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Prepoznavanje razlitij olj - Nafta in naftni proizvodi v vodi - 2. del: Analizne metode in podajanje rezultatov, izhajajočih iz GC-FID in GC-MS nizke ločljivosti

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

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Oil spill identification - Waterborne petroleum and petroleum products - Part 2: Part 2: Analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses

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Foreword

This document (FprCEN/TR 15522-2:2012) has been prepared by Technical Committee CEN/TC “CSS27”, the secretariat of which is held by CCMC.

This document is currently submitted to the Technical Committee Approval.

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Introduction

This Technical Report describes and recommends a forensic methodology for characterizing 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 and 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 minimize 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 minimize 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 characterize 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

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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 TR 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 constraint 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. Still, 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 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)

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3.1.3

sample heterogeneity

non-representative or non-homogenous character of samples caused for example by variable degrees of mixing within a vessel, tank or oil slick

3.1.3

contamination

changes in oil composition which take place during/after the spillage, by mixing with additional compounds, including naturally-occurring chemicals or other products

3.1.4

waterborne oil

petroleum and petroleum products borne by water or available in the water column from marine, estuarial and aquatic environments (includes lakes and rivers but excludes groundwater)

3.1.5

weathering

changes in oil composition which take place after the spillage, including evaporation, dissolution, emulsification, oxidation and biological decomposition. See also Annex G

3.1.6

bilge water

mixture including water and oil collected in the bilge of the machinery space in a ship as a result of leakage, drainage, etc.

3.1.7

slop

mixture of water and oil residues from cargo tanks in oil tankers that may contain oil/water emulsions, wax, sediments and other tank residues

3.1.8

sludge

deposits, generally from the purification of fuel and lubrication oils, consisting of mixtures including oil, wax, sand and water

3.1.9

tank washings

tank washing water containing cargo tank residues including oil, wax, sediment and other foreign matter such as tank cleaning chemicals

3.2 Sample comparison

3.2.1

PW-plot

graph based on GC-FID or GC-MS data of two samples normalised to a non-weathered compound or group of compounds and sorted on boiling point or retention time

Note 1 to entry: The name "PW-plot" is originally a reference to Per Wrang, who introduced the plot in the Nordtest method [36]. In this TR the name PW-plot will be used as an abbreviation of a "Percentage Weathering" plot.

3.2.2

diagnostic ratios (DR)

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

3.2.3**critical difference (CD)**

14 % of the mean value of a ratio for two different samples. The fixed value of 14 % is based on the maximum allowable relative standard deviation of 5 % for the ratios [23, 24, 25]

3.3 Conclusions**3.3.1****positive match**

differences in the chromatographic patterns and diagnostic ratios of samples submitted for comparison are lower than the variability of the method or can be explained unequivocally, for example by weathering. The samples are considered to match to a high degree of scientific certainty

3.3.2**probable match**

differences in chromatographic patterns and diagnostic ratios do not permit an unequivocal positive match, but they can be explained reasonably by external factors, for example weathering in combination with mixing or by non-representative or heterogeneous properties of the available samples. The samples are considered to match to a reasonable degree of scientific certainty

Note 1 to entry: Unavailability of a representative source sample. For example, if a vessel that has discharged all of its bilge water, a representative source sample may not be available. Therefore, when comparing an individual source lubricating oil with the lubricating oil component of a bilge sample, certain differences have to be expected due to other bilge sample components besides the source lubricating oil.

3.3.3**inconclusive**

differences in the chromatographic patterns and diagnostic ratios of the samples submitted for comparison, do not permit a probable or non-match conclusion; for example in case the concentration of the contaminant in a sample is too low

3.3.4**non-match**

differences in the chromatographic patterns and diagnostic ratios of the samples submitted for comparison are pronounced and are larger than the variability of the method, and such differences cannot be explained by any external factors such as weathering, contamination or heterogeneity. The samples are concluded to not match to a high degree of scientific certainty

3.4 Abbreviated terms

CD	Critical difference
DR	Diagnostic ratio
FID	Flame ionisation detection
GC	Gas chromatography
HFO	Heavy Fuel Oil
IUPAC	International Union of Pure and Applied Chemistry
LCO	Light cycle oil
LFO	Light fuel oil
MS	Mass spectrometry

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NR	Normative ratio
PCA	Principal component analysis
RSD	Relative standard deviation
TR	Technical report

4 Strategy for the identification of oil spills sources**4.1 Introduction**

Identification of spilled oils in the context of this Technical Report (TR) implies the comparison of the total chemical composition of the spilled oil with that of candidate source samples.

The likeness of a source and spill sample should be tested by analyzing the samples with GC-FID and/or low resolution GC-MS and by comparing their detailed chemical compositions using a suite of generic and diagnostic petroleum components. If no or only insignificant differences (i.e. differences being smaller than the analytical variability) are observed, a “positive match” should be concluded. On the other hand, if true differences (i.e. differences not related to changes in the chemical composition introduced after the spill, e.g. from weathering, mixing or heterogeneity), that are larger than the variance of the analysis are observed within these diagnostic compounds, it should be concluded that the samples are a “non-match”. Some investigations may result in conclusions intermediate to “positive match” and “non-match”, such as “probable match” or “inconclusive” (see definitions in 3.3).

NOTE It is practically and technically impossible to measure and compare every chemical in spilled oil and its prospective source in order to conclude a positive match exists. Therefore, in practice, two samples are considered to be a positive match if no statistically significant differences in diagnostic metrics determined by GC-FID and GC-MS analysis are present, that cannot be explained by weathering, mixing or heterogeneity. This approach, i.e., looking for differences in diagnostic features instead of similarity among every possible feature, is conceptually more logical and more practically and technically achievable. As such, only distinct differences between samples can be proved. Therefore, when no statistically significant differences between samples are observed, a “positive match to a high degree of scientific certainty” should be concluded.

4.2 Basis for reliable conclusions – Numerical comparisons

The usual practice is to analyse samples qualitatively and then compare the chromatograms and ion chromatograms visually, such as described in the original Nordtest Method (1991) [36] and the ASTM methods [2, 3]. The outcome of such qualitative comparisons is subjective and depends on the experience or bias of the analyst. Because of the high complexity of oils, and the many details that can be compared in the often very complex chromatograms, qualitative comparisons should always form an integral part of oil sample comparisons. However, in order to make conclusions more objective, reproducible, and therefore, more reliable, this technical report also requires the use and comparison of quantitative metrics; i.e., specific peaks or groups of peaks have to be measured and peak ratios have to be calculated and compared.

These ratios are produced in two different ways:

- 1) Measurements of single compounds normalised to hopane – or, if hopane is not sufficiently present, to tetra-methylphenantrene (T-M-phe; see Figure E.2).

Comparing the normalised abundances of compounds spanning the boiling range of oil, in the form of PW-plots, reveals (1) the variance of the analysis and integration, (2) concentration differences between compounds (e.g. biomarkers and PAH's) and (3) the effects of weathering on individual compounds and compound groups, and in turn, on prospective ratios based upon those compounds. When the effects of weathering on a spilled oil are understood, any affected ratio can be eliminated or cautiously considered in when comparing a weathered spill sample to an unweathered source sample.

- 2) Diagnostic Ratios (DRs): for keeping the analytical error low, measurements of compounds (peaks) that are primarily recorded by the same m/z value via GC-MS within a limited retention time range.

NOTE The term “diagnostic ratio” originates from geochemistry, and is related to the diversity in chemical composition of crude oils from different geologic provinces, oil fields, individual wells or reservoirs. DRs are characteristics, which collectively may lead to a unique classification and identification of oils (“diagnosis”: “sorting into categories”). The term “Diagnostic Ratio” is used here in order to pronounce the general differentiation possibilities of these ratios and thus their importance, (see 3.2.2). In addition, this term is widely used in oil spill identification literature [44, 46].

Whereas most of the DRs described in this TR may be used when spills involving crude oil, bunker oil and bilge samples are investigated, only a limited number of DRs may be useful for spills involving lighter fuel oils (e.g. kerosene, diesel, gas oil). The reason for this is because the DRs based upon higher boiling biomarkers may not be present in lighter refined products. Similarly, the higher boiling lubricating oils, normally rich in biomarkers, may not or not sufficiently contain aromatics and n-alkanes, rendering DRs based on these compounds useless.

Because of the need for some flexibility when investigating spills of different oil types, a specific list of normative diagnostic ratios (NRs) generated from potentially diagnostic and more weathering resistant alkanes, PAH compounds and biomarkers has been developed for crude oil and five other types of petroleum (see 6.4.4). This list should be treated as a minimum list, which can be expanded for specific cases and/or oil types. Examples of additional “informative” ratios are given in Annex E. A much more comprehensive review of potentially diagnostic ratios, which may be used/are useful in oil spill identifications, can be found in [46]. The resulting ratios are compared using a critical difference of 14 % (see 3.2 and 6.4.6).

The combined information derived from DRs, PW-plot, and the visual comparison of chromatograms (see Figure 11 and I.7) gives a deep insight in the differences and similarities between two oil samples

NOTE The present methodology is based on semi-quantitative analyses for establishing diagnostic ratios of whole samples (no fractionation in aliphatic and aromatic compounds [1]). For those laboratories who work daily on a “quantitative analytical” level (i.e. internal standards are added and concentrations of individual compounds or compound groups are calculated), and that have good laboratory QA/QC protocols for doing quantitative analysis of the recommended diagnostic compound peaks, the ratios recommended in these guidelines may be established based on quantitative analysis in which the absolute concentrations are used to calculate DRs [15, 16, 23].

4.3 Overview of the procedure

4.3.1 Sampling and sample preparation

When an oil spill has been discovered, samples should be taken from the current spill and from any potential responsible parties such as suspected ships or other sources. The sampling shall be carried out in accordance with CEN/TR 15522-1. When suspected sources are not available, the methodology can still be used to characterize the spilled oil.

All samples should be sent under chain-of-custody either via an authorised “Sampling Coordinator” or directly to a forensic laboratory for oil spill identification.

At the laboratory the samples are visually characterized, described, see 5.2, and prepared for analysis (conservation, extraction and clean-up if needed), see 5.3

4.3.2 GC-FID and GC-MS analysis

Oil sample comparison by GC-FID (see Annex A) and GC-MS (see Annex B) is conducted in both cases by visual (qualitative) comparisons and by numerical (quantitative) comparisons (Figure 1):

GC-FID is used for screening of all samples. Based upon the visual comparison of the gas-chromatograms, source samples that are clearly a different type of petroleum than comprises the spill sample(s) may be ruled out as “non-matching”. For example, a diesel fuel potential source sample might be eliminated from further consideration in a crude oil spill. Differences due to weathering of the spill sample are recognised and visualised by overlays of the gas-chromatograms (Level 1.1). For source samples, which are not clearly