
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

Identifizierung von Ölverschmutzungen - Rohöl und Mineralölerzeugnisse aus dem Wasser - Teil 2: Analytische Methodik und Interpretation der Ergebnisse, basierend auf GC-FID- und GC-MS-Analysen bei niedriger Auflösung

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**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**

Identifizierung von Ölverschmutzungen - Rohöl und
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Analytische Methodik und Interpretation der
Ergebnisse, basierend auf GC-FID- und GC-MS-
Analysen bei niedriger Auflösung

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 19.

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European foreword

This document (prEN 15522-2:2020) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

This document is currently submitted to the CEN Enquiry.

This document will supersede CEN/TR 15522-2:2012.

In comparison with the previous edition, the following technical modifications have been made:

- adding compounds to be analysed in order to include light products in the diesel range;
- adding more information about biodegradation;
- adding a Reporting and a Quality assurance chapter;
- adding Annex C with precision data;
- adding Annex D with likelihood grade conclusions;
- introduction of characterization of FAME in Annex I;
- serious revision of Annexes H, I, J and K, adding new pictures and chromatograms.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

A list of all parts in a series can be found on the CEN website.

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prEN 15522-2:2020 (E)**Introduction**

This document describes a forensic method for characterising and identifying the source of oils spills in the environment as a resulting from accidents or intentional discharges. The method can be used in support of the legal process as evidence for prosecuting offenders. This method is based on the experience gained with its former publications over the years.

EN 15522 is composed of two parts that are described by the following CEN documents:

- EN 15522-1 – Sampling, describing good sampling practice, detailing sampling equipment, sampling techniques and the handling of oil samples prior to their arrival at the forensic laboratory;
- EN 15522-2 – Analytical Method, which covers the general concepts and laboratory procedures of oil spill identification, analytical techniques, data processing, data treatment, interpretation/evaluation and reporting of results.

Oil spill source identification is a complex methodology due to the large variation in sample types 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 (GC-MS). Any chemical difference found between samples is only relevant if this 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 are presented.

In the usual test method standard, instructions are given how to perform an “analytical” procedure. Oil spill identification however comprises of an analytical part and an assessment part. The sample preparation part is described in Chapter 5 and the analytical parts in Annex A for the GC-FID and in Annexes B, E and F for the GC-MS. The other parts of the document describe tools and instructions how to assess the analytical data and how to come to a final conclusion. Because each oil case is different in situation, size, products and weathering, the evaluation part of the method is described as a toolbox. The Annexes J and K evaluate an oil case and show how the tools may be applied. More examples of specific oil cases are available as summary reports of the annual round robins organised by Bonn-OSINet [11] and in literature.

The main purpose of the methodology described in this part of the document is to defensibly identify the source of an oil spill in the environment 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 must be maintained. Even so, a “positive match” between a spilled oil and a suspected source may not be used alone to identify the PRP (potential responsible party), 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 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 with 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 document in defensibly identifying a spilled oil's source depends upon the samples available for chemical study. To minimise the danger for “false positive” and especially “false non-matches”, good sampling

practice is essential, and particularly the need to obtain appropriate suspect source samples, is crucial (as described in Part 1: Sampling).

When oil from suspected sources is not available, this document can 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 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 suspected 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 document is the result of advancements in the field of oil spill identification [e.g. 22, 36, 66, 67 and 78] that have been made since the Nordtest Method [54] 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 changes 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 Proficiency Testing Programs (PTPs; RR-tests) have been conducted to evaluate and improve upon the methodology. Since 2004, in the framework of Bonn-OSINET (Bonn-Agreement Oil Spill Identification Network), annual interlaboratory studies have been organised jointly by RWS-lab (Rijkswaterstaat - Laboratory in the Netherlands) and BSH (Bundesamt für Seeschifffahrt und Hydrographie in Germany) in which laboratories from around the world participate. The studies have covered oil spill cases dealing with light fuel oil distillates (diesel oils), bilge water samples (a mixture of water, gas oils and lubricating oil), crude oils and heavy fuel oils. Findings from these studies have been discussed at annual meetings by the participating analysts and have been taken into account for refining the suggested methodology described herein. The final reports of the interlaboratory studies can be downloaded for free from the Bonn-OSINET part of the Bonn-Agreement website [11].

prEN 15522-2:2020 (E)**1 Scope**

This document describes a method to firstly identify the specific nature of oils spilled in the environment and secondly compare the chemical composition of samples from spilled oil with those of suspected sources. Specifically, the document describes the detailed analytical methods and data processing specifications for identifying the specific nature of 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 can still help to constrain the possible source(s) of the spilled oil.

This methodology is restricted to petroleum related products containing a significant proportion of hydrocarbon-components with a boiling point above 150 °C. Examples are: crude oils, higher boiling condensates, diesel oils, residual bunker or heavy fuel oils, lubricants, and mixtures of bilge and sludge samples, as well as distillate fuels and blends. 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, can have applicability in spills involving this kind of oils.

Paraffin as petroleum product (for candles, etc.) is outside the scope of this method, because too many compounds have been removed during the production process [37]. Still the method can be used to analyse the type of product involved.

This method is not directly intended for identifying oil spills in matrixes like 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”. It is therefore advisable to analyse background sample(s) from seemingly uncontaminated matrix. Including these “non-oil” matrixes in this oil spill identification method can require additional sample preparation (e.g. clean-up) in the laboratory prior to analysis and consideration of the extent to which the matrix can affect the correlation achieved. Evaluating the possible effects in these matrixes is beyond the scope of this document. Whether the method can be used for this kind of matrixes may depend on the oil concentration compared to the “matrix concentration” of the samples. In matrixes containing relatively high concentration of oil, a positive match can still be concluded. In matrixes containing relatively low concentration of spilled oil, a false non-match or an inconclusive match could be achieved due to matrix effects.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 15522-1, *Oil spill identification –petroleum and petroleum products – Part 1: Sampling*

ISO 1998-1:1998, *Petroleum industry — Terminology — Part 1: Raw materials and products*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1998-1:1998 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

3.1 General

3.1.1

chain of custody

practice of ensuring security of the sample so that no one has an opportunity to tamper with or otherwise alter the sample or the results

Note 1 to entry: It includes chronological documentation that records the sequence of sample handling including sampling, sealing, storage, transfer, analysis and disposal to ensure that only documented sample handlers have direct access to the samples.

3.1.2

mixing

mixing of sources containing or consisting of petroleum (products) before, during or after the spillage

Note 1 to entry: Can result in a heterogeneous spill composition (see 3.1.4).

3.1.3

contamination

changes in oil composition which take place during/after the spillage in either sample by addition of non-petroleum compounds from biogenic (e.g. fat from feathers) or anthropogenic sources (e.g. compounds from plastics)

Note 1 to entry: mixing and contamination are used to differentiate between the addition of petroleum products (mixing) and non-petroleum products (contamination)

3.1.4

sample heterogeneity

non-homogenous character of samples caused for example by variable degrees of stirring within a vessel, tank, pipeline or oil slick originally containing oil(product)s with different compositions

3.1.5

duplicate

two times the injection of the same sample extract within a sequence or within an oil case

3.1.6

replicate

two aliquots of a sample or two samples taken from exact the same sample location and at the same time

Note 1 to entry: Two samples taken from different locations of a larger spill are no replicates, but different samples.

prEN 15522-2:2020 (E)**3.1.7****waterborne oil**

petroleum or petroleum product borne by water or available in the water column from marine, estuarial and aquatic environments

Note 1 to entry: Aquatic environments include lakes and rivers, but exclude groundwater.

3.1.8**weathering**

processes that cause changes in oil composition of source and spill samples which can take place after the spillage, including natural processes like evaporation, dissolution, emulsification, photo oxidation, biodegradation, wax redistribution and also processes caused by oil response techniques like chemical dispersion and burning

Note 1 to entry: Sometimes the source is more weathered than the spill. For example when a slop tank contains a mixture of oil and water and is leaking oil into much colder water, the oil in the slop tank can be biodegraded to a higher degree than the spilled oil.

3.1.9**bilge**

water which may be contaminated by oil resulting from things such as leakage or maintenance work in machinery spaces. Any liquid entering the bilge system including bilge wells, bilge piping, tank top or bilge holding tanks is considered oily bilge water

[SOURCE: MEPC. 187(59) ^[48]]

3.1.10**slop (tank)**

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

3.1.11**sludge**

the residual waste oil products generated during the normal operation of a ship such as those from the purification of fuel or lubricating oil from main or auxiliary machinery, separated waste oil from oil filtering equipment, waste oil collected in drip trays, and waste hydraulic and lubricating oils

[SOURCE: MEPC. 187(59) ^[48]]

3.1.12**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 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 [54]. In this document, the name PW-plot is used as an abbreviation of a “Percentage Weathering” plot.

3.2.2

diagnostic ration (DR)

ratio between the peak heights of single compounds or peak areas of compound groups of the same sample selected by their diversity in chemical composition in petroleum and petroleum products, their discriminative power and on their known behaviour in weathering processes

3.2.3

likelihood ratio (LR)

ratio of two probabilities

Note 1 to entry: The numerator is the probability of obtaining the evidence when the prosecutors scenario is true. The dominator is the probability of obtaining the evidence when the defence scenario is true (see Annex D).

3.2.4

critical difference (CD)

14 % of the mean value of a ratio for two different samples

Note 1 to entry: The fixed value of 14 % is based on the maximum allowable RSD of 5 % for the diagnostic ratios (see 7.5.5).

3.2.5

significant difference

difference between a property or analytical result of two samples that cannot be explained as caused by weathering, mixing or contamination

Note 1 to entry: Your skin turning brown or red after a while in the sun, doesn't make you a different person and is therefore not a significant difference.

3.3 Abbreviations

CD	Critical Difference
DR	Diagnostic Ratio
FAMES	Fatty Acid Methyl Esters
FID	Flame Ionisation Detection
GC	Gas Chromatography
HFO	Heavy Fuel Oil
HVO	Hydrotreated Vegetable Oil

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LCO	Light Cycle Oil
LFO	Light Fuel Oil
MS	Mass Spectrometry
NR	Normative Ratio
PTP	Proficiency Testing Program
RR	Round Robin Test;
RSD	Relative Standard Deviation
ULSFO	Ultra-Low Sulfur Fuel Oil
VGO	Vacuum Gas Oil

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

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

NOTE See Annex G for further explanation on composition of oils.

The likeness of a source and spill sample should be tested by analysing the samples with GC-FID and/or GC-low resolution-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 limits defined) 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, contamination 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 can result in conclusions intermediate to “positive match” and “non-match”, such as “probable match” or “inconclusive” (see D.2). All these classifications are used in the descriptions and examples of this document.

IMPORTANT - 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 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) [54] and the ASTM methods [3, 4]. 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 document 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 integration values are used in two different ways:

- a) Measurements of single compounds normalised to hopane – or, if hopane is not sufficiently present, to phytane – or, if phytane is also not sufficiently present, to bicyclic sesquiterpane 10 (BS10).

Comparing two oil samples by the normalised abundances of compounds spanning the boiling range of oil in the form of PW-plots, reveals:

- the variance of the analysis and integration, when comparing duplicates;
- the difference in concentration of compounds (e.g. biomarkers and PAHs) between the two samples;
- 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 DR can be eliminated or cautiously considered when comparing a weathered spill sample to an unweathered source sample.

- b) DRs: for keeping the analytical error low, measurements of compounds (peaks) that are recorded by a m/z value difference of less than 25 via GC-MS.

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NOTE 1 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 leads 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 [66, 67].

Whereas most of the DRs described in this document can 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 crude oil (e.g. condensate) and lighter fuel oils (e.g. kerosene, diesel, gas oil). The reason for this is that 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 aromatic compounds 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 diagnostic and more weathering resistant alkanes, PAH compounds and biomarkers has been developed for relevant types of petroleum (see 7.5.3). Normative ratios should be interpreted as being mandatory. In addition, there are also several informative ratios used at the judgment of the analyst to improve the number of features available for numerical assessment. The full set of normative ratios is sufficient for a sample comparison if at least 80 % of these ratios can be used. If the number of solid/usable ratios is lower, it is recommended to use additional informative ratios to at least base a conclusion on the same overall number of ratios. Examples of additional informative ratios are given in Annex E. A comprehensive review of further potentially DRs, which can be useful in oil spill identifications, can be found in [67]. The resulting ratios are compared using a critical difference of 14 % (see 3.2.3).

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

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NOTE 2 The present methodology is based on semi-quantitative analyses for establishing diagnostic ratios of whole samples (no fractionation in aliphatic and aromatic compounds [2]). 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 this document can be established based on quantitative analysis in which the absolute concentrations are used to calculate DRs [17, 18 and 28].

5 General lab instructions**5.1 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 and sample handling shall be carried out in accordance with EN 15522-1. When suspected sources are not available, the method can still be used to characterise the spilled oil.

At the laboratory the samples are visually characterised, described (see 6.2) and prepared for analysis (conservation, extraction and clean-up if needed) (see 6.3 and 6.4).

5.2 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 (or GC-MS full scan, when a GC-FID is not available) is used for the screening of all samples. Based upon the visual comparison of the gas chromatograms, source samples that are clearly a different type of petroleum than the spill sample(s), can be ruled out as “non-matching”. For example, a diesel fuel potential source sample can 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 a different type of oil than the spill, n-alkanes and isoprenoids, normally the most abundant components of oils, are measured and compound ratios are calculated and compared. A proper visualisation of the results is achieved by GC-PW-plots, where alkane-ratios of the spill sample(s) are plotted against those of the comparison sample(s) (Level 1.2).

NOTE Level 1.2 is optional. Its utility lies in the potential to eliminate some clearly distinct source samples for analysis by GC-MS (Level 2) if justified. However, if it has already been decided to conduct Level 2 GC-MS analysis, Level 1.2 is not essential, except for spills involving light petroleum products like diesel. In this type of spill, the very low concentration of biomarkers in light products and the high concentration of alkanes, the alkane pattern, the isoprenoid ratios and the GC-PW-plot can provide essential input to the final decision.

If there are no obvious or only smaller significant differences evident following Level 1, i.e. differences, which are below or only slightly above the analytical error, Level 2 (Figure 1) is conducted:

GC-MS is used for detailed fingerprinting of the spill and suspected source samples. The steps are the same as given above. In Level 2 however, a large number of compounds representing different compound groups is investigated and compared between the samples. Based upon the visual comparison of the ion chromatograms (can be supported by overlays), at this point suspected source samples that are clearly different from the spill sample(s) due to reasons other than those that might be attributable to weathering, mixing, or sample heterogeneity, can be ruled out as “non-matching” (Level 2.1). For the remaining samples, results are visualised by plotting ratios of the spill sample(s) against those of the comparison sample(s) in form of MS-PW-plots (Level 2.2). Also at this point, a list of “representative” target compounds is measured and DRs are calculated and compared (Level 2.2).

If there are no or only smaller significant differences observed, the final conclusion is reached, whereupon the results from all four steps (Levels 1.1 through 2.2; Figure 1) are collectively evaluated.

Conclusions can be based on match definitions or on likelihood ratios (see Annex D).

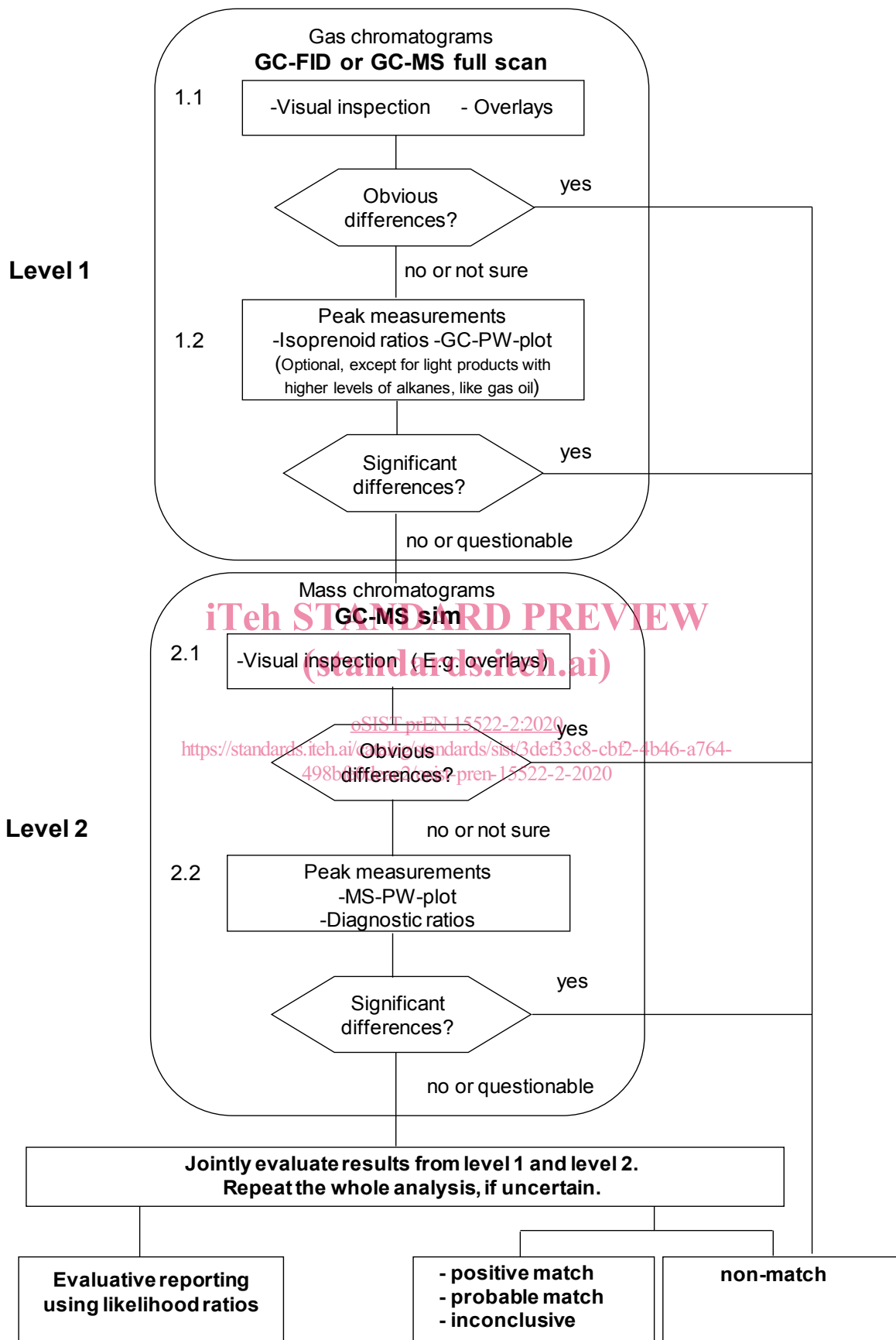


Figure 1 — Protocol/decision chart for oil spill identification