SGS

MINERAL OIL:

PRODUCT INFORMATION AND INSIGHTS

WHEN YOU NEED TO BE SURE

SAMPLING

- Drilling
- Sleaves
- Error Margin

GENERAL

Analytical results

↓

Sampling- Pretreatment– Analysis

An analytical results needs to be interpeted in relation to the circumstances of the test(method).

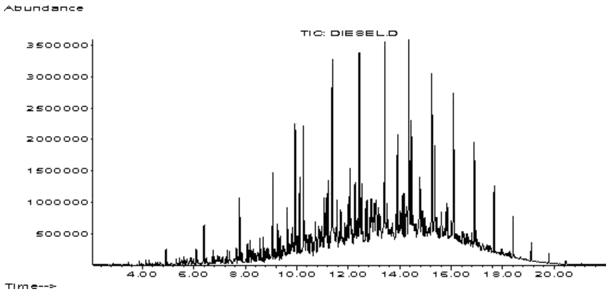
ANALYSES

- Group parameters
  - cheap- general

- Specific analysis
  - expensive- dedicated result

GROUP PARAMETERS

Organic



- Mineral oil GC-FID
- Volatile Mineral Oil
- EOX
- AOX
- VOX
- Fenolindex
- Alifatic-Aromatic split

WHAT

Mineral oil

- ☐ Mixture of both non polar/semi polar substances of aliphatic and aromatic nature.
- ☐ Definition of Mineral oil in environmental research :
  Sum of all substances with a boiling point between n-C10 and n-C40 extracteable with a non polar solvent , no adsorption on florisil, can be separated by means of GC techniques and can be identified using PID
- ☐ Definition is different as defined in other industries and substances who are from a chemical point of view not related to oil will/can contribute to an oil results.

ANALYTICAL TECHNIQUES

- HS-GC/FID
  - Determination of volatile mineral oil (gives an indication on the whole of volatile hydrocarbons (> C5 – C12)

- GC/FID
  - Usual technique for the determination mineral oil

- Aliphatic – Aromatic split
  - GC-FID analysis (specific fractioning)

INTERPRETATION

- Biogenic – Petrogenic
  - Elevated content/presence of biogenic hydrocarbons will/can give raise to falsly elevated TPH
  - Humic acid/
  - ? Bio containing fuels
- PAH – elevated concentrations
- Risk evaluation (TPHCWG – Total Petroleum Hydrocarbon Criteria Working Group → Aliphatic / Aromatic split
  - Analysis is only useful if the nature of the contamination is known and is of petrogenic nature!

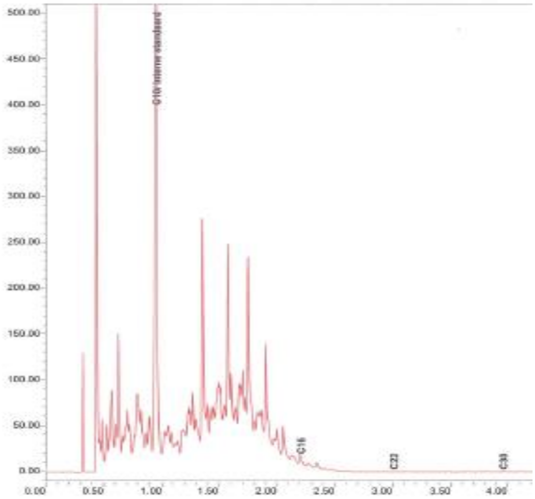
ATTENTION

- Organoleptic evaluation vs oil (labresult <). Presence of volatile oil → analyze for aromatics and volatile oil.
- Organoleptic evaluation: no presence of oil and lab result shows elevated result. Possible presence of high boiling hydrocarbons.
- Elevated concentrations of PAH will contribute to the result for mineral oil. This is mostly possible for soil samples. PAH patern in a chromatogram will be idicated by sharp individual peaks.
- Elevated TPH in water samples can be due to the presence of ftalates. Avoid contact with soft plastic/sampling material.

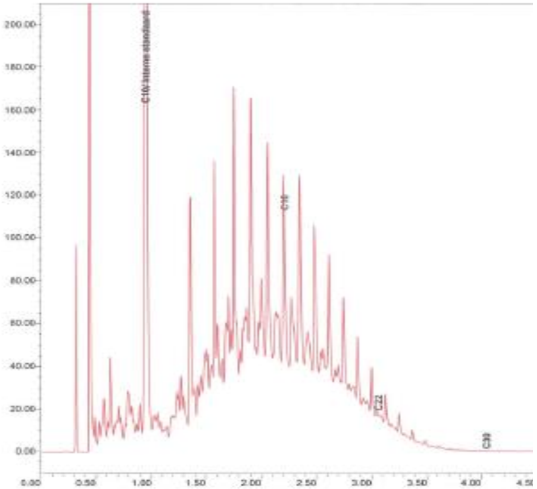
Volatile mineral oil

- The presence of volatile mineral oil (gasoline, wash gasoline) will not be shown in an oil analysis (fraction n-C10 – N-C40) because these are included in the C6- C10 traject.
- Separate analysis of the volatile oil with headspace technique is required
- Combination of volatile and classic TPH will give complete insight in the oil pattern.
- High concentration of VOCl will give false elevated volatile oil concentrations

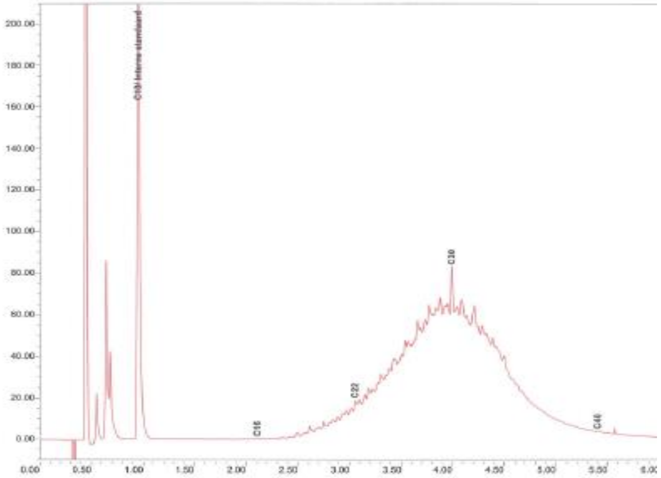
CHROMATOGRAM



Kerosine

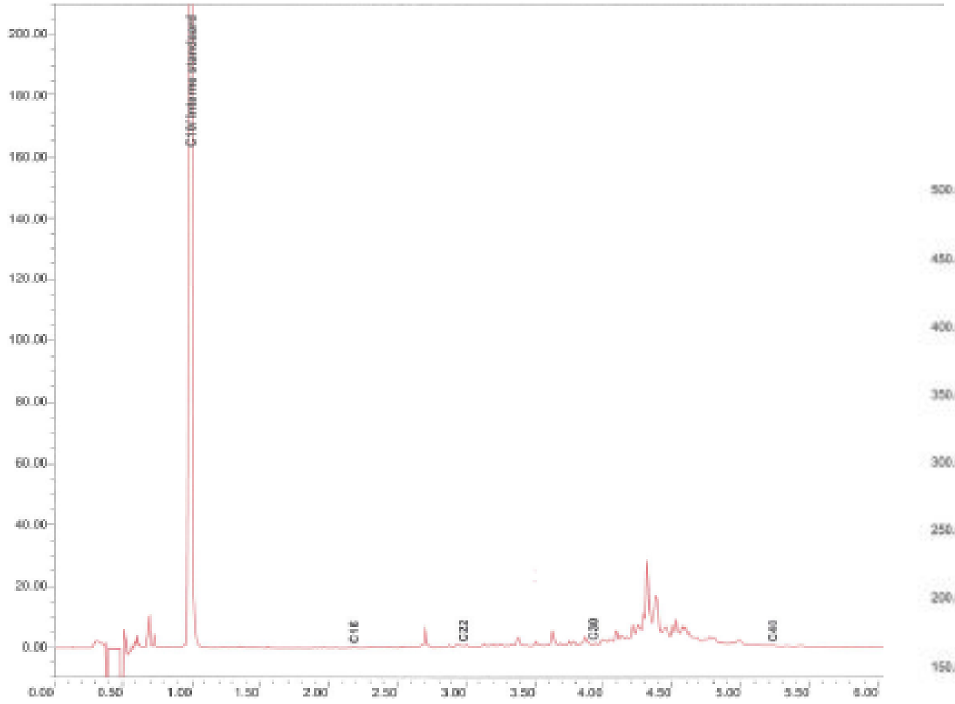


Gasoil



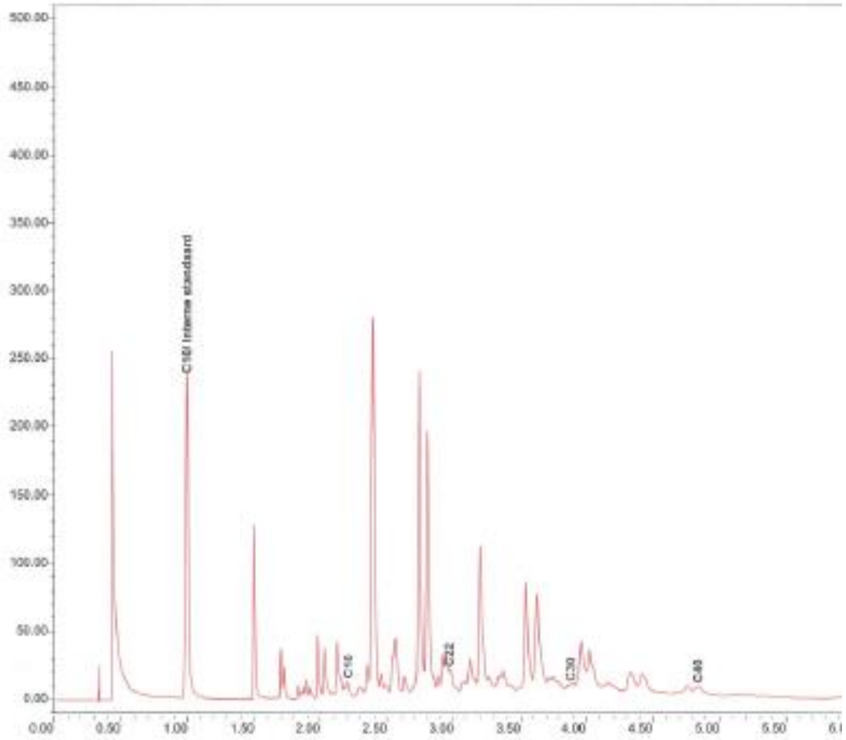
Motor oil

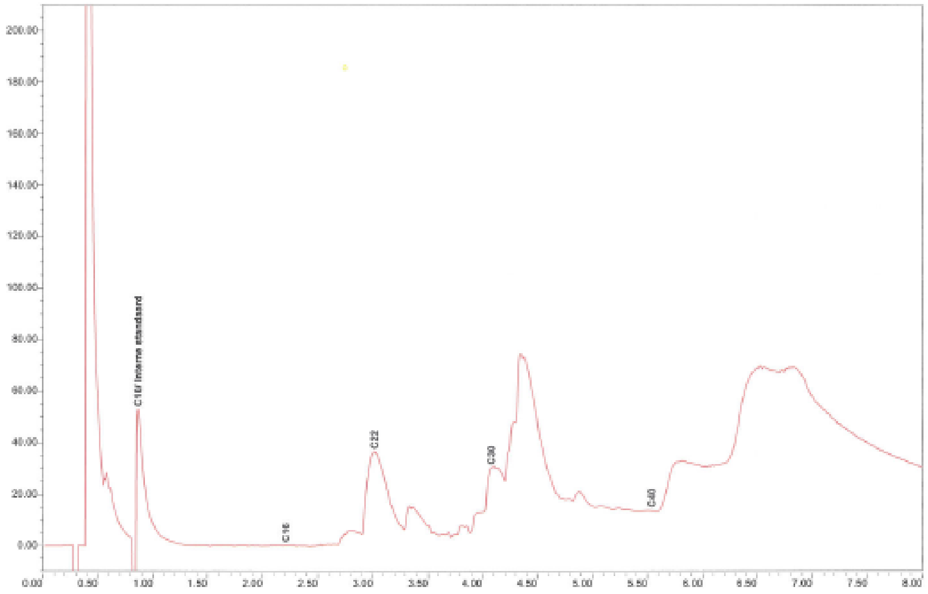
CHROMATOGRAM



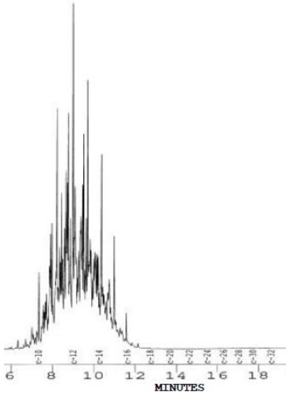
Humic acids

PAH's

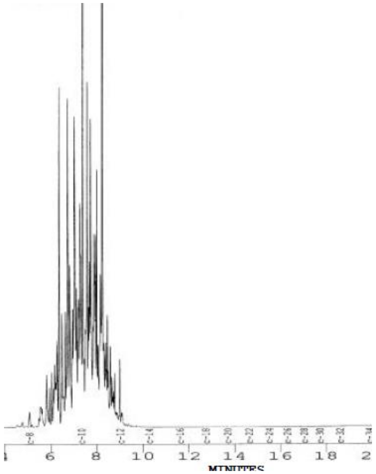



200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
C10/ Interne standaard
C16
C22
C30
C40
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00

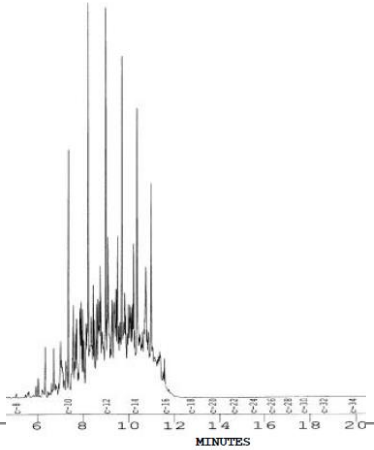
Soja oil



JP-5 JET FUEL C10 – C16



WHITE SPIRIT C8 – C12



KEROSEN C8 – C16

ENVIRONMENTAL FORENSICS
–
OIL SPILLS

ANALYSIS WITH EA-IRMS, GC-C-IRMS AND GC-MS

High End Analytics

SGS Belgium NV - Division IAC

WHEN YOU NEED TO BE SURE SGS

ENVIRONMENTAL FORENSICS – OIL SPILLS

- Allocation of a source of oil residues sampled on beaches, bird feathers, in sediments – deliver, from a juridical point of view, comprehensive prove/link between an oil as source and exposed area and deliver in this way deliver an important tool with respect compensation payments

Different sources
- tankers and discharge of oil
- leaking storage tanks
- pipeline
- natural leaking sources (crude oil sources)

Fig. 5. Coastlines polluted with crude oil (adapted from *Yim et al. 2012*)

ENVIRONMENTAL FORENSICS

- Mineral Oil

→ complex mixture of different compounds

  - Inorganic : Nickel and Vanadium
  - Organic
    - Alkanes
    - Cycloalkanes
    - Mono aromates
    - Polyaromates

- Requires Complex analytical techniques
- Prove relationship between source - contaminant

- **Techniques**
    - GC x GC MS

    - ISOTOPE RATIO - MASS SPECTROMETRY (IR-MS)

- **Methods**

    - Fingerprinting
    - Biomarkers
    - $^{13}C/^{12}C$ verhouding
    - Ni/V

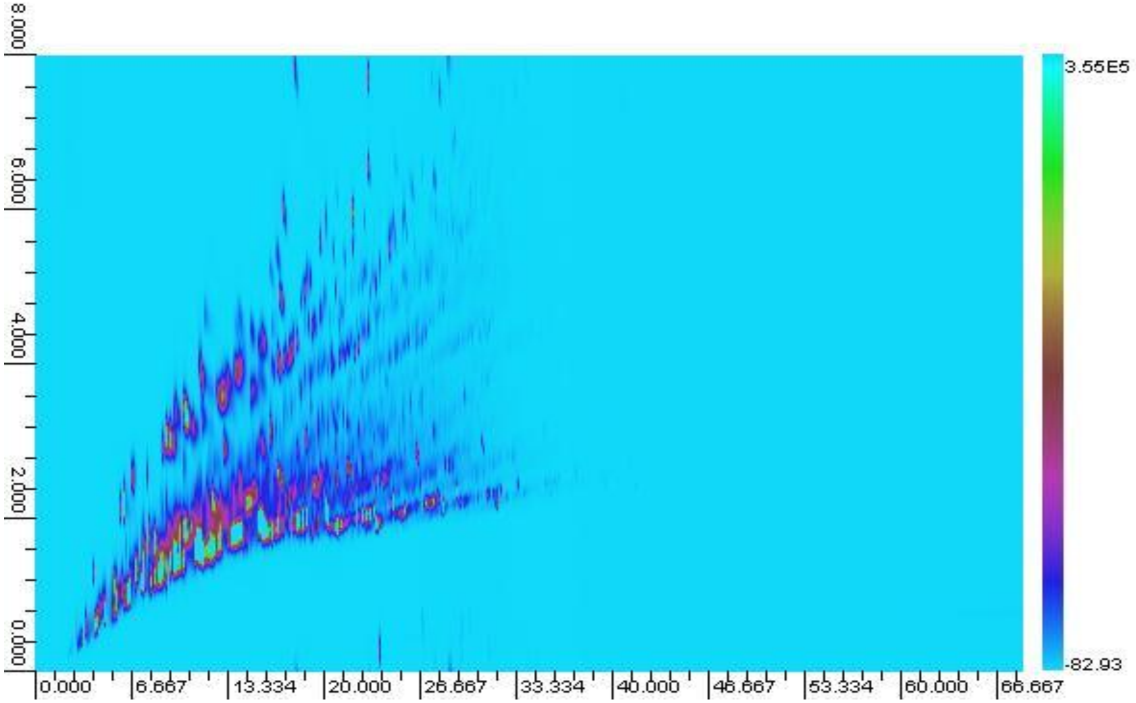
- ☐ **Goal**
  - ☐Reveal analytical data which gives a decisive conclusion/evidence

- ☐**Problems (matrix)**

  - ☐Evaporation
  - ☐Biological phenomena
  - ☐Soluble parts

Fingerprinting : Oil Characterisation

- Determine different groups of organic compounds in oil
- **Paraffin, methyl branched paraffin, ethyl branched paraffin, mono naphthenes and mono aromatics**



❑ Advantages

Separation ability/ High sensivity /
Structured chromatogram / reliable peak identification /
Limited sample clean up

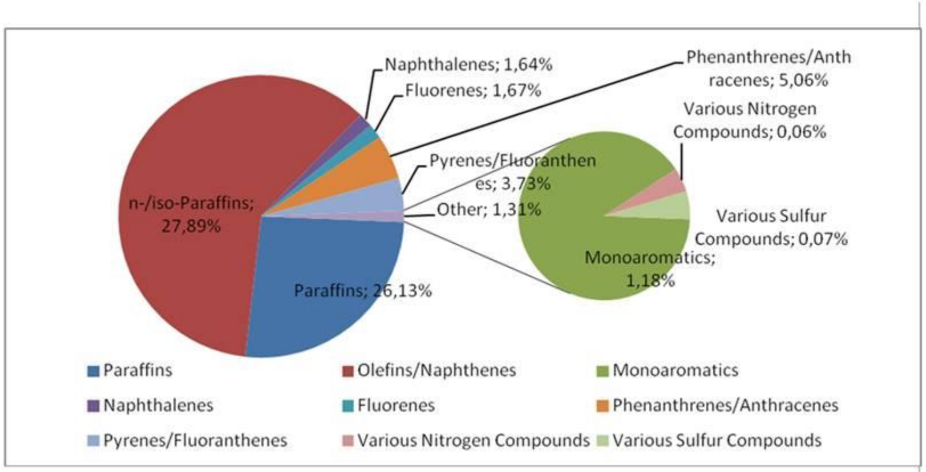
Fingerprinting – Olie karakterisatie

C-nr	Par	Me-Br	Et-Br	H-Br	M-Na	Di-Na	Tri-Na	M-Ar	Na-Mo-Ar	Di-Ar	Na-Di-Ar	Tri-Ar	H-Ar
6													
7													S
8													0,07
9													
10	0,17								0,03	0,05			
11	0,03								0,01	0,06			N
12	0,06								0,02	0,11			0,06
13	0,07	0,06	0,03		0,07				0,03	0,16	0,04		
14	0,12	0,05	0,05		0,14				0,03	0,19	0,13	0,08	
15	0,12	0,02	0,05	0,04	0,29	0,05	0,04	0,02	0,04	0,32	0,13	0,31	
16	0,15	0,13	0,01	0,05	0,30		0,03	0,08	0,01	0,12	0,31	0,76	0,10
17	0,18	0,17	0,10		0,17			0,08		0,08	0,40	0,86	0,28
18	0,32	0,28	0,09	0,08	0,56	0,04	0,32	0,09	0,02	0,11	0,18	0,89	3,36
19	0,50	0,20	0,09	0,23	0,78		0,21	0,21	0,04	0,22	0,22	0,71	
20	0,66	0,37	0,27	0,32	0,95		0,48	0,20	0,03	0,23	0,14	1,46	
21	0,54	0,35	0,30	0,03	0,54		0,74	0,07			0,12		
22	0,72	0,25	0,60	0,33	1,17		0,07	0,08					
23	0,84	0,25	0,53	1,42	2,04		0,20	0,08					
24	1,33	0,26	0,50	0,08	1,06		0,06						
25	1,50	1,10	1,19	0,15	0,90	0,36	15,65						
26	0,84	1,14	0,73	0,08	0,66	1,51							
27	0,69	0,42	0,68		0,56								
28	0,58	0,62	0,88	0,42	0,46								
29	0,42	0,27	0,35		0,17								
30	0,68			25,77	0,85								
31	0,76												
32	0,81												
33	0,29												
34	0,79												
35	0,57												
Total	13,75	5,94	6,45	29,00	11,69	1,96	17,80	0,92	0,26	1,64	1,67	5,06	3,86

C-nr	Carbon number	Tri-Na	Tri-naphthenics
Par	Normal paraffins	Mo-Ar	Mono-aromatics
Me-Br	Methyl branched paraffins	Na-Mo-Ar	Naphthenic-mono-aromatics
Et-Br	Ethyl/dimethyl branched paraffins	Di-Ar	Di-aromatics
H-Br	Heavily branched paraffins	Na-Di-Ar	Naphthenic-di-aromatics
M-Na	Mono-Naphthenics	Tri-Ar	Tri-aromatics
Di-Na	Di-naphthenics	H-Ar	Tetra-Aromatics

Results in % w/w (based on the FID respons factors)

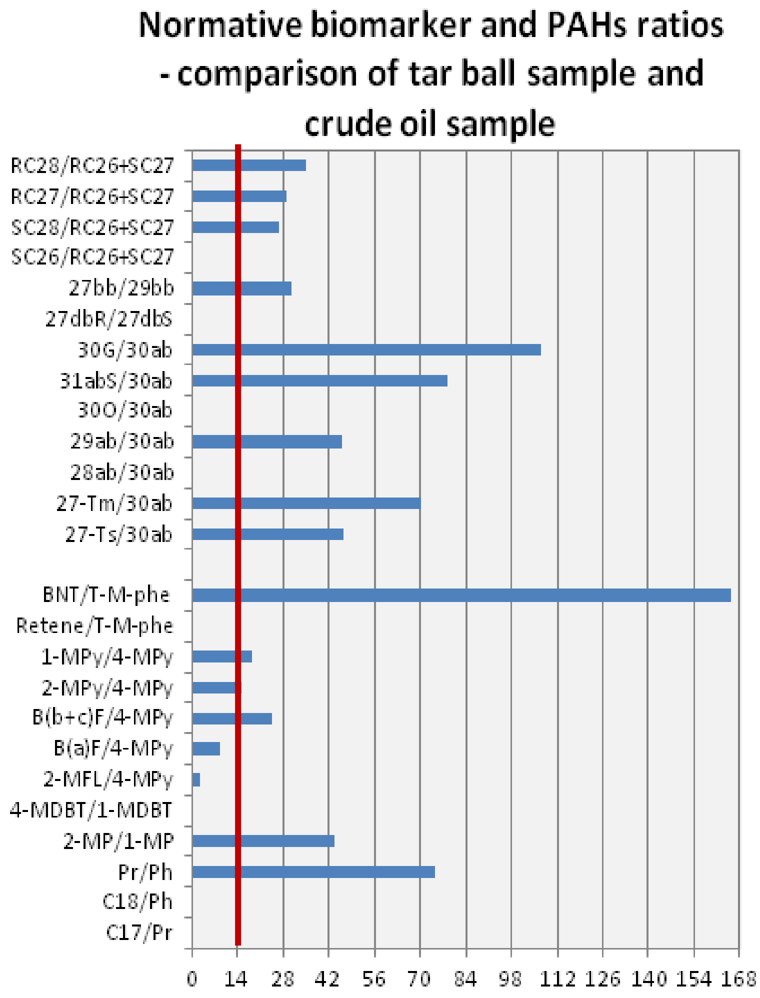
Fingerprinting -



BIOMARKER DETERMINATION WITHGC/MS TECHNIQUE (COMPLEX ORGANIC COMPOUNDS IN “CRUDE OIL” – FORMER LIVING ORGANISM)

	NS1	NS2	NS3	NS4	NS5	NS6	NS7	R1	R2	R3	R4	R5	R6
Terpane (hopane) ratios													
%27Ts	43.8	44.7	62.6	56.9	57.6	51.8	49.2	-	-	-	45.0	45.4	42.0
%28ab	0.0	0.0	0.0	18.2	0.0	7.9	19.3	-	-	-	8.0	4.1	13.3
%25nor30ab	43.4	16.1	0.0	18.2	0.0	8.5	16.7	-	-	-	7.3	2.7	5.6
%30O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-	-	50.6	4.0	70.0
%32abS	55.8	58.1	58.1	57.7	59.2	57.6	58.3	-	-	-	57.9	58.2	59.2
Sterane and diasterane ratios*													
%29aaS	-	-	-	0.0	-	41.4	-	-	-	-	50.0	40.3	38.7
%29bb	-	-	-	68.6	-	20.1	-	-	-	-	24.8	34.8	19.0
%27bbSTER	-	-	-	41.0	-	42.9	59.6	-	-	-	35.1	28.7	22.5
%28bbSTER	-	-	-	27.5	-	34.1	40.4	-	-	-	39.2	38.5	46.4
%29bbSTER	-	-	-	31.5	-	23.0	0.0	-	-	-	25.7	32.7	31.1
Triaromatic steroid hydrocarbon ratios													
%TA21	33.9	18.7	35.9	25.2	33.4	21.1	26.6	-	32.9	-	13.3	15.6	10.0
%TA26	42.7	36.4	30.0	26.1	36.6	39.8	32.4	-	16.2	-	29.7	36.4	19.9
%TA27	48.2	55.5	53.5	51.1	51.0	51.2	49.2	-	26.8	-	50.0	55.7	48.6

OIL SPILL FORENSICS (BIOMARKER)



ISOTOPE RATIO MASS SPECTROMETRY

What?

- Determination of stable isotopes e.g. $^{13}C/^{12}C$

Why?

- Natural process gives different isotope relation

How?

- Determinations on oil (EA-IRMS) and/or on specific compounds (GC-C-IRMS) like: *n*-alkanen, PAHs
- Convertion from compounds into gas phase - C to CO_2
- Relation of light isotopes (e.g. $^{13}C/^{12}C$) vs international standards (Vienna Peedee belemnite for carbon) – conventional δ identification:

$$\delta^{13}C\ (‰) = \frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{VPDB}} - 1$$

- By measuring the isotope ‘finger prints’ of samples we can (as one of the possible techniques) determine a relation between the source and contaminant

Elemental Analyzer (Flash HT)/IRMS – BULK samples isotope ratios

Fig. 2. Flash HT Elemental Analyzer

- Bulk samples (liquids or solid samples)

c.g. oil, tarballs

- Combustion($^{13}C/^{12}C$; $^{15}N/^{14}N$, $^{34}S/^{32}S$)
- High temperature conversion (pyrolysis) ($^{18}O/^{16}O$; $^{2}H/^{1}H$)

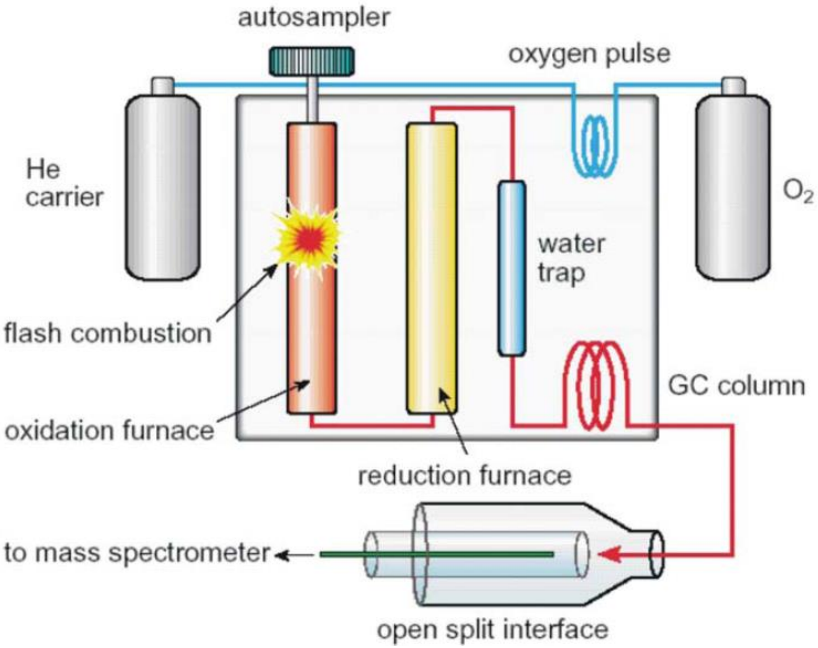


Fig. 3. EA-IRMS schematics (adapted from Thermo Fisher Scientific operating manual)

Gas-Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) - Compound Specific Isotope Analysis (CSIA)

- Measurement will be done on molecular level (chromatografic separation of component) whereafter they :
  - Combusted ($^{13}C/^{12}C$; $^{15}N/^{14}N$) or high temperature conversion ($^{2}H/^{1}H$ or $^{18}O/^{16}O$)

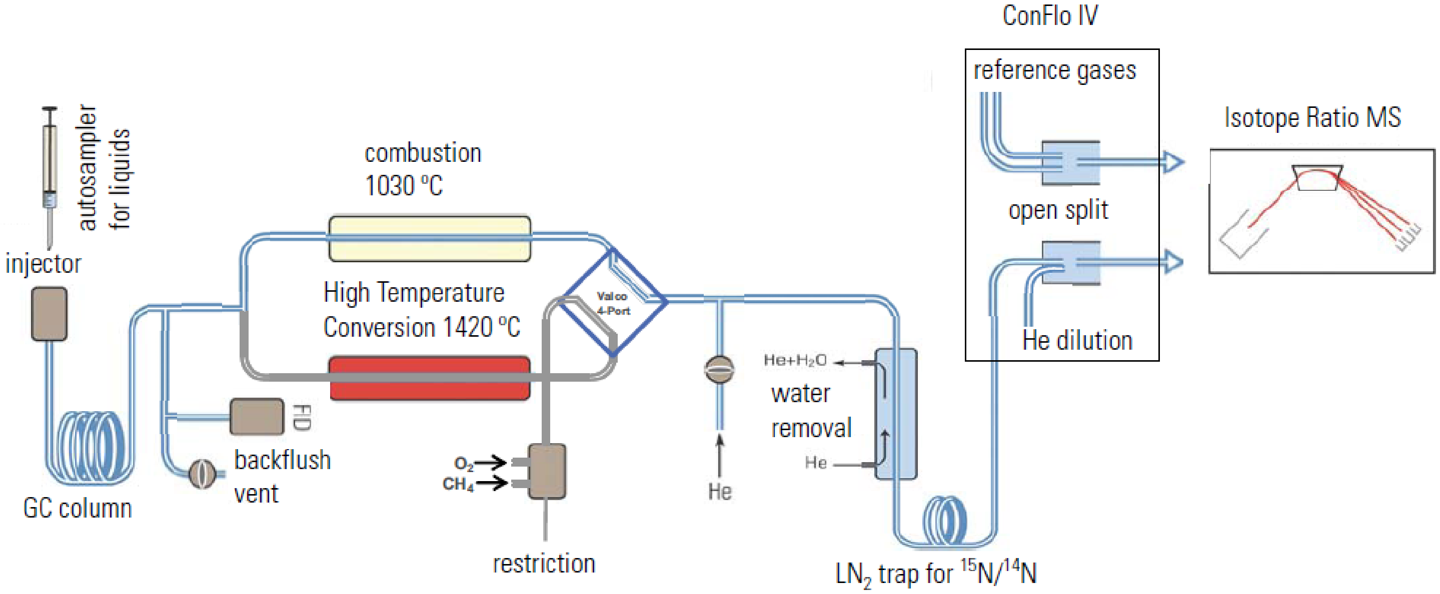


Fig. 4. GC-C-IRMS scheme (adapted from Thermo Scientific operating manual)

ENVIRONMENTAL FORENSICS – OIL SPILLS

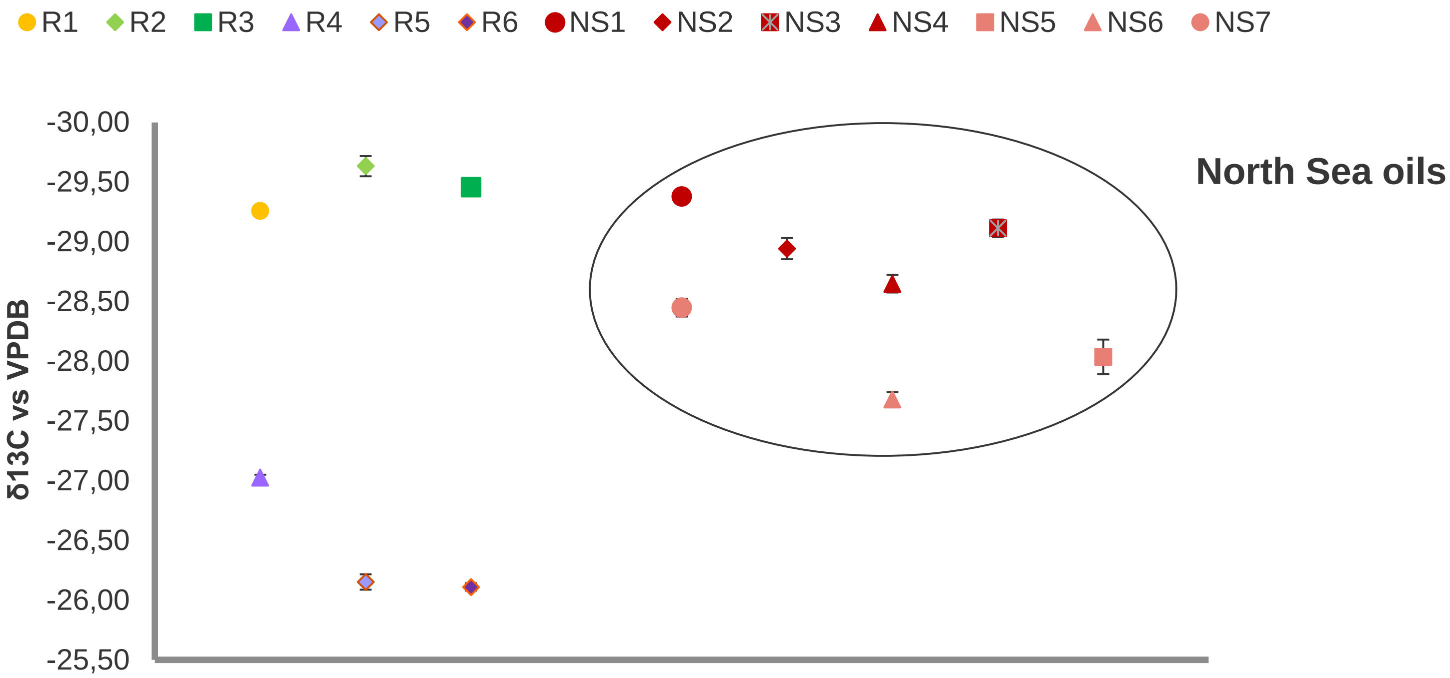
Comparison: Characterisation of different samples crude oil coming from different geografical regions

Geografical origin of oil samples

Sample name	**Oil field**	**Location**	**Sample name**	**Oil field**	**Location**
NS1	Clair	Northern North Sea	R1	Unknown	Algeria
NS2	Forties	Central North Sea	R2	Unknown	Unknown
NS3	Gullfaks	Northern North Sea	R3	Unknown	Libya
NS4	Brent	Northern North Sea	R4	Unknown	Bonny, Nigeria
NS5	Ekofisk	Central North Sea	R5	Burun	Turkmenistan
NS6	Unknown	Southern North Sea	R6	Oyo	Nigeria
NS7	Grane	Northern North Sea			

ENVIRONMENTAL FORENSICS – OIL SPILLS

BULK CARBON ISOTOPES WITH EA-IRMS

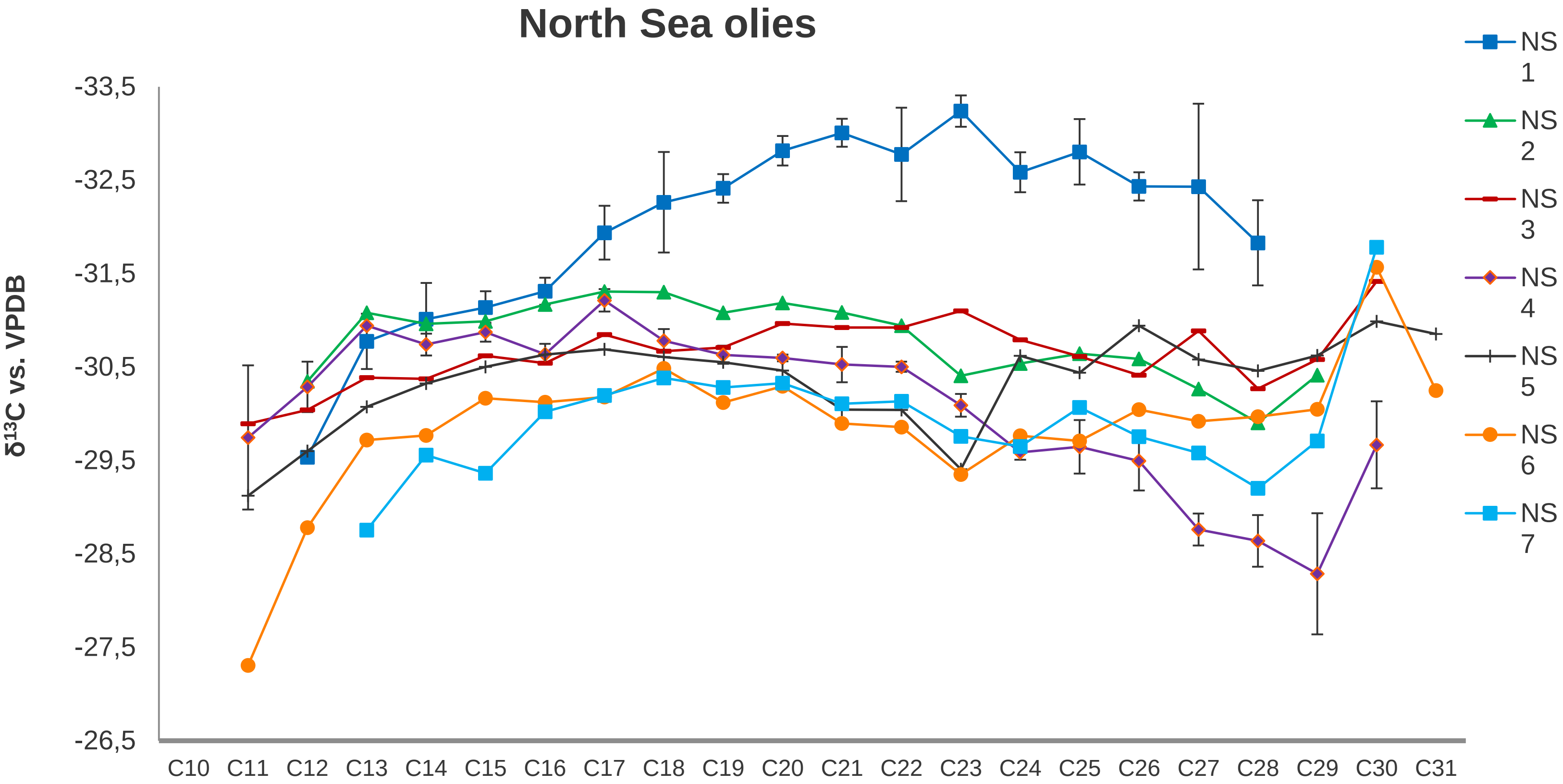


$\delta^{13}C$ of bulk crude oil samples (error bars represent ± 1σ of three repetitions)

- Significant difference in bulk samples Carbon isotope ratios have been found, although some showed same bulk carbon isotope ratio e.g. R5 and R6, NS1 and R1 or R3

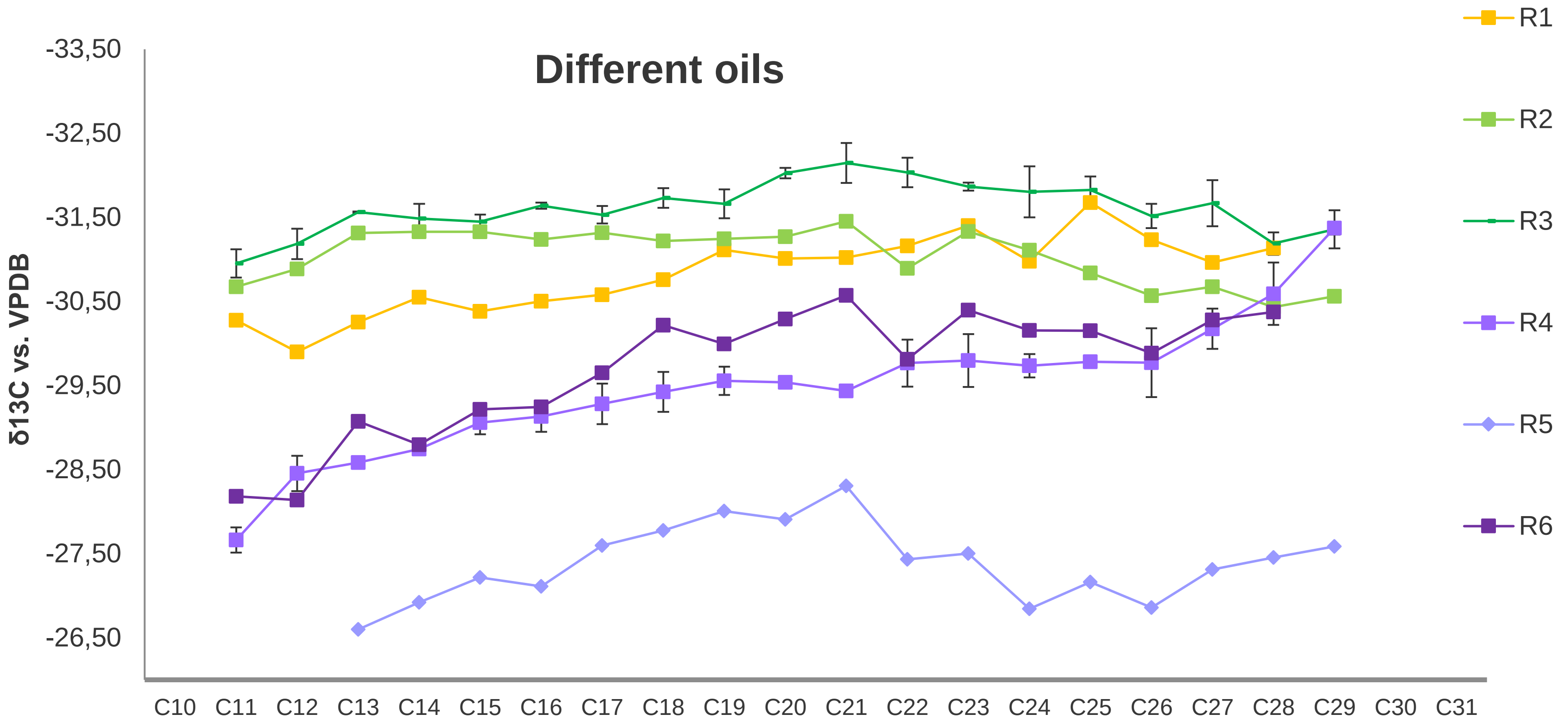
ENVIRONMENTAL FORENSICS – OIL SPILLS

CARBON ISOTOPES IN *n*-ALKANES MET GC-C-IRMS



n-Alkane isotope profiles of North Sea crude oils (error bars ± 1σ of different *n*-alkanes in selected oils, n=3)

ENVIRONMENTAL FORENSICS – OIL SPILLS
CARBON ISOTOPES IN *n*-ALKANES WITH GC-C-IRMS



n-Alkane isotope profile from other crude oils (error bars ± 1σ of different *n*-alkanes in selected oils, n=3)

- *n*-Alkanes f sample R5 showed significant higher ^{13}C in relation with sample R6 (although they have simultaneous bulk carbon isotope ratios)

ENVIRONMENTAL FORENSICS – OIL SPILLS
MEERVOUDIGE TECHNIEKEN

- Significant differences in carbon isotope ratio could be proven in most of the analyzed oil samples
- *n*-alkane Isotope profile could be used as a discriminator between these oil for which an identical bulk carbon isotope ratio was found
- In samples R1 and R3 – no biomarkers could be found and in R2 only one group was present
- NS3 and NS5, impossible to distinguish using biomarker approach alone

ENVIRONMENTAL FORENSICS – OIL SPILLS
MULTIPLE TECHNIQUES

- Conclusion:
  - Carbon isotopic ratio is a very usefull technique which can give valuable information in the investigation with a source contaminant relation → fingerprinting
  - Combined approach by means of biomarker method (EN 15522) give more reliable results
  - Depending on the type of samples GC-c-IRMS can be the only reliable technique for fingerprinting (because of absence of biomarkers)

ENVIRONMENTAL FORENSICS – OIL SPILLS
MULTIPLE TECHNIQUES

- Application:
  - In cases where a contamination can be caused by multiple possible sources, the use of a combination of the mentioned methods, can deliver analytical data giving evidence that will/can be used in the conclusion in the source – contaminant relation
  - Analytical cost for such analysis are limited in relation to remediation costs and allow allocation of remediation cost to the right responsible party and are therefore juridical sound

OUR ORGANIC ANALYTICAL POSSIBILITIES

- Metalspeciation (As III and V, Me-Hg components,…Organotin)
- Dioxin& Dioxin like, markerPCB’s – HRMS techniques
- Brominated compounds: PBDE ‘s, PBDF/D, PBB’s, HBCD, TBBA, …
- Brominated dioxins (PBDD/F)
- Polychlorinated Naphtalenes
- Perfluoro compounds: PFOS, PFOA, PFSE,…
- Residu analyses
- Detergents LCMS techniques
- PPCP’s
- Screening i.e. MultiTrace®
- …

SGS

MAKING THE DIFFERENCE

Questions!

CONTACT - INFORMATION

- More information? Contact us:

Luc De Ren
Environmental Services
Business Development Managar
Mob: +32 (0)470 810 328
E-mail: luc.deren@sgs.com