SINTEF Ocean AS
Address:
Postboks 4762 Torgarden
NO-7465 Trondheim
NORWAY
Switchboard: +47 46415000

Enterprise /VAT No:
NO 937 357 370 MVA

Project Memo

WP-3 PAME – EPPR Methodology for screening properties of New Low Sulphur Marine Fuel

Selection of test parameters

PROJECT NO.	VERSION	DATE
302006029	1.1	2021-04-20

AUTHOR(S)
Per S. Daling, Liv-Guri Faksness, Thor-Arne Pettersen

CLIENT(S)	CLIENTS REF.
Norwegian Coastal Administration	Jon-Arve Røyset

CLASSIFICATION	NO. OF PAGES AND APPENDICES:
Restricted	27 + Appendixes

ABSTRACT
This memo describes the recommended screening test methodology in characterizing properties of "Very Low Sulphur Marine fuels" (VLSFO) and "Ultra Low Marine Fuels" (ULSFO) for use by laboratories within the Arctic member states in the ongoing PAME/EPPR project "Low Sulphur fuels, fate and behaviour in cold water conditions". The purpose of a common methodology is to obtain comparable and consistent results between the different laboratories involved in analyses of oils. The recommended methodology is based on feed-back and suggestions from several laboratories within the PAME /EPPR working group (WP-3).

The suggested test parameters are considered as a best practice methodology for characterizing properties that are relevant for screening the diversity of different marine LSFOs, both connected to fate and behaviour and relative toxicity when spilled in cold or Arctic seawaters. The recommended test methodology will form the basis for an inter-laboratory comparison (Round Robin study) on 2-3 test oils.

This screening test methodology is for characterizing the properties of parent ("fresh") fuel oil samples. Methods for preparation and characterization of weathered samples (e.g. evaporated, emulsified, photo-oxidated) and methods for testing effectiveness of response methods (e.g. dispersant effectiveness, in-situ burning, mechanical recovery) is planned to be performed at a later stage in this PAME / EPPR project, and is therefore not described in this memo.

PREPARED BY	APPROVED BY
Per S. Daling	Kristin Rist Sørheim
Per S. Daling	Kristin R. Sørheim

Document History

VERSION	DATE	VERSION DESCRIPTION
0.1	2021-01-11	Draft version for review
1.0	2021-03-19	Final version after input from the WP-3 working group
1..1	2021-04-20	Signed final version

Table of Contents

1 Background

During WP-1 in this PAME/EPPR project *"Low Sulphur fuels, fate and behaviour in cold water conditions"* (hereafter called LSFO-project), a questionnaire request to 800 ships (??) sailing in the Arctic has gained information on which type of fuel and volume are used on up to. This includes both *"Ultra-Low Sulphur Fuel Oils"* (ULSFO; < 0.1 % S in Emission Control Area (ECA)) and *"Very Low Sulphur Fuel Oils"* (VLSFO; < 0.5% S, Globally 2020 Sulphur Cap). The questionnaire will form a basis for selecting around 10 different fuel oil samples for a "screening" testing performed by relevant laboratories within the member countries in the LSFO-project. These samples may be both Marine Distillate fuels (DM) and Marine Residual fuels (RM), according to the ISO 8217 classification (see Appendix A1).

SINTEF Ocean, Dept. for Climate and Environment (hereafter called SINTEF) has been asked by the Project Management Group (PMG) in the LSFO-project to assist in establishing protocols for screening testing of the fuel oils that will be collected in the LSFO-project.

SINTEF has dedicated oil spill personnel and laboratory test facilities (both bench-scale and meso-scale flume basins) and has over the past four decades performed oil spill weathering and countermeasures testing of an extensive number of crude oils and refined oil products. During the last 4-5 years, SINTEF has performed characterization studies on a selected numbers of marine fuel oils complied to the new IMO-regulations (ULSFOs and VLSFOs). These studies are summarized in the following reports:

- *Weathering Properties and Toxicity of Marine Fuel Oils (Hellstrøm, 2017)*
- *Characterization of Low Sulfur Fuel Oils (LSFO) – A new generation of marine fuel oils (Sørheim, et al. 2020)*

These reports are available at https://www.kystverket.no/Beredskap/forskning-og-utvikling/diesel--og-hybridoljer/

2 Objectives and deliverables

The main objective has been to establish best practice methodology for characterizing properties that are relevant for screening the diversity of different marine LSFOs, both connected to fate and behaviour, and the relative toxicity when spilled in cold or Arctic seawaters. The test methodology will used by selected laboratories within the member countries of the LSFO-project. The purpose is to obtain comparable and consistent results between the different laboratories. High quality, and good laboratory practice, and experienced personnel in oil characterization are therefore a prerequisite.

This final memo is based on response from PAME /EPPR working group (WP-3). The screening protocols include characterizing the physico-chemical properties of the parent ("fresh") fuel oil samples and their relative toxicity. These protocols will form a basis for an inter-laboratory comparison (Round Robin) of 2-3 selected test oils.

Methods for preparation and characterization of weathered samples (e.g. evaporated, emulsified, photo-oxidated) and methodology for testing effectiveness of response methods (e.g. dispersant effectiveness, in-situ burning, mechanical recovery) are planned to be performed at a later stage in this PAME / EPPR LSFO-project, and are therefore not described in this memo.

3 Pre-handling of the samples when arriving the laboratory

Procedures for taking the samples for sending to the laboratories are given in separate memo (and in Appendix B). After the oil samples have entered the laboratory in containers (volume minimum 2-4 L) the following handling is important:

- Registration of the oil samples according to the laboratory's internal QA routines or protocols, including giving the oil unique internal sample number (to maintain "chain of custody", see Figure 4.1 below)
- Visual description or photo documentation, and registration of enclosed paper etc.

Prior to transfer of oil aliquots to smaller bottles, it is very important to check the "homogeneity" e.g. presence of free water, w/o-emulsion, inorganic material on the bottom of the oil in the container. According to the ISO 8217 Fuel standard, the max. sediment content should be < 0.1 wt.% and water content < 0.5wt.%. These parameters are generally documented in *"Certificate of Analysis"* (CoA).

However, to ensure that the arrived oil sample is a representative sample according to the CoA, the following routine-procedures are recommended:

1. The oil container is placed tilted slightly forward, for minimum 12 hours (see Figure 3.1, right photo). A sample is retrieved from the bottom of the container and checked for free water.
    a. If free water is present, the water is removed and volume measured, and a new sample is taken from the bottom of the container.
2. Water content in the bottom sample is measured using Karl Fischer titration (see Table 4.1)
    a. If water content of the bottom sample is low (<1%), the oil is homogenized (step 3).
    b. If the water content is higher, samples are usually taken from the middle and top of the container and water content measured. An assessment is made regarding the total water content of the container. The goal is total water content <2%, preferably <1%.
        i. If the middle and top samples are low in water content, the oil is homogenized.
        ii. If the middle and top samples also contain significant amounts of water, then more water should be removed. Removal of bound water is done by heating the oil container for minimum 1 hour at 50°C. The oil container is then placed tilted slightly forward, minimum 1 hour. Free water is removed, and a new bottom sample is retrieved. This can be repeated several times until water content has become sufficient low.
3. When total water content is satisfactory low, the oil is homogenized by placing the oil container in a water bath at 50°C for 1 hour, it is then put on a shaker for 1 hour. A homogeneous sample is retrieved. Density and water content are measured for this homogeneous sample.

NB! If topping (distillation) of the oil is to be performed at a later stage, the water content must be <2% o safely proceed with distillation.

Figure 3.1 Example of oil containers arriving the SINTEF laboratories, removal of any water on bottom.

4 Physico-chemical properties of the oil

Table 4.1 and Table 4.2 give an overview of the recommended test parameters. Examples of presentation of test-results are exemplified in Appendix A-2. In addition to SINTEF, Environment Canada (ECCC) has specified all the methods and instrumentation for measurement of physical properties. Both laboratories' methods are given in Table 4.1. The ASTM methods are referred as numbers in the table, but their entire titles are provided in the reference list (chapter 9).

Additionally, China (Tongji University) has given positive feed-back for performing the screening testing of Asian LSFOs oil samples according to the test parameters described in table 4.1.

Table 4.1 Analytical methods to determine the physical properties. Upper lines refer to SINTEF, lower line to ECCC.

Physical property	**Analytical method**	**Instrumentation**
Water content	• Volumetric Karl Fisher titration • ASTM E203	• Metrohm 841 Titando • Metrohm 901 and Methrom 915 KF Ti-Touch
Density	• ASTM D4052 at 15.5 °C. Digital densimeter. Oils with high pour point (viscosity, the density measurement if performed at higher temp. (e.g. 50 °C) and density is corrected to 15°C using volume correction factor tables (in ASTM D1250) • ASTM D5002. Density measured at 0 to 15 °C.	• Anton Paar, DMA 4500 • Anton Paar DMA 5000, and Anton Paar Stabinger Viscometer SVM 3000
Pour point	• ASTM D97 / IP 15 / ISO 3016 Standard Test Method for Pour Point of Petroleum Products. Not performed in-house at SINTEF • ASTM D5949	• Performed by Intertek Laboratories (WestLab AS, Stavanger) • Phase Technology 70Xi Pour Point Analyser
Flash point (closed cup)	• ASTM D93: Pensky-Martens Closed Cup • ASTM D7094	• Pensky-Martens Closed Cup Petrotest PMA5 • Grabner MiniFlash FLP of FLPL Analyzer
Viscosity – temperature-sweep	• SINTEF SOP: Dynamic viscosity is measured over a temperature range from 50 down to 0 °C. at shear rates:10 s^{-1} (and 100 s^{-1}). Temperature rate: 1°C/min • Not performed at ECCC	• Anton Paar / Physica MCR 300 /302, PP50 system

Physical property	**Analytical method**	**Instrumentation**
Viscosity (at low temperatures, non-Newtonian behaviour of the oil).	- Viscosity is measured at specific a temperature (e.g. 2 °C)* at different shear rates: 1, 5, 10,50, 100, 500 and 1000 s^{-1}. Shear rate 10 s^{-1} is the main reporting viscosity number (30 sec at each shear). Ref: McDonagh et al, 1995 and SINTEF SOP.	- Anton Paar / Physica MCR 300 /302 / PP50 Rheometer - Paar Physica MC1 / MP 31 (field viscosimeter)
Viscosity for low-viscosity materials (<60 000 mPa.s) (dynamic/kinetic)	- ASTM 7042. Viscosity measurement performed at 15 °C.	- Anton Paar Stabinger Viscometer SVM 3000
Viscosity (for Newtonian and non-Newtonian behaviour of the oil at low and high temperatures (mPa.s)	- ECCC-ESTS in-house method is used for viscometer and rheometers instruments (rotor cup and plate -plate geometries). Viscosity is measured at 0 and 15 °C. For the Non-Newtonian oil, the viscosity is measured at three different shear rates (depending on the oil ranged from 0.0001 to 1000 1/s) at each temperature.	- HAAKE RS6000 Rheometer & HAAKE VTiQ Viscometer
Interfacial tension	- Pendant drop, (25 °C), over 5 min. equilibrium time	- KRUSS gmbH, drop shape syst. DSA 100.
	- ECCC-ESTS in- house methods is used for surface and interfacial tensions. They are determined by a pendant drop technique at air, water and saltwater interfaces at 0 and 15 °C.	- Krüss Drop Shape Analyzer DSA 100
Gas chromatographic analysis (GC/FID)	- The distribution of hydrocarbons (nC_5-nC_{40}) is analyzed by using a Gas Chromatograph coupled with a Flame Ionization Detector (GC-FID. (EPA method 8015)	- Agilent 6890N with a 30m DB1 column. Temp: program: 40°C (1 min) -6°/min.-330°C (10 min). 2.5 ml He /min.
	- In-house method (accredited by CALA)	- GC-FID (Agilent 7890 or higher)
True Boiling point / Distillation curve	- ASTM D 7169 Not performed in-house at SINTEF - Not performed at ECCC	- Simulated Distillation Gas Chromatography (SimDist GC) System. Performed by Intertek Laboratories (Sunbury Technology Centre, UK) -

**Reflecting cold water /arctic seawater temperature.*

Table 4.2 Analytical methods used to determine the chemical properties.

Chemical property	Analytical method	Test procedure
"Hard" asphaltenes (SINTEF) "Soft" asphaltenes (ECCC)	• IP 143 • ECCC-ESTS house method is using precipitation and gravimetric determination of "Soft" asphaltenes	• Precipitation in n-Heptane on "reflux for 1 hour • Asphaltenes are precipitated from the original oil by using excess n-pentane as the precipitating medium (30 mL n-pentane/g of oil).
Wax content	• Bridiè et al, 1980, Modified. • ECCC-ESTS house method is used for wax crystallization and gravimetric determination.	• Precipitation of the maltene fraction (de-asphalted) in a 1:1 2-MEK /DCM* solvent mixture at minus 10°C for 4 hours. 6-fold wt. of solvent to wt. of oil. • Waxes are separated by crystallization in a polar solvent. After quantification of resin, the remaining diluted maltene is rotary-evaporated. Then, it is filtered after mixing with 50 mL of 1:1 (v:v) dichloromethane (DCM)/methyl ethyl ketone (MEK). The flask, funnel, filtering flask, and 1:1 DCM/MEK are placed in the -30 °C freezer to chill overnight before use to be able to crystallize the wax
Sulfur content (%w/w)	• Not performed at SINTEF • ASTM4294	• Thermo Scientific, ARL Quant'X
Vapour pressure (kPa) (limited to low viscosity products only)	• Not Performed at SINTEF • ASTM D6378 used for calibration (pentane) and ASTM D6377 for sample analysis. Performed at 37.8 °C in 4:1 v:v.	• Grabner minivap VPXpert

**MEK: Methyl-ethyl-ketone (2-Butanone); DCM: Dichloromethane*

Table 4.3 Additional parameters that have been suggested by some of the participating laboratories.

Parameter	Analytical method	Test procedure
C, H, N (elemental analysis)	The German laboratory has experience with using the carbon/ Hydrogen (wt-ratio) in an oil to estimate amounts of aromatic compounds	• ASTM D5291.
Elements/metals *	The following metals are suggested: Aluminum Calcium Iron Nickel Silicon Sodium Vanadium Sulfur Copper	• ICP/MS or ICPAES (Inductively Coupled Plasma Atomic Emission Spectrometry).

* *There have been rumors that some of the new low sulfur fuels the oils have caused "catastrophic engine failure" due to remains of "cat fines" or "metal sand" consisting of aluminum and silicon oxide in the fuels.*

5 Chemical characteristics and toxicity testing of Water Accommodated Fraction (WAF)

Standard method for preparation of water accommodated fraction based on CROSERF Low Energy WAF (LE-WAF) is suggested (Aurand and Coelho, 2005). These guidelines were developed to standardize WAF preparation, laboratory exposures to aquatic organisms, and analytical chemistry measurements used to determine the acute toxicity of the water-soluble components in the oil. LE-WAF prepared in closed vessels with calm mixing (no vortex) of water below a surface layer of oil is regarded as a water solution of dissolved oil components.

The same WAF must be used to both chemical characteristics and toxicity testing. Make sure that enough water volume is prepared. For e.g. just chemistry and toxic unit, a 2 L WAF should be appropriate, if e.g. toxicity testing with an algae and a copepod are included, a 10 L WAF system is recommended (Figure 5.1). Target components are listed in Appendix A.3. Some examples of the span in WAF-concentrations and Toxic Unit values from previous projects at SINTEF with marine fuel oils are shown in Appendix A.4

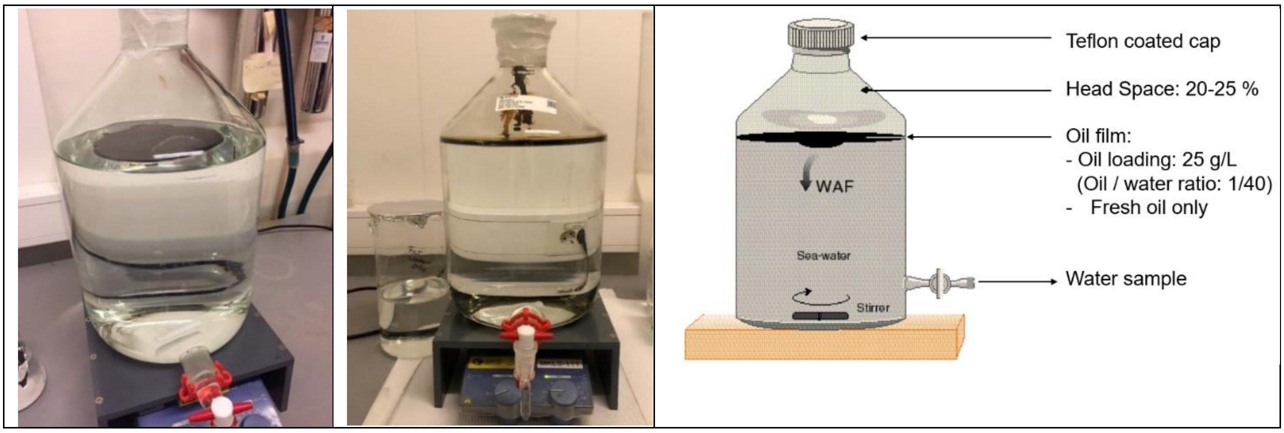


Figure 5.1 Set-up of the CROSERF systems used at SINTEF for preparation of Water Accommodated Fractions (WAF)

5.1 Preparation of water accommodated fraction (WAF)

A volume (9.25 L) of sterile filtered (0.2 μm) natural seawater is added to 10 L bottles giving water to air headspace ratio of 4 to 1. A single WAF is prepared using one oil-to-water loading of 1:40 (i.e. 25 g oil/L seawater). The oil is carefully applied to the water surface. The water is stirred gently with a magnetic stirrer (< 200 rpm) assuring that the oil film rest on the water surface without creating a vortex and without dispersing oil droplets into the water. The preparation should be carried out in darkness at low temperature (approximately 2 °C). Suggested mixing time is 72 hours (equilibrium time will depend on oil type). As suggested by US-EPA: we should be flexible in the WAF-vessel dimension, while maintaining the loading rations and headspace volume. E.g. US-EPA is using WAF-vessels with inserted glass tube sampling of WAF.

Samples for chemical analysis and toxicity testing are collected in glass vials and bottles with Teflon lined caps, allowing no headspace to minimize the loss of volatiles. Samples for chemical analysis were acidified (hydrochloric acid to pH<2) immediately after sampling to avoid biodegradation during storage (in refrigerator). The toxicity tests are initiated the same day as sampling, water samples for chemistry analysis must be extracted within 2 weeks.

5.2 Chemical composition of the WAFs

5.2.1 Sample preparation

Surrogate internal standards (SIS, *o*-terphenyl, naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{12}, phenol-d_6, 4-methylphenol-d_8) are added to the water samples prior to processing, and recovery internal standards (RIS, 5α-androstane, fluorene-d_{10}, and acenaphthene-d_{10}) are added prior to analysis on GC/FID (gas chromatography/flame ionization detection) and GC/MS (gas chromatography/mass spectrometry).

For analyses of semi-volatile organic compounds (SVOC) and total petroleum hydrocarbons (TPH), the water samples are spiked with the appropriate surrogate internal standards and serially extracted with dichloromethane (DCM), thereby following a modification of EPA method 3510C (US EPA, 2015). The combined extracts are dried with sodium sulphate and concentrated to approximately 1 mL using a Zymark Turbovap® 500 Concentrator. The final extract is spiked with the appropriate recovery internal standards and analyzed on GC/FID and GC/MS.

5.2.2 Chemical analysis

The samples are analyzed for SVOC (decalins, PAHs and phenols) using GC/MS, for TPH using GC/FID, and for volatile organic compounds (VOC, C_5-C_9), including BTEX (benzene, toluene, ethylbenzene, and xylenes), by use of P&T GC/MS (Purge and Trap Gas Chromatography Mass Spectrometry). A list of all target analytes is shown in Appendix A.3. This list includes the recommended analytes given by Singer et al. (2000) and is a typical standard list for the target compounds used during post-oil spill damage assessments.

The GC/FID analyses are performed according to a modification of EPA Method 8015D (US EPA, 2015). TPH (resolved plus unresolved petroleum hydrocarbons) is quantified by the method of internal standards using the baseline corrected total area of the chromatogram and the average response factor for the individual C_{10} to C_{36} n-alkanes.

The semi-volatiles are quantified by modifications of EPA Method 8270E (US EPA, 2018). The mass spectrometer is operated in the selective ion monitoring mode to achieve optimum sensitivity and specificity. The quantification of target compounds is performed by the method of internal standards, using average response factors (RF) for the parent compounds. The PAH and phenol alkyl homologues are quantified using the straight baseline integration of each level of alkylation and the RF for the respective parent PAH compound. The response factors are generated for all targets and surrogates versus fluorene-d_{10}.

A total of 35 target volatile organic compounds (VOC) in the C_5 to C_{10} range are determined by Purge and Trap (P&T) GC/MS using a modification of EPA method 8260D (US EPA, 2018). The samples are spiked with SIS (toluene-d_8 and ethylbenzene-d_8) and RIS (chlorobenzene-d_5). The quantification of individual compounds is performed by using the RFs of the individual compounds relative to the internal standards. All standards and samples are analyzed in a full scan mode.

5.3 Toxicity testing

It is agreed that the copepod *Acartia tonsa* is the common test specie for all laboratories. A second, more Arctic relevant specie could also be included as a part of the screening.

Calculation of Toxic Unit should be mandatory for all laboratories preparing WAFs.

If some of the laboratories involved have not established the suggested toxicity test methodologies, it must be evaluated weather those tests should be performed by laboratories that have the test methods implemented.

5.3.1 Acute toxicity to *Acartia tonsa*

Potential effects on primary consumers will be assessed with the marine pelagic copepod *Acartia tonsa*. The bioassays are performed as a modification of ISO/DIS 14669 (1999) with lethal immobilization (LC50 or LC10) as the endpoint. The original protocol is not designed for testing of solutions containing volatiles and has been adapted. The adaptation initiated for testing of WAFs is replacing the recommended test vessels (semi-open flasks (50 mL) with 25 mL test solution) with Erlenmeyer flasks (100 mL) filled to the rim. The flasks are sealed with glass stoppers to avoid loss of volatiles. All bioassays are performed with a fixed number of vessels and a dilution series of WAF ranging from undiluted (100%) to 4% WAF in sea water with a spacing factor of 1.7 and 4 parallel vessels for each dilution. Eight vessels filled with seawater are used as controls.

After preparation of the exposure solutions and control vessels, 10-15 copepodite V or adult *A. tonsa* are transferred to each vessel. After all vessels are supplied with animals, the flasks are left in a temperature-controlled room at nominal 20±2°C under a light regime comparable to the culturing conditions. The vessels should be inspected daily for the next 2 days (48 hours) for immobilized animals and recording of temperature. At the end of exposure, the pH and saturation of oxygen are measured in one vessel in each of the exposure dilutions and in two control vessels.

The calculated values are corrected for mortality in the control series and the effect is calculated within the span 0-100% by constraining the top and bottom of the concentration-effect curve to 100 and 0.

The acute toxicity, expressed as LC_{50}, can be given in percent dilution of the undiluted (or 100%) WAF (relative toxicity, LC_{50} in percent (%)), or as normalized to the total WAF concentration (specific toxicity, LC_{50} in mg/L or ppm). Low values of LC_{50} indicate a high toxicity, while a high value of LC_{50} corresponds to lower toxicity. The two approaches to express toxicity have different applications: Specific toxicity expresses the toxicity of the WAF of a selected oil and test condition and is associated with the concentration of the WAF. Relative toxicity expresses a given dilution to obtain a predefined effect (e.g. LC_{50}) and can be used for comparing the toxicity of WAFs from different oils with different WAF compositions and hence, solubility and chemical composition. Results should be presented both as relative and specific toxicity.

5.3.2 Acute toxicity of optional Arctic species

SINTEF has selected the copepod *Calanus finmarchicus* as a second organism as this copepod has been used for toxicity testing to WAFs of a large number of oils. The same ISO protocol is modified, but the toxicity testing is performed at 10 °C.

5.3.3 Calculation of toxic units (TU)

In the WAFs from petrogenic products, the compounds of concern for toxicity assessment are typically limited to the VOCs and SVOCs, which are structurally classified as Type I narcotics. The target lipid model of narcotic toxicity demonstrates that the acute toxicities of these chemicals vary and are correlated with the octanol-water partition coefficient (K_{ow}) such that LC_{50} decreases with increasing K_{ow} (DiToro et al. 2007).

A regression model for the relationship between the acute toxicity and K_{ow} of target chemicals to estimate the threshold toxic concentration of each compound is used by several authors. It appears to be a linear negative relationship between the log of the median lethal concentration (LC_{50}) to the organisms and the log K_{ow} of compounds exhibiting toxicity by non-specific narcotic action (e.g. McCarty et al. (1992 and 1993) and Di Toro et al. (2007), Neff et al. (2005)). The relationship is described by a linear regression of log LC_{50} (mM/L) against log K_{ow} for each compound:

$$\log LC_{50} = m * \log (K_{ow}) + b \qquad (1)$$

where m is the slope, and b is the intercept of the equation. The slope is related to the partition behavior of the chemical and should therefore be constant from species to species. The y-intercept *b* can be interpreted as the lipid-normalized critical body burden corresponding to the observed endpoint, such as 50% mortality for the LC_{50} for the specific organism being considered. It is variable by species and likely life stage and condition (McGrath and DiToro, 2009).

There are several ways to predict toxicity, and here we have chosen the approach described in e.g. McCarty et al. (1992, 1993) and Neff et al. (2005). The acute toxicity of individual MAHs and PAHs were estimated by the regressions and are given in Table 5.1:

MAHs (McCarty et al.,1992): $\log LC_{50}\ (\text{mM}) = -0.9 * \log (K_{ow}) + 1.71$ (2)

PAHs (Neff et al.,2005): $\log LC_{50}\ (\text{mM}) = -1.162 * \log (K_{ow}) + 2.496$ (3)

The acute toxicity of phenols was estimated with the regression of McCarty et al. (1993) for polar narcosis:
Phenols: $\log LC_{50}\ (\text{mM}) = -0.55 * \log (K_{ow}) + 0.064$ (4)

To calculate TU, LC_{50}s must be given in mg/L:
$LC_{50}\ (\text{mg/L}) = LC_{50}\ (\text{mM}) * M_w$ (M_w = molecular weight) (5)

The predicted toxicities of the individual compounds in the WAFs are given in Table 5.1. They are assumed to be additive and toxic unit (TU) for each compound was summed to produce a toxic unit, which is equivalent to an estimate of the acute toxicity of each WAF. The TU for each component (i) is calculated in the WAF system:

$$TU_i = C_i/LC_{50i} \qquad (6)$$

C_i is the concentration of component *i* in the WAF and LC_{50i} is the estimated acute toxicity for component *i* (Table 5.1) calculated from equations (2) to (4). The estimated toxicity of the total WAF is determined by the sum of the TUs of all component groups. A value of TU > 1 implies toxicity, i.e. the WAF is expected to cause 50% mortality in the test organisms.

The sum TU computed represents the TUs from all measured hydrocarbons in the exposure system. UCM (unresolved complex mixture), which could contribute to more than 90% of the total WAF concentration in e.g. WAFs of heavily weathered oils, is not included in TU calculations.

Table 5.1 Predicted LC_{50} based on logK_{OW}. Equation for MAH is from McCarty (1992), PAHs from Neff et al. (2002), and phenols from McCarty (1993).

Compound	Mw	log Kow	LC_{50} (mg/L)
Decalin	138	5.05	**0.059**
C1-decalins	152	5.63	**0.014**
C2-decalins	166	6.19	**0.0033**
C3-decalins	180	6.75	**0.0008**
C4-decalins	194	7.28	**0.0002**
Benzo(b)thiophene	134	3.13	**9.68**
Naphthalene	128	3.30	**5.87**
C1-naphthalenes	142	3.79	**1.76**
C2-naphthalenes	156	4.24	**0.58**
C3-naphthalenes	170	4.73	**0.17**
C4-naphthalenes	184	5.22	**0.05**
Biphenyl	154	3.94	**1.27**
Acenaphthylene	152	3.44	**4.79**
Acenaphthene	154	3.88	**1.50**
Dibenzofuran	168	3.95	**1.35**
Fluorene	166	3.93	**1.41**
C1-fluorenes	180	4.37	**0.47**
C2-fluorenes	194	4.82	**0.15**
C3-fluorenes	208	5.32	**0.04**
Phenanthrene	178	4.58	**0.27**
Anthracene	178	4.55	**0.29**
C1-phenanthrenes	192	5.04	**0.08**
C2-phenanthrenes	206	5.45	**0.03**
C3-phenanthrenes	220	5.91	**0.01**
C4-phenanthrenes	234	6.36	**0.003**
Dibenzothiophene	184	4.37	**0.48**
C1-dibenzothiophenes	198	4.86	**0.14**
C2-dibenzothiophenes	212	5.33	**0.043**
C3-dibenzothiophenes	226	5.81	**0.013**
C4-dibenzothiophene	240	6.43	**0.0025**
Fluoranthene	202	5.19	**0.059**
Pyrene	202	5.13	**0.069**
C1-fluoranthenes/pyrene	216	5.26	**0.052**
C2-fluoranthenes/pyrene	230	5.56	**0.025**
C3-fluoranthenes/pyrene	244	6.38	**0.003**
Benz(a)anthracene	228	5.74	**0.015**
Chrysene	228	5.78	**0.014**
C1-chrysenes	242	6.19	**0.0049**
C2-chrysenes	256	6.59	**0.0018**
C3-chrysenes	270	5.97	**0,0098**
C4-chrysenes	284	7.42	**0.0002**
Benzo(b)fluoranthene	252	5.57	**0.027**
Benzo(k)fluoranthene	252	6.40	**0.0029**
Benzo(e)pyrene	252	6.45	**0.0025**
Benzo(a)pyrene	252	6.41	**0.0028**
Perylene	252	6,45	**0.0025**
Indeno(1,2,3-c,d)pyrene	276	6.16	**0.0060**
Dibenz(a,h)anthracene	278	7.13	**0.0005**
Benzo(g,h,i)perylene	276	7.47	**0.0002**
Phenol	94	1,50	**16.3**
C1-Phenols	108	1.98	**10.2**
C2-Phenols	122	2.35	**7.21**
C3-Phenols	136	2.70	**5,16**
C4-Phenols	150	3,31	**2.63**
C5-phenols	164	3.50	**2.26**
Benzene	78	1.94	**71.8**
Toluene	92	2.51	**26.0**
Ethylbenzene	106	3.01	**10.6**
m-xylene	106	3.04	**9.98**
p-xylene	106	3.04	**9.98**
o-xylene	106	2.95	**12.0**
C3-benzenes	120	3.58	**3.69**

6 Fingerprinting of the fuel oils according to the OSINET / CEN protocols

The recommended forensic method for characterizing and identifying the source of oil spills in the environment as a result from accidents or intentional discharges is the CEN document CEN/TR 15522-2:2012: "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, 2012). The methodology has been revised recently, and CEN has published a ballot version of the draft European Standard prEN 15522-2 (ballot ends March 6, 2021). More than 40 laboratories world-wide have established and follow this methodology.

As the CEN-method is quite advanced, it is only recommended for the laboratories that already has implemented the methodology (typically a member of the Bonn Agreement Oil Spill Identification Network of Experts (OSINET). More information about OSINET can be found on
http://www.bonnagreement.org/osinet.

For the screening purpose in the present project, a "lighter" version of the method is proposed.
Several of the OSINET-members have access to the online program "Computerized Oil Spill Identification, called COSI, which consists of a large database with several thousands of oils and an automatic evaluation system for the detailed comparison of oil samples (described in Dahlmann and Kienhuis, 2016). COSI is in accordance with CEN (2012) and includes selected diagnostic ratios and ion chromatograms.

It is suggested that the oil samples are analyzed in accordance with CEN (2012) and uploaded in COSI to simplify the reporting of oil fingerprinting. Laboratories that do not have access to COSI can use their inhouse method to calculate the suggested ratios. The recommended ratios are given in Table 6.1. Description of the components and ratios recommended are detailed in CEN (2012) and Kienhuis et al. (2016).

The following parameters are suggested:

- Screening GC/FID
    - GC chromatograms (Example in Figure 6.1)
    - Calculation of the isoprenoid ratios (from COSI)
- GC/MS SIM-analysis (data from COSI)
    - Selected ion chromatograms (Figure 6.2):
        - Hopanes (m/z 191)
        - Triaromatic steranes (m/z 231)
        - C4-phenanthrenes (m/z 234)
        - C1-phenenthrenes (m/z 192)
        - C1-dibenzothiophenes (m/z 198)
        - C1-methylfluoranenes/pyrenes (m/z 216)
- Selected diagnostic ratios (in Table 6.1)

In addition, some of the PAHs containing sulphur are included to see if they can be used to get an indication of the oils sulphur content (ultralow, low, or "high"). A few ratios are suggested, but as this approach has not been investigated yet, the present project and an the ongoing IMAROS (EU-project) will be used to evaluate if the suggested ratios are informative and robust enough for this purpose.

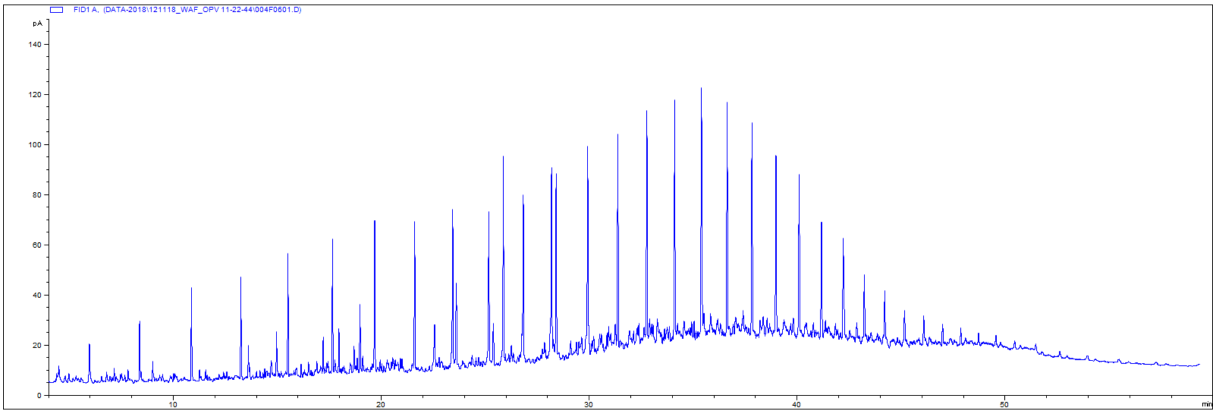


Figure 6.1 Example of GC chromatogram (GC-FID).

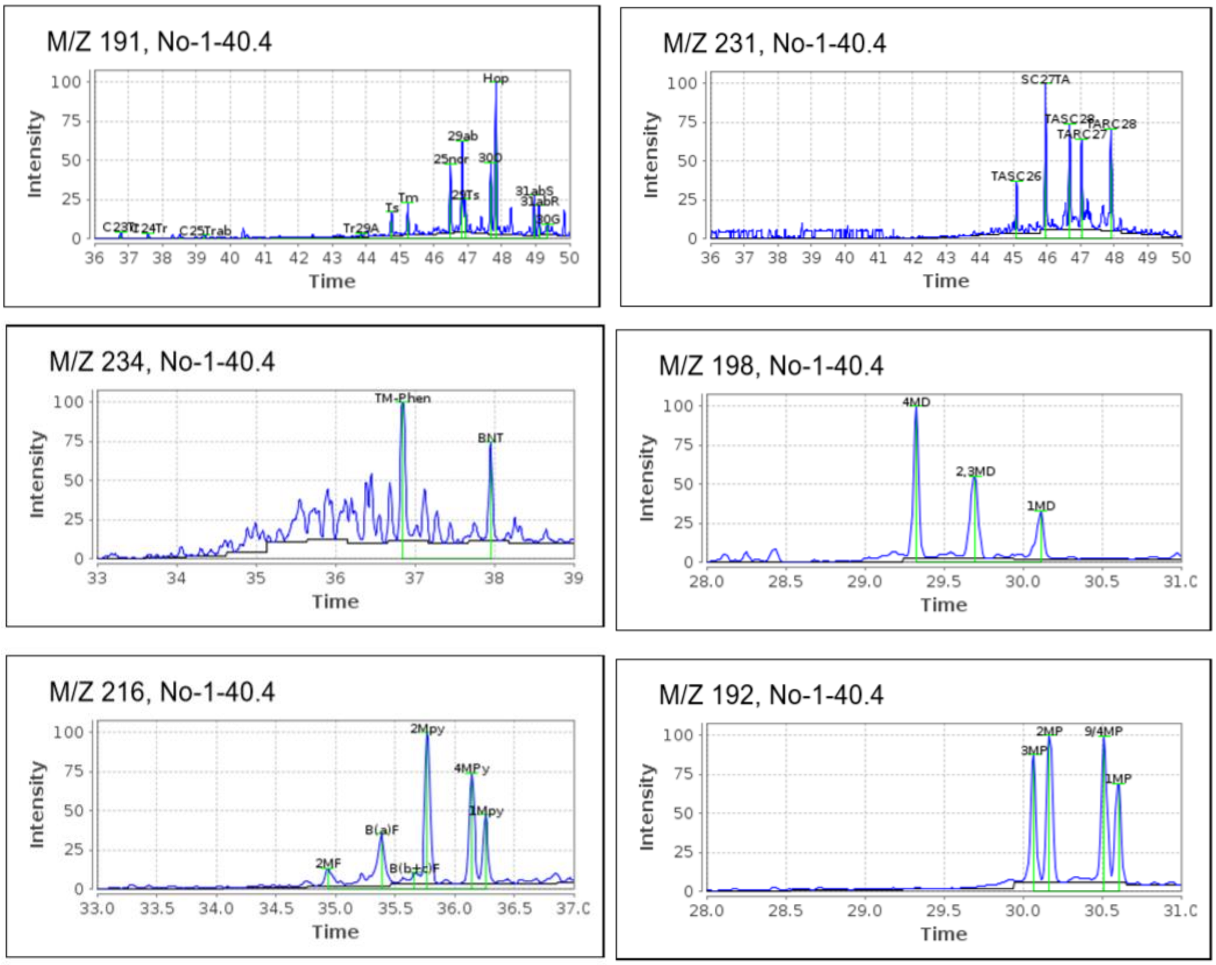


Figure 6.2 Examples of ion chromatograms from COSI (by GC-MS, conditions specified by Dahlmann and Kienhuis, 2016) .

Table 6.1 Overview of diagnostic ratios to be calculated for screening fingerprinting analysis.

	m/z	Ratios	Source
GC/FID		C17/pristane	COSI
		C18/phytane	COSI
		Pristane/phytane	COSI
GC/MS	191	Ts/30ab	COSI
	191	Tm/30ab	COSI
	191	28ab/30ab	COSI
	191	29ab/30ab	COSI
	191	30O/30ab	COSI
	191	31abS/30ab	COSI
	191	30G/30ab	COSI
	217	27dbR/27dbS	COSI
	218	27bb/29bb	COSI
	231	TASC26/RC26+SC27	COSI
	231	TASC28/RC26+SC27	COSI
	231	TARC27/RC26+SC27	COSI
	231	TARC28/RC26+SC27	COSI
	192	2MP/1MP	COSI
	192	MA/1MP	COSI
	198	4MD/1MD	COSI
	216	2MF/4MPy	COSI
	216	B(a)F/4MPy	COSI
	216	B(b+c)F/4MPy	COSI
	216	2MPy/4MPy	COSI
	216	1MPy/4MPy	COSI
	234	Retene/TMPhe	COSI
	234	BNT/TMPhe	COSI
		Sulphur content	
GC/MS	198/191	1M-DBT/30ab	Manual integration
	198/191	4M-DBT/30ab	Manual integration
	234/191	BNT/30ab	Manual integration
		If 30ab is small or not present (lighter products)	
	198/192	1M-DBT/1MP	Manual integration
	198/192	4M-DBT/1MP	Manual integration
	234/192	BNT/TMPhe	Manual integration
		Optional ratios sulphur content	
	212/206	C2-DBT/C2-Phe	Manual integration
	212/206	C3-DBT/C2-Phe	Manual integration
	234/206	BNT/C2-Phe	Manual integration
	162/206	C2-BT/C2-Phe	Manual integration

7 Reporting and presentation of results

To obtain a common and standardized format for the presentation of results from the participating laboratories, it will be worked out customized spreadsheets (Excel templates) for standardizing the reporting of the results from the different participating laboratories, including:

- An overview table of the Physical properties (see example in table A.2.3)
- Figures / graphs of e.g.:
    - Distillation curve (see example in A.2.1)
    - Viscosity Temperature sweep (see example in A.2.4)

- Tables with
    - TPH, SVOC and VOC concentrations in the WAF systems (see target list in A.3)
    - Toxic unit of the WAF systems (individual components and total TU, listed in *Table **5.1***)
    - Results from acute toxicity tests, expressed as relative and specific toxicity (EC50 and/or LC50)

- GC-FID chromatograms (see example in A.2.2) have to be produced by the specific laboratory
    - Oils
    - WAFs

- Oil spill forensics
    - Diagnostic ratios given in Table 6.1
    - GC chromatograms, example shown in Figure 6.1
    - Ion chromatograms, examples shown in Figure 6.2

8 References

ASTM D93 (Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester)

ASTM D97 (Standard Test Method for Pour Point of Petroleum Products)

ASTM E203 (Standard Test Method for Water Using Volumetric Karl Fischer Titration)

ASTM D1250-80 (Standard Guide for Use of the Petroleum Measurement Tables.

ASTM D4052 (Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter)

ASTM D4294 (Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry)

ASTM D5002 (Standard Test Method for Density, Relative Density, and API Gravity of Crude Oils by Digital Density Analyzer)

ASTM D5291:2012 (Standard test method for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants).

ASTM D5949 (Standard Test Method for Pour Point of Petroleum Products (Automatic Pressure Pulsing Method))

ASTM D6377 (Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCRx (Expansion Method))

ASTM D6378 (Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)).

ASTM D7042 (Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity))

ASTM D7094 (Standard Test Method for Flash Point by Modified Continuously Closed Cup (MCCCFP) Tester)

ASTM D7169 (Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography)

ASTM E203 (Standard Test Method For Water Using Volumetric Karl Fischer Titration)

IP 143 (Determination of asphaltenes (heptane insolubles) in crude petroleum and petroleum products)

Aurand, D., Coelho G. (2005). Cooperative Aquatic Toxicity Testing of Dispersed Oil and the "Chemical Response to Oil Spills: Ecological Research Forum (CROSERF)". Ecosystem Management & Associates, Inc., Lusby, MD. Technical report 07-03, 105 pages + Appendices.

Bridié A.L., T.H. Wanders and W.V. Zegweld, H.B. den Heijde (1980). Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse. Marine Poll. Bull., vol 11, pp. 343-348.

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/TR 15522-2:2012.

Dahlmann, G., Kienhuis, P. (2016). Development and application of online computerized oil spill identification – COSIWeb. In Stout and Wang (eds): Standard Handbook Oil Spill Environmental Forensics. Fingerprinting and Source Identification. Second Edition. Elsevier Academic Press, ISBN 978-0-12-809659-8, pp. 729-745.

DiToro, D.M., McGrath, J.A, Stubblefield, W.A. (2007). Predicting the toxicity of neat and weathered crude oil: Toxic potential and the toxicity of saturated mixtures. Environmental Toxicity and Chemistry. 26: 24-36.

Hellstrøm, K.C. (2017). Weathering properties and toxicity of marine fuel oils. Summary report. SINTEF report OC2017-A124, ISBN 978-8-27-174299-7.

ISO [International Organization for Standardization] (1999). Water quality - Determination of acute lethal toxicity to marine copepods (Copepoda, Crustacea). ISO 14669:1999.

ISO (2017). Petroleum products — Fuels (class F) — Specifications of marine fuels. ISO 8217:2017.

Kienhuis, P.G.M., Hansen, A.B., Faksness, L.G., Stout, S.A. Dahlmann, G. (2016). CEN methodology for oil spill identification. In Stout and Wang (eds): Standard Handbook Oil Spill Environmental Forensics. Fingerprinting and Source Identification. Second Edition. Elsevier Academic Press, ISBN 978-0-12-809659-8, pp. 685-728.

McCarty, L.S., Mackay, D., Smith, A.D., Ozburn, G.W., Dixon, D.G. (1992). Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: Neutral narcotic organics. Environmental Toxicology and Chemistry 11, 917-930.

McCarty, L.S., Mackay, D., Smith, A.D., Ozburn, G.W., Dixon, D.G. (1993). Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: Polar narcotic organics. Ecotoxicology and Environmental Safety. 25, 253-270.

McDonagh, M., Hokstad, J. N., Nordvik, A. B. (1995). "Standard procedure for viscosity measurement of water-in-oil emulsions". Marine Spill Response Corporation, Washington, D.C. MRSC Technical Report Series 95-030, 36 p.

McGrath, J.A., DiToro, D.M. (2009). Validation of the target lipid model for toxicity assessment of residual petroleum constituents: Monocyclic and polycyclic aromatic hydrocarbons. Environ. Toxicol. Chem. 28: 1130-1148.

Neff, J.M., Stout, S.A., Gunster D.G. (2005). Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: Identifying sources and ecological hazard. Integr. Environ. Assess. Manag. 1 (1): 22-33.

Sørheim, K., Daling, P.S., Cooper, D., Buist, I., Faksness, L.G., Altin, D., Pettersen, T.A., Bakken, O.M. (2020). Characterization of Low Sulfur Fuel Oils (LSFO) – A new generation of marine fuel oils. SINTEF report OC2020 A-050, ISBN 978-82-7174-385-7.

US EPA, Method 3510C (2015). Separatory Funnel Liquid-Liquid Extraction. https://www.epa.gov/sites/production/files/2015-12/documents/3510c.pdf

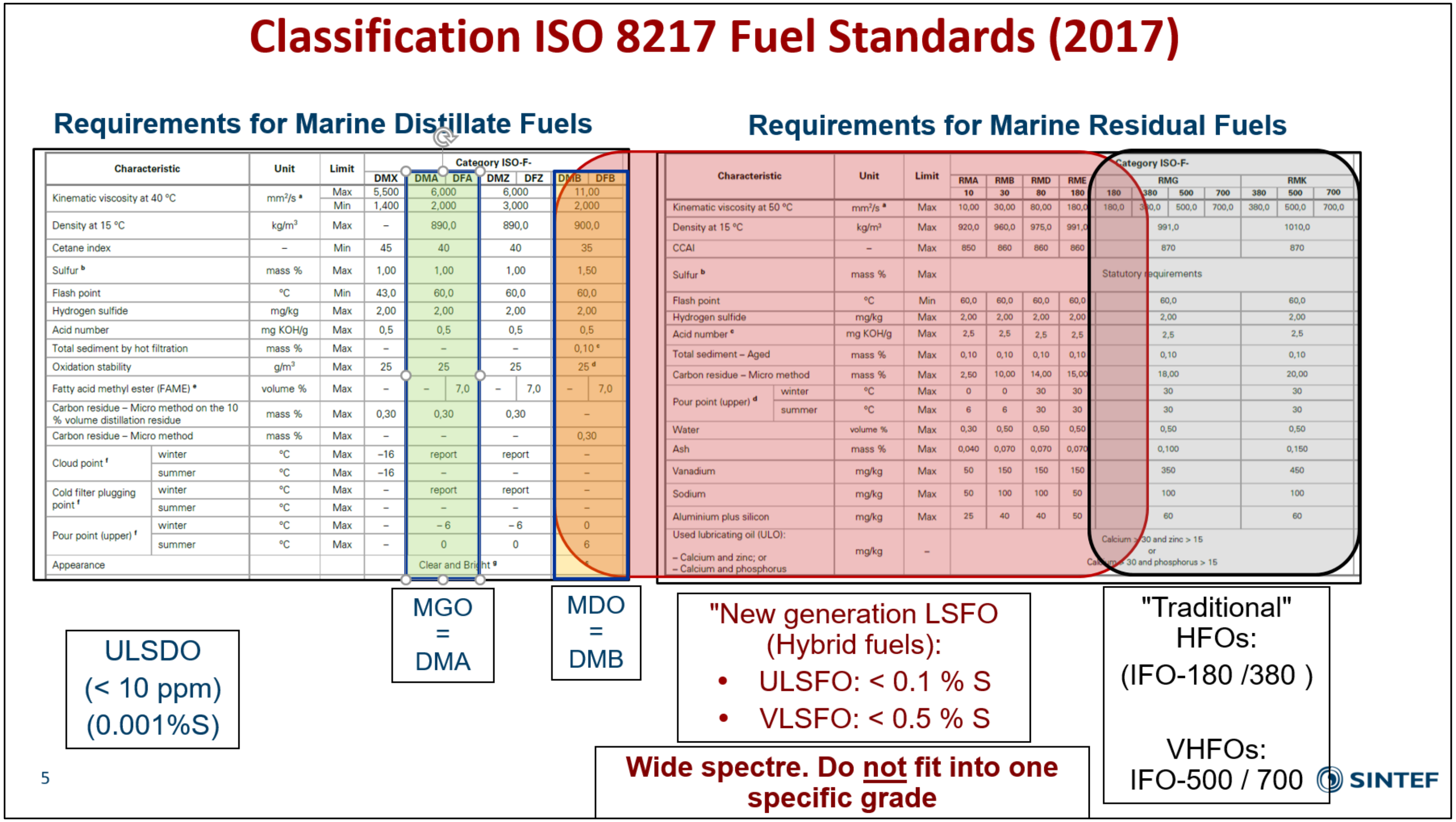
US EPA, Method 8260D (2018). Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS). https://www.epa.gov/sites/production/files/2018-06/documents/method_8260d_update_vi_final_06-11-2018.pdf

US EPA, Method 8270E (2018). Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC-MS). https://www.epa.gov/sites/production/files/2020-10/documents/method_8270e_update_vi_06-2018_0.pdf

US EPA, Method 8015D (2015). Non-halogenated organics using GC/FID. https://www.epa.gov/sites/production/files/2015-12/documents/8015d_r4.pdf

Appendices

A.1 Classification of Marine fuel oils according to ISO 8217 Fuel Standards



Classification ISO 8217 Fuel Standards (2017)

Requirements for Marine Distillate Fuels

Characteristic		Unit	Limit	DMX	DMA	DFA	DMZ	DFZ	DMB	DFB
				Category ISO-F-						
Kinematic viscosity at 40 °C		mm^2/s [a]	Max	5,500	6,000		6,000		11,00	
			Min	1,400	2,000		3,000		2,000	
Density at 15 °C		kg/m^3	Max	–	890,0		890,0		900,0	
Cetane index		–	Min	45	40		40		35	
Sulfur [b]		mass %	Max	1,00	1,00		1,00		1,50	
Flash point		°C	Min	43,0	60,0		60,0		60,0	
Hydrogen sulfide		mg/kg	Max	2,00	2,00		2,00		2,00	
Acid number		mg KOH/g	Max	0,5	0,5		0,5		0,5	
Total sediment by hot filtration		mass %	Max	–	–		–		0,10 [c]	
Oxidation stability		g/m^3	Max	25	25		25		25 [d]	
Fatty acid methyl ester (FAME) [e]		volume %	Max	–	–	7,0	–	7,0	–	7,0
Carbon residue – Micro method on the 10 % volume distillation residue		mass %	Max	0,30	0,30		0,30		–	
Carbon residue – Micro method		mass %	Max	–	–		–		0,30	
Cloud point [f]	winter	°C	Max	–16	report		report		–	
	summer	°C	Max	–16	–		–		–	
Cold filter plugging point [f]	winter	°C	Max	–	report		report		–	
	summer	°C	Max	–	–		–		–	
Pour point (upper) [f]	winter	°C	Max	–	– 6		– 6		0	
	summer	°C	Max	–	0		0		6	
Appearance					Clear and Bright [g]				[illegible]	

Requirements for Marine Residual Fuels

Characteristic		Unit	Limit	RMA	RMB	RMD	RME	RMG				RMK		
				Category ISO-F-										
				10	30	80	180	180	380	500	700	380	500	700
Kinematic viscosity at 50 °C		mm^2/s [a]	Max	10,00	30,00	80,00	180,0	180,0	380,0	500,0	700,0	380,0	500,0	700,0
Density at 15 °C		kg/m^3	Max	920,0	960,0	975,0	991,0	991,0				1010,0		
CCAI		–	Max	850	860	860	860	870				870		
Sulfur [b]		mass %	Max	Statutory requirements										
Flash point		°C	Min	60,0	60,0	60,0	60,0	60,0				60,0		
Hydrogen sulfide		mg/kg	Max	2,00	2,00	2,00	2,00	2,00				2,00		
Acid number [c]		mg KOH/g	Max	2,5	2,5	2,5	2,5	2,5				2,5		
Total sediment – Aged		mass %	Max	0,10	0,10	0,10	0,10	0,10				0,10		
Carbon residue – Micro method		mass %	Max	2,50	10,00	14,00	15,00	18,00				20,00		
Pour point (upper) [d]	winter	°C	Max	0	0	30	30	30				30		
	summer	°C	Max	6	6	30	30	30				30		
Water		volume %	Max	0,30	0,50	0,50	0,50	0,50				0,50		
Ash		mass %	Max	0,040	0,070	0,070	0,070	0,100				0,150		
Vanadium		mg/kg	Max	50	150	150	150	350				450		
Sodium		mg/kg	Max	50	100	100	50	100				100		
Aluminium plus silicon		mg/kg	Max	25	40	40	50	60				60		
Used lubricating oil (ULO): – Calcium and zinc; or – Calcium and phosphorus		mg/kg	–	Calcium > 30 and zinc > 15 or Calcium > 30 and phosphorus > 15										

ULSDO
(< 10 ppm)
(0.001%S)

MGO
=
DMA

MDO
=
DMB

"New generation LSFO
(Hybrid fuels):
- ULSFO: < 0.1 % S
- VLSFO: < 0.5 % S

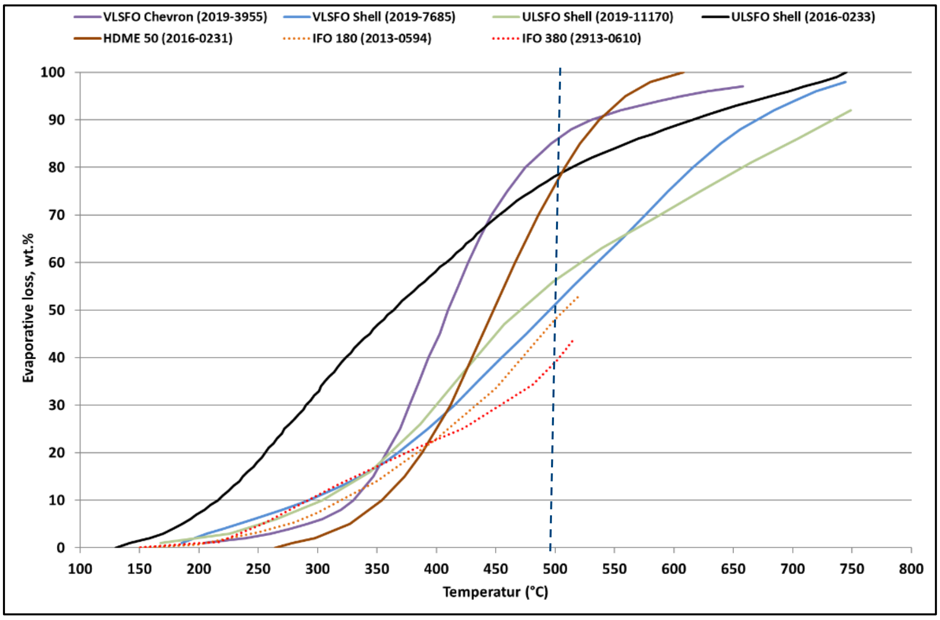
"Traditional"
HFOs:
(IFO-180 /380)

VHFOs:
IFO-500 / 700

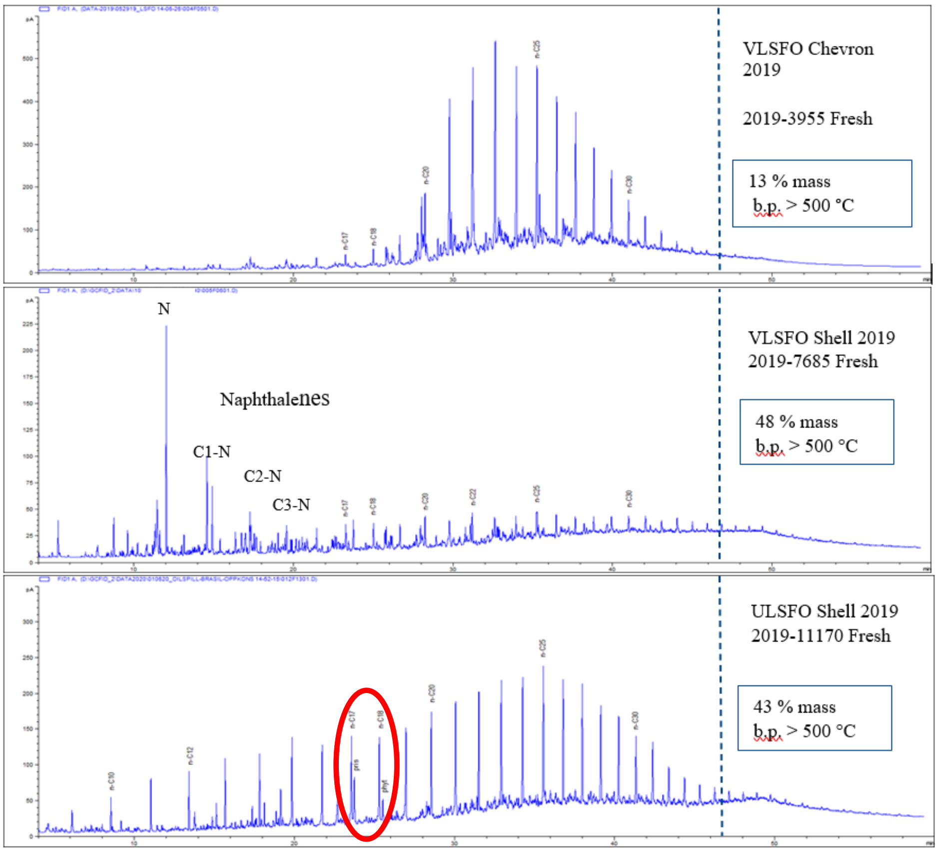
Wide spectre. Do <u>not</u> fit into one specific grade

A.2 Example of presentation of test results

A.2.1 Distillation curves, True Boiling Point (TBP) by GC-Sim.Dist



A.2.2 GC-FID Chromatograms

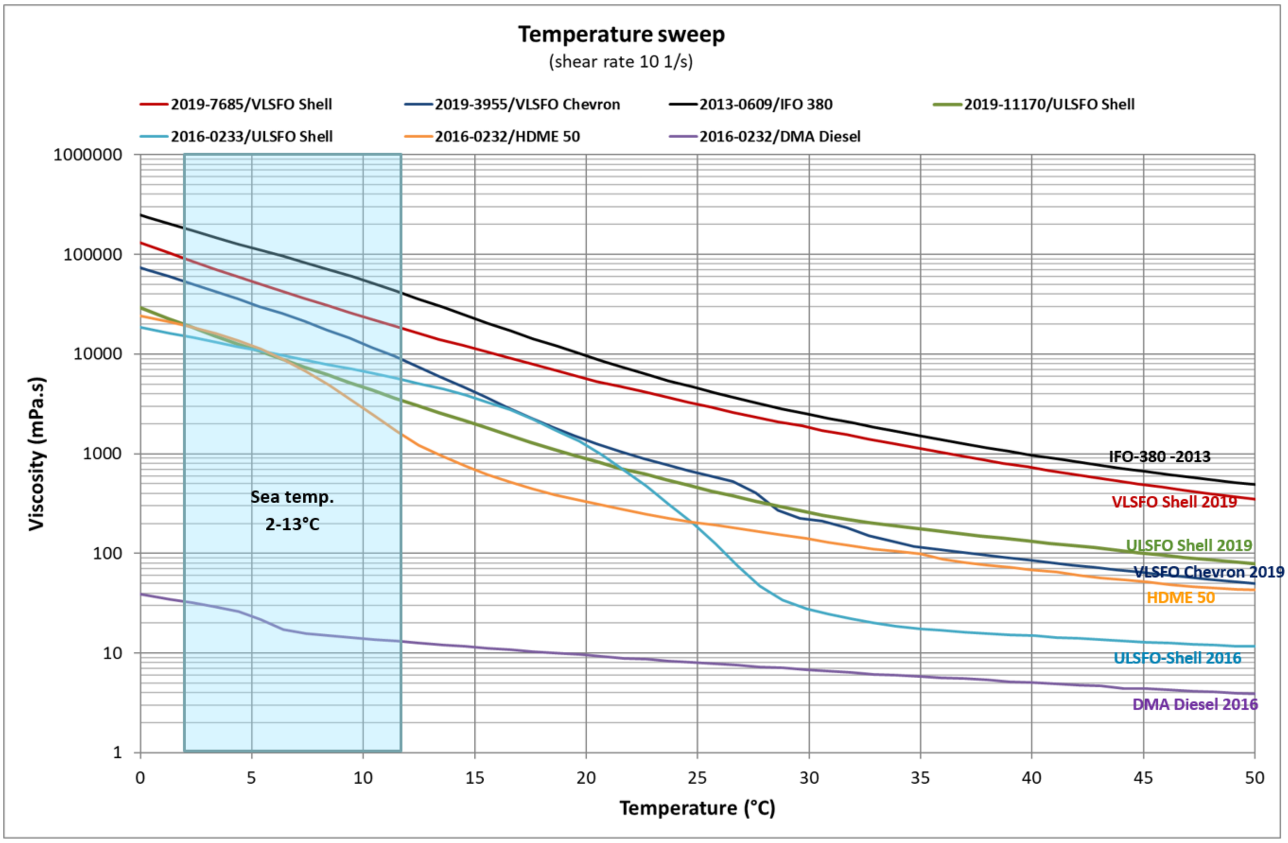


A.2.3 Example of overview table of physico-chemical properties (fresh non-weathered oil samples)

Oil name / (SINTED ID no.)	Asph (wt.%)	Wax (wt.%)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 2°C $10s^{-1}$	Visc. (mPa.s) 2°C, $100s^{-1}$	IFT (mN /m)
VLSFO A (2019-3955)	0.44	4.5	0.989	109	9	71 236	28 399	n.a.
VLSFO B (2019-7685)	4.8	4.9	0.990	100	3	132 46	77 638	n.a.
ULSFO A (2019-11170)	0.14	20.7	0.917	85	24	111 800	21 017	n.a.

Average values of 1-3 parallels

A.2.4 Temperature sweep viscosity measurements

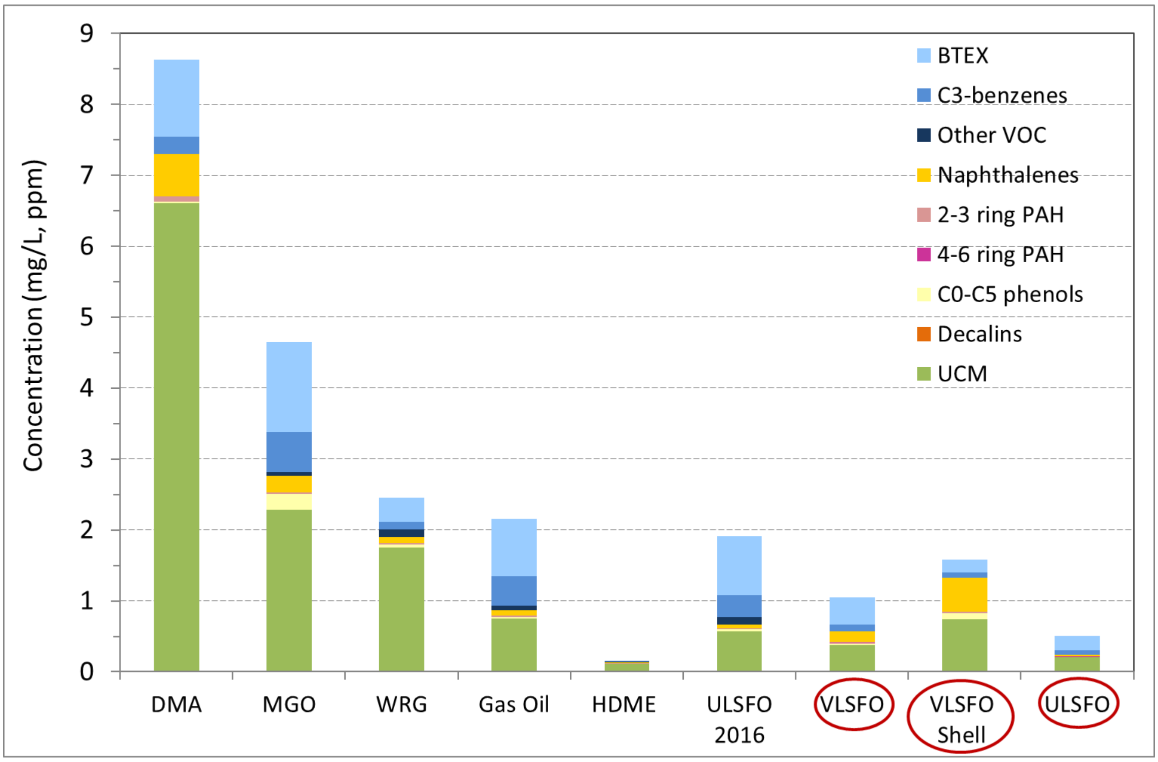


A.3 Target analytical components (in the oils and WAFs)

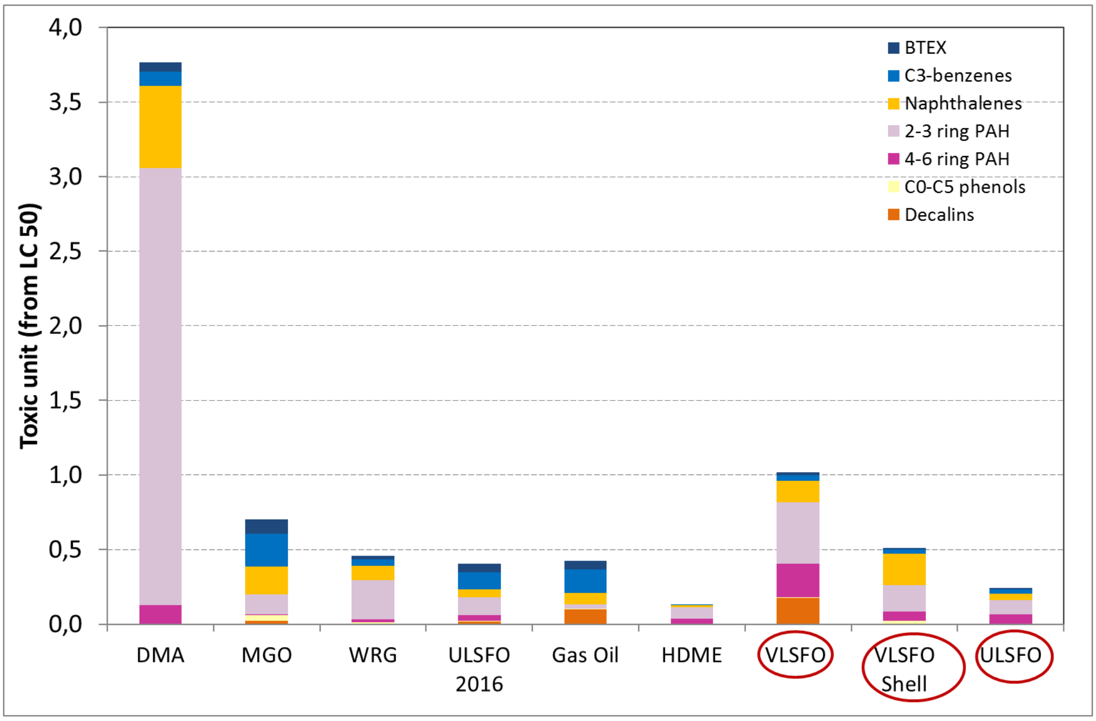
Target organic analytes (SVOC: Semi volatile organic compounds, VOC: Volatile organic compounds, TPH: Total petroleum hydrocarbons, UCM. Unresolved organic materials).

	Compound	Abb	Group	Compound	Abb
Decalins	Decalin	DE	C0-C5 phenols	Phenol	PH
	C1-decalins	DE1		C1-phenols	PH1
	C2-decalins	DE2		C2-phenols	PH2
	C3-decalins	DE3		C3-phenols	PH3
	C4-decalins	DE4		C4-phenols	PH4
Naphthalenes	Naphthalene	N		C5-phenols	PH5
	C1-naphthalenes	N1	Other VOC	Isopentane	
	C2-naphthalenes	N2		n-C5 (Pentane)	
	C3-naphthalenes	N3		Cyclopentane	
	C4-naphthalenes	N4		2-methylpentane	
2-3 ring PAHs	Benzo(b)thiophene	BT		3-methylpentane	
	Biphenyl	B		n-C6 (Hexane)	
	Acenaphthylene	ANY		Methylcyclopentane	
	Acenaphthene	ANA		Cyclohexane	
	Dibenzofuran	DBF		2,3-dimethylpentane	
	Fluorene	F		3-methylhexane	
	C1-fluorenes	F1		n-C7 (Heptane)	
	C2-fluorenes	F2		Methylcyclohexane	
	C3-fluorenes	F3		2,4-dimethylhexane	
	Phenanthrene	P		2-methylheptane	
	Anthracene	A		n-C8 (Octane)	
	C1-phenanthrenes/anthracenes	P1		n-C9 (Nonane)	
	C2-phenanthrenes/anthracenes	P2		n-C10 (Decane)	
	C3-phenanthrenes/anthracenes	P3		n-Butylbenzene	
	C4-phenanthrenes/anthracenes	P4		1,2,4,5-tetramethylbenzene	
	Dibenzothiophene	D		n-pentylbenzene	
	C1-dibenzothiophenes	D1	BTEX	Benzene	
	C2-dibenzothiophenes	D2		Toluene	
	C3-dibenzothiophenes	D3		Ethylbenzene	
	C4-dibenzothiophenes	D4		*m*-xylene	
4-6 ring PAHs	Fluoranthene	FL		*p*-xylene	
	Pyrene	PY		*o*-xylene	
	C1-fluoranthrenes/pyrenes	FL1	C3-benzenes	Propylbenzene	
	C2-fluoranthenes/pyrenes	FL2		1-methyl-3-ethylbenzene	
	C3-fluoranthenes/pyrenes	FL3		1-methyl-4-ethylbenzene	
	Benz[*a*]anthracene	BA		1,3,5-Trimethylbenzene	
	Chrysene	C		1-methyl-2-ethylbenzene	
	C1-chrysenes	C1		1,2,4-trimethylbenzene	
	C2-chrysenes	C2		1,2,3-trimethylbenzene	
	C3-chrysenes	C3			
	C4-chrysenes	C4			
	Benzo[*b*]fluoranthene	BBF			
	Benzo[*k*]fluoranthene	BKF	TPH	C10-C36	
	Benzo[*e*]pyrene	BEP	WAF	Sum of VOC and TPH	
	Benzo[*a*]pyrene	BAP	UCM	TPH - SVOC	
	Perylene	PE			
	Indeno[*1,2,3-c,d]*pyrene	IN			
	Dibenz[*a,h]*anthracene	DBA			
	Benzo(g,h,i)perylene	BPE			

A.4 Examples of the span in WAF-concentrations and Toxic Unit with Marine Distillates and Marine Residual Fuel oils



WAF concentrations of oil products tested in previous studies at SINTEF (Faksness and Altin (2017), compared with the WAFs studied here: VLSFO (Chevron), VLSFO Shell (2019), and ULSFO (Shell 2019) in red circles.



Predicted acute toxicity expressed as TU for WAFs of oil products tested in previous studies at SINTEF compared with the WAFs studied here: VLSFO (Chevron), VLSFO Shell 2019, and ULSFO (Shell 2019) in red circles. A TU>1 indicates mortality of 50% for the tested organisms.

B Guideline for sampling and handling of representative oil samples

Oil samples for screening analysis in the PAME-EPPR LSFO project

Purpose

The purpose with this short guideline, is to obtain high quality and representative samples of the different marine LSFO oils sent to laboratories for screening testing connected to fate and behaviour and relative toxicity when spilled in cold or Arctic seawater.

Amount of oil

Minimum 4 litres of oil (can be delivered in smaller, e.g. 4 x 1-L containers)

Tapping of oil from side stream

The oil must be tapped onto clean and tight containers, e.g. bottles (polypropylene, polyethylene), metal cans or similar tight containers of oil resistant material

- The container can preferably be rinsed beforehand with the relevant oil before tapping.
- The container must not on beforehand be rinsed with any detergent-waters or solvents.
- Avoid that any water (or emulsion) or solids particles from e.g. side stream sampling are coming into the sampling bottle / container during sampling. If needed: drain off some litres from the storage tank before filling the bottle / container, to ensure a homogenous and representative oil sample.

Tapping of oil in storage

Exceptionally, if the sample is taken from a larger container, e.g. an oil barrel, that has been stored for a longer period, it is important that the oil in the container is thoroughly pre-mixed before tapped onto the sampling container, to ensure a representative sample. This is particularly important for oils expected to contain some wax are heated (in addition to the thorough mixing), to blend the wax with the oil. The wax and asphaltenes will most likely be deposited on the bottom of the oil barrel/container during storage. This is very important to ensure a representative sample!

COA

If a *"Certificate of Analysis"* (CoA) is available, enclose a copy of the CoA together with the oil sample when sending to the laboratory.

Labelling of cans/ shipment

The container must be labelled (block letters) with date of sampling, place, type of oil / other sample specifications, contact persons with telephone number. Petroleum is classified as dangerous goods. If larger quantum of oil, it is recommending an AirSea steel drum UN-X approved container for shipment, code 16 and capacity e.g. 25 litres. See the webpage http://www.air-sea.co.uk/ to find your local supplier.

Consignee address for the shipment of oil (if shipped to Norway):

SINTEF Ocean AS,
Dept. for Climate and Environment
Brattørkaia 17 C,
N-7010 Trondheim,
NORWAY
Contact: Kristin Rist Sørheim (+47 982 43 470) of Per S. Daling (+47 98243448)