

Report

Oil spill identification

OSINET – Round Robin 2017

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ABSTRACT

The 12th Oil Spill Identification Round Robin test (RR2017) within the Bonn Agreement Oil Spill Identification Network of Experts (OSINET) has been organized by Rijkswaterstaat, Netherlands. This year's case consisted of two spill samples and three source samples in addition to four samples from In-situ-burning (ISB) from lighter refined products. The samples have been prepared by SINTEF.

A large mysterious oil slick was observed drifting in the Norwegian Sea in the morning and it was assumed that this was an illegal spill done during the night. Some of the oil slick was collected in a fire proof boom and ignited, but parts of the slick were too thin to be ignited. Two samples of the slick were collected, one that was assumed to be a burned residue and one non-burned oil.

Questions for the RR2017; Which of the spill samples is burned, and compare the residue from the in situ burning (ISB) with the three suspected sources. Are there any differences that can be explained by ISB in addition to the weathering processes? SINTEF has followed the provided checklist for the RR2017.

Conclusion:

Spill A and B are from the same source.
Spill B is the burned residue.
Spill versus Source A: Non-match
Spill versus Source B: Positive match
Spill versus Source C: Non-match

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Introduction

The 12th Oil Spill Identification Round Robin (RR2017) test within the Bonn Agreement Oil Spill Identification Network of Experts (OSINET) has been organized by Rijkswaterstaat, Netherlands. This year's samples, two spill samples and three source samples, in addition to two In-situ-burned (ISB) residues and two ISB source samples from lighter refined products, have been prepared by SINTEF, Norway.

To secure that SINTEF received the same aliquot and concentration of samples as other laboratories within OSINET, SINTEF received the samples from Rijkswaterstaat, Netherlands on October 18th, 2017. SINTEF has followed the instructions given by the organizers for analysis and data treatment and compared the samples by means of the CEN (2012). The relevant PAH and biomarkers compounds have been integrated and the results entered in the RR Excel spreadsheet file provided by Paul Kienhuis, vs 71. In addition, all samples have been imported into the COSI database, and several of the chromatograms and figures given in this report are downloaded from the database.

The results from the additional In-situ-burned (ISB) source and two ISB residues samples from lighter refined products is based on results from COSIWEB. The compared results from COSIWEB is given in Appendix E.

1 Sample Information

The scenario for the RR2017 describe a large mysterious oil slick observed drifting in the Norwegian Sea in the morning. It was assumed that this was an illegal spill done during the night. Some of the oil slick was collected in a fire proof boom and ignited, but parts of the slick were too thin to be ignited. Two samples of the slick were collected, one that was assumed to be a burned residue and one non-burned oil

The samples received are described in Table 1.1 and Figure 1.1. Duplicate analyses were performed for all samples.

Table 1.1 Sample description and SINTEF ID.

SAMPLE ID	SINTEF ID	CosiWeb Id:	Sample description
Source A	2017-7289	No-1-24.1 and 24.101	RR2017 Source A
Source B	2017-7290	No-1-24.2 and 24.102	RR2017 Source B
Source C	2017-7291	No-1-24.3 and 24.103	RR2017 Source C
Spill A	2017-7296	No-1-24.4 and 24.104	RR2017 Spill A
Spill B	2017-7297	No-1-24.5 and 24.105	RR2017 Spill B
<i>Additional samples</i>			
ISB Source A	2017-7292	No-1-24.6 and 24.106	RR2017 ISB Source A
ISB Source B	2017-7293	No-1-24.7 and 24.107	RR2017 ISB Source B
ISB Residue A	2017-7294	No-1-24.8 and 24.108	RR2017 Residue A
ISB Residue B	2017-7295	No-1-24.9 and 24.109	RR2017 Residue B



Figure 1.1 Picture of received samples of 18th October 2017.

2 Materials and methods

2.1 Sample preparation and analysis

The provided samples were dissolved in dichloromethane (DCM) at a volume of about 1,8 ml and a concentration of 20 mg/ml. The samples were diluted to a concentration of about 5 mg/ml prior to analysis. No clean-up was performed on the extracts.

Duplicate analyses were performed for all samples on the GC-FID and GC-MS. The GC-FID was equipped with a Zebtron ZB-1 30m column 0.25mm ID and 0.25 μ m film thickness using He as a carrier gas (2mL/min, constant flow), with an injection volume of 1 μ L and the following temperature program: 40°C (1 min), 6°C/min up to 330°C (5 min). Instrument conditions given in CEN (2012) and in the instructions for COSI were used for the GC-MS.

2.2 Quality Assurance (QA)

SINTEF analyse the "SINTEF oil-mix" prior to GC-MS analysis to ensure that all the retention times matches the NR and the DR peaks. In addition, SINTEF follow the Quality Assurance Plan for The BP MC252 Incident for environmental analysis (BP-MC252-QAPP, 2011). More specified MS QA-conditions and the parameters for the MS-analysis are given in Excel-spreadsheet "Oilcomp_100 MS RR2017_NO" and Appendix D.

3 GC-FID results

The GC chromatograms are given in Figure 3.1 to Figure 3.5 and the overlays of the GC chromatograms (from COSI) are given in Appendix A. Results from duplicate analyses in Appendix B. The results are very similar and no DR are deselected for the comparison.

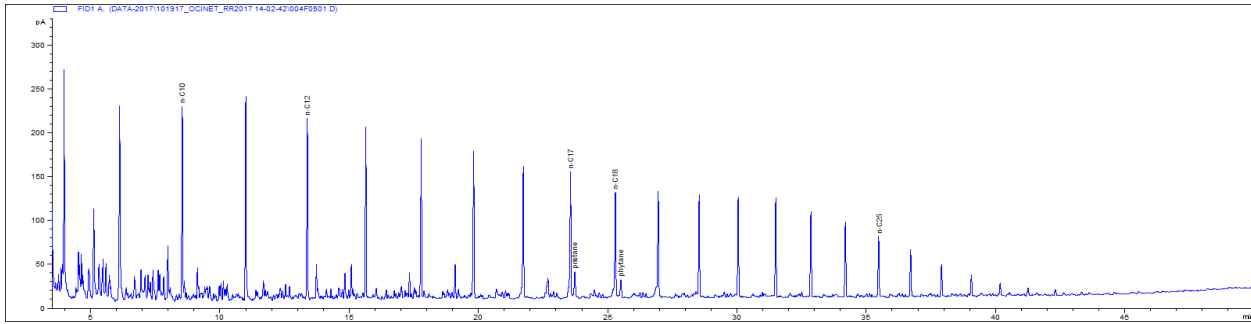


Figure 3.1 Source A (COSI Id.: No1-24.1).

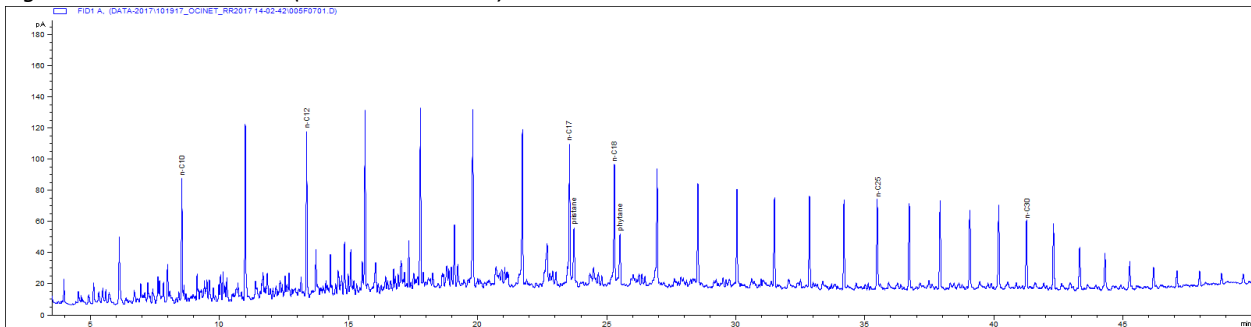


Figure 3.2 Source B (COSI Id.: No1-24.2)

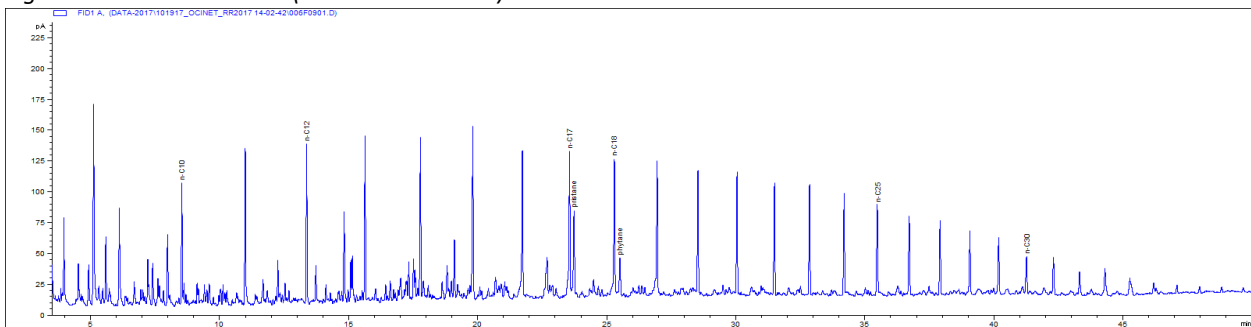


Figure 3.3 Source C (COSI Id.: No1-24.3)

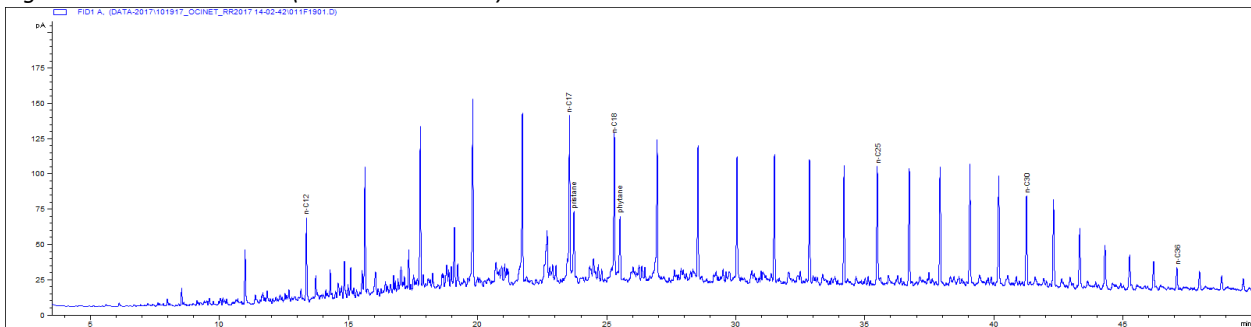


Figure 3.4 Spill A (COSI Id.: No1-24.4)

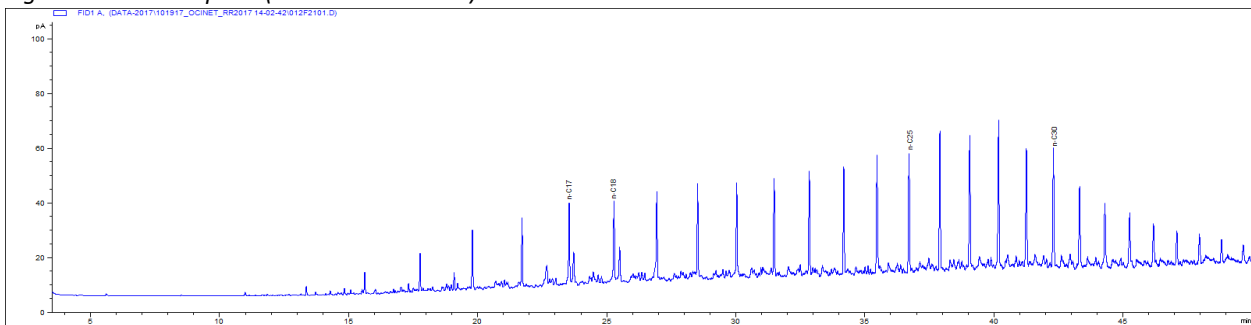


Figure 3.5 Spill B (COSI Id.: No1-24.5)

3.1 Visual inspection, overlays

The overlays of Spill A over Source A, B and C in Appendix A, show that Spill A has a profile that are very similar to Source B, but are slightly more weathered. The Spill samples were collected in the same boom and it was assumed to be one burned residue and one non-burned residue from the same source. The GC-FID chromatograms of the two spill samples are compared in Figure 3.6. Spill A, the blue line, shows a profile typical for an oil which has been weathered on the sea surface, but spill B has a different weathering profile. Spill B has an almost linear evaporative loss up to C23 (Figure 3.8) and has an enrichment of the higher boiling n-alkanes C25-C36 and that might be due to the burning.

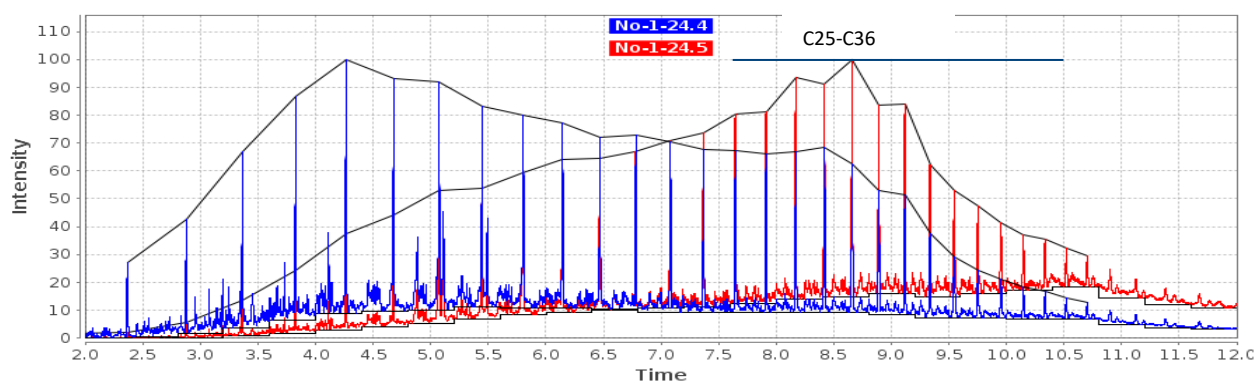


Figure 3.6 Overlays of Spill A (blue) and Spill B (red). (COSI Id.: No1-24.4 and No1-24.5)

3.1.1 Oil type, tentative

The n-alkanes are detected from C9 to C40 in the GC-method applied by SINTEF. Based on the GC-FID screening, the source samples A and C have a chromatographic profile like paraffinic crudes. Source B and the two spill samples might be a mixture of a crude oil and a refined product. The height of the pristane and phytane in Source B and Spill A is about the same. Spill B has a different chromatogram profile showing a high evaporative loss up to C23 and an enrichment of n-alkanes from C25-C35 which is assumed to be due to burning (Figure 3.8). Source B, Spill A and Spill B are possible the same oil type.

It is difficult to conclude on this stage and no source samples can be ruled out. It is recommended to continue with GC-MS fingerprinting analysis of all samples.

3.1.2 Obvious differences

At this stage, the obvious differences are the different degree or type of weathering between the two spill samples due to burning. Spill B has a chromatogram profile showing a high evaporative loss up to C23 (Figure 3.5), and an enrichment of n-alkanes from C25-C35 due to burning. A burning residue seems to have a linear evaporative loss equivalent to the boiling point of the n-alkanes up to C23 (Figure 3.9). Source A and C is most likely crude oils and differ in profile. This is also shown in the difference in height between the isoprenoids and n-alkanes, from Source B and the two spill samples.

3.2 Isoprenoid ratios, GC-PW plots

The isoprenoid ratios are given in Table 3.1 and are calculated by COSI: Source A and Source C differ from Source B and the spills. It looks like the ratio changes by burning e.g. Spill B, and this confirms the discussions in chapter 3.1.1 and 3.1.2.

Table 3.1 The isoprenoid ratios between C17/pristane, C18/phytane, and pristane/phytane, based on peak heights (calculated from COSI).

SAMPLE ID	SINTEF ID	CosiWeb Id:	C17/pristane	C18/phytane	Pristane/phytane
Source A	2017-7289	No-1-24.1	4.68	5.82	1.49
Source B	2017-7290	No-1-24.2	2.41	2.34	1.31
Source C	2017-7291	No-1-24.3	1.67	3.58	2.24
Spill A	2017-7296	No-1-24.4	2.32	2.26	1.10
Spill B	2017-7297	No-1-24.5	2.40	2.26	0.96

The GC-PW plots are from COSI. None of the peaks were removed from the chromatograms prior to preparing the PW-plots. GC-PW plots comparing evaporative loss between the Spill A and Source B are shown in Figure 3.7 and Spill B with Source B are shown in Figure 3.8. The GC-PW plot (Figure 3.8) shows that Spill B compared to Source B is heavily influenced by weathering in addition to burning. However, the difference observed in the PW plot is the same observation done in the overlapping chromatograms. A burned residue has an evaporative loss that looks like the n-alkanes is affected in a gradient which differ from an oil weathered on sea, as seen in the GC-PW plot comparing Spill A with Spill B, Figure 3.9. The GC-PW plots comparing spill Sample A and B with Source A and C gave no useful information and are not shown.

The comparison of samples done by COSI is not as suited as expected when comparing heavily weathered oils with less weathered/fresh oils.

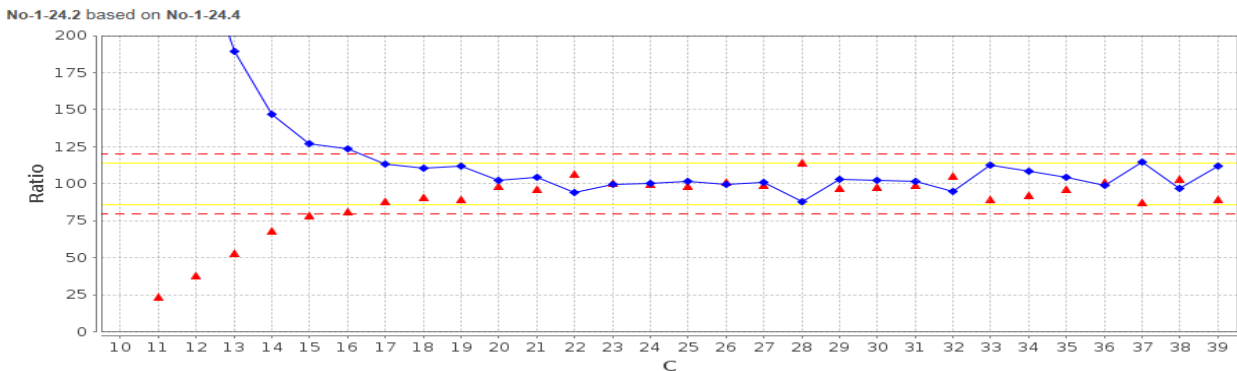


Figure 3.7 GC-PW plots from COSI Spill A (blue) over Source B (red)

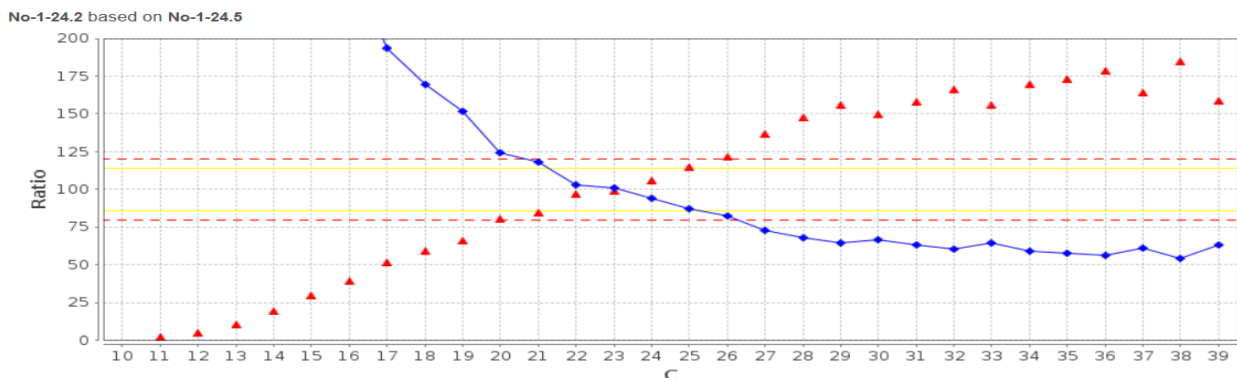


Figure 3.8 GC-PW plots from COSI Spill B (blue) over Source B (red)

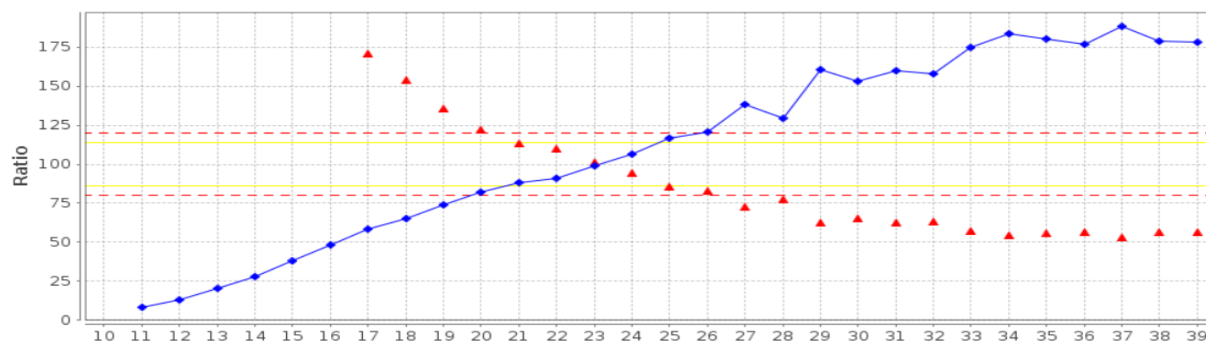


Figure 3.9 GC-PW plots from COSI Spill B (red) over Spill A (blue)

3.3 GC-FID conclusions

The n-alkanes are detected from C9 to C40 in the GC-method applied by SINTEF and the GC screening indicates that the source samples A and C has a chromatographic profile like paraffinic crudes. The chromatograms of Source B and the two spill samples differ from Source A and C and they might be a mixture of a crude oil and a refined product. The heights of the pristane and phytane in Source B and Spill A are about the same and differ in value from Source A and Source C.

Spill B has a high evaporative loss up to C23 and an enrichment of n-alkanes from C25-C35 due to burning (Figure 3.8). A burned residue has an evaporative loss that looks like the n-alkanes is affected in a gradient which differ from an oil weathered on sea, as seen in the GC-PW plot comparing Spill A with Spill B, Figure 3.9. Burning also seems to affect the isoprenoid ratio.

4 GC-MS results

4.1 Visual inspection of the ion chromatograms

Ion chromatograms of m/z 191, 217, 218, 231, 234, 216, 192 and 198 are based on the reports downloaded from COSI (Appendix C.1-C.3) and from MS-chemstation m/z 412, gammacerane (30G) (Appendix C4.).

4.1.1 Oil type

The C1-phenanthrenes/anthracenes (m/z 192) are often used to suggest the oil type. The indication of a refined product is a higher first duplet than the second duplet and a distinct 1-methyl anthracene (MA) peak. These specific features are present in Source B. The MA is not so distinct in Source C as in Source B and in the two spill samples Figure 4.1 to Figure 4.3

MA is not present for Source A, indicating that Source A is a crude oil as seen in Figure 4.1.

If retene (m/z 234) is present, it is an indication of a crude oil and if absent it could be a refined product. Retene is present in Source C, but not the spill samples (Figure 4.3). This indicates that Source C is a crude oil.

The features for a refined product in m/z 192 and m/z 234 are present for Source B.

The spill samples have the same profile for m/z 192 and m/z 234 as Source B, indicating that they also are refined products.

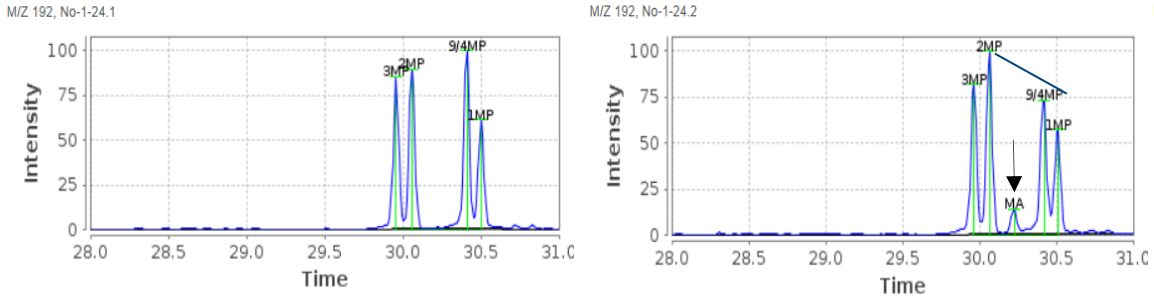


Figure 4.1 Ion chromatograms m/z 192 for Source A and Source B

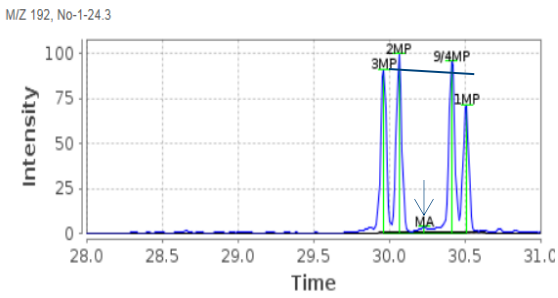


Figure 4.2 Ion chromatograms m/z 192 for Source C

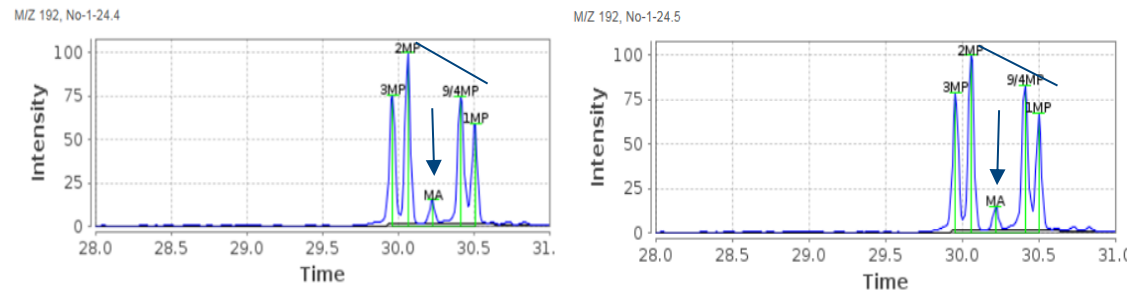


Figure 4.3 Ion chromatograms m/z 192 for Spill A and Spill B

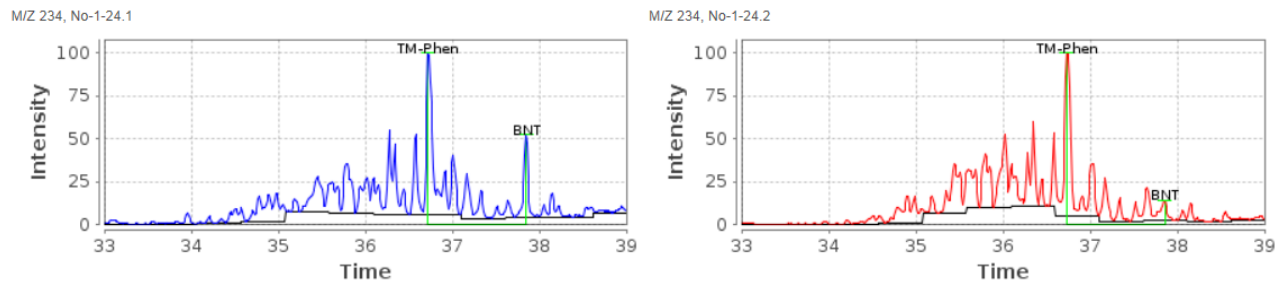


Figure 4.4 Ion chromatograms m/z 234 for Source A and Source B

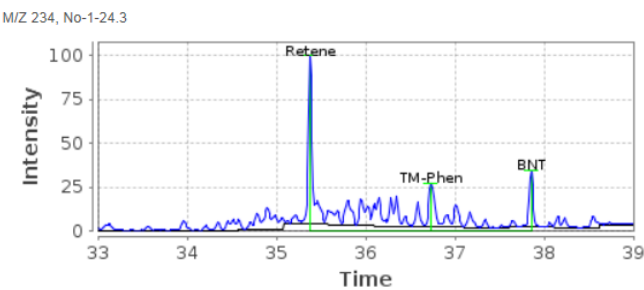


Figure 4.5 Ion chromatograms m/z 234 for Source C

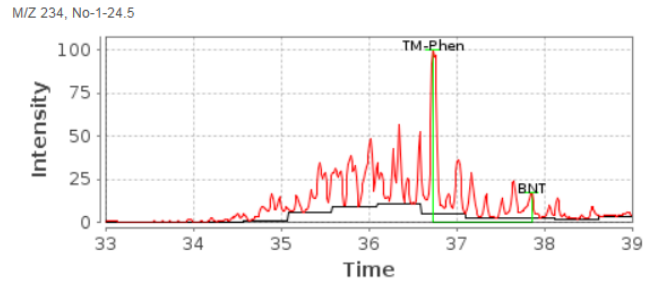
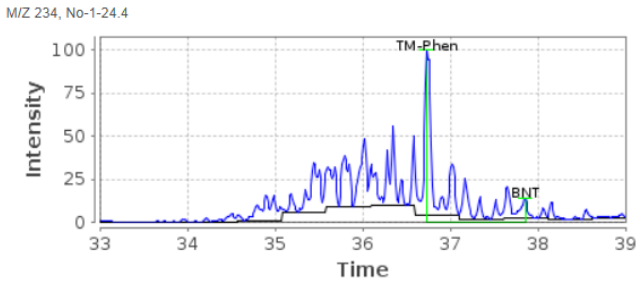


Figure 4.6 Ion chromatograms m/z 234 for Spill A and Spill B

A refined product can be excluded if $B(a)F > 4\text{-Mpy}$ (Malmberg, 2017), meaning that there is always a crude oil if this ratio is > 1 . However, a crude oil can still have a ratio < 1 .

Source C, $B(a)F$ the ratio is > 1 which means that it is not a refined product, but a crude oil (Figure 4.8).

All other samples have a ratio < 1 , indicating that they can be both refined or crude oils based on this ratio (Figure 4.7 and Figure 4.9).

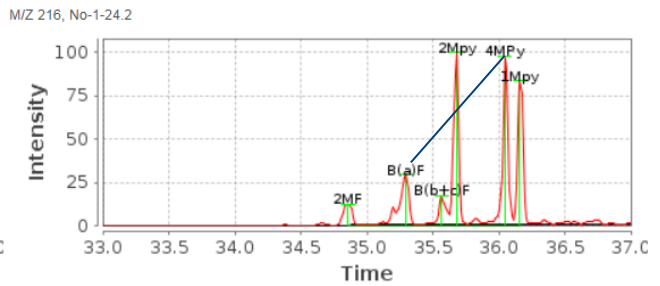
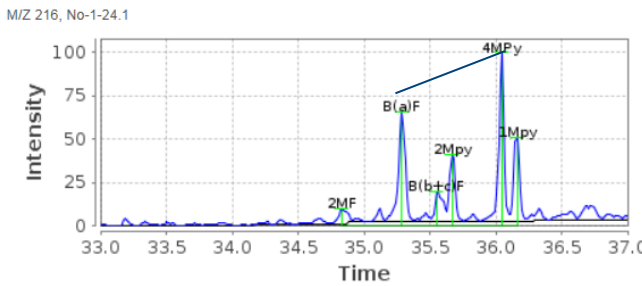


Figure 4.7 Ion chromatograms m/z 216 for Source A and Source B

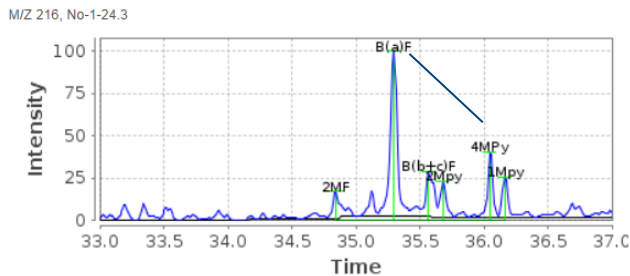


Figure 4.8 Ion chromatograms m/z 216 for Source C

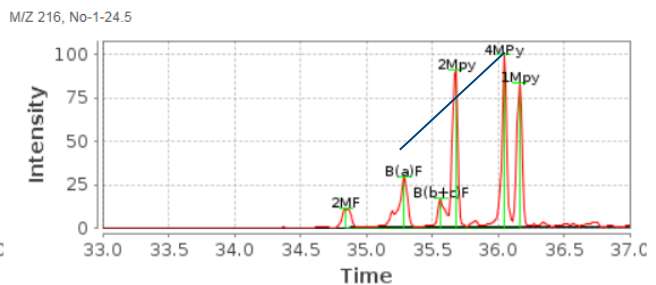
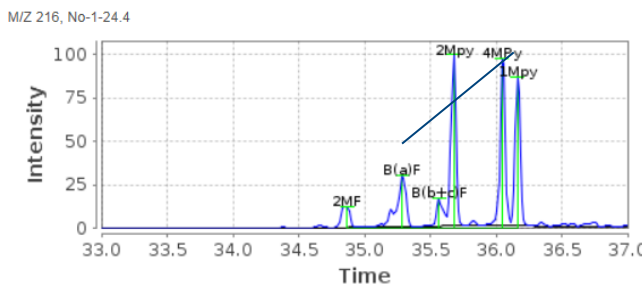


Figure 4.9 Ion chromatograms m/z 216 for Spill A and Spill B

4.1.2 GC-MS obvious differences

Visual inspection of m/z 191:

The height ratio of 29ab and 30ab is significantly different between Source A and Source B, but not so different between Source B and C. The ion chromatograms of m/z 191 of the spill samples is equal to Source B (Figure 4.10).

30G is present in the biomarker chromatogram of m/z 191. 30G is a specific fingerprinting feature and COSI has identified 30G in Source B and in the two spill samples (Figure 4.11). 30G is not present in Source A and Source C.

30G appears to represent a marker for highly saline environments (Peters and Moldowan, 1993). Oils from Libya and some areas in the Mediterranean could contain 30G. Peters and Moldowan (1993) recommend that m/z 412 is used to confirm the presence of gammacerane, but this ion is not included in the MS method described in CEN (2012). SINTEF has included the m/z 412 in the MS-method and the ion chromatograms for m/z 412 is shown in Figure 4.11 and in Appendix C.4.

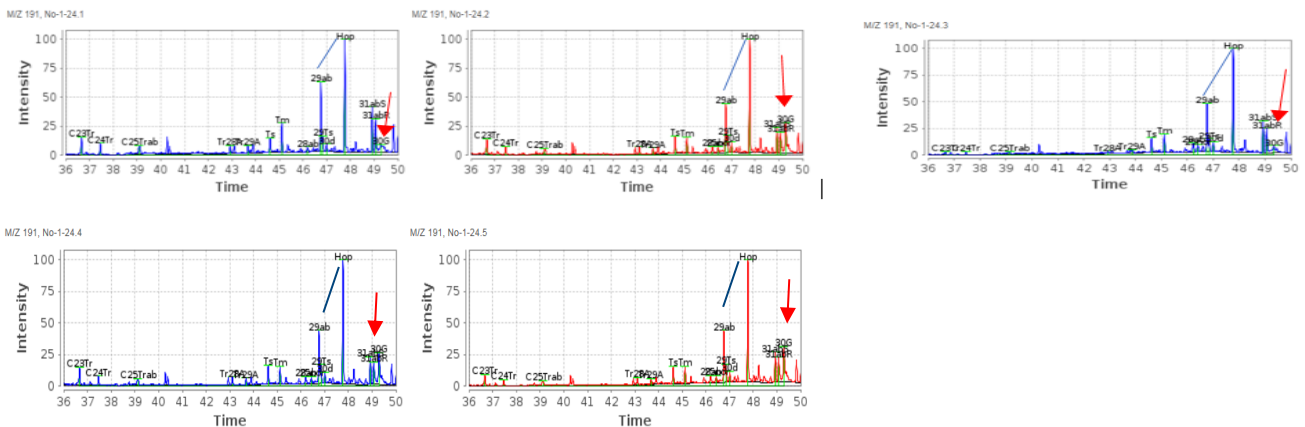


Figure 4.10 Ion chromatograms of m/z 191 hopanes for Source A, B and C and Spill A and Spill B

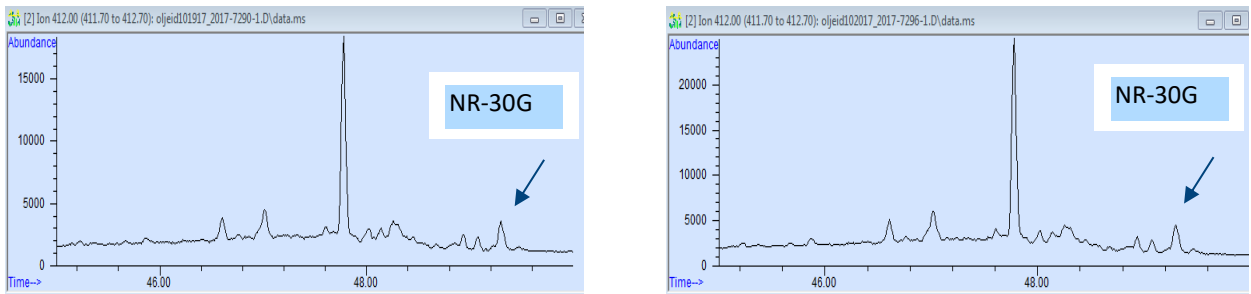


Figure 4.11 Ion chromatograms of m/z 412, Gammacerane Source B (left) and Spill A (right)

Visual inspection of m/z 217 and 218

The significant first two peaks featuring in m/z 217 (RT 39 and 40) are present in Source B, Spill A and Spill B, but not in Source A and Source C.

There are visible differences between Source B and the two spill samples compared to Source A and Source C in the m/z 218 ion chromatogram Figure 4.12

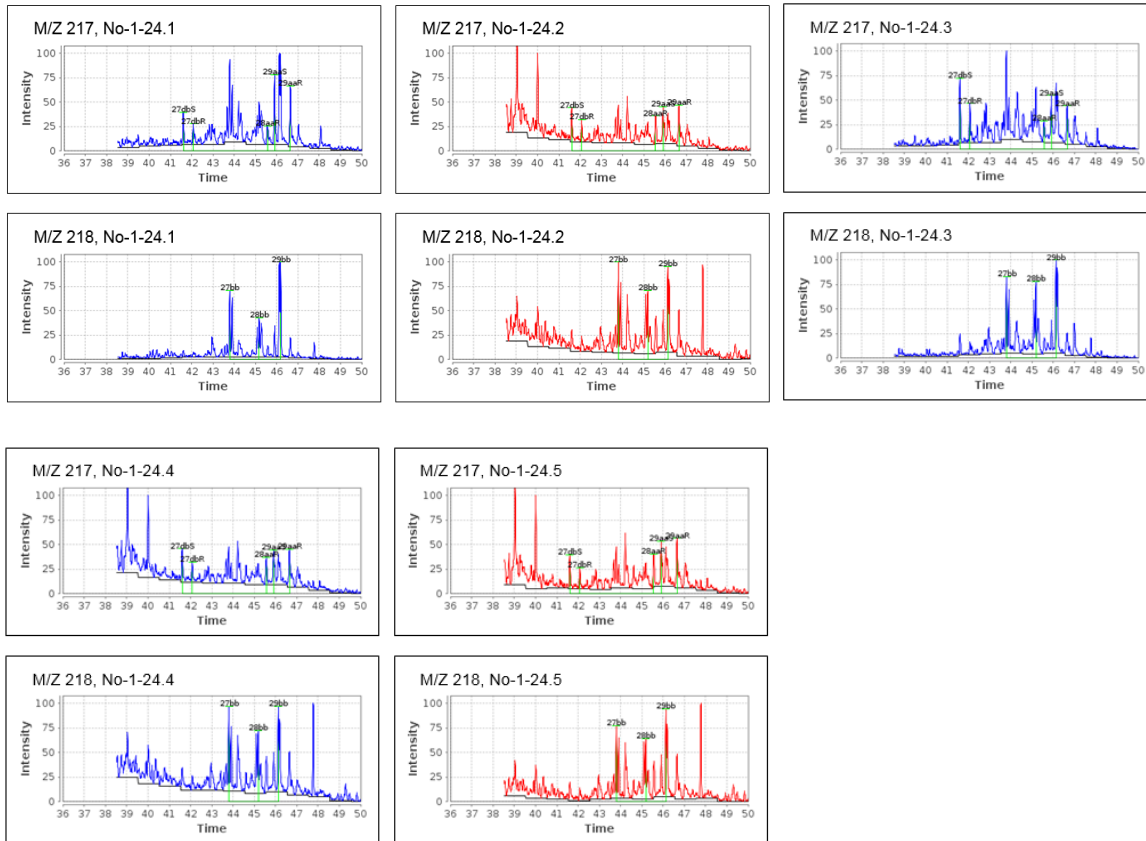


Figure 4.12 Ion chromatograms of m/z 217 and 218 for Source A, B and C, and Spill A and B

Visual inspection of m/z 231:

The characteristic "forrest of peaks" in the first part of the m/z 231 ion chromatogram is typical for refined products and is only present in Source B and the spill samples. Appendix C.1-C.3.

Visual inspection of m/z 234:

Retene (m/z 234) is present in Source C, but not in any of the other samples. Retene is an indication of a crude oil, but not an absolute criterium. The BMT is a significant peak in Source A and C but hardly visible in Source B and the two spill samples (Figure 4.4 to Figure 4.6).

Visual inspection of m/z 192:

The MA is a significant peak in Source B and in the two spill samples, but hardly visible in Source C and not present in Source A (Figure 4.1 to Figure 4.3). MA is a specific feature of a refined product.

Visual inspection of m/z 216

Significant visual differences between the spill samples versus Source A and C are observed for m/z 216. There is no visual difference between Source B and the spill samples (Figure 4.7 to Figure 4.9).

4.2 Peak measurements GC-MS

4.2.1 Duplicate measurements

Results from duplicate measurement of Source B, are shown in Appendix B. The duplicate samples are correlating very well, both the PW-plot and the ratio comparison, according to COSI. This applies to the results plotted in the spreadsheet provided by Paul Kienhuis.

4.2.2 Reasons for selecting/deselecting DRs and data points in PW-plots

None of the normative ratios or data points have been eliminated.

4.2.3 MS-PW plots and diagnostic ratios - significant differences

The MS-PW plots and comparison of the normative diagnostic ratios are given in Figure 4.15 for comparison of Spill B and Source A, B and C. These plots are based on the Excel spreadsheet provided by Paul Kienhuis and duplicate samples are compared.

The difference in the weathering profile between Spill A and Spill B compared with Source B by using the MS-PW plot based on the PAHs and biomarkers, seems to be a good tool to illustrate the difference between Spill A weathered on sea and Spill B weathered/evaporated due to burning (Figure 4.13).

Figure 4.14 shows that several informative ratios (DR) are above 14 % when comparing Spill A with Spill B. This is due to the evaporative loss up to C23 in the Spill B sample caused by burning as discussed in chapter 3.2. For the normative ratios (NR) two ratios are slightly above 14%. This might be due to burning. Only Spill B, the burned residue, will be used in the further discussion and comparison.

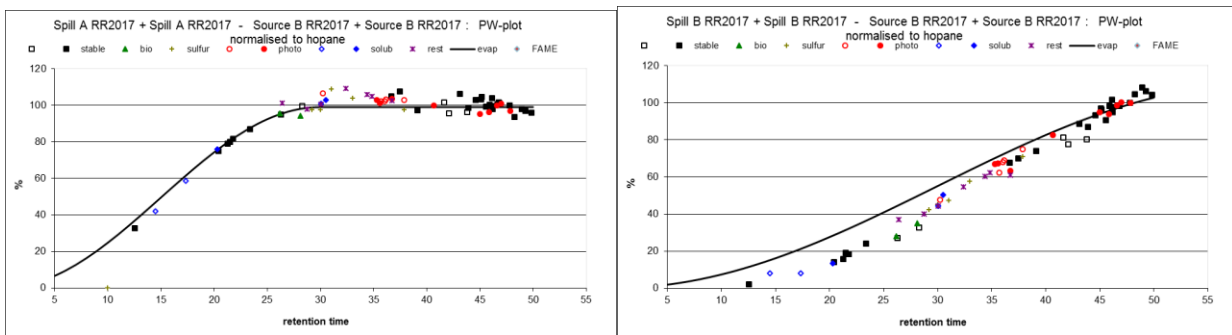


Figure 4.13 Spill A: Weathered on sea

Spill B: Weathered and burned

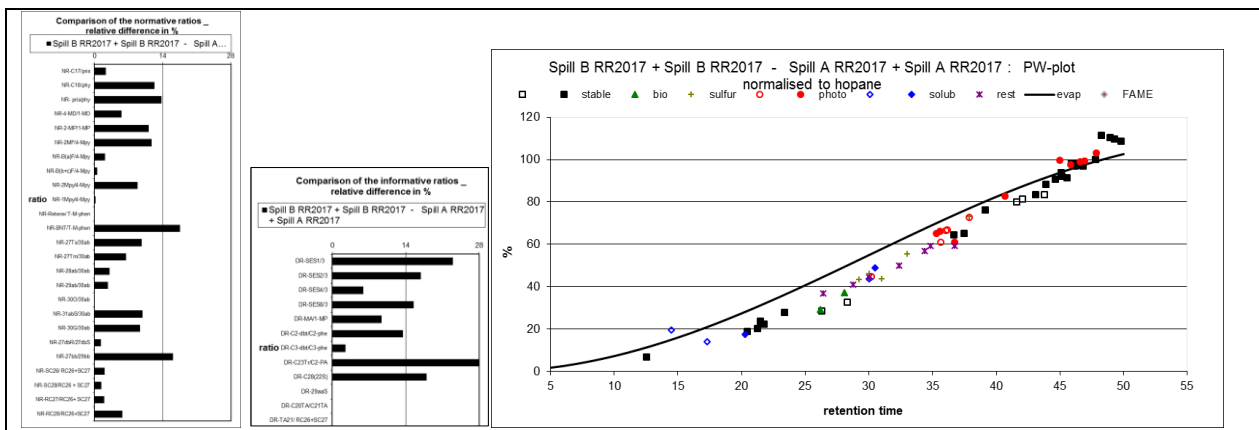


Figure 4.14 MS-PW plots and comparison of the normative and informative diagnostic ratios for Spill B compared to Spill A

The MS-PW plots and the calculated ratios when comparing the Spill B with Source A and Source C, shows that nearly all normative ratios are above 14 % difference. These two source samples can be ruled out as source for the spill samples, which also were indicated from the visual comparison.

When comparing Spill B with Source B, two NRDR are above 14%; Pristane/Phytane and NR27BB/29BB. Both Pristane and NR27BB are components affected by burning.

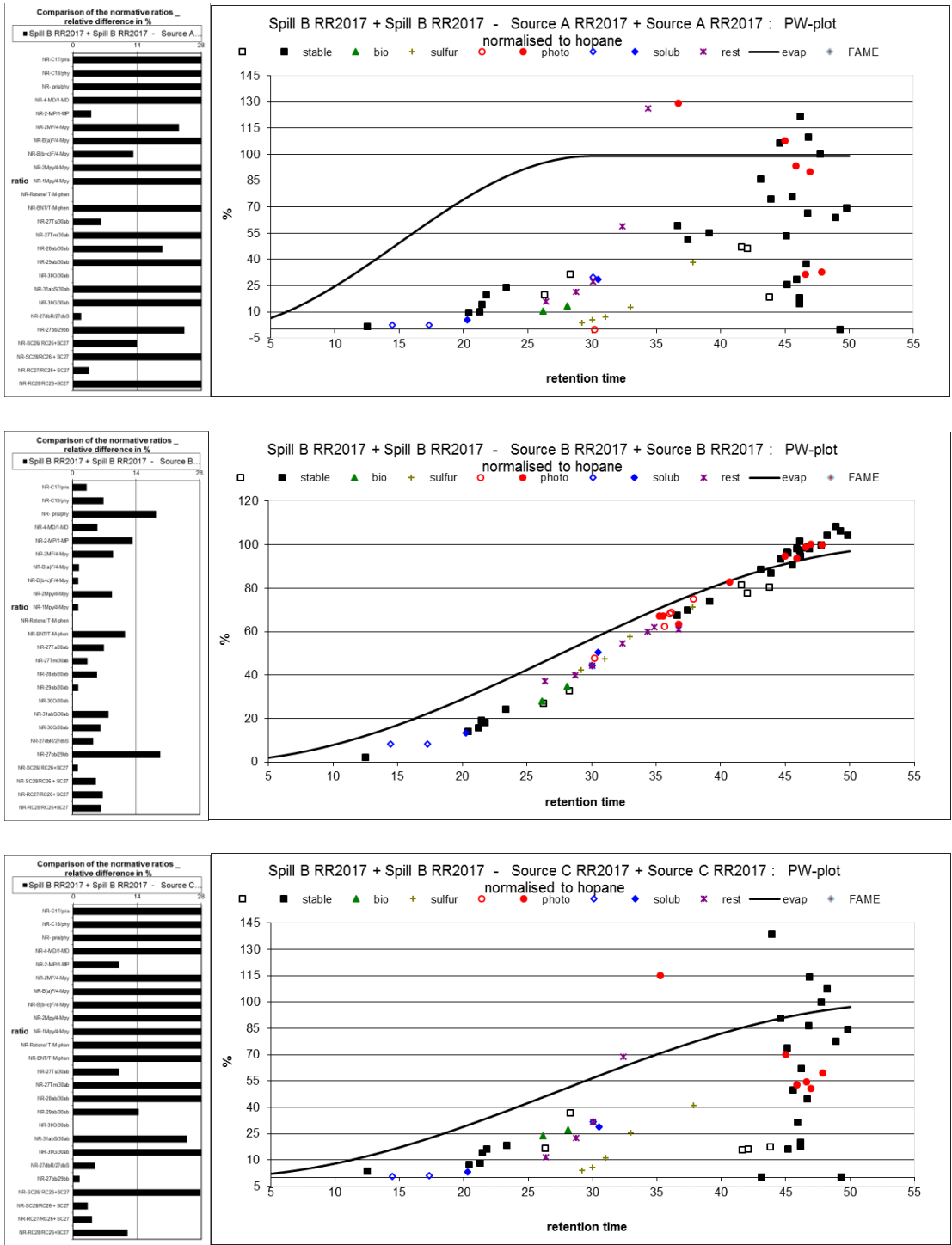


Figure 4.15 MS-PW plots and comparison of the normative diagnostic ratios for Spill B compared to Source A, B and C

4.3 GC-MS conclusions

Based on the MS-PW-plot and the DR we can conclude that Spill A is weathered on sea and Spill B has a weathering/evaporating loss profile due to burning.

It seems there is a need of a complimentary tool for verification of burning in addition to the parameters given in the CEN guidelines today. The distribution of C0-C4 alkylated PAHs can be used to observe differences between oil weathered on the sea surface and oil weathered by in-situ-burning as discussed in Boehm and Saba (2008). Weathering of an oil on the sea surface the petrogenic components of a PAH homologue are affected. By a complete burning, the pyrogenic components of the PAH homologue and the distribution and the profile of the C0 – C4 alkylated PAHs will change as seen in Figure 4.16 (Boehm and Saba (2008)).

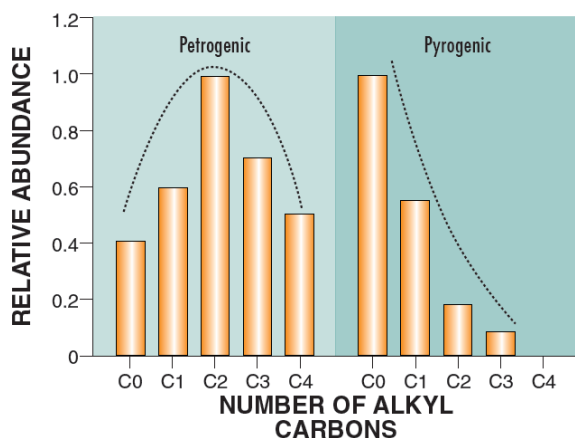


Figure 4.16 Distribution of C0-C4 alkylated PAHs shows differences between oil weathered on the sea and ISB (Boehm and Saba (2008)).

Based on the visual inspections of the m/z: 191, 217/218, 231, 192, 216 and 234 the following conclusion can be made; Source A and Source C are crude oil. Source B and the spill samples are refined products.

Gammacerane appears only in the Source B and in the spill samples. Together with the MS-PW-plot results where only two NR ratios are above 14%, a conclusion can be made on Source B being the source of the spill samples.

There are significant differences between the Source A and Source C and the spill samples which exclude them as possible sources of the spill.

5 Overall results

The scenario for the RR2017 describe a large mysterious oil slick observed drifting in the Norwegian Sea in the morning and it was assumed that this was an illegal spill done during the night. Some of the oil slick was collected in a fire proof boom and ignited, but parts of the slick were too thin to be ignited. Two samples of the slick were collected, one that was assumed to be a burned residue and one non-burned oil

Questions to be answered:

1. The two spill samples were from the same source. Compare them. Is it possible to conclude which one is the burned residue? Explain why.
2. Compare the residue from the in situ burning (ISB) with the three suspected sources. Are there any differences that can be explained by ISB in addition to the weathering processes?

From the GC-FID overlay the Spill A has a weathering profile with the characteristics of an oil which has been weathered on the sea surface. Spill B has a high evaporative loss up to C23 and an enrichment of n-alkanes from C25-C35 due to burning. A burned residue has an evaporative loss that looks like the n-alkanes are affected in the same gradient which differ from an oil weathered on sea. By burning this ratio will not change hence the components evaporates correspondently. However, Pristane has a lower boiling point than Phytane and is more exposed to impact of burning. The ratio of Pristane/Phytane will be affected and was "flagged" as also seen in the additional samples of ISB A and ISB Source A.

There is a need of a complimentary tool for verification of burning in addition to the parameters given in the CEN guidelines today. The distribution of C0-C4 alkylated PAHs and the ratios of these components could be a possible tool.

Based on the conclusions from the GC-FID and GC-MS, there are significant differences between the Source A and Source C and the spill samples which exclude them as sources of the spill.

All significant features (e.g. gammacerane) discussed based on the GC-FID and the GC-MS results the following conclusion can be made that Source B is the source of the two spill samples.

5.1 Match conclusion

Spill A and B are from the same source according to the instruction. Also verified throughout the discussion.

Spill versus Source A: Non-match

Spill versus Source B: Positive match

Spill versus Source C: Non-match

6 Uniqueness of the samples relative to the other samples in the COSI database

The highest "correlation" was obtained with Round Robin samples from other laboratories and with samples analyzed in other cases by SINTEF when comparing samples in the COSI database.

RR2017 Source A has a best correlation with other laboratories reported the RR2017 samples

RR2017 Source B has a match of 99.6 – 99.3 % with RR2016 Source 2 reported by several of the participants in the RR2016 and has match with "no1-18-136" SINTEF (ULSFO Fresh)

RR2017 Source C has a match with SINTEF "no1-18-65 (Norne) and no1-18-86 (Norne Blend)

RR2017 ISB Source A has a match with sample SINTEF sample "no1-18-147" (T-03, MGO)

RR2017 ISB Source B has a match with sample SINTEF sample "no1-11-5" (Diesel)

7 Comments to the use of COSI

COSI is a useful tool, but should be used with caution in data treatment when comparing light fuel oils with no or few biomarkers as in this year's additional samples.

- When inspecting the samples and deleting components that have been integrated by COSI, the deleted components still seems to be reported (Appendix E.1 and E.2).
- Comparing samples with no biomarkers and switch from an evaluation based on Hopane to "TM-Phen" and a selection on only aromatics the user should pay attention. It seems like COSI do a new correlation from the sample selected by the user to the best correlated sample in the database, and at the same time switch back to an evaluation based on Hopane.

- Other comments: Recommend that m/z 412 will be included in future versions of the CEN guideline, as it can be used to confirm the presence of gammacerane.

8 Referances

CEN (2012): Oil spill identification. Waterborne petroleum and petroleum products. Part 2: Analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses. CEN/TR15522-2:2012).

OSINET (2017): Instructions for Oil Spill Identification Round Robin 2017, by Kienhuis, Kraus,

Peters, K.E., and J.M. Moldowan (1993): The biomarker guide. Interpreting molecular fossils in petroleum and ancient sediments. Englewood Cliffs, Prentice Hall, NJ. ISBN 0-13-086752-7, 363 pages.

Jonas Malmberg (2017): A presentation at the meeting in Monaco "HFO vs Crude"

Boehm, P., T. Saba (2008). Identification and allocation of polycyclic aromatic hydrocarbons (PAHs). Exponent Environmental Forensics Notes 4/2008. <http://announce.exponent.com/practice/environmental/ef/vol4/index.html> (downloaded 9.jan, 2018).

BP-MC252-QAPP (2011): Quality Assurance Plan for The BP MC252 Incident for environmental analysis

A Appendix Overlays of GC-FID chromatograms

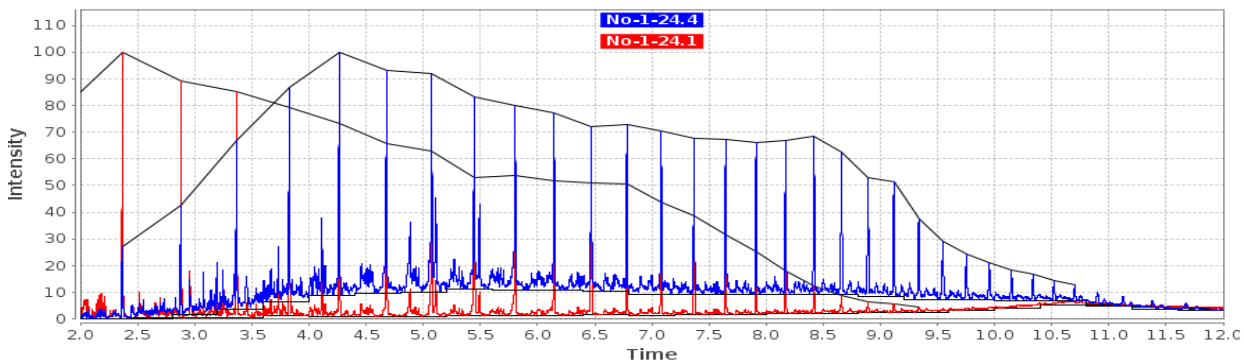


Figure A 1 Overlays of Spill A, blue and Source A, red (COSI Id.: No1-24.4 and No1-24.1)

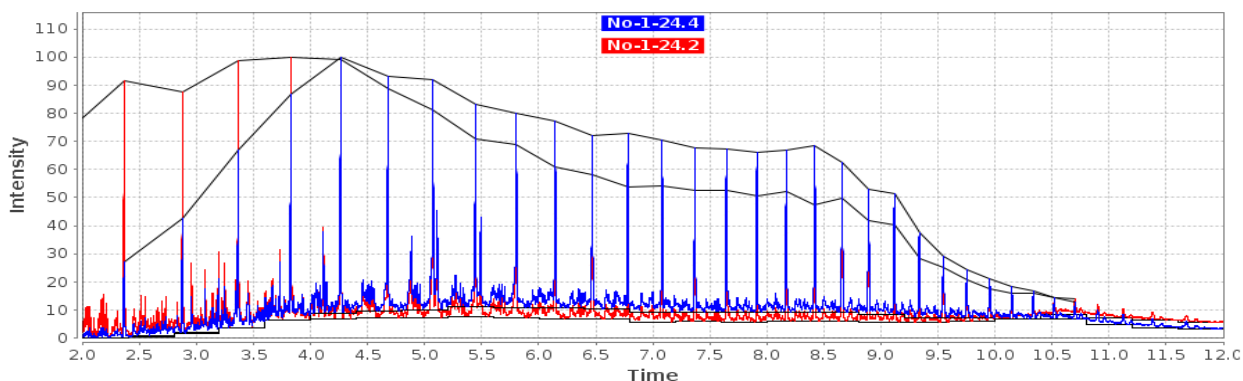


Figure A 2 Overlays of Spill A, blue and Source B, red (COSI Id.: No1-24.4 and No1-24.2)

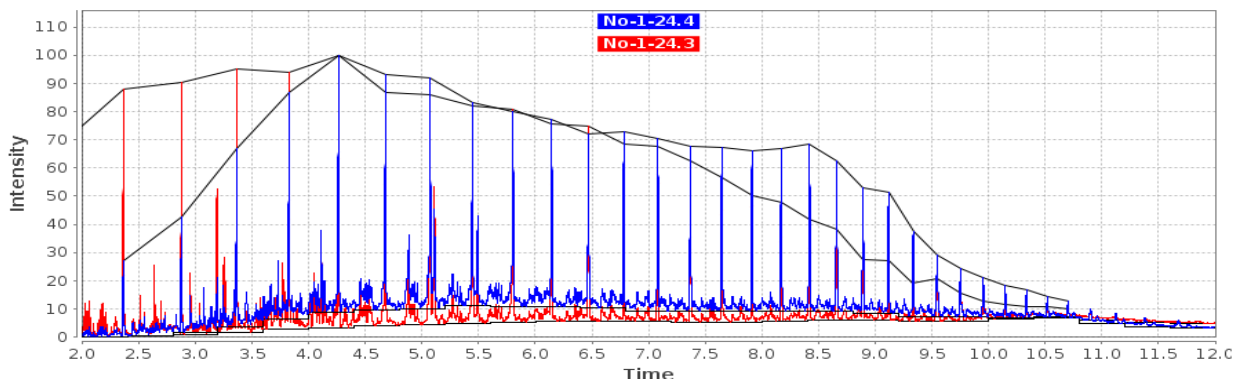


Figure A 3 Overlays of Spill A, blue and Source C, red (COSI Id.: No1-24.4 and No1-24.3)

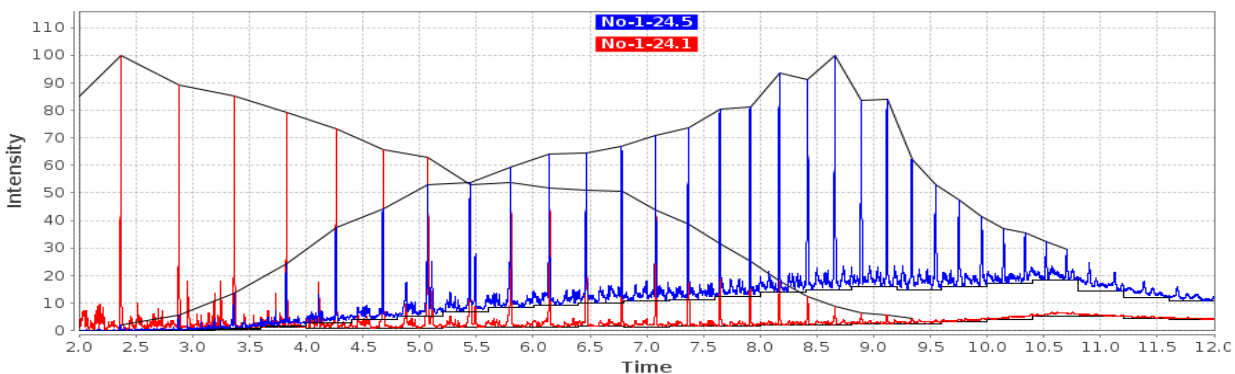


Figure A 4 Overlays of Spill B, blue and Source A, red (COSI Id.: No1-24.5 and No1-24.1)

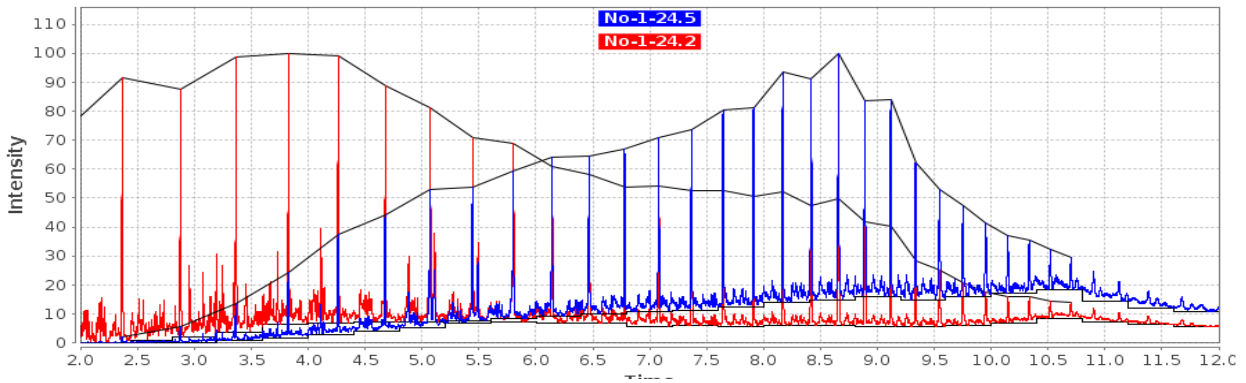


Figure A 5 Overlays of Spill B, blue and Source B, red (COSI Id.: No1-24.5 and No1-24.2)

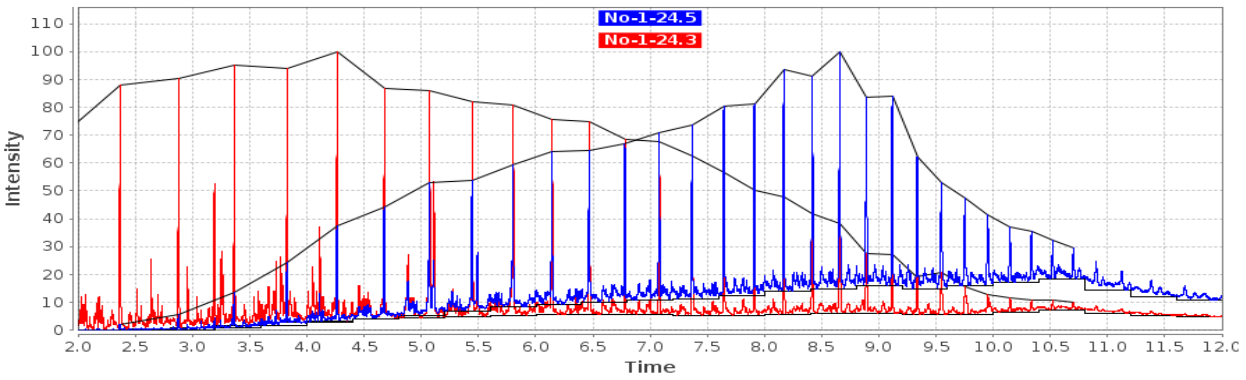


Figure A 6 Overlays of Spill B, blue and Source C, red (COSI Id.: No1-24.5 and No1-24.3)

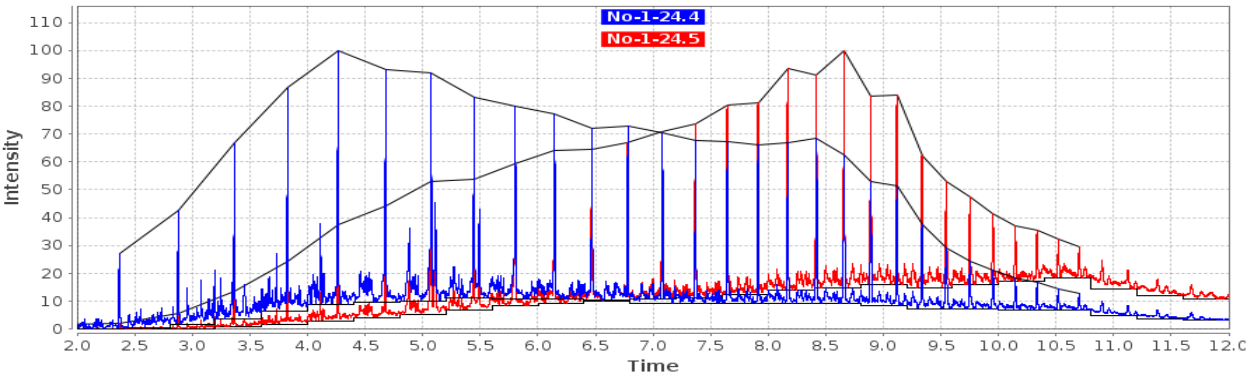


Figure A 7 Overlays of Spill A, blue and Spill B, red (COSI Id.: No1-24.4 and No1-24.5)

B Appendix Duplicate analysis

Result for duplicate analysis for Source B

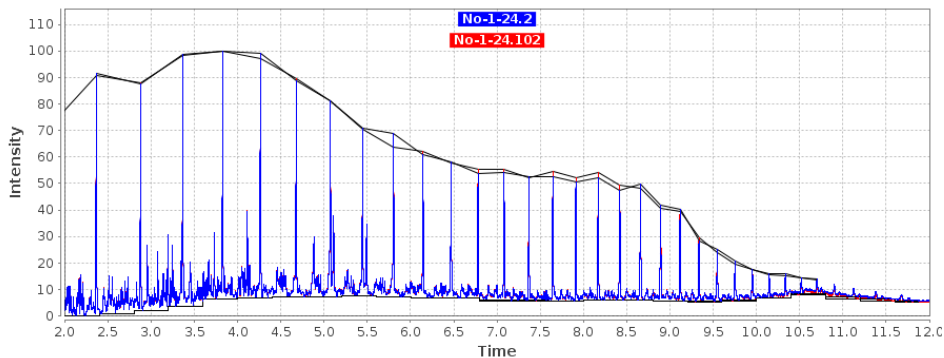


Figure B 1 GC-FID, overlays Source B vs Source B, duplicate.

ratio	No-1-24.2	No-1-24.102	%diff	flag
C17/Pr	2.41	2.45	0.72	
C18/Ph	2.34	2.33	0.23	
Pr/Ph	1.13	1.12	0.47	

Figure B 2 GC-FID, diagnostic ratio Source B, duplicate.

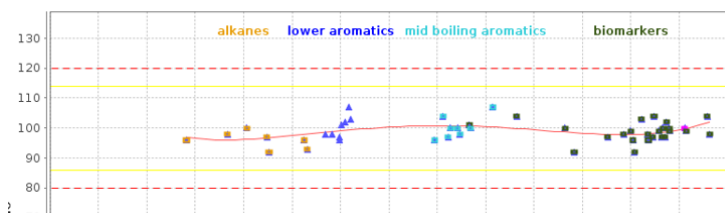
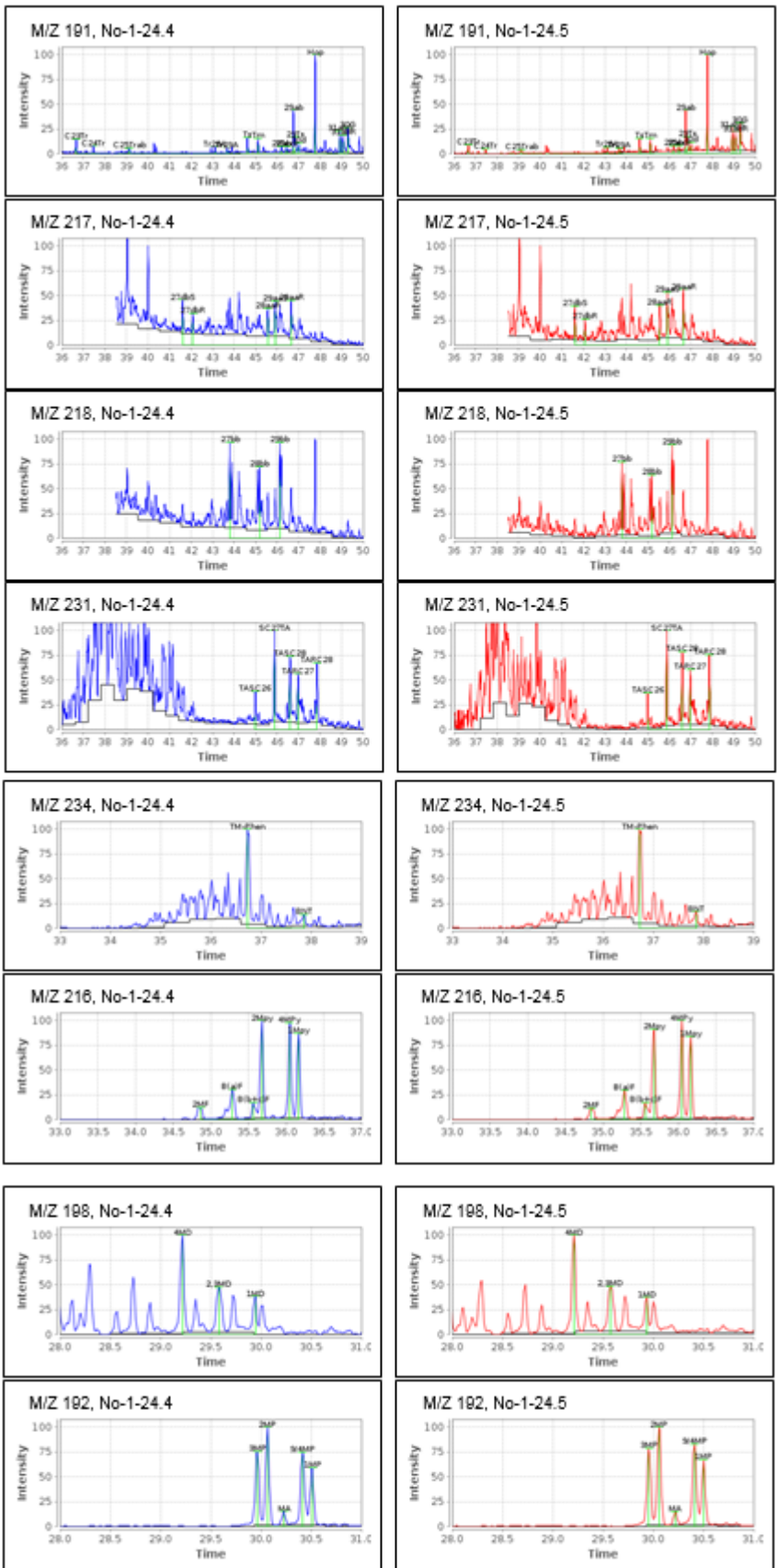


Figure B 3 GC-MS PW-plot for Source B, duplicate

C.3 Ionchromatograms of Spill A and B



C.4 Ionchromatograms of gammacerane m/z 412

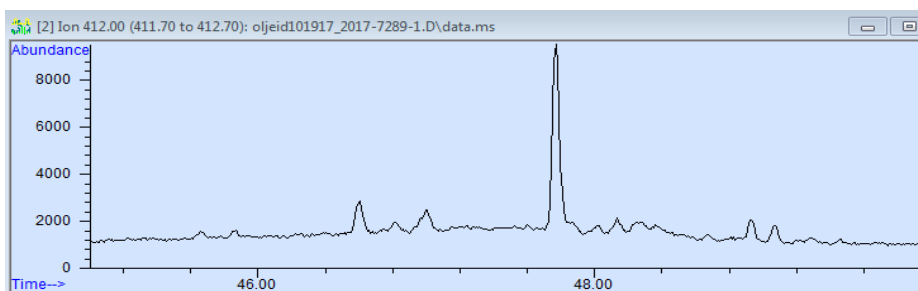


Figure C 1 Source A

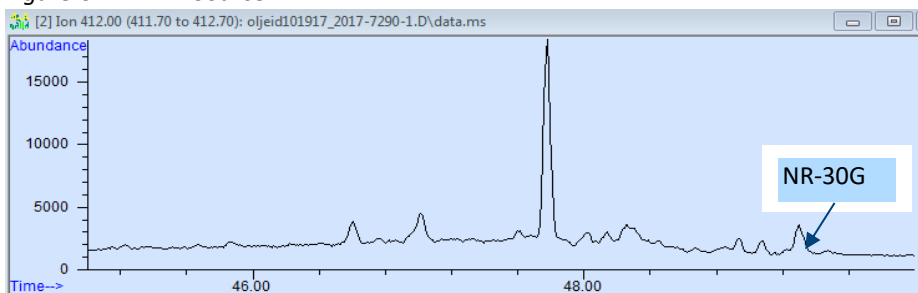


Figure C 2 Source B

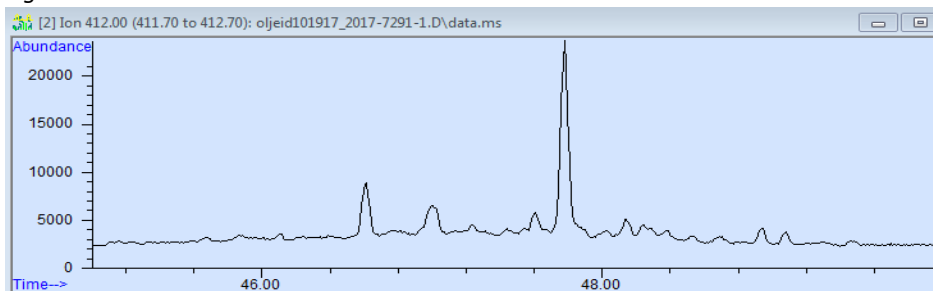


Figure C 3 Source C

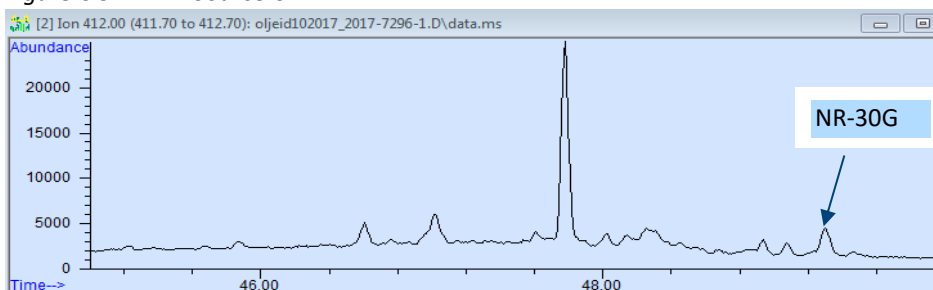


Figure C 4 Spill A

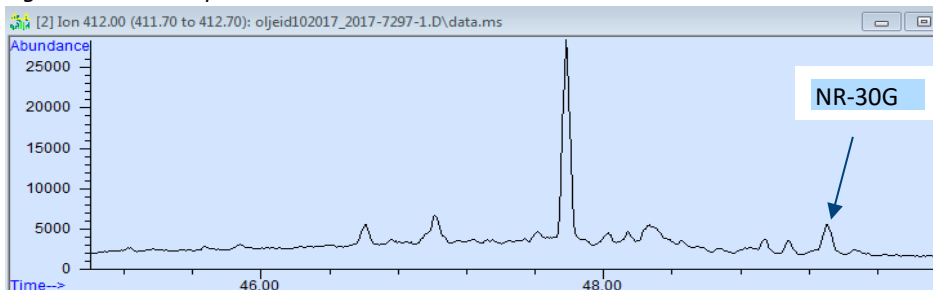


Figure C 5 Spill B

D Appendix QA Performance Criteria

Method Performance Criteria for Extended PAH (Parent and Alkyl Homologs) and Related Compounds

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Tuning/tune evaluation	Prior to every sequence/ every 20-24 hour	Tune as specified in laboratory SOP	Resolve before proceeding.
Initial Calibration (All parent PAH and selected alkyl homologue PAH)	Prior to every sequence, or as needed based on continuing calibration/verification check.		Resolve before proceeding.
Continuing Calibration (CCAL)	Every 12 hours or every 12 field samples	%D ≤ 25 for 90% of analytes %D ≤ 35 for 10% of analytes	Perform instrument maintenance. Re-analyze affected samples.
MC 252 Reference Oil	One per batch/every 20 field samples	Peak resolution >80% of 9-methylphenanthrene from 1-methylphenanthrene (m/z 192). Plus additional criteria to be developed.	Resolve before proceeding.
Procedural Blank	One per batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration >10x blank value	Resolve before proceeding. QA coordinator may be contacted to resolve issues surrounding 'minor exceedance'.
Mass Discrimination	Initial calibration and CCVs (mid-level)	Ratio for the concentration of Benzo[g,h,i]perylene to phenanthrene ≥0.70	Resolve before proceeding.
Internal Standard (IS)	Every sample	50% - 200% of the area of the IS in the associated calibration standard	Resolve before proceeding.

E Appendix Additional samples ISB samples

The results from the additional In-situ-burned (ISB) source and two ISB residues samples from lighter refined products is based on results from COSIWEB.

The isoprenoid ratios between C17/pristane, C18/phytane, and pristane/phytane, based on peak heights (calculated from COSI).

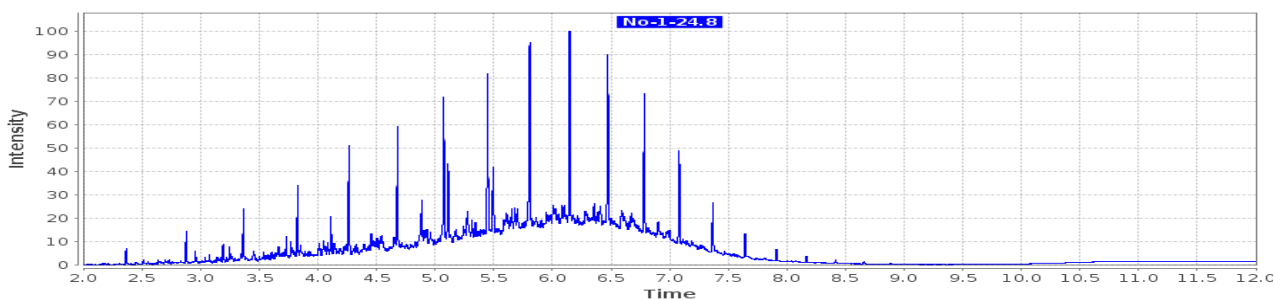
SAMPLE ID	SINTEF ID	CosiWeb Id:	C17/pristane	C18/phytane	Pristane/phytane
ISB Source A	2017-7292	No-1-24.6	1.68	2.47	1.36
ISB Source B	2017-7293	No-1-24.7	1.31	2.25	2.4
ISB Residue A	2017-7294	No-1-24.8	1.78	2.29	1.17
ISB Residue B	2017-7295	No-1-24.9	1.29	2.14	1.98

The results ISB Source A vs residue A and for ISB Source B vs Residue B are compared.

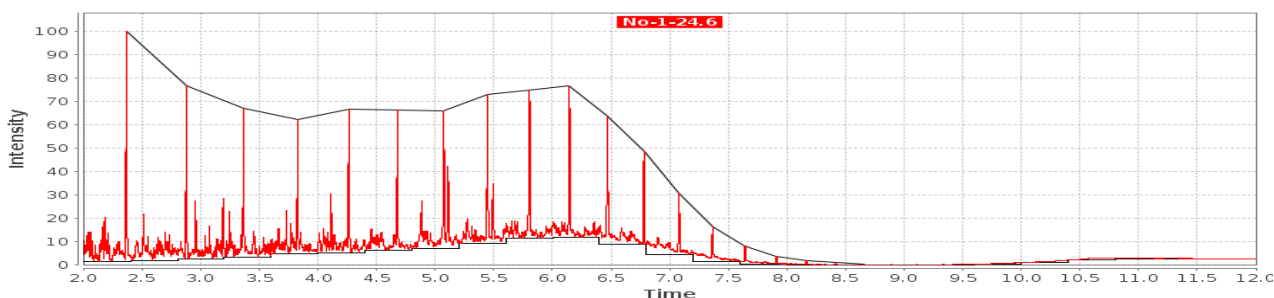
When comparing the samples, only the aromatic ratios have been used since lighter refined products contain none or few biomarkers.

E.1 The compared results for ISB Residue A versus ISB Source A

GC-FID

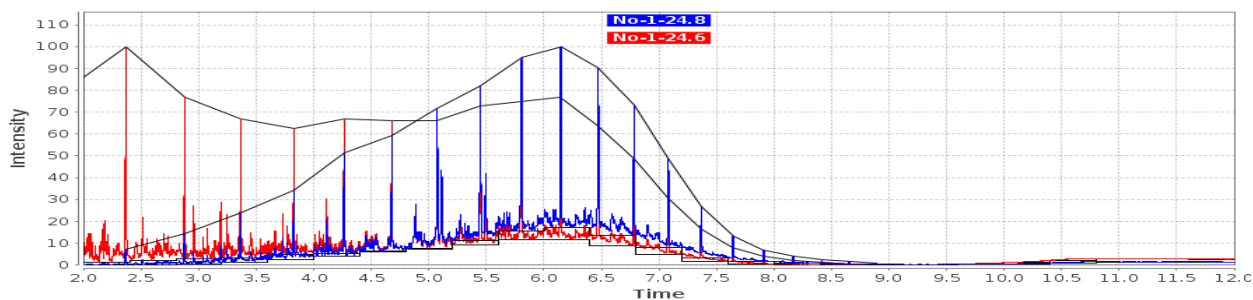


Residue



Source

GC-FID, overlays

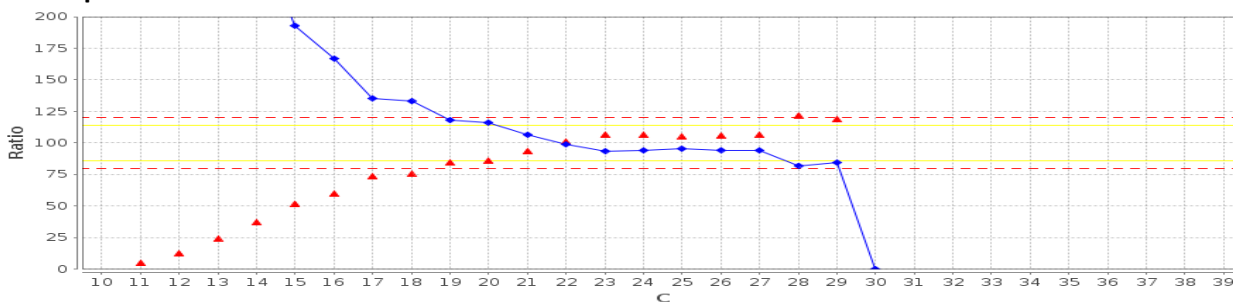


Residue (blue) over Source (red)

Isoprenoid ratios

ratio	No-1-24.8	No-1-24.6	%diff	flag
C17/Pr	1.78	1.68	2.89	
C18/Ph	2.29	2.47	3.76	
Pr/Ph	1.17	1.36	7.60	1

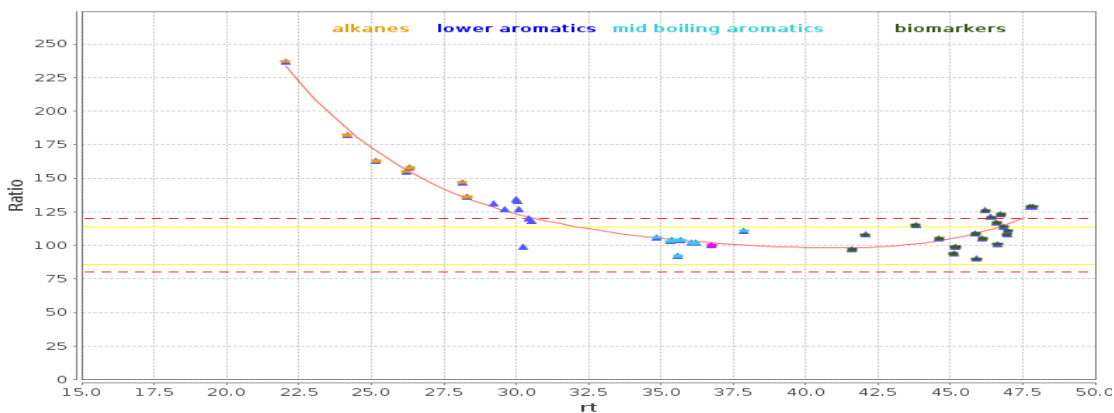
GC-PW-plot



Residue (red) compared with Source(blue)

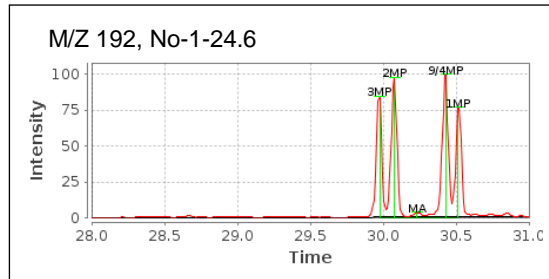
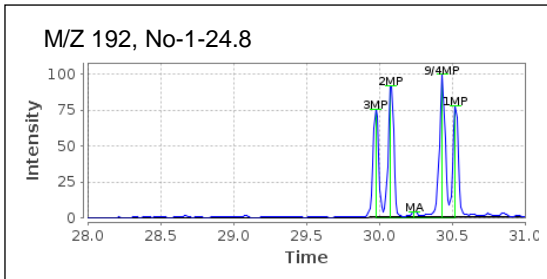
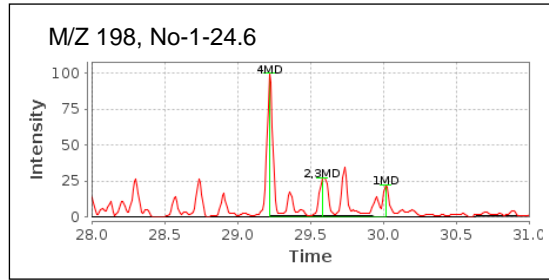
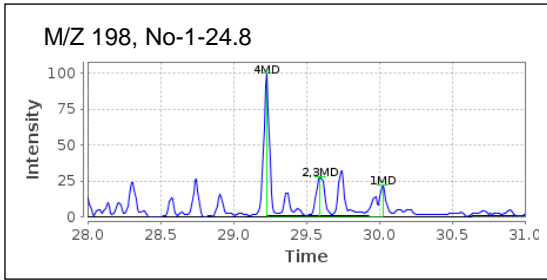
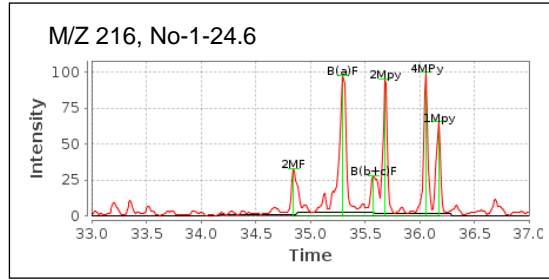
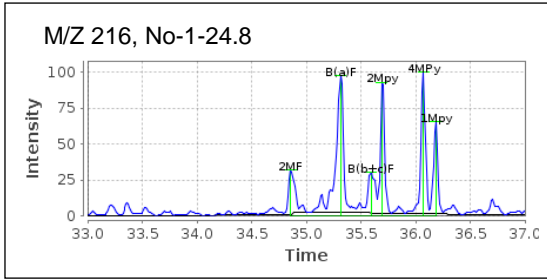
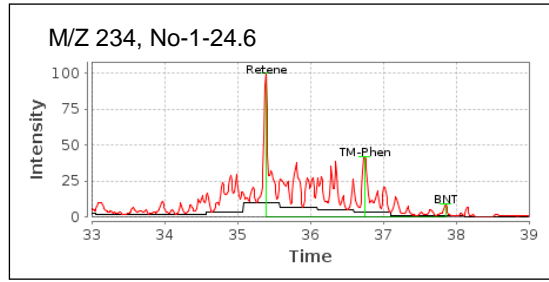
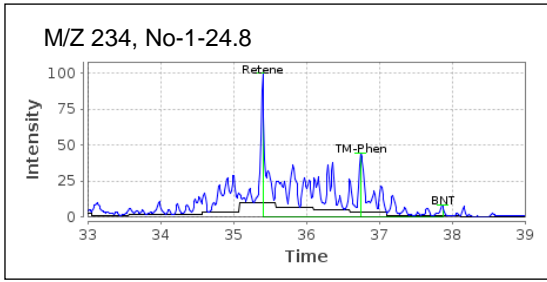
GC/MS analysis

MS-PW-plot



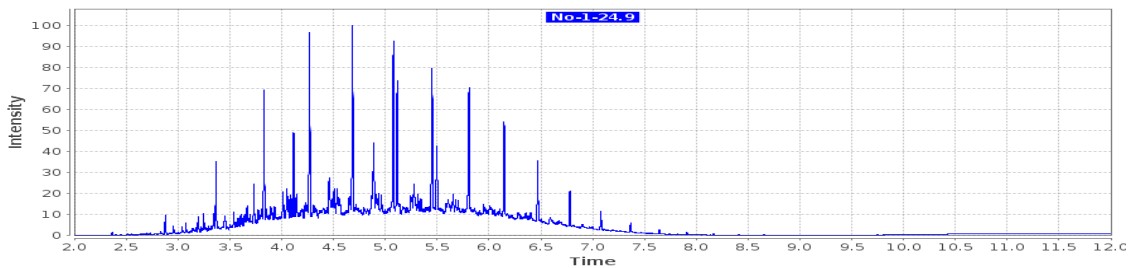
Diagnostic ratios

ratio	No-1-24.8	No-1-24.6	%diff	flag
Ts	0.72	0.58	10.35	1
Tm	0.46	0.34	15.52	1
28ab	0.35	0.34	1.14	
29ab	0.56	0.54	2.24	
30O	0.00	0.00	0.00	
31abS	0.27	0.00	100.00	1
30G	0.05	0.00	100.00	1
27dbR	0.54	0.60	5.46	
27bb	1.91	2.08	4.35	
TASC26	0.00	0.42	100.00	1
TASC28	0.41	0.44	3.70	
TARC27	0.39	0.39	0.23	
TARC28	0.27	0.31	8.28	1
C17/Pr	2.38	2.33	1.10	
C18/Ph	2.35	2.55	4.04	
Pr/Ph	0.91	1.06	7.63	1
2MP	0.92	0.98	2.88	
MA	0.03	0.03	9.17	1
4MD	4.55	4.49	0.73	
2MF	0.32	0.33	1.82	
B(a)F	0.97	0.97	0.33	
B(b+c)F	0.29	0.26	5.32	
2MPy	0.93	0.95	1.26	
1MPy	0.65	0.65	0.04	
Retene	2.18	2.28	2.38	
BNT	0.19	0.21	5.36	

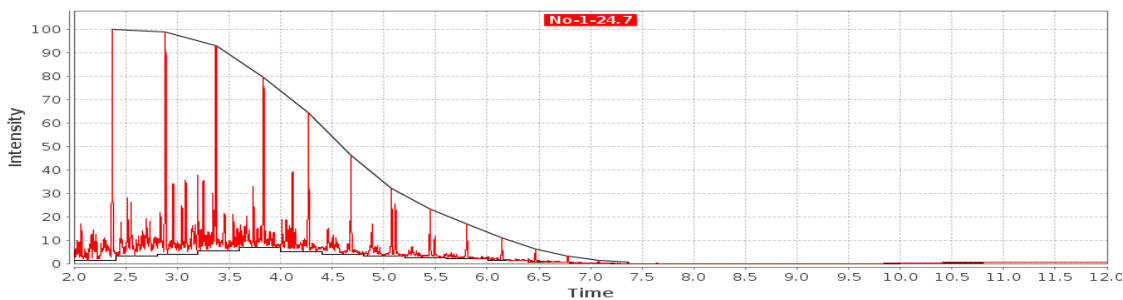
Mass chromatogram


E.2 The compared results for ISB Residue B versus ISB Source B

GC-FID

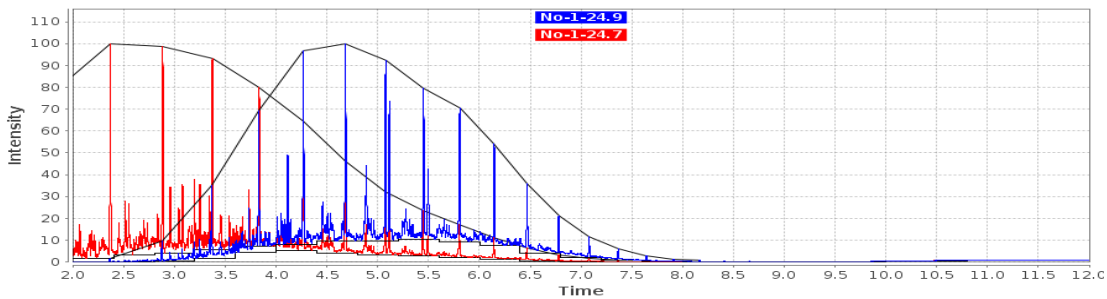


Residue



Source

GC-FID, overlays

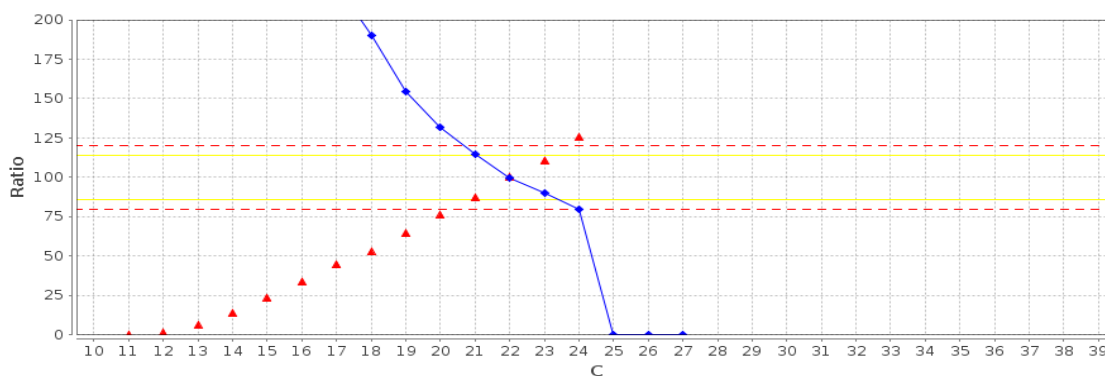


Residue(blue) over Source (red)

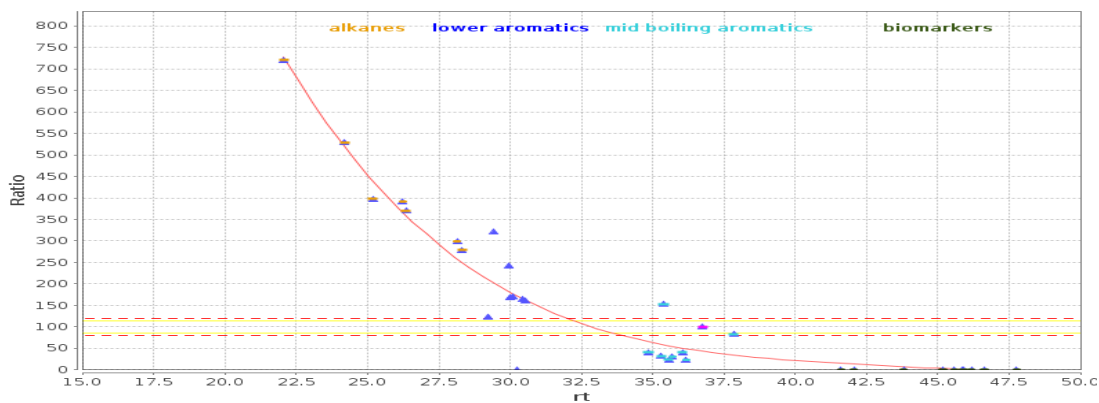
Isoprenoid ratios

ratio	No-1-24.9	No-1-24.7	%diff	flag
C17/Pr	1.29	1.31	0.55	
C18/Ph	2.14	2.25	2.45	
Pr/Ph	1.98	2.40	9.72	1

GC-PW-plot



GC/MS analysis MS-PW-plot



Diagnostic ratios

ratio	No-1-24.9	No-1-24.7	%diff	flag
Ts	0.38	0.00	100.00	1
Tm	0.23	0.00	100.00	1
28ab	0.00	0.00	0.00	
29ab	0.50	0.00	100.00	1
30O	0.00	0.00	0.00	
31abS	0.25	0.00	100.00	1
30G	0.00	0.00	0.00	
27dbR	0.54	0.00	100.00	1
27bb	2.56	0.00	100.00	1
TASC26	0.00	0.00	0.00	
TASC28	0.49	0.00	100.00	1
TARC27	0.42	0.00	100.00	1
TARC28	0.39	0.00	100.00	1
C17/Pr	1.60	1.70	2.89	
C18/Ph	2.07	2.22	3.36	
Pr/Ph	1.48	1.95	13.89	1
2MP	1.06	1.10	2.06	
MA	0.04	0.00	100.00	1
4MD	0.83	0.42	32.13	1
2MF	0.26	0.26	0.23	
B(a)F	0.83	0.66	12.02	1
B(b+c)F	0.29	0.18	25.10	1
2MPy	0.83	0.63	13.10	1
1MPy	0.69	0.39	27.78	1
Retene	3.15	4.84	21.09	1
BNT	0.12	0.10	8.90	1

Mass chromatogram
