TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN/TR 15522-2

November 2006

ICS 75.080

English Version

Oil spill identification - Waterborne petroleum and petroleum products - Part 2: Analytical methodology and interpretation of results

Identification des pollutions pétrolières - Pétrole et produits pétroliers dans l'eau - Partie 2 : Méthodologie analytique et interprétation des résultats

Identifizierung von Ölverschmutzungen - Rohöl und Mineralölerzeugnisse aus dem Wasser - Teil 2: Analytische Methodik und Interpretation der Ergebnisse

This Technical Report was approved by CEN on 25 September 2006. It has been drawn up by the Technical Committee CEN/BT/TF 120.

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

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. CEN/TR 15522-2:2006: E

Contents

Page

Foreword 4
Introduction 5
1 Scope 7
2 Normative references 7
3 Terms and definitions 7
4 Strategy for identification of oil spills 9
4.1 General 9
4.2 Procedure 10
4.3 Decision chart of analytical and data treatment levels 10
5 Sample preparation 12
5.1 General 12
5.2 Visual examination of samples 13
5.3 Preparation 13
5.4 Recommended sample clean up methodology 14
5.5 Recommended injection concentration 15
6 Characterization and evaluation of analytical data 15
6.1 General 15
6.2 Characterization by GC/FID – level 1 15
6.3 Characterisation by GC/MS – level 2 17
6.4 Treatment of the results – level 3 27
6.5 Conclusions 33
7 Reporting 33
8 Quality assurance 34
Annex A (informative) Analytical standards 35
A.1 General 35
A.2 Recommended standards and concentrations 35
A.3 Analytical standards for PAH homologues 36
A.4 Calibration- GC/MS 37
Annex B (informative) Suggested instrument conditions 39
B.1 GC/FID conditions 39
B.2 GC/MS conditions 41
B.3 Sample analysis 42
B.4 Calculations 44
B.5 SIM-sections 45
Annex C (informative) List of PAHs and biomarkers analysed by GC/MS-SIM 46
Annex D (informative) Alkyl homologues patterns of PAHs 49
Annex E (informative) Boiling points of n-alkanes 58
Annex F (informative) General composition of oils – chemical groups 59
F.1 Introduction 59
F.2 Hydrocarbons 59
F.3 Paraffins 59
F.4 Naphthenes 60
F.5 Aromatics 60
F.6 Heteroatomic organic compounds 60

F.7 Resins 60
F.8 Asphaltenes 60

Annex G (informative) Weathering of oils spilled at sea 61
G.1 Introduction 61
G.2 Evaporation 62
G.3 Dissolution 64
G.4 Re-distribution of chemical composition 65
G.5 Biodegradation 66
G.6 Contamination / in-homogeneity 67
G.7 Evaluation of weathering 67
G.8 Optional - Semi-quantitative distribution of PAH homologues - weathering check 69

Annex H (informative) Characteristic Features of Different Oil Types in Oil Spill Identification 70
H.1 Introduction 70
H.2 Light fuel oil (gas oil, diesel, fuel No 2) 70
H.3 Lubricating oil 75
H.4 Heavy fuel oil (HFO, Bunker C, Fuel No 6) 79
H.5 Waste oil (bilge oil, sludge, slops) 87
H.6 Crude oil 93
H.7 Conclusion 98

Annex I (informative) Example of the evaluation of an oil case 100
I.1 Introduction 100
I.2 GC/FID results 100
I.3 GC/MS results 102
I.4 Conclusion 106

Bibliography 107

Foreword

This document (CEN/TR 15522-2:2006) has been prepared by CEN/BT/TF 120 “Oil spill identification”, the secretariat of which is held by SN.

Introduction

This Technical Report gives a recommendation on a forensic methodology for identifying waterborne oils. The methodology may be a support to the legal process as evidence for prosecuting offenders ("potential responsible party" – PRP). This methodology is a technical revision of the Nordtest Method NT CHEM 001 (1991) "Oil spill identification".

This methodology is 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 of results.

Oil spill identification and oil comparison is a complex methodology due to the large variation in samples and oil spill situations, which can be encountered. Part 1 is a compilation of instructions and experiences from experts all over the world and will guide the user in sampling, storing and delivering oil samples. Part 2 will guide the reader through the process by dividing the methodology into 3 tiered levels. It prescribes how to prepare and analyse oil samples with GC/FID and, if necessary, with GC-low-resolution mass spectrometry. Differences found between samples are only relevant if a difference is larger than the analytical variance of the method. Therefore good analytical performance and strict quality assurance are essential. In the annexes of part 2, relevant information concerning different types of oil and oil comparison is presented.

The main purpose of the methodology described in this Technical Report (TR) is to identify oil spills in marine, estuarine and other aquatic environments by comparing samples from spills with those of suspected sources. In oil spill identification cases, both the oil spill and also suspected source(s) may not necessarily be homogeneous in nature e.g. due to the changing/variable nature of oil in the bilge tanks or e.g. mixing of oil spills from several sources in a case of a larger incident. The risk therefore exists that the chemical composition of the reference samples may not be related to that of the spill. In such cases oil spill fingerprinting methodologies in general will have its limitations and may not necessarily lead to firm conclusions. To minimise the danger for “false negative” matches, good sampling practice, and particularly the need to obtain appropriate reference/suspect source samples, is therefore crucial (as described in Part 1 Sampling).

When suspected sources are not available, this methodology may be used to characterise the spill as far as possible with respect to oil type. The identification of the type of oil in a sample can be essential for several reasons:

— if the origin of an oil pollution event is unknown, the investigating authorities must be advised on where to find a possible source. In case of a “mystery” spill, the mere differentiation between pure, unused products or crude oil and waste oil (bilge residues, sludge, slops) is valuable information. Oils must be identified rapidly in such cases because the chances of identifying sources generally decrease with time;

— meaning of analytical results, i.e. their contribution to the overall evidence in criminal proceedings, depends very much on the types of oil that are involved in oil spills. Depending on these types, the search can be more or less focused on a few possible sources, or even a single one;

— in court trials, the differentiation between pure products and waste oil may be highly important because it allows conclusions to be drawn regarding the cause of an oil discharge, e.g. technical failure, inadvertence, intention;

— conclusions obtained from the defensible identification of spilled oil and their correlation to suspected sources will not, however, on their own identify the "potential responsible party" (PRP), but is often a critical part of, and a support to, the legal process.

In these guidelines, some activities are marked as “Optional”. These are suggestions to supplementary diagnostic documentations, e.g. in cases where there may still be uncertainty in drawing conclusions based on the “standard” recommended methodology.

The first draft of the methodology was evaluated through a Round Robin study organised by the CEN/BT/TF 120 *Oil Spill Identification*. This test was limited to crude oils and heavy fuel oils. Two more recent Round Robin tests organised by RIZA in the Netherlands, where fifteen laboratories participated, covered cases with light fuel oil distillates (diesel oils,) and bilge water samples (a mixture of gas oils and lube oil). Findings from these RR-tests have been taken into account for refining the suggested methodology.

1 Scope

This Technical Report (TR) describes a methodology to identify waterborne oils spilled in marine, estuarine and aquatic environments by comparing samples from spills with those of suspected sources . It provides detailed analytical and processing specifications for identifying waterborne oil spills and their correlation to suspected sources. When suspected sources are not available, the methodology may be used to characterise the spill as far as possible with respect to the oil type.

This methodology is restricted to petroleum and petroleum products containing a significant proportion of HC-components with a boiling point above 200 °C. Examples are: Crude oils, condensates, light fuel oils, diesel oils, residual bunker oils, lubricants, and mixtures of bilge and sludge samples. Still, the general concepts described in this methodology have a limited applicability for some kerosenes and some condensates, but may not be applicable for gasoline

NOTE This method is not intended for oil spills to groundwater and soil. The chromatograms of oil extracted from soil and found in ground water may contain reduced and/or additional peaks compared to the source sample. Including such samples in this method makes it necessary to add extraction methods and to describe which compounds are possibly reduced and/or which additional peaks can be expected to change the final conclusion from a probable match into a match. This is beyond the scope of this guideline, however, when case samples completely match according to this method, the method is valid for those samples.

2 Normative references

The following referenced documents are indispensable for the application of this European Standard. 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 and definitions

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

3.1
chain of custody
line of actions taken for samples 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

3.2
contamination
all changes in oil composition which take place during/after the spillage, by mixing with additional compounds, including natural products

3.3
critical difference (CD)
value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 0,95; the critical difference is defined as CD= ((mean *x* $\mathbf{r}_{95\%}$)/(100)

3.4
diagnostic ratios
ratios between the peak height or peak area of single compounds or compound groups selected by their diversity in chemical composition in petroleum and petroleum products and on their known behaviour in weathering processes