SLOVENSKI STANDARD
SIST-TP CEN/TR 15522-2:2008

01-julij-2008

Prepoznavanje razlitij olj - Nafta in naftni proizvodi v vodi - 2. del: Analitske metode in podajanje rezultatov

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

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

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

Ta slovenski standard je istoveten z: CEN/TR 15522-2:2006

ICS:

13.020.40	Onesnaževanje, nadzor nad onesnaževanjem in ohranjanje	Pollution, pollution control and conservation
13.060.99	Drugi standardi v zvezi s kakovostjo vode	Other standards related to water quality

SIST-TP CEN/TR 15522-2:2008 en

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

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

3.5

identity

no differences observed in the chromatographic patterns of GC/FID and GC/MS apart from those changes introduced after the spill (weathering, degradation etc.)

3.6

inconclusive

when differences in chromatographic patterns and diagnostic ratios of the samples submitted for comparison are larger than the analytical variance of the method and may only, to some extent, be explained by external factors like weathering, contamination, heterogeneity of the samples or too low an amount of sample material

NOTE Differences may be due to e.g. heterogeneities of the oil either within the spill or within the suspected source (e.g. within the ship tank), that is not reflected in the available samples analysed, or differences are present because the samples do not originate from the same source.

3.7

non-match

when differences in chromatographic patterns and diagnostic ratios of the samples submitted for comparison are distinct and larger than the analytical variance of the method and they cannot be explained by external factors like weathering, contamination and heterogeneity. The samples are distinctly different

3.8

positive match

when differences in chromatographic patterns and diagnostic ratios of the samples submitted for comparison are lower than the analytical variance of the method or can clearly be explained by weathering. The samples are identical beyond reasonable doubt

3.9

probable match

when differences in chromatographic patterns and diagnostic ratios of the samples submitted for comparison are larger than the analytical variances of the method, but can be explained by external factors like contamination or heterogeneity of the samples

EXAMPLE Comparing lubricating oil with the lubricating oil part of a bilge sample may lead to a probable match.

3.10

repeatability (r)

precision under repeatability conditions

[ISO 5725-2]

3.11

repeatability conditions

conditions where independent test results are obtained by the same method on identical test material in the same laboratory by the same operator (panel leader) using the same equipment within short intervals of time

[ISO 5725-2]

3.12

repeatability limit (r95%)

value less than or equal to the difference between two test results obtained under repeatability conditions which may be expected to be within a probability of 0,95

[ISO 5725-2]

3.13

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)

3.14

weathering

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

4 Strategy for identification of oil spills

4.1 General

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

NOTE Identity, *per se* requires all measurable data to be the same. This definition is practically and technically impossible to fulfill and instead, the definition of identity is rephrased in operational terms: two samples are identical if no differences in the analysed GC/FID and GC/MS data are present that cannot be explained by weathering. The task of looking for differences in chemical composition instead of proving similarity is conceptually more logical and easier to comply with. According to this, only distinct differences between samples can be proved, whereas identity *per se* cannot. Therefore, only when no differences between samples are observed should identity be concluded as being beyond reasonable doubt.

Identity should be tested by analyzing and comparing the detailed chemical composition of the selected samples by chemical fingerprinting of a suite of generic and diagnostic petroleum compounds. If no or only insignificant differences (i.e. differences being smaller than the analytical variance) are observed, identity should be concluded as being beyond reasonable doubt. 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 etc.), that are larger than the variance of the analysis are observed within these diagnostic compounds, it should be concluded that the samples are different.

In the European community oil comparison is performed by laboratories, which analyse oil samples daily, but also by laboratories, which only compare samples a few times a year. Common practice has traditionally been to analyse samples qualitatively and then compare the chromatograms and ion chromatograms visually. The outcome of such comparisons depends on the experience of the analyst. Laboratories, which rarely analyse oil samples, may experience difficulties in reaching the right conclusions, therefore, this guideline introduces the use of diagnostic ratios. The selection of the ratios is based on the known weathering behavior of compounds and the diversity in chemical composition of oils from different wells and oil types [14]. To reduce the variance, ratios are generated by using the area or peak height of compounds, which are recorded by the same m/z value and that are within the same reasonable retention time range. The resulting ratios are compared using the repeatability limit (3.12) as a test method. For those laboratories who work daily on a “quantitative analytical” level, and that have good laboratory routines for doing “exact” quantification of the recommended diagnostic peaks, the ratios recommended in these guidelines may be established based on exact quantitative analysis.

For the comparison of the diagnostic ratios from the GC/MS data, 29 diagnostic ratios, generated from diagnostic PAH compounds and biomarkers, that are robust against weathering have been selected to cope with the differences in oil samples and oil types. Whereas most of the ratios may be used when crude oil, bunker oil and bilge samples are involved, only a limited number may be useful for lighter fuel oils (e.g. kerosene, parafin, diesel, gas oil) because some of the high boiling biomarkers may not be present in such light refined products. In identification cases where the oil spill has been exposed to a low degree of weathering, 3 ratios of acyclic isoprenoids (the n-C_{17} /pristane, n-C_{18} /phytane and pristane/phytane ratios) from the GC/FID analyses and 4 suggested ratios of the sesquiterpanes (in the C_{13} to C_{16} area) may also be included for comparison of diagnostic ratios if a weathering check shows that these compounds have not been exposed to weathering.

Before integrating the compounds applied for calculating the diagnostic ratios, a visual inspection of the diagnostic ion chromatograms (see 6.3.5.2 – 6.3.5.4) should be carried out to eliminate some of the recommended diagnostic peaks that may not be present in sufficient concentrations, used to establish robust diagnostic ratios. Also, a visual comparison of the ion chromatograms is advised to enable exclusion of obviously different samples. After the comparison study of diagnostic ratios(see 6.4), a visual, one by one comparison of the printed ion chromatograms of the relevant samples should also be carried out to verify (ground-truth) the conclusion.

4.2 Procedure

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. All samples should be sent either via an authorised "Sampling Co-ordinator" or directly to a forensic laboratory for oil spill identification.

The oil spill identification methodology is comprised of:

- sampling from the spill and from the suspected sources. When suspected sources are not available, methodology may be used to characterise the spill as far as possible with respect to the oil type. The sampling shall be carried out in accordance with CEN/TR 15522-1;
- visual description of samples, see 5.2;
- preparation of samples, see 5.3;
- gas chromatography combined with flame ionization detection (GC/FID) screening of all involved samples. Evaluation of the chromatograms and calculation of diagnostic ratios, see 4.3.2 and 6.2;
- gas chromatography combined with mass spectrometry (GC/MS) fingerprinting of samples. Evaluation of the chromatograms and calculation of diagnostic ratios, see 4.3.3 and 6.3;
- comparison of diagnostic ratios, see 6.4;
- conclusions and reporting see clause 7.

4.3 Decision chart of analytical and data treatment levels

4.3.1 General

The identification system for oil spills is divided into three levels of decisions, see Figure 1.

4.3.2 GC/FID screening (level 1)

After sample preparation (see 5.3), the chemical fingerprinting analysis in the laboratory starts with the GC/FID screening analysis of all samples, i.e. both samples of spilled oils and suspected sources. The data from this screening should be used for:

- characterising the oil sample(s) by obtaining the overall boiling (carbon) range of the oils, i.e. the total distribution of hydrocarbons including n-alkanes from C_{10} to C_{40} if present, see 6.2.1. For an overview of boiling points of n-alkanes, see Annex E;
- visual inspections of the chromatograms for possible characteristic features and a tentative classification to a type of the spilled oil if possible, see Annex H;
- establishing selected acyclic isoprenoid ratios readily determined using GC/FID, see 6.2.2.1.

If the chromatograms are different and those differences are possibly caused by weathering a "weathering check", either by a chromatographic overlay manipulation or by normalising the distribution of n-alkanes to non-weathered compounds is recommended, see 6.2.2.2 and Annex G.

If the GC chromatograms from the spill samples compared to the suspected sources show differences in the hydrocarbon distribution, the unresolved complex mixture distribution and/or the acyclic isoprenoid ratios (see criteria in 6.2.2.1.) that obviously are not caused by weathering (non-matched samples), should be ruled out and eliminated from additional levels of analysis (see Figure 1). If there are any doubts, the samples should be analysed in accordance with level 2.

See also Annex H, on the evaluation of the GC-screening results (comparison of unresolved envelopes).

4.3.3 GC/MS fingerprinting (level 2)

At this level, analysis of spill and candidate source samples using gas chromatography combined with mass spectrometry that generally operates in the selected ion monitoring mode (GC/MS-SIM) should be performed. This analysis is useful for determining the content and distributions of a suite of diagnostic petroleum biomarkers and PAH target analytes. Data from this analysis should be used for:

- visual inspection of the ion profiles in the chromatograms for possible characteristic features, and an oil type classification of the spilled oil, see Annex H;
- generating a suite of diagnostic ratios based on an evaluation of the presence and “robustness” of the diagnostic PAHs and biomarkers described in 6.3.5.

To give additional diagnostic information, a semi-quantitative histogram established from a suite of selected PAH homologues may be used as a supplementary diagnostic fingerprint and as a check on the weathering of the PAH homologues (optional), see Annex G, Clause 8.

4.3.4 Evaluation of data (level 3)

At level 3, the results obtained from level 1 and 2 should be used for:

- assessing the impact of weathering based on a weathering check of n-alkane data from level 1 and the semi-quantitative distribution of the PAH groups from level 2. The weathering checks are performed optionally;
- deciding which diagnostic ratio can be used for comparison based on oil type and analytical variance, and which samples should be reanalysed because of heterogeneity, see 6.4.2;
- comparison of diagnostic ratios data using repeatability limit, see 6.4.3;
- visual comparison of generated ion chromatograms to check the results of the ratio comparison (ground-truth all data).

The results from all analytical levels should be assessed and the conclusions should be reported for the combined results of the test methodology used, see clause 6.5. Results should be specified either as a Positive Match, Probable Match, Inconclusive or Non-Match.

Note These categories represent four operational and technical defensible conclusion terms (3.6-3.9) to identify or differentiate between oils from a spill and any available candidate sources.

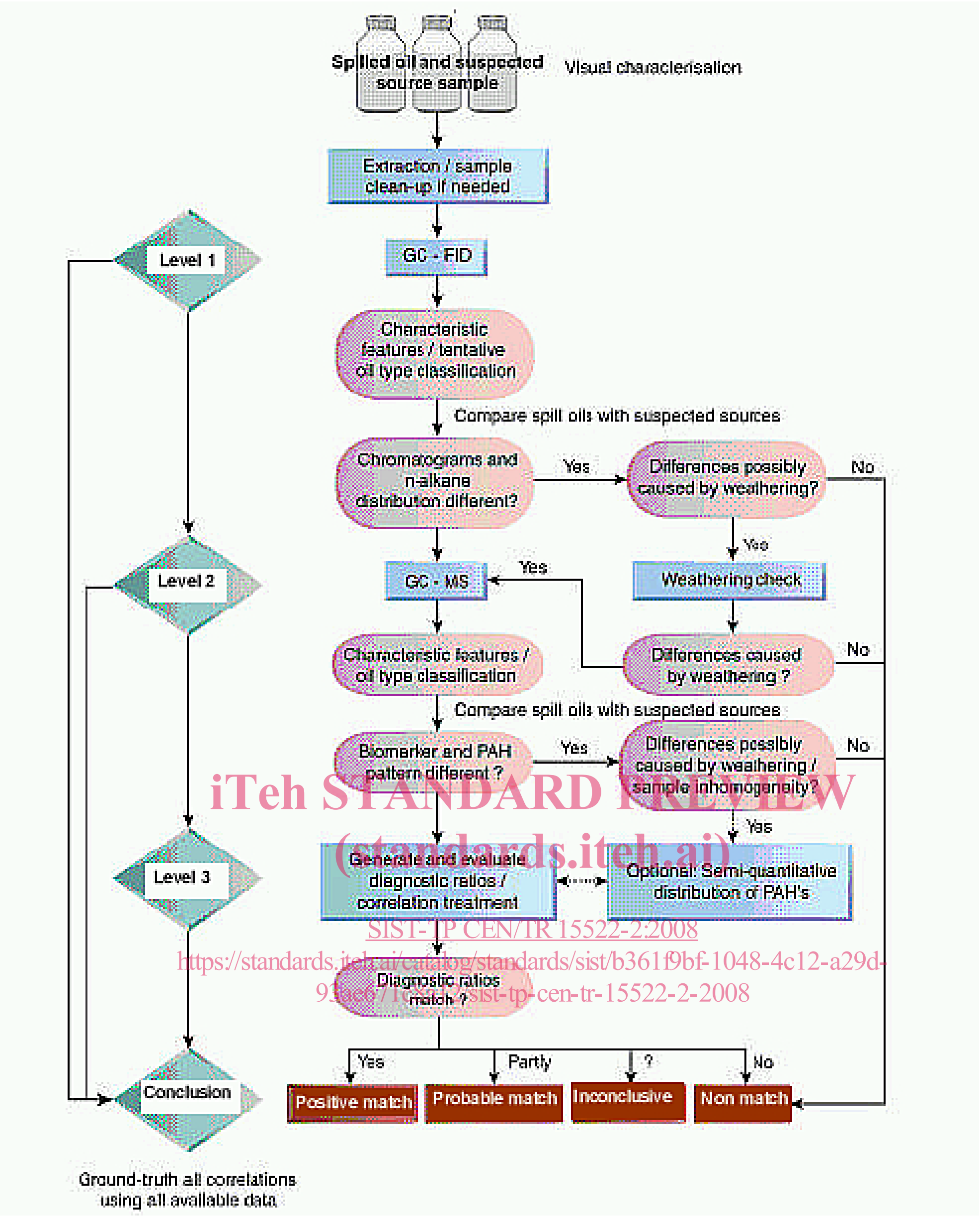

Figure 1 — Protocol/decision chart for oil spill identification

5 Sample preparation

5.1 General

The same sample preparation procedure should be followed for both GC/FID and GC/MS analysis, i.e. the same extracts should be analysed for both analyses. The sample preparation does not generally require asphaltene removal or separation of e.g. aliphatic from aromatic i.e., analysis of a ‘whole oil’ aliquot is recommended.

The present methodology is based on semi-quantitative analysis (i.e. no internal standards are added), for establishing diagnostic ratios.

5.2 Visual examination of samples

Colour, odour, viscosity and content of any free water and debris should be visually noted and reported. It is also recommended that each sample is photographed in order to document its "as-received" condition. Any pieces of wood, fabric, feathers or other debris should be removed from the sample with a pair of tweezers and noted in the report.

5.3 Preparation

5.3.1 General

If a sample contains a significant amount of oil/emulsion, and an aliquot on the sample cannot be immediately prepared after arriving at the laboratory, the sample bottle should be stored in a refrigerator at (5 ± 2) °C. Sample preparation should be carried out as soon as possible, preferably within a week, particularly in cases concerning emulsions.

If a sample contains primarily water and it cannot be immediately extracted, dichloromethane (DCM)[1] should be immediately added after arrival, (e.g. 10 ml to a 1 l water sample). After shaking, the sample should be stored in a refrigerator at (5 ± 2) °C. Further sample preparation should be carried out as soon as possible, preferably within a week.

5.3.2 Water samples

If samples consist primarily of water (no visual oil on the surface), the oily water is transferred to a separating funnel. Use dichloromethane (DCM)[1].Depending on the amount of oil, the sample should be extracted one by one or serially (e.g. 60 ml, 30 ml and 30 ml of solvent if the sample volume is 1 l, less volume if the water sample is smaller). The sample bottle is rinsed inside with DCM[1] before pouring it into the water sample for extraction. The extract is dried with sodium sulphate and diluted or concentrated to a suitable injection concentration. If a concentration step is needed use a gentle evaporation technique (e.g. Kudena Danish, Turbo Vap, N-Evap).

5.3.3 Oil samples from polytetrafluoroethylene (PFTE) net

PFTE net[2] is recommended for sampling thin oil films [39]. The oil should be thoroughly rinsed off the PFTE net using DCM[1] or the PFTE net can be extracted in DCM[1]. After drying with sodium sulphate, the extract should be diluted or concentrated to a suitable injection concentration.

5.3.4 Thick oil and emulsified oil samples

Samples consisting primarily of water or emulsified oil should be allowed to equilibrate at room temperature. Any free water should be decanted into a separating funnel. The oil/emulsion fraction is gently homogenised before an aliquot, 20 mg to 50 mg, is weighed in a tarred volumetric flask (5 ml) and diluted with DCM[1] to the final volume. The extract should be dried with sodium sulphate. Samples consisting of solid oil, e.g. high elastic/viscous HFO, should be adjusted to room temperature. When homogeneity is questionable, take two aliquots, 20 mg to 50 mg, at different spots and treat the aliquots as different samples.

5.3.5 Tar balls and emulsified lumps

Oils weathered for a long time at sea and/or on shore may form very viscous oil lumps (“tar balls”) often centimetres in diameter. Their exposure to weathering may not be homogenous thus in such cases, it is

---

[1] If DCM is not allowed, use another appropriate solvent e.g. hexane.

[2] Teflon® is example of a suitable commercially available product. This information is given for the convenience of users of this CEN Technical Report and does not constitute an endorsement by CEN of this product. An example is Teflon® net manufactured by SEFAR – Internet: www.sefar.com (Sefar Fluortex Product ref.09-150/36).