

DIN CEN/TR 15522-2:2012-12 (E)

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; English version CEN/TR 15522-2:2012

Contents	Page
Foreword	6
Introduction	7
1 Scope	9
2 Normative references	9
3 Terms, definitions and abbreviated terms	9
3.1 General	9
3.2 Sample comparison	10
3.3 Conclusions	11
3.4 Abbreviated terms	11
4 Strategy for the identification of oil spills sources	12
4.1 Introduction	12
4.2 Basis for reliable conclusions - Numerical comparisons	12
4.3 Overview of the procedure	13
4.3.1 Sampling and sample preparation	13
4.3.2 GC-FID and GC-MS analysis	14
4.3.3 Conclusions and reporting	14
5 Sample preparation	16
5.1 General	16
5.2 Visual examination and description of samples	16
5.3 Preparation	16
5.3.1 General	16
5.3.2 Water samples	16
5.3.3 Oil samples from an Ethylene tetrafluoroethylene (ETFE) net	17
5.3.4 Thick oil and emulsified oil samples	17
5.3.5 Tar balls and emulsified lumps	17
5.3.6 Samples from oiled birds, fish and other animals and vegetation	17
5.4 Sample clean-up	18
5.4.1 General	18
5.4.2 Biogenic materials	18
5.4.3 Black oil/HFO (removing of asphaltenes and/or soot particles)	18
5.5 Recommended injection concentration	18
6 Characterisation and evaluation of analytical data	19
6.1 General	19
6.2 Characterisation by GC-FID - Level 1	20
6.2.1 General	20
6.2.2 Evaluation of the influence of weathering on sample comparison	21
6.2.3 Acyclic isoprenoids ratios	22
6.2.4 Level 1 Conclusions	22
6.3 Characterisation by GC-MS - Level 2	22
6.3.1 General	22
6.3.2 Visual inspection and overall characterisation - Level 2.1	23
6.3.3 Treatment of the GC-MS results - Level 2.2	23

6.4	Treatment of the results using the MS-PW-plot- Level 2.2	23
6.4.1	General	23
6.4.2	PW-plot calculations	24
6.4.3	Evaluation of the variability of the analysis and peak integration	24
6.4.4	Evaluation of weathering	26
6.4.5	Evaluation of mixing	29
DIN CEN/TR 15522-2 (DIN SPEC 19269):2012-12 CEN/TR 15522-2:2012 (E) 6.5 Treatment of the		
	results using ratios - Level 2.2	31
6.5.1	General	31
6.5.2	Diagnostic ratios calculation	32
6.5.3	Normative diagnostic ratios	32
6.5.4	Analytical error	35
6.5.5	Match-criterion for ratios	35
6.5.6	Criteria for selecting, elimination and evaluating diagnostic ratios	36
6.5.7	Optional: Evaluation of diagnostic ratios using conventional or multivariate statistics	39
6.6	Conclusions	40
Annex A (normative) GC-FID analysis		
		43
A.1	General	43
A.2	Analytical standards for GC-FID analyses	43
A.2.1	N-alkanes	43
A.2.2	Injection concentration of the standard GC-FID	43
A.2.3	Storage of standard solutions	44
A.3	Suggested instrumental conditions	44
A.4	Measures to improve and verify the accuracy of the method - GC-FID	44
A.4.1	Mass discrimination	44
A.4.2	Column resolution	45
A.4.3	Calibration range	46
A.4.4	Mid-level concentration	46
A.4.5	Variance	47
A.5	Sample analysis with GC-FID	47
Annex B (normative) GC-MS analysis		
		48
B.1	General	48
B.2	Analytical standards for GC-MS analyses	48
B.2.1	General	48
B.2.2	SINTEF oil mixture	49
B.2.3	Analytical standards for PAH homologues	49
B.2.4	Storage of standard solutions	49
B.3	Suggested instrumental conditions	49
B.3.1	GC conditions for the exchange of analytical results	49
B.3.2	MS conditions for full-scan analysis	52
B.3.3	MS preparation for selected ion monitoring (SIM) analysis	52
B.4	Measures to improve and verify the accuracy of the GC-MS method	53
B.4.1	Relative retention time	53
B.4.2	Mass discrimination	53
B.4.3	Peak symmetry and column resolution	53
B.4.4	Patterns	54
B.4.5	Calibration range	54
B.4.6	Mid-level concentration	54
B.4.7	Variance	54
B.5	Sample analysis with GC-MS	54
Annex C (informative) List of PAHs and biomarkers analysed by GC-MS-SIM		
		55
Annex D (informative) Alkyl homologue patterns of PAHs		
		57
Annex E (informative) Diagnostic ratios		
		65

E.1	Diagnostic ratios of PAHs	65
E.2	Diagnostic ratios of biomarkers	69
Annex F (informative) General composition of oils - chemical groups		76
F.1	Introduction	76
F.2	Hydrocarbons	76
F.3	Paraffins	76
F.4	Naphthenes	77
F.5	Aromatics	77
F.6	Heteroatomic organic compounds	77
F.7	Resins	77
DIN CEN/TR 15522-2 (DIN SPEC 19269):2012-12 CEN/TR 15522-2:2012 (E) F.8 Asphaltenes		77
Annex G (informative) Weathering of oils spilled on water		79
G.1	Introduction	79
G.2	Evaporation	80
G.3	Dissolution	82
G.4	Re-distribution of chemical composition	83
G.5	Biodegradation	86
G.6	Photooxidation	86
G.7	Contamination	88
Annex H (informative) Characteristic Features of Different Oil Types in Oil Spill Identification		89
H.1	Introduction	89
H.2	Light fuel oil (gas oil, diesel, fuel No 2)	89
H.2.1	General	89
H.2.2	Analysis, GC screening	90
H.2.3	MS analysis (alternative parameters)	92
H.2.4	Addition of biodiesel	94
H.3	Lubricating oil	95
H.3.1	General	95
H.3.2	Analysis	95
H.4	Heavy fuel oil (HFO, Bunker C, Fuel No 6)	99
H.4.1	General	99
H.4.2	Analysis	99
H.5	Waste oil (bilge oil, sludge, slops)	107
H.5.1	General	107
H.5.2	Analysis	108
H.6	Crude oil	113
H.6.1	General	113
H.6.2	Analysis	113
H.7	Conclusion	118
Annex I (informative) Example of internal documentation - technical report of an oil spill case		120
I.1	General	120
I.2	Sample information	120
I.2.1	General	120
I.2.2	Contact information	120
I.2.3	Request	120
I.2.4	Photo(s) of the samples	121
I.3	Sample preparation and analyses	121
I.4	Quality assurance	124
I.5	GC-FID results	125
I.6	GC-MS results	128
I.6.1	General	128
I.6.2	Comparison of the surface water samples	129
I.6.3	Comparison of the spill samples with bilge Sample 6	130

I.7	Conclusions	131
I.7.1	Surface water Sample 1 with bilge Sample 6	131
I.7.2	Surface water Sample 2 with bilge Sample 6	132
I.7.3	Final conclusion:	132
Annex J (informative) Example of external documentation - identification report of an oil spill identification case		133
J.1	Introduction	133
J.2	Sample information	133
J.3	Analytical procedure	133
J.3.1	Method	133
J.3.2	Dilution/extraction	133
J.3.3	Analyses	133
J.4	Results	133
J.5	Interpretation	134
DIN CEN/TR 15522-2 (DIN SPEC 19269):2012-12 CEN/TR 15522-2:2012 (E) J.5.1 General		134
J.5.2	Positive match	134
J.5.3	Probable match	134
J.5.4	Inconclusive	134
J.5.5	Non-match	134
J.6	Conclusions	134
Bibliography		135