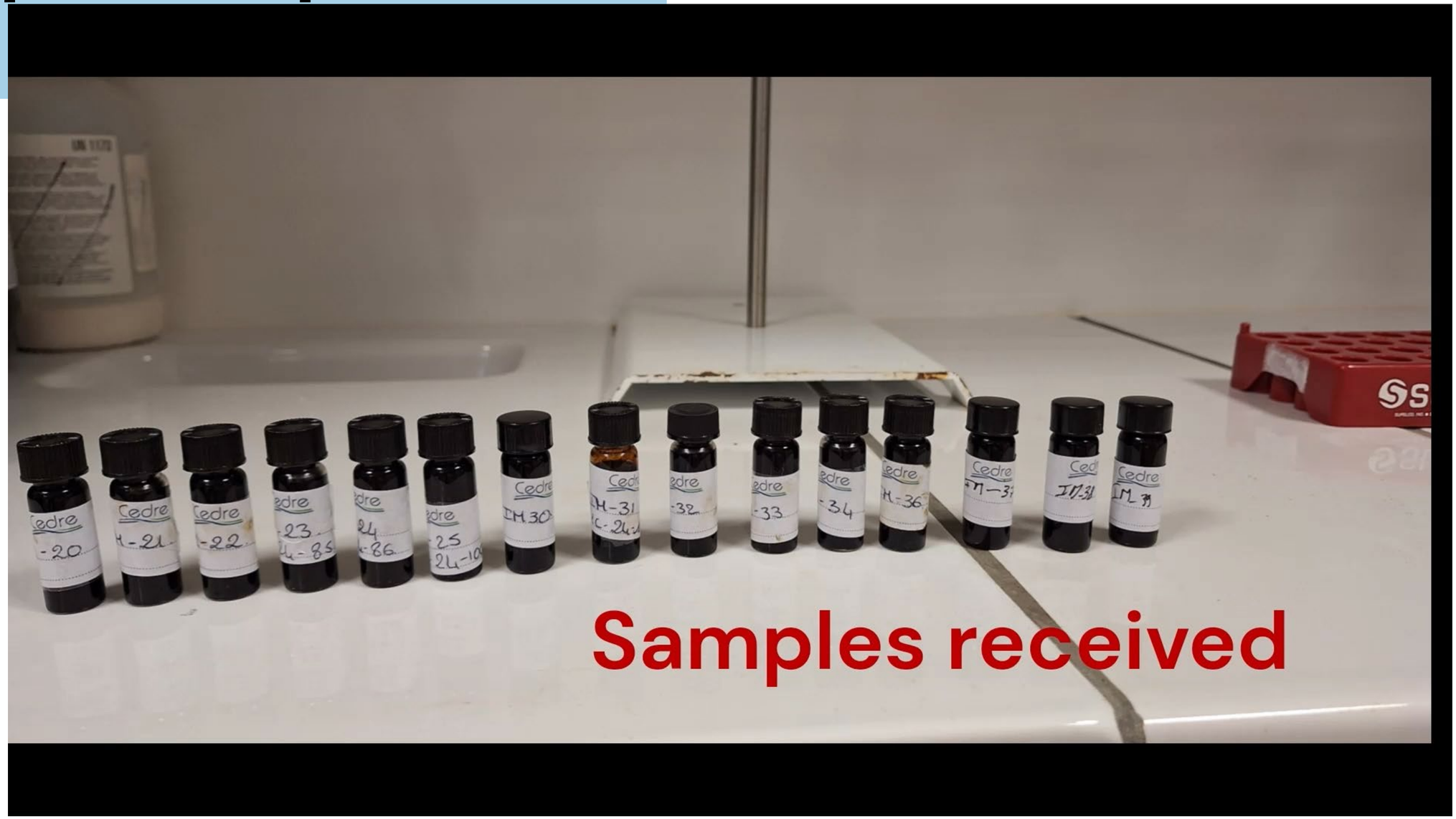


1 µl injected in GC-MS:

- Measured in TIC (total ion count)
- Measured in SIM (single ion monitoring)

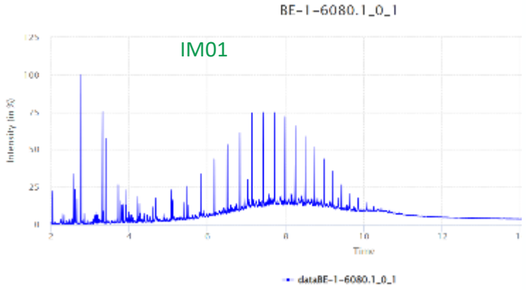
Working list	6119
Number	Sample ID
1	Imaros 2 : IM-20 VLSFO Stena, Sweden
2	Imaros 2 : IM-21 ULSFO Stena, Sweden
3	Imaros 2 : IM-22 VLSFO BunkerOne, Sweden
4	Imaros 2 : IM-23 ULSFO BunkerOne, Sweden
5	Imaros 2 : IM-24 VLSFO Preem AB, Finland
6	Imaros 2 : IM-25 VLSFO Neste, Finland
7	Imaros 2 : IM-30 VLSFO FincoEnergies, Netherlands
8	Imaros 2 : IM-31 VLSFO FincoEnergies, Netherlands
9	Imaros 2 : IM-32 ULSFO FincoEnergies, Netherlands
10	Imaros 2 : IM-33 VLSFO FincoEnergies, Netherlands
11	Imaros 2 : IM-34 ULSFO FincoEnergies, Netherlands
12	Imaros 2 : IM-36 VLSFO Bunker from vessel, Netherlands
13	Imaros 2 : IM-37 VLSFO Bureau Veritas, Malta
14	Imaros 2 : IM-38 VLSFOBureau Veritas, Malta
15	Imaros 2 : IM-39 VSFO Peninsula Antwerp, Belgium
Work list	6119 bis
16	Imaros 2 : IM-27 VLSFO
17	Imaros 2 : IM-28 VLSFO
18	Imaros 2 : IM-29 ULSFO

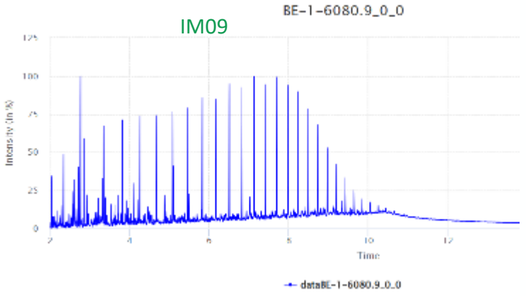
Samples and Sample treatment

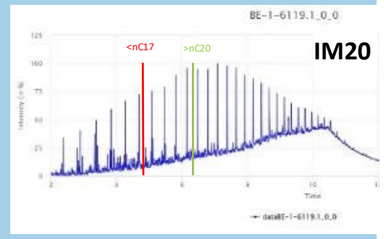


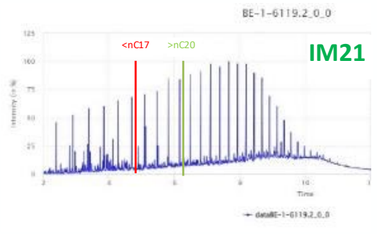
Samples

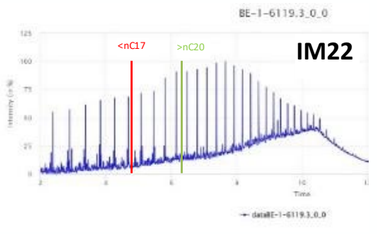
Different patterns : different combinations of naphthalenes, lower alkanes and waxes.

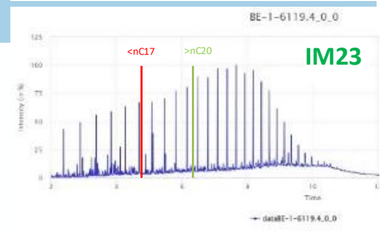


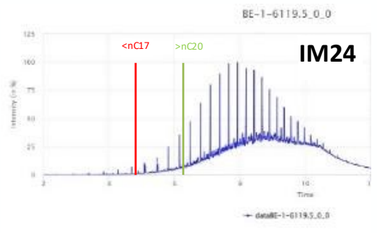


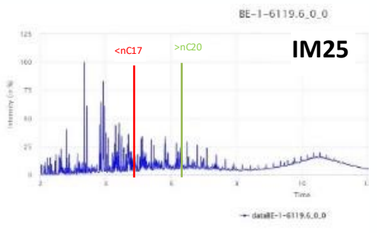


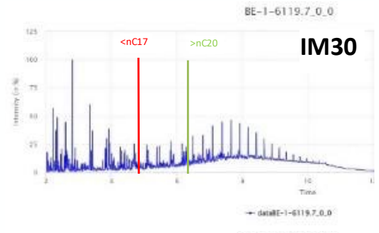


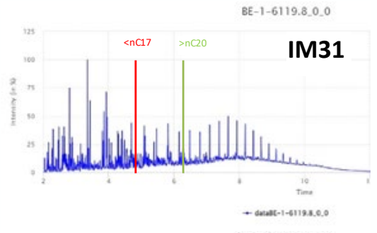


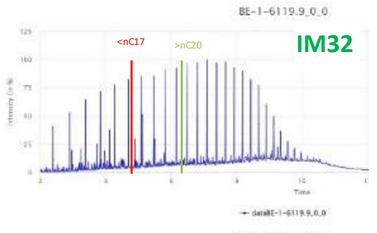


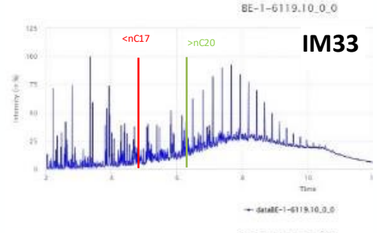


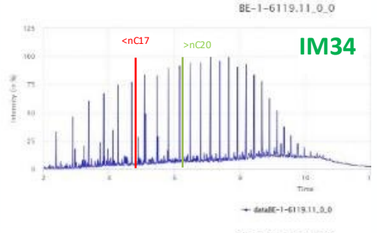


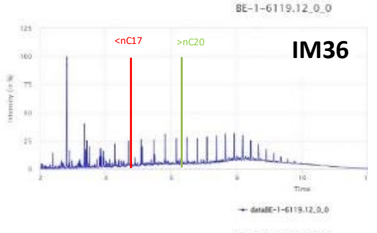


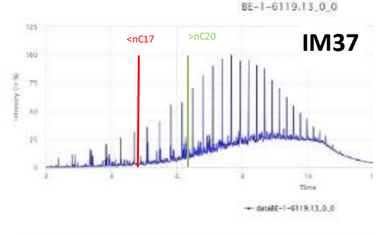


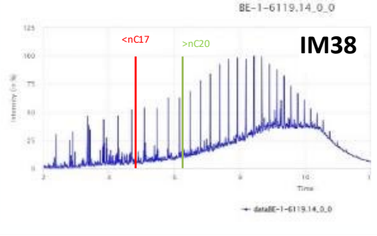


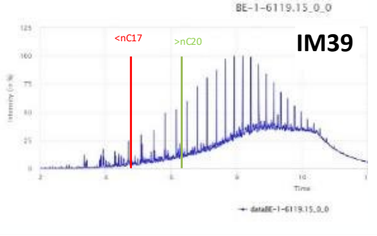


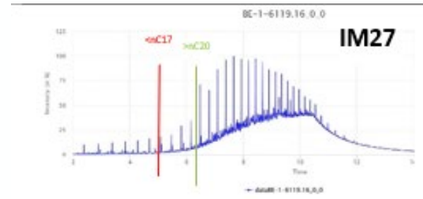


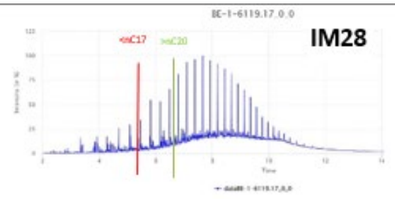


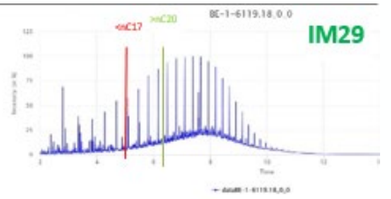


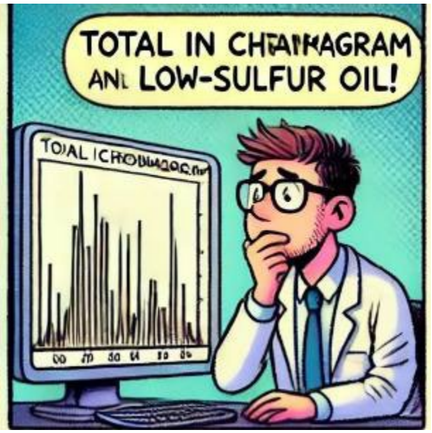












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Ion chromatogram : Retene, Tetra-Methylphenanthrene,

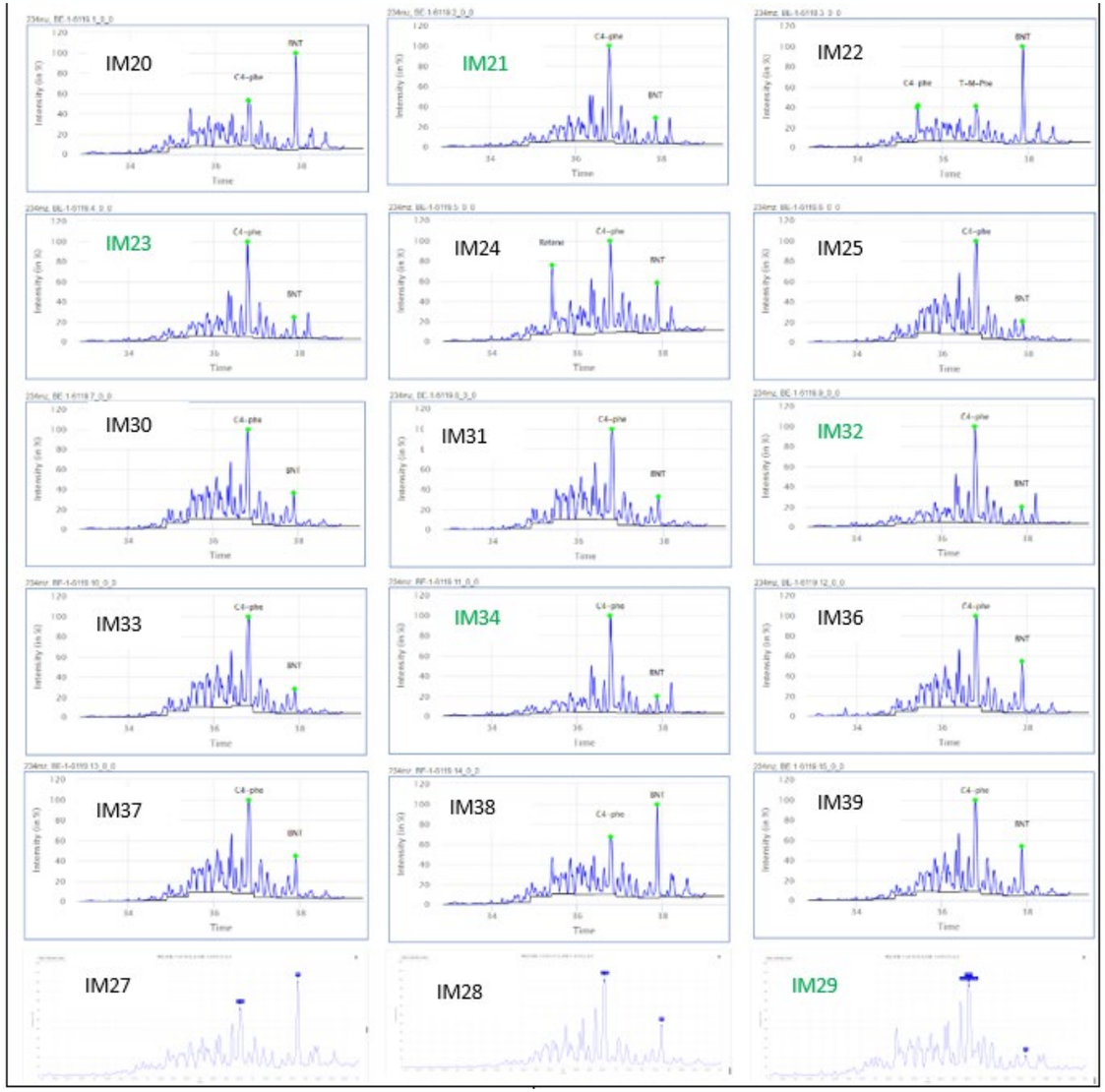
Benzo(b)naphto(1,2-d)-thiophene (BNT) and C4-Phenantrenes (m/z 234)

Characteristic cluster of cracking residues.
BNT contains sulfur.

Samples IMAROS1	BNT/hopane (%)	BNT/C2-phen (%)
IM01	3.7	0.3
IM02	9.1	1.6
IM03	81.2	1.0
IM04	88.9	0.3
IM05	9.7	0.2
IM06	60.0	0.7
IM07	23.5	0.5
IM08	41.4	0.6
IM09	3.6	0.4
IM10	41.5	0.4
IM12	226.1	0.3
IM13	31.9	1.4

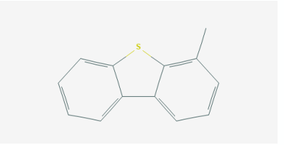
Samples IMAROS2	BNT/hopane (%)	BNT/C2-phen (%)
IM20	32.9	18.13
IM21	4.5	0.34
IM22	36.7	2.66
IM23	3.3	0.31
IM24	7.0	1.12
IM25	220.2	0.12
IM30	104.0	0.35
IM31	87.1	0.29
IM32	2.3	0.30
IM33	59.1	0.24
IM34	2.4	0.32
IM36	79.9	0.54
IM37	41.4	0.55
IM38	18.5	1.62
IM39	17.1	0.57
IM27	13.7	2.01
IM28	59.9	0.62
IM29	3.7	0.14

ULSFO Average BNT/Hopane %	stdev	-2S	+2S
3.4	0.8	1.8	4.9



Ion chromatogram : C1-dibenzothiophenes

(m/z 198)



imaros$_2$

C1-Dibenzothiophenes are very stable.
These compounds contain sulfur.

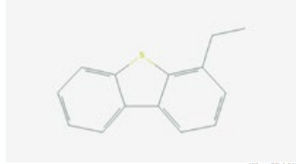
Sample	4-M-Dbt/C2-phe (%)	1-M-Dbt/C2-phe (%)
IM01	1.1	0.3
IM02	2.8	1.1
IM03	1.7	0.5
IM04	2.5	0.5
IM05	1.0	0.4
IM06	2.2	0.5
IM07	3.7	0.7
IM08	1.7	0.4
IM09	1.2	0.3
IM10	2.1	0.5
IM12	1.5	0.3
IM13	1.2	0.3

Sample	4-M-Dbt/C2-phe (%)	1-M-Dbt/C2-phe (%)
IM20	13.6	4.60
IM21	0.7	0.15
IM22	1.7	0.60
IM23	0.7	0.15
IM24	2.0	0.63
IM25	1.1	0.15
IM30	0.9	0.18
IM31	2.5	0.48
IM32	0.9	0.19
IM33	1.1	0.21
IM34	0.9	0.18
IM36	1.7	0.41
IM37	0.9	0.24
IM38	1.0	0.31
IM39	2.5	0.61
IM27	1.2	0.39
IM28	2.2	0.33
IM29	1.2	0.15

4-M-DBT and 1-M-DBT are the lowest in ULSFO

Ion chromatogram : C2-dibenzothiophenes

(m/z 212)



These compounds contain sulfur.
The ratio C2-dibenzothiophenes/C2-phenanthrenes provides information about the sulfur content of the sample.

Sample1 IMAROS1	C2-dbt/C2-phe (%)
IM01	13
IM02	27
IM03	22
IM04	20
IM05	9
IM06	23
IM07	21
IM08	19
IM09	12
IM10	21
IM12	17
IM13	15

Sample IMAROS2	C2-dbt/C2-phe (%)
IM20	163.7
IM21	7.9
IM22	21.6
IM23	7.7
IM24	22.0
IM25	8.4
IM30	10.4
IM31	18.2
IM32	9.8
IM33	10.1
IM34	9.9
IM36	17.4
IM37	12.1
IM38	13.1
IM39	28.1
IM27	15.4
IM28	20.0
IM29	12.2

ULSFO/VLSFO/HFO?

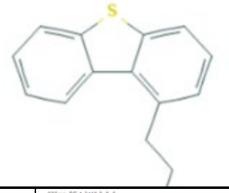
ULSFO	C2-DBT/C2-phe (%)	VLSFO	C2-DBT/C2-phe (%)	HFO	C2-DBT/C2-phe (%)
IM1	13.0	IM2	27	Brent	48
IM9	12.0	IM3	22	Flinterstar tank 4	46
RR2017 sourceB	7.7	IM4	20	RR2020 sourceA	60
IM21	7.9	IM6	23	RR2020 sourceB	36
IM23	7.7	IM7	21	RR2020 sourceC	240
IM32	9.8	IM8	19	RR2017 sourceA	47
IM34	9.9	IM10	21	RR2017 sourceC	43
IM29	11.0	IM12	17		
		IM13	15		
		Flinterstar tank 1	26		
		RR2023 spill1	16		
		RR2023 spill2	16		
		RR2023 source1	13		
		RR2023 source2	15		
		RR2023 source3	22		
		IM22	22		
		IM24	22		
		IM30	10		
		IM31	18		
		IM33	10		
		IM36	17		
		IM37	12		
		IM38	13		
		IM39	28		
		IM27	18		
		IM28	18		

IMAROS1	average %	stdev	-2S	+2S
ULSFO	10.9	2.8	**5.3**	**16.5**
VLSFO	21.1	3.7	**13.7**	**28.5**
HFO	>35			

IMAROS 2	average	std%	-2S	+2S
ULFSO	9.9	2.0	**5.8**	**13.9**
VLSFO	18.5	4.8	**8.9**	**28.2**
HFO	>35			

Ion chromatogram : C3-dibenzothiophenes

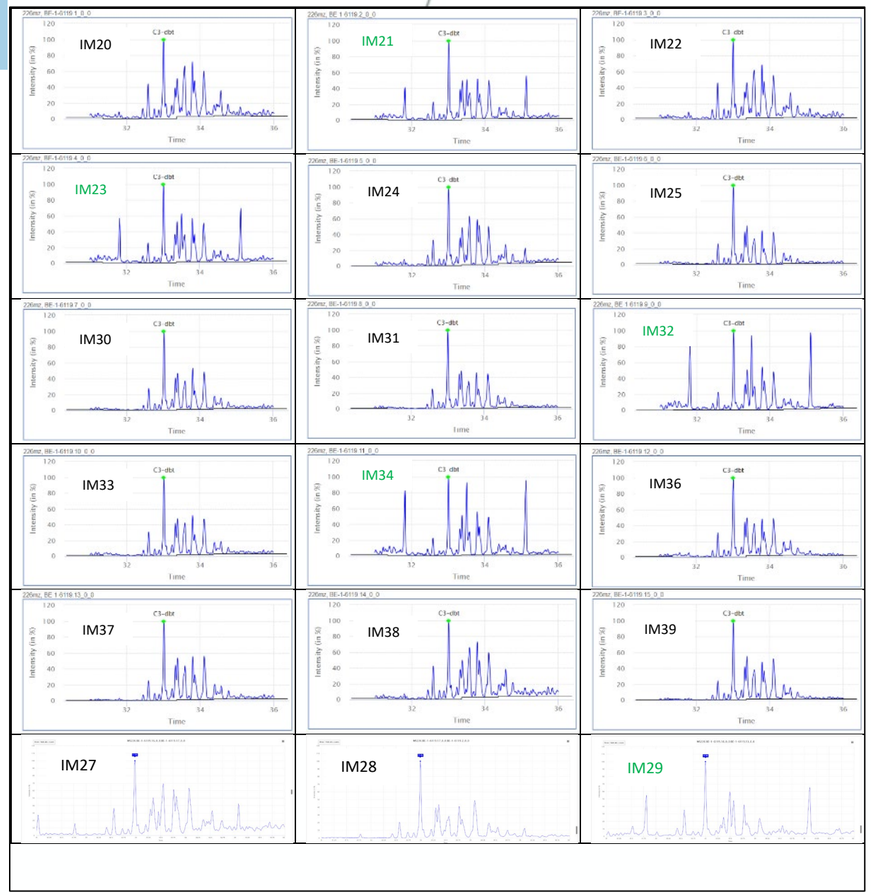
(m/z 226)

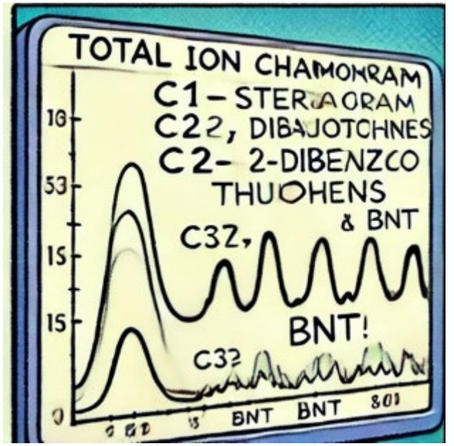


These compounds contain sulfur.

Sample IMAROS1	C3-dbt/C2-phe (%)
IM01	12
IM02	24
IM03	18
IM04	12
IM05	7
IM06	17
IM07	15
IM08	16
IM09	9
IM10	16
IM12	14
IM13	13

Sample IMAROS2	C3-dbt/C2-phe (%)
IM20	173
IM21	7
IM22	22
IM23	7
IM24	23
IM25	6
IM30	10
IM31	12
IM32	8
IM33	9
IM34	8
IM36	15
IM37	13
IM38	16
IM39	24
IM27	18
IM28	18
IM29	11





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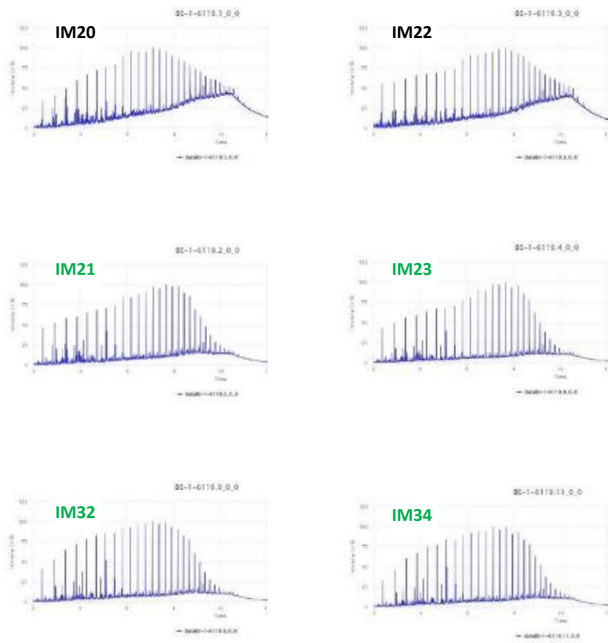
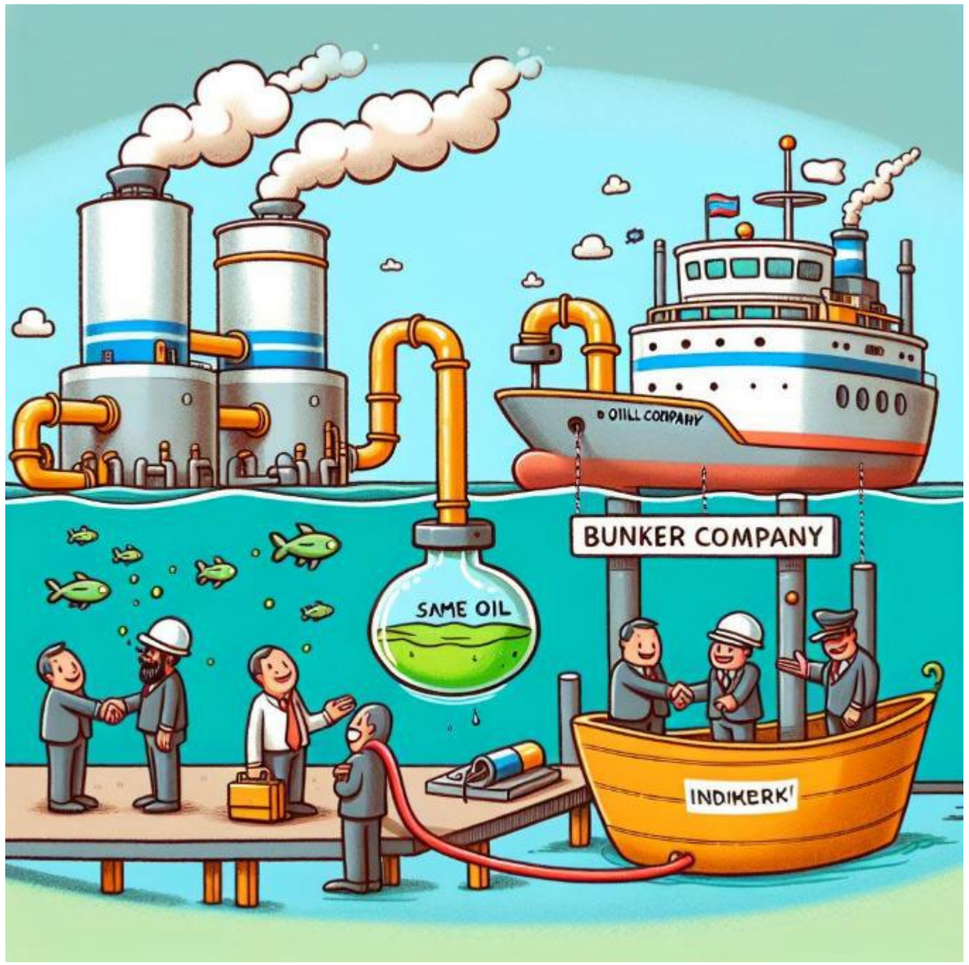
Similar samples

These samples probably originate from the same source:

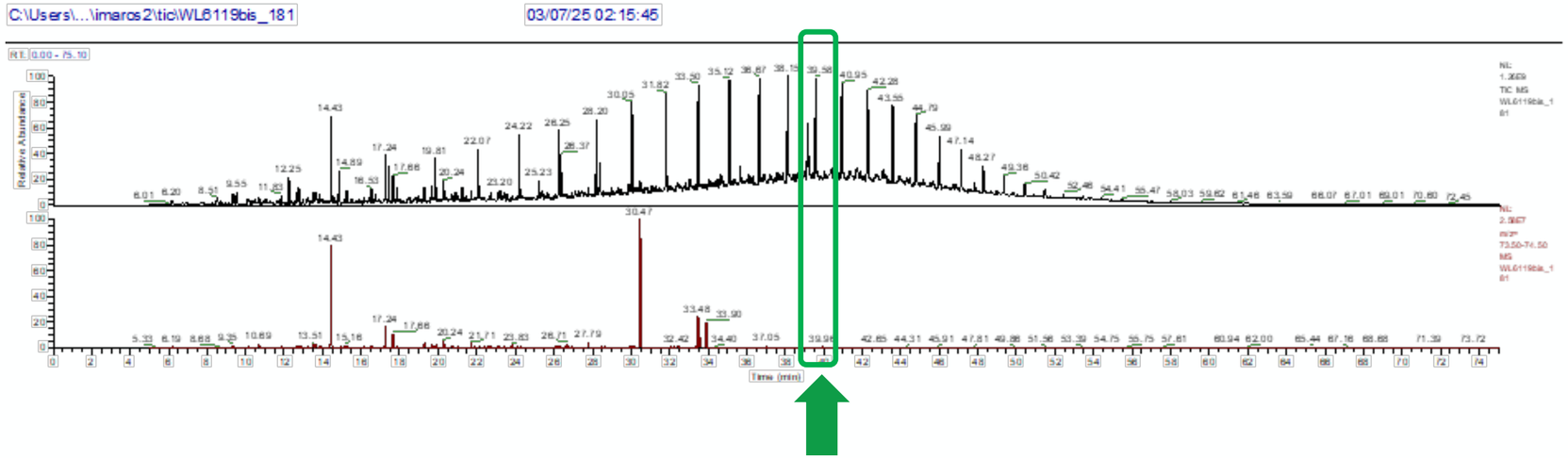
- IM20-IM22
- IM21-IM23
- IM32-IM34





Strange behaviour of sample

IM29



Scan on M/Z 74 (typical for FAMEs)

87% certainty : Phenol,3-(8Z)-8-pentadecen-1-yl

Commonly known as Cardanol

A phenolic industrial compound derived from “Cashew Nut Shell Liquid (CNSL)”

Not pure ULSFO => contains a bio-fraction

Overall conclusion

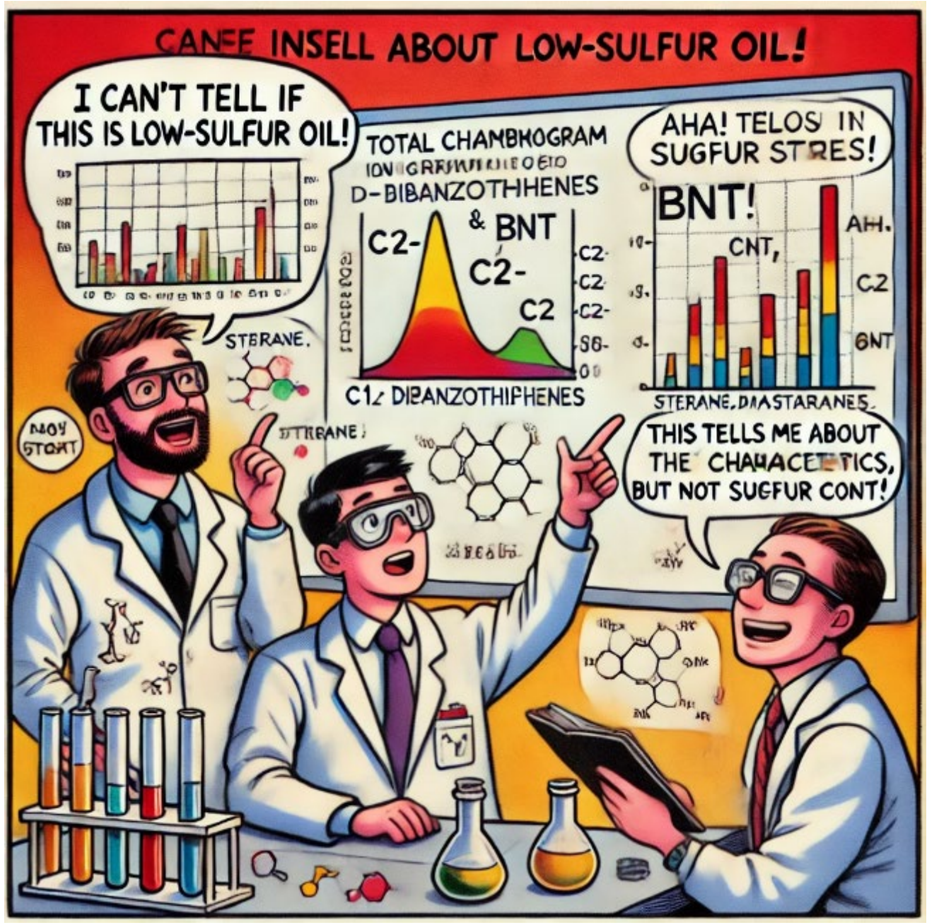
From the Total ion chromatogram, it is not possible to conclude a low sulfur oil.

The Ion chromatograms and the calculations of the C1-, C2-, C3-dibenzothiophenes and BNT can show that there is less sulfur present in an oil.

BNT/Hopane and C2-DBT/C2-Phen are the most effective ratios to be compared.

There were some samples that probably originate from the same source.

One sample contains a bio-fraction.



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