Analysis technique Mineral oil in sediment

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Contents

Sullied Sediments

Sediment Assessment and Clean Up Pilots in Inland Waterways in the North Sea Region

Many of the inland waterways in Europe are under threat due to the introduction of Watch List chemicals that are not currently regulated under the European Water Framework Directive. These chemicals enter our waterways as a result of our day-to-day activities and through industry, and many have been shown to be harmful to wildlife and the wider aquatic environment. Regardless of their source, these pollutants accumulate in the sediments in our rivers and canals over time.

Water regulators and managing authorities do not always know the levels, locations or impacts of these pollutants. Nor do they have the tools to assess sediments confidently and make informed environmental management decisions. To address these issues, the Sullied Sediment project partnership of scientific experts, regulators and water managers is developing and testing new tools that will enable stakeholders to better assess, treat and prevent contamination from these chemicals. This work is being carried out at selected sites in the Elbe, Humber and Scheldt river catchments.

The intention of the Sullied Sediments project is therefore to help regulators and water managers make better decisions with regard to the management, removal and disposal of sediments, thereby reducing economic costs to private and public sector organisations, and the impact of these pollutants on the environment.

The partnership is also working to reduce the extent of chemicals entering the water system by raising awareness about what we, as consumers, are releasing into the environment through the use of common drugs and household products. This includes the involvement of volunteers in a sediment sampling initiative across the North Sea Region, which will inform and empower them as water champions in their local communities.

The Sullied Sediments project has been co-funded by the European Regional Development Fund through the Interreg VB North Sea Region Programme with match funding from the 13 partners involved. The project partnership includes public, private, community and voluntary sector organisations based in the United Kingdom, Germany, Belgium and the Netherlands.

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Website: northsearegion.eu/sullied-sediments

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Abstract

The measured content of mineral oil in sediments often exceeds the threshold that allows the reuse of sediments. The high content can be caused by measuring biogenic mineral oil instead of petrogenic mineral oil. A procedure is validated to ensure that sediment samples are not wrongly classified as contaminated. The clean-up technique for mineral oil in sediments and the removal of biogenic interferences has been investigated and validated. The procedure seems suitable for the analysis of sediment (soil) samples with (slightly) elevated levels of mineral oil (cf. CMA/3/R.1) from locations where contamination with mineral oil of petrogenic origin is very unlikely. By applying the proposed clean-up method, it can be proved that the mineral oil is of biogenic origin.

Introduction

In the past, the VMM (Flanders Environment Agency) indicated that the remediation standard for mineral oil in sediments (cf. CMA/3/R.1) is often exceeded and that this can be caused by measuring biogenic mineral oil instead of petrogenic mineral oil. OVAM (Flemish Waste Agency), as a partner in the European Interreg project Sullied Sediments (Interreg VB North Sea Region Programme), has a procedure investigated to ensure that sediment samples are not wrongly classified as polluted.

The prescribed, Flemish method for determining the content of mineral oil C10-C40 is the method via GC/FID (CMA/3/R.1). However, this method is not specific in the sense that both hydrocarbons of biogenic and petrogenic origin are determined indiscriminately and that both make up the total result. In consultation with the approved laboratory Servaco (Wevelgem), it was examined which methods are currently available for the determination of mineral oil and which modified or adapted methods could possibly be used to eliminate the hydrocarbons of biogenic origin out of the result. The above-mentioned step-by-step method is, as indicated in consultation with the Servaco laboratory, a first line of thought.

Following chapters described the methodology and results. The extensive report can be consulted as appendix.

Methods

In Flanders, the prescribed method for determining the content of mineral oil C10-C40 is the method with GC/FID (cf. CMA/3/R.1). However, this method is not specific in the sense that both hydrocarbons of biogenic and petrogenic origin are determined indiscriminately and that both make up the total result. In consultation with the approved laboratory Servaco (Wevelgem), it was examined which methods are currently available for the determination of mineral oil and which modified or adapted methods could possibly be used to eliminate the hydrocarbons of biogenic origin out of the result.

Research – Part I: Preliminary research and screening

Preliminary research:

- Type of material for clean-up;
- Method of application;
- Detection method;

First indicative research:

- Selection of procedure for further research;

Validation of the selected procedure:

- Selection of the samples:
  - 6 samples with high biogenic load;
  - 2 samples with mixed biogenic and petrogenic load;
- Validation procedure:
  The following research was done on the 8 selected samples:
  - Day 1: Determining of mineral oil existing procedure and new procedure;
  - Day 2: Double new procedure;
  - Day 3: Doping with mineral oil (min. 4 hours ageing and determining of mineral oil new procedure);
- Comparative research between existing procedure and new procedure with clean-up;
- Calculation of reproducibility and correctness;

Research – Part II: Further validation

Procedure for the removal of biogenic interference:

- Extraction of the sample according to CMA/3/R.1;
- Florisil clean-up via cartridge (based on ISO16703:2004);
- Detection method: GC/FID (Flame Ionisation Detector);

Additional validation of the selected procedure:

- Selection of the samples:
  - 6 soil samples containing a petrogenic pollutant (fuel) in a variable concentration;
  - 6 soil and sediment samples likely to contain mainly biogenic individual interferences at variable concentrations;
  - 6 soil and sediment samples likely to contain mixed contamination (biogenic individual interferences on a TPH hump) at variable concentration;

- Validation procedure:
    - 18 selected samples are extracted in duplicate, then each extract is finished according to the standard procedure (= CMA/3/R.1) and the above new procedure with the additional purification to remove the biogenic interferences;
- Comparative research between existing procedure and new procedure with clean-up;
- Calculation of statistical key figures.

Results

Three types of clean-up were investigated that may have a possible positive influence on the removal of biogenic interferents from soil and sludge sample.

- Silica clean-up (based on CMA/3/R.3);
- Florisil clean-up;
- Batch Florisil clean-up excess Florisil (based on CMA/3/R.1);
- Florisil clean-up using cartridges (2 g Florisil) (based on ISO16703:2004);

The exploratory research of the proposed types of clean-up on the basis of 6 types of mineral oil (spread over the complete boiling point range) and 3 samples containing peat.

- Mixture of aliphatic and aromatic compounds (see CMA/3/R.3);
- Alkane series from C10 up to and including C44;
- RIVM oil (50/50 mixture of fuel oil/lubricating oil);
- Engine oil SAE-30;
- Spent engine oil;
- Paraffin;
- 3 actual peat contaminants.

Following results opted to work further with the Florisil cartridge (2 g Florisil) as extra clean-up for the removal of biogenic interferents.were obtained:

- The recovery of mineral oil with the Florisil cartridge is for all investigated types between 90 and 110% compared to the clean-up by the existing procedure for mineral oil determination;
- When use is made of the silica clean-up there is a too high recovery for the mixture of aliphatic and aromatic compounds. This can be explained by the fact that the aromatic compounds elute together with the dichloromethane. The biogenic interferents (that we want to remove) are also partly eluted;
- There is a clear difference between the clean-up with Florisil cartridge and the silica clean-up of the actual peat samples. The Florisil cartridge removes more biogenic interferents than the silica cartridge;
- The excess Florisil batch clean-up cannot remove as many biogenic interferents as with use of the Florisil cartridge.

Eight samples are selected for further validation, 6 of which with mainly biogenic contamination and 2 with mixed (biogenic/petrogenic) contamination. To demonstrate that the Florisil clean-up has taken place efficiently, a biogenic component (e.g. stearyl stearate) is spiked as surrogate just before Florisil cleaning. Stearyl stearate displays a peak in the chromatogram on a retention time corresponding with the retention time of C37. This peak should no longer be present in the final extract.

Comparative investigation between existing procedure and new procedure with clean-gives following results:

- The QC (petrogenic mixture of diesel and lubricating oil) is fully recovered;
- The stearyl stearate peak is still present in the extract with the current procedure. This means that the current procedure cannot remove all biogenic interferents from the extract. With the new procedure with clean-up this peak is fully removed. This shows that clean-up took place efficiently.
- Samples that mainly consist of biogenic individual peaks are reduced by more than 70%;

- For samples consisting of biogenic individual peaks located on a bump, it is noticed that the biogenic individual peaks are removed by the clean-up but the bump is still present. It is as yet unclear if this hydrocarbon bump must be seen as biogenic or petrogenic. Despite the initial presumption of ‘biogenic origin’, this may also concern mixed contamination.
- For samples consisting of mixed contamination the petrogenic fraction stays present, the biogenic individual peaks are removed by the extra clean-up.

The extensive report can be consulted as appendix. An overlay of the chromatograms of the current procedure and the new procedure is given in this report.

Discussion

The current method for the analysis of mineral oil is not able to remove all biogenic interferents. With an extra clean-up the biogenic interferents can be removed without the petrogenic fraction being lost. The Florisil cartridge is the most suitable for this clean-up. Samples with mainly biogenic contamination show a reduction of 70% by use of the clean-up. After validation the procedure appears to suffice with regard to the proposed use and the requirements set for reproducibility and correctness.

Further optimisation with use of an MS detector can be considered for samples consisting of biogenic individual peaks located on a bump. The biogenic individual peaks are removed by the clean-up but the bump is still present. It is as yet unclear if this hydrocarbon bump must be seen as biogenic or petrogenic.

Conclusion

The Flemish method for determining the amount of mineral oil as pollutant in sediment (CMA/3/R.1) is not capable of removing all biogenic interference. By means of an extra clean-up over a florisil cartridge, these biogenic interferences can be removed without significant loss of the petrogenic fraction. The study shows that for samples contaminated with a petrogenic fraction such as heating oil, the loss is less than 10%.

Samples with a mainly biogenic contamination give a reduction of at least 60% by applying the clean-up. After validation, the new procedure appears to comply with the intended use and the proposed requirement for the repeatability variation coefficient.

The procedure seems suitable for the analysis of sediment (soil) samples with (slightly) elevated levels of mineral oil (cf. CMA/3/R.1) from places where contamination with mineral oil of petrogenic origin is very unlikely. By applying the proposed clean-up method, it can be proved that the mineral oil is of biogenic origin.

References

VITO, 2020 CMA - Minerale olie met GC/FID (CMA/3/R.1).

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Partners

The Sullied Sediments project partnership comprises 13 project beneficiaries:

Canal and River Trust (UK)

East Riding of Yorkshire Council (UK)

Ecossa (Germany)

Hamburg Port Authority (Germany)

Hamburg University of Applied Sciences (Germany)

Institut Dr Nowak (Germany)

Openbare Vlaamse Afvalstoffenmaatschappij (Belgium)

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Socotec UK Ltd (UK)

University of Antwerp (Belgium)

University of Hull (UK)

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The partnership also receives expert advice from 12 strategic partners who form our Advisory Group:

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Federal Institute of Hydrology (Germany)

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Hamburg Ministry of the Environment and Energy (Germany)

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Appendix

Analysis technique – Mineral oil in sediment – Removal of biogenic interferents - Report

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ANALYSIS TECHNIQUE MINERAL OIL IN SEDIMENT

REMOVAL OF BIOGENIC INTERFERENTS

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removal of biogenic interferents
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A procedure is validated to ensure that sediment samples are not wrongly classified as contaminated. If the remediation standard for mineral oil is exceeded, it may be due to the measurement of biogenic mineral oil instead of petrogenic mineral oil. The clean-up technique for mineral oil in sediments and the removal of biogenic interferences has been investigated.

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PART I – VALIDATION ANALYSIS TECHNIQUE

1 OBJECTIVE

In the past, the VMM (Flanders Environment Agency) gave the signal that the standard for mineral oil in sediments (cf. CMA/3/R.1) is often exceeded and that this can be caused by measuring biogenic mineral oil instead of petrogenic mineral oil. OVAM (Flemish Waste Agency), as a partner in the European Interreg project Sullied Sediments (Interreg VB North Sea Region Programme), has a procedure investigated to ensure that sediment samples are not wrongly classified as polluted.

The prescribed method for determining the content of mineral oil C10-C40 is the method via GC/FID (CMA/3/R.1). However, this method is not specific in the sense that both hydrocarbons of biogenic and petrogenic origin are determined indiscriminately and that both make up the total result. In consultation with the approved laboratory Servaco (Wevelgem), it was examined which methods are currently available for the determination of mineral oil and which modified or adapted methods could possibly be used to eliminate the hydrocarbons of biogenic origin out of the result. The above-mentioned step-by-step method is, as indicated in consultation with the Servaco laboratory, a first line of thought.

2 RESEARCH

- Preliminary research:
  - Type of material for clean-up;
  - Method of application;
  - Detection method;
- First indicative research:
  - Selection of procedure for further research;
- Validation of the selected procedure:
  - Selection of the samples:
    - 6 samples with high biogenic load;
    - 2 samples with mixed biogenic and petrogenic load;
  - Validation procedure:
    The following research was done on the 8 selected samples:
    - Day 1: Determining of mineral oil existing procedure and new procedure;

    - Day 2: Double new procedure;
    - Day 3: Doping with mineral oil (min. 4 hours ageing and determining of mineral oil new procedure);
  - Comparative research between existing procedure and new procedure with clean-up;
  - Calculation of reproducibility and correctness;
- General conclusion.

3 PROCEDURE

3.1 PRELIMINARY RESEARCH

3.1.1 Type of material for clean-up

Three types of clean-up were investigated that may have a possible positive influence on the removal of biogenic interferents:

- Silica clean-up (based on CMA/3/R.3);
- Florisil clean-up:
  - Batch Florisil clean-up excess Florisil (based on CMA/3/R.1);
  - Florisil clean-up using cartridges (2 g Florisil) (based on ISO16703:2004).

3.1.2 Method of application

3.1.2.1 Silica clean-up (based on CMA/3/R.3)

- Rinse a glass chromatography column with dichloromethane;
- Fill the column successively with 3 g activated silica and 0.5 cm Na_2SO_4;
- Rinse with x ml dichloromethane and remove the eluate;
- Rinse with y ml n-hexane and remove the eluate;
- Bring the n-hexane extract up the column and catch in an ASE vial;
- Rinse again with 3 ml n-hexane and elute with 12 ml n-hexane;
- Then elute with 15 ml dichloromethane/hexane (50/50);
- Collect everything together and evaporate under a gentle nitrogen flow to 1 ml.

3.1.2.2 Florisil clean-up

a. Batch florisil clean-up (based on CMA/3/R.1)
To determine the mineral oil a Florisil ratio of 3 g Florisil per 10 g wet sample (CMA/3/R.1) is taken in account. With high concentrations of biogenic interferents it may be the case that this quantity is not sufficient to remove all biogenic interferents. One uses an excess of Florisil (6 g Florisil per 10 g wet sample) to remove more biogenic interferents from the extract. Florisil is added to the vial of the extract and placed on the shaker

for 10 min. (300 rpm). After settling (and possible centrifuging) the phase above is transferred into a new AS vial.

b. Florisil clean-up using cartridges (based on ISO16703:2004)

See ISO16703. It is very important that the extract is free of acetone (<0.1 vol%). For this, the extract is washed a second time with MgSO4 water before carrying out the clean-up:

- Pre-rinse a Florisil cartridge with 2 x 3 ml hexane;
- Bring the n-hexane extract (1 ml) up the column and catch in an ASE vial - Elute with 3 x 3 ml n-hexane;
- Evaporate under a gentle nitrogen flow to 1 ml.

3.1.3 Detection method

Detection takes place based on GC/FID (Flame Ionisation Detector) to be able to better compare the values obtained with the initial mineral oil result.

3.2 FIRST INDICATIVE RESEARCH

3.2.1 Research

Exploratory research of the proposed types of clean-up on the basis of:

- 6 types of mineral oil (spread over the complete boiling point range):
  - Mixture of aliphatic and aromatic compounds (see CMA/3/R.3);
  - Alkane series from C_{10} up to and including C_{44};
  - RIVM oil (50/50 mixture of fuel oil/lubricating oil);
  - Engine oil SAE-30;
  - Spent engine oil;
  - Paraffin;
- 3 samples with peat.

Peat samples	Concentration mineral oil C10-C40 (mg/kg DM)
Sample A	343
Sample B	376
Sample C	748

Table 1: Concentration of mineral oil in peat samples

3.2.2 Results

3.2.2.1 % recovery of mineral oil types with Florisil cartridge and Silica clean-up compared to batch Florisil clean-up

Type mineral oil	% recovery Florisil cartridge compared to batch Florisil clean-up	% recovery Silica clean-up compared to batch Florisil clean-up
Mixture of aliphatic and aromatic compounds (see CMA/3/R.3)	110	167
Hydrocarbons	93	92
STMO (RIVM oil)	105	109
Engine oil SAE-30	104	111
Waste engine oil	98	105
Paraffine	91	87

Table 2: % Recovery of mineral oil types

3.2.2.2 % % recovery of mineral oil in peat samples with Florisil cartridge, Silica clean-up and excess batch Florisil clean-up compared to usual batch Florisil clean-up

Peat samples	% recovery **Florisil cartridge** relative to batch florisil clean-up	% recovery **Silica clean-up** relative to batch florisil clean-up	% recovery excess **Florisil batch** relative to batch florisil clean-up
Sample A (343 mg/kgDM)	30	50	54
Sample B (376 mg/kgDM)	36	46	62
Sample C (748 mg/kgDM)	16	41	38

Table 3: % Recovery of mineral oil in peat samples

Previous results showed that:

- The recovery of mineral oil with the Florisil cartridge is for all investigated types between 90 and 110% compared to clean-up by the existing procedure for mineral oil determination;
- When use is made of the silica clean-up there is too high recovery for the mixture of aliphatic and aromatic compounds. This can be explained by the fact that the aromatic compounds elute together with the dichloromethane. The biogenic interferents (that we want to remove) are also partly eluted;
- There is a clear difference between the clean-up with Florisil cartridge and the silica clean-up of the actual peat samples. The Florisil cartridge removes more biogenic interferents than the silica cartridge;
- The excess Florisil batch clean-up cannot remove as many biogenic interferents as with use of the Florisil cartridge;

3.2.3 Conclusion

It is opted to work further with the Florisil cartridge (2 g Florisil) as extra clean-up for the removal of biogenic interferents.

3.3 VALIDATION OF THE SELECTED PROCEDURE

Eight samples are selected, 6 of which with mainly biogenic contamination and 2 with mixed (biogenic/petrogenic) contamination. Samples with a concentration > 300 mg/kg DM are selected as given in the table below:

	Matrix	**Origin**	**Contamination**	**Range mineral oil C10-C40 (mg/kg DM)**	**Pre-drying**
Sample 01	Sediment	Coastal polder	Biogenic	± 300	YES
Sample 02	Sediment	Unknown	Biogenic	± 300	YES
Sample 03	Sediment	Ampsin	Biogenic	± 500	YES
Sample 04	Sediment	IJzer polder	Biogenic	± 1000	YES
Sample 05	Sediment	Unknown	Biogenic	± 1000	NO
Sample 06	Sediment	Unknown	Mixed	± 750	NO
Sample 07	Sediment	IJzer polder	Biogenic	± 750	YES
Sample 08	Sediment	Unknown	Mixed	± 1000	YES

Table 4:Selected samples

3.3.1 Surrogate

To demonstrate that the Florisil clean-up has taken place efficiently, a biogenic component (e.g. stearyl stearate) is spiked as surrogate just before Florisil cleaning. Stearyl stearate displays a peak in the chromatogram on a retention time corresponding with the retention time of C37. This should no longer be present in the final extract.

The following investigation was carried out on the 8 selected samples:

- Day 1: Determining of mineral oil current procedure (BCMO) and new procedure (CU):

BCMO procedure	*New procedure*
Bl-01	Bl-01CU
QC-01	QC-01CU
SAMPLE01-01 BCMO	SAMPLE01-01CU
SAMPLE02-01 BCMO	SAMPLE02-01CU
SAMPLE03-01 BCMO	SAMPLE03-01CU
SAMPLE04-01 BCMO	SAMPLE04-01CU
SAMPLE05-01 BCMO	SAMPLE05-01CU

SAMPLE06-01 BCMO	SAMPLE06-01CU
SAMPLE07-01 BCMO	SAMPLE07-01CU
SAMPLE08-01 BCMO	SAMPLE08-01CU

Table 5: Day 1 - Samples examined

- Day 2: Determining mineral oil new procedure (CU):

New procedure
Bl-02CU
QC-02CU
SAMPLE01-02CU
SAMPLE02-02CU
SAMPLE03-02CU
SAMPLE04-02CU
SAMPLE05-02CU
SAMPLE06-02CU
SAMPLE07-02CU
SAMPLE08-02CU

Table 6: Day 2 - Samples examined

- Day 3: Doping with mineral oil 50 µl R463 (± 250 mg/kg DM based on 10 g sample and 100%DM) (min. 4 hours ageing and determining mineral oil new procedure):

New procedure
Bl-03CU
QC-03CU
SAMPLE01-03CU
SAMPLE02-03CU
SAMPLE03-03CU
SAMPLE04-03CU
SAMPLE05-03CU
SAMPLE06-03CU
SAMPLE07-03CU
SAMPLE08-03CU

Table 7: Day 3 - Samples examined

4 RESULTS

4.1 COMPARATIVE INVESTIGATION BETWEEN EXISTING PROCEDURE AND NEW PROCEDURE WITH CLEAN-UP

After extraction the 8 samples are finished through the existing and the new procedure. The mineral oil level is measured by GCFID. The results for the mineral oil level are given in the table below:

	BCMO procedure	new procedure CU
	mg/kg DM	***mg/kg DM***
BL (<25 mg/kg DM)	24	19
QC (500 mg/kg DM)	510	496
sample01	318	89
sample02	280	73
sample03	686	447
sample04	1041	461
sample05	1269	286
sample06	688	459
sample07	814	107
sample08	1040	764

Table 8: Results Analyses

The % recovery from the new procedure (after clean-up) compared to the existing procedure is shown in the following figure:

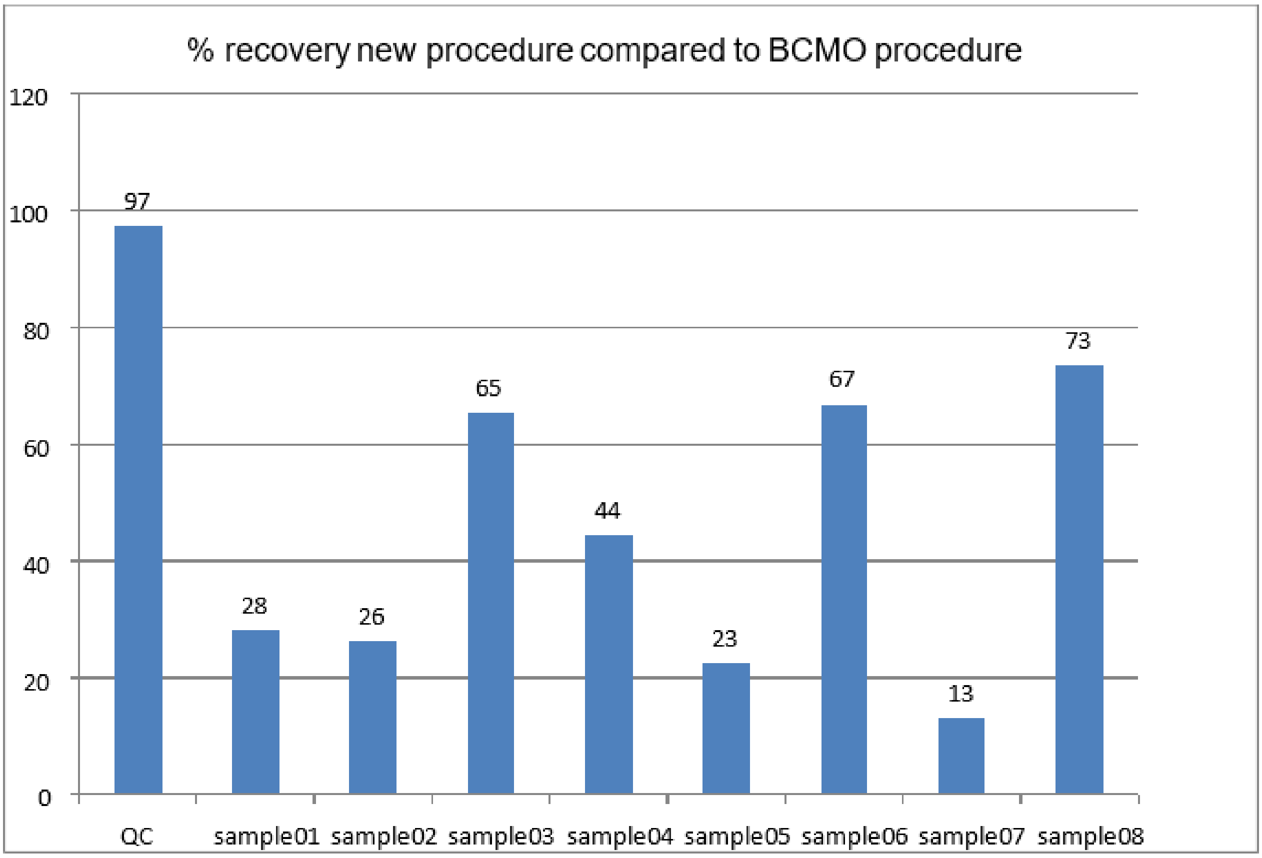

Figure 1: % recovery with the new procedure

An overlay of the chromatograms of the current procedure and the new procedure is annexed for the 8 samples. From the chromatograms and above results it is concluded that:

- The QC (petrogenic mixture of diesel and lubricating oil) is fully recovered;
- The stearyl stearate peak is still present in the extract with the current procedure. This means that the current procedure cannot remove all biogenic interferents from the extract. With the new procedure with clean-up this peak is fully removed. This shows that clean-up took place efficiently.
- Samples that mainly consist of biogenic individual peaks are reduced by more than 70% (e.g. samples 01, 02, 05, 07);
- For samples consisting of biogenic individual peaks located on a bump, it is noticed that the biogenic individual peaks are removed by the clean-up, but the bump is still present. It is as yet unclear if this hydrocarbon bump must be seen as biogenic or petrogenic. Despite the initial presumption of ‘biogenic

origin’, this may also concern mixed contamination. Recovery with these samples therefore also lies a little higher (e.g. samples 03 and 04);

- For samples consisting of mixed contamination the petrogenic fraction stays present, the biogenic individual peaks are removed by the extra clean-up. This also explains the higher recovery with these samples. (e.g. samples 06 and 08).

4.2 CALCULATION OF REPRODUCIBILITY AND CORRECTNESS

Eight different samples were analysed twice under reproducibility conditions (day 1 and day 2). On day 3 the 8 samples were doped with RIVM oil (± 250 mg/kg DM based on 10 g sample and 100 % DM).
The samples are then finished according to the new procedure and analysed in reproducibility. The results for the mineral oil level are given in the table below.

	Day 1	Day 2 duplo	Day 3 Spike	Day 3 Spike
	mg/kg DM	***mg/kg DM***	***mg/kg DM***	***% recovery***
Sample 01	89	93	304	99
Sample 02	73	79	283	95
Sample 03	447	430	657	84
Sample 04	461	451	676	101
Sample 05	286	309	595	93
Sample 06	459	538	682	72*
Sample 07	107	117	300	86
Sample 08	764	799	1010	107

Table 9: Reproducibility
* Sample 06 lies further from the rest but is not significantly higher (see Grubbs test). This sample is therefore also further considered during the further processing of the results.

4.2.1 Reproducibility

$$\boxed{CVr = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{x_{i1} - x_{i2}}{0.5(x_{i1} + x_{i2})}\right)^2}{2n}} * 100\%}$$

CV = variation coefficient, in %

n = number of samples analysed double
xi1 = first analysis result of a double analysis for sample i
xi2 = second analysis result of a double analysis for sample i

The CV must be less than 15 %.

	Variation coefficient CV %
MO C_{10}- C_{40}	6

Table 10: coefficient of variation

<u>Conclusion</u>

The set CV of 15% is obtained.

4.2.2 Correctness

The average recovery and bias are determined.
The absolute value of the bias must be less than 20 %.

	Correctness	
	% recovery	**Bias b**
MO C_{10} – C_{40}	92.2%	-7.8

Table 11: Correctness

$$b = Avg(recovery) - 100\%$$

<u>Conclusion</u>

The absolute value of the correctness (bias) is less than 20%.

5 GENERAL CONCLUSION

The current method for the analysis of mineral oil is not able to remove all biogenic interferents. With an extra clean-up the biogenic interferents can be removed without the petrogenic fraction being lost. The Florisil cartridge is the most suitable for this clean-up. Samples with mainly biogenic contamination show a reduction of 70% by use of the clean-up. After validation the procedure appears to suffice with regard to the proposed use and the requirements set for reproducibility and correctness.

Further optimisation with use of an MS detector can be considered for samples consisting of biogenic individual peaks located on a bump. The biogenic individual peaks are removed by the clean-up, but the bump is still present. It is as yet unclear if this hydrocarbon bump must be seen as biogenic or petrogenic.

PART II – ADDITIONAL VALIDATION ANALYSIS TECHNIQUE

6 OBJECTIVE

OVAM (Flemish Waste Agency), as a partner in the European Interreg project Sullied Sediments (Interreg VB North Sea Region Programme), has a procedure investigated to ensure that sediment samples are not wrongly classified as polluted. The procedure described in Part I will be more extensively validated in this further research.

7 RESEARCH

- Mineral oil procedure for the removal of biogenic interference:
  - Extraction of the sample according to CMA/3/R.1;
  - Florisil clean-up via cartridge (based on ISO16703:2004);
  - Detection method: GC/FID (Flame Ionisation Detector);
- Additional validation of the selected procedure:
  - Selection of the samples:
    - 6 soil samples containing a petrogenic pollutant (fuel salt) in a variable concentration;
    - 6 soil and sediment samples likely to contain mainly biogenic individual interferences at variable concentrations;
    - 6 soil and soil-sludge samples likely to contain mixed contamination (biogenic individual interferences on a KWS hump) at variable concentration;
  - Validation procedure:
    - 18 selected samples are extracted in duplicate, then each extract is finished according to the standard procedure (= CMA/3/R.1) and the above new procedure with the additional purification to remove the biogenic interferences;
  - Comparative research between existing procedure and new procedure with clean-up;
  - Calculation of statistical key figures;
- General conclusion.

8 PROCEDURE

- 1. Procedure for the removal of the biogenic interferences:
  - extraction of the sample according to CMA/3/R.1:
    - Soil and sediment samples with a sufficiently high dry matter content are first mixed with sodium sulphate (Na_2SO_4) as a drying agent and then subjected to a Pressurized Liquid Extraction (PLE) with an n-hexane/acetone mixture (50/50). If the PLE extraction is practically difficult to perform or if the sample intake is insufficient, because of the too low dry matter content (< 70%DS), a soxhlet extraction is performed;
  - Florisil clean-up via cartridge (based on ISO16703:2004);
  - According to ISO16703 it is very important that the extract is free of acetone (<0.1vol%). The extract is washed a second time with $MgSO_4$ water before performing the clean-up:
    - Pre-rinse a Florisil cartridge (6ml / 2000mg) with 2X 3 ml hexane;
    - Apply the n-hexane extract (1 ml) to the column and collect in an ASE vial;
    - Eluate with 3x3 ml n-hexane;
- Evaporate under a gentle stream of nitrogen to 1 ml;
- Detection method:
  - Detection is by means of GC/FID (Flame Ionisation Detector);
- 2. Additional validation of the selected procedure.

8.1 SUMMARY OF SAMPLES USED

Eighteen samples are selected:

- 6 soil samples containing a petrogenic pollutant (fuel salt) in a variable concentration:

Sample	***Matrix***	***Origin***	***Range mineral oil C_{10}-C_{40} (mg/kg DM)***	***Pre-drying***	***Extraction***
1942361-01	Soil	Unknown	± 900	No	PLE
1942361-02	Soil	Unknown	± 700	No	PLE
1942361-03	Soil	Unknown	± 3200	No	PLE
1942361-04	Soil	Unknown	± 1200	No	PLE
1942361-05	Soil	Unknown	± 1300	No	PLE
1942361-06	Soil	Hasselt	± 500	No	PLE

Table 12: Samples with petrogenic contamination

- 6 soil and sediment samples likely to contain mainly biogenic individual interferences at variable concentrations:

Sample	*Matrix*	*Origin*	*Range mineral oil C_{10}-C_{40} (mg/kg DM)*	*Pre-drying*	*Extraction*
1942361-07	Sediment	Haven van Brussel	± 300	Yes	PLE
1942361-08	Soil	Aalst	± 150	No	PLE
1942361-09	Sediment	Haven van Brussel	± 600	Yes	PLE
1942361-10	Sediment	Unknown	± 300	Yes	PLE
1942361-11	Sediment	Unknown	± 300	No	Soxhlet
1942361-12	Soil	Unknown	± 1400	No	Soxhlet

Table 13: Samples with biogenic interferences

- 6 soil and sludge samples likely to contain mixed contamination (biogenic individual interferences on a KWS hump) of variable concentration:

Sample	*Matrix*	*Origin*	*Range mineral oil C_{10}-C_{40} (mg/kg DM)*	*Pre-drying*	*Extraction*
1942361-13	Soil	Unknown	± 350	No	PLE
1942361-14	Soil	Unknown	± 350	No	soxhlet
1942361-15	Soil	Unknown	± 250	No	PLE
1942361-16	Sediment	Unknown	± 300	Yes	PLE
1942361-17	Sediment	Unknown	± 1400	Yes	PLE
1942361-18	Soil	Vichte	± 600	Yes	PLE

Table 14: Samples with mixed contamination

8.2 VALIDATION PLAN

All 18 samples are extracted in duplicate (analysis A and B). Each extract is finished according to the standard procedure (= CMA/3/R.1) and the new procedure with the additional clean-up (CU), to remove the biogenic interferences:

Sample	**Standard procedure (= CMA/3/R.1)**		**New procedure**	
1942361-01	1942361-01 A	1942361-01 B	1942361-01 A CU	1942361-01 B CU
1942361-02	1942361-02 A	1942361-02 B	1942361-02 A CU	1942361-02 B CU
1942361-03	1942361-03 A	1942361-03 B	1942361-03 A CU	1942361-03 B CU
1942361-04	1942361-04 A	1942361-04 B	1942361-04 A CU	1942361-04 B CU
1942361-05	1942361-05 A	1942361-05 B	1942361-05 A CU	1942361-05 B CU
1942361-06	1942361-06 A	1942361-06 B	1942361-06 A CU	1942361-06 B CU
1942361-07	1942361-07 A	1942361-07 B	1942361-07 A CU	1942361-07 B CU
1942361-08	1942361-08 A	1942361-08 B	1942361-08 A CU	1942361-08 B CU
1942361-09	1942361-09 A	1942361-09 B	1942361-09 A CU	1942361-09 B CU
1942361-10	1942361-10 A	1942361-10 B	1942361-10 A CU	1942361-10 B CU

1942361-11	1942361-11 A	1942361-11 B	1942361-11 A CU	1942361-11 B CU
1942361-12	1942361-12 A	1942361-12 B	1942361-12 A CU	1942361-12 B CU
1942361-13	1942361-13 A	1942361-13 B	1942361-13 A CU	1942361-13 B CU
1942361-14	1942361-14 A	1942361-14 B	1942361-14 A CU	1942361-14 B CU
1942361-15	1942361-15 A	1942361-15 B	1942361-15 A CU	1942361-15 B CU
1942361-16	1942361-16 A	1942361-16 B	1942361-16 A CU	1942361-16 B CU
1942361-17	1942361-17 A	1942361-17 B	1942361-17 A CU	1942361-17 B CU
1942361-18	1942361-18 A	1942361-18 B	1942361-18 A CU	1942361-18 B CU

Table 15: Validation plan

8.3 COMPARATIVE EXAMINATION BETWEEN EXISTING PROCEDURE AND NEW PROCEDURE WITH CLEAN-UP

The 18 samples are extracted in duplicate. The extracts are finished using the standard and the new procedure. The mineral oil content is always measured via GC/FID. The results of the mineral oil content are shown in the tables below:

Petrogenic contamination (gasoline)			
Sample	**Standard procedure (CMA/3/R.1)**	**New procedure**	**% recovery new procedure compared to standard procedure**
	mineral oil C_{10}-C_{40}	***mineral oil C_{10}-C_{40}***	
	mg/kg DM	**mg/kg DM**	
1942361-01	893	800	90%
1942361-01 duplo	986	865	88%
1942361-02	713	659	92%
1942361-02 duplo	764	712	93%
1942361-03	3220	2900	90%
1942361-03 duplo	3480	3020	87%
1942361-04	1440	1310	91%
1942361-04 duplo	1190	1140	96%
1942361-05	1450	1330	92%
1942361-05 duplo	1240	1120	90%
1942361-06	490	457	93%
1942361-06 duplo	522	481	92%

Table 16: % recovery of the new procedure compared to the standard procedure for petrogenic impurities

For petrogenic contaminants, the % recovery of the new procedure (after clean-up) compared to the standard procedure is plotted in the following graph:

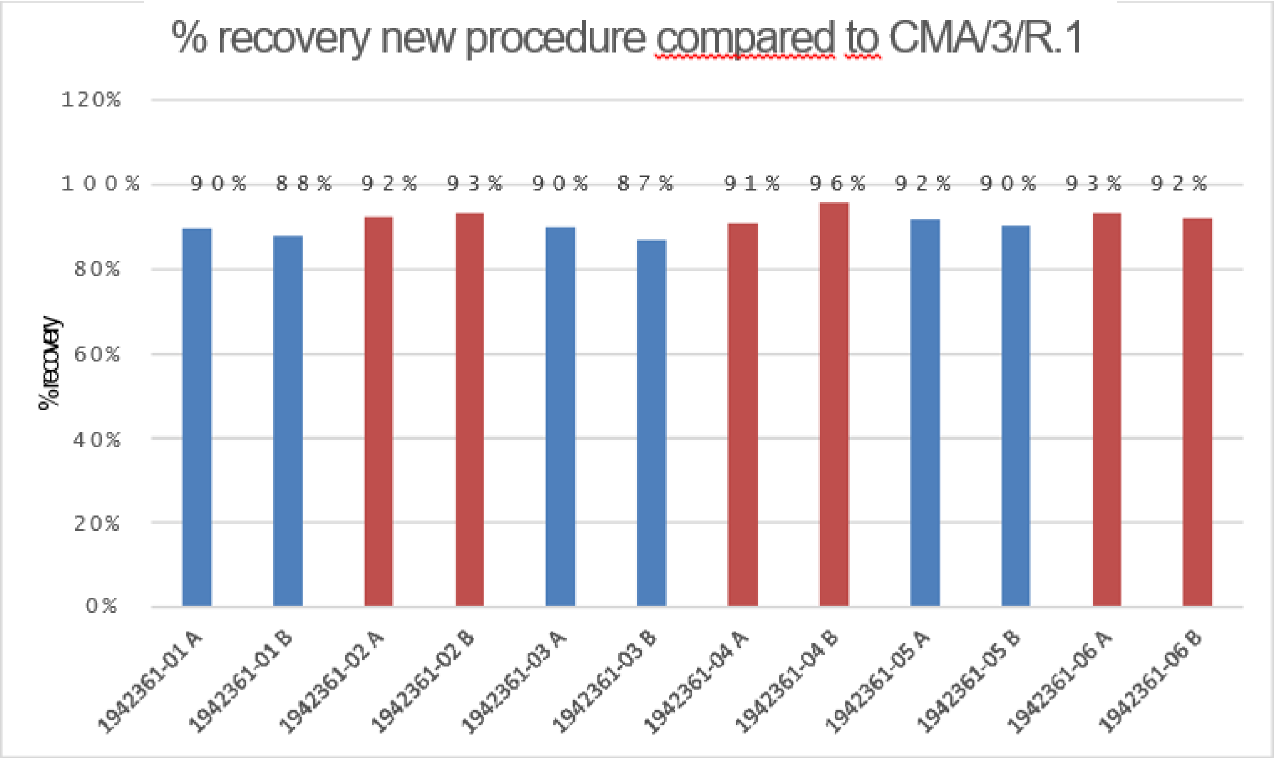

Figure 2: % recovery of the new procedure compared to the standard procedure for petrogenic impurities

Biogenic contamination			
Sample	**Standard procedure (CMA/3/R.1)** ***mineral oil C_{10}-C_{40}*** **mg/kg DM**	**New procedure** ***mineral oil C_{10}-C_{40}*** **mg/kg DM**	**% recovery new procedure compared to standard procedure**
1942361-07	284	45	16%
1942361-07 duplo	295	46	16%
1942361-08	131	<40	/
1942361-08 duplo	183	49	27%
1942361-09	621	96	15%
1942361-09 duplo	572	96	17%
1942361-10	220	86	39%
1942361-10 duplo	395	123	31%
1942361-11	290	96	33%
1942361-11 duplo	317	95	30%

1942361-12[1]	1740	194	11%
1942361-12 duplo	1090	210	19%

Table 17: % recovery of the new procedure compared to the standard procedure for biogenic impurities

For biogenic contaminants, the % recovery of the new procedure (after clean-up) compared to the standard procedure is plotted in the following graph:

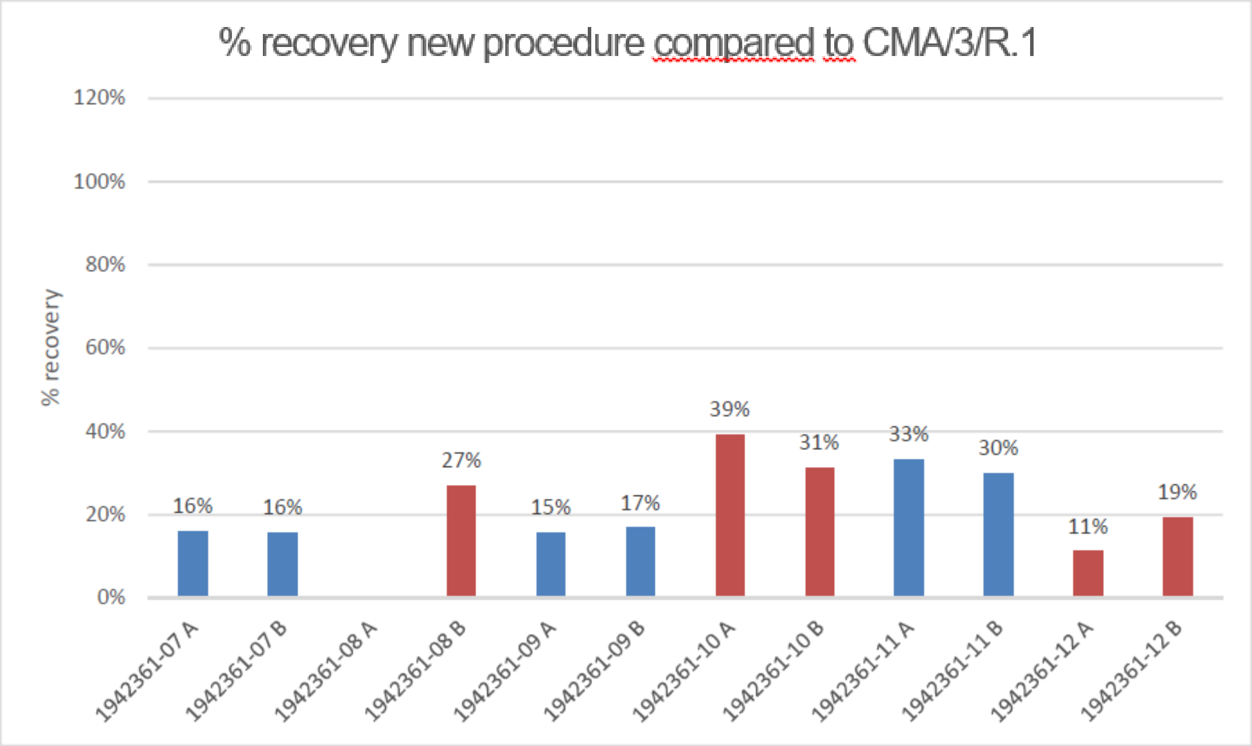

Figure 3: % recovery of the new procedure compared to the standard procedure for biogenic impurities

Mixed contamination **(biogenic individual interferences on a TPH-hump)**			
Sample	**Standard procedure (CMA/3/R.1)**	**New procedure**	**% recovery new procedure compared to standard procedure**
	mineral oil C_{10}-C_{40}	***mineral oil C_{10}-C_{40}***	
	mg/kg DM	**mg/kg DM**	
1942361-13	347	186	54%

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[1] Het chromatogram geeft de indruk dat de fractie minerale olie grotendeels biogeen is en dit wordt bevestigd door clean-up. Dit bodemmonster is geen standaardbodem maar heeft een % organische stof van 70%.

1942361-13 duplo	358	187	52%
1942361-14	342	120	35%
1942361-14 duplo	321	131	41%
1942361-15	244	136	56%
1942361-15 duplo	255	155	61%
1942361-16	304	142	47%
1942361-16 duplo	293	141	48%
1942361-17[2]	1350	950	70%
1942361-17 duplo	1440	1010	70%
1942361-18	625	401	64%
1942361-18 duplo	591	364	62%

Table 18: % recovery of the new procedure compared to the standard procedure for mixed impurities

For mixed impurities (biogenic individual interferences on a KWS hump), the % recovery of the new procedure (after clean-up) compared to the standard procedure is plotted in the following graph:

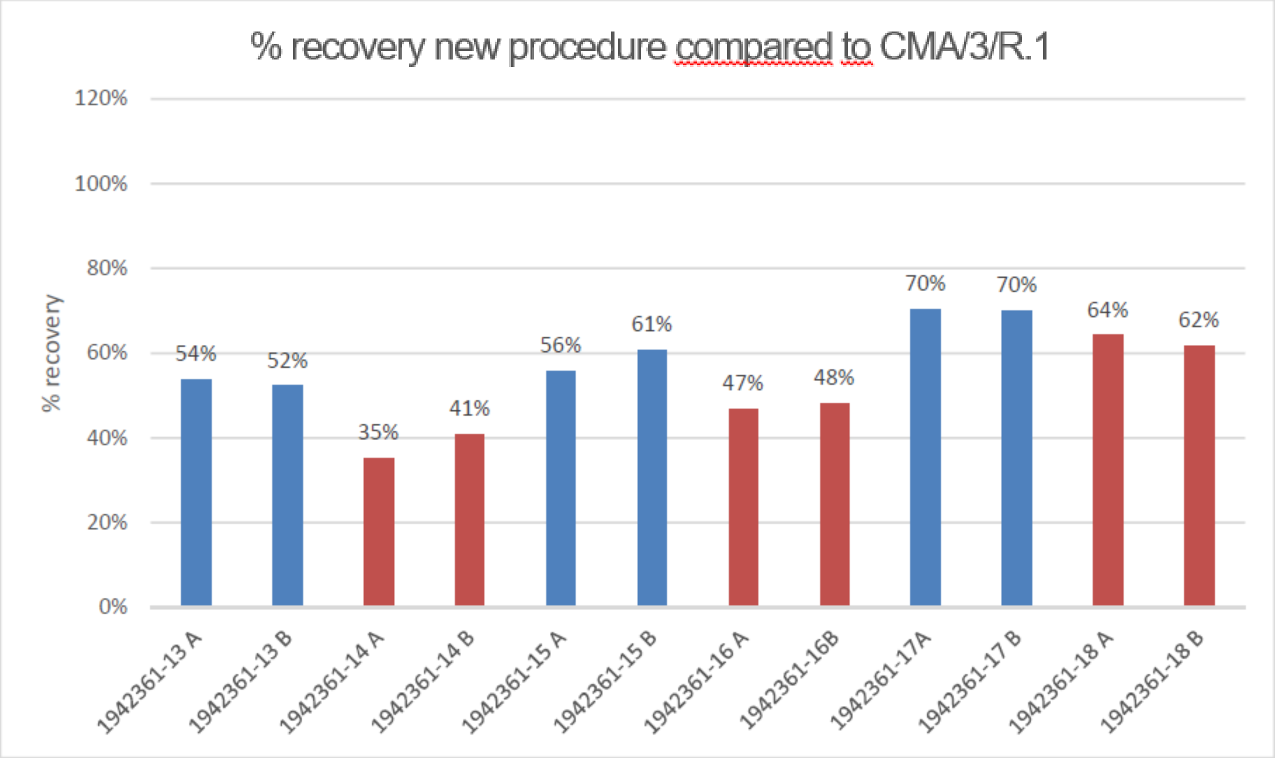

Figure 4: % recovery of the new procedure compared to the standard procedure for mixed impurities

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[2] This soil sample was included to show that the method can also be used at slightly higher concentrations. In practice, clean-up for this soil sample will only be useful if values petrogenic mineral oil are below 1000 mg/kg ds (standard building material).

An overlay of the chromatograms of the current procedure and the new procedure is added for the 18 samples in Annex 2.

From the chromatograms and the above results, we can conclude the following:

- The mean % recovery of the new procedure compared to the standard procedure (CMA/3/R.1) is 91%[3] for the samples with a petrogenic impurity (heating oil);
- Samples consisting mainly of biogenic individual peaks are reduced by at least 60% after application of the new clean-up;
- In the samples with the mixed impurity, which consist of biogenic individual peaks located on a QWS hump, the biogenic individual peaks are removed by the clean-up, the underlying PAH hump remains present.

8.4 DETERMINATION OF THE STATISTICAL KEY FIGURES

3x 6 different samples are analysed in duplicate under repeatability conditions. The samples are finished according to the new procedure. The results of the mineral oil content are shown in the tables below:

Petrogenic contamination (gasoline)			
Sample	**New procedure**	**New procedure (duplicate)**	**% deviation of the duplicate samples**
	mineral oil C_{10}-C_{40}	***mineral oil C_{10}-C_{40}***	
	mg/kg DM	**mg/kg DM**	
1942361-01 CU	800	865	-8%
1942361-02 CU	659	712	-8%
1942361-03 CU	2900	3020	-4%
1942361-04 CU	1310	1140	14%
1942361-05 CU	1330	1120	17%
1942361-06 CU	457	481	-5%

Table 19: Results of repeatability s for petrogenic contaminants

Biogenic contamination			
Sample	**New procedure**	**New procedure (duplicate)**	**% deviation of the duplicate samples**
	mineral oil C_{10}-C_{40}	***mineral oil C_{10}-C_{40}***	
	mg/kg DM	**mg/kg DM**	
1942361-07 CU	45	46	-2%
1942361-08 CU	<40	49	/
1942361-09 CU	96	96	0%
1942361-10 CU *	86	123	-35%

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[3] During reprocessing, a loss of approx. 9 % petrogenic mineral oil is observed . This could be the result of a loss of more volatile components at the evaporation step. , An almost similar loss is observed in the different sediment samples with petrogenic contamination. It is suspected that the lower recovery is not so much the result of a loss during the evaporation step (because then more dispersion of the results would have to be observed) but is perhaps inherent to the procedure itself. During previous validation of pure reference samples, this was not encountered. The former is not a problem if this method or purification is used in addition to an analysis according to the current CMA/3/R.1.

There may also be some loss of petrogenic mineral oil if it concerns obsolete contaminants where degradation has occurred. The more polar compounds formed during degradation may be lost during clean-up together with the biogenic mineral oil. In that case, the original chromatogram will not resemble that of a sample containing biogenic mineral oil, so this can be recognized and overcome during screening.

1942361-11 CU	96	95	1%
1942361-12 CU	194	210	-8%

Table 20: Results of repeatability for biogenic contaminants

* * the larger % deviation of the duplicate samples is most likely due to insufficient homogenity of the sample. Duplicate values showing large differences were also obtained with the standard method (value included in the statistical processing).

Mixed contamination (biogenic individual interferences on a TPH-hump)			
Sample	**New procedure**	**New procedure (duplicate)**	**% deviation of the duplicate samples**
	mineral oil C_{10}-C_{40}	***mineral oil C_{10}-C_{40}***	
	mg/kg DM	**mg/kg DM**	
1942361-13 CU	186	187	-1%
1942361-14 CU	120	131	-9%
1942361-15 CU	136	155	-14%
1942361-16 CU	142	141	1%
1942361-17 CU	950	1010	-6%
1942361-18 CU	401	364	10%

Table 21: Results of repeatability for mixed impurities

8.4.1 Reproducibility

$$CVr = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{x_{i1} - x_{i2}}{0.5(x_{i1} + x_{i2})}\right)^2}{2n}} * 100\%$$

CV = variation coefficient, in %
n = number of samples analysed double
xi1 = first analysis result of a double analysis for sample i
xi2 = second analysis result of a double analysis for sample i

The CV must be less than 15 %.

MO C_{10}- C_{40}	**Reproducibility coefficient CVr %**
Petrogenic contamination	7.4%
Biogenic contamination	11.5%

Mixed contamination	5.7%

Table 22: Reproducibility coefficient

Conclusion:
The proposed CVr of 15% is achieved

9 GENERAL CONCLUSION

The Flemish method for determining mineral oil as a pollutant in sediment (CMA/3/R.1) is not capable of removing all biogenic interference. By means of an extra clean-up over a florisil cartridge, these biogenic interferences can be removed without significant loss of the petrogenic fraction. The study shows that for samples contaminated with a petrogenic fraction such as heating oil, the loss is less than 10%.

Samples with a mainly biogenic contamination give a reduction of at least 60% by applying the clean-up. After validation, the new procedure appears to comply with the intended use and the proposed requirement for the repeatability variation coefficient.

The procedure seems suitable for the analysis of sediment (soil) samples with (slightly) elevated levels of mineral oil (cf. CMA/3/R.1) from places where contamination with mineral oil of petrogenic origin is very unlikely. By applying the proposed clean-up method, it can be proved that the mineral oil is of biogenic origin.

ANNEX 1 : OVERLAY OF THE CHROMATOGRAMS - CURRENT AND NEW PROCEDURE

Overlay of the chromatograms of the current procedure and the new procedure:

- New procedure with clean-up
- Existing procedure

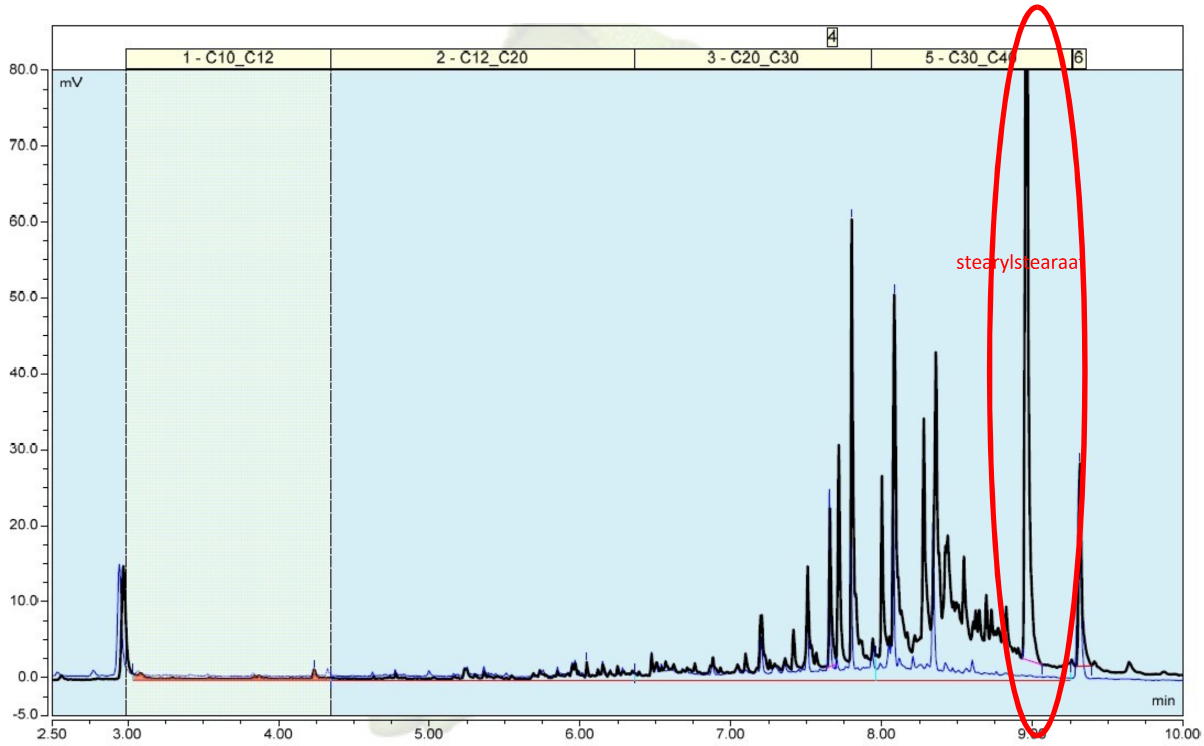

Figure 5: Sample-01:

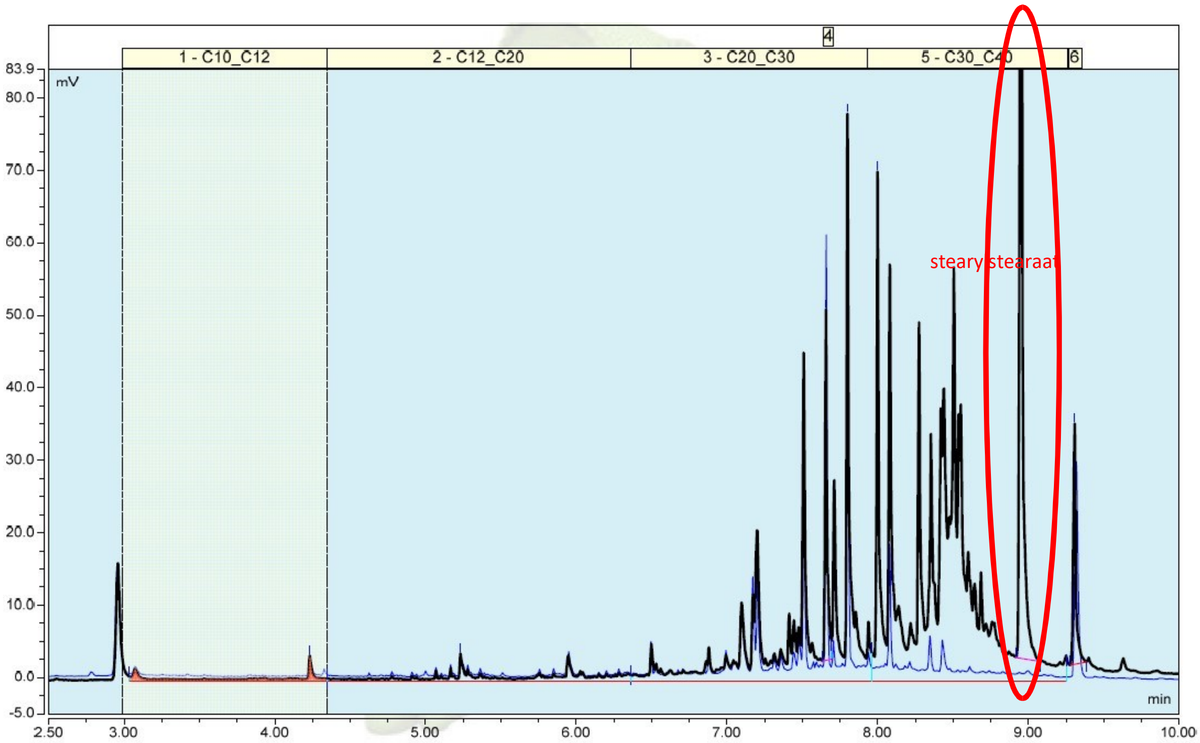

Figure 6: Sample-02

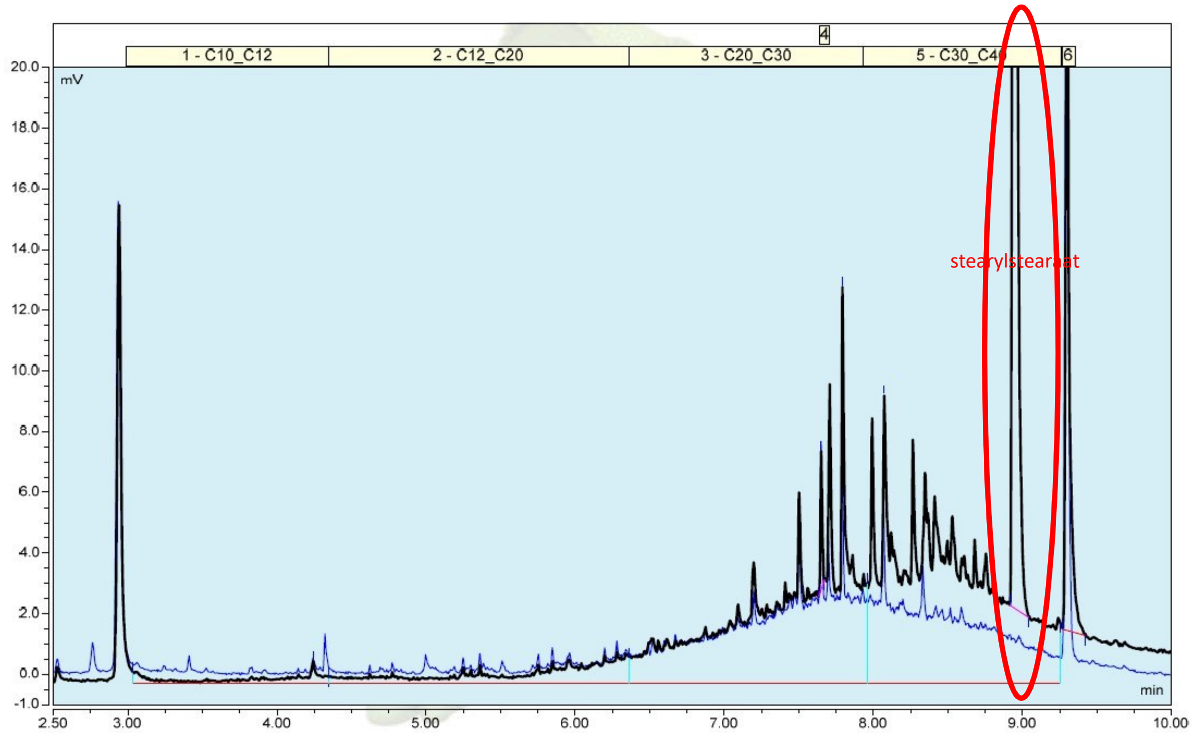

Figure 7: Sample-03

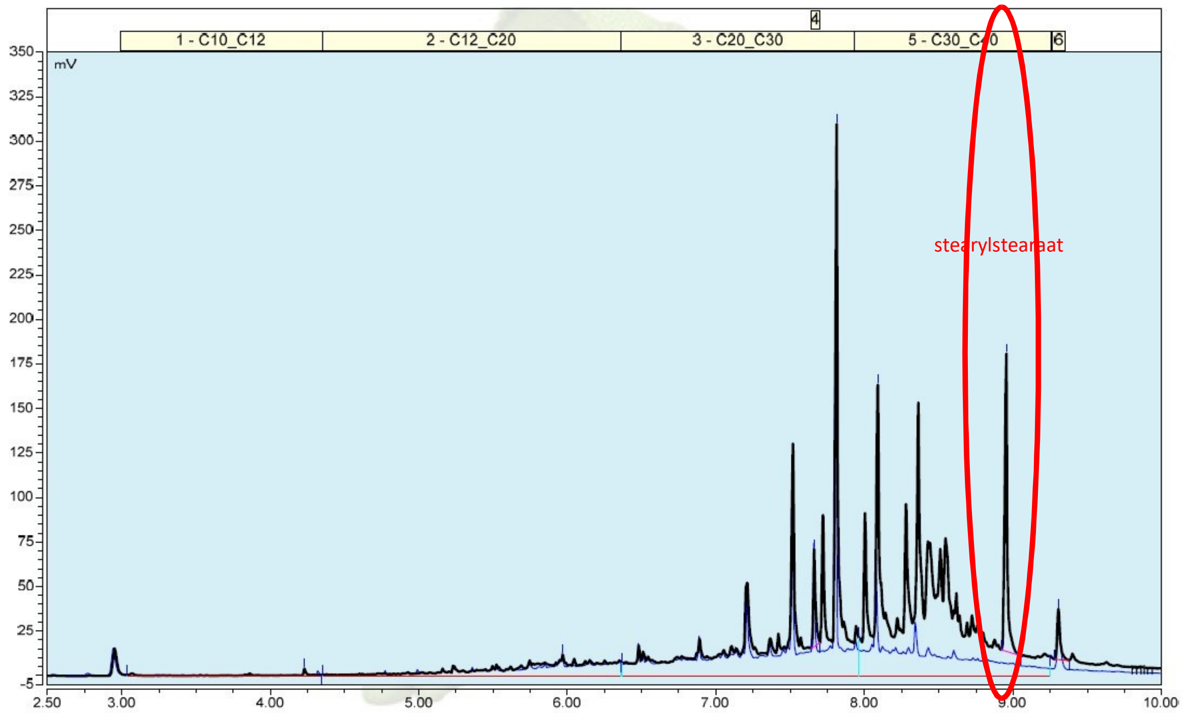

Figure 8: Sample-04

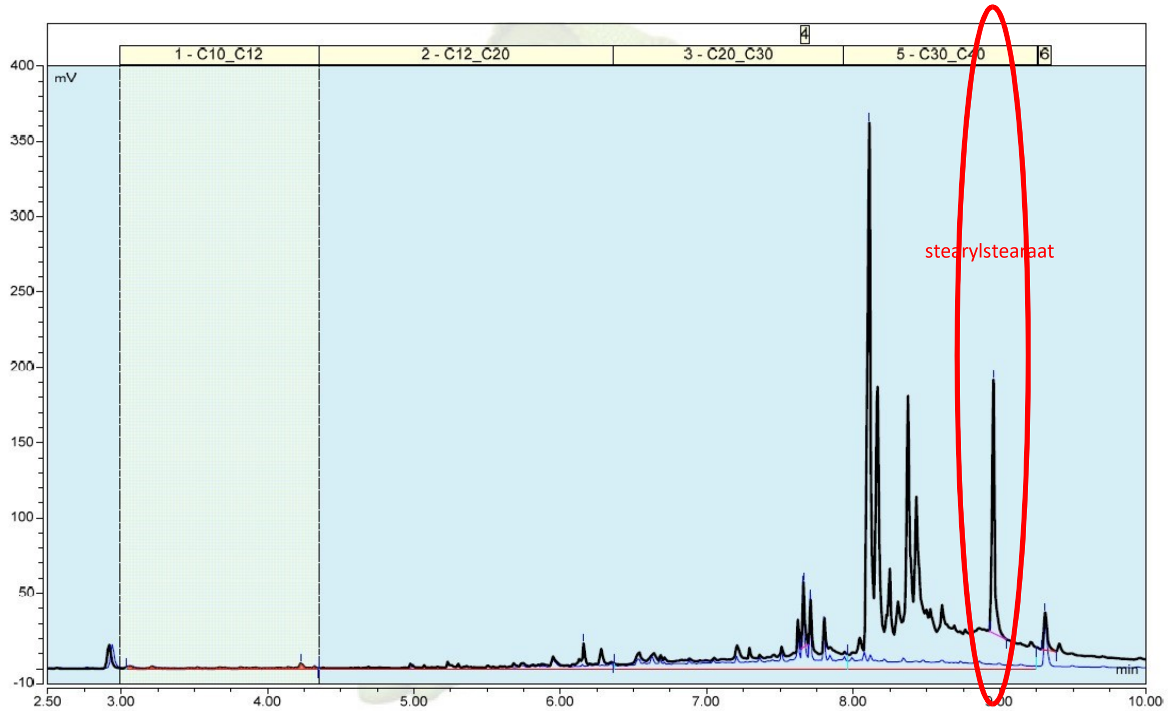

Figure 9: Sample-05

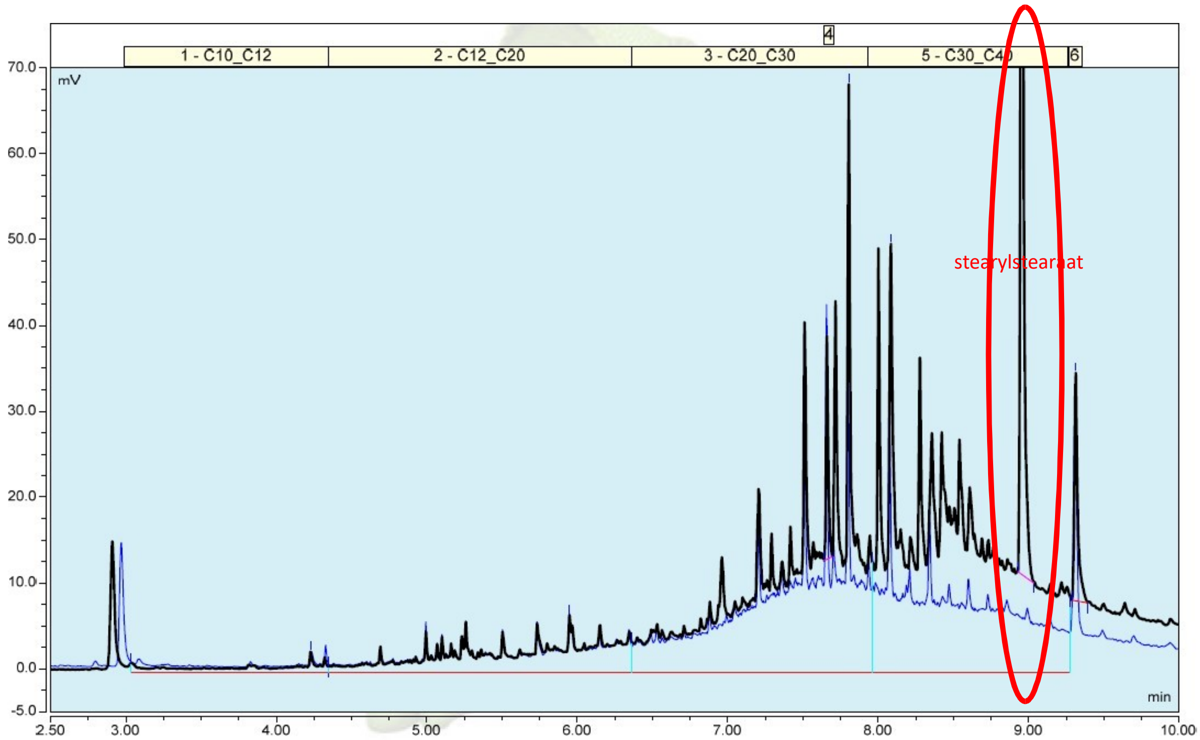

Figure 10: Sample-06

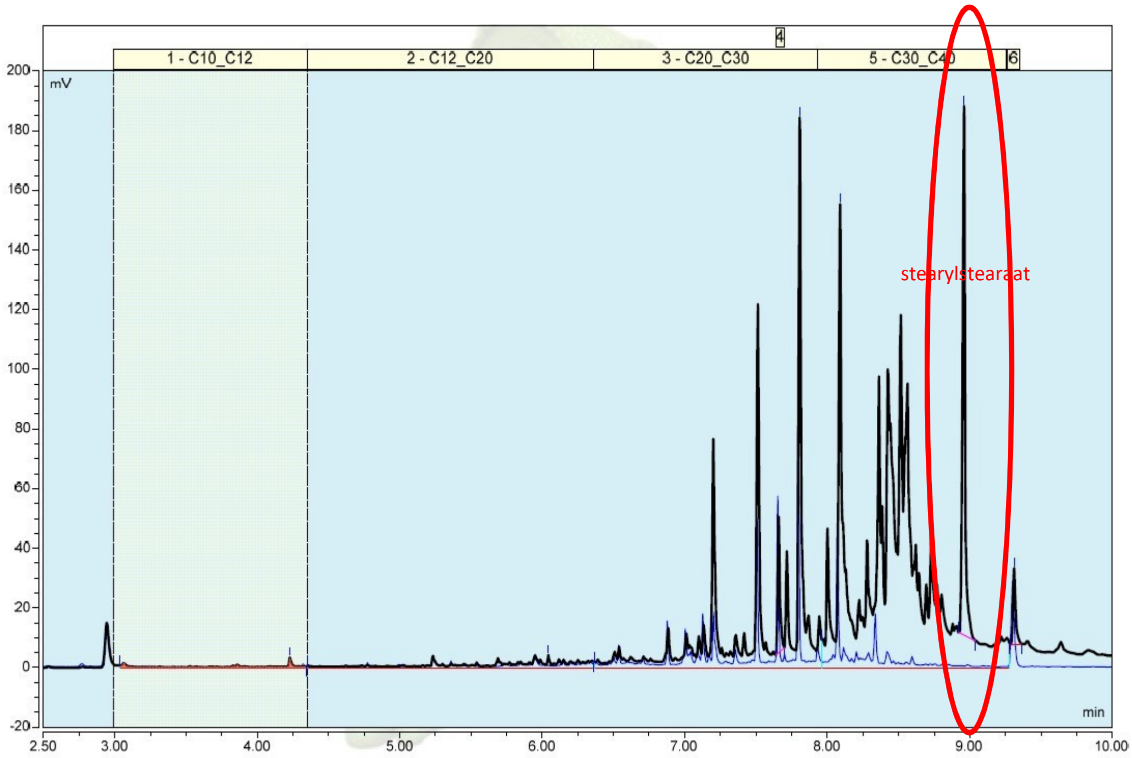

Figure 11: Sample-07

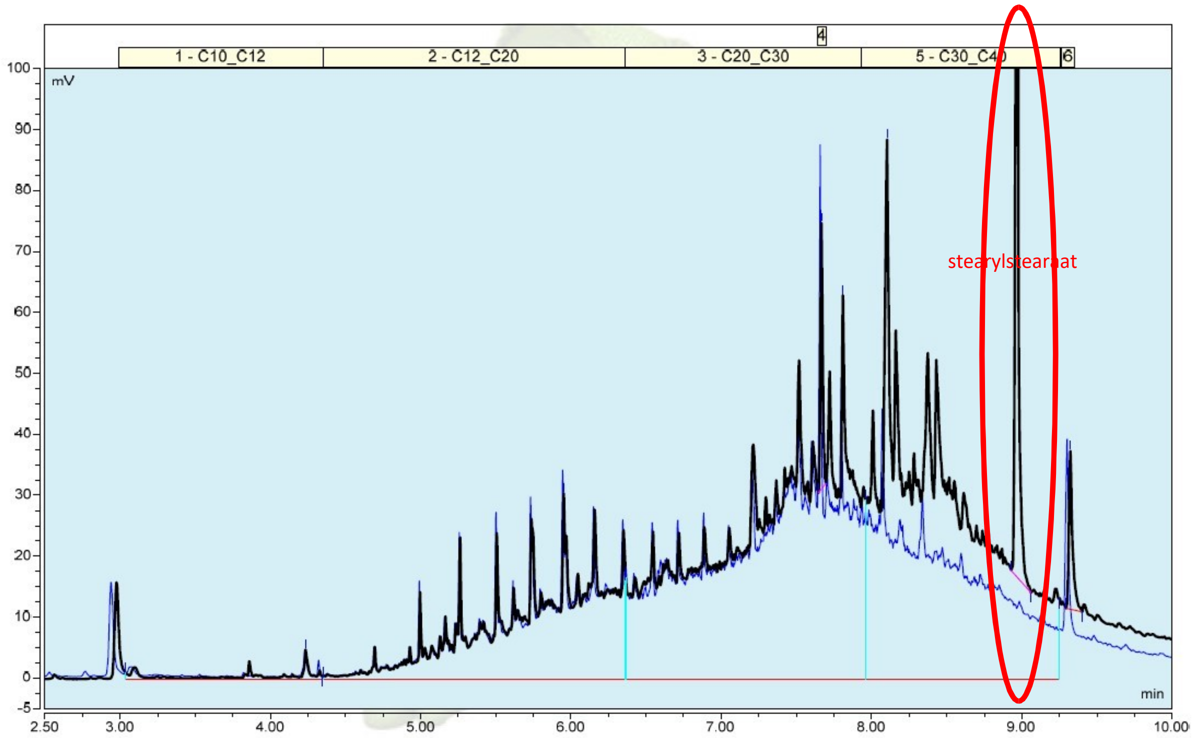

Figure 12: Sample-08

ANNEX 2.1: OVERLAY OF CHROMATOGRAMS - PETROGENIC CONTAMINATION

Overlay of the chromatograms of the current procedure and the new procedure

- New procedure with clean-up
- Existing procedure

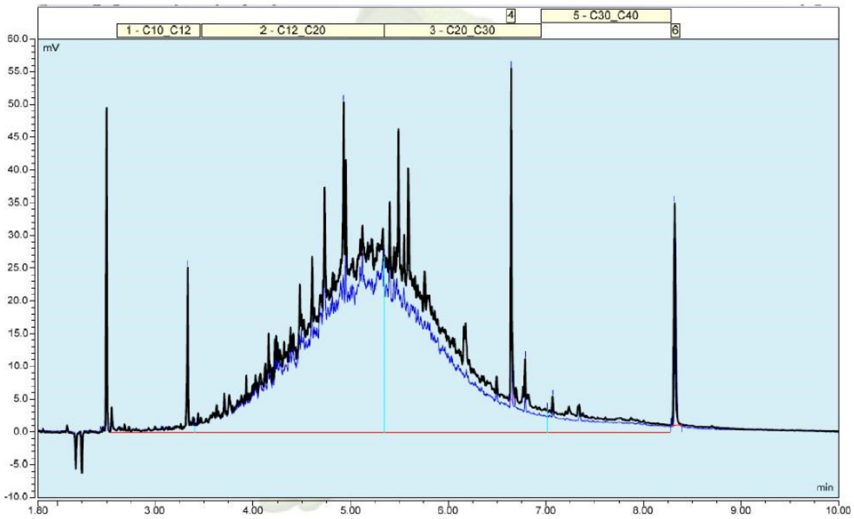

Figure 13: Sample -1942361-01

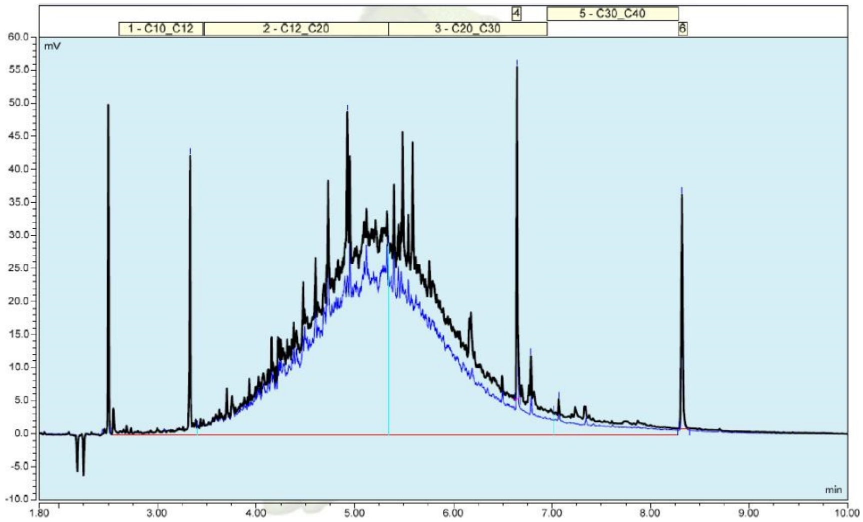

Figure 14: Sample -1942361-01-double

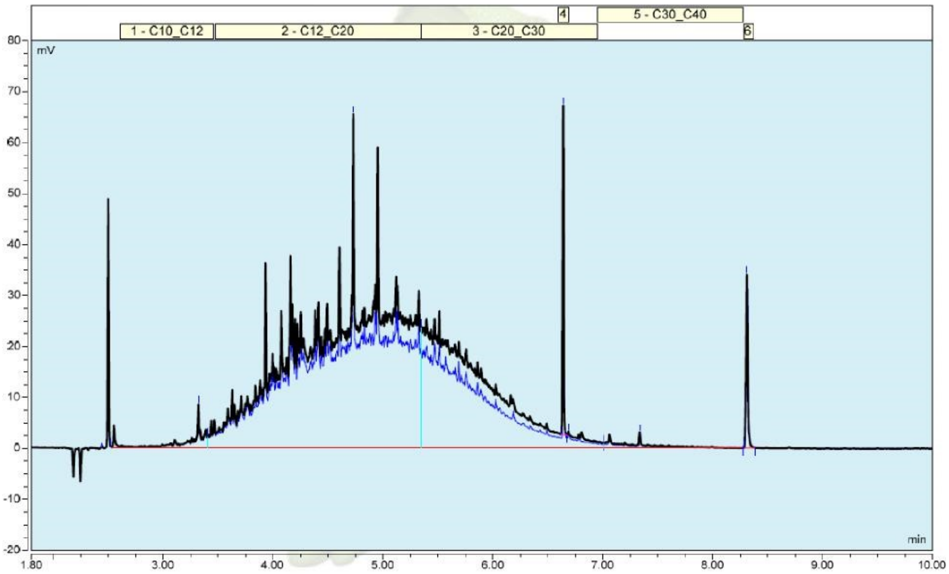

Figure 15: Sample -1942361-02

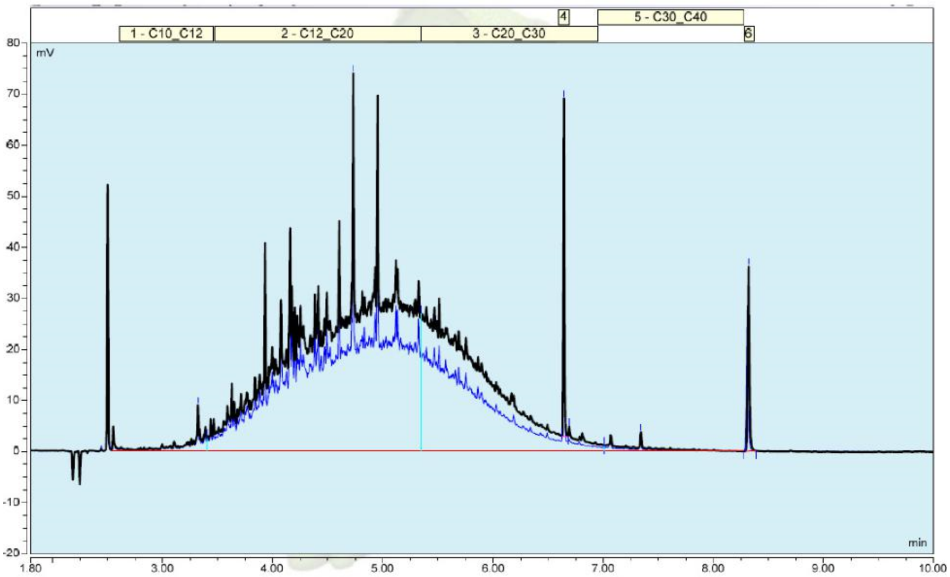

Figure 16: Sample -1942361-02-double

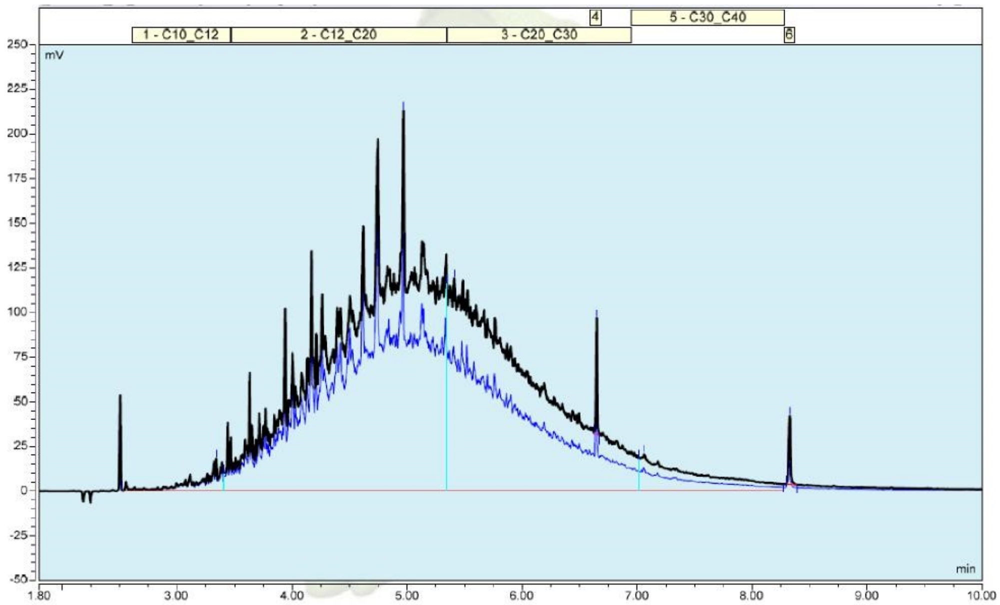

Figure 17: Sample -1942361-03

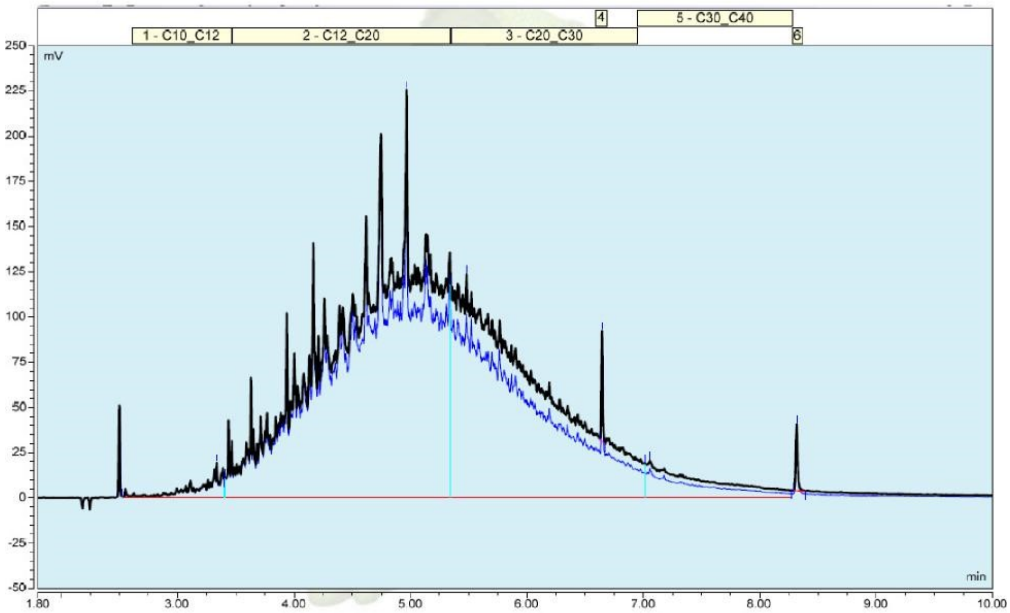

Figure 18: Sample -1942361-03-double

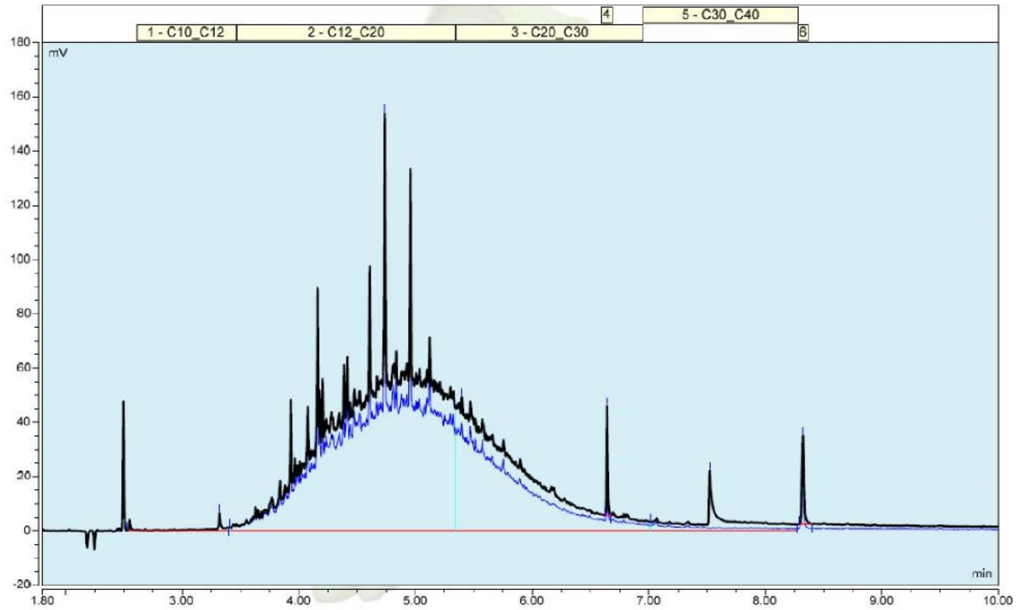

Figure 19: Sample -1942361-04

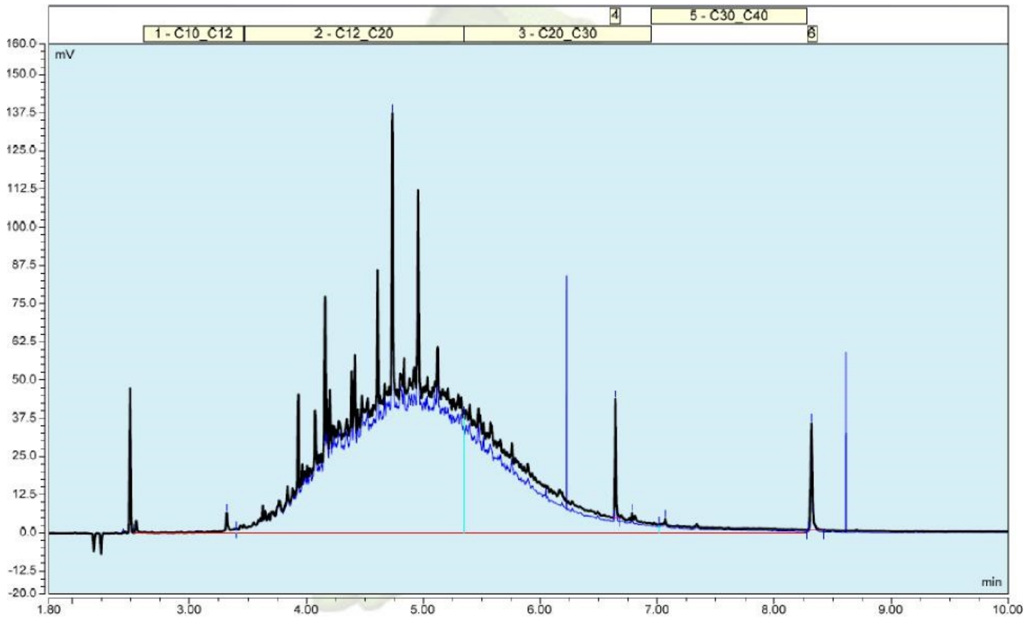

Figure 20: Sample -1942361-04-double

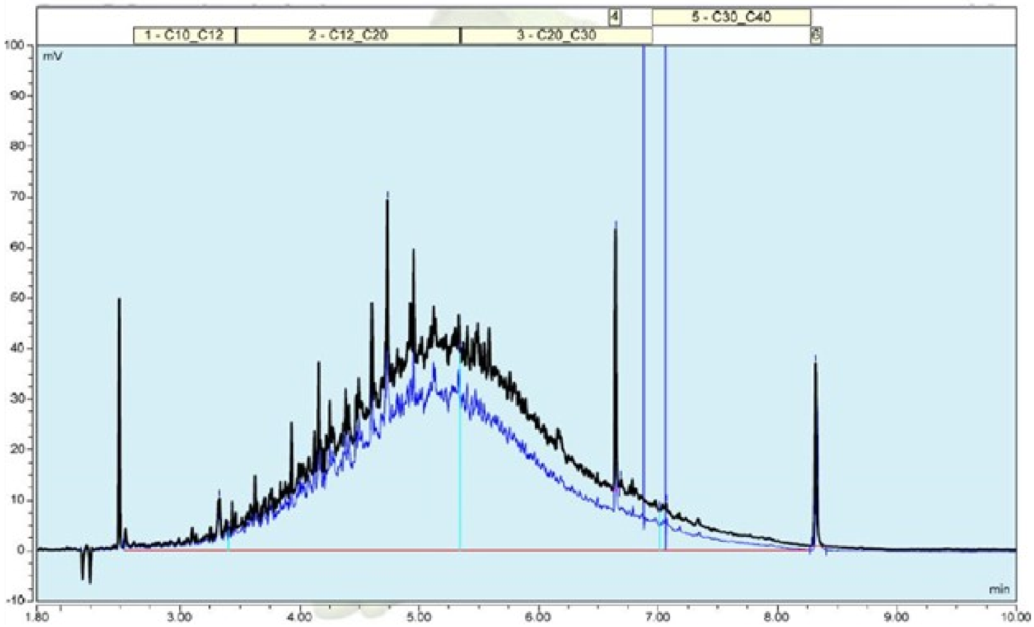

Figure 21: Sample -1942361-05

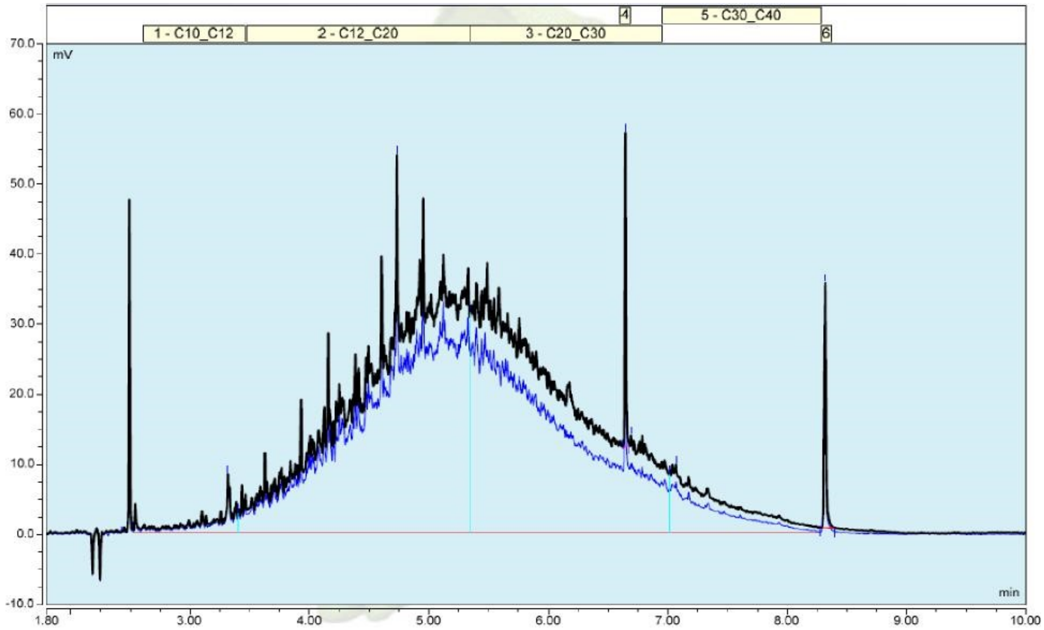

Figure 22: Sample - 1942361-05-double

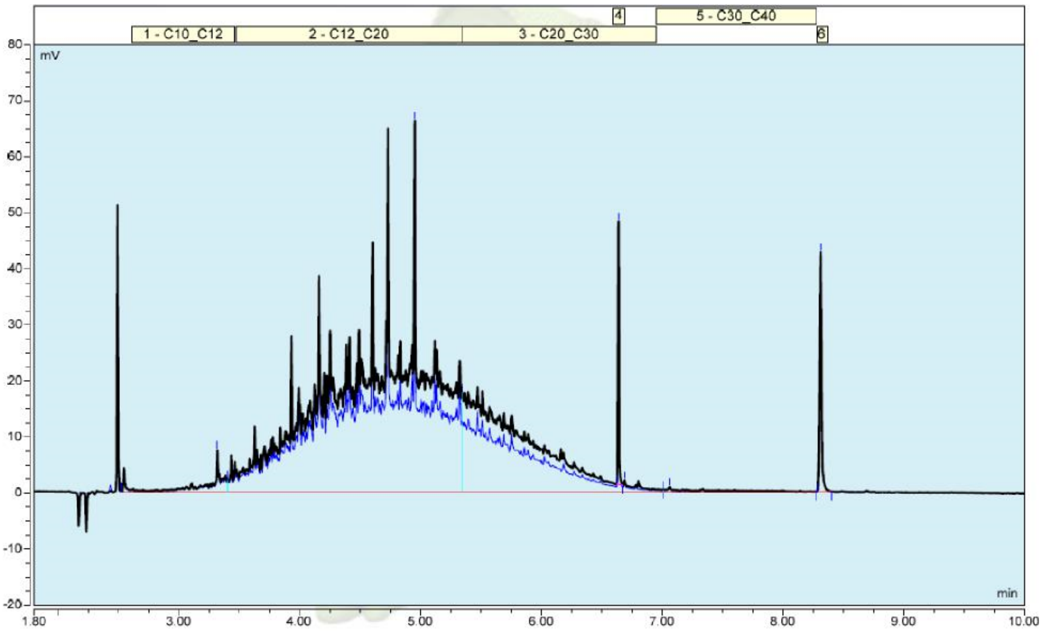

Figure 23: Sample -1942361-06

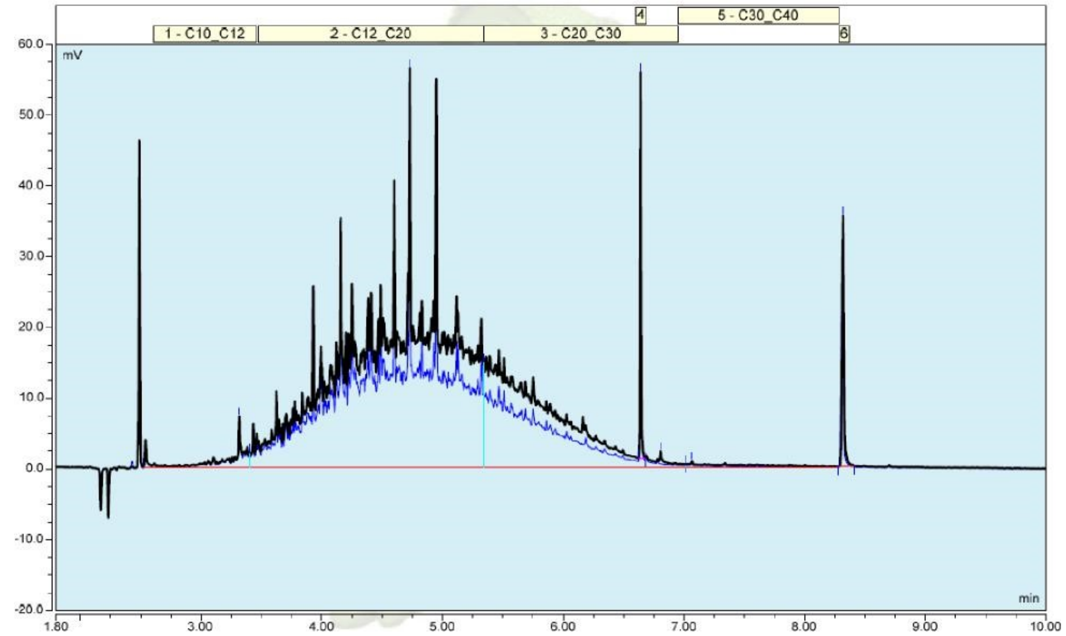

Figure 24: Sample -1942361-06-double

ANNEX 2.2: OVERLAY OF CHROMATOGRAMS – BIOGENIC CONTAMINATION

Overlay of the chromatograms of the current procedure and the new procedure:

- New procedure with clean-up
- Existing procedure

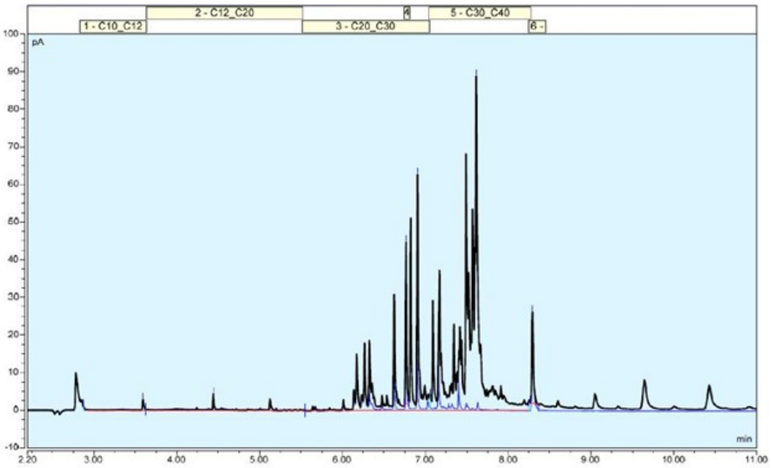

Figure 24: Sample -1942361-07

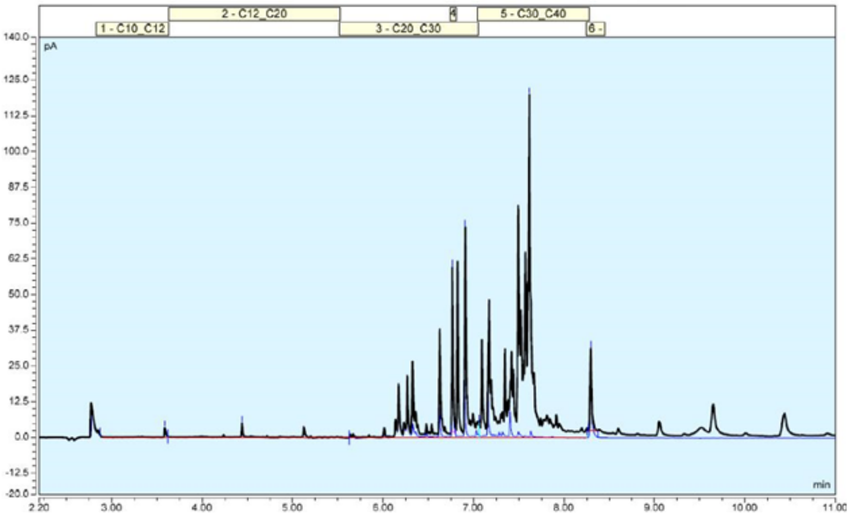

Figure 26: Sample -1942361-07-double

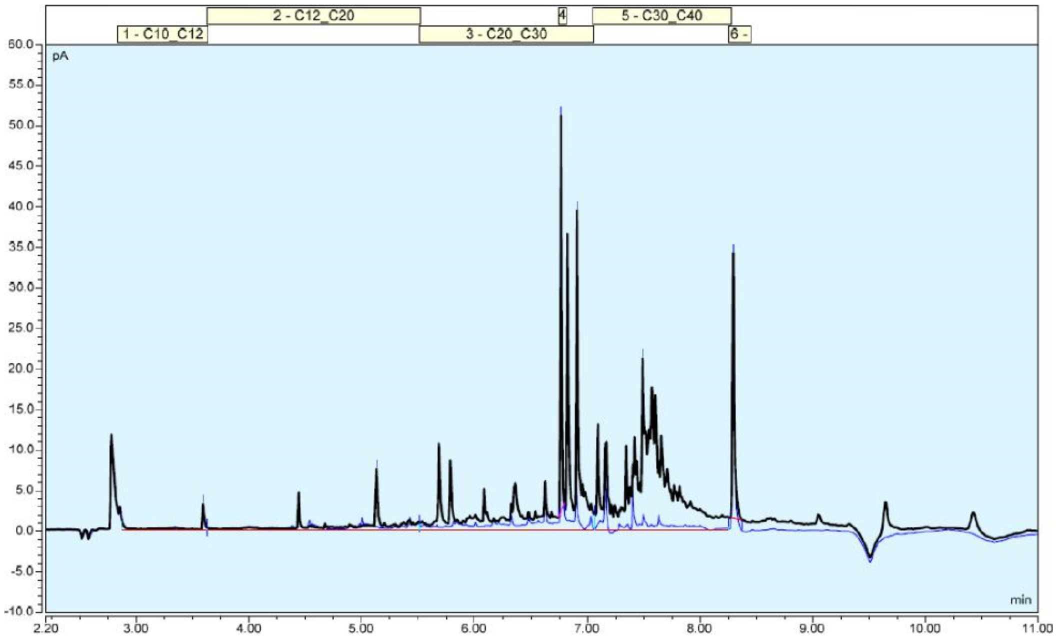

Figure 27: Sample -1942361-08

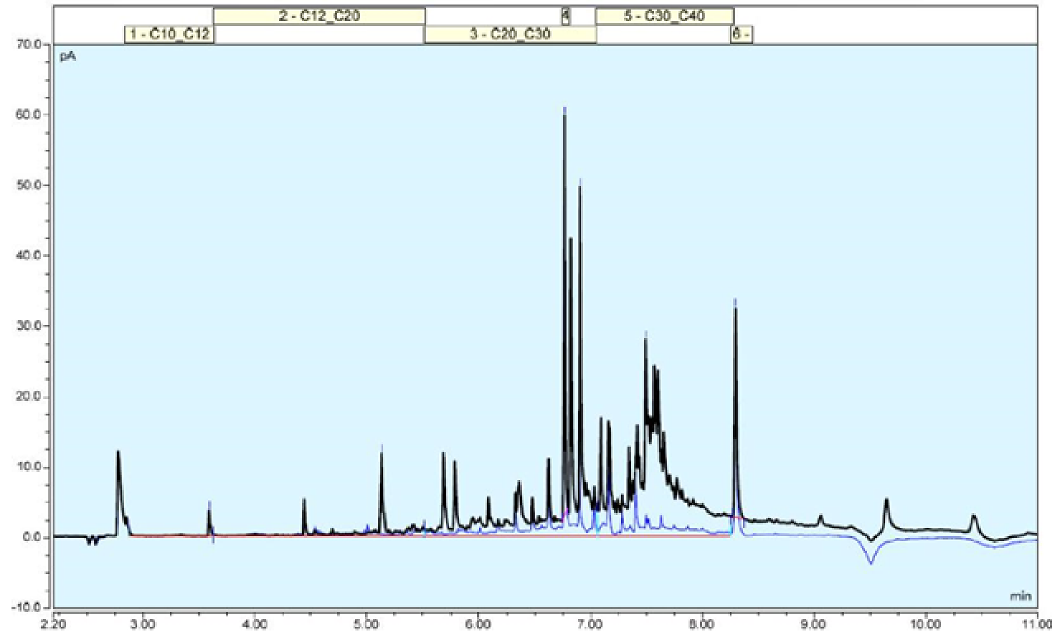

Figure 28: Sample -1942361-08-double

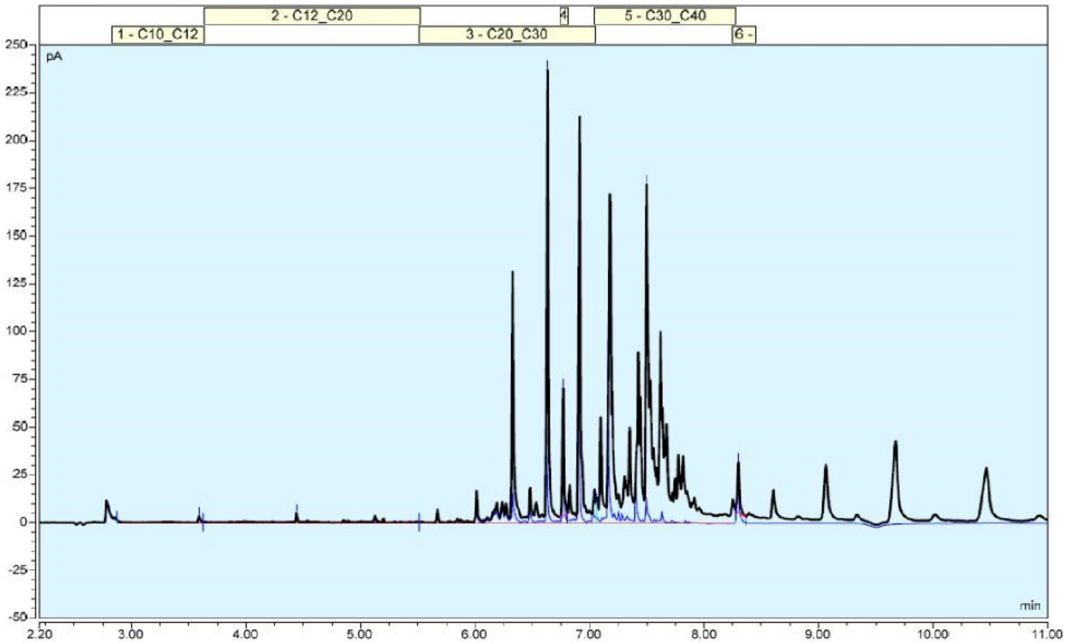

Figure 29: Sample -1942361-09

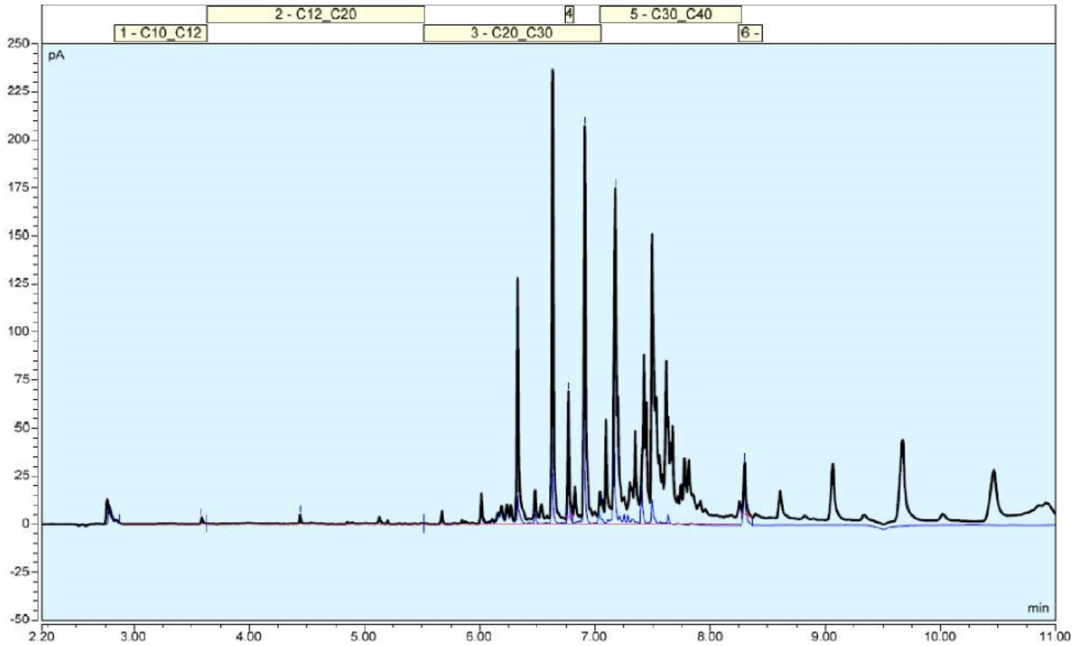

Figure 30: Sample -1942361-09-double

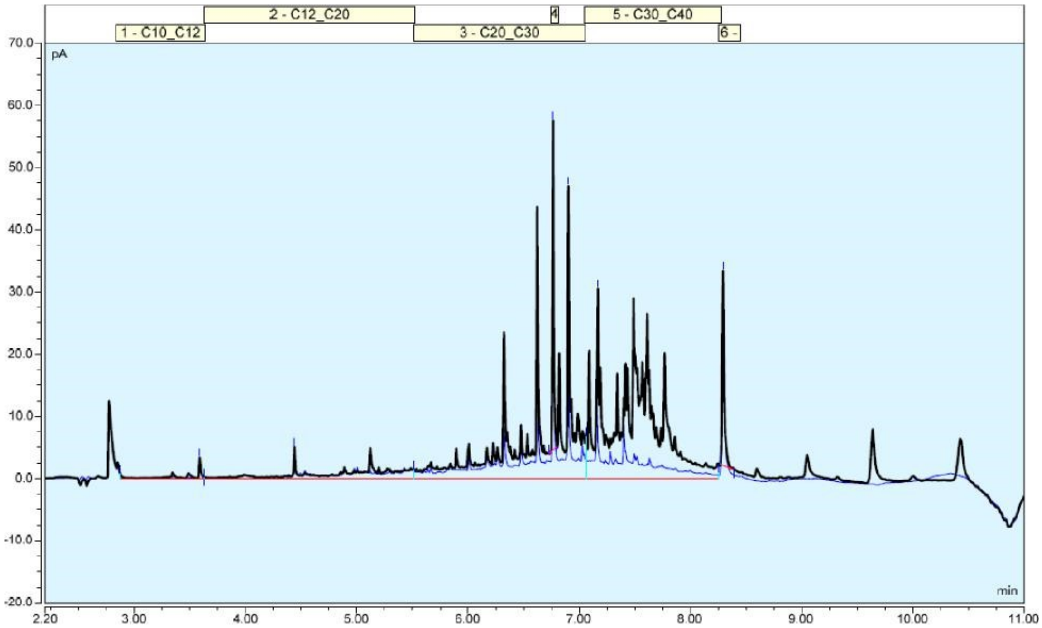

Figure 31: Sample -1942361-10

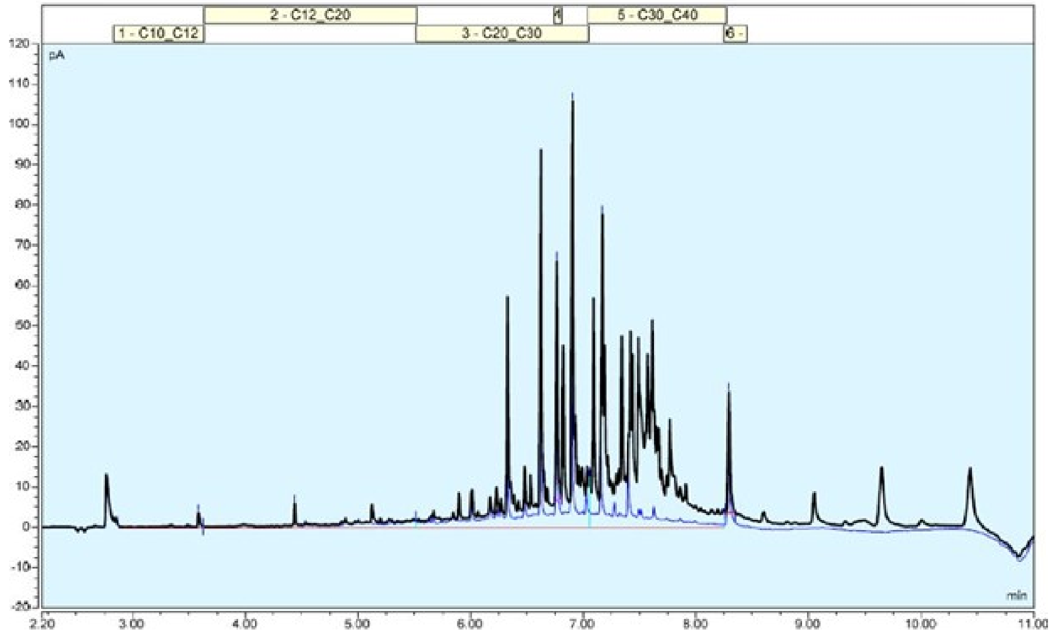

Figure 32: Sample -1942361-10-double

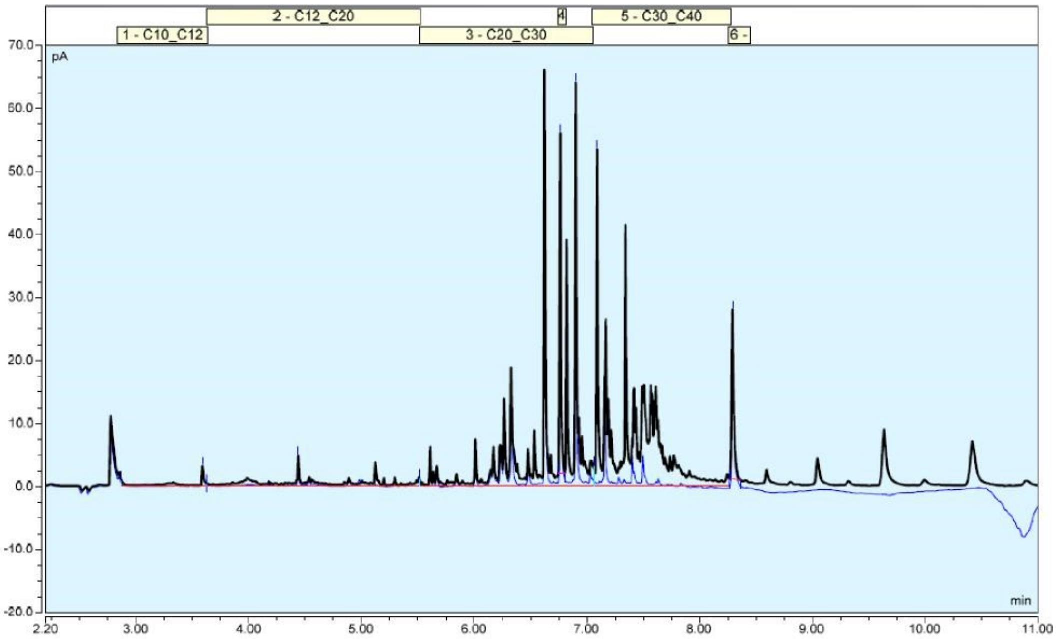

Figure 33: Sample -1942361-11

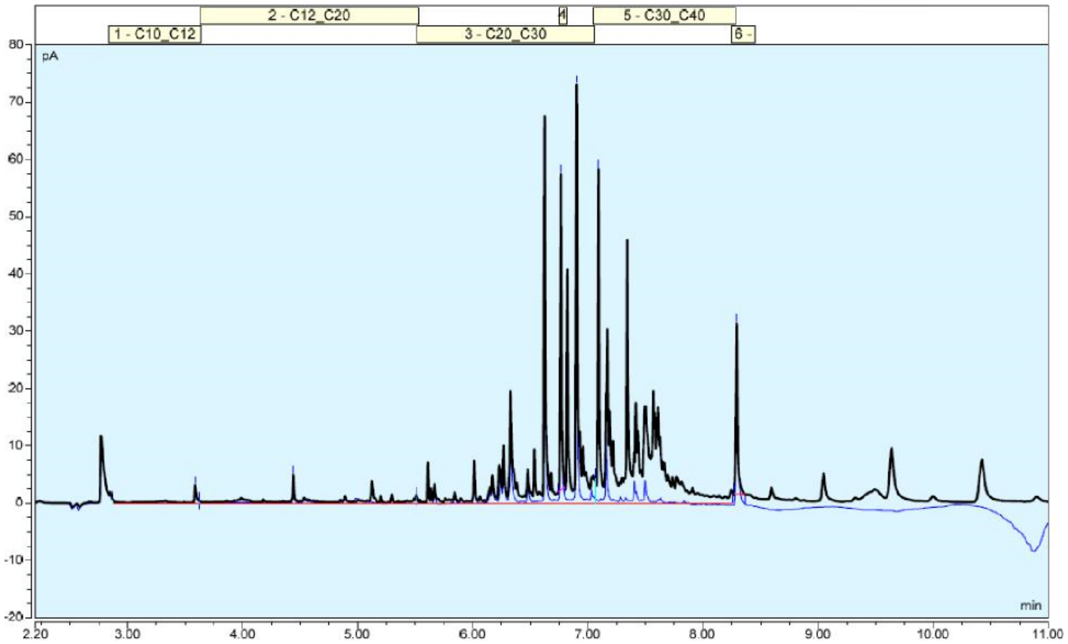

Figure 34: ample -1942361-11-double

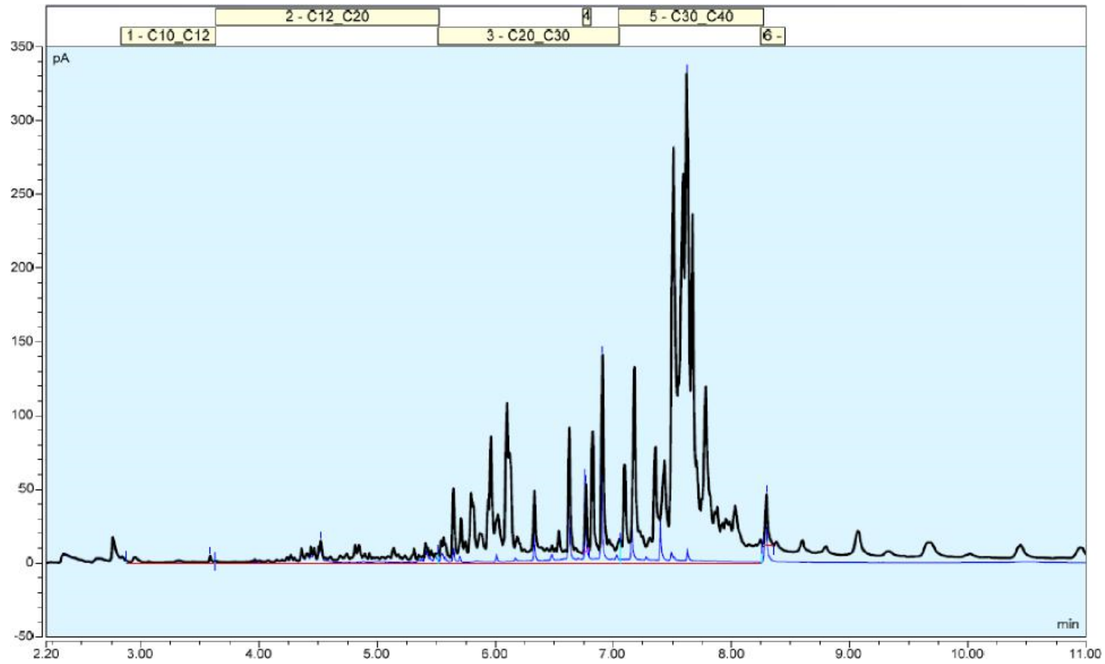

Figure 35: Sample -1942361-12

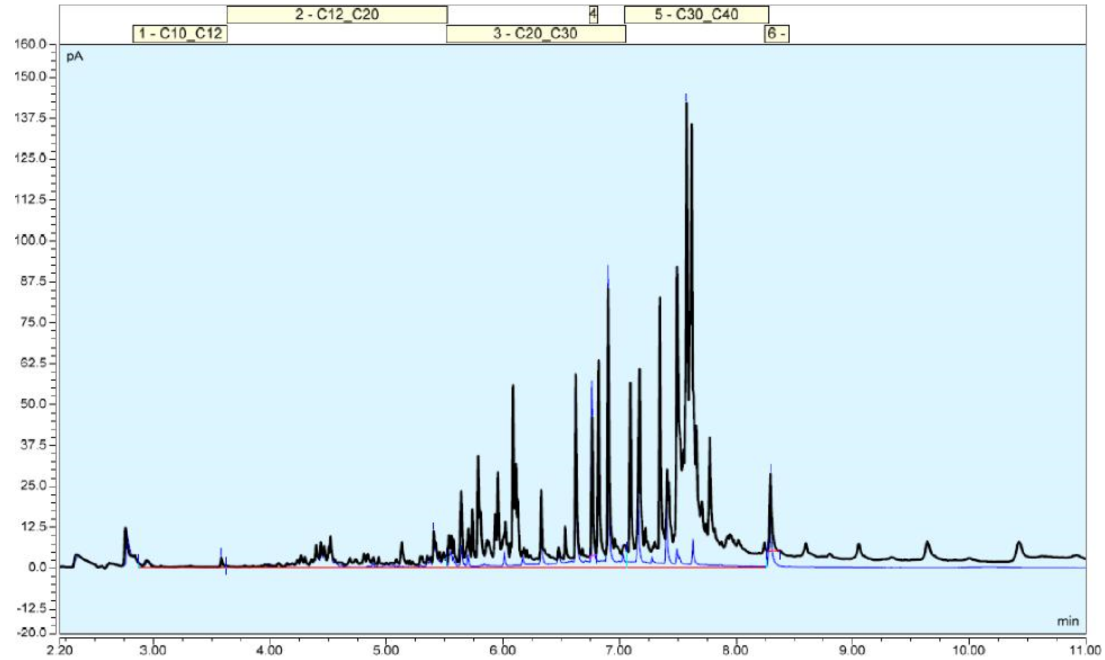

Figure 36: Sample -1942361-12-double

ANNEX 2.3: OVERLAY OF CHROMATOGRAMS – MIXED CONTAMINATION

Overlay of the chromatograms of the current procedure and the new procedure:

- New procedure with clean-up
- Existing procedure

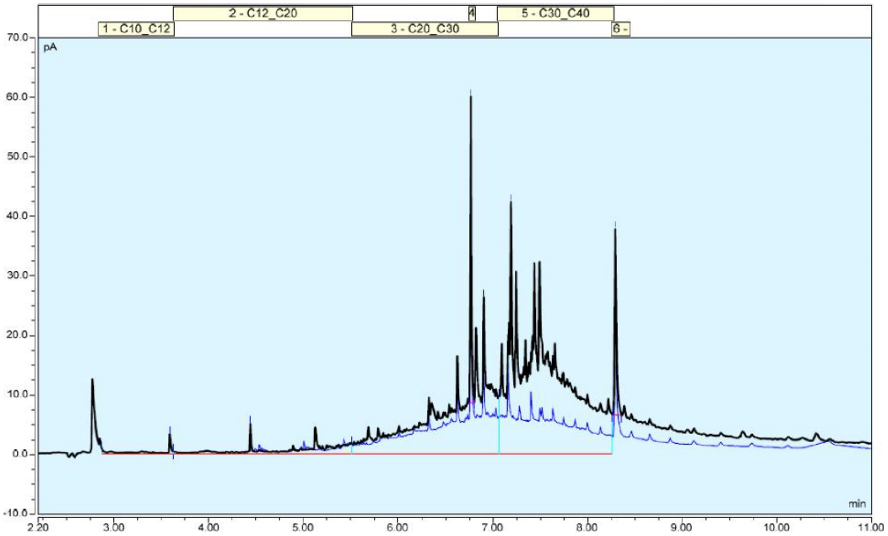

Figure 37: Sample -1942361-13

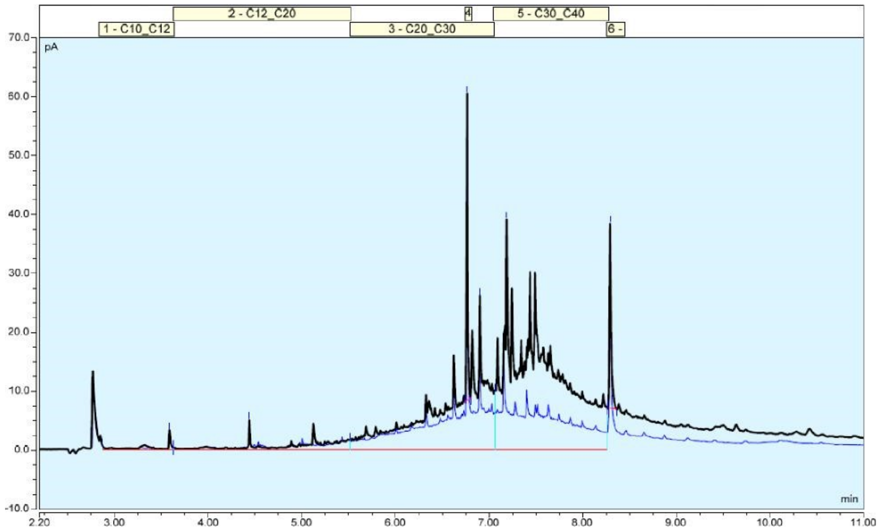

Figure 38:Sample -1942361-13-double

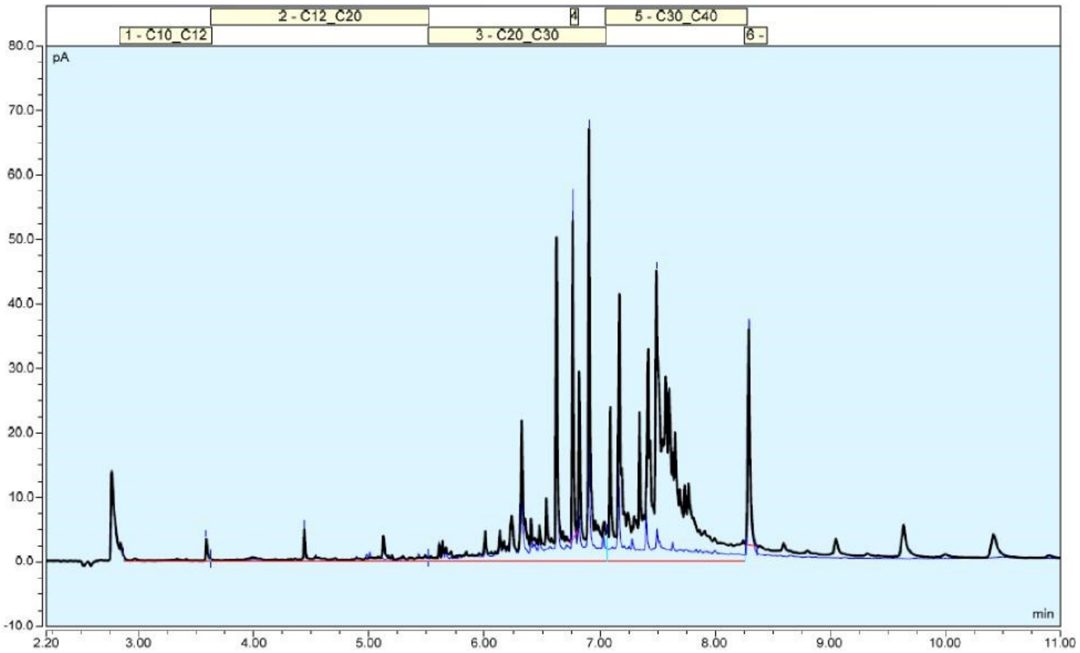

Figure 39: Sample -1942361-14

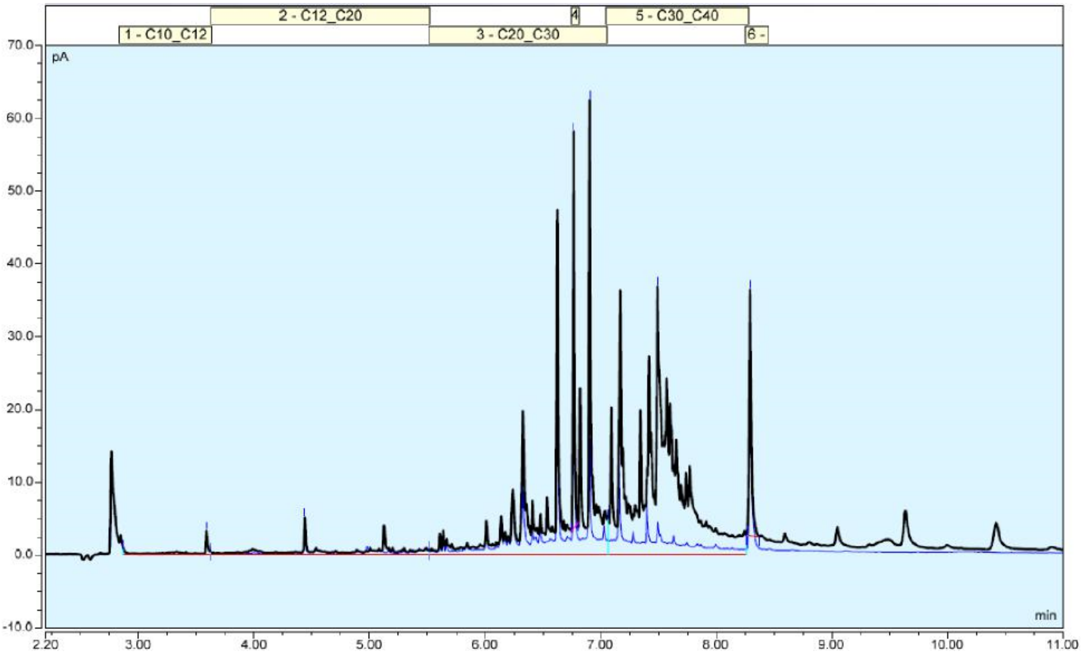

Figure 40: Sample -1942361-14-double

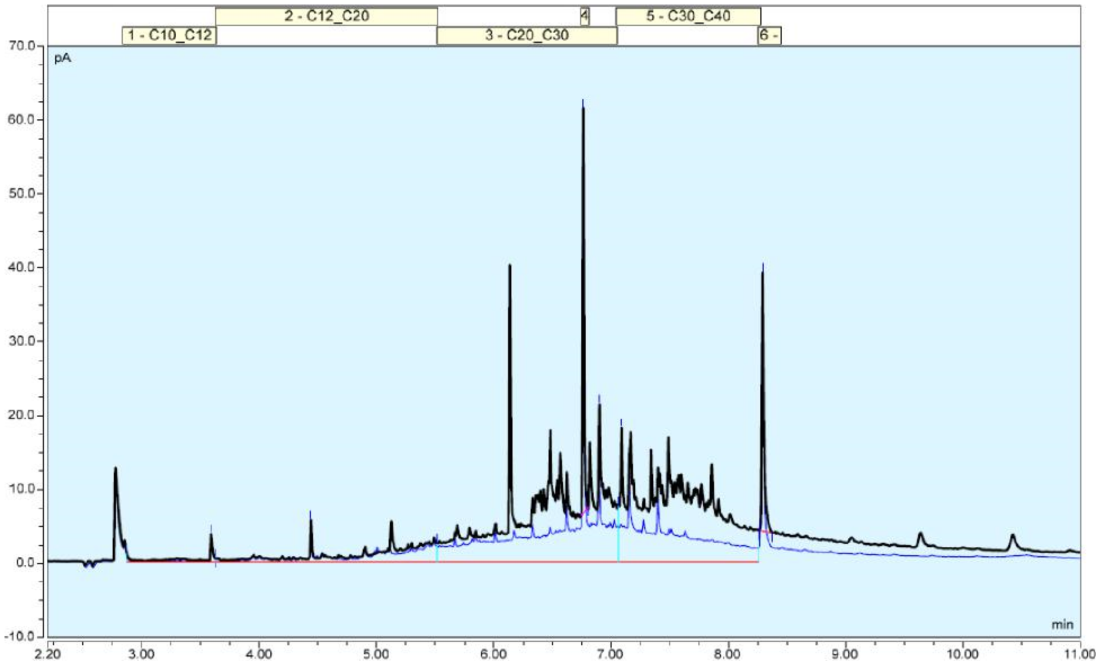

Figure 41: Sample -1942361-15

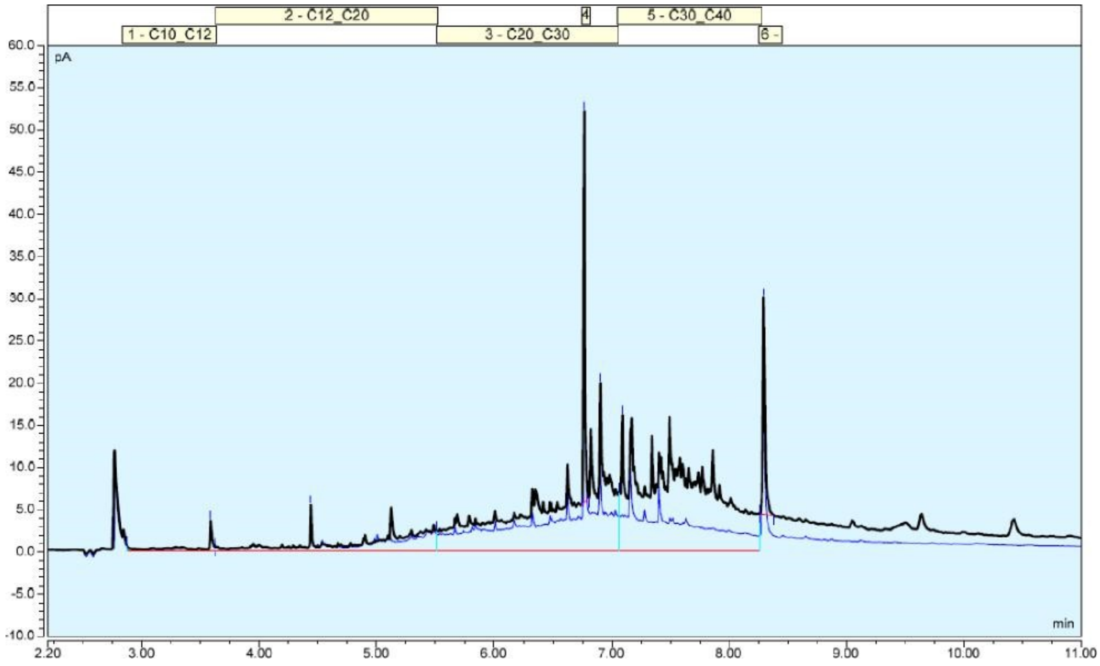

Figure 42: Sample -1942361-15-double

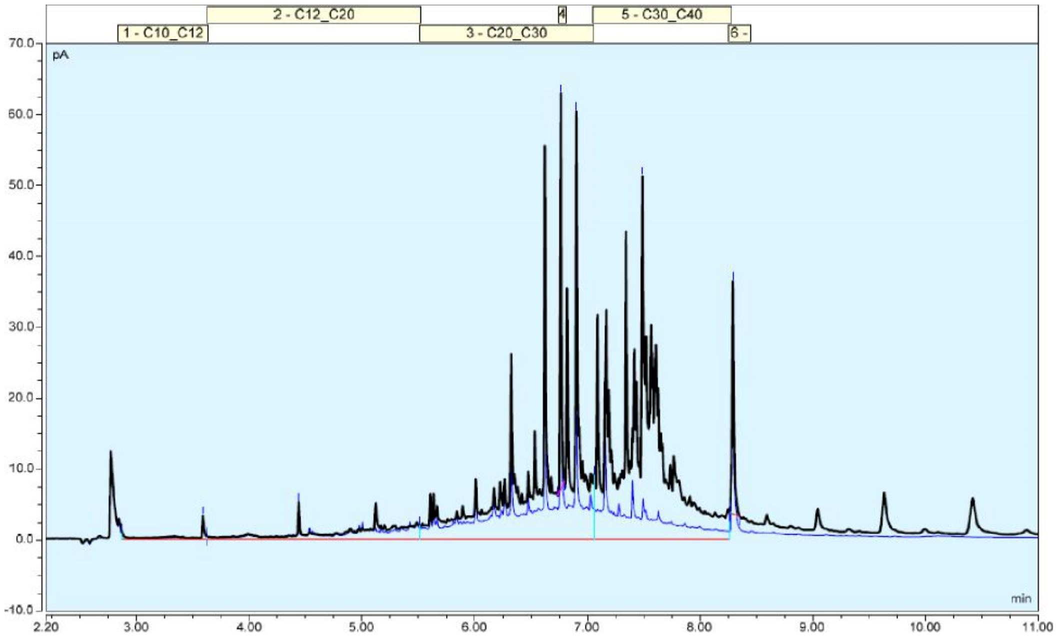

Figure 43: Sample -1942361-16

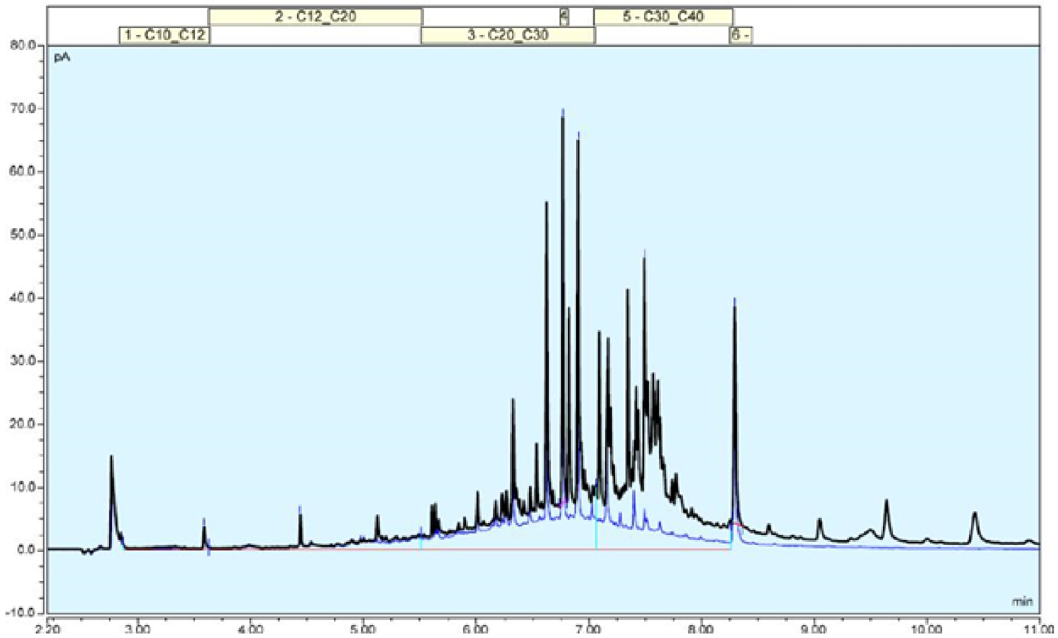

Figure 44: Sample -1942361-16-double

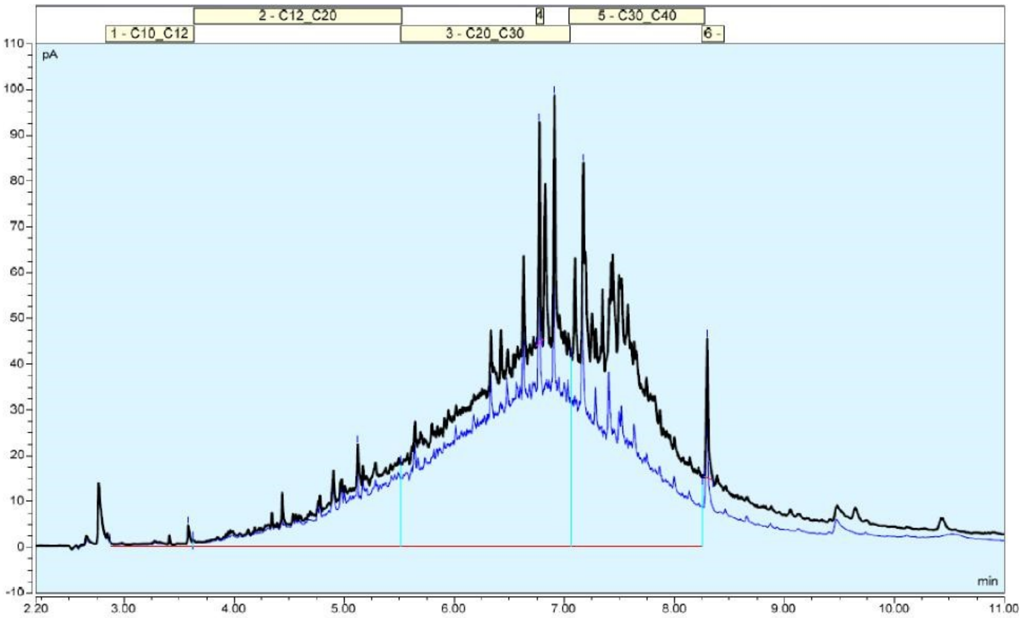

Figure 45: Sample -1942361-17

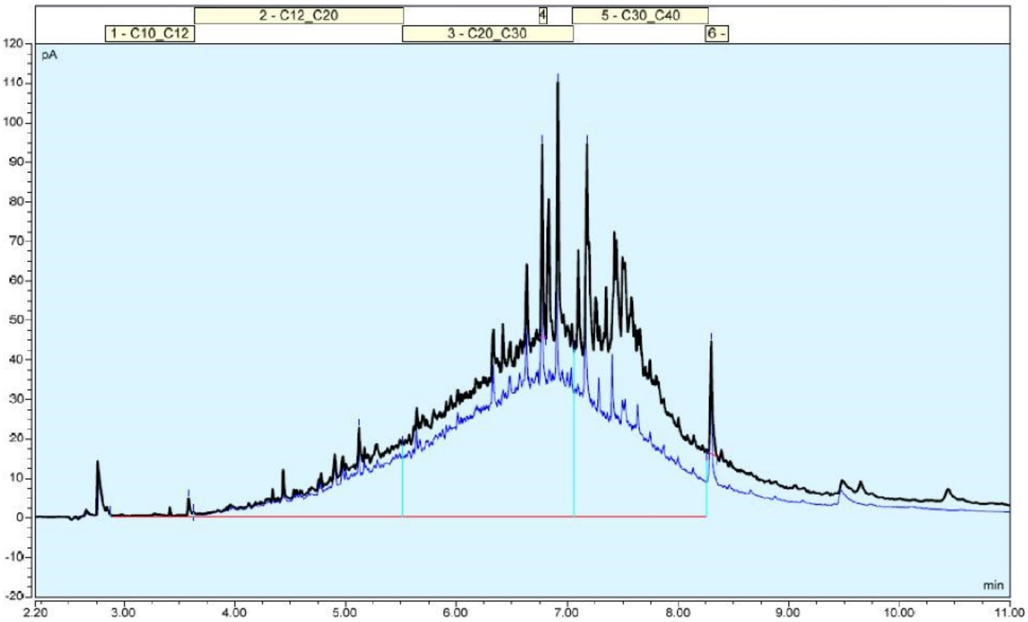

Figure 46: Sample -1942361-17-double

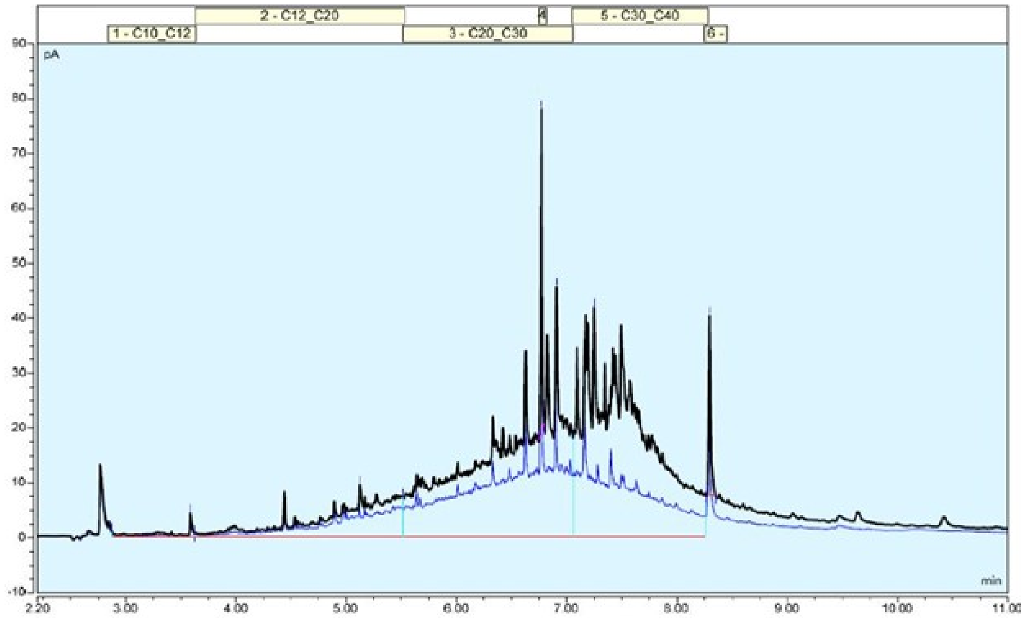

Figure 47: Sample -1942361-18

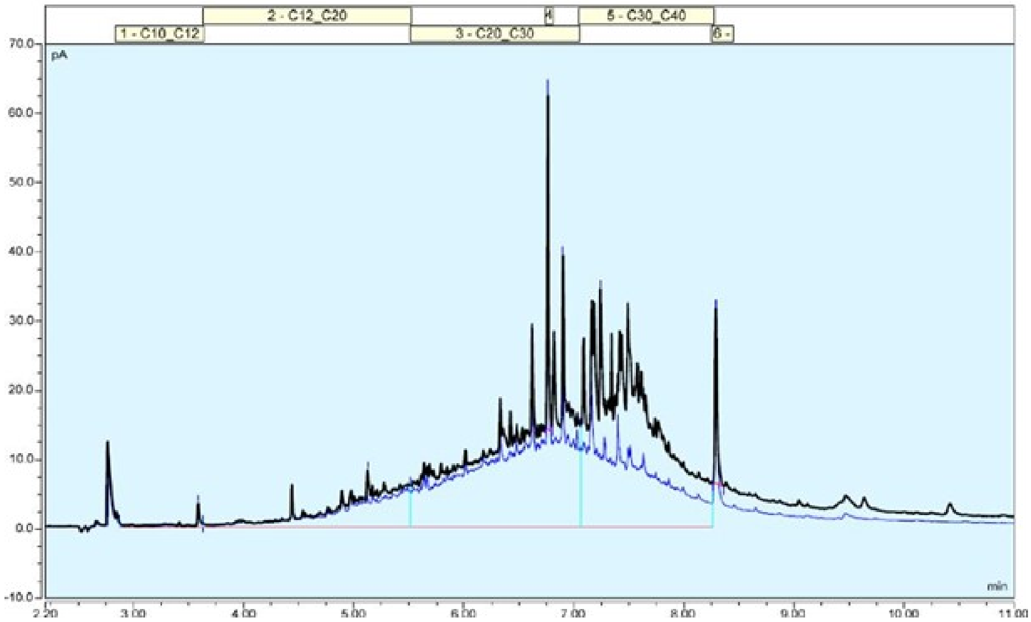

Figure 48: Sample -1942361-18-double