



NSAI
Standards

Standard Recommendation
S.R. 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

S.R. CEN/TR 15522-2:2012

Incorporating amendments/corrigenda/National Annexes issued since publication:

The National Standards Authority of Ireland (NSAI) produces the following categories of formal documents:

I.S. xxx: Irish Standard – national specification based on the consensus of an expert panel and subject to public consultation.

S.R. xxx: Standard Recommendation - recommendation based on the consensus of an expert panel and subject to public consultation.

SWIFT xxx: A rapidly developed recommendatory document based on the consensus of the participants of an NSAI workshop.

This document replaces:
CEN/TR 15522-2:2006

<i>This document is based on:</i> CEN/TR 15522-2:2012 CEN/TR 15522-2:2006	<i>Published:</i> 19 October, 2012 12 December, 2006
---	--

This document was published under the authority of the NSAI and comes into effect on:
19 October, 2012

ICS number:

75.080

NSAI
1 Swift Square,
Northwood, Santry
Dublin 9

T +353 1 807 3800
F +353 1 807 3838
E standards@nsai.ie
W NSAI.ie

Sales:
T +353 1 857 6730
F +353 1 857 6729
W standards.ie

Údarás um Chaighdeáin Náisiúnta na hÉireann

English Version

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

This Technical Report was approved by CEN on 13 August 2012.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

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

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

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

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

Foreword

This document (CEN/TR 15522-2:2012) supersedes CEN/TR 15522-2:2006, which was prepared by CEN/BT/TF 120 "Oil Spill Identification" (now disbanded).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TR 15522-2:2006.

CEN/TR 15522 is composed of the following parts:

- *Part 1: Sampling;*
- *Part 2: Analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses (the present document).*

Introduction

This Technical Report describes and recommends a forensic methodology for characterising and identifying the source of waterborne oils resulting from accidental spills or intentional discharges. The methodology may be used in support of the legal process as evidence for prosecuting offenders ("potential responsible party" – PRP). This methodology is a technical revision of CEN/TR 15522-2 Version 1 published in December 2006.

This methodology is composed of two parts that are described by the following CEN documents:

- *Part 1 – Sampling*: describes sampling techniques and the handling of oil samples prior to their arrival at the forensic laboratory;
- *Part 2 – Methodology*: covers the general concepts and laboratory procedures of oil spill identification methodology, analytical techniques, data processing, data treatment, and interpretation/evaluation and reporting of results.

Oil spill source identification is a complex methodology due to the large variation in samples and oil spill situations that can be encountered. Part 1 is a compilation of instructions and experiences from experts all over the world which will guide the user in sampling, storing and delivering oil samples for laboratory analysis. Part 2 will guide the reader through the analytical process. It prescribes how to prepare and analyse oil samples using GC-FID and GC-low-resolution mass spectrometry (MS). Any chemical differences found between samples are only relevant if a difference is larger than the variability of the method itself. Good analytical performance and strict quality assurance are therefore essential. In the Annexes of Part 2, relevant information concerning different types of oil and oil comparison techniques is presented.

The main purpose of the methodology described in this Technical Report (TR) is to defensibly identify the source of oil spills in marine, estuarine and other aquatic environments by comparing the chemical compositions of samples from spills with those of suspected sources. The underlying basis for this method is the widely variable nature of oils with respect to their specific chemical compositions, which allows oils from different sources to be readily distinguished using the appropriate analytical methods. The method relies upon detailed chemical characterisation and statistical comparison between samples' (i.e., a spilled oil and a suspected source) diagnostic features in order to determine whether they "match". To minimise the danger of "false positive matches", good laboratory practices are necessarily maintained. Even so, a "positive match" between a spilled oil and a suspected source may not be used alone to identify the "potential responsible party" (PRP), but this result is often a critical piece of evidence in proving a case within the legal process.

However, in some oil spill identification cases, both the oil spill and also suspected source(s) may not necessarily be unique or homogeneous in nature, e.g., due to the changing/variable nature of oil in the bilge tanks or due to mixing of oils spilled from several sources in a case of a larger incident. The risk therefore exists that the chemical composition of the available source samples may not match to that of the available spill samples. In such cases, oil spill identification methodologies in general will have limitations and may not necessarily lead to unequivocal conclusions. In other words, the success of this methodology in defensibly identifying a spilled oil's source depends upon the samples available for chemical study. To minimise the danger for "false positive" or "false non-matches", good sampling practice, and particularly the need to obtain appropriate reference/suspect source samples, is crucial (as described in *Part 1: Sampling*).

When oil from suspected sources is not available, this methodology may still be used to characterise the spilled oil in order to determine the spilled oil type and any specific characteristics. The characterisation of a spilled oil sample can still be useful for several reasons:

- If the source of an oil pollution event is unknown, the investigating authorities should be advised on the type of oil in order to aid in the identification of a possible source. For example, in the case of a "mystery" spill, the mere differentiation between pure, unused refined petroleum products (e.g. diesel fuel versus heavy fuel oil) or versus crude oil or waste oil (e.g., bilge residues, sludge, slops) can provide potentially

CEN/TR 15522-2:2012 (E)

valuable information as the possible source(s) for the spill. In such instances, the type of oil spilled should be identified rapidly because the chances of identifying and collecting candidate source oils generally decrease with time.

- In some court trials, the differentiation between pure refined products and waste oil may be very important because it allows conclusions to be drawn regarding the cause of an oil discharge, e.g. technical failure, accidental discharge, intentional discharge.
- In some countries, photos (e.g. taken from an airplane) from a plume behind a ship, combined with the evidence that the plume contains mineral oil, is enough for a condemnation.
- Finally, characterisation of the spilled oil provides a baseline against which future impacts to the affected area/environment might be compared.

This Technical Report is the result of advancements in the field of oil spill identification [e.g., 13, 21, 44, 46 and 50] that have been made since the Nordtest Method [35, 36] was first introduced in 1991. These have included:

- advancements in analytical methodologies;
- improved understanding of the specific chemical compositions and diagnostic features of oils;
- improved understanding of how an oil's composition may change in the environment (e.g., due to weathering);
- improvements in the statistical and numerical analysis of chemical data.

These advancements have been made by researchers around the world and documented in a wide range of peer-reviewed literature. In addition, numerous round robin tests have been conducted to evaluate and improve upon the methodology. Since 2004, in the framework of Bonn-OSINET (Bonn-greement Oil Spill Identification Network), annual round robin tests are organised jointly by RWS-WD (Rijkswaterstaat - Center for Water Management in the Netherlands) and BSH (Bundesamt für Seeschifffahrt und Hydrographie in Germany) in which laboratories from around the world participate. The round robin tests have covered oil spill cases dealing with light fuel oil distillates (diesel oils), bilge water samples (a mixture of gas oils and lube oil), crude oils and heavy fuel oils. Findings from these RR-tests have been discussed at annual meetings by the participating scientists and have been taken into account for refining the suggested methodology described herein. The final reports of the RR-tests can be downloaded for free from the Bonn-OSINET part of the Bonn-agreement website [7].

1 Scope

This Technical Report (TR) describes a methodology to firstly identify the specific nature of oils spilled in marine, estuarine and aquatic environments and secondly compare the chemical composition of spilled oil or oily samples with that of suspected sources. Specifically, the TR describes the detailed analytical methods and data processing specifications for identifying the specific nature of waterborne oil spills and establishing their correlation to suspected sources. Even when samples or data from suspected sources are not available for comparison, establishing the specific nature (e.g., refined petroleum, crude oil, waste oil, etc.) of the spilled oil may still help constrain the possible source(s) of the spilled oil.

This methodology is restricted to petroleum and petroleum products containing a significant proportion of hydrocarbon-components with a boiling point above 200°C. Examples are: crude oils, higher boiling condensates, diesel oils, residual bunker or heavy fuel oils, lubricants, and mixtures of bilge and sludge samples. While the specific analytical methods may not be appropriate for lower boiling oils (e.g. kerosenes, jet fuels, or gasoline), the general concepts described in this methodology, i.e., statistical comparison of weathering-resistant diagnostic ratios, may have applicability in spills involving lower boiling oils.

This method is not directly intended for oil spills impacting groundwater, vegetation, wildlife/tissues, soils, or sediments, and although its application in these matrices is not precluded, it requires caution. The reason for caution is that the extractable compounds in these matrices may alter and/or contribute additional compounds compared to the source sample, which if left unrecognised, can lead to “false non-matches”. Including these “non-oil” matrices in this oil spill identification method may require additional sample preparation (e.g. clean-up) in the laboratory prior to analysis and consideration of the extent to which the matrix may affect the correlation achieved. Evaluating the possible effects in these matrices is beyond the scope of this guideline. Whether the method can be used for this kind of “non-oil” matrices may depend on the oil concentration compared to the “matrix concentration” of the samples. In “non-oil” matrices containing a relative high concentration of oil, a positive match can still be concluded. In “non-oil” matrices containing a relative low concentration of spilled oil, a non-match or an inconclusive match could be achieved due to matrix effects.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

CEN/TR 15522-1, *Oil spill identification – Waterborne petroleum and petroleum products – Part 1: Sampling*

3 Terms, definitions and abbreviated terms

For the purposes of this document, the following terms and definitions apply.

3.1 General

3.1.1

chain of custody

line of recorded actions taken for samples collected from spill and suspected sources at court for safe surveillance and storing; to ensure that the samples have not been tampered with or altered accidentally

3.1.2

mixing

mixing can include chemical changes brought about by (a) the mixing of multiple oils, (b) mixing with pre-existing background compounds from biogenic or anthropogenic sources, or (c) heterogeneity within the sample(s) (e.g., within a vessel, tank, or oil slick)

This is a free preview. Purchase the entire publication at the link below:

[Product Page](#)

-
- [Looking for additional Standards? Visit Intertek Inform Infostore](#)
 - [Learn about LexConnect, All Jurisdictions, Standards referenced in Australian legislation](#)
-